



September 17-22, 2023

8th International Polysaccharide Conference

Graz University of Technology, Austria

www.tugraz.at/events/epnoe2023



Dear colleagues and friends,

We are very pleased to welcome you to the 8th International Polysaccharide Conference held for the first time in Graz, Austria. This congress is an initiative of EPNOE, the Cellulose and Renewable Division of the American Chemical Society (ACS CELL), and the Cellulose Society of Japan (CSJ).



Our ambition is to bring together academia and industry passionate about polysaccharides related R&D and applications. Throughout the years, the EPNOE conference has become **one of the largest events in the field**, and this year gathers over **400 researchers from all over the world**.

This conference is organized by the Austrian University Consortium – **TU Graz, UNI Graz, BOKU Vienna, UNI Vienna, and UNI Innsbruck**.



We hope that you will enjoy the event, have very fruitful discussions, and a great stay in Graz.

Your EPNOE 2023 organizer



Thanks to our sponsors!





Rheology and Dynamic Mechanical Analysis Combined

MCR 702e Multidrive

Full DMA and Rheometer capabilities

Complete characterization of plastics, polymers, and hydrogels

DMA in torsion, tension, bending, or compression modes

Measurements from -160 °C to 1000 °C and under humidity

www.anton-paar.com





polymers

IMPACT
FACTOR
5.2

Indexed in
PubMed

CITESCORE
7.4

Editor-in-Chief:
Prof. Dr. Alexander Böker

ISSN 2073-4360
▶ mdpi.com/journal/polymers
▶ @Polymers_MDPI

Polymers (ISSN 2073-4360) provides an interdisciplinary forum for publishing papers which advance the fields of (i) polymerization methods, (ii) theory, simulation, and modeling, (iii) understanding of new physical phenomena, (iv) advances in characterization techniques, and (v) harnessing of self-assembly and biological strategies for producing complex multifunctional structures.

The scope of *Polymers* includes (but is not limited to):

- Polymer Chemistry
- Polymer Analysis and Characterization
- Polymer Physics and Theory
- Polymer Processing and Engineering
- Polymer Applications
- Biomacromolecules, Biobased and Biodegradable Polymers
- Circular and Green Polymer Science
- Polymer Composites and Nanocomposites
- Polymer Networks
- Polymer Membranes and Films
- Polymer Fibers
- Smart and Functional Polymers



polysaccharides

Editor-in-Chief:
Prof. Dr. Karin Stana Kleinschek

ISSN 2227-9717
▶ mdpi.com/journal/polysaccharides
▶ @MDPIOpenAccess

Polysaccharides (ISSN 2673-4176) provides an advanced forum for studies related to polysaccharides and their derivatives, from basics to applications. *Polysaccharides* publishes reviews, regular research papers, and short communications as well as Special Issues on particular subjects.

The scope of *Polysaccharides* includes (but is not limited to):

- Synthesis, analysis, functionalization and modifications
- Isolation, extraction, purification and degradation
- Chemical-physical properties analysis and characterization
- Structure–property relationships
- Application in drug delivery, medicine, and tissue engineering
- Application in environmental sciences
- Application in food or agricultural science
- Other industrial applications
- Glycobiology



Academic Open Access Publishing
since 1996

MDPI
St. Alban-Anlage 66
4052 Basel
Switzerland

Tel: +41 61 683 77 34
www.mdpi.com
▶ @MDPIOpenAccess

Table of content

Plenary Speakers	1 – 7
Session 1 Keynote	8 – 10
Session 1 Oral	11 – 28
Session 1 Poster	39 – 45
Session 2 Keynote	46 – 47
Session 2 Oral	48 – 67
Session 2 Poster	68 – 72
Session 3 Keynote	73 – 75
Session 3 Oral	76 – 92
Session 3 Poster	93 – 94
Session 4 Keynote	95 – 97
Session 4 Oral	98 – 123
Session 4 Poster	124 – 144
Session 5 Keynote	145 – 147
Session 5 Oral	148 – 171
Session 5 Poster	172 – 185
Session 6 Keynote	186 – 187
Session 6 Oral	188 – 208
Session 6 Poster	209 – 215
Session 7 Keynote	216 – 218
Session 7 Oral	219 – 244
Session 7 Poster	245 – 263
Session 8 Keynote	264 – 266
Session 8 Oral	267 – 290
Session 8 Poster	291 – 300
Session 9 Keynote	301 – 303
Session 9 Oral	304 – 312
Session 9 Poster	313 – 320
Session 10 Keynote	321 – 323
Session 10 Oral	324 – 347
Session 10 Poster	348 – 361

Plenary Speakers

Vincent Eijsnik substituted by Gustav Vaaje-Kolstad

Enzymatic conversion of polysaccharides - from hydrolases to lytic polysaccharide monooxygenases (LPMOs)

Hiroyuki Yano

Driving Toward a Sustainable Society with Nanocellulose Vehicles

Manuel A. Coimbra

Polysaccharides, a source of clean label strategies for food industry

João F. Mano - WINNER EPNOE SCIENCE AWARD

Hydrogels from marine-derived polysaccharides for biomedical applications

Silvia Vignolini

Cellulose engineering: from nature to applications

Didier Letourneur

Clinical use of polysaccharides for molecular imaging and tissue repair: Two examples from IN THE JOURNEY FROM research works to the patients



ENZYMATIC CONVERSION OF POLYSACCHARIDES - FROM HYDROLASES TO LYTIC POLYSACCHARIDE MONOOXYGENASES (LPMOS)

Vincent G. H. Eijsink, Gustav Vaaje-Kolstad

Faculty of Chemistry, Biotechnology and Food Science, Norwegian University of Life Sciences (NMBU), Ås, Norway

Vincent.eijsink@nmbu.no

Nature produces a large arsenal of carbohydrate-active enzymes (CAZymes), which are catalogued in the CAZy database [1]. These enzymes may be exploited for the synthesis, modification and degradation of a wide variety of carbohydrate containing compounds. In this talk, I will focus on enzymatic depolymerization of polysaccharides, which is key to sustainable exploitation of biomass. In the past decades there has been much focus on the saccharification of cellulose and hemicelluloses in (non-edible) plant biomass, to produce sugars for further biotechnological valorization. Enzymatic degradation of cellulose is particularly challenging since cellulose is a crystalline, insoluble material with low enzyme accessibility, that primarily occurs as part of complex, co-polymeric plant cell walls. Chitin, which is abundantly available in side streams from crustacean production, poses similar challenges [2].

Depolymerization of these recalcitrant polysaccharides may be achieved using a combination of endo- and exo-acting hydrolyases and much progress has been made in understanding the structural features that determine enzyme performance and in finding or engineering enzymes with optimal properties for industrial use [3,4]. This classical paradigm of polysaccharide degradation was shattered by the discovery of lytic polysaccharide monooxygenases (LPMOs), which catalyze oxidative cleavage of glycosidic bonds and, by doing so, improve the efficiency of the enzymatic depolymerization reaction [5-12]. LPMOs, which resemble the “decrySTALLIZING” C1 factor hypothesized by Reese et al in 1950 [13], are unique peroxygenases with a single copper co-factor and a flat substrate-binding surface allowing these enzymes to act on fibers rather than on single polysaccharide chains.

In the presentation, I will shortly discuss the various enzyme types involved in processing of cellulose and chitin and then provide an overview of recent developments in the LPMO field, which, notably, include the discovery of LPMOs with functions beyond biomass degradation and with hitherto unknown (carbohydrate?) substrates [14-16].

- [1] E Drula et al., 2022, *Nucleic Acids Res* 50, D571–D577.
- [2] VGH Eijsink et al., 2008, *Trends Biotechnol* 26, 228-235.
- [3] CM Payne et al., 2015, *Chem Rev* 115, 1308-1448.
- [4] YB Chaudhari et al., 2023, *Protein Eng Des Sel* 36, gzad002.
- [5] G Vaaje-Kolstad et al., 2005, *J Biol Chem* 280, 28492-28497.
- [6] G Vaaje-Kolstad et al., 2010, *Science* 330, 219-222.
- [7] B Bissaro et al., 2017, *Nature Chem Biol* 13, 1123-1128.
- [8] M Eibinger et al., 2017, *Nature Commun* 8,894.
- [9] THF Costa et al., 2020, *Biofuels, Bioproducts & Biorefining*, 14, 734-745.
- [10] H Chang et al., 2022, *Nature Commun* 13, 6258.
- [11] EG Kommendal et al., 2023, *Nature Commun* 14,1063.
- [12] B Bissaro & VGH Eijsink, 2023, *Essays Biochem* 67, 575-584.
- [13] ET Reese et al., 1950, *J Bacteriol* 59, 485-497.
- [14] F Askarian et al., 2021, *Nature Commun* 12, 1230.
- [15] F Sabbadin et al., 2021, *Science* 373, 774-779.
- [16] TM Vandhana et al., 2022, *New Phytol* 233, 2380-2396.



DRIVING TOWARD A SUSTAINABLE SOCIETY WITH NANOCELLULOSE VEHICLES

Yano H. ^{*a}

^a *Research Institute for Sustainable Humanosphere, Kyoto university, Japan*

* yano@rish.kyoto-u.ac.jp

Nano Cellulose Vehicle, or NCV is lightweight vehicle of the future, made from the material of cellulose nanofibers, or CNF. 22 organizations, including universities, research institutes and automotive manufacturers, worked together to put the technology to practical use. Applying the nanocellulose technology such as 100% CNF materials, optically transparent CNF materials, surface modification of CNFs, pulp direct kneading method “Kyoto Process ®”, 3D printing technology and so on developed at Kyoto University to automobiles, the NCV project aimed to achieve a 10% reduction in weight. CNFs have outstanding strength allowing them to be used in a variety of parts by making them thinner, foaming them, or using them to replace metals, and contributing to weight savings. NCV achieved a weight saving of 16% through the use of CNF parts, it will reduce CO₂ emissions by a total of 2,000 kg throughout the vehicle’s lifecycle from the production of parts to their disposal.



Fig. 1 Nano cellulose vehicle (NCV)

[1] Development of a Vehicle Using CNF, the Next-Generation Material

<https://www.youtube.com/watch?v=06H8wP9axjU>

[2] Transforming our future - NCV Nano Cellulose Vehicle

https://www.youtube.com/watch?v=28N0YEo_8Ls



POLYSACCHARIDES, A SOURCE OF CLEAN LABEL STRATEGIES FOR FOOD INDUSTRY

Coimbra M.A.

LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Portugal

mac@ua.pt

Globalization resulted in standardized food products, with scarce differentiation all around the world. Half of European consumers are convinced that the food consumed in the past was healthier and had better sensorial characteristics than that found nowadays in supermarket shelves. To counteract scepticism among consumers about the present offer by food industry, new quality related ingredients, formulations, and technologies are under development. They tend to be healthy, tastier, affordable, and appealing foods through personalized “right for me” food, food oriented to specific genders, ages, or lifestyle markets. Total transparency labelling, with less ingredients, minimization of the use of synthetic food additives, minimally processed foods, no allergen warnings, and no genetically modified organisms are the targets.

Polysaccharides and derived oligosaccharides can contribute to the new food industry trends. In this talk, examples of different applications of polysaccharides towards the promotion of clean label strategies are discussed: 1. Anionic polysaccharide-derived oligosaccharides as substituents of polyphosphates by meat industry; 2. Fruit juices with incremental polysaccharide-based soluble dietary fibre and oligosaccharides with potential prebiotic activity; 3. Inulin-rich tuberous roots and derived fructooligosaccharides able to replace sucrose added in processed jams for use in dairy products; 4. Brewers spent yeast glucans and mannoproteins as emulsifiers in vegan mayonnaises [1]; 5. Gelatinized starch derivatives as replacers of titanium dioxide in candies and other white foods; and 6. Chitosan films to produce sulphur dioxide free wines [2,3,4].

- [1] Reis, S.F., Fernandes P.A.R., Martins V.J., Gonçalves S., Ferreira L.P., Gaspar V.M., Figueira D., Castelo-Branco D., Mano J.F., Coimbra M.A. & Coelho E., *Molecules*, 28, 3540, 2023.
- [2] Nunes C., Maricato E., Cunha A., Rocha M.A.M., Santos S., Ferreira P., Silva M.A., Rodrigues A., Amado O., Coimbra J., Silva D., Moreira A., Mendo S., Lopes da Silva J.A., Pereira E., Rocha S.M. & Coimbra M.A. *Green Chem.*, 18, 5331-5341, 2016.
- [3] Rodrigues J.A., Nunes C., Coimbra M.A., Goodfellow B.J. & Gil A.M., *Foods*, 11, 3428, 2022.
- [4] Rocha M.A.M., Ferreira P., Coimbra M.A. & Nunes C., *Carbohydr. Polym.*, 236, 116026, 2020.



HYDROGELS FROM MARINE-DERIVED POLYSACCHARIDES FOR BIOMEDICAL APPLICATIONS

João F. Mano

Department of Chemistry, CICECO - Aveiro Institute of Materials, University of Aveiro, Portugal.

Hydrogels are adequate matrices for the 3D culture of cells and as drug delivery systems. Using bioinspired strategies, and well-designed macromolecular design, basic units of hydrogels can be processed in mild conditions, permitting the encapsulation of living cells and other biological cargo with high efficiency and tuned for envisaged biomedical applications.

From the different sources of biomaterials to produce hydrogels, polysaccharides have been proposed to produce matrices able to interact favourably with cells or to encapsulate bioactive molecules. Some chemical routes that we have employed to extend the chemical versatility of polysaccharides are shown, with particular emphasis on the modification of marine-derived biopolymers. Examples are shown on the processing of hydrogels into different sizes and shapes (e.g. microgels, patches and bioprinted objects) with structural characteristics suitable to be used in tissue engineering and regenerative medicine applications. From a functional point of view an example will be presented on the capacity of laminarin, a storage glucan found in brown algae, to deliver glucose from the own enzymatic degradation process, maintaining the viability of encapsulated cells. Our findings have shown that marine-derived polysaccharides can be valorised to high-added value biomedical applications, upon eventual chemical modifications and adequate processing.



CELLULOSE ENGINEERING: FROM NATURE TO APPLICATIONS

Silvia Vignolini

Max Planck Institute of Colloids and Interfaces, Germany

silvia.vignolini@mpikg.mpg.de

The most brilliant colours in nature are obtained by structuring transparent materials on the scale of the wavelength of visible light. By controlling/designing the dimensions of such nanostructures, it is possible to achieve extremely intense colourations over the entire visible spectrum without using pigments or colorants. Colour obtained through structure, namely structural colour, is incredibly widespread in the plant kingdom. Such natural photonic nanostructures are generally synthesised in ambient conditions using the most abundant biopolymer on the planet: cellulose. Given these limitations, an amazing range of optical structures exists: from very ordered photonic structures to partially disordered to completely random ones. Here, I will introduce some striking example of natural photonic structures and review our recent advances to fabricate bio-mimetic photonic structures using the same material as nature. Developing biomimetic structures with cellulose enables us to fabricate novel photonic materials using low cost polymers in ambient conditions. Importantly, it also allows us to understand the biological processes at work during the growth of these structures in plants.



CLINICAL USE OF POLYSACCHARIDES FOR MOLECULAR IMAGING AND TISSUE REPAIR: TWO EXAMPLES FROM IN THE JOURNEY FROM RESEARCH WORKS TO THE PATIENTS

Letourneur D.

Université Paris Cité, Université Sorbonne Paris Nord, INSERM 1148, LVTS, Hôpital Bichat, F-75018 Paris, France

didier.letourneur@inserm.fr

Biomaterials have been around for centuries. They are found in various forms in cardiovascular, orthopedic, dental, general and aesthetic surgery, ophthalmology, dermatology applications... Initially, they were simply designed to replace missing limbs (legs, feet, hands).

With developments in materials science concerning metals, ceramics and polymers, they have gradually been transformed and some are equipped with substance release systems (active stents). The improvement of biomaterials has therefore been made possible thanks to advances in the properties of the materials used for the manufacture of prostheses, surgical techniques and engineering. The latter continue to evolve by integrating the biological sciences in the fields of tissue engineering and molecular imaging.

Among the materials used, polysaccharides represented a very promising family. Engineers, chemists, biologists, clinicians and entrepreneurs must therefore unite their efforts to develop new biomimetic, bioinspired and biofunctional medical devices and their associated imaging tools using polysaccharides.

Two representative examples of clinical / industrial transfers resulting from our research works will be presented: i) a polysaccharide-based imaging and therapy system that also included a polysaccharide-based agent for thrombus targeting, ii) a 3D porous polysaccharide scaffold for restorative medicine. For each of them, a different development scheme was adopted.

Some recent references

- [1] Aprile P, Letourneur D, Simon-Yarza T. Membranes for Guided Bone Regeneration: A Road from Bench to Bedside. *Adv Healthc Mater.* 2020:e2000707.
- [2] Forero Ramirez LM, Gobin E, Aid-Launais R, Journe C, Moraes FC, Picton L, Le Cerf D, Letourneur D, Chauvierre C, Chaubet F. Gd(DOTA)-grafted submicronic polysaccharide-based particles functionalized with fucoidan as potential MR contrast agent able to target human activated platelets. *Carbohydr Polym.* 2020;245:116457.
- [3] Labour MN, Le Guilcher C, Aid-Launais R, El Samad N, Lanouar S, Simon-Yarza T, Letourneur D. Development of 3D Hepatic Constructs Within Polysaccharide-Based Scaffolds with Tunable Properties. *Int J Mol Sci.* 2020;21:3644.
- [4] Letourneur D, Joyce K, Chauvierre C, Bayon Y, Pandit A. Enabling MedTech Translation in Academia: Redefining Value Proposition with Updated Regulations. *Adv Healthc Mater.* 2020:e2001237.
- [5] Moraes FC, Antunes JC, Forero Ramirez LM, Aprile P, Franck G, Chauvierre C, Chaubet F, Letourneur D. Synthesis of cationic quaternized pullulan derivatives for miRNA delivery. *Int J Pharm.* 2020 Mar 15;577:119041.
- [6] Chauvierre C, Aid-Launais R, Aerts J, Chaubet F, Maire M, Chollet L, Rolland L, Bonafé R, Rossi S, Bussi S, Cabella C, Dézsi L, Fülöp T, Szebeni J, Chahid Y, Zheng KH, Stroes ESG, Le Guludec D, Rouzet F, Letourneur D. Pharmaceutical Development and Safety Evaluation of a GMP-Grade Fucoidan for Molecular Diagnosis of Cardiovascular Diseases. *Mar Drugs.* 2019;17:699.
- [7] Grenier J, Duval H, Barou F, Lv P, David B, Letourneur D. Mechanisms of pore formation in hydrogel scaffolds textured by freeze-drying. *Acta Biomater.* 2019;94:195.
- [8] Li B, Aid-Launais R, Labour MN, Zenych A, Juenet M, Choqueux C, Ollivier V, Couture O, Letourneur D, Chauvierre C. Functionalized polymer microbubbles as new molecular ultrasound contrast agent to target P-selectin in thrombus. *Biomaterials.* 2019;194:139.
- [9] Fricain JC, Aid R, Lanouar S, Maurel DB, Le Nihouannen D, Delmond S, Letourneur D, Amedee Vilamitjana J, Catros S. In-vitro and in-vivo design and validation of an injectable polysaccharide-hydroxyapatite composite material for sinus floor augmentation. *Dent Mater.* 2018;34:1024.
- [10] Juenet M, Aid-Launais R, Li B, Berger A, Aerts J, Ollivier V, Nicoletti A, Letourneur D, Chauvierre C. Thrombolytic therapy based on fucoidan-functionalized polymer nanoparticles targeting P-selectin. *Biomaterials.* 2018;156:204.



SESSION 1:

Advances in polysaccharide analysis, extraction and characterization

Session organizers:

Antje Potthast, Anton Huber, Henk Schols, Manuel Coimbra, Julien Navarro

Keynote speakers:

Harald Pasch

Advanced tools for molecular characterization of biobased and biodegradable polymers

Laura Nyström

Complementary methodologies for detecting weak interactions of neutral soluble polysaccharides



ADVANCED TOOLS FOR MOLECULAR CHARACTERIZATION OF BIOBASED AND BIODEGRADABLE POLYMERS

Pasch H.*, Bungu P.S., Lützow K.

*Department of Multidimensional Polymer Characterization, Institute of Active Polymers,
Helmholtz-Zentrum Hereon, Kantstr. 55, 14513 Teltow, Germany*

e-mail: harald.pasch@hereon.de

Biobased and biodegradable polymers such as hyaluronic acid, polylactides and other aliphatic polyesters possess some interesting properties such as biocompatibility and in-situ hydrolytic degradability. These properties make them suitable for cosmetic and biomedical applications. To establish suitable correlations between the polymer microstructure and the physical properties of polymers, it is imperative to conduct a comprehensive characterization of the materials. Size exclusion chromatography (SEC) coupled to multiple detectors is typically used for molar mass, size and conformation information. For functional group and chemical composition analysis, FTIR and NMR are the methods of choice. The development of suitable HPLC methods for the separation and purification of biodegradable polymers are important since polymers with high purity are valuable for structural and functional studies and applications in e.g. regenerative medicine.

Hyaluronic acid and its acrylate derivatives are important intermediates for various pharmaceutical, biomedical, and cosmetic applications due to their biocompatibility and viscoelasticity properties. However, these polymers are inherently difficult to characterize due to their significant heterogeneity regarding molar mass and chemical composition (e.g. degree of substitution). The work presented here discusses the development of multidimensional approaches for the analysis of biodegradable polymers focusing on methods for modified hyaluronic acid. The analytical protocol is based on a robust solvent gradient HPLC method that is suitable for separating HA regarding differences in functionalization. HPLC fractions and the bulk materials are characterized by NMR for compositional analysis. Coupling techniques such as 2D-LC and LC-FTIR are used for comprehensive structural analysis of a set of samples with regard to composition and molecular size.



COMPLEMENTARY METHODOLOGIES FOR DETECTING WEAK INTERACTIONS OF NEUTRAL SOLUBLE POLYSACCHARIDES

Nyström, L.*^a

^a *Institute of Food, Nutrition and Health, Laboratory of Food Biochemistry, ETH Zurich, Switzerland*

* laura.nystroem@hest.ethz.ch

Polysaccharides in foods belong to dietary fibres and are recognized for their health promoting properties; nevertheless, many of the physicochemical mechanisms behind these effects remain poorly understood. While it is understood that dietary fibres can associate with small molecules influencing the molecular mechanism, by which these associations take place, is still partly unknown. Such interactions are considered as a potential mechanism of action for the regulation of the absorption of nutrients (sugars, minerals, bile acids etc.) in the gut, as well as a potential factor that may hinder the absorption of various substances, be it desired (toxins) or undesired (medications). Yet, measuring such interactions is very challenging in particular for uncharged fibres, as the interactions are relatively weak. Therefore, complementary analytical techniques and detailed fibre characterization is needed to evaluate the structural characteristics and properties of fibre polysaccharides. Until recently the methods to study such interactions have generally been quite unspecific and indirect. Compared to e.g. charged polysaccharides or proteins, the neutral dietary fibres do not have specific binding domains that would govern the binding and interactions, but interact rather non-specifically with each other. We have therefore developed a set of complementary methods based on fibre-tethered gold-nanoparticles and transmission electron microscopy [1], calorimetric titration [2], and electron paramagnetic resonance with spin-labelled probes [3,4] to measure the molecular interactions between a range of linear and linearly branched uncharged soluble polysaccharides (arabinoxylan, mixed linkage β -glucan, galactomannan, and xyloglucan) with various cations and small molecules. Combining information from these studies, together with the structural information of the polysaccharides, will facilitate understanding the interactions between neutral polysaccharides and other molecules in complex matrices.

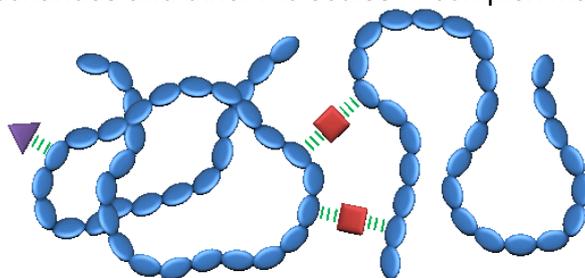


Figure 1 : Neutral soluble fibres possess interactions with other molecules, which may be weak but abundant and therefore important to their functional properties.

- [1] Lupo, C., Boulos, S., Delle Vedove, C., Gram, F., & Nyström, L. *Polysaccharides*, 2, 497-518. 2021.
- [2] Lupo, C., Boulos, S., Gram, F., Wu, X., & Nyström, L. *Carbohydrate Polymers*, 287, 119-229. 2021.
- [3] Wu, X., Boulos, S., Yulikov, M., & Nyström, L. *Carbohydrate Polymers*, 293, 119724, 2022.
- [4] Syryamina, V.N., Yulikov, M. & Nyström, L., *RSC Advances*, 12, 19901, 2022.



UNRAVELLING THE UNIQUE STRUCTURAL MOTIFS OF GLUCURONOXYLAN FROM HYBRID ASPEN WOOD

*Pramod Sivan^a, Emilia Heinonen^a, Louis Escudero^a, Madhavi Latha Gandla^b, Amparo Jiménez Quero^a, Leif J. Jönsson^b, Ewa J Mellerowicz^c and Francisco Vilaplana^{a,d}

^a Division of Glycoscience, Department of Chemistry, KTH Royal Institute of Technology, AlbaNova University Centre, 106 91 Stockholm, Sweden

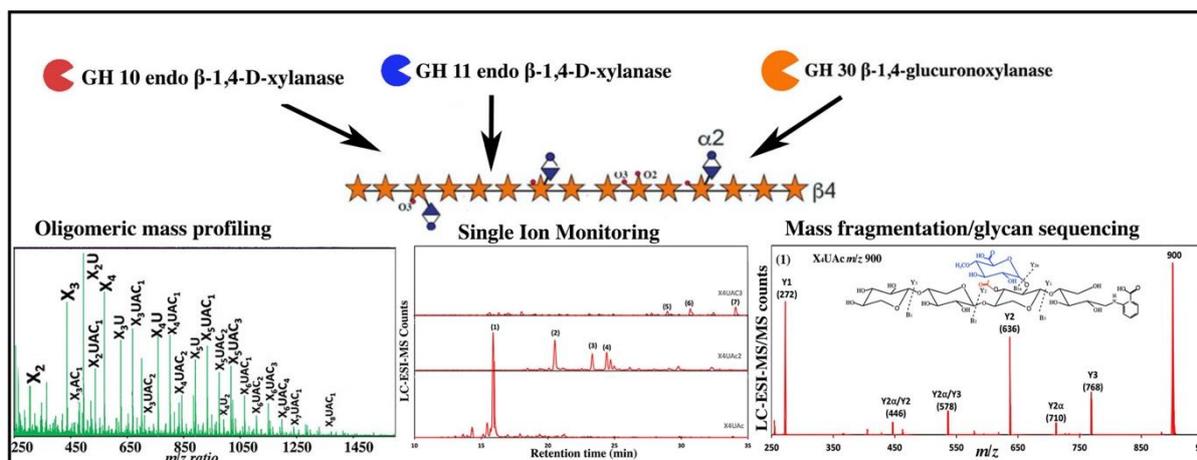
^b Department of Chemistry, Umeå University, 901 87 Umeå, Sweden

^c Umeå Plant Science Centre, Swedish University of Agricultural Sciences, Department of Forest Genetics and Plant Physiology, 901 83 Umeå, Sweden

^d Wallenberg Wood Science Centre, KTH Royal Institute of Technology, 106 44 Stockholm, Sweden

*Presenting author: psivan@kth.se

Cell wall polymers in hardwood biomass are considered as global carbon sink and excellent feedstock for biorefinery applications [1]. Deciphering the structural motifs of hemicellulose that facilitate its complex interaction with cellulose and lignin is fundamental for understanding the structural integrity of plant cell walls and for exploring its potential for industrial applications. In the present study, we investigated the structural motifs of glucuronoxylan (GX) from aspen wood. Easily-extractable GX populations in native (acetylated) form were extracted by subcritical water while recalcitrant populations were extracted with alkali. Both populations were subjected to enzymatic digestions with GH10, GH11 and GH30 xylanases. The mass spectrometric glycan sequencing of xylo-oligosaccharides generated by different xylanases revealed the unique structural motifs in terms of acetylation and glucuronidation patterns present in aspen GX. Motifs with blockwise repeats of even glucuronidation (every 2 xylose units) and a small population of consecutive glucuronidation were unique features of aspen GX and observed for the first time in a hardwood species. Different patterns of relative abundance of xylan motifs were evident in alkaline and subcritical water extracts, correlating with GX interaction with lignin and cellulose and providing new insight into the supramolecular organization of cell wall polymers in a hardwood species. This has fundamental implications for overcoming the lignocellulose recalcitrance during biochemical conversion. Our study also provides evidence for the evolution of GX structure in hardwood species.



[1] Martínez-Abad A., Giummarella N., Lawoko M., & Vilaplana F., *Green Chemistry*, 20, 2534–2546, 2018



DEVELOPMENT OF CHITOSAN DERIVATIVES FOR ANALYTICAL APPLICATION IN CAPILLARY ELECTROPHORESIS

Irene Tagliaro^{1*}, Nadia Maria Porpiglia², Beatrice Pellegrin^{1,3}, Arianna Alessi^{1,3}, Franco Tagliaro², Laura Russo^{4,5}, Francesca Cadamuro⁴, Giacomo Musile², Carlo Antonini¹, Sabrina Bertini³

¹ Department of Materials Science, University of Milano - Bicocca, Milano, 20125 Milan, Italy

² Unit of Forensic Medicine, Department of Diagnostics and Public Health, University of Verona, Verona, Italy. Address: Piazzale L. A. Scuro, 10 - 37134 Verona (VR) Italy

³ Istituto di Ricerche Chimiche e Biochimiche G. Ronzoni, Carbohydrate Science Department, 20133 Milan, Italy

⁴ Department of Biotechnology, University of Milano - Bicocca, Milano, 20125 Milan, Italy

⁵ CÚRAM SFI Research Centre for Medical Devices, National University of Ireland Galway, H92 W2TY, Ireland (L.R.)

*presenting author: irene.tagliaro@unimib.it

Protein analysis by capillary electrophoresis is an established benchmark technique, where electrophoretic separation performances are frequently affected by protein adsorption on capillary walls. The protein-wall interaction can be suppressed or mitigated by the application of the so-called dynamic coating agents. In this study, the potential of chitosan derivatives as dynamic coating was investigated, targeting the separation of the carbohydrate deficient transferrin (CDT), a relevant biomarker in forensic analyses to detect chronic alcohol abuse. To this aim, chitosan was derivatized through different chemical reactions, including nucleophilic substitution, reductive amination, and condensation reaction, to provide different characteristics to the dynamic coatings. After chemical and physical characterization, chitosan derivatives were tested as dynamic coating additives in the buffer separation solution of CDT. Evidence of the improvement in the CDT separation efficiency were found applying PEG-modified chitosan via nucleophilic substitution (Figure 1).

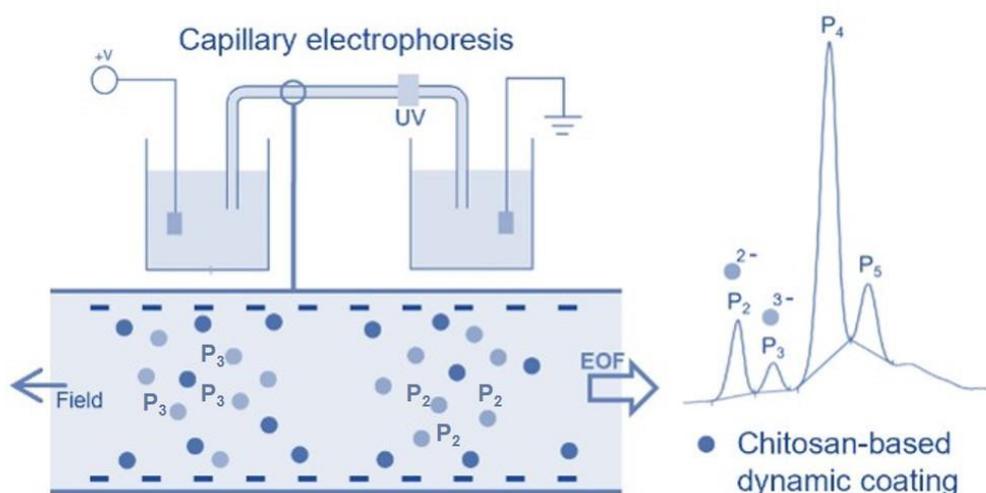


Figure 1 : Effect of derivatized chitosan dynamic coatings on the separation of human transferrin (hTf) glycoforms: disialo-hTf (P2), trisialo-hTf (P3), tetrasialo-hTf (P4), pentasialo-hTf (P5).



$^1\text{H}\rightarrow^{13}\text{C}$ POLARIZATION TRANSFER KINETICS TO INVESTIGATE INTERACTIONS IN POLYSACCHARIDE ASSEMBLIES

X. Falourd^{a*}, V. Aguié-Beghin^c, C. Rondeau-Mouro^b, M. Lahaye^a

a INRAE, UR1268 BIA, F-44316, Nantes, France

b INRAE, UR1466 OPAALE, 17 Avenue de Cucillé, CS 64427, F-35044 Rennes, France

c Université de Reims Champagne Ardenne, INRAE, FARE, UMR A614, 51097 Reims, France.

* xavier.falourd@inrae.fr

The supramolecular structure of polysaccharides is of great interest in many applications, such as in food science [1], in the fields of pharmacology and biological medicine [2] or in biomaterials [3]. Understanding their structure at molecular and supramolecular scales, as well as their hygroscopic properties is essential to develop their use.

Structural and dynamic information of polysaccharide assemblies at the nanometric scale can be assessed by solid state NMR spectroscopy. In particular, the study of the polarization transfer $^1\text{H}\rightarrow^{13}\text{C}$ kinetics allows evaluating different dynamics through relaxation times measurements that are sensitive to non-covalent interactions, including hydrogen bonds between polysaccharides but also with water.

The VCT-CPMAS (Variable Contact Time-Cross Polarization Magic Angle Spinning) sequence used to assess molecular dynamics ($T_{1\rho}^{\text{H}}$, T_{HH} spin diffusion time) in solids is generally underused due to time constraints. Moreover, extraction of the dynamical parameters from the experimental data relies on several complex mathematical models. An optimized VCT-CPMAS experimental and processing pipeline was developed [4] and applied to explore the network of non-covalent bonds in more or less hydrated cellulose-hemicellulose and starch assemblies.

By comparing cellulose from several origins and types at various hydration levels, we demonstrated that different T_{HH} were associated with distinct water locations [5]. We now report that extension of this approach to starch from different botanical origins was also able, associated with classical ^{13}C CPMAS and XRD, to distinguish the impact of water on starch ultrastructure. Furthermore, applied to binary and ternary assemblies of cellulose (with glucomannan and eventually coniferyl acid), our method allowed evaluating the more or less hygroscopic character of each component of these assemblies.

Overall, VCT-CPMAS NMR spectroscopy proved to be a powerful mean for studying interactions in macromolecular assemblies at a nanometer scale that complements other classical methods, as QCM-D or contact angle determination that provide information at the millimeter scale. With the example of different complex polysaccharide assemblies, we were able to define three different spin diffusion times (T_{HH}) which provide information on the localization of water and their involvement in the hydrogen bond network of the assemblies. This method will provide a better understanding of polysaccharides organization at the molecular level and their relationship with water.

[1] Yang X., Li A., Li X., Sun L., & Guo Y., *Trends in Food Science & Technology*, 102, 1-20, 2020.

[2] Mohammed A., Naveed M., & Jost N., *Journal of Polymers and the Environment*, 29, 2359-2371, 2021.

[3] Luo M., Zhang X., Wu J., & Zhao J., *Carbohydrate Polymers*, 266, 118097-118115, 2021.

[4] Falourd X., Lahaye M., & Rondeau-Mouro C., *MethodsX*, 9, 101914-101925, 2022.

[5] Falourd X., Lahaye M., & Rondeau-Mouro C., *Carbohydrate Polymers*, 298, 120104-120115, 2022.



MONITORING NANOCELLULOSE CRYSTALLITE FUSION DURING COLLOID CONDENSATION

Doi Y.*^a, Daicho K.^b, Isobe N.^c, Tanaka R.^d, Kimura S.^e, Fujisawa S.^a, Saito T.^a

^a *Pulp and Paper Science Laboratory, The University of Tokyo, Japan*

^b *Thermal Energy Engineering Laboratory, The University of Tokyo, Japan*

^c *Biogeochemistry Research Center, Japan Agency for Marine-Earth Science and Technology, Japan*

^d *Polysaccharides Chemistry Laboratory, Forestry and Forest Products Research Institute, Japan*

^e *Polymeric Materials Laboratory, The University of Tokyo, Japan*

* doi-yoshinori565@g.ecc.u-tokyo.ac.jp

The crystallinity of cellulose decreases when bundled microfibrils are dispersed in water as cellulose nanofibers (CNFs) or physically separated into finer nanoscale fibrils or single microfibrils. [1] The crystallinity of these CNFs is recovered when they become densely assembled through the dehydration of the dispersion. [2] In this process, multiple CNFs are assumed to partially fuse, leading to the enlargement of crystallite widths. The mechanism of this CNF fusion is, however, not well understood. In this study, the recovery process of the crystallinity of CNFs was monitored by sampling wet CNF gels during condensation from a dilute dispersion to a dense aggregate, followed by wide-angle X-ray diffractometry (WAXD) and solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy analyses after supercritical drying.

In the WAXD analysis, a two-step enlargement in the (2 0 0) crystal size was observed: the first step was a rapid increase in the range of solid content up to 1%, followed by a gradual increase in the range of 1–85% (Figure 1a). The crystallinity index estimated by NMR hardly changed in the range of 0.5–30% but gradually increased in the range of 30–85% (Figure 1b). A portion of the CNF samples, without drying, were also subjected to small-angle X-ray scattering and viscoelasticity analyses, indicating that the inter-CNF contact points in water significantly increased until reaching a solid content of 1%, and then at solid contents higher than 1%, the contact areas of each point gradually expanded. Finally, a mechanism of CNF fusion was proposed based on these results.

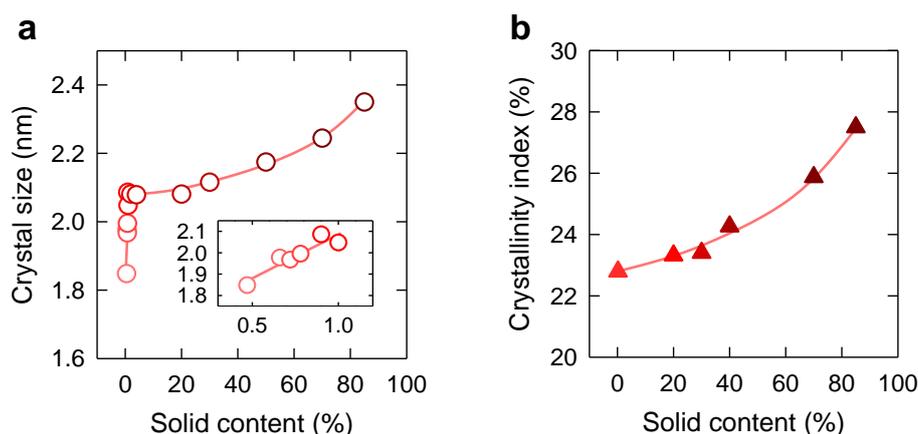


Figure 1 : **a** (2 0 0) crystal size, **b** crystallinity index values of supercritical dried CNF samples

[1] Daicho K., Kobayashi K., Fujisawa S. & Saito T., *Angew. Chem. Int. Ed.*, 60, 24630-24636, 2021

[2] Daicho K., Saito T., Fujisawa S. & Isogai A., *ACS Appl. Nano Mater.*, 1, 5774-5785, 2018



BETA-GLUCAN-RICH EXTRACTS FROM SEVERAL MUSHROOM SPECIES: COMPOSITION, STRUCTURAL PROPERTIES AND IMMUNOSTIMULATORY ACTIVITY

Zaida Pérez-Bassart^a, Christine Bäuerl^b, Maria Jose Fabra^a, Antonio Martínez-Abad^a, Maria Carmen Collado^b, Amparo López-Rubio^{a*}

^a Food Safety and Preservation Department, Institute of Agrochemistry and Food Technology (IATA-CSIC), Valencia, Spain

^b Biotechnology Department, Institute of Agrochemistry and Food Technology (IATA-CSIC), Valencia, Spain

* amparo.lopez@iata.csic.es

Aqueous fractions (FA) and purified aqueous fractions (FAp) from various *Pleurotus* species and from the stipes of *P. ostreatus* were obtained and their macromolecular composition, structure and physicochemical properties were characterised using a broad range of analytical techniques. The carbohydrates present in the aqueous extracts significantly differed in terms of monosaccharide composition, molecular weight (Mw), thermal stability and β -glucan content. Different cell culture models including epithelial NF- κ B-pathway reporter cell lines and, also, THP-1 differentiated macrophages were used to evaluate the immunostimulatory activity of the different *Pleurotus*-derived extracts.

Very good yields were obtained for the aqueous fractions (FA) of the various *Pleurotus* species (ranging between ~27 and 42%). In contrast, a significant lower extraction yield was obtained from *P. ostreatus* residue (stipe) (~17%), probably ascribed to its more recalcitrant nature. The β -glucan content varied from less than 10% to more than 60% and significantly increased after purification, reaching values above 80% for some of the species. The thermal stability and molecular weight profile pointed out to rather different β -glucan structures, further confirmed through NMR and linkage analysis.

Interestingly, these structural differences also resulted in different functional activity of the extracts. Dectin-1 is still considered the most relevant receptor for β -glucan signalling and TLR4 was recently described to synergistically enhance the effects of β -glucan on immune cells [1]. Therefore, a human TLR4 reporter cell line was used to test for NF- κ B activation mediated by TLR4 in both, the presence and absence (basal condition) of the pro-inflammatory TLR4 ligand LPS. Two of the tested extracts could modulate LPS-induced NF- κ B activation, showing a significant anti-inflammatory effect, thus highlighting the potential of these specific fungal fractions as a natural anti-inflammatory extract obtained through a simple and green method. Without the pro-inflammatory LPS, β -glucan FA and FAp exerted varying effects on TLR4 with strong and significant activation of FA and FAp extracts from *P. ostreatus* species (both from the whole mushroom and from the stipes). This strong immunostimulatory activity of *P. ostreatus* FA and FAp was also observed in THP-1 macrophages inducing large amounts of the pro-inflammatory chemokine IL-8 under basal conditions, while five of the tested extracts showed a significant anti-inflammatory effect that reduced LPS-induced IL-8 secretion.

This work thus sets the basis for obtaining new nutraceuticals derived from mushroom biomass.

[1] Kanjan, P., Sahasrabudhe, N. M., de Haan, B. J., & de Vos, P. (2017). Immune effects of β -glucan are determined by combined effects on Dectin-1, TLR2, 4 and 5. *Journal of Functional Foods*, 37, 433–440. <https://doi.org/10.1016/j.jff.2017.07.061>.



SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF WATER INSOLUBLE ALPHA-GLUCANS FROM LACTIC ACID BACTERIA

Ernst L.*^a, Offermann H.^a, Schulz C.^a, Werner A.^a, Müller O.^a, Wefers D.^a

^a*Institute of Chemistry, Food Chemistry – Functional Food, Martin Luther University Halle-Wittenberg, Germany*

*luise.ernst@chemie.uni-halle.de

Lactic acid bacteria produce a broad range of α -glucans, which are synthesized by glucansucrases from sucrose. The most common type are dextrans which are composed of 1,6-linked α -D-glucopyranoses and can be branched at position O2, O3, or O4. Several organisms are also able to form water insoluble glucans, which are characterized by consecutive 1,3-linkages in addition to 1,6- and 1,3,6-linkages. Due to their versatile structures, their simple synthesis by microorganisms or recombinant glucansucrases as well as their occurrence in fermented foods and biofilms, these water insoluble α -glucans are interesting biomaterials. However, detailed knowledge of their structure is limited, but important for potential applications or for investigations on their impact in food and other biological systems. Therefore, the aim of our study was to systematically investigate the structure of a variety of water insoluble α -glucans by various analytical tools.

For this purpose, we synthesized 12 water insoluble α -glucans from different lactic acid bacteria, either by fermentation with the microorganisms or by using recombinant glucansucrases. The obtained glucans were first analyzed for their glycosidic linkage composition by methylation analysis. Because the results may vary depending on the applied ultrasonic treatments and conditions used during hydrolysis, we investigated the influence of these factors on the results obtained for water insoluble α -glucans and other homoexopolysaccharides [1]. For the analysis of the molecular weights, the glucans were dissolved in dimethyl sulfoxide and analyzed by size exclusion chromatography with refractive index detection. Furthermore, we used partial enzymatic hydrolysis to investigate the individual segments of the polysaccharides. By using *endo*-dextranase to hydrolyze the 1,6-linked dextran segments, we were able to isolate and further analyze the remaining water insoluble segments. The application of mutanase to hydrolyze 1,3-linked segments released oligosaccharides which were analyzed by high performance anion exchange chromatography with pulsed amperometric detection.

The yields depended strongly on the production system, but after different clean-up steps, very pure polysaccharides were obtained. The investigated water insoluble α -glucans had different portions of 1,3-linkages besides 1,6-linkages and contained 1,3,6-linked glucose units, however, polysaccharides which were exclusively composed of 1,3- and 1,6-linkages were also obtained. Furthermore, some glucans additionally contained 1,4-linkages. Results from size exclusion chromatography showed varying molecular weight distributions for the investigated water insoluble glucans. Water insoluble fragments obtained by *endo*-dextranase hydrolysis were mainly 1,3-linked, but also contained branched units. Water soluble oligosaccharides, isolated after mutanase hydrolysis of the water insoluble α -glucans, were identified as 1,3-linked nigero-oligosaccharides.

Our results show that water insoluble bacterial α -glucans are complex copolymers which have a broad range of linkage type composition and a varying architecture of their building blocks.

[1] Ernst L., Werner A. & Wefers D., *Carbohydrate Polymers*, 308, 120643, 2023



IN-SITU X-RAY ANALYSIS OF COLD ALKALI DISSOLUTION OF CELLULOSE PULPS OF VARIOUS ORIGIN

Wojtasz-Mucha J^{*a}, Yu S.^b, Bengtsson J.^b, Ulmefors H.^b, Östlund Å.^c, Bernin D.^a

^aChemistry and Chemical Engineering, Chalmers University of Technology, Sweden

^bRISE Research Institutes of Sweden, Sweden

^cTreeToTextile AB, Sweden

* wojtasz@chalmers.se

The global textile fiber production exceeded 100 million tons annually and is constantly increasing. Currently the fossil-based synthetic fibers take the biggest market share, followed by cotton. However, as cotton cultivation is reaching its maximal capacity the demand for cellulosic man-made fibers (eg. Viscose, Lyocell) is growing. There is a need for bio-based, sustainable and inexpensive textile fibers, both to meet the huge demand and for replacement of fossil-based fibers. Therefore, both alternative production methods and sources of cellulose are of great interest.

In this study various cellulose residues were explored as plausible future sources for cellulose dissolving pulp production. The dissolution rate and the ability for the cellulose molecule shows a high dependency on its origin, e.g. plant species and the pretreatment steps. A well-studied dissolution system is the cold sodium hydroxide ($\text{NaOH}_{(\text{aq})}$) solution [1]. This solution is non-toxic, inexpensive (due to high recovery rate), and already used within the pulping industry. It then becomes economically attractive and scientifically interesting to establish a comprehensive understanding of $\text{NaOH}_{(\text{aq})}$ dissolution strategy which works for a broad selection of cellulose origins.

The cellulose- $\text{NaOH}_{(\text{aq})}$ solutions have been studied for a long time, however the dissolution mechanism has still not been fully understood. It is proposed to be enabled by the breakage of hydrophobic interactions and partial deprotonation of the cellulose hydroxyl groups [2]. Swelling of the cellulose structure is the initial step during dissolution, and the degree of swelling has previously been found to differ depending on the temperature of solution [3]. Common methods for studying the solution state, such as rheology, can characterize the state of the final solution, however, do not give insight into the course of the dissolution process. Characterization of cellulose- $\text{NaOH}_{(\text{aq})}$ dissolution using small angle X-ray scattering (SAXS) has been reported in the literature, but are often based on pre-mixed samples of MCC as a model for cellulose [4,5].

To capture the disintegration of the crystalline structure of cellulose during dissolution in-situ synchrotron X-ray characterization (SAXS and WAXS) was applied. Moreover, the X-ray measurements were complemented with NMR measurements and optical microscopy. In order to have a broad approach a range of cellulose origins were investigated and compared with commercially available cellulose.

[1] Sobue H., Kiessig H., *Zeitschrift für Physikalische Chemie*, 43, 309-328 (1939)

[2] Budtova T., and Navard P., *Cellulose* 23, 5-55 (2016)

[3] Gunnarsson M., Hasani M., Bernin D., *Cellulose* 26, 9403-9412 (2019).

[4] Martin-Bertelsen B., Andersson E., Köhnke T., Hedlund A., Stigsson L., Olsson U., *Polymers* 12, 342 (2019)

[5] Swensson B., Lages S., Berke B., Larsson A., and Hasani M., *Carbohydrate Polymers* 274, 118634 (2021)



3D IMAGING AND STRUCTURAL INFORMATION OF THE CHIRAL NEMATIC PHASE OF CELLULOSE NANOCRYSTALS (CNC) BY SECOND HARMONIC GENERATION (SHG) MICROSCOPY

Legat T. ^{*a,b}, Thielemans W.^a, Van Cleuvenbergen S.^b

^a Sustainable Materials Lab, Department of Chemical Engineering, KULAK, KULeuven Etienne Sabbelaan 53, Kortrijk 8500, Belgium.

^b Department of Chemistry, Molecular Imaging and Photonics, KULAK, KULeuven Etienne Sabbelaan 53, Kortrijk 8500, Belgium

* Thibaut.legat@kuleuven.be

In this work, we exploit the inherent confocal effect of Second Harmonic Generation (SHG) microscopy to acquire highly resolved 3D images of the chiral nematic phase of CNCs in a label-free manner. Polarization dependency tests were performed and it was found that the observable response was in accordance with a single dominant tensor component along the director axis of the (chiral) nematic liquid crystal planes. Rotation of the director results in variations in SHG intensity which can be readily linked to the helical pitch. This allowed us to render high contrast 3-dimensional models of the aligned liquid crystals providing unprecedented detail into their structure. Local alignment, morphology and the presence of defects are readily revealed. 3D-FFT analysis enabled the full characterization of the periodicity of the helicoidal structures. We could also obtain a more precise estimate of the helicoidal pitch and identify preferred directions within the investigated volume in comparison to conventional 2D FFT analysis. This work illustrates the numerous benefits of using SHG microscopy for visualizing CNC chiral nematic systems directly in the suspension-liquid state phase. Additionally, by offering a framework for interpreting the images obtained through this technique, we foresee that SHG microscopy will find diverse applications for characterizing various types of aligned CNC structures. [manuscript]

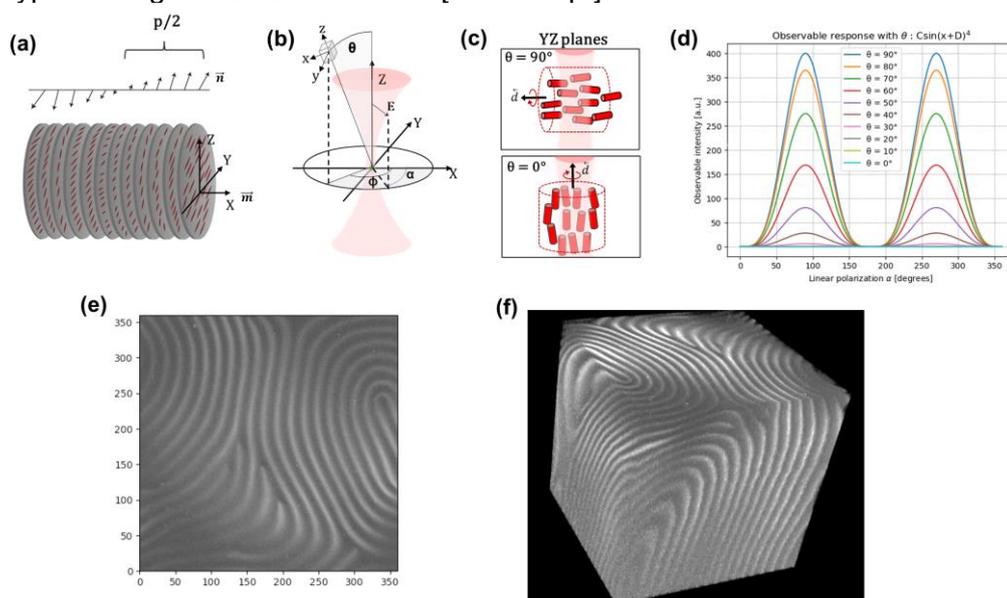


Figure 1: **(a)** Illustration of the chiral nematic alignment of the CNCs, the director (\vec{n}) rotates around the helical axis (\vec{m}) which is along the X axis in a cartesian coordinate system **(b)** Schematic of the angles defining the measuring setup. **(c)** Two YZ planes illustrations of the average orientation of the CNCs in chiral nematic arrangement for angles $\theta = 0^\circ$ and $\theta = 90^\circ$ **(d)** modulated zzz dominant SHG response for varying directors **(e)** 2D SHG **(f)** 3D SHG by SHG focus stacking



APPARENT DEGREE OF POLYMERIZATION OF XANTHAN AND THE CORRELATION TO CALORIMETRIC ENTHALPY

Wintersteller P. ^{*a}, Huber A. ^a

^a *Institute of Chemistry, University of Graz, Austria*

* peter.wintersteller@uni-graz.at

Xanthan is a material that in many ways can be considered a model substance for molecular level tailored materials: twisting a cellulose-type backbone from basically beta-sheet conformation into a helical conformation by introducing charged tri-saccharide branches. Additionally, xanthan is a microbial exo-polysaccharide, and hence, produced on micro-scale by bacteria open for tuning by specific cultivation or genetic modifications of these organisms. In aqueous media xanthan forms hydrocolloidal systems, a screening delivers polymer- and hydrocolloidal characteristics to correlate molecular-level and hydrocolloidal characteristics with controlled material performance. [1]

The degree of polymerization (dp) of xanthan gum is typically used for the calculation of energetic material characteristics. Due to the strong ability of xanthan to form aggregates one determines less reliable apparent values.

A unique alternative approach is to correlate the degree of polymerization with the oxidation enthalpy of building blocks of various homo- and hetero exopolysaccharides (EPS). The oxidation enthalpy depends on patterns of oxidation and substitution plus width of degree of polymerization and molar mass distributions.

With this approach, information on the kind of resulting associates and colloidal objects, the oxidation enthalpy can be correlated with the apparent mean degree of polymerization distributions, obtained at various conditions by AF4 (asymmetric flow field flow fractionation) and SEC (size exclusion chromatography) for the heterogeneous and homogeneous partitions of XWM-systems (xanthan-watermodifier-systems). [2]

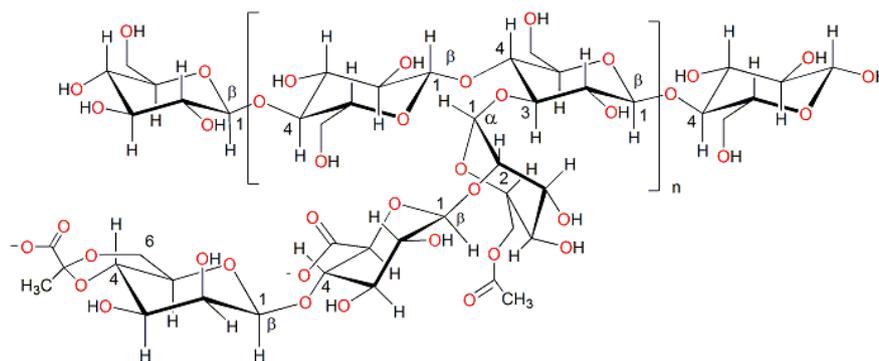


Figure 1: Xanthan repeating unit: β (1 \rightarrow 4) D-glucoses with α (1 \rightarrow 3) linked triose-branches consisting of a partially (60-70%) C6-acetylated mannose β (1 \rightarrow 2) connected glucuronic acid and another optionally (30-40%) C4-pyruvate derivatized β (1 \rightarrow 4) linked mannose.

[1] Morris G. and Harding S., Polysaccharides, Microbial: 482-494., 2009

[2] Wintersteller P., Muriqi A., Bajrami D., Hoti G., Huber A., Current Advances in Biopolymer Processing and Characterization, Chapter 4, Xanthan in aqueous media: Molecular and Hydrocolloidal Characteristics, 2017



EXTRACTION AND CHARACTERIZATION OF PRIMARY CELL WALL XYLOGLUCAN FOR THE SYNTHESIS OF REINFORCING AGENTS FOR CELLULOSIC MATERIALS

Josselin Mante ^{*a,b}, Julien Leguy ^a, Laurent Heux ^b

^a FunCell 601 rue de la Chimie, 38610 Gières, France

^b CERMAV, CNRS, Univ Grenoble Alpes, (UPR 5301), Saint Martin d'Hères, France

* josselin.mante@funcell.fr / josselin.mante@cermav.cnrs.fr

In a context of emancipation from hydrocarbons for obtaining materials, one of the alternatives is the recovery of waste from the food industry via the extraction of natural polymers and in particular polysaccharides. The challenge lies in the complexity of the plant cell walls, which leads to difficulties in isolating and characterizing these carbohydrates. Hemicelluloses are a family of natural polymers that have the particularity of having a very variable chemical structure. Among them, xyloglucan (Xg) is the hemicellulose that constitutes 15 to 20% of the primary walls of dicots [1]. Although widely cited in academic works for its physicochemical properties in association with cellulose, few works allow to characterize the diversity of primary cell wall xyloglucans as a polymer depending on their origin and extraction procedures.

We investigate the structural diversity of xyloglucan from different sources. We established well controlled extraction and purification processes, to obtain highly pure fractions of xyloglucans. Using liquid and solid-state NMR, ion exchange chromatography (Figure 1) and permethylation sugar component analysis, we deciphered the structural differences between xyloglucans of three different origins and investigated their physico-chemical properties. One goal is to compare xyloglucans' structures depending on the extraction conditions used and discuss structure-properties relationships.

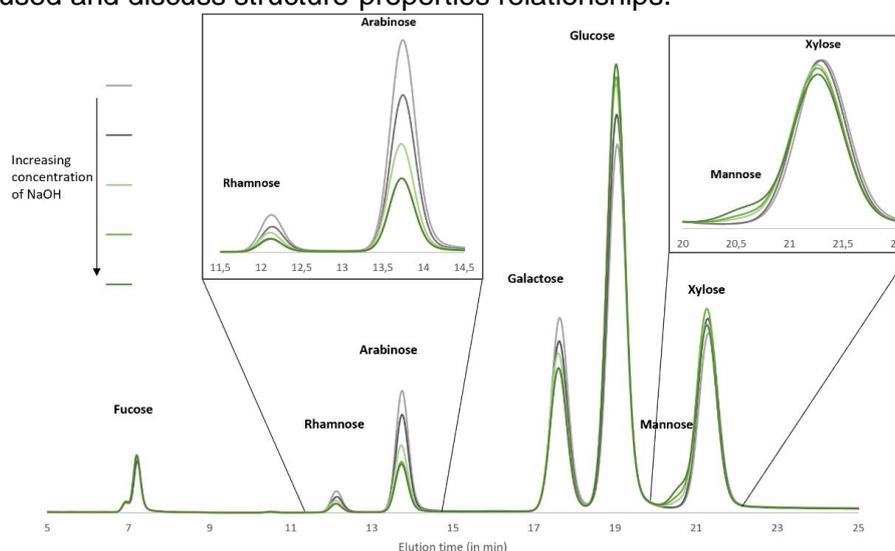


Figure 1 : Osidic compositions of primary cell wall xyloglucan fraction by ionic chromatography, depending on concentrations of sodium hydroxide used

[1] Scheller, H. V.; Ulvskov, P. *Annu. Rev. Plant Biol.* 61 (1), 263–289, 2010

[2] Jean, B., Heux, L., Dubreuil, F., Chambat, G., & Cousin, F., *Langmuir*, 25(7), 3920-39236, 2009



RE-INVESTIGATING DEHYDRATION REACTIONS DURING THERMOSTABILIZATION OF CELLULOSE FIBERS BY SOLUTION STATE NMR

Lukas Fliri,^{a,*} Chamseddine Guizani,^{a,b} Minjeong Jang,^{c,d} Sung-Soo Kim^c and Michael Hummel^a

^a Department of Bioproducts and Biosystems, Aalto University, P.O. Box 16300, FI-00076, Espoo, Finland

^b VTT Technical Research Centre of Finland, Tietotie 2, FI-02150 Espoo, Finland

^c Carbon Composite Materials Research Center, Korea Institute of Science and Technology, 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeollabuk-do 55324, Republic of Korea

^d School of Chemical Engineering, Jeonbuk National University, 567 Baekje-daero, Jeonju-si, Jeollabuk-do 54896, Republic of Korea

* email of presenting author: lukas.fliri@aalto.fi

Although cellulosic fibers were one of the first starting materials in carbon fiber production, nowadays they got effectively replaced by fossil-fuel based precursors like polyacrylonitrile (PAN) or pitch. A major reason for this shift can be found in the intrinsically low char yields upon cellulose carbonization, which also impair the resulting fibers' properties. This is due to a competing pyrolysis pathway leading to the formation of levoglucosan and other low molecular weight volatile products. It is known that different chemical pre-treatment strategies or low heating rates / isothermal treatments in the temperature range of 150 °C – 250 °C can significantly increase the char yields of cellulosic materials. This effect was ascribed to dehydration along the cellulose backbone and crosslinking reactions during “low temperature” stabilization. However, despite the longstanding research interest the occurring reactions and the mechanistic background are still controversially discussed and not generally agreed on. Several partly contradicting proposals can be found in literature, often only attempting to describe the process on a kinetic basis. We were interested in obtaining a better understanding of the structures formed in the solids after thermostabilization to develop new entry points for chemical pretreatment strategies to enhance the char yield. For this endeavor we applied a solution state NMR protocol relying on a tetra-*n*-butylphosphonium acetate ([P₄₄₄₄][OAc]) – DMSO-*d*₆ (1:4 wt%) electrolyte to re-examine isothermally heat-treated cellulosic materials in the temperature range of 150 °C – 250 °C. 2D HSQC and HMBC NMR experiments clearly evidenced the formation of levoglucosan moieties at the reducing ends – formed through depolymerization of the cellulose backbone – as first and major occurring reaction. Both the depolymerization and an expected thermal re-polymerization of the levoglucosan containing fragments were also visible in complementarily conducted size exclusion chromatography (SEC) measurements. However, these reactions are known to be reversible, cannot explain the dehydration and are more commonly connected to the expulsion of levoglucosan during pyrolysis [1]. Samples treated at 250 °C for longer periods of time showed the formation of an additional phase, insoluble in both the NMR electrolyte and the SEC dissolution medium. This agreed with previous similar investigations where a so called “condensed thermostable phase” formed and even resisted hydrolysis with concentrated hydrochloric acid [2]. The appearance of this phase also coincided with emerging carbonyl bands in FTIR spectroscopy. We surmise that the observed “thermostable phase” is the consequence of dehydration reactions and ultimately responsible for char formation at higher temperatures. However, given that this phase showed a drastically different dissolution and hydrolysis behavior compared to cellulose, it seems unlikely that it consists of simply dehydrated polysaccharidic moieties.

[1] Kawamoto H., *Current Organic Chemistry*, 20 (23), 2444-2457, 2016.

[2] Pastorova I., Arisz P.W. & Boon J.J., *Carbohydrate Research*, 248, 151-165, 1993.



DISCLOSING BREWER'S SPENT YEAST POLYSACCHARIDES TOWARDS THE IMPACT ON INNATE IMMUNE SYSTEM RESPONSE

Bastos R.^a, Lima T.^b, Marin-Montesinos I.^c, Ferreira S.S.^a, Mentink-Vigier F.^d, Sardo M.^c, Mafra L.^c, Vilanova M.^{b,e,f}, Coimbra M.A.^a, Coelho E.^{*a}

^a REQUIMTE-LAQV, Department of Chemistry, University of Aveiro, Portugal

^b I3S, Institute for Research in Innovation in Health, University of Porto, Portugal

^c CICECO, Department of Chemistry, University of Aveiro, Portugal

^d National High Magnetic Field Laboratory, Tallahassee, Florida, United States of America

^e IBMC, Institute for Molecular and Cell Biology, University of Porto, Portugal

^f ICBAS, School of Medicine and Biomedical Sciences, University of Porto, Portugal

* ecoelho@ua.pt

Brewer's spent yeast (BSY) is the second major by-product of the brewing industry. BSY polysaccharides have gained particular interest for biomedical applications. [1] BSY polysaccharides, namely glucans and mannoproteins, are present in the cell walls that undergo modifications during the brewing process. [2] This work aimed to disclose glucan structural features of industrial *Saccharomyces pastorianus* BSY and their impact on innate immune system response, exploiting therefore the BSY potential for biomedical applications. *S. pastorianus* cell wall glucans were isolated through sequential alkali extractions. The BSY residue left upon 4M KOH extraction was mainly composed of glucose (96 mol%), (1→4)- and (1→3)-linked (57.8 and 16.3 mol%), with (1→4,6)-Glc (4.9 mol%) and (1→3,6)-Glc (3.0 mol%) branching points. Magic-angle spinning dynamic nuclear polarization (MAS-DNP) NMR showed the covalent linkage of (β1→3)-glucans to glycogen through a (β1→4)-linkage. Hydrolysis with zymolyase, cellulase, and lichenase solubilize high molecular weight (HMW) fractions of glycogen, while amylase yielded HMW of mannoproteins. Zymolyase hydrolysate (94.3% of sugars; 74 mol% of (1→4)-Glc), analysis by liquid state and MAS-DNP NMR, evidenced that β-Glc linked residues can occur as glycogen branches at C6 position, including terminal β-Glc, (β1→3), and (β1→6)-glucans. It was also found evidence of covalent linkage between (α1→4) and (β1→6)-glucans through (α1→6) glycosidic linkage. HPAEC-PAD analysis of enzymatic released oligosaccharides confirmed the covalent linkage of (α1→4)-glucans with (β1→3)-, (β1→6)-, and (β1→4)-glucan motifs.

Upon alkali or subcritical water extractions of BSY, a residue with a preserved 3D structure was obtained as a porous microcapsule. The diameter of microcapsules ranged on average between 3-4 μm and they had a negative surface charge potential (-5.2 to - 13.2 mV). Using a reporter cell line that overexpresses Dectin-1 (β1,3-glucan receptor), all microcapsules were able to promote receptor activation. Innate immune system response to BSY microcapsules was evaluated using murine (BMDC) and monocyte-derived dendritic cells (mdDC). All microcapsules were able to promote the expression of cell maturation markers and the activation of BMDC and mdDC, leading to the secretion of proinflammatory cytokines. Moreover, BSY microcapsules were successfully uptake by mdDC, supporting their potential as carriers for drug delivery and targeted immunotherapy applications. The polysaccharide network forms resistant and glucan balanced microcapsules, which are able to be recognized and uptake by dendritic cells, supporting the development of target BSY drug delivery systems.

[1] Bastos R., Oliveira P.G., Gaspar V.M., Mano J.F., Coimbra, M.A., & Coelho, E., *Carbohydrate Polymers*, 277, 118826, 2022.

[2] Bastos R., Coelho, E. & Coimbra, M.A., *Carbohydrate Polymers*, 124, 322-330, 2015.

The authors acknowledge the FCT/MEC financial support of project Yeast4FoodMed (POCI-01-045-FEDER-030936), LAQV/REQUIMTE (UIDB/50006/2020), and CICECO (UIDB/50011/2020) through national funds, co-financed by the FEDER, within PT2020 Partnership Agreement. R Bastos was supported by FCT (PD/BD/114579/2016), I M-Montesinos by GAS2MAT-DNPSENS (POCI-01-0145-FEDER-028), and E Coelho thanks the research contract (049-88-ARH/2018) funded by national funds (OE), through FCT, Decree-Law 57/2016. National NMR Network partially supported by Infrastructure Project 022161.



MICROBIAL CAPSULAR POLYSACCHARIDES AND THEIR STRUCTURE-SHAPE-ACTIVITY

Corsaro M.M.^{a*}, Casillo A.^a, Schiraldi C.^b, Paduano L.^a

^aDepartment of Chemical Sciences, University of Naples Federico II, Naples, Italy

^bDepartment of Experimental Medicine, University of Campania "Luigi Vanvitelli", Naples, Italy

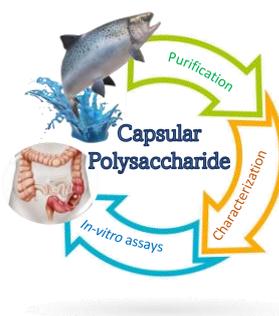
* corsaro@unina.it

The majority of bacteria display on their surface, as prevailing features, glycoconjugates. Among these, capsular polysaccharides are usually retained on the cellular surfaces through intermolecular forces or covalently linked to a lipid portion in Gram-negative microorganisms or the peptidoglycan in some Gram-positive ones. [1]

Some capsular polysaccharides play a critical role during the mechanism of microbial virulence and for this reason, they are considered the target for vaccine formulation. In some other cases, capsules are beneficial for human microbiota and are therefore used as prebiotic substances.

Extremophiles are microbes that experience the limits of life where they thrive, in environments that humans consider extreme. For this reason, they have certainly developed peculiar molecular strategies, including the production of unusual capsular polysaccharides, to cope with harsh environments.

Here we present our data about the primary structure of two different CPS isolated from two cold-adapted Gram-negative bacteria, i.e. *Shewanella vesiculosa* HM13 and *Pseudoalteromonas nigrifaciens* Sq02-Rif^r. Both microorganisms have been isolated from fish living at low temperatures. In addition, experiments on the anti-cancer activity and physicochemical properties of the two polymers will be discussed. [2,3]



[1] Whitfield C., Wear S.S. & Sande C., *Annu. Rev. Microbiol.* 74, 521-543, 2020.

[2] Di Guida R., Casillo A., Stellavato A., Kawai S., Ogawa T., di Meo C., Kawamoto J., Kurihara T., Schiraldi C., Corsaro M. M., *Carbohydr. Polym.* 278, 118908-118917, 2022.

[3] Casillo A., Di Guida R., Cavasso D., Stellavato A., Rai D., Yokoyama F., Kamasaka K., Kawamoto J., Kurihara T., Schiraldi C., Kulkarni S., Paduano L., Corsaro M. M., *Carbohydr. Polym.* 297, 120036-120047, 2022.



COLORIMETRIC SENSORS BASED ON METHYLCELLULOSE/ANTHOCYANINS/CACL₂ FOR MONITORING FISH FRESHNESS

Silva, R. R. A.^a, Otoni, C. G.^a, Mattoso, L. H. C.^{ab*}, Stringheta, P. C.^c, Soares, N. F. F.^c

^a PPGCEM/DEMa, Federal University of São Carlos (UFSCar), Brazil

^b Brazilian Agricultural Research Corporation (EMBRAPA), Brazil

^c Federal University of Viçosa (UFV), Brazil

* luiz.mattoso@embrapa.br

Animal-derived foods, particularly fish, stand out as extremely susceptible to spoilage and to cause human disease. Among the various types of intelligent packaging, sensors using polysaccharides as matrix have been developed to identify and inform food contamination, enabling real-time monitoring of the physicochemical factors of foodstuffs. Here, we report on a novel methylcellulose-based colorimetric sensor to accurately monitor the freshness of Lambari fish. The ionic strength of the methylcellulose solution was adjusted using CaCl₂ at 0 (control), 25, 50, 250, and 500 mM to, after casting and drying, absorb moisture and plasticize the solid-state matrix. To the film-forming formulation, açai phenolic extract was incorporated at 2 vol.% to serve as signal detector and transducer.^[1] The materials were characterized structurally by Fourier-transform infrared (FTIR) spectroscopy, mechanically by uniaxial tensile test, and sensing efficiency through *in vitro* volatile ammonia (NH₃) detection and real-time storage monitoring assays of actual Lambari fish.

As the ionic strength increased from 0 to 500 mM, the greater equilibrium moisture content (confirmed by FTIR) led to an absolute increase in elongation (from 41 to 120%) and a decrease in Young's modulus (from 1.09 GPa to 3.7 MPa), confirming the indirect plasticizing effect of CaCl₂. Moreover, increasing the ionic strength enhanced the detection sensitivity of NH₃ and total volatile basic nitrogen (TVB-N). The colorimetric change in the control sensor was perceptible to the human eye after 20 min (Figure 1a). In contrast, for sensors with 500 mM CaCl₂, this human perception threshold was reduced to 5 min, reaching a total color difference ΔE^* greater than 3.0 (Figure 1b). Furthermore, sensor irreversibility—which is relevant against counterfeit—was achieved for ionic strength values above 250 mM and maintained even after 60 days of storage. Finally, using principal component analysis, sensors with 0 and 25 mM were able to classify Lambari fish freshness into three levels (fresh, medium fresh, and spoiled) according to the TVB-N levels required by Brazilian and European legislations. Thus, it can be concluded that the ionic strength and hygroscopicity controlled by the addition of CaCl₂ into anthocyanin-loaded methylcellulose exhibits a dual functionality by acting as a plasticizer and regulating the chromatic properties of the sensor to accurately monitor the quality and safety of foods during their shelf-lives.

Acknowledgement: FAPESP proc. 2018/22214-6.

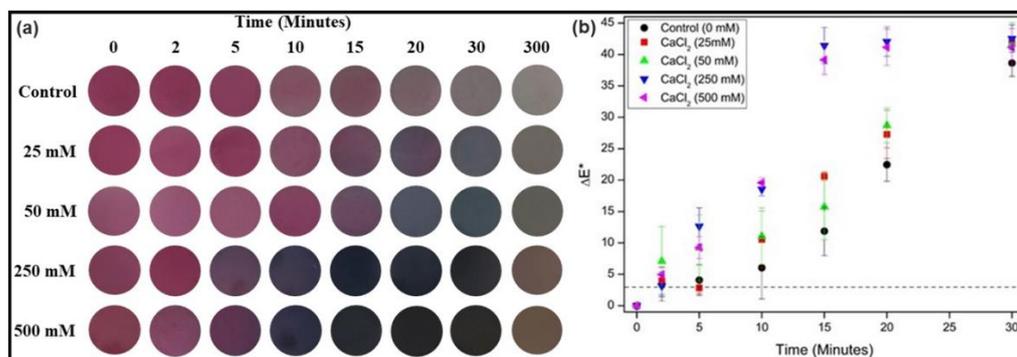


Figure 1: (a) Images of the sensors both before and after NH₃ contact for up to 5 h and (b) total color difference (ΔE^*) upon contact with NH₃ for 30 min in *in vitro* assays.

[1] Silva, R.R.A. et al. *Food Biophysics*, 17, 59–74, 2022.



LIPOSOME SURFACE COATING USING DISTINCT β -GLUCANS FRACTIONS FROM *PLEUROTUS ERYNGII*

Mariana M. de Carvalho,^{1*} Andrea Angelov,¹ Marianne Hiorth,¹ Anne Berit Samuelsen¹

¹, Department of Pharmacy, University of Oslo, P.O.Box 1068 Blindern, NO-0316, Oslo, Norway

*m.m.carvalho@farmasi.uio.no

β -glucans present immunomodulatory activity, making them potential sources for the development of drug delivery platforms targeting to the immune system¹. In that sense, as far as we know, their application as coating materials for liposomes remains to be investigated. Therefore, the present work aims to analyze the ability of different fractions of β -glucans from *Pleurotus eryngii* in coat liposome surfaces. After alkali extraction and solvent fractionation of the fruiting bodies of *P. eryngii*, two polysaccharide fractions named PEA2-SS and PEA2-SP were obtained. From the methylation and 1D,2D NMR analyses it was possible to infer that both fractions contain 1 \rightarrow 3 linked β -glucan branched by a glucose unit at O-6 and 1 \rightarrow 6 linked β -glucan branched by a glucose unit at O-3. Size exclusion chromatography coupled to laser light scattering showed that PEA2-SS and PEA2-SP presents molar mass (Mw) of 7.1 and 36.1 kDa, respectively. Solutions of PEA2-SS and PEA2-SP were used to coat the liposome formulation named LipC (SoyPC: DOTAP) which was synthesized by the thin-film method. The zeta potential, size and PDI were measured by a zetasizer. Both fractions were able to promote a change in the zeta potential from 31.8 mV to approximately 0 mV. An increase in size from 134 nm to 315 and 1249 was observed after the coating of LipC with PEA2-SP and PEA2-SS, respectively. In addition, a lower PDI could be obtained after the coating with PEA2-SP (0.273) compared with PEA2-SS (0.721). Therefore, considering the size distribution, it is possible to infer that the β -glucans with the higher Mw (PEA2-SP) presented a better interaction with the liposome surface when compared to the lower Mw one (PEA2-SS). As another evidence of the importance of Mw, PEA2-SP was submitted to an enzymatic hydrolysis using an endo-1,3-beta-glucanase. The coating of LipC with the degraded LipC-2SP gave rise to a formulation presenting size and PDI of 5311 nm and 0.925, respectively. This result indicates the β -glucans in PEA2-SP had lost their ability in successful coat LipC after depolymerization, suggesting lower Mw is detrimental for the obtainment of a suitable liposome formulation based on β -glucans. Therefore, beta-glucans can be used as source material for coating materials of liposomes. The development of such formulation opens the perspective of the employment of β -glucans as drug delivery systems able to carry both hydrophobic and hydrophilic drugs for the immune system cells. The novel β -glucans coated liposomes could be used in the treatment of infectious diseases, cancer therapy and as vaccine adjuvants. The study of the interaction of the coated liposomes with the immune cell receptors is ongoing.

REFERENCES

(1) Su, Y.; Chen, L.; Yang, F.; Cheung, P. C. K. Beta-d-glucan-based drug delivery system and its potential application in targeting tumor associated macrophages. *Carbohydr Polym* **2021**, 253, 117258. DOI: 10.1016/j.carbpol.2020.117258 From NLM Medline. Lehtovaara, B. C.; Gu, F. X. Pharmacological, structural, and drug delivery properties and applications of 1,3-beta-glucans. *J Agric Food Chem* **2011**, 59 (13), 6813-6828. DOI: 10.1021/jf200964u From NLM Medline.



SOLUTION-STATE NMR IS NOW AN ACCESSIBLE TOOL FOR THE ANALYSIS OF CRYSTALLINE CELLULOSES

Koso T.^{*a}, Fliri L.^b, Heise K.^b, Hummel M.^b, Thielemans W.^c, King A. W. T.^{*a}

^a *Bioinspired Materials Team, VTT Technical Research Centre, Finland*

^b *Department of Bioproducts and Biosystems, Aalto University, Finland*

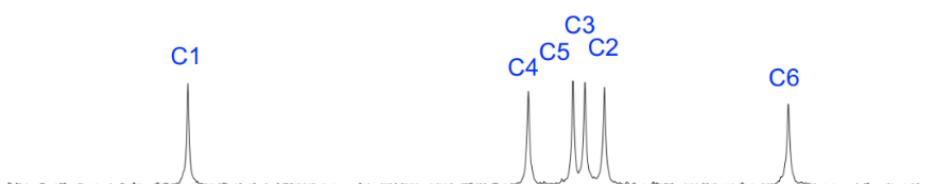
^c *Department of Chemical Engineering, KU Leuven, Belgium*

* tetyana.koso@vtt.fi

Our well-established method of the direct-dissolution of cellulose samples in the tetrabutylphosphonium acetate electrolyte ([P₄₄₄₄][OAc]:DMSO-d₆) is gaining broader application in the solution-state NMR analysis of chemically modified crystalline celluloses [1,2]. While solid-state NMR method is invaluable for the structural peculiarity and crystallinity determinations, it has somewhat limited application accurately specifying chemically modified cellulose analysis. On the other hand, solution-state NMR allows for a huge increase in resolution of signals (Figure 1). This allows us to separate chemical species even at low abundance, such as, reducing end groups of cellulose nanocrystals [3] or surface confined modifications [4]. This is also a valid tool for estimating the processes in well-known reactions of cellulose, including those with other natural derivatives.

The aim of this abstract is to demonstrate this approach to the wider audience, explain benefits of the method and tell about recent advances in this field.

Quantitative solution-state (¹³C) – MCC



Semi-quantitative solid-state (¹³C CP MAS) - MCC

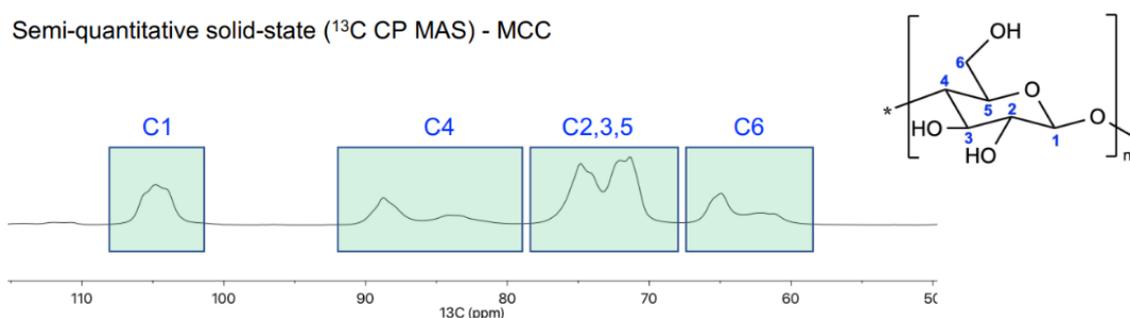


Figure 1. Comparison of solution (top) vs solid (bottom)-state NMR analysis of two common cellulose samples.

[1] Fliri L., Heise K., Koso T., Todorov A., Rico del Cerro D., Hietala S., Fiskari J., Kilpeläinen I., Hummel M., King A. W. T. *Nature Protocols*, in press, **2023**.

[2] King A. W. T., Mäkelä V., Kedzior S. A., Laaksonen T., Partl G. J., Heikkinen S., Koskela H., Heikkinen H. A., Holding A. J., Cranston E. D., & Kilpeläinen I. *Biomacromolecules*, **19**(7), 2708–2720, **2018**.

[3] Heise K., Delepierre G., King A. W. T., Kostianen M. A., Zoppe J., Weder C., Kontturi, E. *Angewandte Chemie International Edition*, **60**(1), 66–87, **2021**.

[4] Koso T., Beaumont M., Tardy B. L., Rico del Cerro D., Eyley S., Thielemans W., Rojas O. J., Kilpeläinen I., King A. W. T. *Green Chemistry*, **24**(14), 5604–5613, **2022**.



IN VITRO BATCH FERMENTATION OF (UN)SATURATED HOMOGALACTURONAN OLIGOSACCHARIDES BY HUMAN INOCULA

Jan Willem Zwolschen^{1*}, Paul Vos² and Henk Schols¹

¹ *Laboratory of Food Chemistry, Wageningen University & Research, Wageningen, The Netherlands*

² *Wageningen Food & Biobased Research, Wageningen, The Netherlands.*

* Janwillem.zwolschen@wur.nl

Pectin, a predominant polysaccharide found in the plant cell wall and a major contributor to the total weight of agricultural waste, has been commended as a promising prebiotic dietary fiber that exerts specific health effects. Such beneficial effects may strongly depend on pectin's molecular weight, methyl-esterification and level and type of neutral sugar side chains. Yet, the health effects and structure function relation of pectin derived galacturonic acid oligosaccharides (GalA-OSs), that can be released from agricultural waste using enzymes, are underexplored. This study aims to further expand on the bioactivity of GalA-OS by revealing the effect of methyl-esterification, Δ 4,5 unsaturation and size on the *in vitro* fermentation of enzymatically produced GalA-OSs. To do so, the utilization, metabolite production and extent of methyl-esterification of saturated (sGalA-OSs) and Δ 4,5 unsaturated GalA-OSs (uGalA-OSs) were monitored during 43h of *in vitro* batch fermentation using adult fecal inoculates of three healthy donors. HPAEC analysis revealed that both sGalA-OS and uGalA-OSs were fermentable at a reduced rate compared to the prebiotic reference fructo-oligosaccharides (FOS) regardless of methyl-esterification. Methyl-esterified GalA-OSs were shown by MALDI-TOF MS and HILIC-LC-MS to ferment at a vastly reduced rate compared to the same mixture of saponified, methyl-ester free GalA-OSs, confirming that methyl-esterification of GalA-OSs hinders fermentation by gut microbiota. Fermentation of sGalA-OS and uGalA-OS substrates induced the production of the short chain fatty acids acetate, butyrate and propionate. Yet, fermentation of uGalA-OSs increased the production of butyrate, while fermentation of sGalA-OS increased the production of propionate. Through 16S rRNA sequencing, it was revealed that this difference in metabolite production was likely a result of the stimulation of distinct microbiota compositions caused by the fermentation of the structurally different substrates. These substrate dependent changes in microbiota composition will be discussed. The results shows that the Δ 4,5 unsaturated bond established at the non-reducing end through β -elimination by pectin lyase plays a part in the bioactivity of galacturonic acid oligosaccharides and should be considered in future pectin structure-function research.



UNRAVELLING THE STRUCTURE-ACTIVITY RELATIONSHIP OF RHAMNOGALACTURONAN-I RICH PECTIN AND GALECTIN-3

Kleijn A.F. ^{*a}, Mutter M.^b, Schols H.A.^a

^a *Laboratory of Food Chemistry, Wageningen University and Research, The Netherlands*

^b *G3P Inc, Burlington, USA*

* anne.kleijn@wur.nl

Rhamnogalacturonan(RG)-I enriched pectin shows high binding activity to galectin-3 (gal-3), a protein that is known to be upregulated in individuals with cardiovascular disease and may cause fibrosis[1]. Using gal-3 as a target, this pectin therefore presents a promising preventative treatment for fibrosis and has been shown to prevent and revert fibrosis in mice models[2]. RG-I rich pectin consists of a backbone of alternating galacturonic acid and rhamnose units, of which rhamnose can be decorated with arabinose and galactose containing side chains. This pectin can be released through enzymatic treatment of pectin-rich plant material, such as *Cucurbita* (squash) species.

RG-I is generally considered a dietary fiber, reaching the colon as it is undigestible in the upper digestive tract. However, a direct systematic effect of RG-I rich pectin is suggested due to its partial absorption into the blood circulation, exerting its gal-3 mediated effects throughout the body[3]. Currently, determination of the presence of poly- or oligomeric pectin in plasma or urine is hardly described. This project therefore includes the development of a sufficiently sensitive method to detect RG-I rich pectin in these biological samples. Constituent sugars were released from plasma spiked with squash-derived RG-I rich pectin using various acids and reaction conditions. These monosaccharides were analysed using either gas chromatography or high performance anion exchange chromatography. Pectin-derived monosaccharides could be recovered at 6 µg/ml pectin concentrations at 300 µl plasma sample volume. Samples from an *in vitro* Caco-2 intestinal model system to test barrier passage and from *in vivo* human studies using RG-I supplements are analysed for the presence of pectin. Results will be discussed and will help to elucidate the mechanisms of mediation of fibrosis by RG-I rich pectin.

[1] Stegmayr J., Zetterberg F., Carlsson M. C., Huang X., Sharma G., Kahl Knutson B., Schambye H., Nilsson U. J., Oredsson S., Leffler H., *Scientific Reports*, 9 (1), 2186-2186, 2019

[2] Pozder C., van der Velde A. R., Meijers W. C., Silljé H. H. W., Muntendam P., Dokter M. M., van Gilst W. H., Schols H. A., de Boer R. A., *Current Research in Translational Medicine*, 70 (1), 103321, 2022

[3] Pedrosa L. D. F., Raz A., Fabi J. P, *Biomolecules*, 12 (2), 289, 2022



Session 1 Poster



INCREASE IN OXYGEN PERMEABILITY OF REGENERATED CELLULOSE DUE TO SWELLING AND MOLECULAR MOVEMENT CAUSED BY WATER

Okugawa A.^a, Yamane C.^b, Yuguchi Y.^{a*}

^a Graduate School of Engineering, Osaka Electro-Communication University, Japan

^b Faculty of Home economics, Kobe Women's University, Japan

* yuguchi@osakac.ac.jp

The application of regenerated cellulose for packaging films and coatings of paper food containers must be expanded as alternatives to synthetic polymers. In this field, gas barrier properties are strongly required. The gas barrier of regenerated cellulose films is extremely high in a dry state. However, gas permeates easily in a wet state. In this study, the reason why the oxygen permeability coefficient (OP) of regenerated cellulose significantly increases with increasing water regain focusing on swelling behavior as a macroscopic phenomenon and relaxation phenomenon as molecular motion by water was investigated.

The OP of the regenerated cellulose film in the dry state was remarkably low (Fig. 1). However, the OP at 90% water regain increased to $150 \times 10^{-15} \text{ cm}^3 \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$. This value was similar to that of low-density polyethylene film, which has inferior gas barrier properties. The film thickness increased with increasing water regain and was approximate twice the dry film thickness at 80% water regain. Small angle X-ray scattering (SAXS) in edge view showed that the spacing of microcrystals in the thickness direction increased from about 4 nm in a dry state to 6.5 nm at 100% water regain. This indicates that the oxygen molecules have passed through the space between the cellulose molecules created by the water. Contrary, the film width did not change by the water. This anisotropic swelling is probably caused by the uniplanar orientation of the (110) crystal plane parallel to the film surface. Thus, water permeates the amorphous region along the hydrophilic surface of the (110) plane, expanding the space in the thickness direction. In addition, storage modulus (E') decreased by two orders of magnitude with increasing water regain, and a broad peak of $\tan \delta$ was observed at around 90% water regain, indicating that the micro-Brownian motion of the cellulose main chain was released. Therefore, the increase in OP of the regenerated cellulose is due to the micro-Brownian motion of the cellulose main chain caused by the space between cellulose and widening of space caused by water.

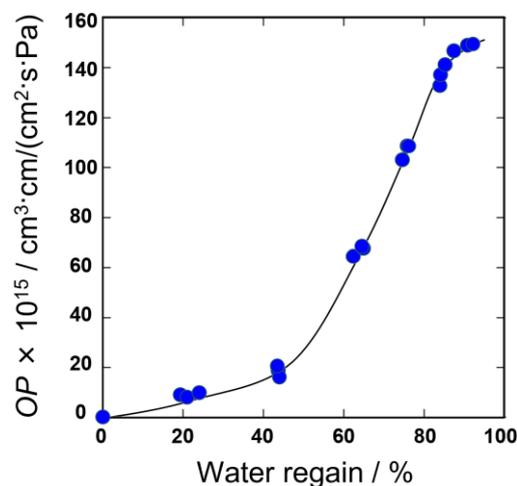


Figure 1 : Effect of water regain on OP of regenerated cellulose



COMPLEX FORMATION OF SEAWEED POLYSACCHARIDE AND WHEY PROTEIN

Yuguchi Y. ^{*a}, Kawashima S. ^a, Thanh Thi Thu T. ^b

^a Osaka Electro-Communication University, Japan

^b Institute of Chemistry, Vietnam Academy of Science and Technology (VAST), Vietnam

* yuguchi@osakac.ac.jp

We can find ionic polysaccharide with sulfate groups in seaweeds, for example, carrageenan, fucoidan, ulva and so on. They are applied for food additives or supplement. Fucoidan has physiological activities as anticoagulant, immunomodulatory, antitumor, etc. The mechanism of these effects is complicated and not clear.

We focused on the complex formation of such ionic polysaccharide and whey protein. In this study the interaction and complex structure of ionic polysaccharide and protein was studied not only to measure the strength of each interaction but also to investigate the complicated structure of fucoidan and/or ulva.

The carrageenan family, fucoidan, ulva mixed with β -lactoglobulin (β -Lg) were used for samples. The small angle X-ray scattering measurement (SAXS) was performed to analyze the associated structure. The time-resolved SAXS during making low pH by addition of gluconolactone (GDL) was also carried out. The mixture solution becomes turbid at low pH, indicating the aggregation. The variation of SAXS pattern indicated the aggregation process of ionic polysaccharide and protein at nano-order level.

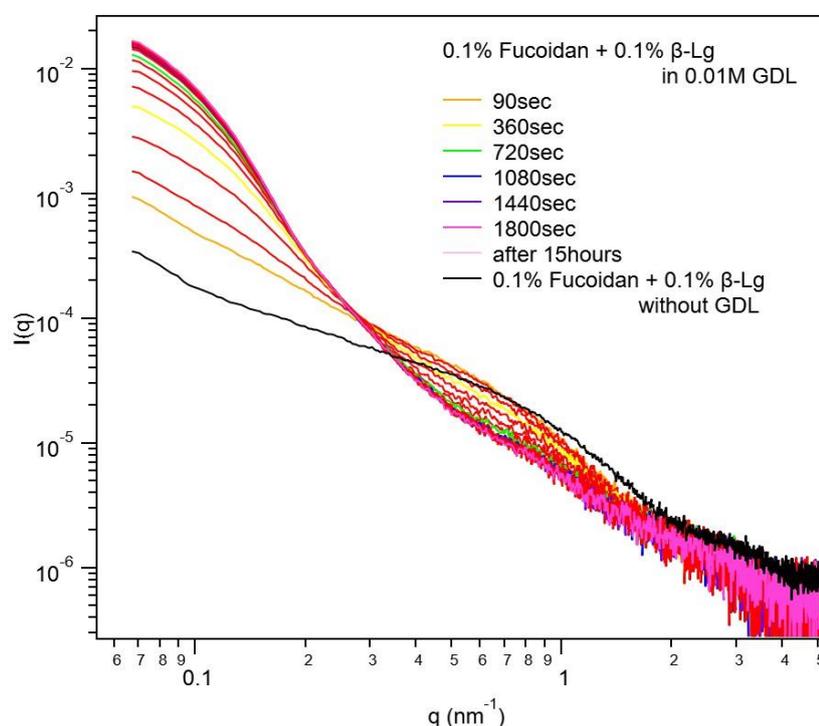


Figure 1 : Kratky plots for time resolved SAXS during aggregation of fucoidan and β -Lg. Here $I(q)$ is scattering intensity, q is the magnitude of scattering vector.

Acknowledgement: This project was supported by JSPS and VAST under the JSPS-VAST joint Research Program (120239602). We thank prof. T. Konishi in univ. of the Ryukyus to provide fucoidan sample.



WHEAT AND RYE ARABINOXYLANS ARE DIFFERENTLY SUSCEPTIBLE TO FENTON-OXIDATION

Pandeirada C.O.*^a, Boulos S.^a, Nyström L.^a

^aLaboratory of Food Biochemistry, ETH Zurich, Switzerland

* carolina.pandeirada@hest.ethz.ch

Extrusion of wheat bran changes the functional properties and structure of arabinoxylan (AX) [1], a major dietary fiber in cereals. A possible reason for AX structural change is Fenton-oxidation, causing AX depolymerization and introduction of carbonyl and carboxyl groups [1,2]. Despite being studied for wheat AX (WAX), it is still unclear if modifications through Fenton-oxidation are similar for different AXs. Thus, AXs from wheat and rye (WAX and RAX) were Fenton-oxidized and structurally characterized.

WAX and RAX were Fenton-oxidized and freeze-dried, yielding ox-WAX and ox-RAX, respectively. (ox-)AXs were analyzed for their molecular weight (Mw; HPSEC-TI/RALS/LALS) and sugar composition (HPAEC-PAD). (ox-)AXs were enzymatically digested with endo-xylanase (GH11) and exo-xylosidase (GH43), NaBD₄-reduced, and the oligosaccharides were purified by solid phase extraction and analyzed by HILIC-ESI-qTOF-MS.

After Fenton-oxidation, the Mw of WAX and RAX decreased 75 and 45%, respectively, indicating that the used WAX material is more prone to depolymerization under the chosen Fenton-oxidation conditions than the RAX material. 75% (w/w) and 89% of the sugars present in WAX and RAX were recovered in ox-WAX and ox-RAX, respectively. This indicates that 10-15% of the sugar units were modified during oxidation, highlighting the AX structural change. HILIC-ESI-qTOF-MS analysis of the oxidized oligosaccharides after NaBD₄-reduction revealed that the structural change was due to the introduction of carbonyl and carboxyl groups, and cleavage of the sugar ring with release of CH₂O+O. Remarkably, the HILIC-ESI-qTOF-MS oligosaccharide profiles derived from both ox-AXs were different, species with *m/z* 268.11, 254.10, and 400.16 were exclusively observed for ox-WAX.

This study shows that depolymerization and AX structural changes via Fenton-oxidation is AX-structure dependent, which raises attention to the fact that the functional properties of (ox-)AXs might as well be differently modified.

[1] Demuth T., Betschart J. & Nyström L., *Carbohydrate Polymers*, 240, 116328, 2020.

[2] Demuth T., Boulos S. & Nyström L., *Analyst*, 145, 6691, 2020.



CHEMICAL MODIFICATION AND FLUORESCENT LABELING OF CELLULOSE NANOFIBRILS: STED SUPER-RESOLUTION IMAGING OF A SINGLE FIBRIL AND ITS EMBEDDING IN A COMPOSITE

X. Jiang^{*a}, J. B. Mietner^a, J. R.G. Navarro^a

^a *Institute of Wood Science, Universität Hamburg, Germany*

* xuehe.jiang@uni-hamburg.de

In this work, our team pursued two main objectives. The first was to create a multifunctional platform using cellulose nanofibrils (CNFs) that could be easily adapted for various applications. Our approach involved chemically modifying CNFs into a CNF-based macroinitiator (CNF-MI)¹ and a subsequent synthesis route combining surface-initiated controlled radical polymerization (SET-LRP) and Cu^I-catalyzed azide-alkyne click-chemistry (CuAAC). Secondly, we used this synthesis process to label the surface-modified CNFs with fluorescent dyes, which we then observed directly using super-resolution microscopy to study the behavior of a single fibril and its embedding in composites.²

SET-LRP has been widely used as a robust and versatile tool for synthesizing vinyl polymers with well-defined functionality. In this study, monomers comprised di (ethylene glycol) ethyl ether acrylate (DEGEEA) and acrylic acid 3-trimethylsilyl-prop-2-ynyl ester (TMSPgA). We used TMSPgA to introduce luminescent dyes on the CNF surface via CuAAC, while DEGEEA was used to increase the stability of the CNFs in selected solvents (DMSO&H₂O) and act as a spacer between neighbor luminescent dyes by spacing the reactive clickable monomers.

The novelty of our work lies in the morphology study of modified CNFs investigated through confocal laser scanning microscopy (CLSM) and stimulated emission depletion (STED) microscopy. The study explored the behaviors of CNFs dried from DMSO, including single fibrils, fibril networks, bundles, and clusters. The distribution and morphology of modified CNFs embedded in a PVA composite with a thickness of approx. 10 μm were revealed through a widefield microscope and CLSM/STED microscopes. This morphology observation, which could not be realized with traditional electron microscopy techniques (SEM, AFM), was possible with the STED.

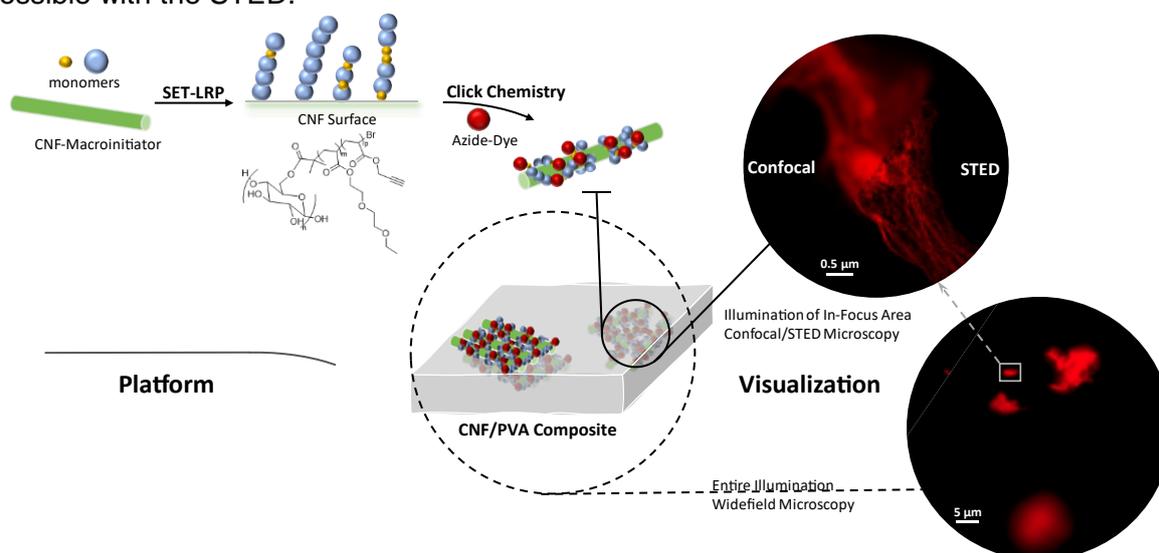


Figure 1: Surface modification of CNFs and STED super-resolution imaging of a single fibril and its embedding in composites.

- [1] Navarro, J. R. G.; Rostami, J.; Ahlinder, A.; Mietner, J. B.; Bernin, D.; Saake, B.; Edlund, U., *Biomacromolecules* **2020**, 21 (5), 1952–1961.
 [2] Jiang, X.; Mietner, J. B.; Navarro, J. R. G., *Cellulose* **2023**, No. 0123456789.



BIOFABRICATION OF FUNCTIONAL PULLULAN – CONTROL OF THE PULLULAN PRODUCTION AND MOLECULAR WEIGHT

De Ceulaer F. ^{*a}, Van den Eynde K.^a, Boon V.^a, Fardim P.^a

^a Department of Chemical Engineering, Chemical and Biochemical Reactor Engineering and Safety (CREaS), KU Leuven, Belgium

* femke.deceulaer@kuleuven.be

Pullulan is a linear polysaccharide produced by the polymorphic fungus *Aureobasidium pullulans*, which consists of repeating maltotriose units joined together via α -(1,6)-glycosidic bonds. The unique linkage pattern and the presence of nine hydroxyl groups on the repeating units provides pullulan with an inherent physiological activity, a high potential for chemical modification and remarkable physicochemical properties, which improves its application in the food, cosmetic, and pharmaceutical industry [1]. Although pullulan is gaining great attention as a functional material for biomedical applications, the commercial use of pullulan-based biomaterials is limited due to its cost intensive biofabrication process [2]. A precise control of the pullulan yield, molecular weight, and melanin production by varying the fermentation conditions is required to minimize this biofabrication cost. In this study, the influence of the carbon source, nitrogen source concentration and aeration rate on the pullulan production by *A. pullulans* ATCC 42023 is examined in batch fermentation experiments. Different pullulan yields and molecular weights were obtained by altering the biofabrication parameters. The chemical structure of the produced pullulan was characterized via NMR and FTIR, while the molecular weight distribution was analyzed via GPC [3]. The change in cell morphology of *A. pullulans* over the batch time was observed via optical microscopic images and linked to the pullulan yield and melanin production.

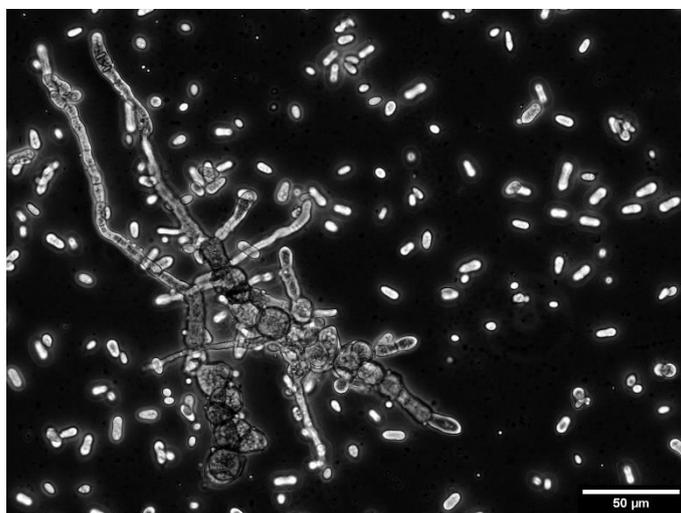


Figure 1: Optical microscopic image of the polymorphic fungus *Aureobasidium pullulans* inside the fermentation medium after 96 hours at pH 5.00 (Erlenmeyer flask), illustrating the presence of yeast-like cells, blastospores, chlamydospores and hyphae.

- [1] Singh R.S., Kaur N. & Kennedy J.F., Carbohydrate Polymers, 123, p.190-207, 2015
 [2] Singh R.S., Kaur N., Rana V. & Kennedy J.F., Carbohydrate Polymers, 171, p. 102-121, 2017
 [3] Van de Eynde K., Boon V., Gaspar R.C. & Fardim P., Molecules, 6, 2478 ,2023



PHYSICO-CHEMICAL CHARACTERIZATION OF POLYSACCHARIDES FROM EDIBLE SEAWEEDS

Patricia Murciano Martinez. ^{*a}, Sarah Michel^a, Delphine Curti.^a

^a Nestlé Research, Rte du Jorat 57, 1000 Lausanne, Switzerland

* patricia.murcianomartinez@rd.nestle.com

Edible seaweeds are gathering more attention in regions where their consumption is not greatly spread among the population such as Latin America or Europe. This is, among other reasons, due to the ability of seaweeds to sequester CO₂ and, therefore the potential of seaweed farming to contribute to net-zero greenhouse gas emissions [1]. Furthermore, studies highlight the potential of a number of seaweed compounds such polysaccharides or micronutrients and their positive impact on animal and human health. Seaweeds are a great source of polysaccharides widely used as ingredients in the food and cosmetic industry because of their unique techno-functional properties such gel formation, thickening and encapsulation of bioactive compounds.

There are large variations in the chemical composition and structure of seaweed polysaccharides depending on the species, harvesting location and season. Understanding the relationship between the fine chemical structure and physical properties of polysaccharides from the different seaweed species of commercial interest in a specific region is key for the design of new food products containing substantial amounts of seaweeds and relevant to consumers.

[1] DeAngelo et al., *Nature plants*, 9, 45-57, 2023



REACTIVE DISSOLUTION OF 6-HALO-6-DEOXYCELLULOSES AND THEIR CHARACTERIZATION BY SOLUTION-STATE NMR

Dryś M.^{*a}, Koso T.^b, Kilpeläinen P.^c, Rinne-Garmston K.^c,
Todorov, A.^a, Wiedmer S.K.^a, King A.^b

^a Department of Chemistry, University of Helsinki, Finland

^b VTT Technical Research Centre of Finland

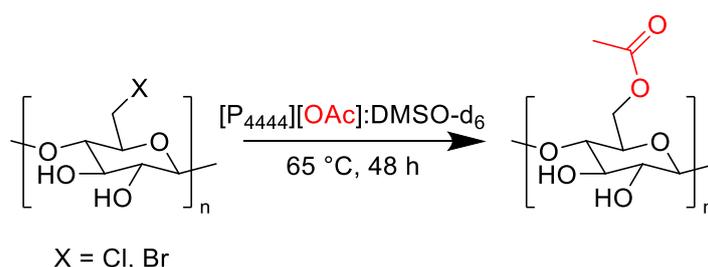
^c Natural Resources Institute Finland (Luke)

* magdalena.drys@helsinki.fi

6-Halo-6-deoxycelluloses are versatile intermediates for synthesizing cellulose derivatives with high regioselectivity at carbon 6 (C6) and maximum degree of substitution (DS₆). These are unique features that may lead to the development of new products with fine-tuned properties. Yet, currently available methods for characterizing 6-halo-6-deoxycelluloses are clearly insufficient, since they allow only for estimating total DS or require laborious derivatization procedures in order to utilize more advanced analytics. Modern solution-state NMR techniques offer the possibility for detailed structure elucidation and quantitative analysis; however, the essential insolubility of 6-halo-6-deoxycelluloses in organic solvents or water has been a major setback, and the potential of cellulose derivatives with high regioselectivity at C6 remains underexplored.

Herein we present a protocol for direct and rapid DS₆ determination of 6-halo-6-deoxycelluloses with solution-state NMR, utilizing the well-established ionic liquid (IL) electrolyte, [P₄₄₄₄][OAc]:DMSO-d₆. [1,2] The IL electrolyte simultaneously acts as a reactant in a reactive dissolution process, in which 6-halo-6-deoxycelluloses are quantitatively converted into 6-monoacetylcellulose (**Scheme 1**), which remains soluble, enabling high-resolution NMR measurements without the need for isolation and purification of the acetylated product.

Our method is attractive both in terms of accuracy and minimal requirements for resources or workload, and has the potential to be extended to polysaccharides beyond 6-halo-6-deoxycelluloses. We believe that the presented analytics will be useful for optimizing syntheses of regioselectively functionalized cellulose derivatives.



Scheme 1: Reactive dissolution of 6-halo-6-deoxycellulose in [P₄₄₄₄][OAc]:DMSO-d₆ to yield 6-monoacetylcellulose

[1] King A.W.T. *et al.*, *Biomacromolecules* 19(7), 2708–2720, 2008.

<https://doi.org/10.1021/acs.biomac.8b00295>

[2] Koso T. *et al.*, *Cellulose* 27, 7929-53, 2020.

<https://doi.org/10.1007/s10570-020-03317-0>



DISTRIBUTION-ANALYSIS OF AQUEOUS POLYSACCHARIDE-SYSTEMS BELOW OVERLAPPING-CONCENTRATION

Wintersteller P. ^{*a}, Huber A. ^a

^a Institute of Chemistry, University of Graz, Austria

* peter.wintersteller@uni-graz.at

Depending on chemistry of their repeating unit, degree of polymerization and conditions of aqueous media polysaccharides partially may: be molecular dissolved, partially form hydrated aggregates and associates, partially form long ranging colloidal-type gel-constituting networks. Dimensions of each of these fractions show up as distributions, and hence, analysis needs separation approaches as well for homogeneous as for heterogeneous components.

Size-exclusion chromatography (SEC) is a well working approach for molecular dissolved fractions. Asymmetric Flow Field Flow Fractionation (AF4=AF4) represents an powerful approach for dispersed heterogeneous or even mixes of homogeneous and heterogeneous fractions.

Application of both, SEC and AF4, to size-distribution analysis of the mix of homogeneous and heterogeneous fractions of a charged polyanionic polysaccharide in aqueous media, provides data to discuss XWM-systems. Such systems, constituted by Xanthan (X) in continuous aqueous phase (W) in the presence of dissolved modifying compounds (M), are investigated upon hydrodynamic radii of dissolved molecules, sphere-equivalent radii of hydrated supermolecular structures and non-dissolved colloidal objects. To obtain information close to intrinsic conditions investigations were performed below overlapping concentration c^* .

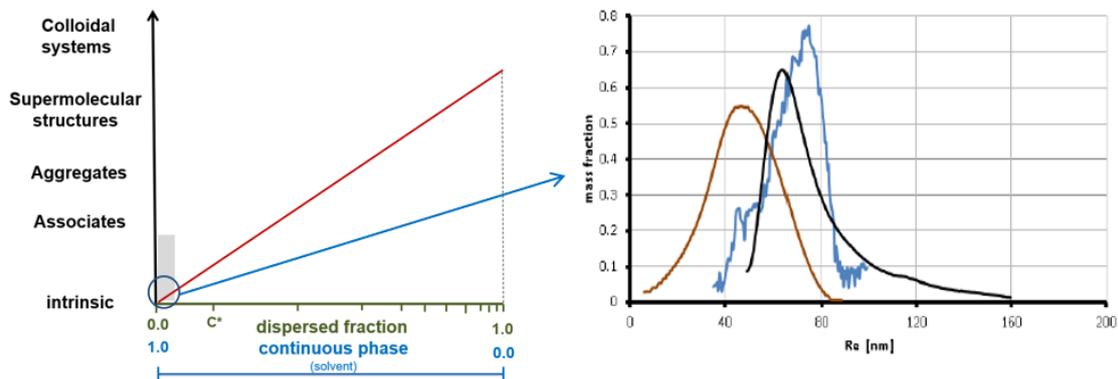


Figure 1: *Left*: shows the domain, where separation techniques (SEC, AF4) combined with multiple detectors, provide information of the homogeneous fraction with SEC and of both the homo- and heterogeneous fraction with AF4; *Right*: shows distribution of sphere equivalent radii in an XWM-system with SEC-analysis of the homogeneous fraction  and AF4-separation of both, the homo- and heterogeneous fraction.  (mixed at 60°C) and  (hydrated with an ultrasonic finger) are both XWM-systems prepared with 2 different techniques. [1]

[1] Wintersteller P., Muriqi A., Bajrami D., Hoti G., Huber A., Current Advances in Biopolymer Processing and Characterization, Chapter 4, Xanthan in aqueous media: Molecular and Hydrocolloidal Characteristics, 2017



RESPONSE CAPABILITY OF AQUEOUS POLYSACCHARIDE-SYSTEMS BEYOND OVERLAPPING CONCENTRATION

Wintersteller P. ^a, Huber A. ^{*a}

^a *Institute of Chemistry, University of Graz, Austria*

* anton.huber@uni-graz.at

Aqueous colloidal systems with exo-polysaccharides (EPS), like Xanthan show strong increase in viscosity even at low concentrations.

Beyond the overlapping concentration, are typically the systems of interest for technological applications. Polysaccharide-characteristics emerge as apparent information, based on intrinsic properties that are unaffected by concentration effects.

With increasing concentration, the systems are dominated by interaction phenomena, the higher the fraction percentage in aqueous media.

In addition, the way and history of preparation of such systems also contribute to actual system states and correlated apparent data.

A polysaccharide system constituted by Xanthan in aqueous media prepared by various approaches (mechanical mixing, ultra sound, conventional heating...) has been investigated upon response capability on applied shear stress and with respect to changes in solid/liquid-ratio characteristics.

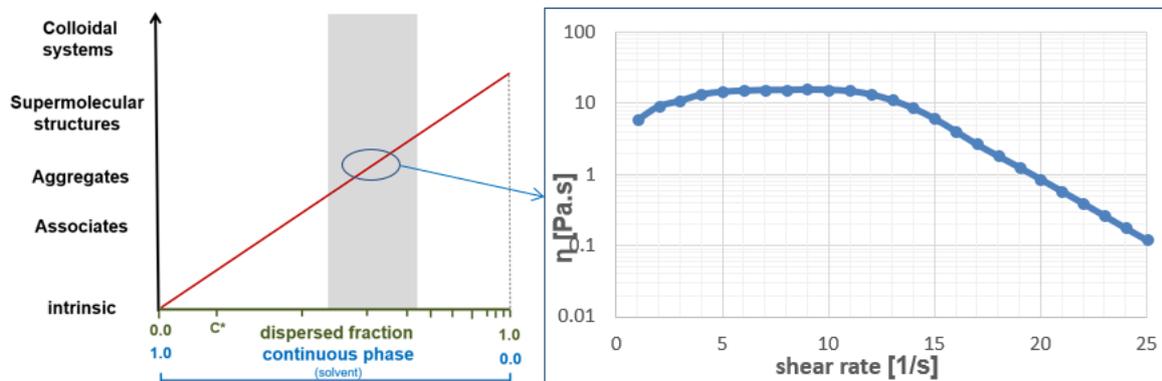


Figure 1: Left shows the domain, where Rheology can provide important information
Right: shows a flow curve of an XWM-system heat treated; \bullet FNCS 5 [mg/mL], shear thinning with increasing shear stress,



ANTARCTIC BACTERIA AS SOURCE OF BIOACTIVE POLYSACCHARIDES

Casillo A.^{*a}, D'Angelo C.^b, Gallucci N.^a, Paduano L.^a, Tutino M.L.^a, Parrilli E.^a, Corsaro M.M.^a

^a Department of Chemical Sciences, University of Naples Federico II, Naples, Italy

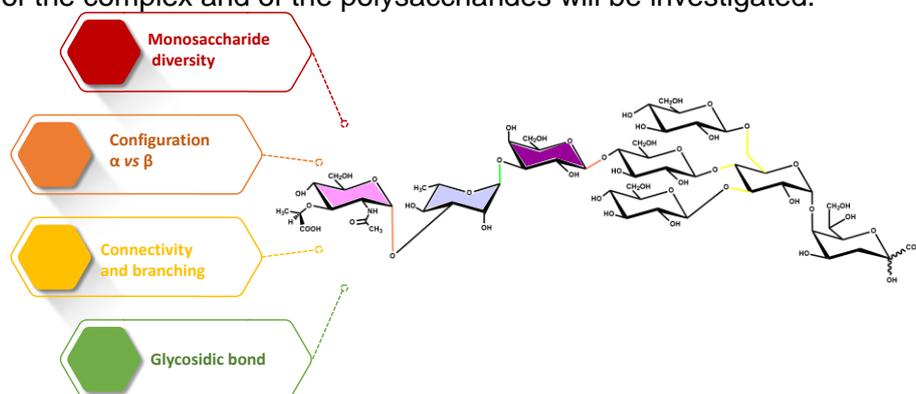
* angela.casillo@unina.it

Glycans isolated from marine resources are unique in terms of function and structure. Arctic and Antarctic bacteria have developed chemical adaptation strategies that allow them to maintain their cellular integrity in extreme conditions. One of these strategies is the biosynthesis of extracellular polysaccharides (EPS), which constitute a slime and hydrated matrix that keep the cells embedded, protecting them from environmental stress (desiccation, salinity, temperature, and radiation). EPSs have gained interest for their unique properties such as structural complexity, biodegradability, biological activities, and biocompatibility.[1] With the development of marine biotechnologies, the potential of marine polysaccharides as an innovative source for new bioactive molecules has emerged and gained considerable attention.

Psychrobacter sp. TAE2020 is an aerobic γ -proteobacterium isolated from an Antarctic coastal seawater sample.[2] This marine bacterium can produce and secrete surfactants and emulsifier, and its cell-free supernatant strongly affected some specific virulence features of *P. aeruginosa* isolates from CF patients.[2]

We recently isolated and purified the anti-adhesive and emulsifying polysaccharide-protein complex, CATASAN. The complex can reduce biofilm formation and the detachment of biofilm of the nosocomial bacterium *S. epidermidis*. [3]

Here we reported the purification and the characterization of the polysaccharide portion of CATASAN produced from *Psychrobacter* sp. TAE2020. Finally, the physicochemical properties of the complex and of the polysaccharides will be investigated.



[1] Casillo A. et al., Exopolysaccharides from Marine and Marine Extremophilic Bacteria: Structures, Properties, Ecological Roles and Applications. *Marine Drugs* 2018, 16(2), 69

[2] Riccardi, C.; D'Angelo, C.; Calvanese, M.; Ricciardelli, A.; Tutino, M.L.; Parrilli, E.; Fondi, M. Genome Analysis of a New Biosurfactants Source: The Antarctic *Bacterium* *Psychrobacter* sp. TAE2020. *Mar. Genom.* **2022**, 61, 100922.

[3] D'Angelo C. et al., CATASAN Is a New Anti-Biofilm Agent Produced by the Marine Antarctic Bacterium *Psychrobacter* sp. TAE2020. *Mar. Drugs* 2022, 20(12), 747.



SWEETSEP™ AEX200 A NEW STATIONARY PHASE FOR FAST AND HIGH-RESOLUTION SEPARATION OF CARBOHYDRATES USING HPAEC-PAD

Daniel Vetter*; H.J. Brouwer, J.P. Chervet, C. Marvelous, T. Mulder, M. Eysberg, N.J. Reinhoud

Antec Scientific, Alphen a/d Rijn, The Netherlands

* d.vetter@antescientific.com

High-Performance Anion Exchange Chromatography in combination with Pulsed Amperometric Detection (HPAEC-PAD) is the method of choice for the analysis of carbohydrates in a large variety of sample matrices. It combines superior selectivity with sensitive detection down to femtomole levels without the need for derivatization or complicated sample preparation. Since the introduction of HPAEC-PAD in the early 1980's the research on new anion-exchange stationary phases resulted in significant improvements in column performance over the years. The use of smaller polymeric particles, down to 4 μm , in combination with improved chemistries & stationary phase architecture enabled fast, high-resolution anion-exchange separation of complex carbohydrates samples. However, it is evident that smaller particle sizes will give rise to higher system back pressures, so the use of 4 μm columns put some constraints on the metal-free ion chromatography (IC) instrumentation which can be used.

A novel agglomerated pellicular anion-exchange stationary phase SweetSep™ AEX200 (Antec Scientific) has been developed. AEX200 is based on a monodisperse 5 μm resin of highly crosslinked poly(divinylbenzene-co-ethylvinylbenzene) copolymer coated with quaternary amine functionalized nanoparticles. The high uniformity and monodispersity of the AEX200 resin allow for rapid, high-resolution separations of carbohydrates that can rival the performance of some stationary phases based on 4 μm particle technology, but operate with significantly lower back pressures. The size and exchange capacity of the latex nanoparticles was optimized to enable the analysis of a wide variety of carbohydrates samples ranging from mono- to tetrasaccharides present in food, plants and glycoproteins, up to oligosaccharides such as FOS (fructo-oligo-saccharides) and N-linked glycans. As an example, neutral sugars and uronic acids typically present in biomass hydrolysates are shown in figure 1.

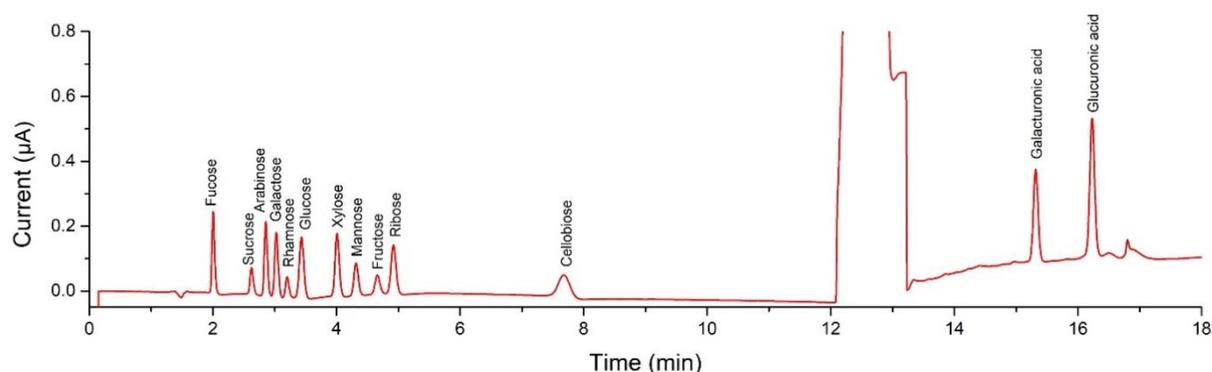


Figure 1: Separation of a 10 μM standard mixture of 11 neutral sugars and 2 uronic acids using SweetSep™ AEX 200 column



EFFECT OF ULTRASONIC TREATMENT ON THE B-GLUCAN OF DICTYOPHORA: STRUCTURE, MORPHOLOGY AND SOLUTION PROPERTIES

Zhe Wang ^{*a}, Junyi Yin ^a, Shaoping Nie ^a

^a State Key Laboratory of Food Science and Technology, Nanchang University, China

* 13361654548@163.com

β -glucan can be used as food excipients because of its good biological activity. As a common food processing method, ultrasound may lead to changes in the structure of polysaccharides and thus lead to changes in their activity. Therefore, it is necessary to systematically understand the structural information of β -glucan after ultrasound. In this study, we treated dictyophora β -glucan (DIPP) with ultrasound and then investigated the changes in DIPP through the characterization of molecular weight, glycosidic bond type, surface morphology, and viscosity. The results showed that the glycosidic bond type and branching degree of DIPP did not change significantly with the extension of ultrasonic time. However, the molecular weight and intrinsic viscosity of DIPP decreased, and the surface morphology changed from filamentous to spherical. These results indicated that ultrasonic treatment only reduced the molecular weight of dictyophora β -glucan but did not affect the structure of the repeating unit. Therefore, ultrasound has potential applications in the preparation of β -glucan with different polymerization degrees. [1]

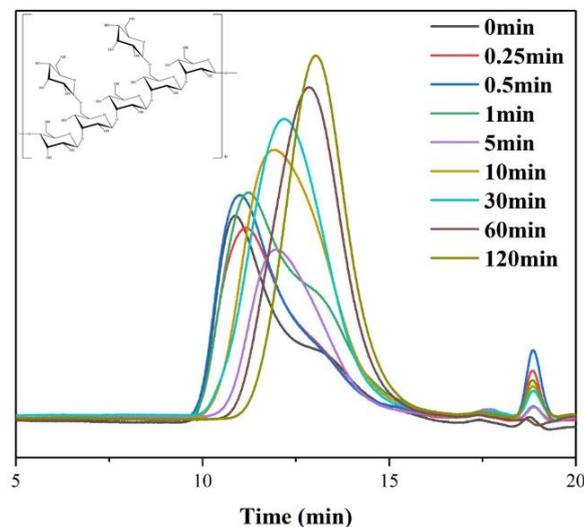


Figure 1 : Liquid phase diagram of DIPP treated with different ultrasound times

[1] Cui, R., & Zhu, F., *Trends in Food Science & Technology*, 107, 2020.



SIMPLE ANALYTICAL METHODS AS BASIS FOR PHYSICS INFORMED NEURAL NETWORKS REVEALING VALID MODELS FOR REACTIVE DIFFUSION OF VOLATILES THROUGH PAPER

Serebrennikova A. ^{a,d}, Teubler R. ^{*b,d}, Hoffellner L. ^{b,d}, Leitner E. ^{b,d}, Hirn U. ^{c,d}, Zojer K. ^{a,d}

^a *Institute of Solid State Physics, Graz University of Technology, Austria*

^b *Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Austria*

^c *Institute of Bioproducts and Paper Technology, Graz University of Technology, Austria*

^d *Christian Doppler Laboratory for Mass Transport through Paper, Graz University of Technology, Austria*

* raimund.teubler@tugraz.at

Predictive models for the transport of volatile organic compounds in paper need to consider the complex interplay of diffusion, adsorption, desorption, or chemical reactions. The relative importance of each of these processes is determined by the polarity of the volatile. Hence, it is challenging to pick a valid theoretical model that correctly predicts transport regardless of the polarity. Here, physics-informed neural networks (PINNs) assess which of five different models correctly describe transport of DMSO as polar and n-tetradecane as non-polar model compound: (i) a pseudo first-order adsorption model for an irreversible sorption process, (ii) a first-order kinetics model allowing reversible sorption, (iii) a second-order model with a reversible process, and an effective diffusion model accounting for a constant (iv) and for a variable effective diffusivity (v). Each tested model is given as set of partial differential equations (PDE). Considering the model under testing and experimentally obtained, PINNs predict concentration of the volatiles and associated material constants such as sorption constants and effective diffusion coefficients by solving the inverse problem.[1] The experimental data, obtained in advance by analytical and chromatographic methods, include spatially and temporally resolved concentration profiles through paper stacks and the corresponding saturation concentration of volatiles on a paper layer. These analytical methods were developed to provide a rapid, simple, and reproducible way to collect transport and sorption data of a wide range of different volatile organic compounds in different temporal domains which can be applied directly in PINNs.

Our PINNs revealed two models, pseudo first-order sorption and second-order reversible sorption, that correctly predict concentration profiles and polarity-driven differences in sorption times. While a PINN-based picking of valid transport models has important implications for the development of effective methods for controlling emission of volatiles from paper materials, PINNs represent a versatile mathematical tool to validate or refute the capability of PDE-based theoretical models to describe experimental data.[2]

[1] Serebrennikova A., Teubler R., Hoffellner L., Leitner E., Hirn U. & Zojer K., *Transport in Porous Media* 145, 3, 589-612, 2022.

[2] Serebrennikova A., Teubler R., Hoffellner L., Leitner E., Hirn U., & Zojer K., DOI: 10.13140/RG.2.2.32837.01769



ELECTROMECHANICAL BEHAVIOUR OF CHITOSAN-BASED BIONANOCOMPOSITES

Dayana Guzmán^a, Qiancheng Zhang^b, Paula M. Vilarinho^a, Cláudia Nunes^{a*}, Antti Vehkaoja^c, Brian J. Rodriguez^b, Paula Ferreira^a

^aDepartment of Materials and Ceramic Engineering, CICECO – Aveiro Institute of Materials, University of Aveiro, Portugal; dlguzmans@ua.pt, paula.vilarinho@ua.pt, claudianunes@ua.pt, pcferreira@ua.pt

^bSchool of Physics, University College Dublin; srikanth.kolagatla@ucd.ie, qiancheng.zhang@ucdconnect.ie, brian.rodriguez@ucd.ie

^cDepartment of Automation Science and Engineering, Tampere University of Technology, Finland; antti.vehkaoja@tuni.fi

* claudianunes@ua.pt

The study of the electromechanical properties of chitosan-based composites is an exciting and rapidly growing field of research with numerous potential applications in electronics, sensing, and biomedicine[1]. This study aims to provide a better understanding on the performance of bionanocomposites made from polysaccharides, specifically in the context of their potential use for flexible electronic applications in the future. It has been challenging to identify the origin of its electromechanical performance which is different depending on the fabrication conditions and measurement methodologies. A systematic characterisation of chitosan pristine films was performed. The X-Ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) methods were performed for structure characterization. The mechanical properties of the films were evaluated through tension until rupture tests following ASTM D 882 and 883 practices. The electromechanical performance of the films was characterized through piezoelectric force microscopy (PFM) technique including the analysis of the second harmonic signal[3], combined with piezoelectric sensitivity measurements. The results allowed us to conclude that the main contribution of its electromechanical performance comes from electrostrictive and electrostatic effects, raising new questions on the approaching of non-piezoelectric components in dielectrics[2]. Furthermore, the electrostrictive component of chitosan-based bionanocomposites was studied, comparing the effect of chitin nanostructures and barium titanate nanoparticles in the electromechanical performance of the films produced through solvent casting method.

[1] M. Jian, Y. Zhang, Z. Liu, *Natural Biopolymers for Flexible Sensing and Energy Devices*, Vol. 38, 2020.

[2] J. Yu, P. Janolin, J. Yu, P. J. Defining, G. Electrostriction, *A. Physics*, 2022, 131.

[3] B. J. Rodriguez, S. V. Kalinin, J. Shin, S. Jesse, V. Grichko, T. Thundat, A. P. Baddorf, A. Gruverman, *J. Struct. Biol.* 2006, 153, 151.

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). Also, this work was funded by national funds, through FCT, IP, in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, changed by Law 57/2017. FCT is acknowledged by the PhD fellowship ref. UI/BD/151142/2021.



STABILITY INVESTIGATION OF NOVEL SUPERBASE IONIC LIQUID

Melikhov I.^{*a}, Sulaeva I.^b, Barbini S.^a, Sriranganadane D.^a, Rosenau T.^a, Kilpeläinen I.^c, Potthast A.^a

^a University of Natural Resources and Life Sciences, Vienna, (BOKU); Department of Chemistry, Institute for Chemistry of Renewable Resources; Konrad-Lorenz Strasse 24, 3430 Tulln an der Donau, Austria

^b University of Natural Resources and Life Sciences, Vienna, (BOKU); Core Facility Analysis of Lignocellulosics (Alice); Konrad-Lorenz Strasse 24, 3430 Tulln an der Donau, Austria

^c University of Helsinki, Department of Chemistry, Helsinki Institute of Sustainability Science (HELSUS), Yliopistonkatu 3, 00014, Helsingin yliopisto, Finland

* ivan.melikhov@boku.ac.at

Cellulose fibers are gaining popularity as an environment-friendly alternative to synthetic fibers due to their renewable and biodegradable nature. However, current production methods have limitations in terms of efficiency, scalability, and environmental impact. To address these concerns, Ionic Liquids (ILs) have emerged as promising "green" solvents for cellulose, offering low volatility, flammability, and tunable properties. Nevertheless, only a limited number of ILs have proven effective for direct dissolution of cellulose. Herein, the stability of a novel superbase IL (SIL) [mTBNH][OAc] was investigated under different conditions, including thermal decomposition in presence of different amounts of water or wood polysaccharides and its natural degradation over a period of two years.

As other guanidine-base IL [mTBDH][OAc], which is used in the IONCELL process [1], [mTBNH][OAc] also undergoes a two-step degradation process, namely hydrolysis and subsequent acetylation of the newly-formed amine group [2].

The novel mTBNH showed superior stability under thermal conditions (95°C, 10% water). However, the IL's capacity to endure degradation while retaining its ability to dissolve cellulose and produce spun fibers is a question of further investigation.

While thermal degradation pathways can be readily tracked using NMR; the natural degradation occurs to a small extent only, necessitating more sensitive investigation methods. In our study, we employed supercritical fluid chromatography coupled with mass spectrometry (SFC-QToF-MS) to detect degradation products, establish their elemental composition, and optimize flash chromatography separation conditions for certain compounds to elucidate their structure with NMR. Through our investigations, we have determined that also oxidation is one of the primary degradation reactions under storage conditions (rt, no light).

The insights gained from the present study of mTBNH will contribute to a better understanding of this class of ILs. Furthermore, the methodologies developed can be applied to investigate other promising IL candidates in the future, as well as certain important parameters of the spinning process, such as the content of residual IL in spun fibres.

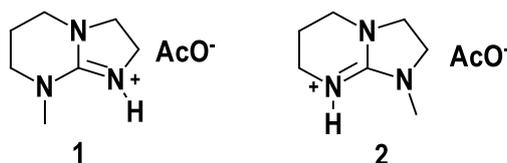


Figure 1 : The two isomers of the ionic liquid [mTBNH]⁺[AcO⁻]: 5-methyl-1,5,7-triazabicyclo[4.3.0]non-6-enium acetate (1) and 7-methyl-1,5,7-triazabicyclo[4.3.0]non-6-enium acetate (2).

[1] Michud A., Tantt M., Sixta H., *Textile Research Journal*. 86(5), 543-552, 2016

[2] Schlapp-Hackl I., Witos J., Ojha K., Uusi-Kyyny P., Alopaeus V & Sixta H., *Ind. Eng. Chem. Res.* 61, 259-268, 2022



RESEARCH ON CHITOSANS CARBOHYDRATE, VACCINES AND SACCHARIDES PURIFICATION, ANALYSATION, DETERMINATION

Dauwe C.*^a, Bures K.^b, Dauwe J.^a, Schulze V.^a, Dauwe S.^a

^a AppliChrom GmbH Research & Development, 16515 Oranienburg, Germany

^b Analytical Science Dr. Bures CEO, 14624 Dallgow-Döbernitz, Germany

* christian.dauwe@applichrom.de

Since liquid chromatography was invented 1850 by Prof. Runge in Oranienburg this technology has continued to several innovations.

Saccharides, special oligosaccharides that are important in vaccination process, polysaccharides like **chitosans**, important in pharmaceutical applications must get purified, analysed and determined to get a product that is economic and safe. Ligand exchange, ion exclusion and size exclusion chromatography (SEC) respective gel permeation chromatography (GPC) are tools for analysation and determination, in special cases also for purification.

GPC respective SEC has been all well established method for polymer characterisation. Its primary and oftentimes only use is to measure the molecular weight and to qualitatively compare different polymer samples.

There are still 2 challenges - 1: molecular weight, size, determination

However, adding a viscometer and light scattering detector to a GPC creates new and challenging dimensions in polymer characterization. Tripel Detection and especially **Volume Matched In situ Tripel Detection** yields data of unsurpassed correctness. Its not only molecular weight, size (radius of gyration R_g) and structure (branching) but also enter the co-polymer analysis.

Challenge 2 – pure SEC method for chitosans:

Size Exclusion Chromatography (SEC) analysis of polycations like chitosan is not easy to handle and this is further compounded by less the optimum reliability of the methods.

Solution: Through a complete re-invention of the stationary SEC phase, it is now possible to access an entire line of SEC columns to carryout analysis of polycationic sugars like chitosan. This new SEC line covers the range from oligomers up to 20 million Daltons with high recovery. This novel SEC packing media shows superior performance with high recovery rates even at low salt concentrations, and for even very large molecular sizes. High resolution is obtained from small size molecule up to + 20 million Dalton. The SEC media is even suitable for systems where polycation blocks are combined with polyanion blocks (partial oxidized product).

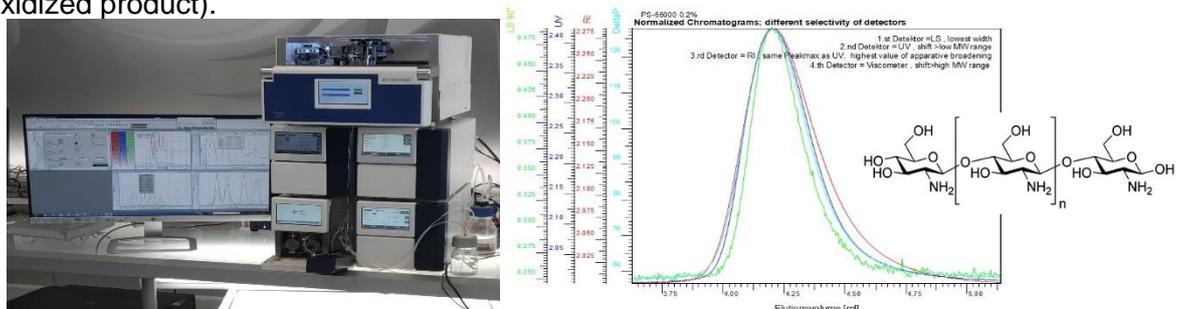


Figure 1: Complete SEC-Solution for Analysis and Determination of Chitosans

SESSION 2

CHALLENGES AND PROGRESS IN POLYSACCHARIDE CHEMISTRY

Session organizers:

Martin Gericke, Thomas Rosenau, Kevin Edgar, Yoshinobu Tsujii

Keynote speaker:

Hiroshi Kamitakahara

Design, synthesis, and functions of cellulosic diblock copolymers: from organic chemistry to biomass refinery



DESIGN, SYNTHESIS, AND FUNCTIONS OF CELLULOSIC DIBLOCK COPOLYMERS: FROM ORGANIC CHEMISTRY TO BIOMASS REFINERY

Kamitakahara H. ^{*a}

^a *Chemistry of Composite Materials, Division of Forestry and Biomaterials Science,
Graduate School of Agriculture, Kyoto University, JAPAN*

* kamitakahara.hiroshi.3n@kyoto-u.ac.jp

Block copolymers have been paid attention in the field of macromolecular science. As far as my knowledge, Ceresa for the first time reported the synthesis of block copolymers of cellulose and its derivatives in 1961. [1] After Ceresa's report of cellulosic block copolymer, cellulose scientists have not been much interested in this research field for about a half century. We have published our first paper regarding cellulosic diblock copolymers in 2005. [2] Progress of analytical instruments such as NMR and MALDI-TOF MS have promoted us to study the chemistry of cellulosic diblock copolymers. Introduction of functional groups at the reducing- and non-reducing ends can be monitored, meaning that end-groups of linear polysaccharides can be reacted with the second polymeric residues to afford diblock copolymers.

We have prepared cellulose acetate-based diblock copolymers. [3] Moreover, methylcellulose-based diblock cooligomers and copolymers have been intensively studied. [4,5,6] End-functionalization of cellulose derivatives has been monitored. It is of crucial importance to purify the reaction products, diblock copolymers, to know structure-property relationships of polysaccharide-based diblock copolymers. We found that aqueous solution of diblock methylcellulose with unmodified cellobiose (DP about 28) exhibits thermo-reversible gelation property at human body temperature. [5] To enhance the function of methylcellulose-based diblock copolymers, our research focuses on methylcellulose-*block-oligo*(amino acid)s. [7] Slow release of model drugs from hydrogel of methylcellulose-*block-oligo*(amino acid)s have been achieved based on the ionic interaction between oligo(amino acid) and model drugs.

Recently, the importance of biorefinery concept has been increasing to decrease the impact of CO₂ emission from human activities. Cellulose must play an important role in the biorefinery concept. Two-thirds of Japan's land is covered in forest. From the viewpoint of cellulose science, I had thought that we have to consider the cost to isolate cellulose from wood. Currently, hemicellulose and lignin are mainly burnt as black liquor under the Kraft pulping process. We have succeeded in the preparation of cellulosic diblock copolymer directly from wood, not via isolated cellulose, together with hemicellulose and lignin derivatives separately. [8]

[1] Ceresa, R. J., *Polymer*, 2, 213-219, 1961.

[2] Kamitakahara, H.; Nakatsubo, F., *Cellulose*, 12 (2), 209-219, 2005.

[3] Kamitakahara, H.; Baba, A.; Yoshinaga, A.; Suhara, R.; Takano, T., *Cellulose*, 21 (5), 3323-3338, 2014.

[4] Kamitakahara, H.; Nakatsubo, F.; Klemm, D., *Cellulose*, 13 (4), 375-392, 2006.

[5] Nakagawa, A.; Fenn, D.; Koschella, A.; Heinze, T.; Kamitakahara, H., *J. Polym. Sci., Part B: Polym. Phys.*, 49 (21), 1539-1546, 2011.

[6] Yamagami, M.; Kamitakahara, H.; Yoshinaga, A.; Takano, T., *Carbohydr. Polym.*, 183, 110-122, 2018.

[7] R. Suhara, M. Yamagami, H. Kamitakahara, A. Yoshinaga, Y. Tanaka and T. Takano, *Cellulose*, 26, 355-382, 2019.

[8] K. Miki, H. Kamitakahara, A. Yoshinaga, Y. Tobimatsu and T. Takano, *Green Chemistry*, 22, 2909-2928, 2020.



SEMI-SYNTHESIS OF GLYCOSAMINOGLYCANS MIMETICS FROM SUSTAINABLE SOURCES

Esposito F.^{*a}, Traboni S.^a, Iadonisi A.^a, Bedini E.^a

^a Department of Chemical Sciences, University of Naples Federico II, Naples, Italy

* fabiana.esposito3@unina.it

Sulfated glycosaminoglycans (GAGs) are highly complex, anionic, linear polysaccharides extracted from extracellular matrix of animals cells. Some of them are exploited in already approved therapeutic treatments, and a significant number of novel drugs are currently under development.¹ Nonetheless, naturally occurring GAGs exhibit variable chemical compositions and biological activities, which could cause unpredictable results during applications (e.g. heparin crisis in 2007). However, sulfated polysaccharides can also be obtained in a semi-synthetic way: the introduction of sulfate groups into the backbones of natural unsulfated polysaccharides allows to endow them with bioactivities similar to sulfated GAGs but without risks derived from their typical animal sources.² This work is focused on the development of semi-synthetic strategies for the regioselective modification of polysaccharides to obtain new polysaccharide-based products, which can be proposed as substitutes for GAG-based drugs already existing but obtained from less eco-sustainable sources. The regioselective derivatizations that are carried out aim at the insertion of negatively charged functionalities (sulfate or phosphate groups), in order to mimic the structural characteristics of natural GAGs. The starting materials are polysaccharides extracted from bacterial or algal sources. In particular, the attention is focused on the development of suitable multi-step sequences all relying upon protection-derivatization-deprotection sequences.^{3,4}

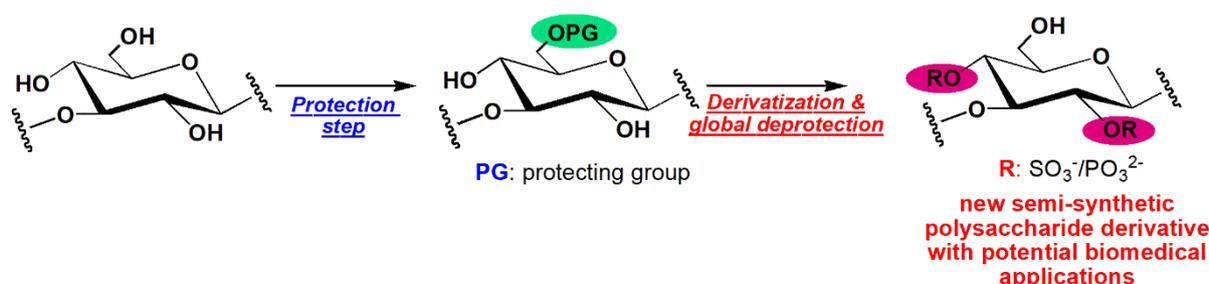


Figure 1 : General scheme of the employed multi-step semi-synthetic approach

[1] Köwitsch, A., Zhou, G., Groth, T., *Journal of Tissue Engineering and Regenerative Medicine*, 12, 23, 2018.

[2] Arlov, Ø., Rüttsche, D., Korayem, M. A., Öztürk, E., Zenobi-Wong, M., *Advanced Functional Materials*, 31, 2010732, 2021.

[3] Vessella, G., Esposito, F., Traboni, S., Di Meo, C., Iadonisi, A., Schiraldi, C., Bedini, E., *Carbohydrate Polymers*, 269, 118324, 2021.

[4] Esposito, F., Vessella, G., Sinquin, C., Traboni, S., Iadonisi, A., Collic-Jouault, S., Zykwinska, A., Bedini, E., *Carbohydrate Polymers*, 283, 119054, 2022.



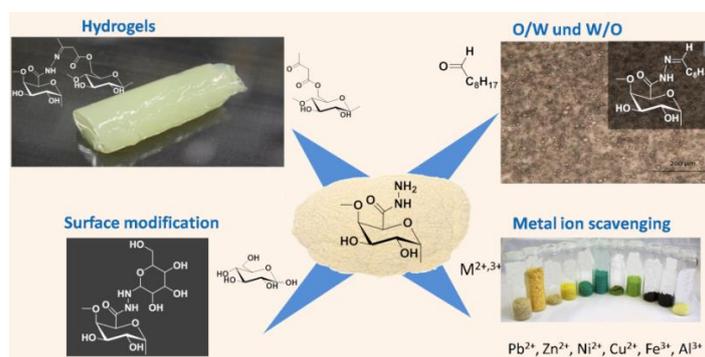
HETEROGENEOUS ONE-POT SYNTHESIS OF REACTIVE PECTIN DERIVATIVES: PECTIN HYDRAZIDE AS NOVEL NUCLEOPHILE

Würfel, H.^a, Geitel, K.^a, Heinze, T.^a

^aCenter of Excellence of Polysaccharide Research, Institute of Organic Chemistry and Macromolecular Chemistry Friedrich Schiller University Jena Humboldtstraße 10, 07743 Jena, Germany

* email: hendryk.wuerfel@uni-jena.de

Pectin, as one of the most abundant polysaccharides, has found little use outside the food industry so far. This situation may be changed if chemical modifications are carried out. A major drawback of the biopolymer is its insolubility in almost any organic solvents due to the polyanionic nature, thus preventing efficient homogeneous chemical modifications except some reactions in ionic liquids (IL), like 1-butyl-3-methylimidazolium chloride.[1] The high cost of ILs and the lack of recycling strategies and difficult purification processes make them unattractive for industrial applications. Reactions in other media lead to partial transformation of the pectin structure only.[2] Water -as a good solvent for pectins- is not well suited for chemical reactions concerning the conversion of the hydroxyl- or carboxyl function and leads to partial degradation and side reactions during transformation. In addition to that, even heterogeneous conversions of pectin are difficult to proceed.



Pectin hydrazide as versatile nucleophile for the formation of hydrogels, emulsions, sugar conjugates and metal scavenging scaffolds.

In our studies it was found that an efficient reaction is the heterogeneous and technically feasible reaction of polygalacturonic acid with hydrazine hydrate in 2-propanol generating the corresponding hydrazide derivatives in high yields with almost quantitative conversion.[3] The hydrazide derivatives can be allowed to react with carbonyl compounds forming Schiff-bases, which can be stabilized to the substituted hydrazides by reduction. This reaction sequence was demonstrated by attaching glucose to the hydrazide moiety in aqueous medium at room temperature.[4] Saccharides play a key role for cell-cell communication and immune responses. Throughout the hydrazide modification, the pectin derivatives retain their multivalent metal ion induced gel forming ability, which will allow the generation of sugar decorated microcapsules for drug delivery systems in the future.

[1] Würfel, H., Kayser, M. & Heinze, T., *Carbohydrate Polymers*, 207, 791-795, 2019.

[2] Würfel, H., Kayser, M. & Heinze, T., *Macromolecular Chemistry and Physics*, 220(9), 1900002, 2019

[3] Würfel, H., Geitel, K. & Heinze, T., *Carbohydrate Polymers*, 261, 117838, 2021.

[4] Würfel, H., Geitel, K. & Heinze, T., *Macromolecular Chemistry and Physics*, 223(23), 2200241, 2022.



FUNCTIONAL POLYSACCHARIDE GELS THROUGH SELECTIVE CROSSLINKING BY CLICK-CHEMISTRY-REACTIONS

Gericke M. *, Skodda L. H., Atmani Z., Heinze T.

Friedrich Schiller University of Jena, Institute of Organic Chemistry and Macromolecular Chemistry, Germany

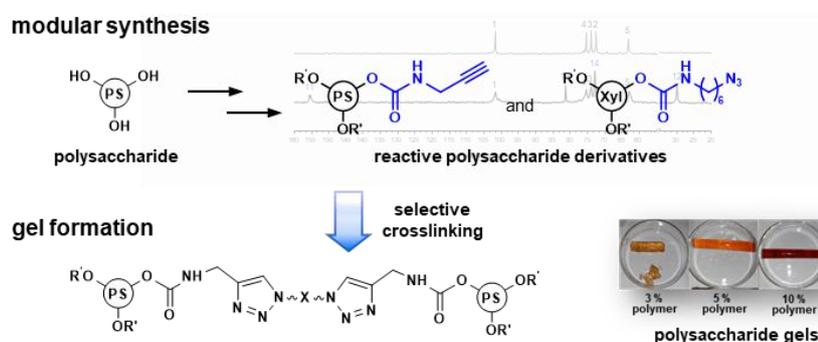
* martin.gericke@uni-jena.de

Polysaccharide gels are of great interest for applications in biomedicine, environmental technologies, and agriculture. Compared to synthetic polymer gels, polysaccharide-based materials provide inherent advantages with respect to sustainability, biocompatibility, and biodegradability. Key development challenges are (i) tailoring of the physical, chemical, and biological gel properties and (ii) the ability to introduce additional functionalities to support specific performances. Both requires direct control over the gelation process and the molecular structure of the biopolymers, which is targeted in this work by exploiting “click-chemistry-approaches”.

Reactive xylan- and cellulose derivatives with “click-chemistry-groups” were synthesized by a modular approach that uses phenylcarbonates as activated compounds. [1,2] The compounds were converted quantitatively into reactive carbamate derivatives by aminolysis with amines carrying the desired “click-chemistry-groups”. [3] The advantage of this modular approach is that a large variety of different reactive groups could be introduced with high efficiency (e.g., azide / alkynyl for 1,3-dipolar cycloaddition, furan / maleimide for Diels-Alder reaction). The degrees of substitution (DS) could be tuned over a broad range from around 0.5 up to almost complete conversion of all hydroxy groups. Moreover, it is demonstrated that mixed carbamates with tailored solubility properties were accessible in a convenient one-pot reaction.

Gels were prepared by selective covalent crosslinking of the reactive polysaccharide carbamates through “click-chemistry-reactions” in aqueous and organic media. The gelation kinetics were monitored by rheological experiments and gelation times ranging from several seconds to several hours were observed depending on concentration, amount of crosslinker, temperature, and the particular crosslinking reaction. The gel properties were characterized and correlated with comprehensive information on the molecular structure of the biopolymer-based materials.

Fields of application that are currently studied for these novel polysaccharide gels are drug-delivery as well as water storage and release (for pharmaceutical and agricultural purposes). Moreover, conversion into aerogels by critical-point-drying (with supercritical CO₂) and freeze-drying (with cryo-protectants) is studied.



- [1] Gericke M., Gabriel L., et al., *Carbohydrate Polymers*, 193, 45-53, 2018
 [2] Gabriel L., Gericke M., Heinze T., *Carbohydrate Polymers*, 207, 782-790, 2019
 [3] Gericke M., Skodda L. H., Heinze T., *Carbohydrate Polymers*, 300, 120251, 2022



DESIGN OF LIGNOCELLULOSIC MODEL SYSTEMS AND BIOINSPIRED MATERIALS BY MITSUNOBU REACTION

Elschner T. ^a, Fischer S.^a

^a Institute of Plant and Wood Chemistry, Technische Universität Dresden, Germany

* thomas.elschner@tu-dresden.de

The Mitsunobu reaction is used as selective one-step procedure for the synthesis of hydroxycinnamic acid esters of polysaccharides. Cellulose esters of ferulic-, p-coumaric-, and caffeic acid are synthesized by applying triphenylphosphine and diisopropyl azodicarboxylate in N,N-dimethylacetamide/LiCl [1]. Similar conditions in N-methyl-2-pyrrolidone can be used for the modification of arabinoxylan [2].

With cellulose, the reaction takes place highly selective at primary hydroxyl groups according to S_N2 mechanism. Moreover, the method is tolerant regarding double bonds and phenolic hydroxyl groups of hydroxycinnamic acids. Thus, protecting group chemistry is not necessary and side products can be removed easier compared to the Steglich procedure [3]. Interestingly, in the case of arabinoxylan, chloride ions of the solvent system lead to the formation of deoxychloro moieties (Appel product).

The novel synthesis of polysaccharide hydroxycinnamates allows the tailoring of antioxidative biomaterials, on the one hand. On the other, it makes lignocellulosic model compounds accessible to achieve progress in biorefining. Investigations on natural plant cell walls are very difficult due to their complex architecture. Therefore, cell wall polysaccharides can be shaped into nanometric thin films to perform online monitoring of the lignification process on surfaces by quartz crystal microbalance with a dissipation monitoring (QCM-D). For example, cellulose ferulate is trimethylsilylated and spin-coated from ethyl acetate to yield model films by deprotection of trimethylsilyl groups with HCl vapor. Thus, ferulate anchor groups are obtained on a smooth cellulose surface to study dehydrogenative polymerization of coniferyl alcohol in a QCM-D device in the presence of H_2O_2 and adsorbed horseradish peroxidase (Figure 1) [4].

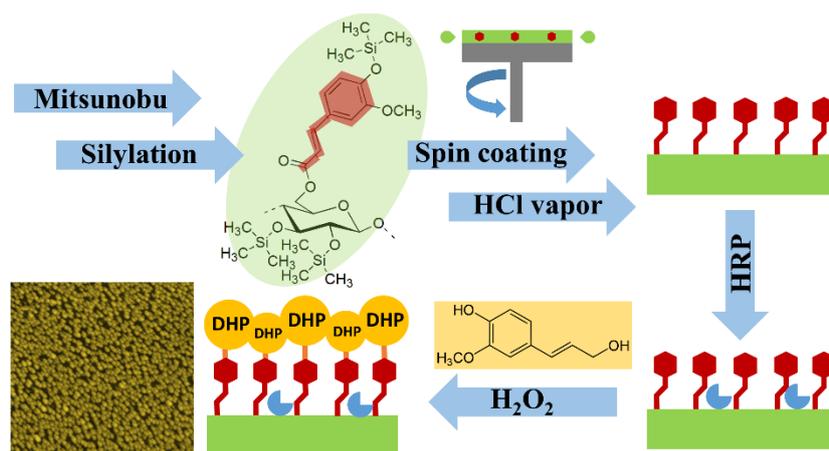


Figure 1 : Growing of artificial lignin on cellulose ferulate thin films [4].

[1] Elschner T., Brendler E. & Fischer S., *Macromol. Chem. Phys.*, 2100232, 2021

[2] Elschner T., Brendler E. & Fischer S., *Cellulose*, 30, 2111–2121, 2023

[3] Trombino S., Cassano R., Bloise E., Muzzalupo R., Leta S., Puoci F., Picci N., *Macromol. Biosci.*, 8, 86, 2008

[4] Elschner T., Adam J., Lesny H., Joseph Y. & Fischer S., *Biomacromolecules*, 23, 2089–2097, 2022



TOWARDS TAILORED DIALDEHYDE CELLULOSE DERIVATIVES: ACCESS TO RENEWABLE THERMOPLASTICS

Simon J.*^a, Fliri L.^b, Zieher J.^a, Sapkota J.^c, Ristolainen M.^c, Hummel M.^b, Rosenau T.^a,
Potthast A.^a

^a Department of Chemistry, Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences Vienna (BOKU), Austria

^b Department of Bioproducts and Biosystems, Aalto University, Finland

^c NE Research Center, UPM Pulp Research and Innovations, Finland

* jonas.simon@boku.ac.at

Our modern society works on solutions to replace fossil-based materials with biobased alternatives. In this regard, dialdehyde cellulose (DAC) – obtained by periodate oxidation of cellulose – presents a promising alternative to conventional, fossil-based materials for various applications across different fields, such as material science, sensor technology, medical applications, and drug delivery. However, unmodified DAC shows no thermoplastic behavior due to interchain cross-linking of the aldehyde groups in the form of hemiacetals and hemiacetals. Thus, further derivatization of the aldehyde groups is required to plasticize DAC. Depending on the extent and type of modification, the materials' glass transition temperature (T_g) can be tuned. This offers access to biomaterial-derived thermoplastics with high stability, high molecular weight, and glass transition temperatures in the range of commercially available thermoplastics (e.g., polyethylene terephthalate or polystyrene).

Here, we present the reduction,^[1] reductive amination^[2], and oximation of DAC as routes to thermoplastic cellulose-derived materials. We investigated the influence of the introduced sidechains on the thermal properties and the course of the reaction. Already low degrees of substitution can result in thermoplasticity. State-of-the-art analytical techniques (e.g., solution state cellulose NMR spectroscopy, GPC-MALLS) revealed occurring side reactions, which often have been disregarded in DAC chemistry.

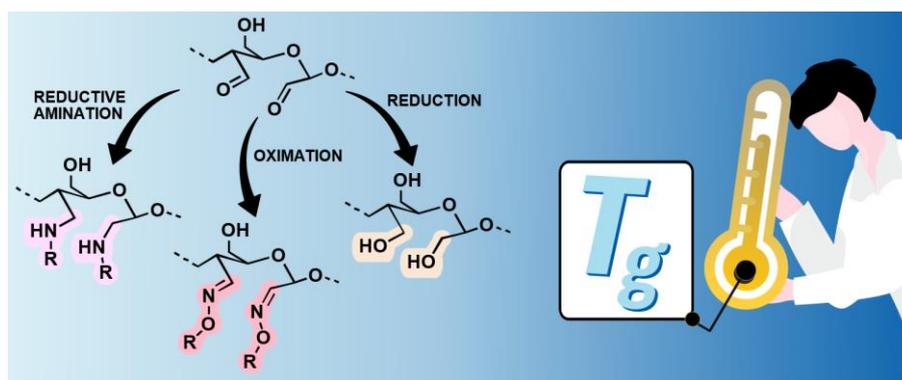


Figure 1: Different synthetic strategies (reductive amination, oximation, and reduction) to modify dialdehyde cellulose (DAC) into thermoplastic materials with tunable glass transition temperature (T_g).

[1] J. Simon, L. Fliri, F. Fröhlich, J. Sapkota, M. Ristolainen, M. Hummel, T. Rosenau, A. Potthast, *ChemSusChem*, submitted, 2023.

[2] J. Simon, L. Fliri, J. Sapkota, M. Ristolainen, A. S. Miller, M. Hummel, T. Rosenau, A. Potthast, *Biomacromolecules*, 24, 166–177, 2023.



SUGARFUN²: CARBOHYDRATE FUNCTIONALISED CARBOHYDRATES

Wrodnigg T.M. ^{*a}, Spormann C. ^c, Dorn T. ^a, Koschella A. ^b, Heinze T. ^b, Lindhorst T. [©]

^a *Graz University of technology, Institute of Chemistry and Technology of Biobased Systems, 8010 Graz, Austria Affiliation*

^b *Friedrich Schiller University of Jena, Institute for Organic Chemistry and Macromolecular Chemistry, 07743 Jena, Germany*

^c *Christiana Albertina University of Kiel, Otto Diels Institute of Organic Chemistry, Otto-Hahn-Platz 3-4, D-24118 Kiel, Germany*

* t.wrodnigg@tugraz.at

The use of biopolymers from renewable resources for the fabrication of novel and sophisticated materials for technological as well as medicinal applications is an important research field today. As a matter of fact, carbohydrates are amongst the most abundant class of biomolecules, mostly biodegradable as well as non toxic which makes them highly versatile raw materials to be used in this respect. Derivatization of polysaccharides is the most important path to impart further functionalities into the biopolymers and to tailor properties of the biopolymers.[1] In the field of cellulose chemistry, many derivatives have been developed and some are even produced in industrial scale.[2]. In order to tailor the properties of biobased materials and systems, chemical modification of oligo- and polysaccharides to introduce customised functionalisation is an expedient approach.

We have functionalized cellulose with different monosaccharides by azide-alkyne click chemistry approach. [3] Depending on the monosaccharide scaffold different properties can be introduced to the polymeric backbone. For example, if the decorating sugar entity presents the *D-manno* configuration, the obtained mannose-modified cellulose derivatives are potential ligands for manno-specific lectins such as FimH of 1-fimbriated bacteria. Details on synthetic approaches and biological evaluation will be presented.

[1] Xiao R., Grinstaff M. W., *Progress in Polymer Science*, 74, 78 - 116, 2017.

[2] Arca H. C., Mosquera-Giraldo L. I., Bi V., Xu D., Taylor L. S., Edgar K. J., *Biomacromolecules*, 19, 2351 - 2376, 2018.

[3] Koschella A., Chien C-Y., Iwata T., Thonhofer M. S., Wrodnigg T. M., Heinze T., *J. Macromol. Chem. Phys.*, 221(1), 1900343 (1-8), 2019.



REVERSIBLE AND SPATIOSELECTIVE SURFACE ESTERIFICATION FOR THE PRODUCTION OF FUNCTIONAL CELLULOSE NANOFIBRILS

Beaumont M. ^{*a}, Tardy B. ^b, Cianciosi A. ^c, Jungst T. ^c, Potthast A. ^a, Rojas O.J. ^d, Rosenau T. ^a

^a Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences, Vienna (BOKU), Austria

^b Department of Chemical Engineering, Khalifa University of Science and Technology, United Arab Emirates

^c Institute of Functional Materials and Biofabrication, University of Würzburg, Germany

^d Bioproducts Institute, The University of British Columbia, Canada

* marco.beaumont@boku.ac.at

To fully realize the potential of nanomaterials derived from biomass, careful attention must be paid to their native chemical and physical structure. Cellulose nanofibrils, obtained through a top-down approach from cellulose fibers, have significantly advanced the field of materials science in the last decade. However, a major obstacle in this field has been the development of a mild and efficient technique for generating precisely defined and regioselectively modified nanocelluloses [1].

Here we introduce a methodology to extract elementary C6-OH-succinylated cellulose nanofibrils (C6SA-CNFs) by treatment of dissolving pulp with *N*-succinylimidazole, which can be reverted using mild post-treatments [2]. No polymer degradation, cross-linking, nor changes in crystallinity occurred under the mild processing conditions, yielding negatively charged C6SA-CNFs decorated with carboxylate moieties. C6SA-CNFs are strongly shear-thinning and can be post-modified at the free C2,C3-OHs position to yield multifunctional C6SA-CNFs for various applications. They can be, e.g., used as inks in direct ink writing, enabling the preparation of hydrogels with functional and mechanical gradients. Alternatively, the native C6SA-CNFs can be processed into nanopaper and/or treated in alkali to remove the succinate groups. The latter offers the important opportunity of reconstitution of the chemical and structural interfaces associated with the natural states of cellulose microfibrils which for instance does not exist anymore in the case of irreversibly modified, TEMPO-oxidized materials.

In conclusion, the regioselective succinylation offers new opportunities for post-modification, yielding a physically more preserved (multi)functional C6SA-CNF. Moreover, the reversible nature of the modification allows the mimicry of native cellulose interactions in arbitrary geometries to increase interfibrillar interactions and improve mechanical properties.

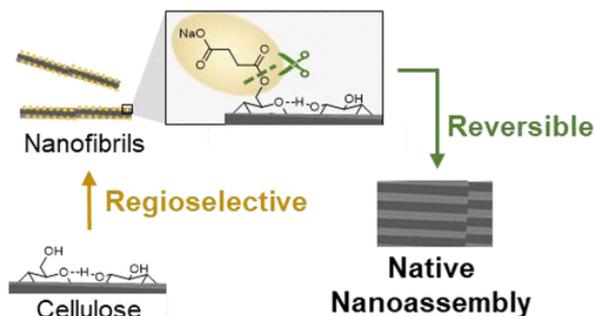


Figure 1 : Maximum one figure or table [2].

[1] Heise, K.; Koso, T.; King, A. W. T.; Nypelö, T.; Penttilä, P.; Tardy, B. L.; Beaumont, M. Spatioselective Surface Chemistry for the Production of Functional and Chemically Anisotropic Nanocellulose Colloids. *J. Mater. Chem. A* **2022**, 10, 23413–23432.

[2] Beaumont, M.; Tardy, B. L.; Reyes, G.; Koso, T. V.; Schaubmayr, E.; Jusner, P.; King, A. W. T.; Dagastine, R. R.; Potthast, A.; Rojas, O. J.; Rosenau, T. Assembling Native Elementary Cellulose Nanofibrils via a Reversible and Regioselective Surface Functionalization. *J. Am. Chem. Soc.* **2021**, 143, 17040–17046.



CELLULOSE NANOFIBRILS CROSS-LINKED THROUGH LYSINE ANALOGUE RESIDUES

Schober K.^a, Bučak Gasser D.^a, Steindorfer T.^a, Bračič M.^b, Kargl R.^{a,b}

^a *Institute for Chemistry and Technology of Biobased Systems (IBIOSYS), Graz University of Technology, Austria*

^b *Laboratory for Characterization and Processing of Polymers (LCPP), University of Maribor, Slovenia*

* rupert.kargl@tugraz.at

Cellulose nanofibrils (NFC) are one of the most promising biobased nanomaterials for a future bioeconomy. [1] The properties of NFC can significantly be altered by chemical surface modifications and cross-linking in the gel form. [2] Among many chemical derivatives of cellulose and other glycans are polysaccharide peptide conjugates, which also allow for biofunctionalization and cross-linking of these materials. [3] To imitate naturally occurring cross-linking processes of protein chains, lysine analogue residues were grafted to cellulose surfaces in the work presented here. These residues were further cross-linked to form covalent NFC networks, potentially relevant for applications in tissue culture. The conditions for grafting and cross-linking were studied in detail, including the mechanical properties of the resulting gels. Surface and charge analytical methods were employed to elucidate the distribution and density of the lysine analogue residues in the networks. The cross-linking procedure was then applied to extrusion 3D printed NFC constructs, allowing for a relatively mild and bio-compatible processing of NFC gels. The NFC networks are meant to imitate fibrous collagenous tissue.

[1] Li, T.; Chen, C.; Brozena, A. H.; Zhu, J. Y.; Xu, L.; Driemeier, C.; Dai, J.; Rojas, O. J.; Isogai, A.; Wågberg, L.; Hu, L., Developing fibrillated cellulose as a sustainable technological material. *Nature* 2021, 590, (7844), 47-56.

[2] Rol, F.; Belgacem, M. N.; Gandini, A.; Bras, J., Recent advances in surface-modified cellulose nanofibrils. *Progress in Polymer Science* 2019, 88, 241-264.

[3] Mohan, T.; Kleinschek, K. S.; Kargl, R., Polysaccharide peptide conjugates: Chemistry, properties and applications. *Carbohydr. Polym.* 2022, 280, 118875.



TOWARDS THE SEMI-SYNTHESIS OF PHOSPHORYLATED GLYCOSAMINOGLYCANS

Esposito F.^a, Traboni S.^a, Iadonisi A.^a, Bedini E.^a

^a Department of Chemical Sciences, University of Naples Federico II, Naples, Italy

* ebedini@unina.it

A very important class of animal-sourced polysaccharides is constituted by sulfated glycosaminoglycans (GAGs). They are highly negatively charged, linear biomacromolecules, composed of disaccharide repeating units, that are extensively decorated with sulfate groups. GAG sulfation is a dynamic, complex post-translational modification process that seems to be a result of evolution in order to let sulfated GAGs play key roles in many physiological and pathological processes typical of higher animals. [1]

GAG mimics carrying phosphate rather than sulfate anionic groups have been poorly investigated, in spite of their interesting perspectives. Indeed, phosphate vs. sulfate differences in size, polarity, acid-base and chelation properties could lend unreported activities to phosphorylated GAGs (pGAGs), as indicated by a recent *in silico* study comparing the structural flexibility and intra- and intermolecular interaction patterns of native GAGs with their phosphorylated counterparts. [2] Indeed, this theoretical investigation suggested that pGAGs could bind proteins generally with a stronger affinity than their sulfated counterparts and the differences in the binding modes might be highly protein target-dependent. This would propose pGAGs as promising, new species to specifically control biochemical processes where the mediating role of sulfated GAGs is crucial. Nonetheless, the introduction of phosphate groups on polysaccharide backbones presents several concerns: i) the rather harsh conditions required by the commonly employed methods, ii) the low degrees of derivatization that are generally achieved; iii) the very limited number of reports dealing with the regioselective phosphorylation of polysaccharides. [3] With the aim to fill the lack of an access to pGAGs, in this communication we present the results of a screening of several standard and recently proposed phosphorylation methods on an unsulfated chondroitin polysaccharide deriving from the fed-batch fermentation of *Escherichia coli* O5:K4:H4 [4] and three partially protected derivatives thereof.

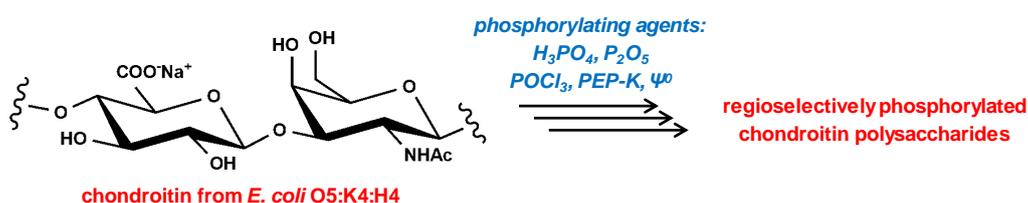


Figure 1 : General scheme of the screening study towards phosphorylated GAG mimics

[1] Perez S., Makshakova O., Angulo J., Bedini E., Bisio A., de Paz J.L., Fadda E., Guerrini M., Hricovini M., Lisacek F., Nieto P.M., Pagel K., Paiardi G., Richter R., Samsonov S.A., Vivès R.R., Nikitovic D., Ricard-Blum S. *J. Am. Chem. Soc. Au*, 3, 628–656, 2023.

[2] Bojarski K.K., Becher J., Riemer T., Lemnitzer K., Möller S., Schiller J., Schnabelrauch M., Samsonov, S.A. *J. Mol. Struct.*, 1197, 401–416, 2019.

[3] Illy N., Fache M., Ménard R., Caillol S., David G. *Polym. Chem.*, 6, 6257–6291, 2015.

[4] Cimini D., Restaino O.F., Schiraldi C. *Emerg. Top. Life Sci.*, 2, 349–361, 2018.



SYNTHESIS OF CHITOTRIAZOLAN DERIVATIVES FOR ANTIBACTERIAL ACTIVITY

Sankar R.*^a, Martha Á. H.^b, Mikkel B. T.^c, Már M.^a

^a Faculty of Pharmaceutical Sciences, University of Iceland, Reykjavík, Iceland

^b Department of Biomedical Science, University of Iceland Reykjavík, Iceland

^c Department of Chemistry, University of Copenhagen, Denmark

* sankar@hi.is

“Click chemistry” reaction has gained significant attention in recent years due to its remarkable efficiency, high yield, and specificity. The most commonly used click reaction is the copper-catalyzed azide-alkyne cycloaddition (CuAAC), which involves the reaction of an azide and an alkyne in the presence of a copper catalyst. This reaction has found applications in a wide range of fields, including drug discovery, materials science, and bioconjugation [1]. Chitosan is a naturally abundant biopolymer that exhibits many biomedical properties due to its biocompatibility, biodegradability, and non-toxic [2, 3]. There have been few studies on the modification of chitosan to triazoles via click chemistry [4, 5].

The work creates a new class of chitosan derivatives by transforming all C-2 primary amino groups to aromatic chito-1,2,3-triazoles (Chitotriazolan) [6]. Additionally, common chitosan derivatives, such as TMC, TAC, HTC, HPC, and CMC, were synthesized with partial substitution so that the remaining primary amino groups could be transformed to triazole via CuAAC reaction. IR and NMR spectroscopy were employed to characterize these derivatives, and size exclusion chromatography was utilized to determine their molecular weight. Chitotriazolan products were synthesized using two approaches with and without the protection of hydroxy groups with TBDMS. A previous study reported that chitosan could not be converted by more than 40% from amine to triazole through *N*-azidated chitosan [5]. However, we successfully synthesized water-soluble chitotriazolan derivatives and chitotriazolan with partially substituted common derivatives. The degree of azidation to 1,2,3-triazole was confirmed to be over 90% through 1H-NMR. To assess their antibacterial activity, the derivatives were evaluated against *S. aureus*, *E. faecalis*, *E. coli*, and *P. aeruginosa* at pH 7.2. The cationic chitotriazolans and mixed chitotriazolans were active against bacteria, except chitotriazolan derived from CMC, which lacked activity.

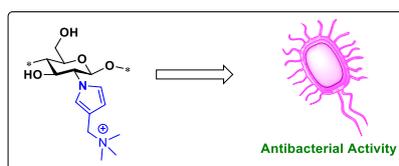


Figure 1. Antibacterial activity of chitotriazolan

References :

1. H.C. Kolb., et al., (2001). *Angew. Chem*, 40, 2004-2021.
2. P. Sahariah., et al., (2017). *Biomacromolecules*, 18, 3846-3868
3. S. Rathinam., et al., (2020) *Int. J. Biol. Macromol.* 160, 548-557
4. F. Zhang., et al., (2008). *Helvetica Chimica Acta*, 91, 608-617
5. R. Kulbokaite., et al., (2009). *Reactive & Functional Polymers*, 69, 771-778
6. S. Rathinam., et al., (2021) *Carbohydrate polymers*, 267, 118162.



SYNTHESIS OF NON-CONVENTIONAL CELLULOSE-BASED CHIRAL STATIONARY PHASES FOR ENANTIOSEPARATION BY HPLC

Lehrhofer A.F.*^a, Bui C.V.^a, Malysenko A.^b, Rosenau T.^{a,c}, Hettegger H.^a

^a Institute of Chemistry of Renewable Resources, Department of Chemistry, University of Natural Resources and Life Sciences, Vienna (BOKU), Austria

^b Institute of Biotechnology, Department of Life Sciences, IMC University of Applied Sciences Krems, Austria

^c Faculty of Science and Engineering, Laboratory of Natural Materials Technology, Åbo Akademi University, Åbo/Turku, Finland

* anna.lehrhofer@boku.ac.at

Enantiomers are pairs of chiral molecules with structures that are mirror images of each other. For their application in many fields, such as the pharmaceutical or food industry, the production of enantiopure compounds is crucial, as the bioactivities of two enantiomers often significantly differ. However, due to their almost identical chemical structure and physicochemical properties, they are difficult to distinguish. Besides asymmetric synthesis, the direct separation of mixtures of enantiomers is one way to obtain single enantiomers. This can be conducted, *inter alia*, using advanced chromatographic techniques, such as HPLC with chiral stationary phases (CSPs). For the preparation of the latter, cellulose represents an ideal raw material for the synthesis of homochiral selectors, as it is a natural chiral polymer and highly abundant. [1]

In our work, we exploit the inherent chirality of cellulose and utilize its derivatives for enantioseparation. To explore new possibilities for the fabrication of cellulose-based chiral selectors, one focus is placed on non-conventional cellulose derivatives using a bottom-up approach. [2] This method, starting from glucose, allows precise and regioselective modification of hydroxy groups. The chiral selectors are subsequently coated onto porous silica particles as a chromatographic support material. Additionally, studies towards new methods for chemical immobilization on the support materials are conducted. All new compounds are comprehensively analytically characterized, and their enantioseparation power is evaluated using a set of representative chiral test analytes. This way, structure-property relationships and molecular interactions leading to enantioseparation can be derived.

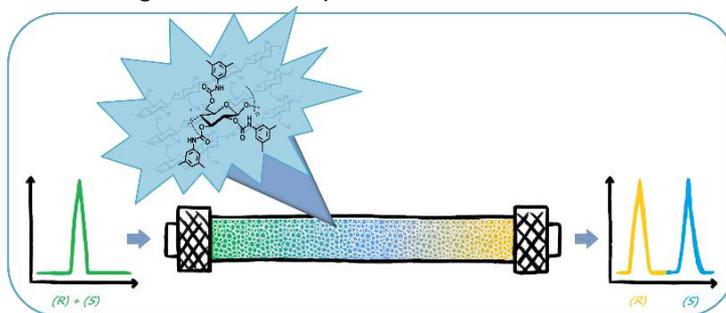


Figure 1: Enantioseparation of racemates on cellulose-based CSPs

[1] Bui, C. V., Rosenau, T. & Hettegger, H., *Molecules*, 27, 1384, 2022

[2] Lehrhofer, A. F., Goto, T., Kawada, T., Rosenau, T. & Hettegger, H., *Carbohydrate Polymers*, 285, 119222, 2022



SYNTHESIS DEVELOPMENT AND OPTIMIZATION OF N,N,N-TRIMETHYL CHITOSAN (TMC) WITH HIGH DEGREE OF TRIMETHYLATION

V. Nagy ^{*a}, H. L. Lauzon^b, M. Másson^a

^a *University of Iceland, Faculty of Pharmaceutical Sciences, School of Health Sciences, Hofsvallagata 53, 107 Reykjavík, Iceland*

^b *Primex, Oskarsgata 7, 580 Siglufjordur, Iceland*

* vin2@hi.is

Chitosan is a marine polysaccharide obtained from crustaceans such as shrimp, crab, and lobster shells. Chitosan is an antimicrobial, non-toxic, biodegradable, and biocompatible polymer. However, it possesses poor aqueous solubility, limiting its applications at physiological pH [1].

With chemical modification resulting in chitosan derivatives, the biological properties can be enhanced. *N,N,N*-Trimethyl chitosan (TMC) has significant antibacterial activity and enhanced aqueous solubility compared to unmodified chitosan [2]. The aim of the current work was to develop and optimize a one-pot process for the synthesis of TMC with high degree of trimethylation (D-TM) which would be suitable for economical production.

The optimization was done through the Design of Experiment (DOE) approach, involving systematic investigation of the effect of different reaction parameters on the degree of trimethylation (D-TM). In these designs reaction parameters like molar ratios, solvent system, alkylating agent, reaction steps, base, base addition, temperature, and time were varied throughout several Fractional Factorial and Full Factorial designs. The D-TM (%) was estimated using ¹H NMR spectroscopy. The results were analyzed using MODDE (Sartorius) software.

With the help of the DOE approach the significant factors of the TMC synthesis were established (temperature, base addition, reagent). It was found that time is an insignificant factor for the yield and D-TM (%) responses, which is beneficial for the economic production of TMC. Most publications on the synthesis of TMC use NaOH or NaHCO₃ base, however they can lead to viscosity issues and gas production. To overcome this, several new potential bases were tried, and the use of *N,N*-diisopropylethylamine (DIPEA) was implemented successfully. The highest obtained D-TM in one step was 72%, which is a significant increase in trimethylation compared to the initial design as well as the currently available published methods.

References:

- [1] P. Sahariah, M.Á. Hjálmarsdóttir, M. Másson. Antimicrobial properties of chitosan and chitosan derivatives, "Marine Glycobiology: Principles and Applications", CRC Press, 2017.
- [2] Ö.V. Rúnarsson, J. Holappa, S. Jónsdóttir, H. Steinsson, M. Másson. N-selective 'one pot' synthesis of highly N-substituted trimethyl chitosan (TMC), *Carbohydrate Polymers*, Volume 74, Issue 3 (2008), Pages 740-744.



DICARBOXYMETHYL CELLULOSE POLYMER: APPLICATIONS AND POTENTIALITIES

Gago D.^a, Chagas R.^b, Ferreira L. M.^a, Coelho I.^{*a}

^a LAQV-REQUIMTE, Departamento de Química, NOVA School of Science and Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

^bFood4Sustainability-Associação para a Inovação no Alimento Sustentável, Centro Empresarial de Idanha-a-Nova, Zona Industrial, 6060-182 Idanha-a-Nova, Portugal.

* imrc@fct.unl.pt

Cellulose materials have been researched throughout the years, due to their appealing physicochemical characteristics, availability and low cost. Dicarboxymethyl cellulose (DCMC) can be produced by the heterogeneous etherification of cellulose with a halogenated malonate compound. The polymer has a wide working pH range and can perform cation exchange at low pH (2.5-3.5). [1]

DCMC has been successfully used in the adsorption of methylene blue (MB) from aqueous solutions [2], protein adsorption [3] and white wine protein stabilization [4]. Membrane filtration is increasingly used in several processes. However, disadvantages such as membrane fouling often contribute to reduced process performance over time. Therefore, the use of adsorption coupled with membrane filtration has great potential, since it can prevent direct solute(s) contact with the membrane. Adsorption of MB with DCMC was coupled with regenerated cellulose ultrafiltration membranes with excellent performance. Adsorbent and membrane reusability studies were performed and DCMC polymer presented 93.9% desorption efficiency with NaCl 1 M solution, whereas none of the membranes desorbed the sequestered dye. This high desorption efficiency suggests that the polymer may be reused in consecutive cycles, thus contributing to a more sustainable and economical process.

This approach will be applied also for proteins (cytochrome C and lysozyme) and may be implemented for white wine stabilization.

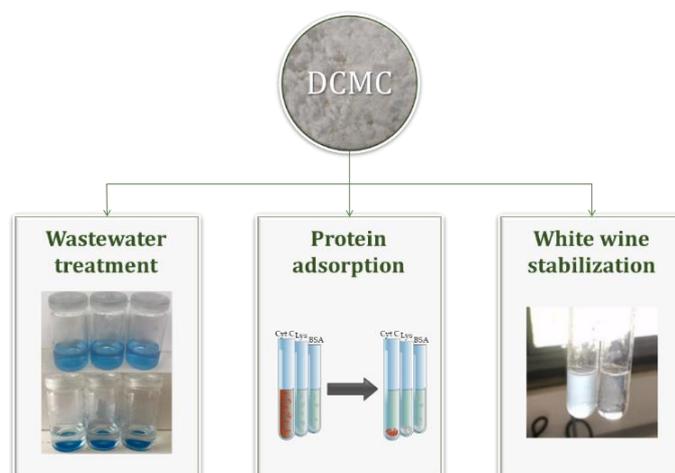


Figure 1: Applications of the DCMC polymer

[1] Ferreira, L.; Chagas, R.; Ferreira, R.B.; Coelho, I.; Velizarov, S. Compound, method of production and uses thereof. WO2019/197884 A1.

[2] Gago, D., Chagas, R., Ferreira, L.M., Velizarov, S., Coelho, I. *Membranes*, 10, 2020.

[3] Gago, D., Corvo, M.C.; Chagas, R.; Ferreira, L.M.; Coelho, I. *Polymers*, 14, 5122, 2022.

[4] Gago, D., Chagas, R., Ferreira, L.M., *Beverages*, 7, 2021.



AMINO-DECORATED NANOSTRUCTURED CELLULOSES AS A POTENTIAL CARRIER SYSTEM FOR BIOACTIVE COMPOUNDS

Ronchetti R. ^{*a}, Beaumont M.^b, Wojtyła, P.^a, Francesconi S.^c, Balestra G. M.^c, Giovagnoli S. ^a, Rosenau T,^b Camaioni E.^a

^a Department of Pharmaceutical Sciences, University of Perugia, Perugia, Italy.

^b Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences, Vienna (BOKU), Austria.

^c Department of Agriculture and Forest Sciences (DAFNE), University of Tuscia, Viterbo, Italy.

* Presenting author: riccardo.ronchetti00@gmail.com

Nanocellulose has emerged as a promising material for many applications, including crop protection.[1] The unique physicochemical properties of nanocellulose (NC), such as high specific surface area, biocompatibility, and biodegradability, make it an ideal carrier for the controlled release of agrochemicals. To improve the adsorption of bio-active components onto NC, chemical modification is often necessary to introduce functional groups onto the NC surface. The main challenge is in this regard to establish “green” protocols, which are efficient and versatile.

In the present work, functional NCs decorated with epoxide groups were prepared and investigated for application in crop protection. Epoxide groups can be selectively and efficiently post-modified with a myriad of nucleophiles and offer a high versatility, but so far, they have been mainly introduced using the toxic and potentially cancerogenic chemical, epichlorohydrin. [2] We chose an alternative and more sustainable procedure using glycidol and investigated it for the preparation of NCs loaded with bio-active components. The etherification was performed with a binary ionic liquid mixture of [EMIM][OAc] as solvent, and a sulfonated imidazolium as catalyst. **(Figure 1)** This modification was directly compared to the traditional epoxidation using epichlorohydrin. Both NCs were post-modified with ammonia to introduce amino groups onto the NC surface, and tested for loading of bio-active phenolic acids. The modified celluloses were characterized by nuclear magnetic resonance spectroscopy and infrared spectroscopy, and compared to traditionally functionalized cellulose using epichlorohydrin. The amount of adsorbed phenolic acids and their release was evaluated and the loaded NCs were used for formulation of drug delivery systems for crop protection. Epoxidation of cellulose using glycidol mediated by ionic liquids enabled the introduction of a higher amine content with higher adsorption capability than the traditional method using epichlorohydrin, and the functionalized amino-NCs show high promise for the development of sustainable agrochemical formulations.

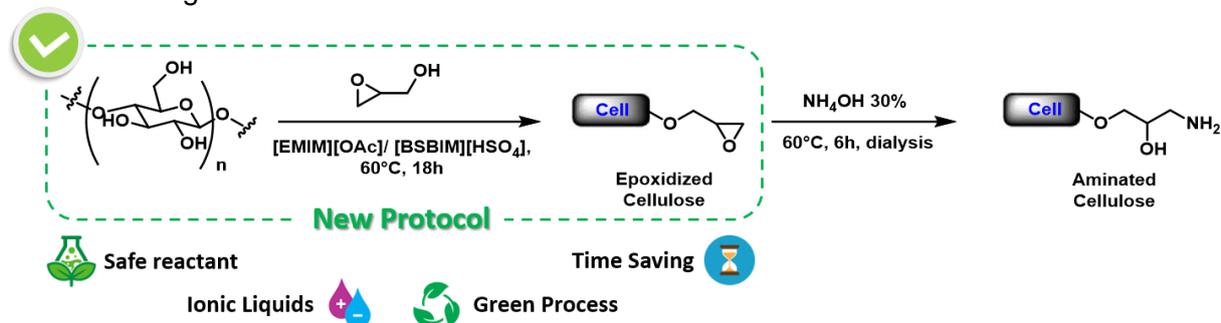


Figure 1: Synthetic pathway for the synthesis of amino-decorated cellulose.

[1] Schiavi D., Ronchetti R., Di Lorenzo V., Salustri M., Petrucci C., Vivani R., Giovagnoli S., Camaioni E. & Balestra, G. M., *Applied Sciences*, 12, 2604, 2022.

[2] Dong S., Cho J., Woo L. Y. & Roman, M., *Biomacromolecules*, 15, 1560-1567, 2014.



DEVELOPMENT OF SYNTHETIC METHODOLOGIES TO OBTAIN DICARBOXYMETHYL CELLULOSE WITH DIFFERENTIATED STRUCTURE AND PROPERTIES

Gago D.^a, Corvo, M.^b, Chagas R.^c, Coelho I.^a, Ferreira L. M.*^a

^aLAQV-REQUIMTE, Departamento de Química, NOVA School of Science and Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal. ^bi3N/Cenimat, Materials Science Department, NOVA School of Science and Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal. ^cFood4Sustainability-Associação para a Inovação no Alimento Sustentável, Centro Empresarial de Idanha-a-Nova, Zona Industrial, 6060-182 Idanha-a-Nova, Portugal.

* lpf@fct.unl.pt

Dicarboxymethyl cellulose (DCMC) is a polyelectrolyte cellulose ether synthesized via the heterogeneous reaction of cellulose with a halogenated malonate compound. Our team recently developed and explored this compound [1-4], which has a tunable water solubility and double the number of ionizable groups compared to the well-known polymer carboxymethylcellulose (CMC) with the same degree of substitution (DS). As a result, DCMC exhibits a higher charge density over a wide range of pH values.

However, achieving precise control over this etherification reaction is a non-trivial task. The resulting products may display an unpredictable DS and variable selectivity of the cellulose hydroxyl groups. To address this issue, we have focused on promoting the dissolution of cellulose in inert solvents that do not interfere with the etherification reagents.

Here we used solid-state nuclear magnetic resonance (ssNMR) experiments to investigate the production of DCMC under homogeneous and heterogeneous conditions. Our results show that these predefined synthetic conditions can yield DCMC with different substituted positions, varying degrees of substitution, and backbone selectivity. This can result on the tunability of DCMC properties like that observed for CMC, which also has distinct properties based on its degree of substitution and backbone selectivity.[5]

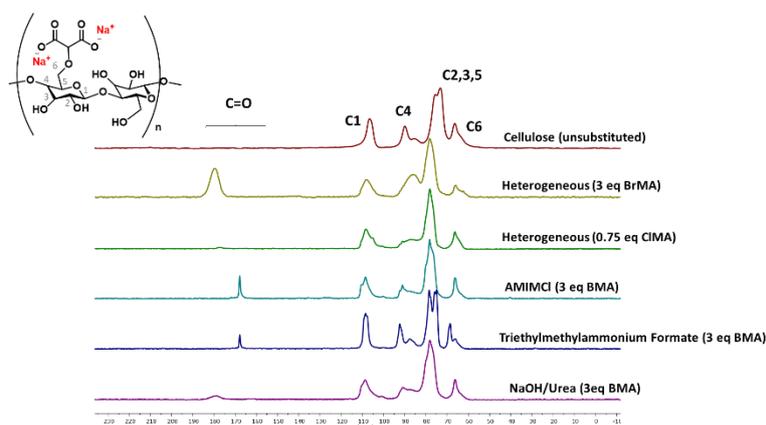


Figure 1 : ssNMR results for DCMC made in different conditions (homogeneous and heterogeneous) with different electrophiles. BrMA – bromo malonic acid, CIMA – chloro malonic acid.

[1] Ferreira, L.; Chagas, R.; Ferreira, R.B.; Coelho, I.; Velizarov, S. Compound, method of production and uses thereof. WO2019/197884 A1.

[2] Gago, D., Chagas, R., Ferreira, L.M., Velizarov, S., Coelho, I. *Membranes*, 10, 2020.

[3] Gago, D., Corvo, M.C.; Chagas, R.; Ferreira, L.M.; Coelho, I. *Polymers*, 14, 5122, 2022.

[4] Gago, D., Chagas, R., Ferreira, L.M., *Beverages*, 7, 2021.

[5] Cai, Z. X.; Wu, J.; Du, B.Q.; Zhang, H. B. *Food Hydrocolloids*, 76, 150, 2018.



THERMO-SENSITIVE HYDROGELS BASED ON CARBOXYMETHYL CELLULOSE COPOLYMERS DUALY FUNCTIONALIZED BY PASSERINI THREE COMPONENT REACTION

Remy L.^{*a}, Couturaud B.^b, Sudre G.^c, Fleury E.^a, Charlot A.^a,

^a *Université de Lyon, CNRS, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, UMR 5223, Ingénierie des Matériaux Polymères F-69621 Cédex, France*

^b *Univ Paris Est Créteil, CNRS, Institut de Chimie et des Matériaux Paris-Est (ICMPE), UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France*

^c *Université de Lyon, CNRS, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, UMR 5223, Ingénierie des Matériaux Polymères F-69622 Cédex, France*

* laurent.remy@insa-lyon.fr

Chemical modifications of polysaccharides have been an ever-growing interest of chemists to adjust the properties of this valuable biomass. Multicomponent reactions constitute a versatile chemical tool to sustainably (multi)functionalize polymers thanks to their good atom economy and their achievement in mild and “one-pot” conditions. In particular, in the case of the Passerini three component reaction (P-3CR), a carbonyl (aldehyde or ketone), an isocyanide and a carboxylic acid react together to lead to a single final structure. Recently, we demonstrated the feasibility to modify carboxymethyl cellulose (CMC) by P-3CR [1] in aqueous medium with various aldehydes and isocyanides, and we extended this reaction to the use of ketones in order to generate chemical hydrogels showing a thermo-induced and reversible shrinkage [2]. The present work is a continuation of this topic and focuses on the design of new thermo-sensitive physical hydrogels based on tailor-made CMC grafted copolymers obtained by P-3CR. Various isocyanide-terminated Jeffamine segments, differing in their composition and molar mass, and exhibiting a LCST, were grafted onto CMC backbone, conjointly with an aliphatic aldehyde molecules, by P-3CR in water medium. In this way, a series of dually modified CMC copolymers was conveniently synthesized, and their behavior in aqueous solutions was fully investigated. It appears that physical hydrogels are formed upon a temperature elevation (Figure 1). The thermosensitive response was characterized at different scales, by rheology, turbidimetry, DSC and NMR spectroscopy. Additionally, SAXS experiments allowed to elucidate the internal organization as a function of temperature [3]. The influence of the copolymer concentration, the presence of salt, as well as the jeffamine structure, on the temperature-triggered response, was evaluated. It results that the thermosensitivity is controlled by these parameters, and that the dual chemical grafting brought by the Passerini reaction leads to a noticeable change of the association temperatures, in comparison with more common architectures, described in literature [4].

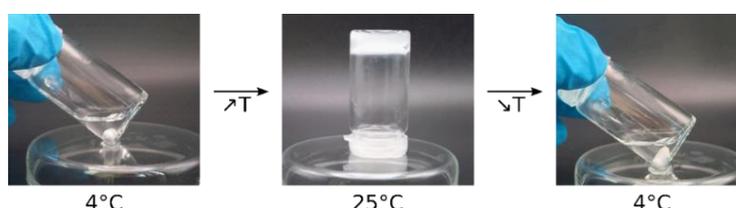


Figure 1 : Thermo-induced gelation of dually grafted CMC copolymers in water

[1] Pettignano, A., Daunay, A., Moreau, C., Cathala, B., Charlot, A., Fleury, E., *ACS Sustain. Chem. & Eng.*, 2019, 7, 17, 14685

[2] Remy, L., Sudre, G., Charlot, A., Fleury, E., *Carbohydr. Polym.*, submitted

[3] Remy, L., Couturaud B., Sudre, G., Fleury, E., Charlot, A. in progress.

[4] Dulong, V., Mocanu, G., Picton, L., Le Cerf, D. (2012). *Carbohydr. Polym.*, 2012, 87, 2, 1522–1531.



PASSERINI THREE-COMPONENT REACTION FOR THE HYDROPHOBIZATION OF MICROFIBRILLATED CELLULOSE: A GREEN STRATEGY TOWARD ADVANCED PAPER PACKAGING

HAMZAH O. ^{*a}, CURMI H. ^b, DARPENTIGNY C. ^b, JEAN B. ^a, HEUX L. ^a

^a Univ. Grenoble Alpes, CNRS, CERMAV, 38000 Grenoble, France

^b Centre Technique du Papier, 38000 Grenoble, France

* Oussama.hamzah@cermav.cnrs.fr

Recent studies indicate that coating paper or cardboard with microfibrillated cellulose (MFC) can enhance their barrier properties. However, the hydrophilic nature and sensitivity to humidity of native MFC-coated papers hinder their development, limiting their potential applications in industries such as food packaging [1]. The first step involves chemically modifying oxidized MFCs using the Passerini three-component reaction (P-3CR, shown in Fig. 1) to confer a partial hydrophobic character on them. The P-3CR combines an aldehyde, a carboxylic acid, and an isocyanide into an α -acyloxycarboxamide function, making it possible to dually functionalize MFCs [2]. In the second step, the hydrophobized MFCs are coated onto paper to provide them with enhanced barrier properties that can withstand humidity and temperature variations.

To achieve efficient hydrophobic grafting of MFCs, we systematically varied key parameters of the P-3CR, such as the nature of the oxidation (into carboxylic acid using TEMPO-mediated or into aldehydes using periodate [3]), the degree of oxidation (DO) of the starting MFCs, the amount and nature of hydrophobic substituents, and co-solvents. Advanced spectroscopic techniques, including ATR-FTIR and CP-MAS ^{13}C NMR, were used to characterize the products and quantitatively measure the degree of substitution (DS, Fig. 1). Results showed highly efficient hydrophobic grafting up to DS=0.33 when using heptanoic acid, tert-butyl isocyanide, and periodate oxidized MFCs of DO=1.1, while preserving the atom economy character of P-3CR. Furthermore, using cosolvents enables the grafting of low-soluble moieties (e.g., undecanoic acid). The hydrophobic MFCs produced were deposited onto flexible packaging paper sheets using the wet lamination method [4]. The homogeneity of the coatings was investigated using SEM, and the barrier properties were tested using suitable methods. Initial results showed good oil barrier properties with only a 5 g/m² coating weight.

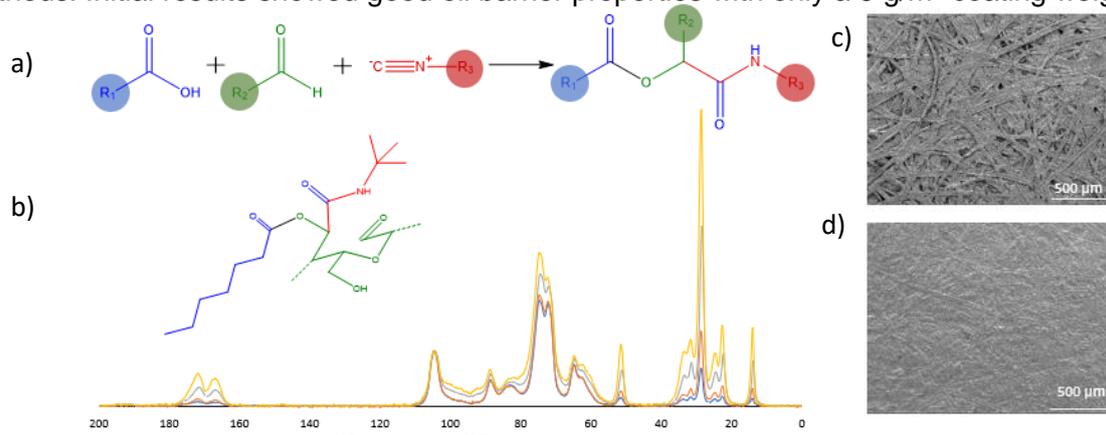


Figure 1: P-3CR scheme (a). ^{13}C NMR spectra of Passerini-modified periodate oxidized MFCs showing increasing DS (b). SEM image of non-coated (c) and coated (d) paper.

[1] Nechita P., & Roman M., *Coatings*, vol. 10, no. 6, pp 566, 2020 [2] Pettignano A., Leguy J., Heux L., Jean B., Charlot A., & Fleury E. *Green Chemistry*, vol. 22, no. 20, pp 7059–7069, 2020 [3] Leguy, J., Nishiyama, Y., Jean, B., & Heux, L. *ACS Sustainable Chemistry & Engineering*, vol 7, no.1, pp 412–420, 2019 [4] WO 2016174348 A1



ONE-POT FUNCTIONALIZATION OF PULLULAN BY FERULIC ACID USING ENZYMATIC CATALYSIS.

Boundaoui K. ^{*a}, Rihouey C.^a, Picton L.^a, Le Cerf D.^a, Dulong V.^a

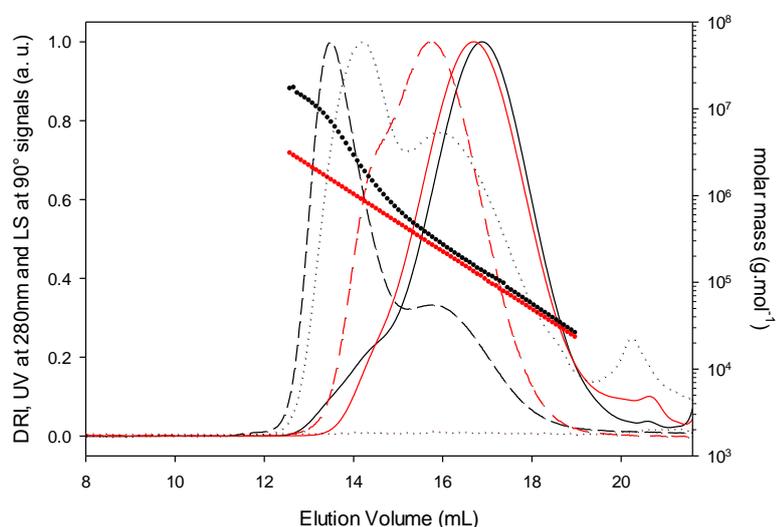
^a *PBS laboratory UMR 6270, University of Rouen Normandy, France*

Koceila.boundaoui@univ-rouen

Polysaccharides are natural abundant polymers widely used in many fields as texturizer, gelling, adsorption, filtration agents.... In order to improve their properties and better adapt them to targeted applications, they are subject to functionalization which may bring more reactivity or new properties and functions (e.g.: amphiphilicity [1], antioxidant [2], antibacterial properties [3],...).

In our project, an enzymatic functionalization, green chemistry respectful, is considered to bring new properties to polysaccharides by the addition of phenolic compounds. The latter is based on the activity of a family of oxidoreductase enzyme "laccases" able to specifically oxidize many natural phenolic compounds (e.g., ferulic acid, caffeic acid, catechin...) and catalyse polysaccharides-phenolic compounds reaction [4]. To well understand this kind of conjugation, the functionalization of Pullulan, a neutral polysaccharide, by Ferulic acid (an antioxidant molecule) has been done. The success of this latter was proved by an apparition of UV-Vis signal and new FTIR bands relative to the chemical incorporation of Ferulic acid into Pullulan. A maximum grafting amount of 6.8 mg of Ferulic acid per g of product was obtained thanks to the Folin-Ciocalteu method. The macromolecular parameters determined by SEC/MALS analysis showed a non-degrading synthesis condition. It also showed an apparition of intra and intermolecular hydrophobic interactions between the grafted Ferulic acid. This amphiphilic behaviour was highlighted via fluorescence measurements with pyrene probe by the apparition of a critical aggregation concentration. The impact of this incorporation on the

rheology of Pullulan was monitored and showed a slowing down of chains reptation in the entangled system. Finally, the antioxidant activity of functionalized Pullulan has been studied.



Elution profile of Pull red) and Pull-FA 0.4 (black) in filtered LiNO₃ 0.1M at 25°C Light diffusion scattering at 90° (dashed line), refractive index (full line) and UV absorbance at 280 nm (dotted line). and molar masses distribution.

[1] Duval-Terrié C., Huguet J. & Muller G., *Colloids and Surfaces*, 220, 105, 2003

[2] Dulong V., Kouassi M-C., Labat B., Le Cerf D. & Picton L., *Food Chemistry*, 262, 21, 2018

[3] Kouassi M-C., Thébault P., Rihouey C., Dé E., Labat B. & Picton L., *Biomacromolecules*, 18, 3238, 2017.

[4] Aljawish A., Chevalot I., Jasniewski J., Revol-Junelles A-M., Scher J. & Muniglia L., *Food Chemistry*, 161, 279, 2014.



CATALYST-FREE ACETYLATION OF STARCH USING GREEN DEEP EUTECTIC SOLVENTS AS REACTION PROMOTERS

Portillo-Perez G.A.^a, Skov K.B.^a, Martinez M.M.^a

^a Center for Innovative Food (CiFOOD), Department of Food Science, Aarhus University, AgroFood Park 48, 9200, Aarhus N, Denmark

gportillo@food.au.dk

Starch is widely regarded as a promising starting macromolecule for bio-based materials due to its polymeric and green nature, as well as its abundance. Therefore, modification and functionalization of starch for the improvement of its mechanical and barrier properties as packaging material has become a focus of research in the past years. Nevertheless, if modified starch is to be widely adopted as a sustainable alternative, its production process needs to be sustainable, both environmentally and financially. Herein, a sustainable, catalyst-free acetylation is presented. Using choline chloride/urea (ChCl:Ur) natural deep eutectic solvent (DES) as both solvent and reaction promoter, a high degree of substitution (DS) could be obtained, while maintaining a high average molecular weight (Mn). DS was calculated via ¹H NMR and further confirmed by ¹³C solid state NMR. The system proved to be highly efficient, achieving values of DS=2.2 after only one hour, and reaching a full theoretical DS of 3.2. However, under certain conditions, reactions between solvent and reagents took place, resulting in either acetyl urea or starch carbamates. The reaction conditions were analyzed by response surface methodology and optimized to reduce reaction times while keeping high DS, obtaining DS=2,87 after only 30 min, and substrate loads of 20 wt%. Thermal properties were analyzed via TGA and DSC. Results showed an increase in thermal stability and glass transition temperatures, with a degradation temperature of 392 °C (an increase of 62 °C from native starch). Similarly, glass transition onset temperature increased from 65 °C for starch to 158,9 °C for fully substituted starch. Results for Mn were obtained by HP-SEC-MALS, showing a reduction in Mn from 1.04x10⁸ Da for starch, to 1,6x10⁵ Da for the most substituted samples. The high DS and Mn values, as well as the short reaction times proved that ChCl:Ur is an efficient solvent and reaction promoter to result in high derivatization levels while keeping starch chain degradation low.

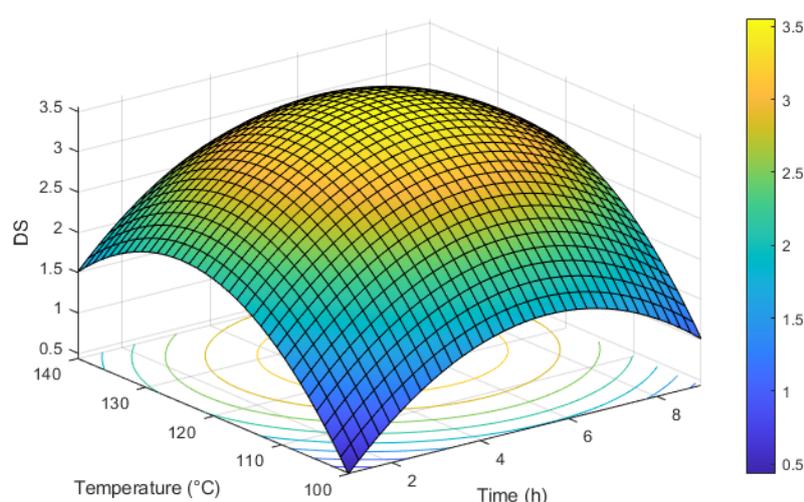


Figure 1 Response surface plot of the catalyst-free acetylation reaction using a ratio of acetic anhydride to starch of 15.



MOLECULAR ENGINEERING OF NANOCELLULOSE-POLY(LACTIC ACID) BIO-NANOCOMPOSITE INTERFACE BY REACTIVE SURFACE GRAFTING FROM COPOLYMERIZATION

Gaoyuan Ye¹, Qiwen Yong¹, Liqiu Hu¹, Emil Rosqvist², Wenyang Xu^{1,*}, Chunlin Xu¹

¹ Laboratory of Natural Materials Technology, Åbo Akademi University, Turku FI-20500, Finland

² Laboratory of Molecular Science and Engineering, Åbo Akademi University, Turku FI-20500, Finland

*Presenting author: Wenyang.Xu@abo.fi

Poly (Lactic acid), a prominently biodegradable polymer, yet limited by its weak toughness and poor crystallinity, the practical application-efficacy has been significantly restricted. In the present study, the surface modified cellulose nanocrystal (CNC) *via* copolymerization of caprolactone and allyl caprolactone (ACL) as a reinforcement, was designed to improve mechanical performances of PLA. Reactive core-shell nanofiller (allyl polycaprolactone-grafted CNC, *i.e.*, CNC-*g*-APCL) of surface molecular engineering facilitated interfacial compatibilization between PLA and CNC *via* covalent stitching through a facile *in situ* reactive extrusion process. The presence of elastic polycaprolactone (PCL) rendered a good energy dissipation as revealed by an improved toughness and elongation at break of the PLA/CNC hybrid composites. Most importantly, the integrated CNC composite presented an extremely high crystallinity of 45.1%, which is top-ranking among all existed studies regarding PLA/CNC nanocomposites. In a nutshell, this research presents an enticing approach of formulating nanocomposites with improving interfacial compatibility among matrix and components, supplying a generic remedy for mechanical and crystalline weakness of biodegradable polymers.

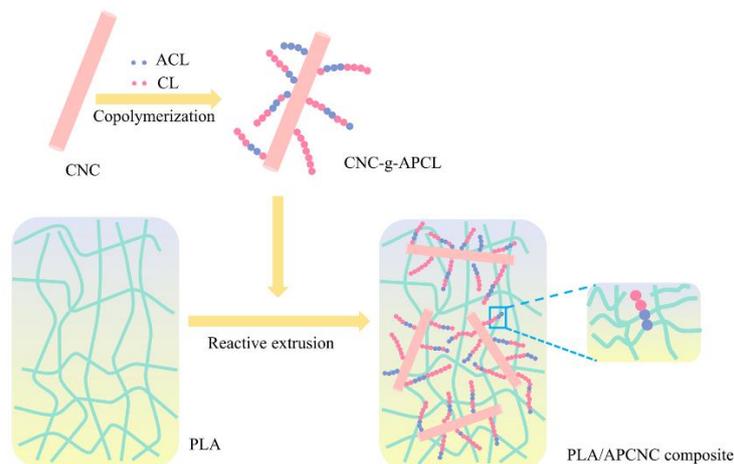


Figure 1. Schematic illustration of interfacial compatibilization of PLA/CNC composite through CNC surface *grafting from copolymerization*



Session 2 Poster



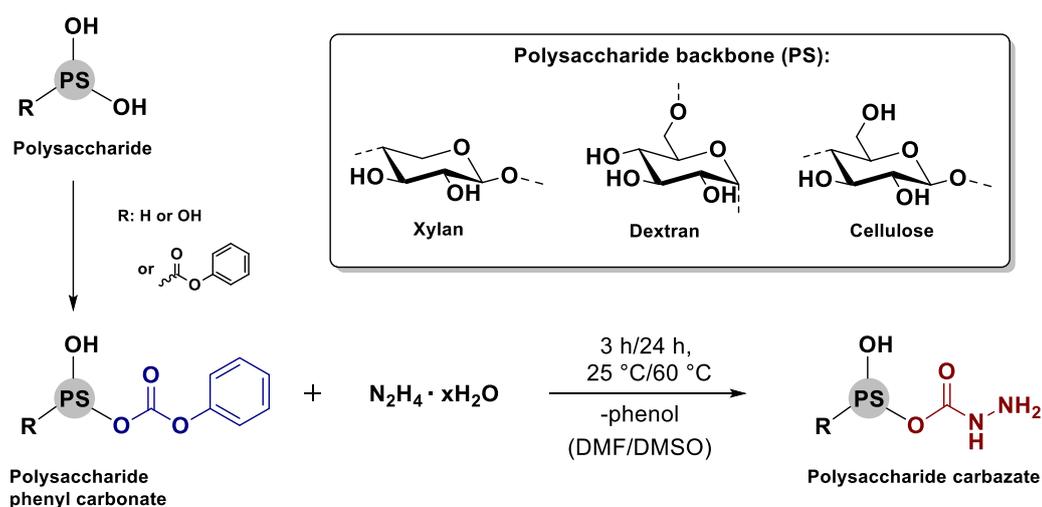
SYNTHESIS AND CHARACTERIZATION OF POLYSACCHARIDE CARBAZATES

Geitel K.*, Würfel H., Heinze T.

Center of Excellence of Polysaccharide Research, Institut of Organic Chemistry and Macromolekular Chemistry Friedrich Schiller University Jena Humboldtstraße 10, 07743 Jena, Germany

* email: katja.geitel@uni-jena.de

Highly substituted phenyl carbonates of xylan, dextran, and cellulose were converted with hydrazine hydrate to introduce nucleophilic carbazate groups in the polysaccharide backbone. The nucleophilic replacement reaction was carried out in aprotic solvents under various reaction conditions. Different molar ratios of hydrazine hydrate allow the adjustment of the degree of conversion, which enables the preparation of highly substituted derivatives or derivatives with bifunctional reactive groups. The subsequent functionalization of the derivatives is feasible with nucleophilic substituents via the phenyl carbonate group and, in addition, the linkage of aldehydes or ketones is possible by the carbazate groups. Thus, this conversion could be successful carried out by the reaction of those carbazate groups with 4-fluorobenzaldehyd.



Scheme: Reaction scheme of the formation of polysaccharide carbazates by conversion of polysaccharide phenyl carbonates with hydrazine hydrate.



SULFATED POLYSACCHARIDES SUBSTITUTED WITH BIFORKED GROUPS: THEIR EFFECT ON PHYSICOCHEMICAL PROPERTIES OF SUSPENSIONS AND MECHANICAL PROPERTIES OF FILMS

Wojno S.^{b,c}, Sonker A.^{a,c}, Feldhusen J.^a, Kádár R.^{b,c}, Westman G.^{a,c}

¹Department of Chemistry and Chemical Engineering, Division of Chemistry and Biochemistry, Chalmers University of Technology, Sweden

²Department of Industrial and Material Science, Division of Engineering Materials, Chalmers University of Technology, Sweden

³Wallenberg Wood Science Center, Chalmers, Sweden

* jelka@student.chalmers.se

Sulfonated cellulose nanocrystals, CNC, have been researched for many years. Most of the chemical modification has been on the plenty-fold hydroxyl groups on the surface, whereas the sulfate groups have been somewhat neglected as a handle for chemical modification. Herein we present our work on conjugation to the already existing sulfate groups on carrageenan and sulfonated CNC with Azetidinium salts which gives biforked dialkylamine substituents (Figure 1a). Different dialkyl amines were used with varying alkyl chain lengths and functional groups to gain CNC derivatives with different physicochemical properties and application possibilities. The CNC-suspensions behavior was studied by rheology and passive drying of suspensions yielded flexible transparent films (Figure 1b and 1c). The poster/paper will present the synthesis of azetidinium salts, their conjugation to carrageenan and CNC, and the characterization of suspensions and films formed therefrom.

The synthesis of several azetidinium salts was investigated for the purpose of utilizing them to modify the surface of. Azetidinium salts are produced in a two-step reaction by reacting epichlorohydrin with dialkyl amines, producing the ring-open intermediate, Chloro-2-hydroxypropyl-N,N-dialkylamines. The final product is gained by self-cyclization of the ring-open intermediate, mediated in a polar solvent at elevated temperatures. FTIR and NMR were used to gain knowledge on the formation of Chloro-2-hydroxypropyl-N,N-dialkylamines as well as the ring closed azetidinium salt, monitoring the reaction to unfold the kinetics.

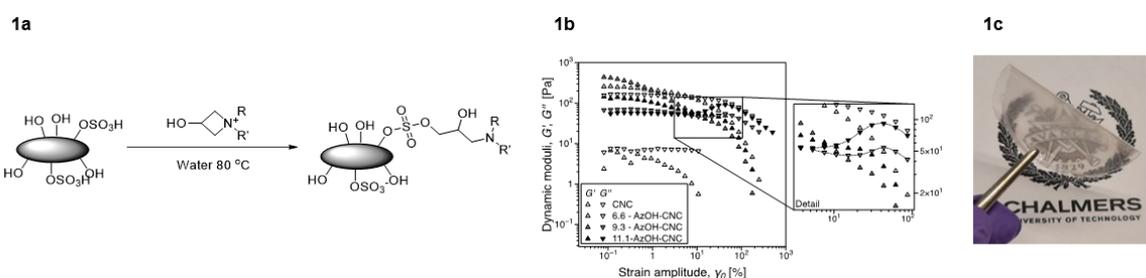


Figure 1: a) Illustration of conjugated azetidinium salt to sulfate groups. b) Graph illustrating the changes occurring for the dynamic moduli as different salts with varying chain length are conjugated to CNC. c) Picture of modified CNC film.



POSSIBILITIES OF USING STARCH ESTERS IN PACKAGING APPLICATIONS

Römhild K.^{*a}, Krypczyk A.^a, Lindemann H.^b, Hermann P.^b, Heinze Th.^b

^a*Thuringian Institute for Textile and Plastics Research Rudolstadt (TITK), Competence Center Polysaccharide Research, Germany*

^b*Institute for Organic Chemistry and Macromolecular Chemistry, Competence Center Polysaccharide Research Friedrich-Schiller-University Jena (FSU), Germany*

*roemhild@titk.de

In recent decades, biopolymers have become increasingly important as a replacement for synthetic plastics due to economic and environmental constraints and societal demand. Starch as a biopolymer is one of the most frequently occurring renewable raw materials, which can be chemically modified in a targeted manner and hence its molecular structure, giving it thermoplastic properties. Due to their historically very long use, they are available in consistent quality and purity. However, the full potential of these natural products is far from being known and exhausted. Their molecular and supermolecular structural properties can be widely varied by means of a targeted chemical modification of the hydroxyl groups and specifically adapted for a wide variety of applications. Starch fatty acid esters produced in this way are therefore the perfect, biogenic raw material to be used in food packaging as a thermoplastically deformable material. After the first successful studies on synthesis on a laboratory scale,¹ studies will be presented in the which should ensure a later transfer to the technical scale. In addition to films, film composites with other materials of biogenic origin and coatings are also products of interest.

[1] Liebert, T.; Nagel, M. C. V.; Jordan, T.; Heft, A.; Grünler, B.; Heinze, T. *Macromolecular Rapid Communications*, 32 (17), 1312–1318, 2011.



CELLULOSE MODIFICATION WITH SMALL SUGAR ENTITIES AS BACTERIAL ANTI-ADHESIVES

Prasch H.^{a*}, Dorn T.^a, Spormann C.^b, Koschella A.^c, Heinze T.^c, Lindhorst T.^b, Wrodnigg T.M.^a

^a Institute of Chemistry and Technology of Biobased Systems, Graz University of Technology, 8010 Graz, Austria

^b Otto Diels Institute of Organic Chemistry, Christiana Albertina University of Kiel, D-24118 Kiel, Germany

^c Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University of Jena, 07743 Jena, Germany

* herwig.prasch@tugraz.at

Polysaccharides, such as cellulose, are amongst the most abundant biopolymers and because of the non-toxic nature are of great interest for the fabrication of new materials for medicinal applications. Derivatization of the polysaccharide, introducing bioorthogonal ligation handles such as alkynes or azides, enables further functionalization using click-chemistry.[1]

Bacterial infections are a serious threat to human health due to the evolution of multi-resistant bacterial strains against available antibiotics. Bacterial diseases are often triggered by the binding of the pathogens to the surface of host cells.[2] In this respect, many bacteria use carbohydrate specific lectins for adhesion to human cells. Therefore, new therapeutic approaches interfering with the interaction of the bacteria with human cells are highly in demand. Many different approaches aiming for the prevention of bacterial adhesion have been reported, including affecting adhesion biosynthesis, use of anti-adhesion antibodies, or any type of adhesion analogs.[2-4]

In this respect, functionalization of biopolymers with potent lectin binding inhibitors can be used for development of polyvalent epitopes for anti-adhesion therapy.

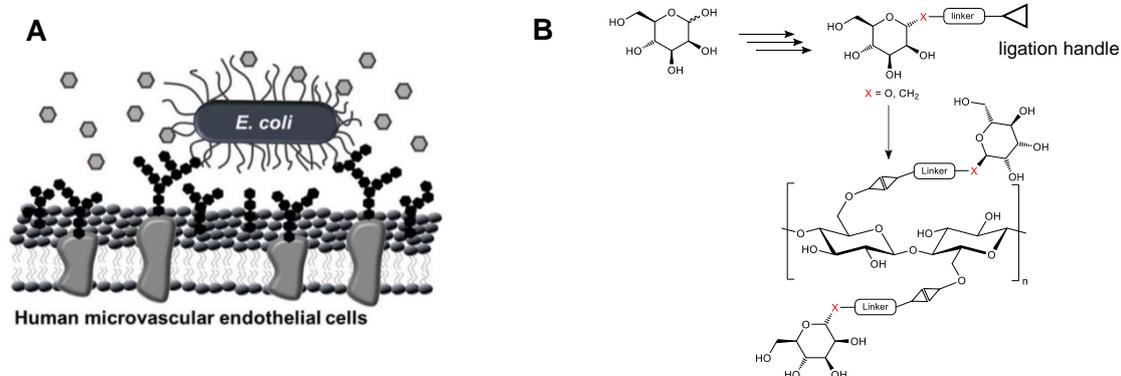


Figure 1: A) *E. coli* binds to human cells using FimH.[6] B) Synthesis of D-mannoside derivatives for a covalent linkage to modified cellulose.

As an example, uropathogenic *Escherichia coli* (UPEC) binds to the cell surface of host cells by the D-mannoside selective lectin FimH (Figure 1A). In our approach, we have functionalized cellulose with different D-mannosides to obtain potential polyvalent ligands for lectin FimH presenting 1-fimbriated bacteria (Figure 1B). Synthetic details and biological evaluation will be presented.

[1] Koschella A., Wrodnigg T., Heinze T. et al., *J. Macromol. Chem. Phys.* 221, 1900343, 2019.

[2] Krachler A.M., Orth K., *Virulence*, 4, 284-294, 2013.

[3] Ofek I., Hasty D. L., Sharon N., *FEMS Immunol Med Microbiol.*, 38, 181-191, 2003.

[4] Okuda K., Hanada N., Usui Y. et al., *Arch Oral Biol.*, 55, 754-762, 2010.

[5] Moon H.W., Bunn T. O., *Vaccine*, 11, 213-220, 1993.

[6] Möckl L., Lindhorst T. K. et al., *Biochimica et biophysica acta*, 1860, 2031, 2016.



Session 3

Progress in bulk, surface and interactions of polysaccharide through experimental and computational methods

Session organizers:

Wim Thielemans, Isabelle Capron, Ali Khodayari, Hubert Hettegger, Katja Heise

Keynote speakers:

Yu Ogawa

Drying-induced structural modifications of nanocelluloses: 4D STEM and molecular dynamics simulation study

Peter Fischer

Structure and rheology of stimuli-responsive nanocellulose interfacial layers



DRYING-INDUCED STRUCTURAL MODIFICATIONS OF NANOCELLULOSES: 4D STEM AND MOLECULAR DYNAMICS SIMULATION STUDY

Yu Ogawa^{a, *}

^a *Univ. Grenoble Alpes, CNRS, CERMAV, 38000 Grenoble, France*

* yu.ogawa@cermav.cnrs.fr

Fine morphological details of nanocelluloses, such as fibrillar twists and defects, have recently attracted attention for their potential consequences in the material properties. These nanoscale structural features are characterized primarily using transmission electron microscopy (TEM) and atomic force microscopy (AFM) in dry conditions where nanocelluloses are dried from aqueous suspensions on a supporting substrate. While the surface tension of water is immense at the nanoscale and thus is expected to affect the nanocellulose structure, the actual effects of drying on the nanoscale morphology of cellulose remain largely elusive.

In this contribution, I present our recent efforts in analyzing the drying-induced structural changes of nanocelluloses at the single crystal level based on both experimental and theoretical approaches. The combination of nanobeam electron diffraction and cryoTEM revealed that the twisted morphology of CNCs is susceptible to the drying process during the sample preparation. The drying on carbon film alters the native continuous twists of CNCs into discontinuous sharp twists and extended flat regions [1]. The morphology of kink defects of CNCs is also affected by the drying. Low-angle kinks are partly straightened upon drying on a flat substrate, resulting in the underestimation of the kink population in the standard dry observation conditions [2]. Such a susceptibility of cellulose crystals to the drying stress presumably originates from the lateral flexibility of cellulose crystals, as we recently demonstrated using atomistic molecular dynamics simulations. [3]

These observations highlight the importance of the drying effects in the nanoscale structure and morphology of cellulose nanoparticles. A better understanding of such structural modifications will facilitate our efforts to precisely correlate the structure, morphology, and material properties of nanocelluloses.

References

- [1] Ogawa, Y. (2019) *Nanoscale*, 11 (45), 21767-21774.
- [2] Lim, J.H. et al., (2023) *J. Phys. Chem. Lett.*, 14 (16), 3961-3969.
- [3] Ogawa, Y. et al., (2020) *Cellulose*, 27 (17), 9779-9786.



STRUCTURE AND RHEOLOGY OF STIMULI-RESPONSIVE NANOCELLULOSE INTERFACIAL LAYERS

Fischer P.*^a

^a *Institute of Food, Nutrition and Health, ETH Zurich, 8092 Zurich, Switzerland*

* peter.fischer@hest.ethz.ch

The use of particles such as nanocelluloses, i.e. cellulose nanocrystals (CNC) and nanofibrils (CNF) received increasing attention for the Pickering stabilization of fluid interfaces [1]. The adsorption of nanocellulose and nanocellulose-protein composites at oil-water or air-water interfaces facilitates the formation of stable and biocompatible emulsions and foams but depends heavily on the particles' surface properties. In this contribution, we review the structure of differently designed adsorption layers by neutron reflectivity and interfacial rheology measurements as a function of physico-chemical boundaries conditions (pH, salts, enzymes) [2, 3], surface properties of the cellulose crystals (natural, methylation, esterification) [4, 5], and protein or polysaccharide addition [6]. Native unmodified CNC (hydrophilic, negatively charged, and anisotropic nanoparticles) showed negligible viscoelasticity that could be increased by charge screening due to a shift from repulsive to attractive CNC interactions. Methylated CNCs formed dense monolayers with higher dynamic moduli compared to native CNCs and could be thermo-gelled into multilayers. The esterified CNCs formed aggregated clusters at the interface, resulting in a Maxwellian frequency behavior with distinctive relaxation times, a rarely observed phenomenon for interfacial layers. Scattering length density profiles obtained from neutron reflectivity measurements are used to elucidate the thickness and roughness of the adsorption layer, and in case of nanocellulose-protein composites, their spatial composition. Supported by in vivo digestion experiments in humans we rationalize the design principles of nanocellulose-stabilized emulsions and foams for food and drug delivery vehicles [7-9].

[1] Bertsch P, Fischer P: *Advances in Colloid and Interface Science* 276 (2020) 102089

[2] Bertsch P, Fischer P: *Langmuir* 35 (2019) 7937.

[3] Scheuble N, Geue T, Windhab EJ, Fischer P: *Biomacromolecules* 15 (2014) 3139.

[4] Bertsch P, Diener M, Adamcik J, Scheuble N, Geue T, Mezzenga R, Fischer P: *Langmuir* 34 (2018) 15195.

[5] van den Berg MEH, Kuster S, Windhab EJ, Adamcik J, Mezzenga, R, Geue T, Sagis LMC, Fischer P: *Langmuir* 34 (2018) 10932.

[6] Scheuble N, Lussi M, Geue T, Carriere F, Fischer P: *Biomacromolecules* 17 (2016) 3328.

[7] Bertsch P, Bergfreund J, Windhab EJ, Fischer P: *Acta Biomaterialia* 130 (2021) 32

[8] Scheuble N, Schaffner J, Schumacher M, Windhab EJ, Liu D, Parker HL, Steingoetter A, Fischer P: *ACS Applied Materials and Interfaces* 10 (2018) 17571.

[9] Bertsch P, Steingoetter A, Arnold M, Scheuble N, Bergfreund J, Fedele S, Liu D, Parker HL, Langhans W, Rehfeld JF, Fischer P: *Food & Function* 13 (2022) 9010.



PROBING CELLULOSE–SOLVENT INTERACTIONS WITH SELF-DIFFUSION NMR: ONIUM HYDROXIDE CONCENTRATION AND CO-SOLVENT EFFECTS

Medronho B.^{*a,b}, Pereira A.^a, Duarte H.^a, Gentile L.^c, Rosa da Costa A.M.^d, Romano A.^a, Olsson U.^{c,e}

^a *MED-Mediterranean Institute for Agriculture, Environment and Development, Universidade do Algarve, Faculdade de Ciências e Tecnologia, Campus de Gambelas, Ed. 8, 8005-139 Faro, Portugal*

^b *FSCN Research Center, Surface and Colloid Engineering, Mid Sweden University, SE-851 70 Sundsvall, Sweden*

^c *Dipartimento di Chimica, Università di Bari “Aldo Moro” & CSGI (Consorzio per lo Sviluppo dei Sistemi a Grande Interfase), Via Orabona 4, Bari I-70126, Italy*

^d *Algarve Chemistry Research Centre (CIQA), Faculdade de Ciências e Tecnologia, Universidade do Algarve, 8005-139 Faro, Portugal*

^e *Physical Chemistry, Chemistry Department and Biochemistry and Structural Biology, Chemistry Department, Lund University, P.O. Box 124, SE-22100 Lund, Sweden*

* bfmedronho@ualg.pt

Cellulose has a peculiar hierarchical organization and complex network of interactions which makes its processing into novel advanced materials (e.g., fibres, films, or foams) a non-straightforward task. As cellulose cannot be melted without chemical derivatization, it often requires initial solubilization. The list of suitable solvents is rather restricted and the key mechanisms governing such process are still debatable. Among other factors, a good solvent for cellulose involves high diffusivity, aggressiveness in decrystallization, and capability of disassociating the cellulose chains. Over the years, several classes of efficient cellulose solvents from widely different chemical families have been developed. A successful example relies on using strong hydroxides composed of bulky organic ions, such as tetrabutylammonium hydroxide (TBAH). TBAH belongs to a family of aqueous solvents based on alkylammonium hydroxide (also referred to as onium hydroxides) which display notable capacity of solubilizing large cellulose concentrations in reasonably mild conditions. In this work, the molecular self-diffusion coefficients were accessed in solutions of microcrystalline cellulose, dissolved in 30 wt% and 55 wt% TBAH (aq), and in mixtures of 40 wt% TBAH (aq) with an organic co-solvent, dimethylsulfoxide (DMSO), through pulsed field gradient stimulated echo NMR measurements [1]. A two-state model was successfully applied to estimate α (*i.e.*, average number of ions that “bind” to each anhydroglucose unit) and P_b (*i.e.*, fraction of “bound” molecules of DMSO, TBAH or H₂O to cellulose) parameters. The α values suggest that TBA⁺ ions can bind to cellulose within 0.5 TBA⁺ to 2.3 TBA⁺/AGU. On the other hand, the P_b parameter increases when raising cellulose concentration for TBA⁺, DMSO and water in all solvent systems. Data suggests that TBAH interacts with the ionized OH groups from cellulose forming a sheath of bulky TBA⁺ counterions which consequently leads to steric hindrance between cellulose chains.

[1] Medronho, B.; Pereira, A.; Duarte, H.; Gentile, L.; Costa, AMRD; Romano, A. & Olsson, U. Probing cellulose-solvent interactions with self-diffusion NMR: Onium hydroxide concentration and co-solvent effects. *Carbohydr. Polym.* 2023, 303, 120440

Acknowledgments: This work was supported by funding from the Portuguese Foundation for Science and Technology (FCT) through the projects UIDB/05183/ 2020, PTDC/ASP-SIL/30619/2017 and the researcher grant CEECIND/ 01014/2018.



DETERMINATION OF THE MOLECULAR INTERACTIONS BETWEEN POLYSACCHARIDES IN AQUEOUS MEDIA BY FLUORESCENCE SPECTROSCOPY

Hucher N., Cordinier A., Grisel M.*

URCOM, 25 rue Philippe Lebon, BP 1123, 76063 Le Havre Cedex

* Michel.grisel@univ-lehavre.fr

Nowadays, due to their natural origin, reasonable price and abundance, a variety of polysaccharides are widely used in many industries such as the food or cosmetics for their gelling or thickening properties. Among all the polysaccharides available, it is established that some may interact together thus inducing large increasing of viscosity and/or new properties such as gel forming.

Xanthan and galactomannan gum mixtures are well-known to behave this way [1,2]. For years researchers mainly [1,3,4] based their studies on macroscopic analysis techniques to investigate the association mechanism; however, no-one has yet proposed a universal model of interactions due to controversy on the mechanisms proposed. This may be explained by the diversity of chemical structures of the xanthan and galactomannan macromolecules. To solve this problem, we started to investigate fully characterized polysaccharides [5] at the molecular level, by using molecular probes, and mainly fluorescence ones in order to 1) identify the different intermolecular interactions being implied in the synergy between both polysaccharides and 2) quantify each interactions energy in order to rank them.

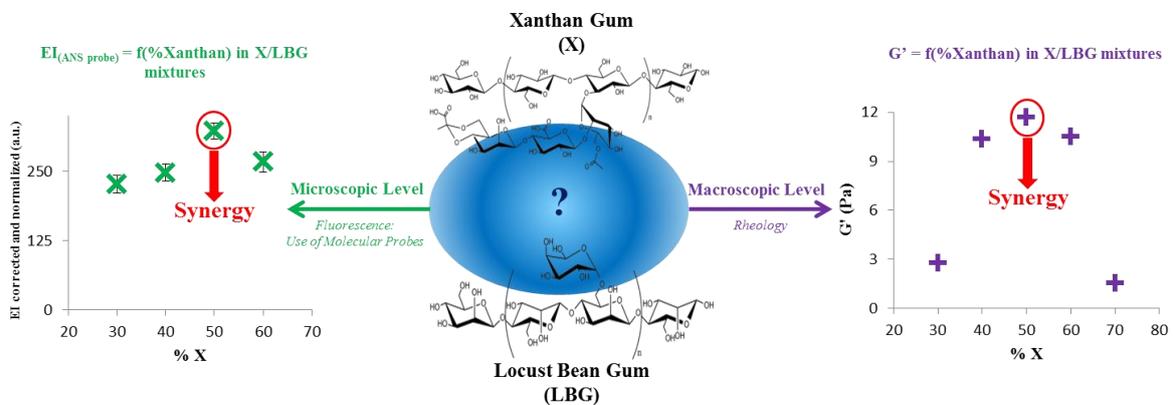


Figure 1 : Molecular / Macroscopic evidencing of Xanthan/LBG interactions

Fluorescent measurements were conducted in parallel with other techniques such as NMR spectroscopy and rheology to link together the properties at both the molecular and the macroscopic scales. Such an approach aims to propose a universal tool to understand the behaviour of polymers alone or when mixed with other molecules in aqueous solution.

- [1] Dea, I. C. M. et al., *Carbohydr. Res.* **1977**, 57, 249–272.
- [2] Higiro, J. et al., *Food Res. Int.* **2006**, 39 (2), 165–175.
- [3] Tako, M. et al., *Agric. Biol. Chem.* **1984**, 48 (12), 2995–3000.
- [4] Cheetham, N. W. H. et al., *Carbohydr. Polym.* **1988**, 9 (3), 195–212.
- [5] Grisel, M. et al., *Food Hydrocoll.* **2015**, 51, 449–458.



ELECTROSPINNING OF CELLULOSE NANOCRYSTALS

Khodayari A.^{*a}, Vats, S.^b, Fuentes C.A.^{ab}, Seveno D.^a

^a Department of Materials Engineering, KU Leuven, Leuven 3000, Belgium

^b Department of Materials Research and Technology, Luxemburg Institute of Science and Technology, L-4940 Hautcharage, Luxemburg

*ali.khodayari@kuleuven.be

Electrospinning cellulose nanoparticles in cellulose acetate solutions using Acetone/Acetic acid as solvents offers a promising approach for producing high-performance cellulose fibers that can reinforce composites with exceptional mechanical properties. However, electrospinning cellulose alone is a challenging process. Therefore, cellulose acetate fibers are electrospun first, then deacetylated and regenerated back to cellulose. The alignment of cellulose nanocrystals along the electrospun fibers is crucial in providing the desired mechanical properties to the composite material. In this study, we use KOH to regenerate cellulose fibers (Fig 1(R)) and further utilize molecular dynamics simulations to investigate the effects of various factors such as the cellulose acetate polymeric chains, filler type (i.e., cellulose nanocrystals or nanofibrils), and the overall composition on the electrospinning process and filler alignment.

Our results suggest that the cellulose acetate polymeric chains align well on the surface of the fillers and form connections between them, leading to the alignment of the filler particles along the electrospun fibers. Furthermore, we observed that the alignment of the cellulose acetate polymers themselves is also affected by the concentration of the constituents and the type of filler. However, we also found that the use of Acetone/Acetic acid significantly decreased the dynamics of the system compared to water solutions. The movement of the fillers in Acetone/Acetic acid solutions was comparably slower than in water solutions. Despite the higher dynamics of water, it cannot be used to electrospin cellulose in practice. Our ongoing simulations and experiments aim to further elucidate the underlying mechanisms governing the electrospinning process and the effects of different solvent systems on the filler alignment and mechanical properties of the composite material.

In addition, our upcoming research will focus on exploring the in-situ regeneration of cellulose from cellulose acetate solutions, in contrast to the current multi-step deacetylation process. This step is crucial and innovative in the electrospinning process suggested by our study, for obtaining fibres with exceptional mechanical performance. Regeneration affects the properties of the electrospun fibers, such as their porosity and mechanical strength, and understanding the underlying mechanisms can aid in the design of high-performance sustainable composite materials.

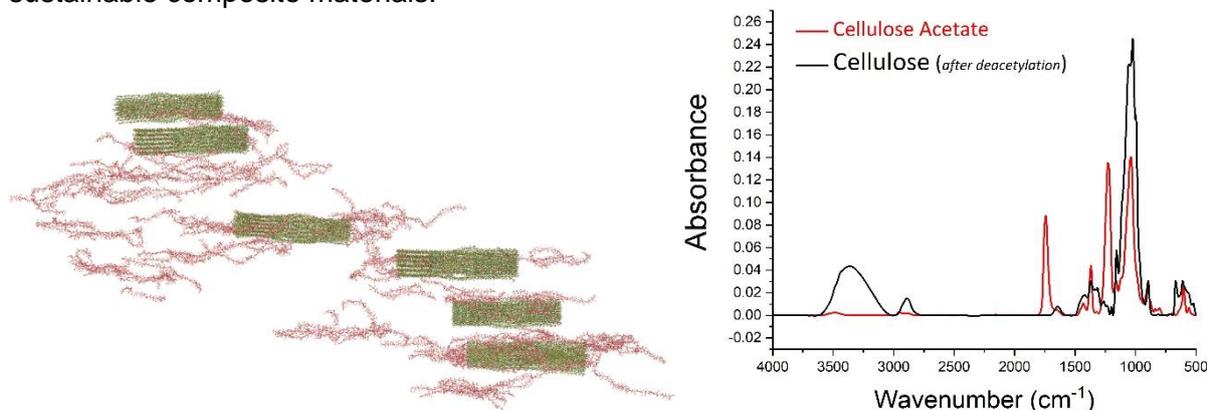


Figure 1: (L) A snapshot of the cellulose nanofibrils in a solution of cellulose acetate, aligned by the electric field. (R) FT-IR Spectra peaks confirming regenerated cellulose.



MANUFACTURE OF SUPERHYDROPHILIC CELLULOSE FILMS

Orelma H.^{*a}, Lohtander-Piispa T.^a, Kontturi K.S.^a, Mäkelä T.^b, Kunnari V.^a, Torvinen K.^a, Harlin A.^a

^a VTT Technical Research Centre of Finland, Biomaterial processing and products, Finland

^b VTT Technical Research Centre of Finland, Sensing solutions, Finland

* hannes.orelma@vtt.fi

Superhydrophilic surfaces (WCA = 0°) are a relatively new group of materials that has many applications such as self-cleaning surfaces, anti-fogging surfaces, water purification and evaporation films, packaging film, and microfluidic substrates. The surface chemistry of such films is opposite to superhydrophobic surfaces which have been widely studied with many substrate materials for applications mimicking nature. Water wets superhydrophilic surfaces evenly, enabling preparation of self-cleaning surfaces. On such surface, water can penetrate between dirt and the surface, releasing the adhered dirt particles. The prevention of formation of water droplets on the surface prevents fogging of transparent films. Cellulose materials are naturally hydrophilic due to abundant surface hydroxyl groups of cellulose. Moreover, typically cellulose materials contain hemicellulose fractions that are hydrophilic. When cellulose material is cast into a form of a film, the hydrophilic characteristics of the material are replicated to the prepared film. Pure cellulose does not fill the criteria of superhydrophilic surfaces, having WCA about 40°. Thus, post-treatment of the material is required to improve the surface hydrophilicity. In this work, we have investigated methods for preparation of superhydrophilic cellulose films. The properties of the prepared superhydrophilic cellulose films were investigated with a water contact angle goniometer (WCA), a dynamic vapor sorption device (DVS), and imaging techniques. The application potential of the films was demonstrated in relevant applications.

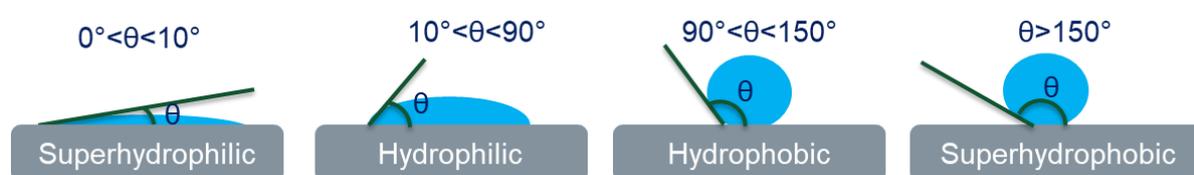


Figure 1 : Schematic of superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic wetting states



CELLULOSE THIN FILM INTERACTIONS WITH IONIC LIQUIDS

Pachernegg L.^{*a}, Waldner C.^a, Spirk S.^a

^a Institute of Bioproducts and Paper Technology, Graz University of Technology, Austria

*lpachernegg@tugraz.at

Ionic liquids possess unique physical and chemical properties which make them attractive for a range of applications, including gas separation membranes and separators for electrochemical devices.^[1] Ionic liquids often lack the mechanical properties required for these applications and need to be combined with supporting materials, such as polysaccharides.^[2] However, the interfacial interaction between many commercially available ionic liquids and polysaccharides is a crucial parameter for designing effective membrane systems, but remains poorly understood. Here we demonstrate the interaction of 20 commercially available ionic liquids with cellulose thin films and the influence of physiochemical parameters, such as surface tension and viscosity of the liquids. We employ various models, including the MKT-model, force-driven approaches, and a power law, to predict drop spreading on thin films.^[3-5] To validate the different models, these results are compared to experimental data. Our results demonstrate that the cation plays a significant role in the interfacial interaction, whereas the influence of the anion size is relatively small (Figure 1). Our approach provides a powerful tool for designing ionic liquids tailored to specific interactions with polysaccharides and help to better understand the underlying mechanisms.

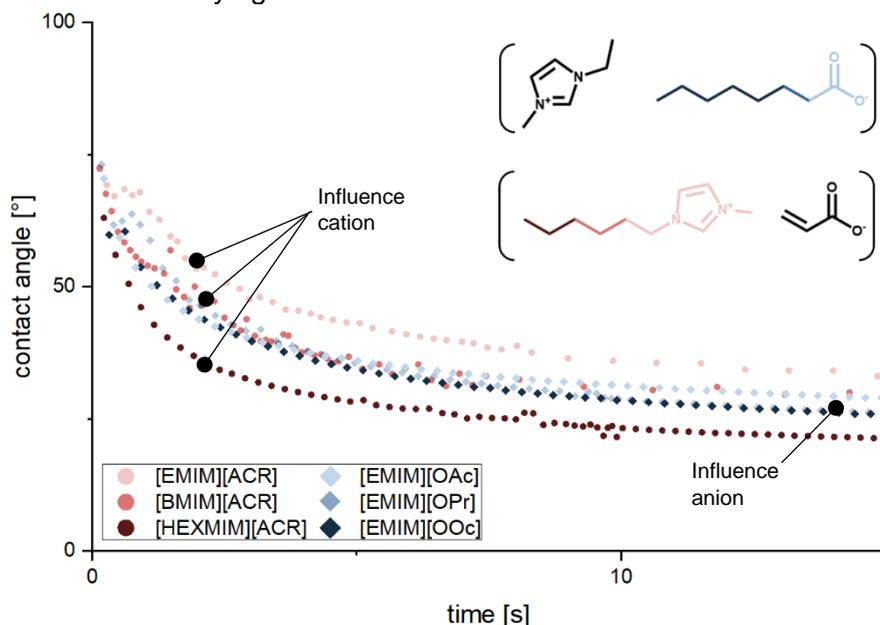


Figure 1: Drop evolution of six ionic liquids on a cellulose thin film.

- [1] Wang J., Luo J., Feng S., Li H., Wan Y. & Zhang X., *Green Energy Environ.*, 1, 43-61, 2016
 [2] Noble, R. D. & Gin D. L., *J. Membr. Sci.*, 1-2, 1-4, 2011
 [3] Pereira M. M., Kurnia K. A., Sousa, F. L., Silva N. J. O., Lopes-Da-Silva J. A., Coutinho J. A. P. & Freire M. G., *Phys. Chem. Chem. Phys.*, 47, 31653-31661, 2015
 [4] Härth M., Schubert D. W., *Macromol Chem Phys*, 6, 654-665, 2012
 [5] Li H., Sedev R. & Ralston J., *Phys. Chem. Chem. Phys.*, 9, 3952-3959, 2011



DIALCOHOL XYLAN THIN FILMS AND THEIR SWELLING PROPERTIES

Palasingh C. ^{*,a}, Kargl R. ^{b,c}, Stana Kleinschek K. ^{b,d}, Schaubeder J. ^e, Spirk S. ^e, Ström A. ^a, Nypelö T. ^{a,f}

^a Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Sweden

^b Institute of Chemistry and Technology of Biobased Systems, Graz University of Technology, Austria

^c Laboratory for Characterization and Processing of Polymers, University of Maribor, Slovenia

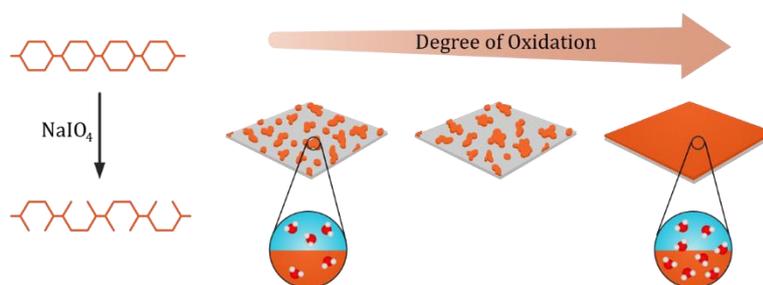
^d University of Maribor, Institute of Automation, Faculty of Electrical Engineering and Computer Science, Slovenia

^e Institute of Bioproducts and Paper Technology, Graz University of Technology, Austria

^f Wallenberg Wood Science Center, Chalmers University of Technology, Sweden

* chonnipa.palasingh@aalto.fi

Many xylans liberated from wood are only partially soluble in water despite being hydrophilic polysaccharides. However, polysaccharides are often processed into films from water solutions fabricating excellent network structures, and this manufacturing step is involved in a facile way of engineering nature-based components into materials. The aim was to facilitate solution-based processing opportunity for sparsely water-soluble wood xylans. Influence of the degree of oxidation (DO) on xylan solubilization and consequent film formation and film stability toward humidity was investigated. The modification involved periodate oxidation and borohydride reduction to generate dialcohol xylans. The highest DO (77 %) within a series exhibited the smallest hydrodynamic diameter (D_h) of 60 nm in dimethylsulfoxide (DMSO), while others with a lower DO (42% and 63 %) did not reveal significant change in D_h comparing to unmodified xylan. A continuous film was only obtained from solution of highest DO and this film demonstrated a significant moisture uptake that depended on the film mass and was not observed with the other modified grades or unmodified xylan.



TUNABLE EMULSIONS BASED ON CELLULOSE NANOCRYSTALS MODIFIED BY ACYL CHAINS AND CELLULOSE DERIVATIVES

Isabelle Capron^{*a}, Francesco D'Acierno^a, William Dufefoi^a, Benjamin Dhuiège^b, and Gilles Sèbe^b

^a INRAE, UR BIA, Nantes, France

^b Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, Pessac, France

* isabelle.capron@inrae.fr

The development of new functional sustainable materials is needed. Cellulose nanocrystals (CNCs) are good candidates to raise materials' sustainability. However, CNCs are hydrophilic and show colloidal stability only in aqueous suspension. To extend their use to various applications, their surface chemistry needs to be modulated.

We studied two ways of modification: i) grafting covalently (acylation with model functional vinyl esters) linear acyl chains of 2 to 6 carbons with varying in degree of substitution to reach different hydrophilic/hydrophobic balance at their surface [1], and ii) by physical adsorption of two alkyl cellulose derivatives, namely methyl cellulose (MC) and ethyl cellulose (EC), maintaining unaltered their sustainable nature [2]. such CNC modifications are discussed in terms of preparation facility, modulable wetting and emulsification properties.

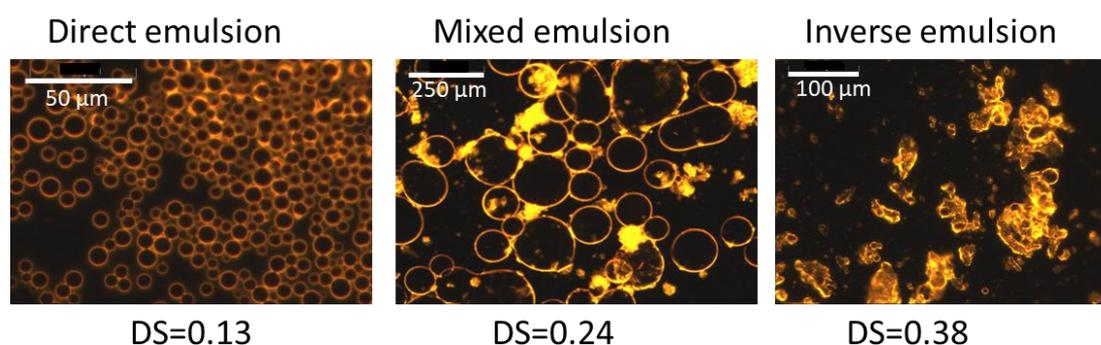


Figure 1 : Image of a typical direct O/W emulsion, intermediate and inverse W/O emulsion varying the acylation surface degree of substitution

[1] Dufefoi, W., Dhuiège, B., Capron, I., & Sèbe, G. (2022). Controlled hydrophobic modification of cellulose nanocrystals for tunable Pickering emulsions. *Carbohydrate Polymer Technologies and Applications*, 3(April). <https://doi.org/10.1016/j.carpta.2022.100210>.

[2] Francesco D'Acierno and Isabelle Capron (*submitted*)



DOES XYLAN HAVE A POSITIVE EFFECT IN THREE-DIMENSIONAL?

Biegler V. ^{*a}, Schaubeder J.^b, Orzan E.^c, Spirk S^b., Nypelö T^d., Bismarck A.^a

^a*Institute for Materials Chemistry and Research, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria*

^b*Institute of Bioproducts and Paper Technology, Graz University of Technology, Inffeldgasse 23, 8010 Graz, Austria*

^c*Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Kemivägen 10, 412 96 Gothenburg, Sweden*

^d*Department of Bioproducts and Biosystems, Aalto University, Vuorimiehentie 1, FI-00076 Aalto, Finland*

*veronika.biegler@univie.ac.at

Cellulose Pulp Fibres mainly comprise cellulose microfibrils and hemicellulose. The most frequent ones are xylans, which interact with cellulose microfibrils the pectin matrix in primary cell wall and provide strength to the plant fibre walls. Depending on the origin the structure of xylans differ. Xylan from biomass of woody tissues are a linear β -(1,4)-D-xylopyranan backbone substituted with a number of different side chains/groups. In the preparation of two-dimensional fibre networks, the role of xylan has been investigated; xylan provides surface charge, which influences fibre-fibre interaction positively affecting the network strength.

We will discuss the effect of xylan on cellulose surfaces on the frothability of aqueous pulp suspensions and its influence on structural properties of cellulose pulp fibre foams. Foams with enzymatically degraded bleached softwood kraft pulp as well as with additionally adsorbed beechwood xylan were prepared. The change of foaming behaviour and foam formation was evaluated and the morphology and surface properties were tested by SEM, iGC and Zeta potential. Additionally, the interaction of the foam with water molecules of and its influence on the surface within the fibre network was investigated. An additional focus is placed on the mechanical foam properties to derive the structure-property relationship from the xylan content on cellulose fibres.



COMBINING ORDERED CELLULOSE NANOCRYSTALS AND MOBILE SILK PROTEINS: REVEALING PARAMETERS FOR BIOPOLYMER INTERACTIONS

Leppänen I.*^a, Arola S.^a, King A.W.T.^a, Unger M.^b, Stadler H.^b, Nissen G.S.^c, Zborowski C.^d, Virtanen T.^a, Salmela J.^e, Setälä H.^e, Lésage S.^c, Monika Österberg M.^d, Tammelin T.^a,

^a *Biomaterial processing and products, VTT Technical Research Centre of Finland Ltd., Finland*

^b *Bruker Nano Surfaces Division, Germany*

^c *Oxford Biomaterials Ltd., United Kingdom*

^d *Department of Bioproducts and Biosystems, Aalto University, Finland*

^e *Spinnova PLC, Finland*

* ilona.leppanen@vtt.fi

Natural materials, such as silk and cellulose, have intriguing properties, which can be exploited in novel material engineering. Here, we have combined cellulose nanocrystals (CNCs) and regenerated silk fibroin (RSF), to tentatively demonstrate their suitability for filament formation. CNCs are expected to bring order along with reinforcing ability, whereas RSF provides soft and more mobile regions to further facilitate the alignment of the final filament structure. We use CNCs with varying surface functionalities (sulfate and/or aminosilane groups) and emphasize detailed characterization thereof. By modification, we can *i*) modify the surface charge of the CNCs by controlling the degree of surface substitution and *ii*) use it as a platform for further grafting, i.e. covalent 'amine-amine' crosslinking between CNCs and RSF. We investigate the interactions and compatibility of the different CNCs and RSF to reveal the interactions most suitable for filament formation by using quartz crystal microbalance with dissipation monitoring (QCM-D) and photothermal atomic force microscopy (AFM-IR). We show that ionic interactions induce sufficient binding between the two components and no covalent crosslinking is needed. Further, to visualize the alignment of the materials under shear and to determine their suitability for spinning, we utilize shear-induced polarized light imaging (SIPLI). These results support the QCM-D studies and show that silk can orientate with the CNCs when not covalently bound. Moreover, the CNCs with the higher negative charge showed the best alignment, in flow, with RSF. Finally, preliminary spinning experiments were conducted for mixtures of CNCs and RSF, using dry-spinning, which takes inspiration from the way natural fibers are produced.



TUNING THE PROPERTIES AND THE WATER INTERACTIONS OF CELLULOSE NANOFIBRIL HYDROGELS USING WILLOW BARK EXTRACT

Huynh N. ^{*a}, Valle-Delgado J. J. ^{a,b}, Fang W. ^a, Arola S. ^{a,c}, Österberg M. ^{a,b}

^a *FinnCERES Materials Bioeconomy Cluster, Finland*

^b *Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland*

^c *VTT Technical Research Center of Finland Ltd*

* Email: ngoc.huynh@aalto.fi

Cellulose nanofibrils (CNF) are increasingly used in several composite forms such as foams and films from hydrogel precursors where dewatering or drying is especially challenging in practice due to CNF's high affinity to water [1]. Therefore, it is desirable to control their water interactions without compromising the mechanical properties. At the same time, there is a clear interest in green approaches to provide CNF-based materials with additional functionalities through surface modification of nanofibrils using natural compounds. In this study, we tackled these goals by incorporating extracts from willow bark waste stream as a plant-based modifier for CNF hydrogels. Willow bark extract (WBE) obtained by hot-water extraction contained several bioactive phenolic compounds (in line with previous studies [2]) together with potassium salt and traces of magnesium salt, as confirmed by high-performance liquid chromatography (HPLC) and X-ray photoelectron spectroscopy (XPS).

We employed quartz crystal microbalance with dissipation monitoring (QCM-D) as well as bulk characterization methods (rheological and swelling tests) to study the interactions between WBE, CNF and water in CNF hydrogels. Both TEMPO-oxidized and mechanically fibrillated CNF were used to highlight the effect of surface charge and surface area on the WBE uptake. QCM-D experiments revealed a strong affinity of WBE phenolic compounds for CNF. The addition of WBE increased the storage modulus and reduced the swelling ratio of CNF hydrogels in water considerably, without affecting the intrinsic shear thinning behavior of pure CNF hydrogels. The effect of WBE phenolic compounds and salts on the rheological and swelling behavior of CNF hydrogels will be discussed. In summary, WBE has high potential to control water interactions and dewatering in large scale processing of CNF, and it also offers the possibility to add useful functionalities to CNF materials like antioxidant and UV-shielding properties [3].

- [1] Fall, A., Henriksson, M., Karppinen, A., Opstad, A., Heggset, E. B., & Syverud, K. (2022). *Cellulose*, 29(14), 7649–7662.
- [2] Dou, J., Xu, W., Koivisto, J. J., Mobley, J. K., Padmakshan, D., Kögler, M., Xu, C., Willför, S., Ralph, J., & Vuorinen, T. (2018). *ACS Sustainable Chemistry and Engineering*, 6(4), 5566–5573.
- [3] Lohtander, T., Grande, R., Österberg, M., Laaksonen, P., & Arola, S. (2021). *Frontiers in Chemical Engineering*, 3(August), 1–13.



MODELING LIQUID PENETRATION INTO CELLULOSE FIBER NETWORKS BASED ON SUBSTRATE AND LIQUID SURFACE ENERGIES

Carina Waldner^{a,b}, Ulrich Hirn^{a,b*}

^a Graz University of Technology, Inffeldgasse 23, 8010 Graz, Austria

^b CD Laboratory for Fiber Swelling, Inffeldgasse 23, 8010 Graz, Austria

* ulrich.hirn@tugraz.at

The widely used Lucas-Washburn (LW) equation depends on the contact angle between liquid and substrate as the driving force for liquid penetration. However, the contact angle depends on both, the liquid and the substrate. It would be desirable to predict the penetration into porous materials, without the requirement to measure the solid-liquid interaction. Here, we propose a novel modeling approach for liquid penetration from mutually independent substrate- and liquid properties. For this purpose, the contact angle in the LW-equation is replaced by polar and dispersive surface energies, utilizing the theories of Owens-Wendt-Rabel-Kaelble (OWRK), Wu, or van Oss, Good, Chaudhury (vOGC).

The proposed modelling approach is validated exhaustively by measuring penetration speed for 96 substrate-liquid pairings and comparing the results to model predictions based on literature- and measured data. Liquid absorption is predicted very well ($R^2= 0.8-0.9$) with all three approaches, spanning a wide range of penetration speed, substrate- and liquid surface energy, viscosity, and pore size. The models for liquid penetration without measurement of solid-liquid interaction (contact angle) performed well. Modeling calculations are entirely relying on physical data of the solid and the liquid phase (surface energies, viscosity and pore size), which can be measured or retrieved from databases.

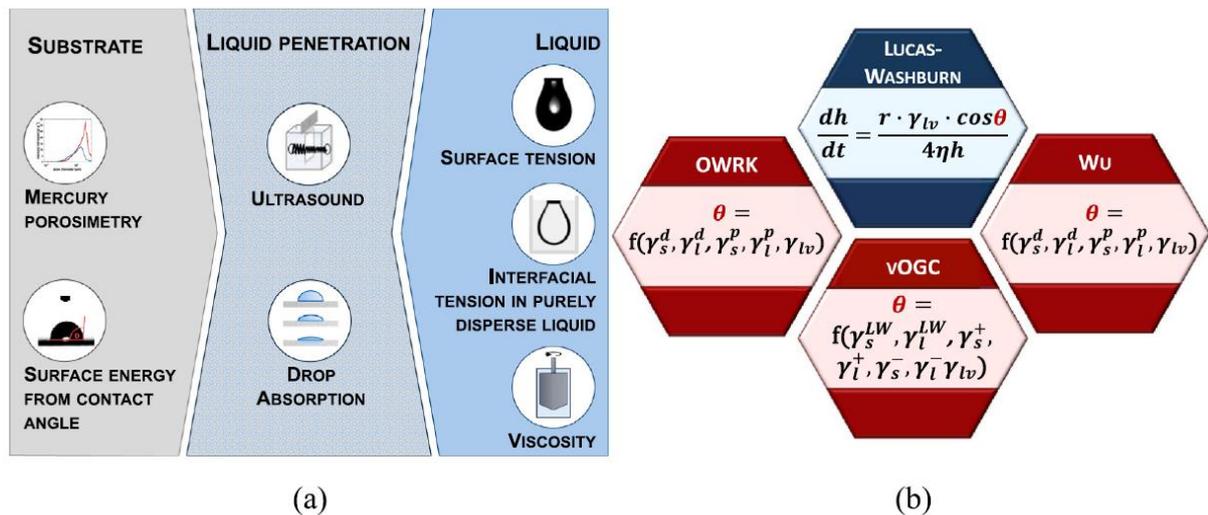


Figure 1 : (a) Overview of measurement methods used. Liquid penetration speed measured with ultrasound and drop absorption is predicted from substrate surface energy and pore size, as well as liquid viscosity and surface tension components. (b) Overview of modelling approaches used. OWRK, Wu and vOGC theory are used to replace the contact angle in the Lucas-Washburn equation with substrate surface energies and liquid surface tensions.

MOLECULAR SWELLING FROM ESTERIFICATION OF MICROFIBRILLATED CELLULOSE OR PVA FILMS

François Brua, Sonia Boisseau ^a, Karim Mazeau ^a, Claire Monot^b, Eline Bartolamib, Philippe Martinez^b, Laurent Heux* ^a

^a CERMAV, CNRS, Univ. Grenoble Alpes, UPR 5301, 38400, Saint-Martin-d'Hères, France

^b Centre Technique du Papier, 38400, Saint-Martin-d'Hères, France

* laurent.heux@cermav.cnrs.fr

Microfibrillated cellulose films exhibit very good oxygen and oil barrier properties, while being very sensitive to water or water vapor diffusion. In order to overcome the avidity of cellulose for water, hydrophobization of the surface with apolar molecules has been proposed for decades but is not so simple to implement. We have developed at CERMAV a gas-phase technique that allows to modify the surface of cellulose aerogels with high efficiency and yields up to very high degrees of substitution [1]. In parallel, CERMAV and the Centre Technique du Papier (CTP) have developed a technology called chromatogeny which allows the modification of the surface of cellulosic substrates by depositing and grafting acyl chloride reagents by flushing the surface with a hot air blade [2].

However, this chromatogeny technique is not suitable for the modification of the dense layer of MFCs because the reagent does not penetrate inside the film. During the European project Celluwiz [3], we demonstrated that one of the mechanisms of hydrophobization is related to the huge molecular expansion that accompanies the modification of the cellulose backbone, as shown by molecular modeling (see Figure 1a). We also showed that by opening the structure of the MFC films, we were able to achieve very high levels of grafting that can be monitored by SSNMR (see Figure 1b). The results will be discussed in comparison with PVA coatings for which the mechanisms are very different because the reagent penetrates from the surface to the interior of the film.

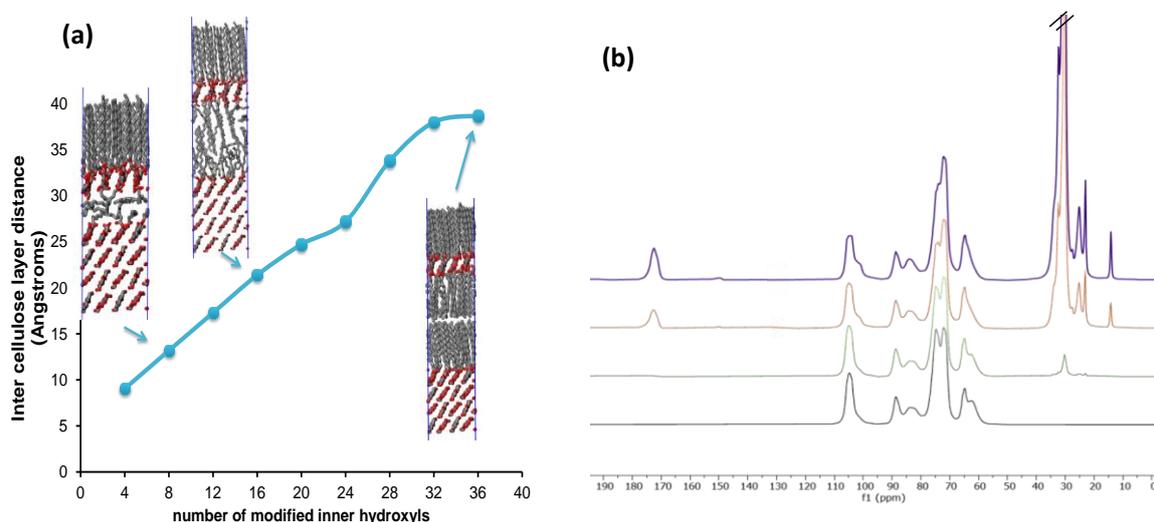


Figure 1 : (a) molecular modelling of grafting (b) SSNMR spectrum of modified films

[1] Fumagalli, M.; Ouhab, D.; Boisseau, S.; Heux L., , *Biomacromolecules* , 3246-3255 (2013)

[2] Berlioz, S., Stinga, C., Condoret, J., & Samain, D. *Int. J.Chem. Reactor Eng.*, 6(1) (2008).

[3] <http://www.celluwiz.eu/>



FIBRE MORPHOLOGY CONSERVING CELLULOSE DERIVATIZATION IN THE HIGH-CONSISTENCY REGIME

Heckel S. *, Arjona A., Schilling, T., Zahel M.

Papiertechnische Stiftung (PTS), Business Division Fibres & Composites, Germany

* sandra.heckel@ptspaper.de

Derivatized or surface-modified cellulose fibres have the potential to contribute substantially to bioeconomy, i. e. the transition from fossil resources towards the utilisation of renewable raw materials. Whereas hydrophobised fibres may act as reinforcement of biopolymers, ionised fibres (such as carboxymethylcellulose) can adsorb a variety of functional fillers to yield specialty, such as conductive, papers. However, current modification technologies work either at a lab scale at 2-5 wt.% consistency due to otherwise high viscosities of the fibre solutions, which is not economically scalable, or as high consistency reactive extrusion with consistencies up to 50 wt%, which inevitably causes fibre shortening due to the high shear forces during extrusion.^[1,2]

In this work, we present a new reaction technology that is based on reactive filtration. In absence of a stirrer, reactions are taking place in a pressurized filter chamber. As a result, it is possible to derivatize cellulose fibres at consistencies from 10 wt.% upwards without mechanical fibre shortening.

To illustrate we present two application scenarios of the reactor: Firstly, the derivatization of cellulose to dialdehydcellulose, which is the precursor of dialcoholcellulose. Dialcoholcellulose is a thermoplasticised cellulose derivative with promising properties for bio-based packaging. Secondly, we show an charge introducing reaction like carboxymethylation. By introducing additional charges, these are able to generate strength in papers made from unrefined pulp. Refining is one of the most energy-requiring steps of paper production and its replacement therefore has the potential to reduce CO₂ production in papermaking.

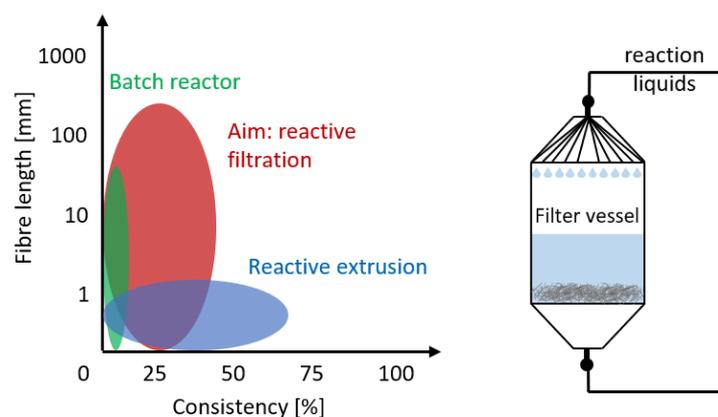


Figure 1 : Schematic illustration of aimed consistency range and filtration reactor

[1] A. Feldner, M. Zahel, T. Arndt, *Modellunterstützte Auslegung von Extrusionsschnecken Für Die Faserstoffextrusion*, ongoing research work at PTS, 2020.

[2] T. Heinze, O. A. El Seoud, A. Koschella, *Principles of Cellulose Derivatization*, 259–292, 2018.



CHEMICAL “ON-SURFACE” MODIFICATION AND ANALYSIS OF CHITOSAN THIN-FILMS

Dorn T.*^a, Finšgar M.^b, Katan T.^a, Kleinschek K. S.^a, Wrodnigg T. M.^a, Kargl R.^a

^a Institute of Chemistry and Technology of Biobased Systems, Graz University of Technology, Austria

^b Faculty of Chemistry and Chemical Engineering, University of Maribor, Slovenia

* tobias.dorn@tugraz.at

C-Glycosides, where the glycosidic linkage consists of a carbon-carbon bond, are stable against most chemical reactions as well as hydrolysis in biological systems compared to the naturally occurring O- and N-glycosides. [1] This stability makes C-glycosides interesting candidates for therapeutics against various diseases and for technological applications. With the introduction of ligation handles, such stable compounds can be covalently linked to polysaccharides via orthogonal conjugation methods. [2] Thus, specific biological properties of the polysaccharide backbone can be introduced by target specific choice of the sugar based small molecule entity.

For example, chitosan (poly- β -1,4-D-glucosamine) can be used as a support to bind different molecules, like amino acids or peptides, by chemical modification of the free amino moieties. [3] Due to the water solubility of chitosan, we already prepared thin-film coatings on various substrates and modified them with simple amino acids. [4] As a further proof-of-concept study, we synthesized a fluorescently marked C-glycosidic monosaccharide and modified chitosan thin-films with this compound and other fluorescent molecules. The surfaces were analyzed by fluorescence spectroscopy, atomic force microscopy, X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. Synthetic details and the results of the surface analysis will be presented.

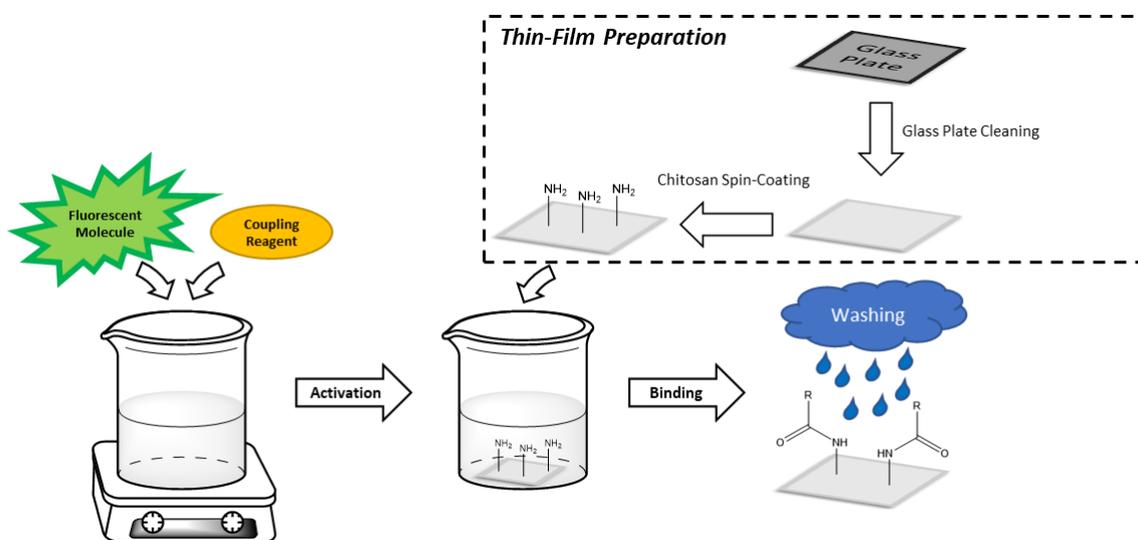


Figure 1: Schematic representation of the chitosan modification process.

[1] J. Ati, P. Lafite, R. Daniellou, *Beilstein journal of organic chemistry*, 13, 1857, 2017

[2] A. Koschella, C.-Y. Chien, T. Iwata, M. S. Thonhofer, T. M. Wrodnigg, T. Heinze, *Macromol. Chem. Phys.*, 221, 1900343, 2020.

[3] W. Neugebauer, R.E. Williams, J-R Barbier, R. Brzezinski, G. Willick, *Int. J. Peptide & Protein Res.*, 47, 269-275, 1995.

[4] T. Katan, R. Kargl, T. Mohan, T. Steindorfer, M. Mozetič, J. Kovač, K. Stana Kleinschek, *Biomacromolecules*, 23, 731-742, 2022.



CHITOSAN-GLUCAN/ COLLAGEN HYBRID SCAFFOLD: PREPARATION AND CHARACTERIZATION

Abdellatif A.^{*a,b}, Radwan R^a, Kelnar I^a

^a Institute of Macromolecular Chemistry, Czech Academy of Sciences, Czech Republic

^b CEITEC-Central European Institute of Technology, Brno University of Technology, Czech Republic

* abdellatif@imc.cas.cz

Hybrid biocomposite scaffolds (HBS) that serve as a carrier for cell proliferation and differentiation are increasingly used for tissue regeneration¹. The 3D hybrid scaffold based on collagen-grafted-chitosan-glucan fiber (CO-g-CGF-HBS) was prepared by freeze-drying technique. The swelling percentage, hydrolytic stability, and modulus of elasticity of HBS were enhanced after the chemical modification of CO with CGF. Pore size and porosity of HBS were decreased with an increased CGF ratio. HBS exhibits a higher reduction rate against different types of bacteria compared with a control sample. Thus, chemical modification of CO with different ratios of CGF significantly improved the physicochemical, antibacterial properties of HBS. From *in vitro* measurements, the cell viability of HBS was enhanced in comparison with native CO using mesenchymal stem cells (MSCs). The viability of MSCs suggests a potential for a range of therapeutic and biomedical applications especially for bone regeneration purposes.

Table 1: Different composition of grafted hybrid biocomposite scaffold (HBS) using different ratios between CO and CGF.

Sample codes	Weight ratio between CO to CGF	Wt. of CO (g)	Wt. of CGF (g)
Native CO scaffold	0	0.5	0
CO-g-CGF (70/30)	70/30	0.375	0.125
CO-g-CGF (50/50)	50/50	0.25	0.25
CO-g-CGF (30/70)	30/70	0.125	0.375
Native CGF scaffold	0	0	0.5

References:

[1] Abdel-Rahman R. M., Kelnar I. & Abdel-Mohsen A.M. International journal of biological macromolecules, 202, 671-680, 2022.

Acknowledgments:

This work was supported by LUAUS23004 Inter-Excellence Grant from MEYS CR is greatly appreciate.



INFLUENCE OF CHITOSAN AND CELLULOSE NANOCRYSTALS ON THE SURFACE CHARGE OF CELLULOSE ACETATE COMPOSITE FILM

Kramar A.^{*a,b}, Luxbacher T.^c, González-Benito J.^{a,b}

^a Department of Material Science and Engineering and Chemical Engineering, Universidad Carlos III de Madrid UC3M, Spain

^b Álvaro Alonso Barba Institute of Chemistry and Materials Technology, UC3M, Spain

^c Anton Paar GmbH, Austria

* akramar@ing.uc3m.es

In this work, we report the preparation, by solution casting method [1], of cellulose acetate (CA) composite films using chitosan (CS) or cellulose nanocrystals (CNC) as fillers. After casting, the zeta potential of films was measured with SurPASS 3 analyzer (Anton Paar, GmbH) using the streaming potential method, over a range of pH 2.5-9.5 for films containing CNC and of pH 4.0-9.5 for films containing chitosan. In addition to composite films, we have also determined the surface charge of pure CS and CNC cast films. The results presented in Figure 1 show how the surface charge of CA films is changing upon the addition of reinforcing fillers, which can have a significant impact on the final application of the prepared films.

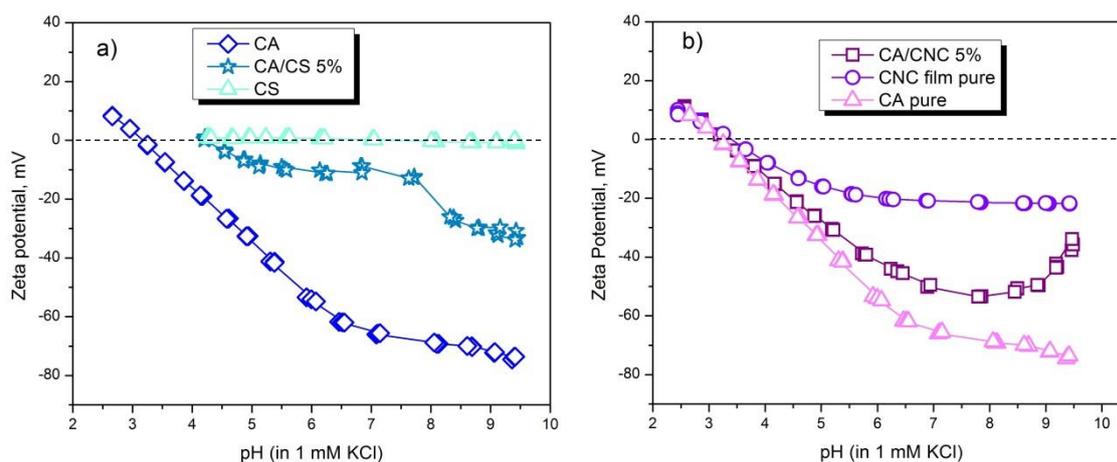


Figure 1: Zeta potential as a function of pH for: a) cellulose acetate (CA) composite film with chitosan (CS), and b) CA composite film with cellulose nanocrystals (CNC)

As expected, the surface charge of the CA/CS composite film, represented by the plateau value of the zeta potential and the isoelectric point (IEP) is found between that of pure CA and CS. Similar results were obtained for CA/CNC, pointing out that IEPs of CA, CNC, or CA/CNC coincide at pH 3.2. The addition of nanocrystals has an enhanced effect on the zeta potential plateau value. Current studies are focused on the investigation of the concentration of components influencing the CA zeta potential curves, taking into account molecular interaction between components as well as surface roughness, which is likely to affect the zeta potential [2].

[1] Kramar A., Rodriguez Ortega I., Gonzalez Gaitano G. & Gonzalez-Benito J., *Cellulose*, 30, 2037–2052, 2023.

[2] Drechsler A., Caspari A., Synytska A., *Surface and Interface Analysis*, 52, 991– 995, 2020.



Session 3 Poster



LEEK-INSPIRED BIO-BASED FILMS WITH OPTICAL AND SELF-CLEANING FUNCTIONALITIES

Daghigh Shirazi H. ^{*a}, Mirmohammadi S.M. ^a, Mousavi S.M. ^a, Markkanen M. ^a, Halme J. ^b, Jokinen V. ^a, Vapaavuori J. ^a

^a Department of Chemistry and Materials Science, Aalto University School of Chemical Engineering, Espoo, Finland.

^b Department of Applied Physics, Aalto University School of Science, Espoo, Finland.

* Presenting author: Hamidreza.daghighshirazi@aalto.fi

Optimum performance of solar cells requires maximizing and retaining the incident light, which can be ensured by proper light management and removing dirt or other obstructions for light path. [1] Partially bio-based films, such as transparent wood composites, have already been introduced as an efficient and environment-friendly light management layer for solar cells, due to the possibility of optimizing their light transmittance and haze. [2]

In this work, we present a bioinspired approach to produce fully bio-based films with high total light transmittance and superhydrophobicity. These characteristics are obtained by replicating the hierarchical surface structures of leek leaves onto cellulose acetate (Figure 1a). Inspired by leek's epicuticular wax, the subsequent addition of carnauba wax coating integrates the inherent hydrophobicity of the wax and hierarchical surface features, providing anisotropic superhydrophobicity. This superhydrophobicity enables self-cleaning behavior, which tackles the accumulation of dirt and dust, while high transmittance and haze lead to higher absorption of light in the active layer of solar cells.

Owing to the periodical surface roughness and low surface energy of carnauba wax microfeatures, the superhydrophobic surfaces demonstrate an anisotropic wetting characteristic with advancing contact angles of up to 160° and 156° in cross directions (Figure 1b). Furthermore, the films show an anisotropic light scattering (Figure 1c), with high light transmittance of 94% and a haze of 54% at the wavelength of 550 nm.

Employing these films as the light management layer on the outmost layer of perovskite solar cells was shown to contribute to light trapping and result in a 6% efficiency improvement. Moreover, surface water repellence facilitates self-cleaning to maintain photovoltaic performance over time. Hence the developed renewable and environment-friendly solution offers a suitable route toward sustainable light management layers for photovoltaics with improved lifetime and efficiency.

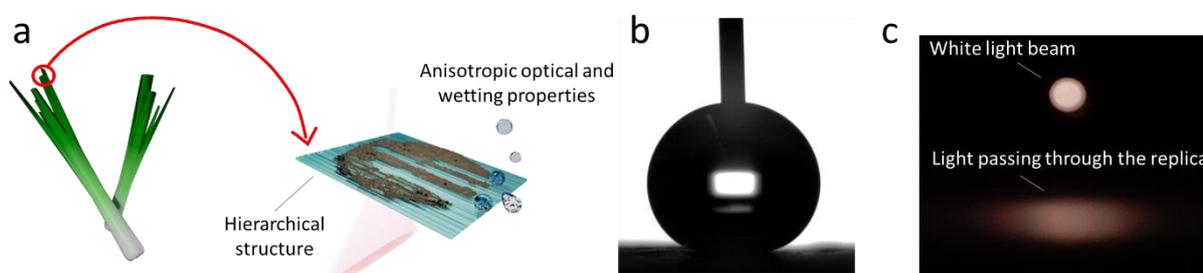


Figure 1: a) A leek-inspired solution for b) high water contact angle and c) high anisotropic light transmittance

[1] Heo S.Y., Koh J.K., Kang G., Ahn S.H., Chi W.S., Kim K., Kim J.H., *Advanced Energy Materials*, 4, 1300632, 2014.

[2] Zhu M., Li T., Davis C.S., Yao Y., Dai J., Wang Y., AlQatari F., Gilman J.W., Hu L., *Nano Energy*, 26, 332, 2016.



Session 4

Emerging polysaccharide based (nano)materials

Session organizers:

Stefan Spirk, Anna Roig Serra, Magnus Norgren, Silvia Vignolini

Keynote speakers:

Katariina Torvinen

Emerging bio-based solutions in wearable and energy storage applications

Tobias Keplinger

Desing of Smart High-Performance Cellulose Materials based on Wood



DESIGN OF SMART HIGH-PERFORMANCE CELLULOSE MATERIALS BASED ON WOOD

Keplinger Tobias ^{*a,b}

^a Wood Materials Science, ETH Zurich, Switzerland

^b Agrobiogel GmbH, Austria

* tobias.keplinger@agrobiogel.com

Sustainable materials design and fabrication based on renewable resources is one of the key challenges in materials science and development. Wood as a prominent example for an abundant, CO₂ storing, green resource possesses enormous potential to play an important role in future materials advancement. Particularly, functional materials fabrication by bottom-up approaches using wood inherent cellulosic building blocks has attracted increasing attention over the last 20 years. Their vast amount of reaction sites, large surface area and superb mechanical properties make them a very promising raw material.

However, the need for energy intense disassembly processes and limitations in terms of reassembly, raise questions regarding scalability and the potential to transfer their excellent mechanical properties on the micro- and nanoscale to the bulk material level. Hence, the presentation covers recent developments regarding alternative manufacturing and functionalization processes that are based on a top-down approach utilizing the hierarchical structure of native wood or the wood inherent cellulose scaffolds. Structure retaining delignification of wood, optional matrix infiltration and a subsequent densification result in high performance cellulose materials characterized by excellent tensile properties with elastic moduli of up to 70 GPa and 600 MPa strength. Wet cellulose scaffolds can also be easily shaped which provides elements with high curvatures and cellulose fibres perfectly adapting to the shape. Smart lay-up manufacturing enables elements with mechanical gradients that facilitates force transfer.

In addition, cellulose scaffold functionalization strategies are highlighted, such as the in-situ formation of Metal Organic Frameworks or Stimuli Responsive Polymers, to develop novel functional cellulose materials.



EMERGING BIO-BASED SOLUTIONS IN WEARABLE AND ENERGY STORAGE APPLICATIONS

Katariina Torvinen*, Tia Lohtander, Chamseddine Guizani

^a *VTT Technical Research Centre of Finland, Biomaterial processing and products, Finland*

*Katariina.torvinen@vtt.fi

The global consumption of material resources expected to more than double between 2015 and 2050. There is a growing need of sustainable and renewable solutions to avoid problems of overconsumption and fossil-based raw material usage. Our ambition is the implementation of bio based materials as a new normal in printed and hybrid electronics, diagnostics, wearables, optics and energy storage devices. Novel lignocellulose-based materials offers a wide selection of substrate and structural material components including bio based, compostable and recyclable materials depending on end-application needs. Wearable electronics is a rapidly growing market, and the next generation of conformable wearable skin patch electronics for monitoring health and well-being is emerging. Herein, we produced composite films from cellulose nanofibers (CNF) and polymeric cellulose ethers or physical cellulosic fibers. The films were characterized by their strength and ductility, from which the latter is essential for producing conformable skin patches. The electronic components were integrated as a reusable unit to enable facile end-of-life management. Finally, the performance of the integrated skin patch as an electrocardiogram device was verified. Overall, these findings benchmark the potential of renewable cellulosic materials for high-end wearable electronics besides conventional paper and packaging applications.

An annual energy storage demand is expected to increase from 200 GWh to 10 000 GWh in 20 years period and solutions are needed to fight against climate change. Renewable materials can provide novel chemistries and meet different end-application needs both in battery and advanced supercapacitor devices. Understanding structure-function-performance relationships is crucial to reach novel advanced energy storage devices with different end-use requirements. In this paper, we will present recent results of the processing of different lignin based hard carbon grades and the generation of electrical characterization methods.



STIMULI-RESPONSIVE (CHEMI-)LUMINESCENT WOOD MEMBRANES

Ritter M.^{*a,b}, Burgert I.^{a,b}, Panzarasa G.^{a,b}

^a Wood Materials Science, ETH Zürich, Switzerland

^b WoodTec group – Cellulose and Wood Materials, Empa, Switzerland

* maxritter@student.ethz.ch

Wood is a renewable and CO₂-storing material with excellent mechanical properties. Among additional functions wood can be enabled with, optical and photonic properties are extremely promising in view of sustainable indoor lighting applications.

However, state-of-art wood-based lighting applications require several modification steps, such as lignin removal, infiltration with refractive index-matching materials, and use of heavy metal-based quantum dots as fluorophores, which can compromise the inherent sustainability of wood. [1-2]

Here we demonstrate an innovative approach that makes use of the unique hierarchical wood structure to achieve the necessary light transmission while maintaining the valuable wood aesthetics and sustainability, as well as allowing for easier process scalability. We studied how light propagates inside wood as a function of different parameters (wood species, cutting direction, lignin composition, Figure 1a) and then impregnated wood with environmentally friendly fluorescent metal-organic complexes (Figure 1b). In addition to their strong photoluminescence, these metal-organic fluorophores are also responsive to acidic or basic gases, allowing their use as sensors of indoor air quality. [3]

Building on this idea, we made chemiluminescent (CL) wood membranes. In nature, decaying wood can be colonised by bioluminescent fungi, resulting in a “glow-in-the-dark” behaviour. By functionalising the wood with suitable CL species, we are able to mimic this process in an artificial way. Depending on the trigger, the chemiluminescent system and wood pre-treatment, long lasting CL can be achieved (Figure 1 c,d).

References

[1] Q. Fu et al., *ACS Nano*, vol.14, pp. 13775–13783, 2020

[2] L. A. Berglund and I. Burgert, *Adv. Mater.*, vol.30, pp. 1-15, 2018

[3] M. Ritter, I. Burgert and G. Panzarasa, *Mater. Adv.*, vol.3, pp. 1767-1771, 2022

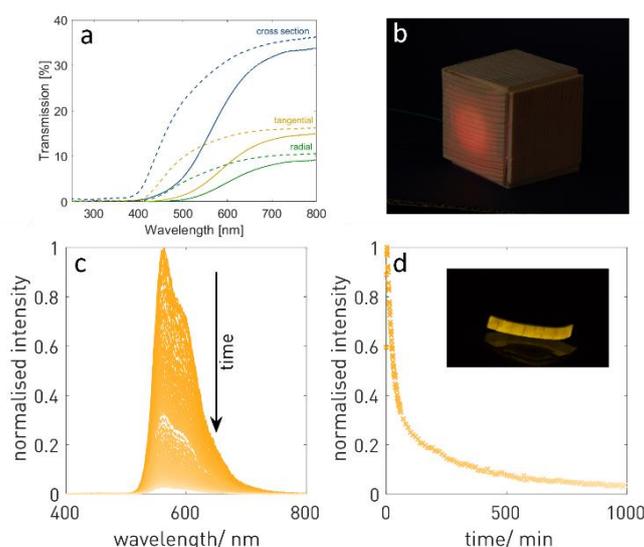


Figure 1 : Light transmission through different native (full lines) and delignified (dotted lines) wood cuts. (a) Wooden cube demonstrator (4x4x4 cm³) with a functionalised wooden face and a small UV LED inside (b). Chemiluminescent spectra of functionalised native spruce over time (c) and the maximum intensity of the CL signal plotted over time (d).



BACTERIAL CELLULOSE NANOFIBRES AS A REINFORCING MATERIAL AND BEYOND

Roig A.^{*a}, Malandain N.^{a,b}, Roig-Sanchez S.^a, Mira-Cuenca C.^a, Meslier T.^a, Sanz-Fraile H.^b, Farre, R.^b, Otero, J.^b, Kam D.^{c,d}, Sachyani-Keneth E.^c, Shoseyov O.^d, Magdassi S.^c, Laromaine A.^a

^a Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Spain

^b Unitat de Biofísica i Bioenginyeria, Universitat de Barcelona, Spain

^c Institute of Chemistry, The Hebrew University of Jerusalem, Israel

^d Plant Sciences and Genetics in Agriculture, The Hebrew University of Jerusalem, Israel

* roig@icmab.es

Bacterial cellulose (BC) is a biosynthesized polymer gaining popularity in the medical field. By blending the as-obtained BC pellicles we can produce bacterial cellulose nanofibers (BCf) and prove them versatile to elevate the properties of synthetic or natural soft hydrogels. The first example concerns polyacrylate hydrogels (PAA) which are worth considering as soft tissue implants as they can be photocurable and sustain customized shapes through 3D bioprinting. However, acrylate-based hydrogels present weak mechanical properties and significant dimensional changes when immersed in liquids. I will present the fabrication of PAA/BCf double network hydrogels which are more resistant to cracks, show increased stiffness, and lower water swelling [1]. In a second example, I will show how type I collagen hydrogels can be efficiently reinforced with BCf without the inclusion of cross linkers. In addition, a cell-laden hydrogel scaffold could be cast in a single step by mixing, type I collagen, BCf, and cells (human bone marrow mesenchymal stromal cells or human fibroblasts), resulting in homogenous 3D cell cultures viable for at least seven days [2]. Finally, I will explain how we can enlarge the palette of potential uses of BC with an original approach. To control the spatial distribution of inorganic nanoparticles on a BC film resulting in a variety of patterns and designs. This is done by screen-printing BCf functionalized with inorganic nanoparticles over BC wet pellicles as shown in the figure below [3].

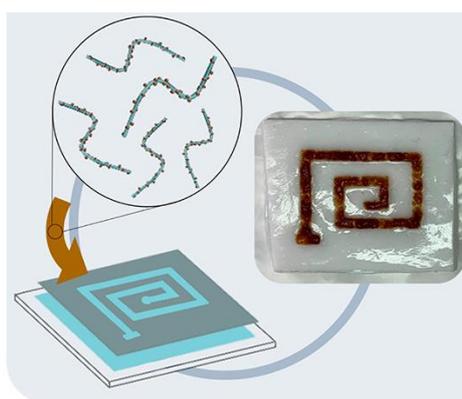


Figure 1: Screen-printed magnetic bacterial cellulose fibers on a BC pellicle.

[1] Roig-Sanchez S., Kam D., Malandain N., Sachyani-Keneth E., Shoseyov O., Magdassi S., Laromaine A., Roig A., *Carbohydrate Polymers* 294, 119778, 2022.

[2] Malandain N., Sanz Fraile, H.; Farre, R.; Otero, J.; Roig, A.; Laromaine, A., *ACS Applied Bio Materials*, in print, 2023.

[3] Mira-Cuenca C., Meslier T., Soledad Roig-Sanchez S., Laromaine A., Roig A., *ACS Appl. Polym. Mater.*, 3, 10, 4959, 2021.



BIOPOLYMER OPTICAL FIBERS FROM CELLULOSE FOR SENSING APPLICATIONS

Aayush Kumar Jaiswal^{*a}, Ari Hokkanen^a, Markku Kapulainen^a, Olli Ikkala^b, Hannes Orelma^a

^aVTT Technical Research Centre of Finland, Espoo, Finland

^bDepartment of Applied Physics, Aalto University, Espoo, Finland

*aayush.jaiswal@vtt.fi

Optical fibres (OFs) are the backbone of modern telecommunication infrastructure and are widely used in sensing applications. Glass optical fibres (GOFs) and polymer optical fibers (POFs) are the two main classes of commercial fibers. Although possessing excellent optical properties, both GOFs and POFs lack active sensing capability and that has led to the exploration of alternative materials for OF fabrication. Recently, cellulose has entered the OF domain as a novel candidate material [1-3]. Cellulose-based OFs offer exciting features such as active sensing capability with fast wetting and drying, renewability, biocompatibility, and biodegradability, which conventional OFs lack. Such features, especially biocompatibility, makes cellulose OFs attractive for biomedical applications.

In this work, we present the fabrication of OFs from carboxymethyl cellulose (CMC) and demonstrate the application of such OFs in various sensing systems. CMC OFs were prepared via dry-jet wet spinning of CMC hydrogels into a coagulation bath. The spun hydrogel fibers were crosslinked with Al^{3+} ions in wet-state and then dried to obtain strong (tensile strength ~ 150 MPa), flexible, and optically clear multimode OFs. The light transmission window for the CMC OFs was 550-1350 nm, wherein, the minimum attenuation was measured to be $1.6 \text{ dB}\cdot\text{cm}^{-1}$ (at 637 nm), meaning CMC OFs have good waveguiding properties in the visible (red) to near infrared range. Further, exploiting the rapid moisture sorption of CMC, we demonstrated respiratory rate monitoring with CMC OFs. A touch sensor was also prepared. Additionally, we demonstrated high-speed (150 Mbit/s) optical signal transmission through CMC fibers in both air and water media, indicating potential applications involving bodily fluids. Our work shows the technical potential of cellulose optical fibers in advanced sensing applications, for instance in environmental sensing and in the biomedical domain.

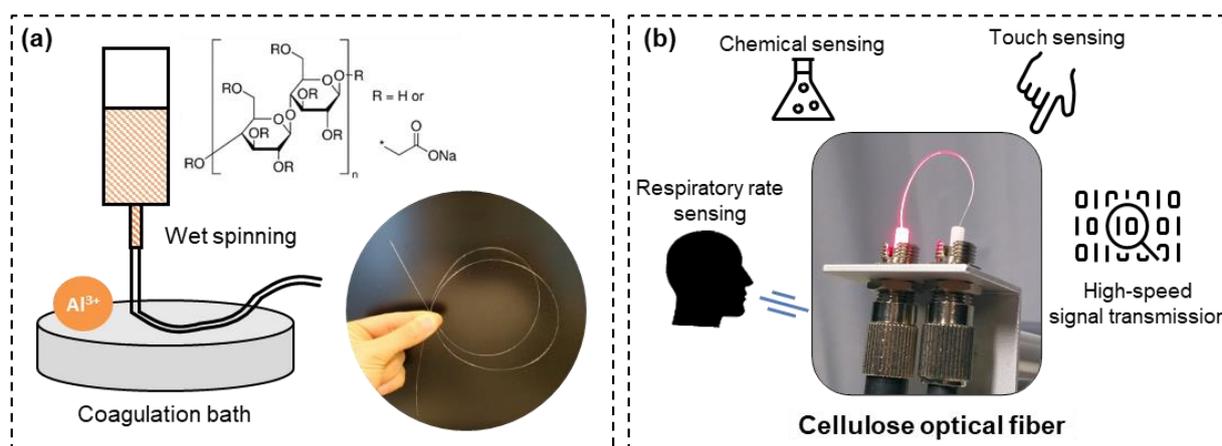


Figure 1: (a) Schematic of CMC OF fabrication, (b) application demonstrated for CMC OFs.

[1] Orelma, H., Hokkanen, A., Leppänen, I. et al., *Cellulose*, 27, 1543–1553, 2020.

[2] Hynninen, V., Chandra, S., Das, S. et al., *Small*, 17, 2005205, 2021.

[3] Jaiswal, A., Hokkanen, A., Kapulainen, M. et al., *ACS Applied Materials & Interfaces*, 14(2), 3315–3323, 2022.



PHOTORESPONSIVE COVALENTLY LINKED DEXTRAN NETWORKS

Knaipp K.^{*a}, Kargl R.^b, Stana Kleinschek K.^b, Makuc D.^c, Plavec J.^c, Gescheidt G.^a

^a Institute of Physical and Theoretical Chemistry, Graz Technical University, Austria

^b Institute of Chemistry and Technology of Biobased Systems, Graz Technical University, Austria

^c Slovenian NMR Centre, National Institute of Chemistry, Slovenia

* kknaipp@tugraz.at

Functional materials that can take up and release guest molecules upon stimulation with light can find applications in the area of targeted drug release. [1] Such systems are often based on azobenzene, a molecular photoswitch that can be photoisomerized between its *cis* and *trans* isomers. [2] The bacterial polysaccharide dextran and its modifications have been used in a wide variety of drug delivery systems. [3]

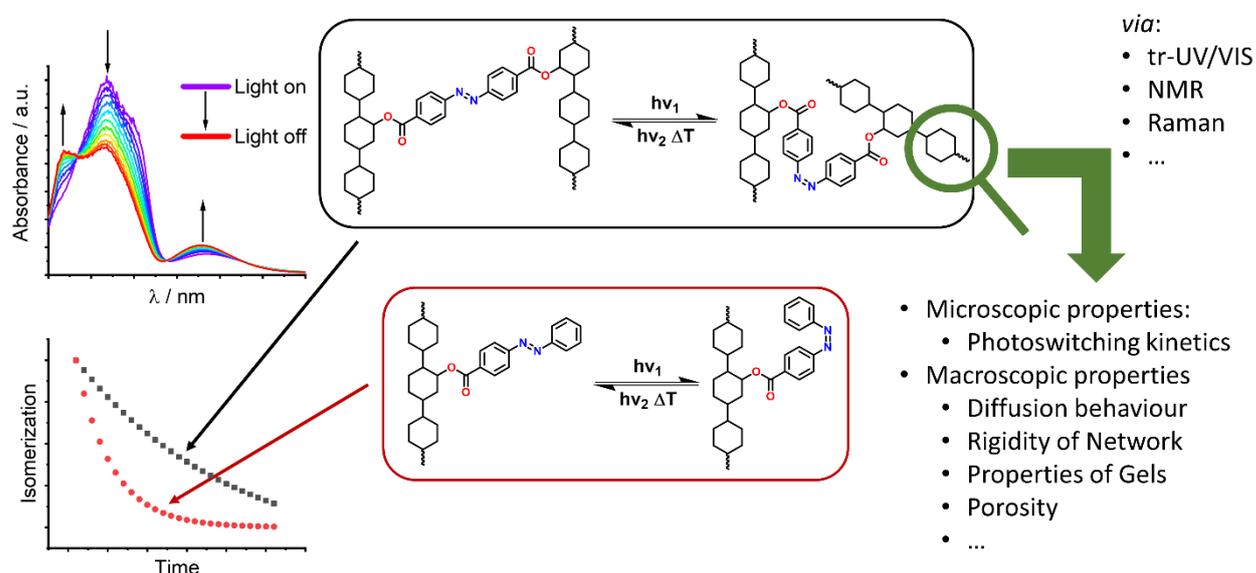


Figure 1: Azobenzene-crosslinked dextran molecules show photoswitching activity, paving the way towards photo-triggered catch-and-release devices.

Here a previously unreported doubly-covalent ester link by azobenzene moieties opens the way for a photo-triggered porous device for the release and capture of small molecules. We have been exploring the potential of such materials by varying the degree and fashion of crosslinking. The preparations of gels *via* this procedure has been demonstrated.

Control experiments indicate remarkably different material properties when the azobenzene linker is attached by one or two covalent bonds. We have been following the kinetics of *trans*↔*cis* isomerizations of the azo-moiety and the micro- and macroscopic properties of the crosslinked dextran network using a wide variety of analytical techniques, including time-resolved UV/VIS spectroscopy, NMR spectroscopy and Raman spectroscopy.

- [1] Y. Zhou, H. Ye, Y. Chen, R. Zhu, L. Yin, *Biomacromolecules*, 19, 1840–1857, 2018
 [2] L. Dai, J. Lu, F. Kong, K. Liu, H. Wei, C. Si, *Adv. Compos. Hybrid Mater.*, 2, 462–470, 2019
 [3] Q. Hu, Y. Lu, Y. Luo, *Carbohydr. Polym.* 264, 117999, 2021



NANOCELLULOSE AND PROTEIN AMYLOID FIBRILS: A PARTNERSHIP FOR THE DESIGN OF FUNCTIONAL SUSTAINABLE NANOMATERIALS

Carmen S.R. Freire

CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

* cfreire@ua.pt

Polysaccharides and proteins are extensively used for the design of advanced sustainable materials. Specially, nanocellulose (nanofibrillated cellulose and bacterial nanocellulose) and protein amyloid fibrils are gaining growing popularity amongst the catalog of nanostructures exploited in panoply of fields, including nanocomposites industry, paper and packaging, environmental remediation, electronics, energy, and biomedical applications [1]. The enormous potential of these biobased nanofibrils is related to their high aspect ratio and specific surface area, ease of modification, high mechanical strength and thermal stability, renewability, biodegradability, and biological functionalities, particularly for the case of protein amyloid fibrils. They are normally blended with other (bio)polymers and processed following different methodologies envisioning the fabrication of diverse nanomaterials.

In this communication, a summary of recent studies regarding the combination of nanofibrillated cellulose and lysozyme amyloid nanofibrils for the design of distinct functional fibrous nanomaterials, *viz.* patches, films and hydrogels, for various applications (e.g. tissue regeneration, 3D-bioprinting and water remediation) will be presented and discussed. This set of works highlight the potential of the simple assembly of these two types of biobased nanofibrils for the development of high performance and functional sustainable nanomaterials.

[1] Silva A.C.Q., Silvestre A.J.D., Vilela C. & Freire C.S.R., *Front. Bioeng. Biotechnol.*, 10, 2022.

Acknowledgments: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials (UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020) financed by national funds through the FCT/MEC (PIDDAC). FCT is acknowledged for the research contract under Scientific Employment Stimulus to C.S.R.F. (CEECIND/00464/2017).



PASSIVE CLIMATE REGULATION WITH TRANSPIRING WOOD FOR BUILDINGS WITH INCREASED ENERGY EFFICIENCY

Yong Ding ^{*a,b}, Christopher H. Dreimol ^{a,b}, Robert Zboray ^c, Kunkun Tu ^{a,b}, Tobias Keplinger ^{a,b}, Guido Panzarasa ^{a,b}, Ingo Burgert ^{a,b}

^a Wood Materials Science, Institute for Building Materials, ETH Zürich, Switzerland

^b WoodTec Group, Cellulose & Wood Materials, Empa, Switzerland

^c Center for X-ray Analytics, Empa, Switzerland

* yoding@ethz.ch

Keywords: wood, passive regulation system, hygrothermal effect, moisture buffer effect, thermal energy storage, energy-efficient building materials.

Abstract:

About 20% of the energy consumption worldwide is used for maintaining a comfortable indoor climate. Therefore, passive systems for indoor temperature and humidity regulation that can respond to environmental changes are very promising to reduce buildings' energy consumption. We developed a process to improve the responsiveness of wood to humidity changes by laser-drilling and incorporating a hygroscopic salt. The resulting "transpiring wood" allows to regulate humidity and temperature by the exchange of moisture between the surrounding air. We proved that the hygrothermal performance of transpiring wood can be used to regulate indoor climate in various climate types with associated energy savings, favoring broad application in the building sector. The reduction of temperature fluctuations, thanks to the buffering of temperature peaks, can lead to an indirect energy saving of about 10% for cooling and of between 4-27% for heating depending on the climate. Furthermore, our transpiring wood meets in full different sustainability criteria, from raw materials to the fabrication process, resulting in a product with a low overall environmental impact and which is easy to recycle. [1]

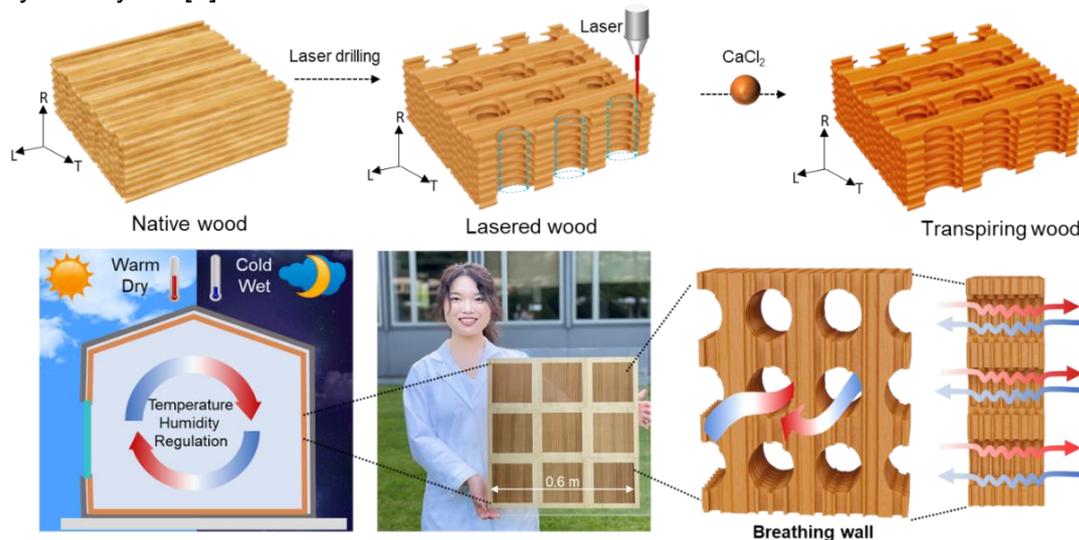


Figure 1: Fabrication process and working principle of the 'transpiring wood'.

[1] Ding Y, Dreimol C H, Zboray R, et al. Passive climate regulation with transpiring wood for buildings with increased energy efficiency. *Materials Horizons*, 2023.



EFFECT OF NANOCELLULOSE IN ENHANCING THE PERFORMANCE OF HYBRID NANOCELLULOSE/CARBON NANOTUBE ELECTROCHEMICAL SENSORS

Kontturi K. S.*^a, Durairaj V.^a, Tammelin, T.^a, Laurila, T.^b

^a VTT Technical Research Centre of Finland, Finland

^b School of Electrical Engineering, Aalto University, Finland

* katri.kontturi@vtt.fi

Electrochemical sensing is a powerful method for fast and easy detection of biomolecules in both *in vivo* and *in vitro* systems. Carbon serves as an optimal electrode material for such applications due to low cost, high stability, and wide operation potential. Carbon nanomaterials have a potential of radically improving the sensitivity of bulk carbon electrodes due to their high reactive surface area, low charge transfer resistance, and improved reaction kinetics compared to bulk materials. However, creating controlled carbon nanotube (CNT) network architectures optimal for sensing applications is a challenge due to the limited dispersibility of the rather hydrophobic CNTs in different solvents.

Nanocellulosic materials enable particle-stabilized dispersing of CNTs into water and further casting the mixture to form a stable cellulose/carbon nanoparticle hybrid film, providing a straightforward route for the development of electrochemical sensor platforms. Besides providing the means for dispersion, tuning the surface chemistry and geometry of nanocellulose can be utilized for tailoring the properties of the cast electrodes.

Here, we study the effect of the characteristics of nanocellulosic species on the architecture and electroanalytical performance of the nanoparticle hybrid sensor. With such sensor, it is possible to detect drugs or biomolecules at low concentrations by using cyclic voltammetry, making the system applicable for fast point-of-care diagnostics. It appears that the nanocellulose/nanocarbon hybrid architecture based on cellulose nanocrystals (CNCs) builds up denser than that based on nanofibers (CNFs). The more open and hygroscopic CNF-based architecture shows higher surface area and sensitivity towards biomolecules. The nanocellulose-containing hybrids outperform commercial CNT-based electrodes, and their electroanalytical performance remains on a high level even in presence of physiologically relevant interfering molecules or protein foulants.

[1] Durairaj V., Li P., Liljeström T., Wester N., Etula J., Leppänen I., Ge Y., Kontturi K.S., Tammelin T., Laurila T., Koskinen, J., *ACS Applied Nano Materials*, 4, 5842-5853, 2021.

[2] Durairaj V., Liljeström T., Wester N., Engelhardt P., Sainio S., Wilson B.P., Li P., Kontturi K.S., Tammelin T., Laurila T., Koskinen J., *Cellulose*, 29, 9217-9233, 2022.



HARNESSING NATURE AND NANOTECHNOLOGY: ADVANCES IN BACTERIAL CELLULOSE-BASED BIOHYBRID MATERIALS

Soledad Roig-Sánchez, Irene Anton-Sales, Nerea Murugarren, Thomas Meslier, Anna Roig, Anna Laromaine

Nanoparticles and Nanocomposites Group (nn.icmab.es) Institut Ciència de Materials de Barcelona (ICMAB-CSIC) Campus UAB, 08193 Bellaterra, Spain

alaromaine@icmab.es

Biopolymers, such as cellulose, derived from natural sources, are playing a pivotal role as environmentally-friendly materials in various industries. Cellulose (C) and nanocellulose (NC) are gaining attention as sustainable, green materials for the fabrication of advanced composites, garnering interest from industries, governments, and consumers alike.

Nanoparticles (NPs) offer unique properties that can be tailored through chemical and structural modifications. By combining raw materials like cellulose with nanoparticles, new opportunities arise for developing innovative materials that leverage the synergies of nanotechnology and nature.

In this context, our latest research focuses on the development of novel stimuli-responsive materials using bacterial cellulose (BC). We have explored the modification of BC during the biosynthesis steps or through post-synthesis treatments to create multifunctional bacterial cellulose laminates and spherical BC structures with the incorporation of various types of nanoparticles. This approach allows us to precisely control the composition and structure of the resulting biohybrid materials, expanding the range of intriguing possibilities for their potential applications.

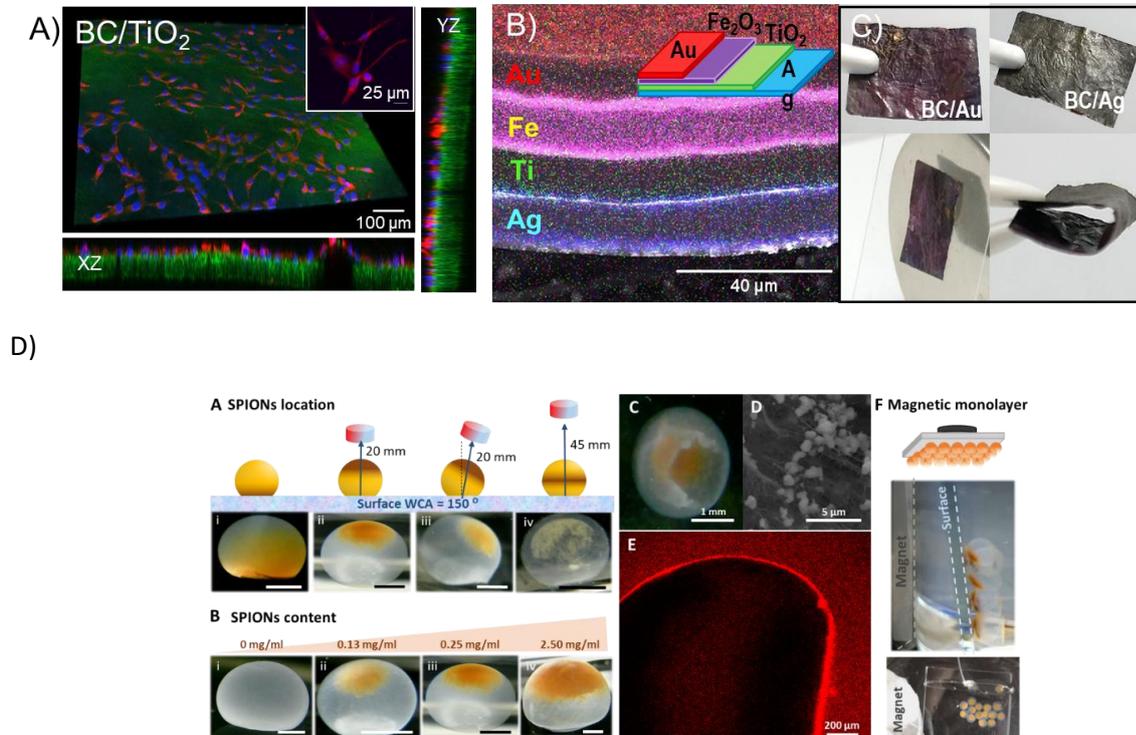


Figure: BC Composites of: A) Titania nanoparticles where we cultured fibroblast cells, B) Multilaminate BC composites C) Flexible BC nanocomposites. D) BC spheres composite with SPIONs to afford magnetic responsible biomaterials.



DIRECT 3D BIOFABRICATION OF BACTERIAL NANOCELLULOSE VIA SOFT MATTER TEMPLATING

Lu Y. ^{*a}, Chun Y. ^a, Su X. ^a, Shi X. ^a, Mehling M. ^a, Kamkar M. ^{b,a}, Fuller G.G. ^c, Rojas O.J. ^{a,d}

^a Bioproducts Institute, Department of Chemical and Biological Engineering, Department of Chemistry and Department of Wood Science, University of British Columbia, Canada

^b Department of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, Canada

^c Department of Chemical Engineering, Stanford University, Stanford, USA

^d Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland

* yi.lu@ubc.ca

Biofilms of bacterial nanocellulose (BNC) grown at the air/water interface are promising structural materials due to their green production and remarkable mechanical strength. In principle, BNCs can be fermentatively produced at the oil-water interface, *i.e.*, under-liquid biofabrication, since air can permeate through many hydrophobic oils as a supply for the proliferation of aerobic nanocellulose-producing bacteria (*e.g.*, *Komagataeibacter medellinensis*). Such development is essential to guiding BNC growth into three-dimensional structures through emulsion templating. Herein, we evaluate the performance of cellulose-producing activities under different oil conditions. Air transport efficiency impacts the physiochemical properties of the produced biofilms, including the fibril morphology and scale, surface area, and mechanical strength. Combining the new understanding of living microbials with various soft matters systems, we highlight the 3D biofabrication of nanocellulosic soft materials with well-controlled morphologies, including BNC capsules/foams (*via* emulsion) and layered composites (*via* multiple interfaces). This approach paves the avenue to investigate living soft matter systems, for potential applications in the fields of biomedical, bioremediation, and arts designs.

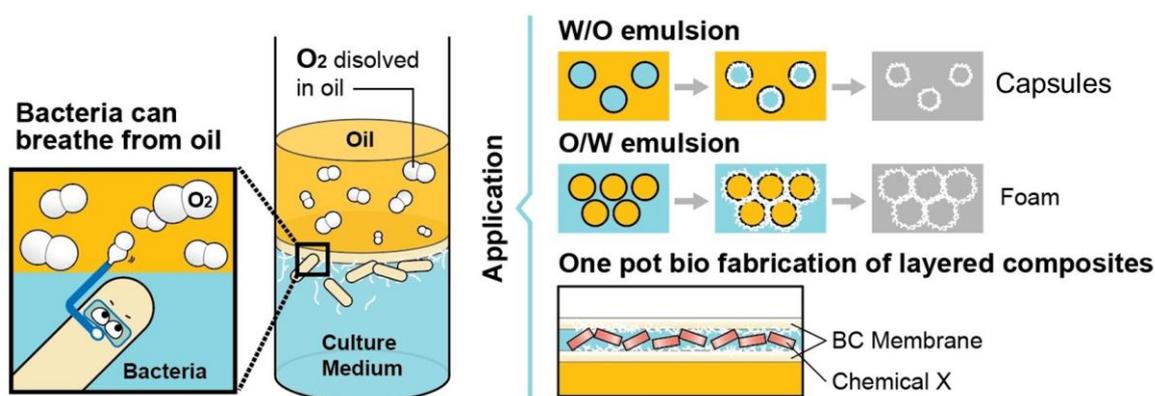


Figure 1 : Soft matter-templated 3D biofabrication of BNC



DEVELOPMENT OF CELLULOSIC NANOCOMPOSITES WITH CONTROLLED STRUCTURING BY ULTRAFILTRATION AND ULTRAVIOLET CURING

Mandin S.^{*a}, Metilli L.^b, Karrouch M.^a, Lancelon-Pin C.^b, Chèvremont W.^c, Hengl N.^a, Jean B.^b and Pignon F.^a

^a L. Rhéologie et Procédés, Univ. Grenoble Alpes, CNRS, Grenoble INP, Grenoble, France

^b CERMAV, Univ. Grenoble Alpes, CNRS, CERMAV, Grenoble, France

^c ESRF, The European Synchrotron, Grenoble, France

* samuel.mandin@univ-grenoble-alpes.fr

The number of techniques for fabricating nanocomposites based on cellulose nanocrystals (CNC) [1] has been constantly growing in recent years. These processes aim at controlling the organization of the nanoparticles in the composites to confer functional properties, such as mechanical, optical or barrier properties. In this context, frontal ultrafiltration combined with ultraviolet (UV) cross-linking appears to be an innovative technique. Indeed, thanks to the application of pressure fields in the filtration cell at the membrane surface, ultrafiltration makes it possible to structure and orient nanoparticles on a nanometric scale. However, in order to maintain nano-structured and oriented materials in a solid material, it is necessary to fix this structure *in situ* before it relaxes. Accordingly, a UV curing strategy using poly(ethylene glycol) diacrylate (PEGDA) has been developed. This polymer was chosen because it is curable under UV light with the addition of a photoinitiator, is water soluble and allows the colloidal stability of CNC to be maintained. In this study, a PEGDA/CNC suspension was filtered and then UV cured under different operating conditions. The combination of scanning electron microscopy (SEM) and small angle X-ray scattering (SAXS) analyses showed that it was possible to organize and orient the CNCs at very high concentrations (started from a 2 wt% suspension and reached 74 wt%) and to maintain this organization in the nanocomposite over a very broad lengthscale (nm to μm) (Figure 1).

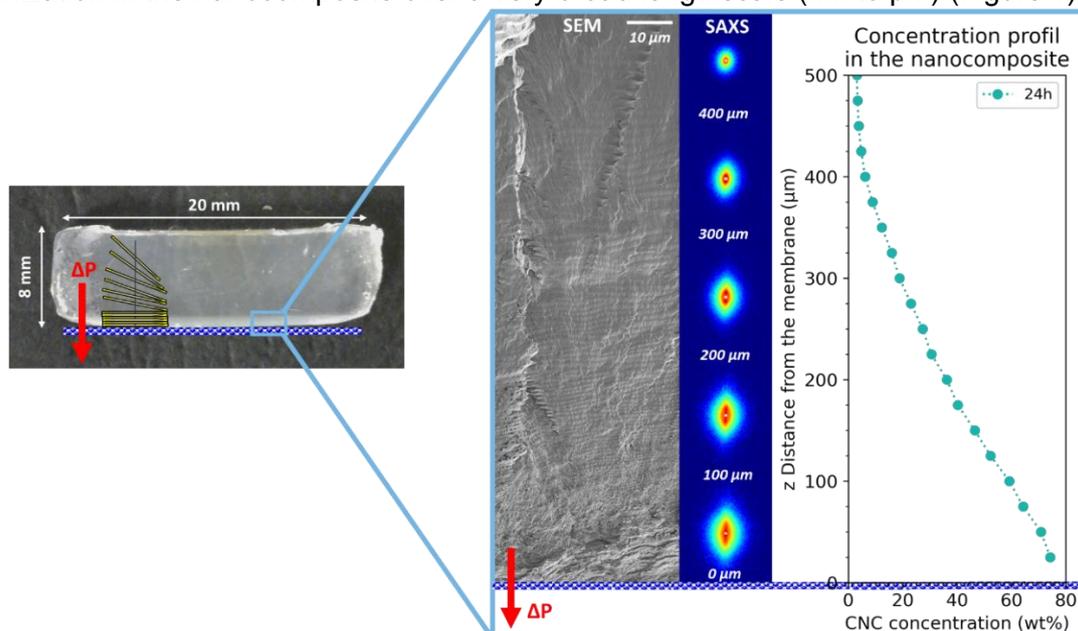


Figure 1: Image of a PEGDA/CNC nanocomposite (left) and SEM image of the CNC deposit formed near the membrane and the CNC concentration profile in the nanocomposite deduced from the analysis of the SAXS measurements.

[1] Semeraro E. and al, Colloids and Surfaces A, 584, 124030, 2020.



NANOCELLULOSE MODIFICATION BY THE INCORPORATION OF CORE-SHELL NANOLATEXES SYNTHESIZED THROUGH PISA

Jerlhagen Å. ^{a,b}, Malmström E. ^{a,b,c}

^a Division of Coating Technology, KTH Royal Institute of Technology, Sweden

^a FibRe - A Centre for Lignocellulose-based Thermoplastics, KTH Royal Institute of Technology, Sweden

^b Wallenberg Wood Science Centre (WWSC), KTH Royal Institute of Technology, Sweden

* asaje@kth.se

Cellulose nanofibrils (CNFs) constitute one of the most promising biobased building blocks for the development of sustainable materials for the future. One such application is the replacement of fossil-based plastics by CNF-based nanopapers, which are both biobased and biodegradable. But to make nanopapers suitable as drop-in alternatives to plastics, some of their inherent weaknesses must be overcome, such as sensitivity to moisture and brittleness in low humidity environments.

Polymeric core-shell nanolatexes are one of the most promising classes of additives for the modification of CNF-based materials, and have been shown to effectively modify water resistance and mechanical properties.^{1,2} Nanolatexes are synthesized through reversible-fragmentation chain-transfer (RAFT)-mediated polymerization-induced self-assembly (PISA) in water. The PISA process makes for a flexible platform in the synthesis of functional nanolatex with tunable size, softening temperature and chemical surface functionality. This means that nanolatexes can be tailored to interact specifically with cellulosic surfaces, both in the dispersed and in the dry state.

The exploration of these nanolatexes as CNF-additives is still in its infancy, but early results have shown the great potential of cationic nanolatexes for modifying mechanical properties of nanopapers.¹ Depending on nanolatex additive amount, the effect can be tailored to be stiffening or plasticizing of the resulting materials. Further work aims to develop a holistic understanding as to the importance of particle size, charge and chemical functionality by extending investigations to anionic and non-charged nanolatex systems.

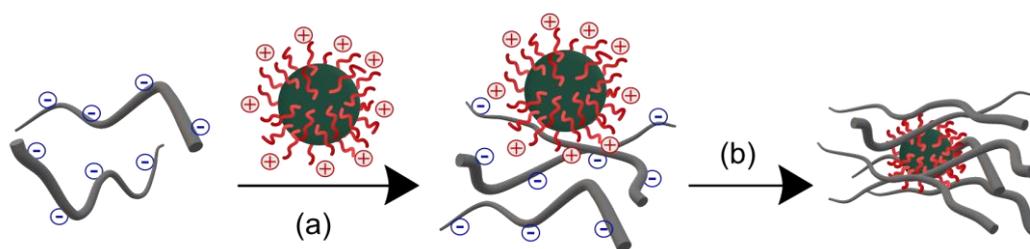


Figure 1 : Schematic of fabrication method for cellulose nanofibril – nanolatex hybrid materials ; (a) electrostatic adsorption in dispersion and (b) dewatering. Adapted from [2].

[1] Engström, J., Hatton, F. L., Wågberg, L., D'Agosto, F., Lansalot, M., Malmström, E., & Carlmark, A., *Polymer Chemistry*, 8(6), 1061-1073, 2017

[2] Alexakis, A. E., Jerlhagen, Å., Leggieri, M. R. T., Eliasson, A., Bensselfelt, T., & Malmström, E., *Macromolecular Chemistry and Physics*, 224(1), 2200249, 2023



POLYMER MODIFIED CNF CROSS-LINKED WITH A VARIETY OF NANOPARTICLES IN A ONE-STEP SURFACE-INITIATED CONTROLLED RADICAL POLYMERIZATION (SI-SET-LRP)

Mietner J. B.*^a, Jiang X.^a, Navarro J. R. G.^a

^a Institute of Wood Science, University Hamburg, Germany

* jakob.benedikt.mietner@uni-hamburg.de

Cellulose nanofibrils (CNF) are a versatile material that can acquire new properties by combining them with inorganic nanoparticles (NP). Our team devised a synthesis pathway to surface-modify CNF with polymers and cross-link them with various NP *in situ*. This involves chemically modifying CNF into a CNF-based macroinitiator (CNF-MI), which allowed grafting various acrylate monomers, such as sterayl acrylate (SA) and di (ethylene glycol) ethyl ether acrylate (DEGEEA), onto the CNF surfaces via surface-initiated radical polymerization (SET-LRP).^{1,2} We also successfully chemically modified different types of NP, including barium titanate (BTO)², cobalt iron oxide (CFO)³, lanthanide-doped upconversion nanoparticles (UCNP)⁴ and Nano-GdF₃, with acrylate containing surface ligands and incorporated them in the modified CNF network.

To confirm the chemical transformation of these modified CNF-based hybrid gels, we conducted various analyses, such as IR, TGA, XRD and SEM etc.. We also investigated their properties and performance with the addition of NP. For instance, magnetic and electrochemical properties of CNF grafted with poly-SA and CFO (CNF-PSA-CFO) were monitored via magnetic moment measurements³; NIR-sensitive upconverting properties and nanostructure of CNF-PSA-UCNP were analyzed with confocal microscopy and small-angle X-ray scattering (SAXS)⁴. Furthermore, we discovered that all these hybrid gels exhibit outstanding 3D gel-printing performance.

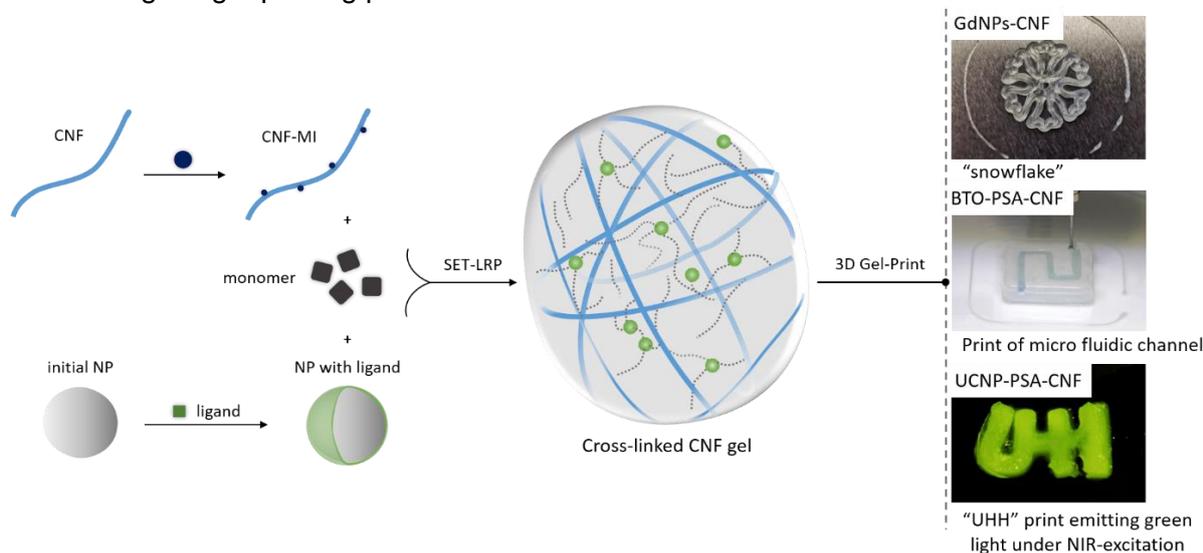


Figure 1: Modified CNF-based hybrid gel: syntheses and 3D printing applications.

- [1] Jiang, X.; Mietner, J. B.; Navarro, J. R. G., *Cellulose* **2023**, No. 0123456789.
- [2] Navarro, J. R. G.; Rostami, J.; Ahlinder, A.; Mietner, J. B.; Bernin, D.; Saake, B.; Edlund, U, *Biomacromolecules* **2020**, 21 (5), 1952–1961.
- [3] Mietner, J. B.; Willruth, S.; Kompan, R.; Gimmler, C.; Nehmeh, B.; Navarro, J. R. G., *Fibers* **2022**, 11 (1), 2.
- [4] Jiang, X.; Mietner, J. B.; Harder, C.; Kompan, R.; Chen, S.; Strelow, C.; Sazama, U.; Fröba, M.; Gimmler, C.; Müller-Buschbaum, P.; Roth, S. V; Navarro, J. R. G., *ACS Appl. Mater. Interfaces* **2023**, 15 (4).



STRUCTURE PROPERTIES RELATIONSHIPS FOR NATURAL RUBBER FILLED WITH CELLULOSE NANOCRYSTALS

Fadoua ELLASSADI*, Emmanuel BEYOU^a, Florent DALMAS^b, Matthieu FUMAGALLI^a

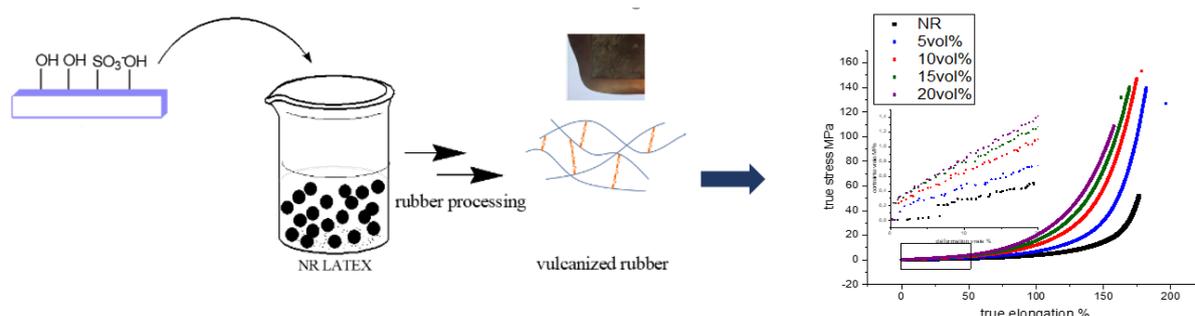
^aUniv Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, F- 69621 VILLEURBANNE Cédex, France

^b Université de Lyon, INSA-Lyon, CNRS, MATEIS, UMR 5510, F-69621 Villeurbanne, France

* fadoua.ellassadi@univ-lyon1.fr

Using nanocellulose as a reinforcing filler for rubber materials is gaining more and more attention as its characteristics (biosourced origin, low density, anisotropic morphology and mechanical properties) could give more sustainable materials and with original properties in comparison with conventional fillers.[1] Previously, we have shown that nanocellulose aerogel can be designed to be melt dispersed in SBR and that the linear modulus of the vulcanized materials show a reinforcing effect comparable to those reported for silica filled materials. [2]

Alternatively, materials can be wet-processed from colloidal suspensions of cellulose nanocrystals and rubber latex, such approach being less energy intensive and offering the possibility to tune the material microstructure through the processing. As a first illustration of that process, we prepared materials by freeze drying colloidal suspensions of cellulose nanocrystals and natural rubber latex while varying the filler loading from 0 to 20% v/v. The microstructure and mechanical reinforcement of the related vulcanized materials have been characterized combining TEM, DMA and tensile tests. The specific reinforcement effect observed in those materials have then been discussed considering both mechanical models (Halpin Kardos and percolation) and previous works from the literature.



[1] Low, D. Y. S., Supramaniam, J., Soottitantawat, A., Charinpanitkul, T., Tanthapanichakoon, W., Tan, K. W., & Tang, S. Y. (2021). Recent developments in nanocellulose-reinforced rubber matrix composites: A review. *Polymers*, 13(4), 550.

[2] Fumagalli, M., Berriot, J., de Gaudemaris, B., Veyland, A., Putaux, J. L., Molina-Boisseau, S., & Heux, L. (2018). Rubber materials from elastomers and nanocellulose powders: Filler dispersion and mechanical reinforcement. *Soft Matter*, 14(14), 2638-2648.



HIGHLY TRANSPARENT HEAT-SEALABLE CNF FILMS THROUGH ESTERIFICATION AND ULTRASONIC TREATMENT

Matias Lakovaara^{a,*} · Juho Antti Sirviö^a · Luyao Wang^b · Jouko Peltonen^c · Chunlin Xu^b · Henrikki Liimatainen^a

^a Fibre and Particle Engineering Research Unit, University of Oulu, Oulu, Finland

^b Laboratory of Natural Materials Technology, Åbo Akademi University, Turku, Finland

^c Laboratory of Molecular Science and Engineering, Åbo Akademi University, Turku, Finland

* matias.lakovaara@oulu.fi

Cellulose nanofiber (CNF) films have attracted interest among researchers because of their biodegradability and green origin combined with good mechanical and oxygen barrier properties [1]. However, CNF film strongly interacts with water, so their intriguing properties are lost when exposed to humid conditions [2]. This research introduces a unique type of CNFs using cellulose esterification and ultrasonic treatment in ethanol. The films made from CNF had excellent optical properties with transparency of 92–93% and without haziness or scattering (Figure 1). The CNF film exhibited water vapor permeability of 2.34 g·µm/m²·d·kPa, which was significantly better than neat CNF film (18.67 g·µm/m²·d·kPa). Moreover, the CNF film displayed a good liquid water resistance, since dry and wet mechanical properties were statistically the same (13.6 MPa and 13.1 MPa respectively). The CNF film had heat-sealing properties, which was illustrated by fabricating a small package filled with rice. In addition, heat-sealing barrier test was performed, which showed that bottle could be heat-sealed to achieve barrier against moisture.

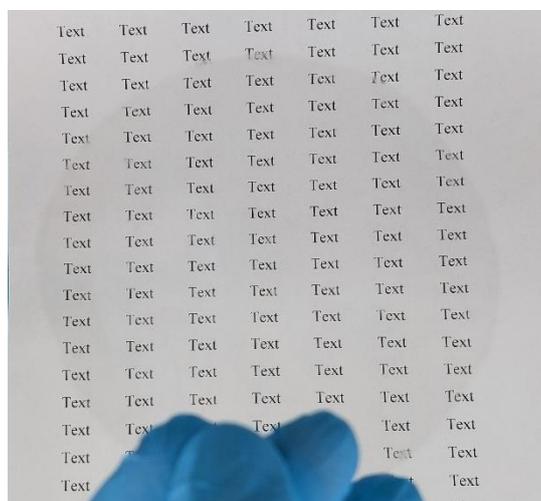


Figure 1. Transparent heat-sealable CNF film

[1] Aulin, C.; Gällstedt, M.; Lindström, T. Oxygen and Oil Barrier Properties of Microfibrillated Cellulose Films and Coatings. *Cellulose* 2010, 17 (3), 559–574.

[2] Wang, J.; Gardner, D. J.; Stark, N. M.; Bousfield, D. W.; Tajvidi, M.; Cai, Z. Moisture and Oxygen Barrier Properties of Cellulose Nanomaterial-Based Films. *ACS Sustainable Chem. Eng.* 2018, 6 (1), 49–70.



CELLULOSE-MOF SUSPENSIONS: TOWARDS SELF-SUPPORTED POLYFUNCTIONAL MATERIALS DESIGNED FROM ULTRAFILTRATION

Lorenzo Metilli^{a*}, Héloïse Ugo^b, Cyril Picard^b, William Chèvremont^c, and Frédéric Pignon^a

^aUniv. Grenoble Alpes, CNRS, Grenoble INP (Institute of Engineering Univ. Grenoble Alpes), LRP, 38000 Grenoble, France

^bUniv. Grenoble Alpes, CNRS, LIPhy (Laboratoire Interdisciplinaire de Physique), University Grenoble Alpes, 38000 Grenoble, France

^cESRF, The European Synchrotron, 38043 Grenoble, France

lorenzo.metilli@cermav.cnrs.fr

Metal-organic frameworks (MOFs) are promising materials to address critical issues such as petrochemical and gas separation, filtration, catalysis, sensing and energy storage [1]. Large-scale deployment of MOFs is however hampered by their crystalline powder state, which results in poor processability. Recently, the hybridization of MOFs with biopolymers has emerged as a greener, biocompatible strategy with improved processability into membranes, films, and porous materials [2]. Nevertheless, the physiochemical properties of the biopolymer-MOF mixtures, and their relationship to the composite structure and functionality, need to be investigated to promote their use in real applications. The present work focuses on the preparation of thin nanocomposites from commercial ZIF-8 (a synthetic zeolite) and cellulose nanocrystals (CNCs) aqueous suspensions using membrane ultrafiltration. Results showed that small amounts of CNCs (1:20 CNC:ZIF-8 volume ratio) are sufficient to disperse the ZIF-8 particles, preventing further aggregation and phase separation, and enabling the formation of a compact deposit under filtration. The stabilization derived from the electrostatic interaction between the CNCs and ZIF-8, leading to the formation of a layer of adsorbed CNCs on the surface of ZIF-8 particles, as observed by TEM. The rheology of ZIF-8 suspensions shifted from shear-thinning to a Newtonian behaviour in presence of CNCs. The filtration process was investigated *in situ* with Small-Angle X-Ray Scattering (Figure 1), showing that the deposition of ZIF-8 particles occurred concurrently to the formation of a layered structure of CNCs, perpendicular to the transmembrane pressure. Finally, the porosity of ZIF-8 to water was tested with a custom-made porosimeter [3], showing that the adsorbed CNCs did not affect the intrusion/extrusion pressure, or the available pore volume in the hybrid material.

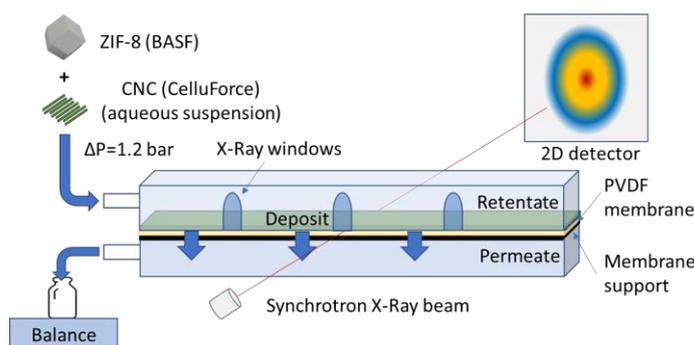


Figure 1. Scheme depicting *in situ* SAXS analysis during filtration of CNC and ZIF-8 suspensions.

[1] Freund et al., *Angew.Chem.Int.Ed.* 60, 23975–24001, 2021.

[2] El Hankari et al., *Prog. Mater. Sci.* 106, 100579–100616, 2019.

[3] Guillemot et al., *Rev. Sci. Instrum.* 83, 105105–105113, 2012.



INVESTIGATING THE ROLE OF AgNO₃-DERIVED SILVER NANOPARTICLES SUPPORTED ONTO TEMPO-OXIDIZED CELLULOSE NANOFIBERS IN PROMOTING Cd²⁺ CATIONS ADSORPTION

Riva L.^{*a}, Dotti A.^a, Meneghini C.^b, Iucci G.^b, Venditti I.^b, Battocchio C.^b, Corsi I.^c, Punta C.^a

^a Department of Chemistry, Materials, and Chemical Engineering, Politecnico di Milano, Italy

^b Department of Science, Roma Tre University of Rome, Italy

^c Department of Physical, Earth and Environmental Sciences, University of Siena, Italy

* laura2.riva@polimi.it

Cd²⁺ adsorption on cellulose is widely reported in literature, attributing the interaction mainly to electrostatic attractions between the negative charges of the deprotonated groups of this bio-polymer and the positive charges of the ion. [1] It is also possible to detect interesting works on Silver Nanoparticles (AgNPs) interacting with Cd²⁺, and the use of AgNPs as sensors and for water decontamination is gaining increasing attention towards the scientific community. On the other hand, problems related to the use of nanoparticles in the context of environmental contamination suggest the development of ecologically sustainable media to prevent undesirable eco-toxic effects. [2]

Due to the limited number of examples describing cellulose-AgNPs hybrids as Cd²⁺ adsorbents, in our research work we decided to investigate in depth what phenomena regulate this interesting interaction. Moreover, in-depth *in vivo* eco-toxicological analyses were conducted on non-oxidized (CNF) and TEMPO-oxidized cellulose nanofibers (TOCNF), to test their effects in the marine environment and evaluating their eco-toxicity before the decoration with AgNPs.

In order to study the interaction mechanisms, we first started with the production of TEMPO-oxidized cellulose (TOC) and TOCNF, and through *in situ* physical deposition with AgNO₃ solutions we obtained the Silver-decorated materials (TOC-Ag and TOCNF-Ag).

Adsorption tests on 150 ppm Cd²⁺ solution were performed and we were able to observe that the significantly highest sorption capacity values were obtained with the TOCNF-Ag and TOCNF_b materials, highlighting the key role of silver and deprotonated carboxyl groups on the surface of the nanocellulose.

XPS and XAS analyses on samples before and after sorption experiments were conducted and through an in-depth semi-quantitative data analysis we were able to detect negatively charged residues which could be the responsible for the efficient interaction with positively charged Cd²⁺ ions, suggesting a strong electrostatic sorbent-cation interaction with the contribution of chelation phenomena, also underlining the role of Silver, since its presence is able to increase the exposure of the COO⁻ groups involved in the adsorption process. These hypotheses were further confirmed by adsorption tests in presence of Na⁺ and Ca²⁺, which revealed a decrease in adsorption capacity of the material in the presence of large amounts of interfering cations.

[1] Hokkanen S., Repo E., Suopajarvi T., Liimatainen H., Niinimaa J., & Sillanpää M., *Cellulose* 21(3),1471, 2014.

[2] Corsi I., Winther-Nielsen M., Sethi R., Punta C., Della Torre C., Libralato G., Lofrano G., Sabatini L., Aiello M., Fiordi L., Cinuzzi L., Caneschi A., Pellegrini D., & Buttino I., *Ecotoxicol. Environ. Saf.* 154, 237, 2018.



COPPER OXIDE NANOPARTICLE-DOPED NANOFIBER MATS FOR EFFECTIVE AIR FILTRATION

Anisiei A. ^{*a}, Bejan A.^a, Marin L.^a

^a "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

* anisiei.alexandru@icmpp.ro

Chitosan is a natural polysaccharide that is biodegradable and biocompatible, produced by deacetylating chitin from renewable sources such as insect and fungal exoskeletons. Materials derived from chitosan have several bioactive properties such as antimicrobial, hemostatic, spermicidal, CNS depressant, and anti-tumor effects. However, its bioactive properties are low in solid state, blending with other potent bioactive compounds being necessary for practical applications. In this regard, encapsulation of noble metals, such as silver and gold, are currently investigated in order to attain materials with improved performances. Nevertheless, the high cost of the noble metals strongly limits their applications [1]. Another research direction dedicated to the improvement of the chitosan' activity, is its transformation in chitosan derivatives, e.g. quaternized chitosan, which improve the antimicrobial and antiviral activity, and beside the adhesivity and anchoring ability of metals [1,2].

In this context, the aim of this study was to obtain new materials with improved properties for application in air filtration. To this aim, nanofibers mats based on chitosan and quaternized chitosan dopped with copper oxide nanoparticles were prepared by electrospinning. CuO nanoparticles were chosen due to their high antimicrobial activity and low cost, which recommend them as noble metal counterparts [3]. The obtained materials were structural and morphological characterized, and their specific properties as air filters were investigated. They proved high mechanical properties, antioxidant and antimicrobial activity, and good vapor and water permeability. The filtration efficiency of the electrospun fibers was evaluated using PM2.5 sensors, which measure the concentration of particulate matter with diameters less than 2.5 micrometers. The test conducted under controlled airflow conditions showed that the electrospun fibers exhibit good air filtration efficiency, effectively reducing the concentration of PM2.5 particles.

[1] Andreica B.-I., Cheng X., Marin L., *European Polymer Journal*, 110016, 2020.

[1] Guo Z., Xing R., Jiu S., Zhong Z., Ji X., Wang L., Li P., *Carbohydrate Research*, 342(10), 1329–1332, 2007.

[3] Javed R., Rais F., Kaleem M., Jamil B., Ahmad M.-A., Yu T., Qureshi S.-W., Ao Q., *International Journal of Biological Macromolecules*, 167, 1452-1467, 2021.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PCE2/2021 within PNCDI III



DIRECT SILVER NANOPARTICLES SYNTHESIS ONTO NANOCELLULOSE FOR ANTIBACTERIAL CELLULOSE-BASED FOOD PACKAGING

Aouay M. ^a, Aguado R.J. ^b, Fiol N. ^b, Putaux J.L. ^c, Boufi, S. ^a, Delgado-Aguilar M. ^{*b}

^a LMSE, University of Sfax, Tunisia

^b LEPAMAP-PRODIS research group, University of Girona, Spain

^c CNRS CERMAV, Université Grenoble Alpes, France

* m.delgado@udg.edu

The food industry will have to face important challenges in a near future, some of them in the field of food packaging. Considering that several strategies worldwide are aligned with the reduction of plastic use, particularly those designed for a single use, most of the food packaging solutions available in the market will require of a sustainable modification, conception or even substitution for non-plastic products. A clear example is the Directive (EU) 2019/904 of the European Parliament and the Council (of 5 June 2019), broadly known as the SUP directive. Despite the negative environmental impacts of plastic-based packaging, there is no doubt that the barrier performance that mono-material and multi-material plastic structures can offer is much greater than those based on paper. Paper is a porous structure that needs to be properly modified to provide certain barrier to gases, namely through the use of appropriate coatings. In the recent years, several strategies related to polysaccharide-based coatings, either modified or not, have appeared, such as the use of alginates, chitosan, pullulan or nanocellulose. However, the barrier performance that polysaccharide-coated paper can provide is still far from the requirements for food packaging, and the system must be supported by active strategies for increasing shelf life of food and, thus, preventing its spoilage.

In this work, we report the use of TEMPO-oxidized cellulose nanofibers (TOCNFs) modified by means of periodate oxidation to obtain 2,3-Dialdehyde cellulose (DAC) as reducing agent for silver, while providing barrier to gasses. The use of TOCNFs as feedstock for the production of DAC revealed that periodate oxidation can be performed under milder conditions, while keeping a high reduction potential. In addition, the *in situ* reduction of the silver present in the Tollen's reagent ($\text{Ag}(\text{NH}_3)_3^+$) onto the TOCNFs surface is of great interest, as the resulting gel can be directly coated onto paper for developing antibacterial surfaces. It was found that the antibacterial activity was significantly enhanced, generating a wide halo around the coated papers when they were in contact with *Bacillus subtilis* (Figure 1). Overall, the present work shows a promising approach to develop antibacterial paper, ensuring the presence of silver nanoparticles attached to the surface of the nanocellulose coating.

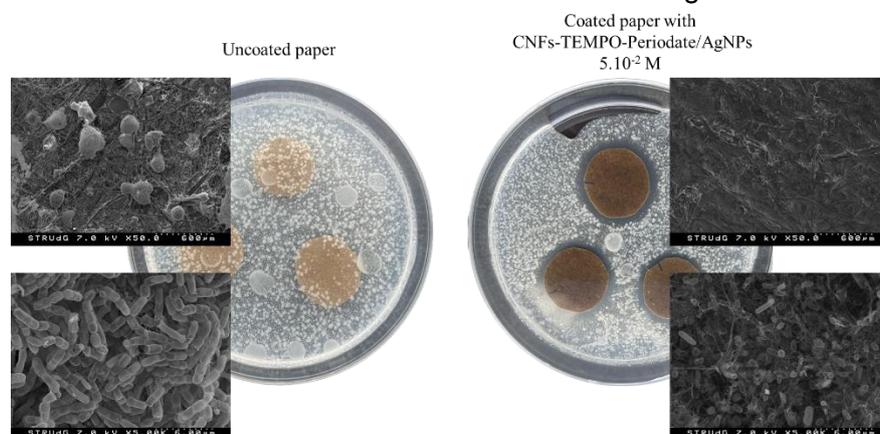


Figure 1 : Visual aspect of uncoated and coated papers with TOCNFs/AgNPs and SEM images of their surface



MANURE AS SOURCE FOR (MODIFIED) NANOCELLULOSE, ENERGY AND MORE...

Weiland K. ^a, Mautner A. ^{a,b}, Bismarck A. ^{*a}

^a Institute for Materials Chemistry, Faculty of Chemistry, University of Vienna, Austria

^b Institut für Umweltbiotechnologie, Universität of Bodenkultur, Konrad-Lorenz-Straße 20, 3430 Tulln an der Donau, Austria

* alexander.bismarck@univie.ac.at

Manure is mainly used as farm fertilizer and substrate for biogas production or simply considered as waste. Utilizing herbivore manure as source for cellulose outsources biomass collection to animals and disintegration of plant biomass—commonly not used for pulp production—into fibres occurs in their digestive system, which could reduce the energy input for fibre production. We proposed a manure management system (Fig. 1), in which not only biogas and fertilizer precursors but also high-value materials in the form of (nano)cellulose are produced. We will show that high biogas yields can be achieved using manure as substrate and that the remaining fermentation residue allows for effortless isolation of cellulose nanofibres, leading to a significant reduction of the environmental impact compared with traditional systems based on wood. Ruminants only convert about 50% of the consumed feed to sustain their life and the remains are excreted. Therefore, the faeces of these animals still contain significant amounts of fibrous materials originating from their feed. For demonstration purposes we used elephant and horse manure as a model system due to the high content of lignocellulosic fibres of around 70 wt.%. We will focus here on the properties of the cellulose materials obtained.

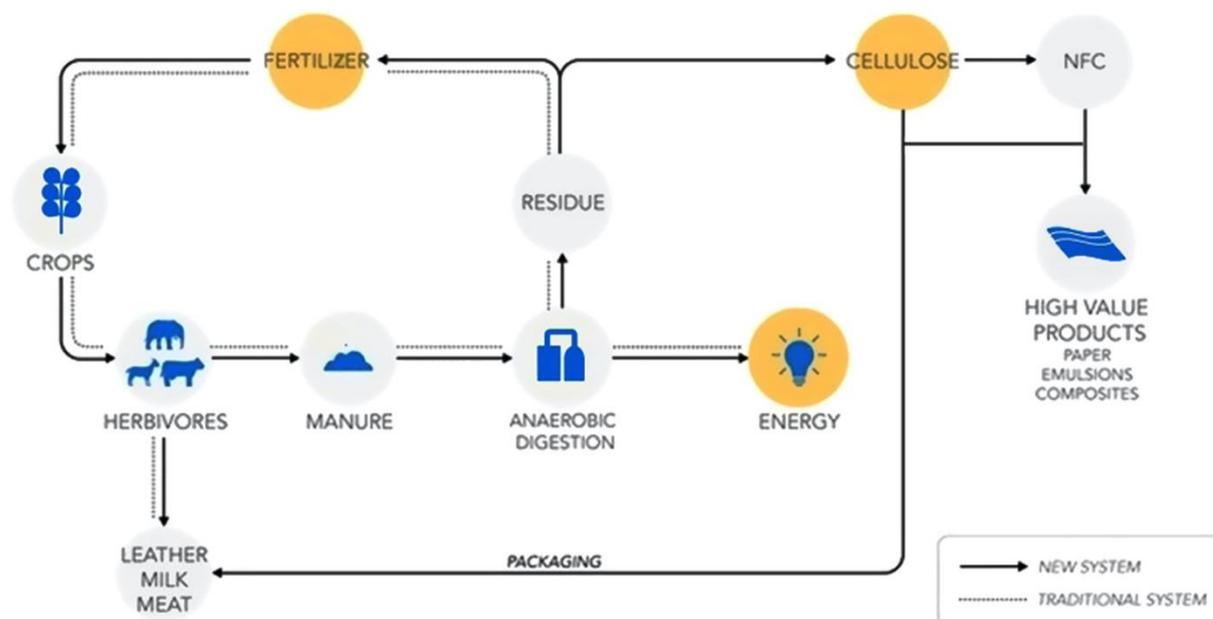


Fig. 1 : The graphic shows the proposed production chain of biogas and cellulose from animal manure: conventional use of manure (traditional system, dotted line) and proposed production system (new system, solid line) [1]

[1] Weiland, K., Wlcek, B., Krexner, T., Kral, I., Kontturi, K., Mautner, A., Bauer, A., Bismarck, A. ACS Sust. Chem. Engin. 2021 (46), 15506-15513.



TRIBOELECTRIC PERFORMANCE OF REGENERATED CELLULOSE

Dahlström, C.^a, Eivazi, A.^a, Pettersson, T.^d, Rojas, O.^{a,e,f}, Zhang, R.^b, Medronho, B.^{a,c}, Norgren, M.*^a

^a Surface and Colloid Engineering, FSCN Research Centre, Mid Sweden University, Sweden

^b Material Physics, FSCN Research Centre, Mid Sweden University, Sweden

^c MED–Mediterranean Institute for Agriculture, Environment and Development, Universidade do Algarve, Portugal

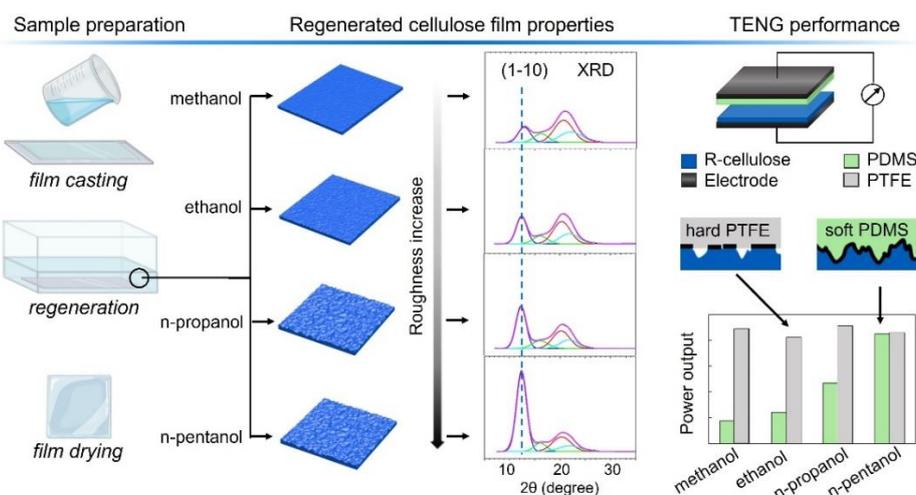
^d Fibre and Polymer Technology, KTH Royal Institute of Technology, Sweden

^e Bioproducts Institute, University of British Columbia, Canada

^f Department of Bioproducts and Biosystems, Aalto University, Finland

* magnus.norgren@miun.se

Cellulose has shown great potential in the development of green triboelectric nanogenerators (TENG) [1]. Particularly, regenerated cellulose (R-cellulose) has shown remarkably high output power density but the structural features and key parameters that explain such superior performance remain unexplored. In this work, wood cellulose fibers were dissolved in a LiOH(aq)-based solvent to produce a series of R-cellulose films. Regeneration in different alcohols (from methanol to n-pentanol) was performed and the films' structural features and triboelectric performance were assessed. Nonsolvents of increased hydrophobicity led to R-cellulose films with higher hydrophilic character; the films showed a (1-10) diffraction peak of larger amplitude and higher apparent crystallinity. An open-circuit voltage (VOC) of up to ca. 260 V and a short-circuit current (ISC) of up to ca. 150 μ A were measured for R-cellulose against polytetrafluoroethylene (as negative counter-layer). However, R-cellulose showed an increased VOC of 175% (from 88.1 V) against polydimethylsiloxane from methanol to n-pentanol. The corresponding ISC and output power also increased by 76% (from 89.9 μ A) and by 382% (from 8.8 W m⁻²), respectively. The higher R-cellulose hydrophilicity, combined with soft counter-layer that follow the surface structures increasing the effective contact area, are the leading reasons for a superior triboelectric performance.



[1] Zhang, R., Dahlström, C., Zou, H., Jonzon, J., Hummelgård, M., Örtegren, J., Blomquist, N., Yang, Y., Andersson, H., Olsen, M., Norgren, M., Olin, H. & Wang, Z.L. *Adv. Mater.* 32, 2002824, 2020; <https://doi.org/10.1002/adma.202002824>



POLYSACHARRIDE FROM CRICKETS AS BIOMASS SOURCES FOR CARBON ELECTRODES IN ELECTROCHEMICAL CAPACITOR

Lemieux J. ^{*a}, Backovic G.^a, Eyley S.^a, Thielemans W.^a

^a *Sustainable Materials Lab, KU Leuven Campus Kortrijk, Belgium*

*Julien.lemieux@kuleuven.be

The increasing demand for sustainable energy sources has led researchers to explore alternative materials for energy storage. Biomass, derived from plant and animal sources, has shown potential as a renewable resource for carbon electrodes in energy storage devices such as electrochemical capacitors. In this study, cricket biomass was utilized for the first time as a precursor for electrochemical capacitor electrodes. Cricket is a commonly consumed insect in many parts of the world, and its exoskeleton cuticles are rich in chitin, chitosan, and proteins. The carbon structure and nitrogen doping of the cricket materials can bring significant benefits to electrochemical capacitors, including improved electrical conductivity, surface area, and stability, resulting in higher capacitance and better electrochemical performance.

Cricket flour was carbonized at different temperatures (1000-900-800-700 °C) and activated in KOH under an argon atmosphere. Devices with a thick electrode (250 μm) and mass loading (>10 mg/cm²) were assembled in a Swagelok configuration. Our results show that cricket-derived chitin and protein carbon exhibits excellent electrochemical properties, with high specific capacitance (> 240 F/g at 1 A/g in 1 M H₂SO₄), interesting nitrogen content (>3-4 at.%) and good rate capabilities and cycling stability. The material was also characterized via WAXS, SAXS, SEM, EA, nitrogen adsorption isotherms, and electrochemical methods.

In conclusion, this study highlights the potential of cricket biomass as a renewable resource for energy storage applications. Our findings provide a new perspective on utilizing insect biomass for sustainable energy solutions, which have often been overlooked, and offer an exciting avenue for future research in the field of electrochemical capacitors technology. The use of cricket biomass as a precursor for electrochemical capacitor electrodes offers a sustainable and eco-friendly alternative to traditional electrode materials and has the potential to pave the way for the development of biodegradable energy storage devices



EFFECTS OF ELECTRODEPOSITION MODE ON THE ELECTROCHEMICAL PERFORMANCE OF CELLULOSE NANOCRYSTAL BASED COMPOSITE ELECTRODES FOR HIGH-ENERGY-DENSITY SUPERCAPACITORS

Backović G., Lemieux J., Eyley S., Thielemans W.

Sustainable Materials Lab, Department of Chemical Engineering, KU Leuven, campus Kulak Kortrijk, Etienne Sabbelaan 53, 8500 Kortrijk, Belgium

gordana.backovic@kuleuven.be

This work focuses on the development of conductive polypyrrole-cellulose nanocrystal porous scaffolds as supercapacitor electrode. Polypyrrole (PPy), an intrinsically conductive polymer, was combined with carboxylated cellulose nanocrystals (oCNC) in the presence of KCl as supporting electrolyte, to introduce the desired electrochemical properties. Nanostructured network-like composite electrodes (oCNC-PPy+KCl) were prepared via different electrodeposition modes, i.e. potentiostatically (PS), potentiodynamically (PD), and galvanostatically (GS). X-ray diffraction and electron microscopy were used to study the crystalline nature and morphologies of the deposited films. The electrochemical properties were investigated using cyclic voltammetry and charge/discharge tests. The results revealed that the electrochemical performance of the as-obtained composite electrodes depended on the electrodeposition mode. The electrochemical properties of composite films prepared potentiostatically exhibited the highest capacitance values amounting to 2.15 F/cm^2 at a current density of 2 mA/cm^2 (corresponding to a specific capacitance of 297 F/g at 0.3 A/g), with 49% capacitance retention at a high current density of 20 mA/cm^2 (3 A/g). Moreover, a symmetric supercapacitor was assembled and exhibited an energy density of $48.5 \mu\text{W h/cm}^2$ (6.9 W h/kg) with outstanding cycling performance that can be attributed to the CNC template. The results herein obtained point out CNC-PPy composite material as a promising system for the development of sustainable energy storage devices.

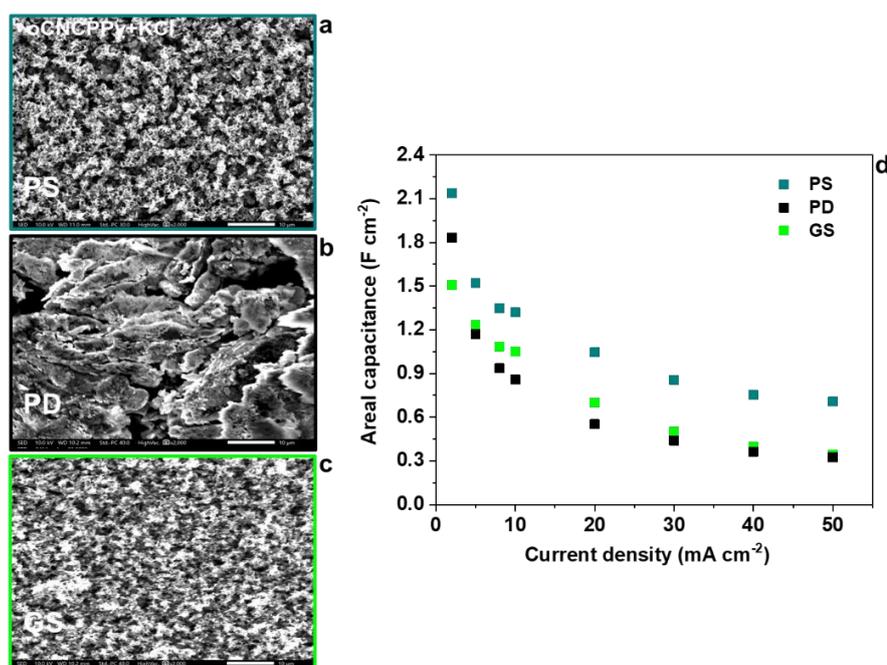


Figure 2 : SEM images of electrodes prepared via different electrodeposition modes: potentiostatic (a), potentiodynamic (b), and galvanostatic (c) along with respective evolution of areal capacitance with the current density (d).



MICROSPHERES FROM CELLULOSE ESTERS AS ELECTRODE MATERIAL FOR ENERGY STORAGE DEVICES

Fischer J. ^{*a,b}, Thümmler K. ^a, Mikhailova D. ^b, Fischer S. ^a

^a *Institute of plant and wood chemistry, TU Dresden, Germany*

^b *Leibniz Institute for Solid State and Material Research, Dresden, Germany*

* Johanna.fischer1@tu-dresden.de

A lot of different porous carbons are already used in electrochemical storage systems. Materials based on cellulose and its derivatives might be a more environmentally friendly and more sustainable alternative to other carbons.

Bead cellulose is already well characterized and is a promising material for carbons with a large specific surface area due to its porosity and high internal surface. [1] Here, microspheres of cellulose acetate and cellulose acetate butyrate prepared by the acetate method are used as the cellulose source. With cellulose acetate butyrate, the surface functionality of the microspheres is modified and an increase of the C amount can be received. The effect of a stepwise replacement of cellulose acetate by cellulose acetate butyrate on the resulting beads was investigated. It can be shown that the characteristics of the microspheres obtained from the different cellulose esters differ considerably, especially in terms of particle size, porosity, internal and surface structure.

The strong influence of the properties and the structure of the microspheres on the characteristics of the resulting carbons was studied. After carbonization of the cellulose acetate butyrate microspheres already a specific surface area of $567 \text{ m}^2 \text{ g}^{-1}$ was obtained without any further activation step. The (activated) carbons prepared from cellulose acetate and cellulose acetate microspheres show promising results as electrode material in symmetric supercapacitors.

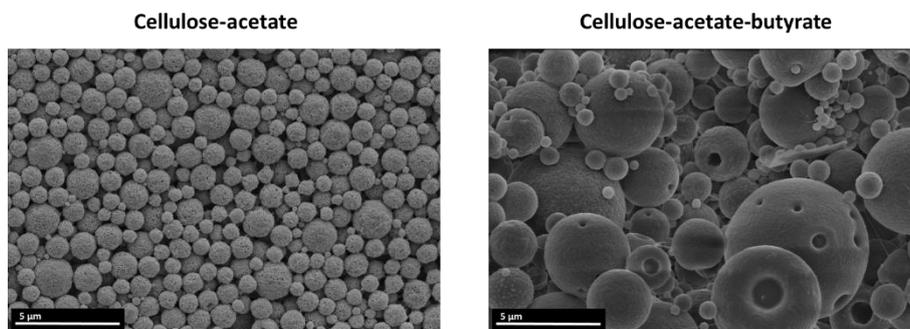


Figure 1 : Scanning electron microscope image of cellulose acetate and cellulose acetate butyrate microspheres

[1] Thümmler K., Fischer S., Feldner A., Weber V., Ettenauer M., Loth F. & Falkenhagen D., *Cellulose*, 18, 135-142, 2011



FACILELY PREPARED STARCH-BASED ION-CONDUCTIVE HYDROGEL, BATTERIES, AND SELF-POWERED SENSORS WITH STRAIN-SENSITIVITY

Ma C. ^a, Liu P. ^{a,b}, Xie F. ^{* b}

^a School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou, 510006, China

^b School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom

* david.xie@newcastle.ac.uk

Herein, we report an entirely starch-based hydrogel for flexible electronics including strain-sensitive batteries and self-powered wearable sensors. This biodegradable hydrogel is only based on natural high-amylose maize starch (HAMS), CaCl_2 , and glycerol, and the preparation method is green and facile (namely stirring at 70 °C for 1 h). This hydrogel is highly stretchable, flexible, reprocessible, and self-healable. Based on this hydrogel, we developed a galvanic cell-type Zn-Cu battery (composed of one starch-based hydrogel additionally incorporated with zinc powder and the other with CuCl_2 and copper powder), which has a voltage of 0.81 V and its output current positively correlated with compression deformation. Based on this Zn-Cu battery, a self-powered (SP) wearable sensor was further constructed, which has high sensitivity (1.5371 kPa^{-1}) even under weak compression stress. This SP sensor can be used to detect human activities involving small strain such as wrist pulse and throat vibration with strong, clear and stable signals. Considering the easy processability, cost-effectiveness, high strain-sensitivity, robustness, and greenness of the starch-based hydrogel and electronics, their application prospect is foreseen. Read more [1].

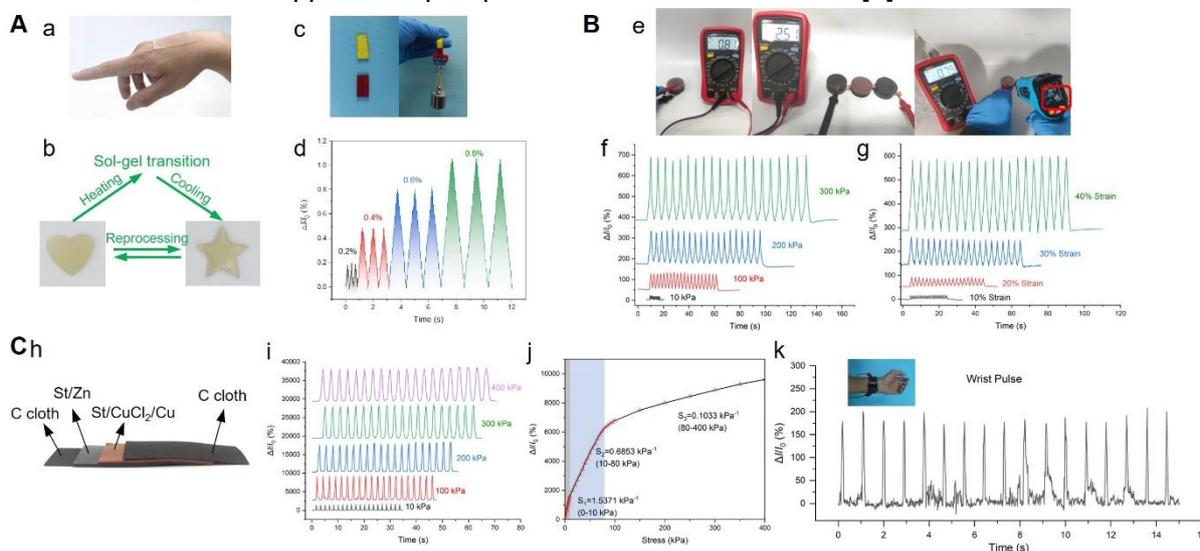


Figure 1: A) Starch-based hydrogel: a) the hydrogel attached to skin, b) reprocessability, c) self-healability, and d) change in current change ($\Delta I/I_0$) under different stresses of stretching; B) Starch-based Zn-Cu battery: e) voltages of the battery measured at room temperature, connected in series, and after freezing, f) change in $\Delta I/I_0$ under different stresses of compression, and g) under different strains of compression; C) Starch-based flexible, self-powered sensor: h) the composition of the sensor, i) change in $\Delta I/I_0$ under different stresses of compression, j) $\Delta I/I_0$ vs. compression stress curve, and k) change in $\Delta I/I_0$ when being used to detect wrist pulse.

[1] Ma C., Xie F., Wei L., Zheng C., Liu X., Wang L. & Liu P. *ACS Sustainable Chemistry & Engineering*, 10, 20, 6724–6735, 2022



EXPLOITING THE UNIQUE PROPERTIES OF BIOMASS IN ARID AREAS TOWARDS NEW CLASSES OF BIOPRODUCTS

Qian Liu ^{*1,2,3} and Blaise Leopold Tardy^{1,2,3}

¹ *Research and Innovation Center on CO₂ and Hydrogen & Center for Membrane and Advanced Water Technology, Khalifa University, UAE*

² *Research and Innovation Center on CO₂ and Hydrogen & Center for Membrane and Advanced Water Technology, Khalifa University, UAE*

³ *Department of Chemical Engineering, Khalifa University, UAE*

*100062555@ku.ac.ae

Removal of lignin from wood result in the formation of, so-called, nanowood that bears the inherent structural properties of wood while also opening new avenues in terms of post-processes and functional properties [1]. Other plant-based “scaffolds” can be obtained by applying the same chemistry of deconstruction. The chemistry of delignification of wood is herein applied to plant-based biomass that is readily accessible in arid areas as a viable alternative to traditional nanowood.

In this study, we utilized date seeds waste as a raw material to evaluate the impact of delignification. The process involves treating the date seeds with NaOH solution (mild soda pulping), followed by immersion in a mixed solution of H₂O₂/CH₃COOH for further delignification. This results in a pure white material due to the removal of lignin. The unique cellular micro structure of nano date seeds imbued new property to the final material and the mechanics, porosity, and water response were evaluated. The prepared material is hydrophilic and is expected to have a high specific surface area, making it ideal for water treatment applications. Our research shows the potential of plant wastes to produce a sustainable and cost-effective nanowood-like material to areas typically scarce in forest areas.



Figure 1 : (a) Raw date seeds and (b) processed date seeds as nonwood nanowood

- [1] C. Chen, Y. Kuang, S. Zhu, I. Burgert, T. Keplinger, A. Gong, T. Li, L. Berglund, S.J. Eichhorn, L. Hu, *Nat Rev Mater.* 5 (2020) 642–666.



ECOTOXICITY AND CYTOTOXICITY OF ANTIMICROBIAL ACTIVE NANOCELLULOSE

Vanja Kokol^{a*}, Sara Novak^b, Veno Kononenko^b, Monika Kos^b, Vera Vivod^a, Nina Gunde-Cimerman^b, Damjana Drobne²

^a Faculty of Mechanical Engineering, University of Maribor, Smetanova ul. 17, 2000 Maribor, Slovenia

^b Department of Biology, Biotechnical Faculty, University of Ljubljana, Večna pot 111, 1000 Ljubljana, Slovenia

*vanja.kokol@um.si

Dialdehyde cellulose nanofibrils (CNF) and nanocrystals (CNC) were prepared via periodate oxidation (CNF/CNC-ox) and subsequently functionalized with hexamethylenediamino (HMDA) via the Schiff-base reaction [1]. This resulted in a porous and micro-sized (0.5-10 μm) particles (CNF/CNC-ox-HMDA, Figure 1) that can catch bacteria by multi-targeted (ionic and hydrophobic) non-specific modes of action, and prevent them from growing at minimum nontoxic (both *in vitro* to human lung cells and *in vivo* to *Daphnia magna*) concentrations (< 0.2 wt%). The hydrodynamically smaller (0.5-1 μm) CNC-ox-HMDA decorated with aldehyde, anionic, amino and hydrophobic surface groups was found to be the most effective, with up to log 9 of bacteria reduction at >0.4 wt.% and a bactericidal effect. While the antimicrobial less-active CNF/CNC-ox were fully biodegradable in composting soil within 24 weeks, this process was inhibited considerably for CNF/CNC-ox-HMDA, indicating their different stability and disposal after use (e.g. composting vs. recycling). As such, however, they can serve as an alternative to nano-biocides (such as metal nanoparticles), which are limited by their toxicity for humans and the environment [2]. Some application potentials will be presented [2-5].

Acknowledgements: This project has received funding from the Slovenian Research Agency (Grant Agreement No. J2-1719 and Research Program P2-0424).

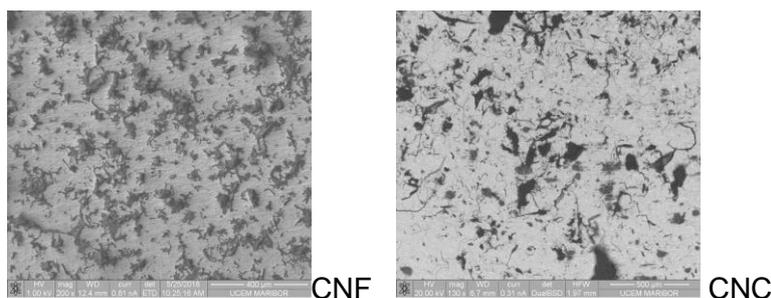


Figure 1: SEM images of spray-dried water-suspended CNF/CNC-ox-HMDA

- [1] Kokol V. et al. functionalized cellulose decontamination agent, Patent pending LU102795 (29.4.2021) PCT/EP061122 (26.4.2022).
- [2] Kokol V. et al. Antibacterial and degradation properties of dialdehyded and aminohexamethylated nanocelluloses. *Carbohydrate polymers*. 2023, 311, 120603, 16 pages.
- [3] Kokol V. et al. Antimicrobial properties of viscose yarns ring-spun with integrated amino-functionalized nanocellulose. *Cellulose*. 2021, 28, 545-6565.
- [4] Kokol V. et al. Cationised fibre-based cellulose multi-layer membranes for sterile and high-flow bacteria retention and inactivation. *Membranes*. 2023, 13(13), 284, 23 pages.
- [5] Vivod V. et al. Highly efficient film-like nanocellulosebased adsorbents for the removal of loose reactive dye during textile laundering. *Textile research journal*. 2019, 89(6), 975-988.



Session 4 Poster



GRAPHENE OXIDE POLYSACCHARIDE/POLYETHYLENIMINE CONJUGATES. SYNTHESIS, CHARACTERIZATION AND PROPERTIES

Papadakis R.*^a

^a TdB Labs, 75651, Uppsala, Sweden

* rafpapadakis@gmail.com

Graphene-based materials (GBMs) are currently more and more considered for a large variety of technologies and applications [1-2] Graphene itself holds a range of outstanding properties such as mechanical, electronic, electrical, (physico)chemical, photochemical etc. Nonetheless, for a range of special applications graphene and other members of the graphene family, are not satisfactorily applicable by themselves, thus appropriate modification is required. [2-3] A relatively new trend is to combine the beneficiary properties of GBMs and those of other materials in order to conform to the demanded properties corresponding to specific applications. This is pronounced in biorelevant applications where a range of material properties are required e.g. biocompatibility, low toxicity, biodegradability etc. [4] Polysaccharides, due to their bio-occurrence, biocompatibility, high abundance and sustainable way of production are often proposed as conjugates to GBMs with application in drug delivery, detection of bio-relevant analytes, bioimaging, etc. [5]

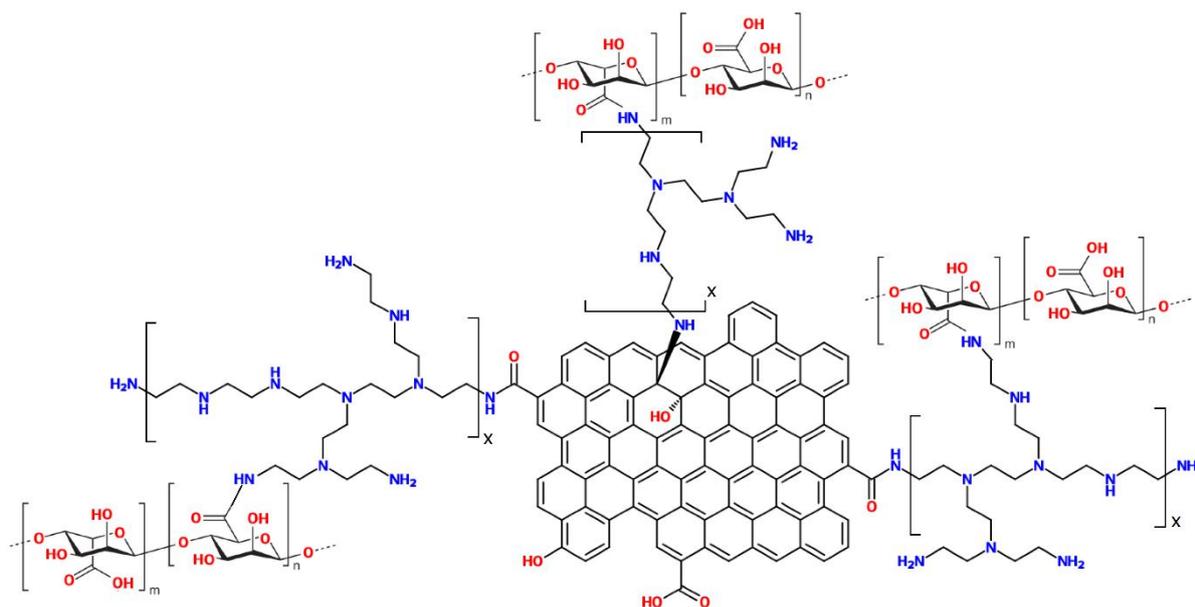


Figure 1 : Proposed structure of Graphene oxide (GO) - Polyethylenimine (PEI) – Alginate (Alg.) material discussed in this communication.

In this communication, the synthesis, spectral and physicochemical properties of novel GO-based materials involving PEI and polysaccharides will be presented.

- [1] Razaq A., Bibi F. *et al.*, *Materials* 15(3), 1012, 2022
- [2] Zheng X., Zhai R. *et al.*, *Molecules* 27(6), 2018, 2022
- [3] Georgakilas, V., Otyepka, M., *et al.*, *Chem. Rev.* 112, 11, 6156–6214, 2012
- [4] Cheng, C., Li, S., *et al.* *Chem. Rev.* 117, 3, 1826–1914, 2017
- [5] Li H., Papadakis R., *Polymers* 13(1), 142, 2021



OPTIMIZED CARBOXYMETHYL CELLULOSE FOR LITHIUM-ION BATTERIES

Petermann, O. ^{*a}, Bayer, R., Engelhardt, J. ^a et al.^a

^a *International Flavors and Fragrances (IFF), Pharma Solutions, Germany*

* oliver.petermann@iff.com

Sodium carboxymethyl cellulose (CMC) is a naturally-derived water soluble polymer obtained from wood or cotton linter cellulose. It is widely used as viscosity modifier, thickener, binder and film former in food, pharmaceutical, home & personal care and industrial applications.

With the increasing demand for lithium-ion batteries in various industries, particularly in automotive, there has been a need to improve CMC performance. CMC is used as a binder and enables the processability of the aqueous graphite anode slurry. This results in a homogenous particle distribution, the formation of a conducting network and the improvement of electron transport kinetics¹. It has been observed that CMC impurities, particularly partially dissolved CMC in the form of gel particles, can result in lower battery performance.

In this work, we introduce optimized CMC for lithium-ion batteries, with reduced gel impurities. This optimized CMC improves the specific discharge capacity of the battery at high C-Rates and increases charging speed. We are also observing an increased specific discharge capacity over multiple use cycles, indicating that lithium-ion batteries made with CMC with low gel impurities lengthen battery life.

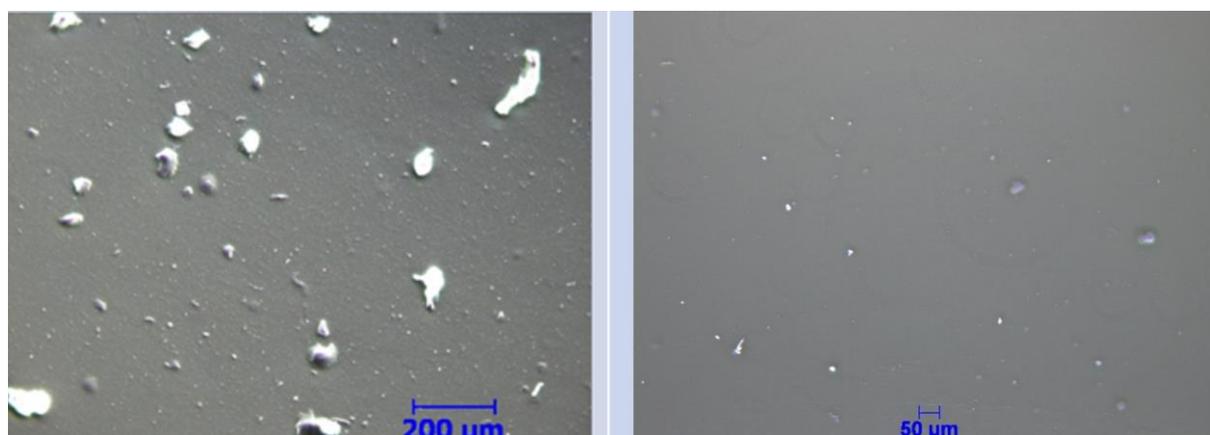


Figure 1: Gel impurities of standard CMC (left) and optimized CMC (right)

[1] Gordon, R., Kassar, M, Willenbacher, N, ACS Omega, 5, 11465-11465, 2020.



SUSTAINABLE SUPERBLACK MATERIALS FROM WOOD FOR LIGHT MANAGEMENT

Khakalo A.^{*a}, Zhao B.^b, Shi X.^c, Khakalo S.^{a,d}, Miettinen A.^e, Turpeinen T.^a, Rojas O.^{b,c}, Mattos B.^b

^a VTT Technical Research Centre of Finland Ltd., Finland

^b Department of Bioproducts and Biosystems, Aalto University, Finland

^c Bioproduct Institute, The University of British Columbia, Canada

^d Department of Civil Engineering, Aalto University, Finland

^e Department of Physics, University of Jyväskylä, Finland

* alexey.khakalo@vtt.fi

Superblack materials display ultralow light reflectance and are essential for maintaining the high resolution of optical devices, e.g. telescope and lens, via managing undesirable light scattering (i.e., stray light). Superblack materials are usually fabricated by growing vertically aligned carbon nanotube (VACNT) arrays on a metal substrate using chemical vapor deposition (CVD). However, large-scale applications of VACNT array are limited by the cost, low CNT growth rate, low thickness (< 400 μm) and poor mechanical properties of VACNT coatings. We have fabricated sustainable wood-based superblack materials by carbonization of delignified wood to achieve ultralow light reflectance. High-temperature carbonization was optimized to maximise the number of graphitic structures responsible for light absorption. To further decrease the light reflectance, the effect of wood anatomical elements dimensions was assessed by finite element modeling. Consequently, controlled partial wood delignification was employed to engineer the wood nano-microstructure to enhance the light absorption. The radial section of wood carbon materials displayed 3-10% light reflectance whereas the light reflectance was lowered down to superblack levels, i.e., to $\sim 0.3\%$ due to vertically aligned carbon fiber arrays formation in the cross section of delignified wood during high-temperature carbonization. Superblack wood carbon materials have several advantages over CNT-based technologies regarding mechanical robustness, manufacturing cost and sustainability.

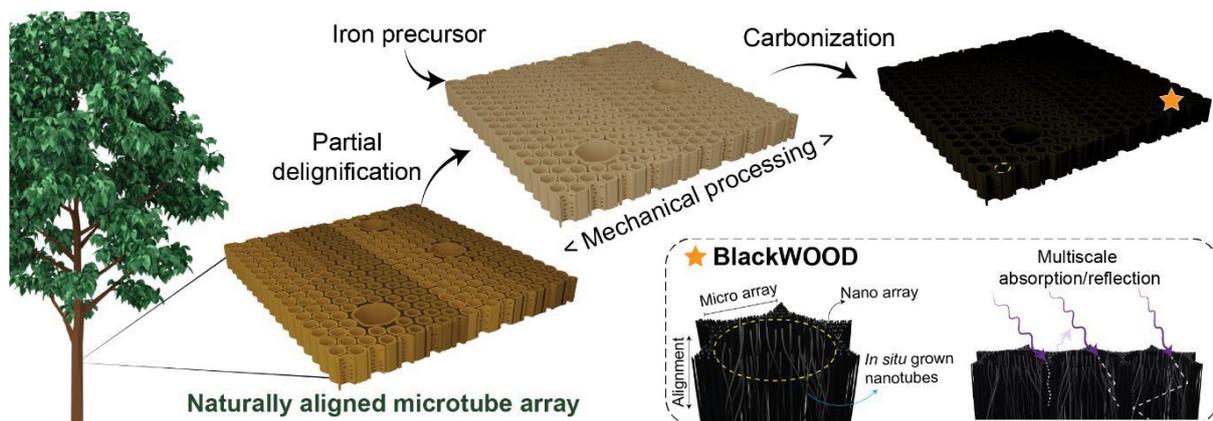


Figure 1 : Fabrication of superblack materials by high temperature carbonation of delignified wood.



NOVEL MAGNETIC IRON OXIDE-DEXTRAN SULPHATE NANOCOMPOSITES WITH PROMISING PROTEIN-REPELLENT PERFORMANCE

Plohl O. ^{*a}, Zemljč Fras L. ^a, Vesel A. ^b, Gyergyek S. ^c, Bračič M. ^a

^a *Laboratory for Characterization and Processing of Polymers, Faculty of Mechanical Engineering, University of Maribor, Slovenia*

^b *Department of Surface Engineering, Jožef Stefan Institute, Slovenia*

^c *Department for Materials Synthesis, Jožef Stefan Institute, Slovenia*

* olivija.plohl@um.si

Polysaccharides with protein-repelling properties, especially those containing sulfone groups, have recently attracted much attention because this ability allows them to act as anticoagulants, for example. However, their removal and reusability after the process is difficult and often impossible. Therefore, the magnetic nanoparticles (MNPs) modified with sulfo group-containing MNPs may be a good option to overcome the mentioned drawbacks. In this study, we synthesized maghemite MNPs and coated them with sulfo-dextran (i.e., MNPs@s-dext) to achieve protein repellency. The MNPs@s-dext were characterized by transmission electron microscopy (TEM) to reveal their morphology (Figure 1), while the success of modification and introduction of new functional groups were monitored by infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The zeta potential, thermogravimetric and magnetic properties were studied and compared with the bare MNPs. Their protein repellent properties were investigated by QCM using albumin and fibrinogen proteins. The result showed the successful formation of a thin coating of MNPs with s-dext and their pronounced anti-adsorption potential towards proteins compared to bare MNPs.

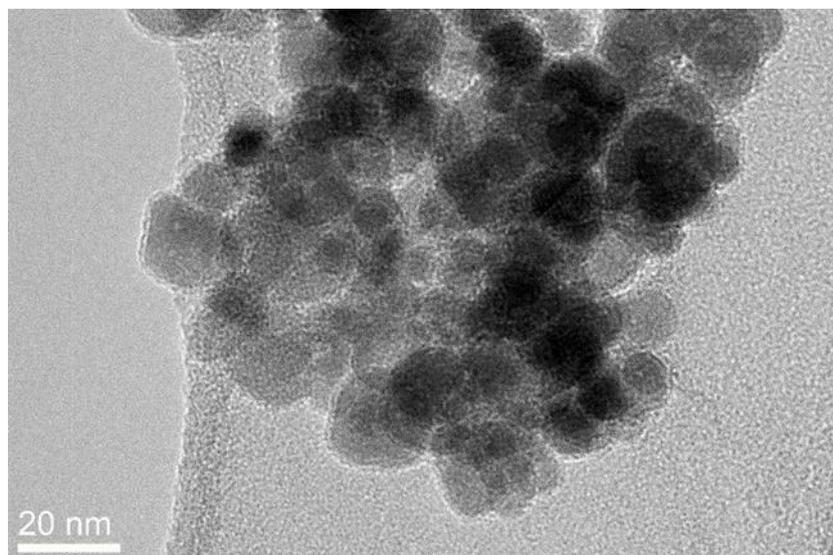


Figure 1 : TEM image of MNPs@s-dext.



DIRECT ELECTROCHEMICAL SENSOR DEVELOPMENT USING NANOCELLULOSE / NANOCARBON HYBRID MATERIALS

Durairaj V.^{*a}, Kontturi K.S.^a, Tammelin T.^a, Laurila T.^b

^a *Bioinspired materials, VTT Technical Research Centre of Finland Ltd., Espoo, Finland*

^b *School of Electrical Engineering, Aalto University, Espoo, Finland*

* vasuki.durairaj@vtt.fi

Direct electrochemical sensing is one of the simplest, fastest, and most economical methods available for reliable, point-of-care detection of a large range of electrochemically active biomolecules. Two major limitations hindering the widespread application of this method include sensitivity and selectivity. Use of high surface area electrode materials such as carbon nanotubes can significantly improve the sensitivity, enabling detection of very low, physiologically relevant concentrations of drugs and other biomolecules. However, the inherent hydrophobicity of carbon nanotubes results in strong bundling effects, rendering them hard to disperse in either organic or inorganic solvents. This in turn poses several challenges to developing functional electrode architectures from carbon nanotubes, without losing their intrinsic electrochemical activity.

Nanocellulosic materials, especially those modified with highly charged functional groups, have been shown to be very efficient in dispersing carbon nanotubes in stable aqueous suspensions [1]. We have developed functional nanocellulose / carbon nanotube hybrid electrochemical sensors using nanocellulosic materials with different physical and chemical properties [2]. We demonstrated the structure-property relationships between the nanocellulose / carbon nanotube hybrid material architectures and their electrochemical sensing performance [3]. Cationic small molecules (such as the neurotransmitter – dopamine) are seen to be preferentially enriched in hybrid electrodes containing highly negatively charged nanocellulosic materials, enabling both excellent sensitivity and selectivity. Interestingly, neutral molecules (such as paracetamol) are also seen to be highly enriched in this same hybrid material, indicating that in addition to electrostatic effects, the nanocellulose dictated hybrid membrane architectures also drastically affect the electrochemical sensor performance.

Compared to commercial carbon nanotube-based electrodes without nanocellulosic materials, our hybrid nanocellulose / carbon nanotube electrode materials show significantly higher sensitivity towards various small molecules in physiologically relevant concentrations. In addition to effectively dispersing the carbon nanotubes, the nanocellulose component also improves the hygroscopicity of the hybrid material, thereby enabling higher electrochemically active carbon nanotube surface area to be available for sensing. Further, these amphiphilic nanostructured hybrid materials also offer superior resistance to fouling from common proteins present in human plasma and can therefore be highly promising alternatives in the development of direct electrochemical point-of-care sensors for medical applications.

References:

- [1]. Hajian, Alireza, et al. "Understanding the dispersive action of nanocellulose for carbon nanomaterials." *Nano letters* 17.3 (2017): 1439-1447.
- [2]. Durairaj, Vasuki, et al. "Functionalized nanocellulose/multiwalled carbon nanotube composites for electrochemical applications." *ACS Applied Nano Materials* 4.6 (2021): 5842-5853.
- [3]. Durairaj, Vasuki, et al. "Role of nanocellulose in tailoring electroanalytical performance of hybrid nanocellulose/multiwalled carbon nanotube electrodes." *Cellulose* 29.17 (2022): 9217-9233.



MAKING WOOD LUMINESCENT WITH STYRIAN PUMPKIN SEEDS

Ritter M.^{*a,b}, Burgert I.^{a,b}, Panzarasa G.^{a,b}

^a Wood Materials Science, ETH Zürich, Switzerland

^b WoodTec group – Cellulose and Wood Materials, Empa, Switzerland

* maxritter@student.ethz.ch

Wood is a highly promising material for developing sustainable optical and photonic devices, especially for smart building applications e.g. indoor lighting purposes. Thanks to its inherent hierarchical structure, and the possibility to chemically modify its natural chromophores (especially lignin), it can be used to transmit, and even guide, light of controllable wavelengths.^[1] However, state-of-art studies make use of potentially toxic quantum dots or other unsustainable fluorophores, and use petrol-based polymers to improve the matrix transparency, thus compromising the inherent sustainability of wood^[2,3].

Here, we took advantage of the *shine-through* effect^[4] in which a fluorophore is applied to one side of a thin wood membrane and excited with UV radiation so that the emitted light is allowed to travel through the wood matrix while the UV light is blocked. As fluorophore, we selected a natural red-emitting protochlorophyllide extracted from the seeds of *Steirischer Ölkürbis* (*Cucurbita pepo* subsp. *pepo* var. *styriaca*). Impregnation of the wood matrix with bio-based refractive index-matching materials resulted in a fully sustainable transparent luminescent wood. In addition to photoluminescence, wood functionalised with this fluorophore can also display chemiluminescent properties.

References

- [1] Y. Ding, Z. Pang, K. Lan, Y. Yao, G. Panzarasa, L. Xu, M. Lo Ricco, D. R. Rammer, J. Y. Zhu, M. Hu, X. Pan, T. Li, I. Burgert, L. Hu, *Chem. Rev.* **2023**, *123*, 1843.
- [2] Q. Fu, I. Burgert, K. Tu, C. Goldhahn, T. Keplinger, M. Adobes-Vidal, M. Sorieul, *ACS Nano* **2020**, *14*, 13775.
- [3] L. A. Berglund, I. Burgert, *Adv. Mater.* **2018**, *30*, 1.
- [4] M. Ritter, I. Burgert, G. Panzarasa, *Mater. Adv.* **2022**, *3*, 1767.



3D GEL-PRINTING OF A TOUGH POLYMER COMPOSITE GEL INK REINFORCED WITH CHEMICALLY MODIFIED CELLULOSE NANOFIBRILS SHOWING SELF-HEALING BEHAVIOUR

Feras Dalloul*, J. Benedikt Mietner and Julien R. G. Navarro

Institute of Wood Science, University Hamburg, Germany

*feras.dalloul@uni-hamburg.de

Three-dimensional (3D) gel printing, also called direct ink writing, is a rapidly expanding technology that enables the creation of intricate, multi-layered structures with a high degree of precision and accuracy. This study aims to demonstrate that chemical-modified cellulose nanofibrils (CNF) can be used as a renewable and sustainable reinforcement agent to render polymers printable. Precise surface chemistry were achieved using a procedure known as Single-Electron Transfer Living Radical Polymerisation (SET-LRP)¹. A polymer consisting of ureidopyrimidinone (UPy) and di(ethylene glycol) ethyl ether (DEGEEA) units have been synthesized, and UPy-grafted cellulose nanofibrils (CNF-g-UPY) were used to produce the composite (UPy-DEGEEA/CNF-g-UPY). Results revealed significantly improved mechanical properties (3.7-fold in storage modulus and 2.8-fold in loss modulus). Also, it showed shear thinning properties, enabling the extrusion in a uniform and stable structure. Self-healing characteristics of the polymer have been transferred to the composite with minimal loss of structure during the repairing process².

These results highlight the potential of modified CNF in designing advanced composite materials, leading to the development of innovative products with functionalities and performance in various applications, notably biomedical engineering, robotics and portable electronics.

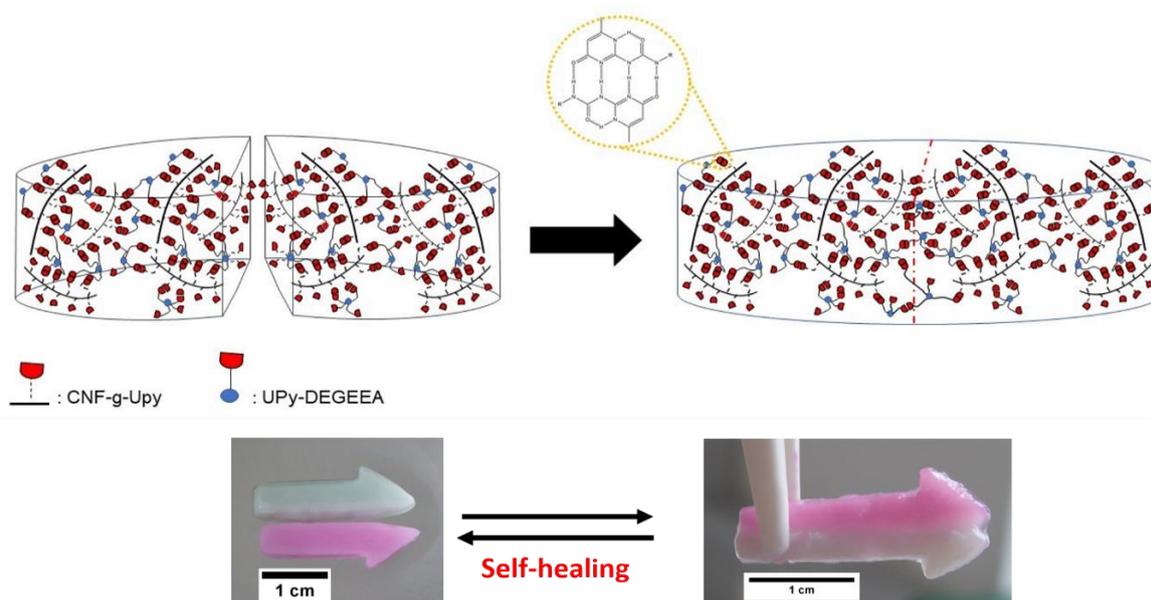


Figure 1. Schematic representation of the self-healing process

- [1] Rosen BM, Jiang X, Wilson CJ, Nguyen NH, Monteiro MJ, Percec V. *J Polym Sci Part A Polym Chem*; 47(21) : 5606-5628. 2009;
- 2] Dalloul F, Mietner JB, Navarro JRG.. Published online April 6, 2023. doi:10.1021/acscapm.2c02065



KINETIC/SELECTIVITY STUDY AND REAL-TIME MONITORING STRATEGY FOR TEMPO-MEDIATED OXIDATION

Mazega A. ^{*a,b}, Aguado R.J. ^{a,b}, Tarrés Q. ^{a,b}, Alexandre Ferreira Santos ^c, Luiz Pereira Ramos ^c, M. Àngels Pèlach ^{a,b}, Marc Delgado-Aguilar ^{a,b}

^a LEPAMAP-PRODIS Research Group, University of Girona, Spain

^b Department of Chemical and Agricultural Engineering and Agrifood Technology, University of Girona, Spain

^c Department of Chemical Engineering, Universidade Federal do Paraná, Brazil

* andre.mazega@udg.edu

This study examines the practicality of using a monitoring system in real-time for TEMPO-mediated oxidation, through the relationship between NaOH consumption and carboxyl content in a temperature range from 5 to 35 °C. Kinetic constants between 0.58 to 5.50 s⁻¹ were determined, indicating a first-order reaction system. Furthermore, an activation energy of approximately 73.70 kJ/mol for a 16 g/kg addition of TEMPO was quantified, as mentioned in previous researches [1,2]. A linear correlation between NaOH consumption and carboxyl content for different TEMPO catalyst amounts (ranging from 2 to 32 g/kg) was found, while the carboxyl content of oxidized fibers decreases significantly, particularly for lower concentrations of TEMPO. The selectivity of soluble polysaccharides oxidation is intrinsically linked to the proportion of available oxidizer (NaOCl) and catalyst (TEMPO). However, increasing the amount of TEMPO beyond 16 g/kg did not improve the kinetics significantly but could significantly increase oxidation selectivity. The study also investigated the effect of different NaOCl concentrations (2-12 mmol/g) versus TEMPO concentrations (2-32 g/kg) on morphology and kinetics of reaction. The results showed that changes in morphology could expose more sites susceptible to oxidation, while minimizing depolymerization of the fibers. These results demonstrate the suitability of scaling up TEMPO-mediated oxidation and suggest that with proper reaction conditions, it is possible to achieve higher proportions of carboxyl content/degree of polymerization. The study provides valuable insights into the factors that affect the reaction path and the characteristics of the resulting oxidized cellulose.

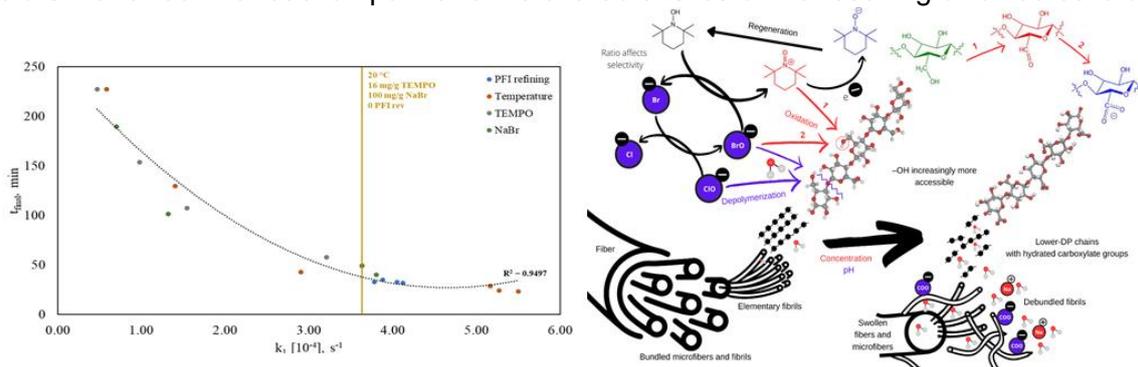


Figure 1 - Correlation between t_{final} and k_1 for all the tested conditions/Schematic representation of oxidation, depolymerization, hydration, and partial disruption of fibers and microfibrils [3].

[1] Dai, L., Dai, H., Yuan, Y., Sun, X., & Zhu, Z., *BioResources* 6, 2619 – 2631, 2011.

[2] Sun B, Gu C, Ma J, Liang B., *Cellulose* 12, 59 – 66, 2005.

[3] Mazega, A., Santos, A.F., Aguado, R. et al. Kinetic study and real-time monitoring strategy for TEMPO-mediated oxidation of bleached eucalyptus fibers. *Cellulose* 30, 1421–1436 (2023).



REGENERATED CELLULOSE TENG WITH COLOUR PRINTED SURFACE FOR INCREASED PERFORMANCE

Stolpe A. ^{*a}, Eivazi A. ^a, Norgren M. ^a, Zhang R. ^b, Dahlström C. ^a

^a Surface and Colloid Engineering, FSCN Research Centre, Mid Sweden University, Sweden

^b Material Physics, FSCN Research Centre, Mid Sweden University, Sweden

* amanda.stolpe@miun.se

Triboelectric nanogenerators (TENGs) are ideal to meet the increasing need for green and efficient energy solutions, e.g., in small wireless and/or wearable applications. Regenerated cellulose is an exemplary material regarding both power output and mechanical performance, and it is environmentally friendly and economically favourable. To further improve the triboelectric performance of the cellulose, colour printing was done on the surface with conventional laser printing. Printer toners commonly contain substances with different triboelectric properties. [1]

In this work, cellulose fibres were dissolved using a LiOH/urea solvent and regenerated in an ethanol bath and eventually dried under controlled conditions. Thereafter the resulting transparent cellulose films were run through a conventional laser paper printer to apply toners of different colour and patterns on the surface. Cyan, magenta, yellow and black was printed in one layer. In addition, black was printed in certain patterns from low to high coverage and in several layers to evaluate the effect of applied amount. The samples were analysed using SEM, AFM, XRD, FTIR and a TENG was assembled in the contact-separation mode to investigate the triboelectric performance.

The printed cellulose films were found to give enhanced triboelectric output. The results show an interesting and simple processing route to enhance the performance of cellulose-based TENG materials that can be useful in the development of cheap and sustainable small wireless electrical generators or sensors.



Figure 1 : Example of a regenerated cellulose film with colour printing on the surface.

[1] Zhang, R.; Hummelgård, M.; Örtengren, J.; Andersson, H.; Olsen, M.; Chen, W.; Wang, P.; Eivazi, A.; Dahlström, C.; Norgren, M., *Adv. Engin. Mater.*, 2023, in press, <https://doi.org/10.1002/adem.202300107>



WASTEPAPER-BASED TRIBOELECTRIC NANOGENERATORS

Zhang, R.^a, Hummelgård, M.^a, Örtengren, J.^a, Andersson, H.^b, Olsen, M.^a, Eivazi, A.^c, Dahlström, C.^c, Norgren, M.*^c, Wang, P.^d, Chen, W.^e

^a Material Physics, FSCN Research Centre, Mid Sweden University, Sweden

^b Electronic Design, STC Research Centre, Mid Sweden University, Sweden

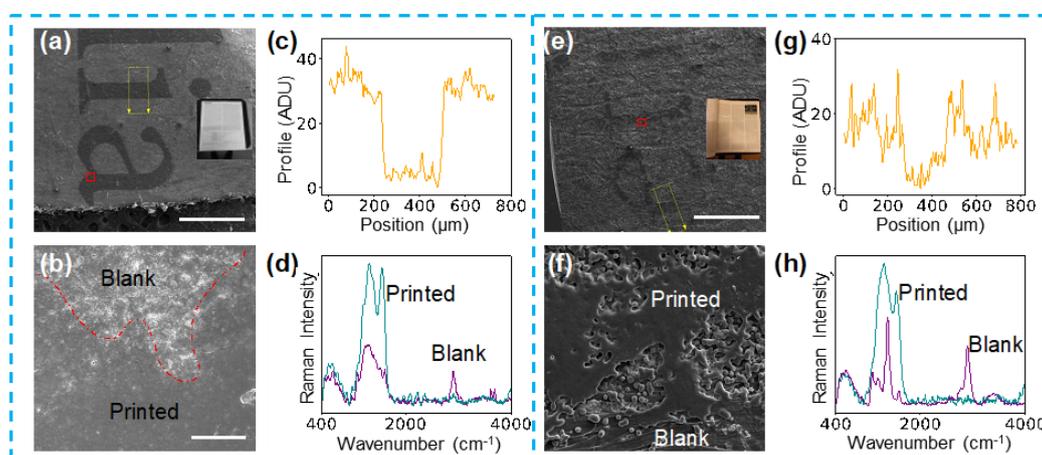
^c Surface and Colloid Engineering, FSCN Research Centre, Mid Sweden University, Sweden

^d School of Materials Science and Engineering, Anhui University, China

^e Key Laboratory of Biobased Material Science and Technology, Northeast Forestry University, China

* magnus.norgren@miun.se

Inks and toners used for printing contain materials, such as polyester, with strong triboelectric properties to enhance the binding effects, making wastepaper, such as magazines and newspapers, good candidates for triboelectric materials. In this study, we report high-output power triboelectric nanogenerators (TENGs) that utilize wastepaper as triboelectric layers (wastepaper-based triboelectric nanogenerators (WP-TENGs)) [1]. Journal paper and office copy paper wastes are investigated. The results show that the maximum power densities of the WP-TENGs reach $43.5 \text{ W}\cdot\text{m}^{-2}$, which is approximately 250 times the previously reported output of the TENG with a recycled triboelectric layer made from wastepaper [2]. The maximum open circuit voltage (V_{OC}) and short circuit current (I_{SC}) are 774 V and 3.92 mA (784 mA m^{-2}), respectively. These findings can be applied to extend the life cycle of printed papers for energy harvesting, and they can later be applied for materials recycling to enhance the sustainable development of our society.



[1] Zhang, R., Hummelgård, M., Örtengren, J., Andersson, H., Olsen, M., Chen, W., Wang, P., Eivazi, A., Dahlström, C. & Norgren, M. *Adv. Engin. Mater.*, in press, 2023; <https://doi.org/10.1002/adem.202300107>

[2] Zhang, Z., Jie, Y., Zhu, J., Zhu, Z., Chen, H., Lu, Q., Zeng, Y., Cao, X., Wang, N. & Wang, Z. *Nano Res.* 15, 1109, 2022; <https://doi.org/10.1007/s12274-021-3612-8>



CHITOSAN SELF-ASSEMBLY CONTROLLED IN TIME BY A PH CLOCK REACTION

Panzarasa G.^a

^a *Wood Materials Science, ETH Zürich, Switzerland*

* guidop@ethz.ch

Chitosan is a pH-responsive natural polysaccharide, biocompatible and biodegradable, with countless practical applications and of great interest for developing sustainable functional materials.

Here we take advantage of its pH-dependent solubility in water to program its autonomous self-assembly into colloidal particles. To this end, we use the methylene glycol-sulfite (MGS) system, an acid-to-alkali clock reaction which is able to produce sharp changes of pH (from ca. 5.5 to about 11) after a tailorable induction time. We show that the time of chitosan precipitation i.e. of particle formation, as well as the size of the resulting particles, can be controlled by tuning the initial conditions of the clock reaction.

References

- [1] G. Panzarasa, A. Osypova, A. Sicher, A. Bruinink, E. R. Dufresne *Soft Matter* **2018**, *14*, 6415–6418.



LOWERED WETTABILITY AND ENHANCED BARRIER PERFORMANCE OF PAPERBOARD THROUGH FULLY BIO-BASED CELLULOSE NANOFIBRILS/POLYMERIZED LIGNIN COATING MATERIALS

Liqiu Hu ^{*a}, Wenyang Xu ^a, Jan Gustafsson ^a, Martti Toivakka ^a, Chunlin Xu ^a

^a *Laboratory of Natural Materials Technology, Åbo Akademi University, Henrikinkatu 2, Turku FI-20500, Finland*

* Email of presenting author: liqiu.hu@abo.fi

Coating materials made from cellulose nanofibrils (CNF) obtained from plant cell walls have attracted an increased interest for packaging and coating applications as alternatives to petroleum-based materials. CNF is biodegradable and renewable, providing excellent barrier and mechanical properties [1, 2]. However, CNF's hygroscopic nature presents a challenge in maintaining its water vapor and oxygen barrier properties in humid conditions. To address this issue, we have developed a new CNF-based coating material that is manufactured in water phase and in a single step through in situ laccase-catalyzed polymerization of lignin on CNF.

In this study, we prepared various lignin soluble fractions with well-defined characteristics using the solvent fractionation methodology. The fractions included crude lignin (BLN) and those soluble in isopropyl alcohol (iPrOH), ethanol (EtOH), and methanol (MeOH). We selected the iPrOH lignin fraction with a high degree of polymerization to synthesize the CNF/polymerized lignin coating material. The resulting material, prepared in a fiber suspension with a loading amount of 15 wt% lignin and a reaction duration of 6 hours, had an even distribution of lignin nanoparticles on the fiber surfaces. The homogenous films formed using the casting method showed increased hydrophobicity (water contact angle approximately 120°) compared to neat CNF films.

More importantly, when we applied the CNF/polymerized lignin coating materials onto the surface of paperboard they significantly enhanced the barrier properties (2-fold reduction for water vapor and 52-fold for oxygen), as shown in **Fig. 1a**. The coating also exhibited excellent grease barrier (KIT value of 12) and low wettability within 45 s (**Fig. 1b**). These results suggest that the CNF/polymerized lignin coating material has the potential to serve as a fully bio-based coating material for packaging and barrier applications.

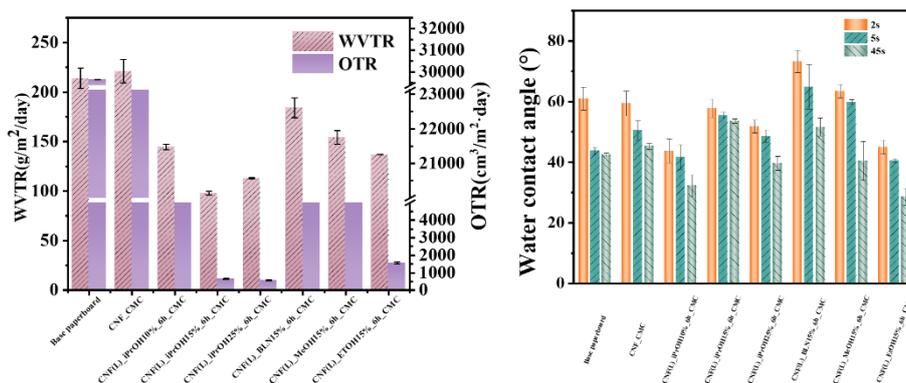


Figure 1. (a) water vapor transmission rate (WVTR) and oxygen transmission rate (OTR), and (b) the water contact angle for base paperboard and paperboard coated with CNF and CNF/polymerized lignin coating materials. CMC: carboxymethylated cellulose

- [1] Ahankari, S. S., Subhedar, A. R., Bhadauria, S. S., & Dufresne, *Carbohydrate Polymers*, 255, 117479, 2021.
 [2] Wang, J., Gardner, D. J., Stark, N. M., Bousfield, D. W., Tajvidi, M., & Cai, Z. *ACS Sustainable Chemistry & Engineering*, 6(1), 49-70, 2017.



CELLULOSE NANOCRYSTALS BASED FLOCCULANTS FOR MARINE MICROALGAL HARVESTING

Tyagi S. ^{*a,b}, Rao N.R.H. ^{a,b}, Muylaert K. ^a, Thielemans W. ^b

^a Aquatic Biology, Department of Biology, KU Leuven, Belgium

^b Sustainable Materials Lab, Department of Chemical Engineering, KU Leuven, Belgium

* sakshi.tyagi@kuleuven.be

Polysaccharide-based flocculants are gaining traction for harvesting saltwater microalgae. However, some polysaccharides do not perform well in saltwater conditions due to the high ionic strength of the medium, which results in their coiling and reduced efficacy. Furthermore, unless subjected to chemical modification, polysaccharides do not possess cationic properties at pH > 9, which corresponds to the pH of the anionic microalgal cells during the harvesting process. Cellulose nanocrystals (CNCs) are a novel class of flocculants that provide benefits over other polysaccharides due to their crystalline structure, which inhibits their coiling in high ionic strength environments. The hydroxyl groups present on the surface of CNCs can be readily modified chemically with cationic quaternary ammonium groups, leading to the production of flocculants that exhibit pH-independent flocculation. This study aims to evaluate the performance of two CNC-based flocculants: (a) unmodified CNCs and (b) pyridinium-modified CNCs that possess cationic quaternary ammonium groups, for separating the saltwater microalgae *Nannochloropsis oculata* via flocculation-flotation. The CNCs were extracted from cotton wool through sulfuric acid hydrolysis, and the extent of grafting was determined using FTIR, elemental analysis, TGA, and XPS spectroscopy, while crystallinity and morphology were confirmed using WAXS and SEM, respectively.

With increasing dose of functionalised CNCs the separation efficiency increased, resulting in a maximum separation of >90% at 50 mg/L. The efficiency then declined but remained stable at ~80% with further increases in the flocculant dose. In contrast, the non-functionalised CNCs failed to induce any separation. This study also found that the amount of modified CNCs required to separate the microalgae was less than what was needed for chitosan, another polysaccharide-based flocculant¹. Thus, our work demonstrates that cationic, crystalline and chemically modified nanocellulose has significant potential as a flocculant in high ionic strength solutions.

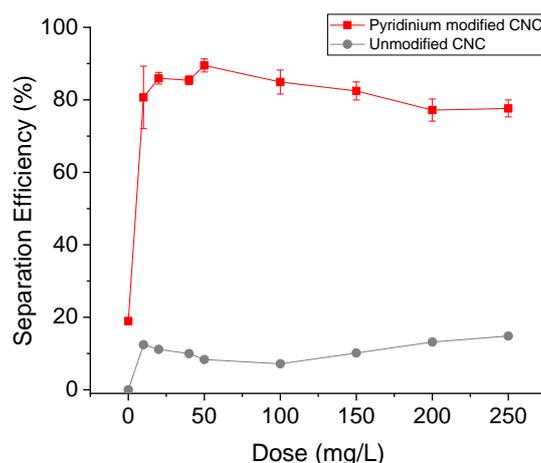


Figure 1 : Dose-response curves for pyridinium modified and unmodified CNCs with DAF as separation process for *Nannochloropsis oculata* species.

[1] Blockx J., Verfaillie A., Thielemans W., Muylaert K. *ACS Sustainable Chem. Eng.* 2018, 6, 9, 11273–11279



DECREASING UNCERTAINTY IN ENZYMATIC HYDROLYSIS AS PRETREATMENT FOR CELLULOSE MICRO/NANOFIBERS PRODUCTION: CORRELATION BETWEEN STRUCTURAL CHANGES AND PROCESS PARAMETERS

Mazega A. ^{*a,b}, Aguado R.J. ^{a,b}, Tarrés Q. ^{a,b}, Marc Delgado-Aguilar ^{a,b}

^a LEPAMAP-PRODIS Research Group, University of Girona, Spain

^b Department of Chemical and Agricultural Engineering and Agrifood Technology, University of Girona, Spain

* andre.mazega@udg.edu

The present study provides the correlation between different structural characteristics of cellulose fibers with process parameters, aiming at providing real-time monitoring systems during enzymatic hydrolysis for cellulose nanofibers production. Bleached kraft hardwood pulp was treated with enzyme cocktail (mostly endoglucanases) using dosages in a range of 80-320 $\mu\text{g/g}$ with a residence time varying from 30 to 240 min. In order to acquire a better idea of how the process of hydrolysis develops and affects the supramolecular structure of the fibers, particularly at mild conditions compared to those implemented for biofuel and/or sugar production, the reactions were monitored throughout several experiments. Energy consumption of the stirring system was found to correlate the concentration of reducing sugars in the reaction media, making it possible to draw a rough idea of the treatment effects on the fiber based only on the rheological behavior within a specific reaction time. Measurements of intrinsic viscosity presented a different pattern of evolution throughout the reaction for each enzymatic load. We hypothesized that enzymes will preferentially act on more available and smaller fibers, first reducing the proportion fines/fibers and later reducing the viscosity by affecting the DP of larger fibers [1]. It was possible to see an increase in viscosity on every condition, with a sharp increase followed by a decrease on the condition with highest enzymatic load. Morphological analysis of the fibers confirmed this shift on size distribution on a macroscale. Further morphological investigation with microscopic techniques were required to confirm if the viscosity is being affected not only by a shift on size distribution of the samples, or also by structural changes on a molecular level. The interaction in between elementary cellulosic chains being compromised leading to an increase in surface area without significantly affecting the size of the chains, explaining the increase followed by the decrease in viscosity measurements.

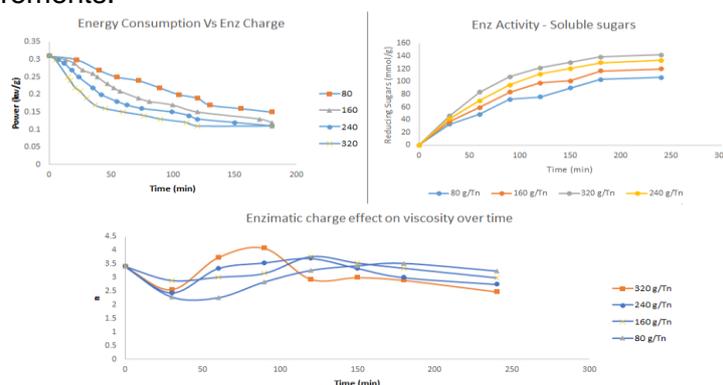


Figure 1 – Effect of enzymatic treatment in the stirring system, reducing sugars concentration and viscosity for different conditions of enzymatic charge and reaction time.

[1] Sigoillot, J. C., Berrin, J. G., & Bey, M. (2012). Cellulolytic enzyme activities in biomass conversion: measurement methods and comparison. *Critical Reviews in Biochemistry and Molecular Biology*, 47(3), 172-205.



BIOACTIVITY OF BACTERIAL CELLULOSE INDUCED BY SPRAY-DRIED GELATIN AND GELATIN-NISIN MICROPARTICLES

Hren M. ^a, Trček J. ^b Hribernik S. ^c and Gorgieva S. ^{*a}

^a Faculty of Mechanical Engineering, University of Maribor, Slovenia

^b Faculty of Natural Sciences and Mathematics, University of Maribor, Slovenia

^c Faculty of Electrical Engineering and Computer Science, University of Maribor, Slovenia

* selestina.gorgieva@um.si

As an ultrapure material, bacterial cellulose (BC) does not trigger undesirable reactions when used in contact with human tissues, which is highly advantageous from a medical perspective [1, 2]. Such "inertness" may also restrict targeted interactions with other (bio)molecules, reducing the foreign-body reactions [3]. At the same time, this means a lack of bioactivity, arising as an issue in specific applications where bioactivity is required, such as regenerative medicine. More generally speaking, lack of bioactivity means missing cell-recognition moieties for attracting (human) cells to attach and lacking any active function towards any organism, which can also be desirable, such as antimicrobial activity. Herein, we produce spray-dried gelatin and gelatin-nisin microparticles, stabilised by dehidrotermal treatment and apply them onto the BC membrane by dispersion-casting procedure (Figure 1). Further, we assess the relationship between production parameters with obtained properties (morphology, size distribution and stability). Mineralisation pattern after immersion in saturated simulated body fluid was explored, as well as antimicrobial action using selected Gram-positive and Gram-negative bacterial strains: *Pseudomonas aeruginosa* ATCC 27853, *Staphylococcus aureus* ATCC 29213, *Escherichia coli* ATCC 25922, *Enterococcus faecalis* ATCC 29212, utilising disc diffusion method. We aim to highlight microparticles' structural and compositional effect on the bioactivity of modified BC, in comparison with neat BC and evidence for rationality behind such modification procedure.

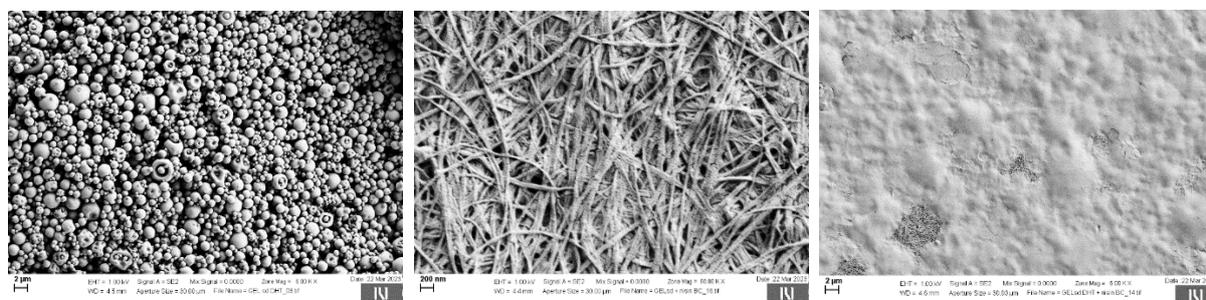


Figure 1. (left to right) Gelatin/nisin microparticles and BC membrane before and after their application.

ACKNOWLEDGMENTS

The authors acknowledge the Slovenian Research Agency funding (project J2-2487 *Bioactive, in situ modified, fibrous membranes based on bacterial cellulose: processing, characterisation and assessment of biomedical potential* and program P2-011 Textile Chemistry and Advanced Textile Materials) and Ministry of Education, Science and Sport (M.Era.Net - BioCell3D)

REFERENCES

- [1] Gorgieva S (2020) *Processes*, DOI: 10.3390/pr8050624.
- [2] Gorgieva S and Trček J (2019) *Nanomaterials*, DOI: 10.3390/nano9101352.
- [3] Gorgieva S and Hribernik S (2019) *Nanomaterials*, DOI: 10.3390/nano9020303.



SURFACE CHEMICAL AND ENZYMATIC HYDROPHOBIZATION OF CELLULOSE NANOCRYSTALS

Makeu O. ^{*a,b}, Le Cerf D.^a, Capron I.^c, D'Avierno F.^c, Dulong V.^a, Dubessay P.^b, Michaud P.^b, Picton L.^a

^a PBS, UMR6270, Normandie Univ., UNIROUEN, I CNRS, France

^b Université Clermont Auvergne, Clermont Auvergne INP, IP, CNRS, France

^c UR1268 INRAE Nantes, BIA, France

*Olive.makeu-sokamte@univ-rouen.fr

Pickering emulsions are systems where the interface of the droplets is stabilized by solid particles. There are direct (oil in water), inverse (water in oil) and multiple emulsions [1].

The objective of the project “Drywater” funded by the French National Research Agency is to prepare Pickering water-in-oil emulsions stabilized by cellulose nanoparticles (CNC). The surface of cellulose nanocrystals is globally hydrophilic and leads only to the preparation of oil-in-water emulsions when they are used for their emulsifying properties [2]. The stabilizing particles usually used in water-in-oil emulsions must be mainly hydrophobic. Therefore, to be used in Pickering water-in-oil emulsions, the surface affinity of CNC for the dispersant phase (oil) needs to be increased while maintaining a partial affinity for the dispersed phase (water) [3]. It is necessary to modify their surface to increase their hydrophobicity. For that, a chemical grafting route for phenolic compounds had been used to obtain a first coating. The grafting of ferulic acid by esterification was carried out based on the chemistry of imidazoles (carbonyldiimidazole) [4]. It was validated by infrared spectroscopy, UV-Visible spectrophotometry and ¹H NMR. Time turbidity measurements in water also confirm the phenolic coating. The contact angle (water used as solvent) was evaluated at $34^\circ \pm 4$ for the CNC grafted ferulic acid (CNC-FA) versus $23^\circ \pm 2$ for the non-grafted CNC.

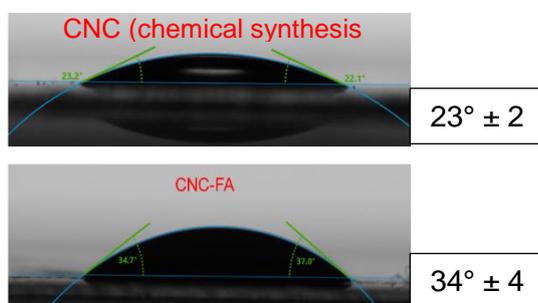


Figure 3: Contact angles of CNC (chemical synthesis blank) and CNC-FA measured with water

Then, laccases have been chosen to increase the amount of ferulic acid and at the same time the surface hydrophobicity. Laccases are enzymes that can oxidize low molecular weight molecules such as phenols while reducing oxygen to water [5]. Two of them from *Bacillus subtilis* and *Trametes trogii* had been evaluated by cyclic voltammetry on ferulic acid, on CNC and CNC-FA. They have shown activity on ferulic acid and not on CNC. On this basis, tests are in progress to graft ferulic acid onto the CNC-FA and thus obtain more hydrophobic particles.

- [1] Chevalier Y., Bolzinger M-A., Colloids and Surfaces A: Physicochemical and Engineering Aspects, 439, 23–34, 2013
- [2] Capron I., Rojas OJ. & Bordes R., Current Opinion in Colloid & Interface Science, 29, 83–95, 2017
- [3] Fujisawa S., Togawa E. & Kuroda K., Sci Technol Adv Mater, 18, 959–971, 2017
- [4] Hadrich A., Dulong V., Rihouey C., Labat B., Picton L. & Le Cerf D, Carbohydr Polym, 250, 116967, 2020
- [5] Witayakran S., Ragauskas AJ., Adv. Synth. Catal, 351, 1187–1209, 2009



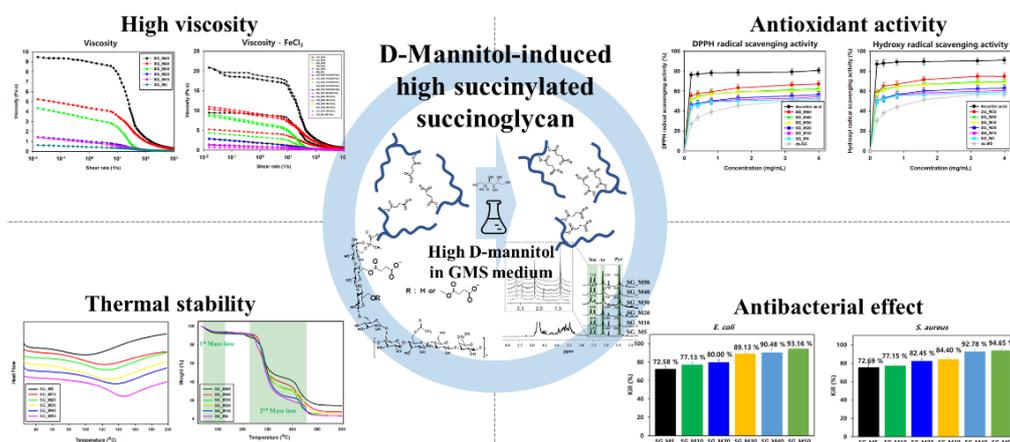
HIGH VISCOSITY, ANTIBACTERIAL AND ANTIOXIDANT PROPERTIES OF D-MANNITOL-INDUCED HIGHLY SUCCINYLATED SUCCINOGLYCAN PRODUCED BY *SINORHIZOBIUM MELILOTI* RM 1021

Yohan Kim^{a*}, Sohyun Park^a, Younghyun Shin^a, Jaeyul Kim^a, Jae-pil Jeong^a, and Seunho Jung^{a,b}

^a Department of Bioscience and Biotechnology & ^b Department of System Biotechnology, Microbial Carbohydrate Resource Bank (MCRB), Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, South Korea

* shsks1@hanmail.net

As social and environmental awareness has recently increased, highly viscous microbial polysaccharide is one of the essential raw materials for various industries as a novel natural rheological agent to replace synthetic chemicals [1]. Among natural polymers, microbial exopolysaccharides (EPS) have great advantages as ecofriendly biodegradable polymers with significant potential to provide a wide range of their rheological properties [2]. Succinoglycan (SG) isolated from *Sinorhizobium meliloti* (*S. meliloti*) Rm 1021 contains non-carbohydrate substituents, such as pyruvate, succinate, and acetate groups, in repeating octasaccharide unit [3]. The physical properties of SG are constant even under high temperature, shear rate, and salt condition, it is used in commercial products such as thickeners, stabilizers, emulsifiers, and gelling agents [4]. The rheological and physiological properties of D-mannitol-induced highly viscous SG produced by *Sinorhizobium meliloti* Rm 1021 have been investigated. When the concentration of D-mannitol as a carbon source in the GMS medium increased, SG exhibited a higher degree of succinylation. The viscosity of highly succinyl-substituted SG remarkably increased up to 7.726 Pa·s at a shear rate 10 s^{-1} , about 24.75 times higher than normal SG. As the degree of succinyl substitution increased, the thermal stability of SG also increased. In particular, as the concentration of D-mannitol increased, the rheological properties of G' of SG proportionally improved. In addition, this highly succinyl-substituted SG solution showed the enhanced antibacterial effects against *E. coli* and *S. aureus* and scavenging activities against DPPH and hydroxyl radical.



[1] Rana, S., & Upadhyay, L. S. B. *International journal of biological macromolecules*, 157, 577-583, 2020.

[2] Sutherland, I. W. *Trends in biotechnology*, 16(1), 41-46, 1998.

[3] Andhare, P., Goswami, D., Delattre, C., Pierre, G., Michaud, P., & Pathak, H. *Applied Biological Chemistry*, 60(3), 339-348, 2017.

[4] Jahanbin, K., Moini, S., Gohari, A. R., Emam-Djomeh, Z., & Masi, P. *Food Hydrocolloids*, 27(1), 14-21, 2012.



CHITOSAN/QUATERNIZED CHITOSAN NANOFIBERS DESIGNED FOR BIOMEDICAL APPLICATIONS

Andreica B.-I.^{*a}, Anisiei A.^a, Rosca I.^a, Sandu A.-I.^a, Mititelu-Tartau L.^c, Marin L.^a

^a “Petru Poni” Institute of Macromolecular Chemistry, Grigore Ghica Voda Alley, Iasi, Romania

^c “Grigore T. Popa” University of Medicine and Pharmacy, Iasi, Romania

* andreica.bianca@icmpp.ro

Over the past few decades, there has been a significant focus on quaternized chitosan-based (nano)fibers for the development of materials with applications as wound dressings, air and water filters, drug delivery scaffolds, antimicrobial textiles, energy storage systems, alkaline fuel cells, and more. The unique properties of quaternary groups, such as hydrophilicity, bioadhesiveness, antimicrobial, antioxidant, hemostatic, and antiviral activity, and ionic conductivity, have contributed to this interest [1]. Nevertheless, the ionogenic nature of quaternary chitosan hampers its electrospinning, and co-spinning with a synthetic polymer has been necessary to produce high-quality fibers. Additionally, a high degree of quaternization can lead to cytotoxicity, making it challenging to use these fibers for *in vivo* applications that require biodegradability and biocompatibility. To address these challenges, a new approach has been proposed, to prepare chitosan/quaternized fibers, using poly(ethylene glycol) with a double role: co-electrospinning agent and sacrificial component [2].

The success of this strategy has been demonstrated through FTIR and NMR spectroscopy and TGA analysis, which showed the complete removal of poly(ethylene glycol). SEM analysis showed that the fibers had an average diameter of around 160 nm, while X-ray diffraction corroborated with POM indicated their semicrystalline nature. The fibers swelled in water and in media of physiological pH, partially dissolved in these media, and biodegraded in the presence of lysozyme, with biodegradation rates controlled by HTCC's content and pH. The fibers also exhibited breathability, as evidenced by reversible water vapor adsorption/desorption curves. The mechanical properties of the fibers varied, but the overall results were superior to those of many fibers from synthetic polymers or of human skin. The adhesive force to chicken skin increased as the content of HTCC increased, pointing to good bioadhesion, a fact also observed for the mucoadhesion tests, evaluated by UV-vis and Zeta potential measurements on mucin mixtures. Additionally, small amounts of samples containing HTCC inhibited the growth of *E. coli* and *S. aureus* in less than 6 h, and 24 h respectively, while materials based only on chitosan showed a limited antimicrobial effect. *In vitro* tests demonstrated cytocompatibility suitable for biomedical applications, while *in vivo* testing on rats by subcutaneous implantation showed no toxicity or allergic effect and did not perturb the immune system.

Overall conclusions revealed that a moderate quantity of HTCC can provide good balance between the physical properties and biological activities of the nanofibers, making them valuable biomaterials for biomedical devices, especially implantable ones, and promising candidates for wound healing applications.

Acknowledgment: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE2020-2717, within PNCDI III, no. PCE 2/2021 and from the project H2020- MSCA-RISE-2019, SWORD-DLV-873123.

[1] Andreica B.-I., Cheng X., Marin L., *European Polymer Journal*, 139, 2020.

[2] Andreica B.-I., Anisiei A., Rosca I., Sandu A.-I., Pasca A. S., Mititelu-Tartau L. & Marin L., *Carbohydrate Polymers*, 302, 2023



NANOCELLULOSE-FUNCTIONALIZED AFM PROBES: PROBING SURFACE INTERACTION AT THE NANOSCALE WITH NATURAL ORGANIC MATTER IN THE LIQUID PHASE.

Houssine Khalili^{*a}, Edouard Pesquet^b, and Aji P Mathew^a

^a Department of Materials and Environmental Chemistry, Stockholm University, 10691 Stockholm, Sweden.

^b Department of Ecology, Environment and Plant Sciences, Science for Life Laboratory, Stockholm University, 10691 Stockholm, Sweden.

* Email of presenting author: houssine.khalili@mmk.su.se

Nanocellulose stands out as an incredibly versatile biobased material with numerous uses in environmental applications. With its distinctive surface chemistry and nanostructured morphology¹, nanocellulose has gained recognition as a promising resource for water treatment, an emerging field in which it exhibits significant potential. The use of nanocellulose as an effective agent to prevent fouling in membranes has been suggested, but the specific mechanism behind its antifouling properties remains unclear. Therefore, the objective of this study was to develop nanocellulose-functionalized AFM probes and utilize them as force sensors to investigate the intermolecular forces between the nanocellulose and organic foulant, which presents a major obstacle in water treatment processes. The AFM probes were successfully developed and examined using high-resolution scanning electron microscopy (SEM) and fluorescence techniques. Phosphorylated cellulose nanofibers (PCNF) exhibited lower adhesion force towards bovine serum albumin foulant (BSA) compared to TEMPO-oxidized cellulose nanofibers (TOCNF). Suggesting low that PCNF has a low affinity toward BSA than TOCNF.

AFM: Atomic force microscopy.

(1) Zhu, C.; Monti, S.; Mathew, A. P. Cellulose Nanofiber–Graphene Oxide Biohybrids: Disclosing the Self-Assembly and Copper-Ion Adsorption Using Advanced Microscopy and ReaxFF Simulations. *ACS Nano* **2018**, *12* (7), 7028–7038. <https://doi.org/10.1021/acsnano.8b02734>.



AGGREGATION STUDIES ON THE DISSOLUTION AND REGENERATION OF BIOPOLYMERS FROM HEMP (CANNABIS SATIVA) USING IONIC LIQUIDS

Vilaró P. ^{*a}, Rodríguez M.^b, Reyes A. L.^c and Moyna, G..^d

^a *Espacio de Ciencia y Tecnología Química, CENUR Litoral Noreste, Universidad de la República, Uruguay*

^b *Ciencias Físicas y sus Aplicaciones, CENUR Este, Universidad de la República, Uruguay*

^b *Unidad de Espectroscopía Electrónica, Facultad de Ciencias, Universidad de la República, Uruguay*

^d *Departamento de Química del Litoral, CENUR Litoral Norte, Universidad de la República, Uruguay*

* pilar.vilaro@cut.edu.uy

From the approval of new regulations on Cannabis sativa (CS) a growing hemp industry has started to emerge. Though, in the current situation, flowers are sold un-transformed, leaving farmers little to no profit. In this scenario, we proposed the use of non-traditional hemp products for the development of new materials. Hemp residues were kindly donated by Innovaterra (Salto, Uruguay). Dried and sieved primary and secondary branches residues (125-500 μ m) were dissolved in [C4mim] [Cl] (Liotec) using either oil bath with stirring at 90°C for 24h or subjected to microwave 1s - 2s pulses for 1-5 min [1]. After dissolution and centrifugation, a cellulose rich material fraction (CRM) was obtained by precipitation with either acetone-water, ethanol or acetonitrile. Structural carbohydrate and soluble and insoluble lignin content was carried out following NREL/TP-510-42618. The materials obtained were then characterized using traditional techniques (FTIR, PXRD, DSC, TGA analysis and SEM microscopy). A yield of dissolution of up to 83% was obtained for the biomass and for CRM was about 40%. In the CRM, lignin content was variable with a 50% reduction in the principal stems sample (A), and the cellulose content remained constant in most of the fractions in both secondary and primary fractions. Granulometry was found to be the leading factor of DSC behavior of the samples, regardless of the variation in its composition. In conclusion, firstly, a simple dissolution methodology of hemp residues was successfully applied to be further investigated in its application for film or wet- spinning. Secondly and more importantly, promise is held for the use of aggregation as a controlling factor for the development of bio-based materials.

[1] Shamshina, J.L., et al., In Search of Stronger/Cheaper Chitin Nanofibers through Electrospinning of Chitin–Cellulose Composites Using an Ionic Liquid Platform. ACS Sustainable Chemistry & Engineering, 2018, 6,14713-14722.



Session 5

Polysaccharide gels, porous materials, emulsions

Session organizers:

Tatiana Budtova, Falk Liebner, Bernard Cathala, Henrikki Liimatainen

Keynote speakers:

Kirsi Mikkonen

Transforming hemicelluloses' distinctive properties to unique benefits

Christophe Chassenieux

Stabilization of water in water emulsions and their use as precursors of porous hydrogels and microgels



TRANSFORMING HEMICELLULOSES' DISTINCTIVE PROPERTIES TO UNIQUE BENEFITS

Mikkonen K.S. ^{a,b}

^a *Department of Food and Nutrition, University of Helsinki, Finland*

^b *Helsinki Institute of Sustainability Science HELSUS, University of Helsinki, Finland*

* kirsi.s.mikkonen@helsinki.fi

Established industrial wood biorefining processes are optimized for cellulose recovery, but they often lead to at least partial degradation of hemicelluloses into low molar mass fractions. Impurities, such as lignin bring compositional variation, which together with the incomplete water-solubility of hemicelluloses complicates hemicellulose valorization for potential applications. At the same time, there is a significant demand by food, pharmaceutical, cosmetics, and chemical industries for intermediate-to-low molar mass polysaccharides with low viscosity in aqueous solutions and with capability to stabilize dispersed systems. The stabilizing capacity is generally enhanced by amphiphilic structures. Lignin impurities introduce such amphiphilicity in hemicelluloses, so they can be viewed as natural functionality enhancers. The unique composition and colloidal properties of hemicelluloses make them efficient stabilizers against emulsion breakdown and lipid oxidation. Furthermore, a potential utilization route of hemicelluloses is as prebiotic fibers for healthy lifestyle. Hemicelluloses from various different wood biorefinery processes are a significant underexploited natural resource with broad future outlook. [1]

[1] Mikkonen, K.S. *Green Chemistry*, 22 (4), 1019-1037, 2020



STABILIZATION OF WATER IN WATER EMULSIONS AND THEIR USE AS PRECURSORS OF POROUS HYDROGELS

Chassenieux C.

Le Mans University-CNRS, IMMM UMR 6283, France

* christophe.chassenieux@univ-lemans.fr

Water-in-water emulsions are obtained by mixing solutions of two incompatible water-soluble polymers, of which polysaccharides are widely used. Due to the very low interfacial tension between the two aqueous phases and the length scale involved, their stabilisation is a challenging problem that has been approached in several ways. Most commonly, it is achieved by a Pickering effect associated with the use of solid particles sitting at the interface¹. Again, in that attempt, whiskers, microgels and self-assemblies based on polysaccharides have been widely reported in the literature^{2,3}. Often, Pickering stabilisation is coupled with gelation of the continuous phase², which prevents the emulsions from sedimenting or creaming, giving them the potential to be transformed into hydrogels with controlled porosity. I will illustrate some of these issues and show how the water-in-water interface can be further used to produce polysaccharide/proteins complexes of interest⁴.

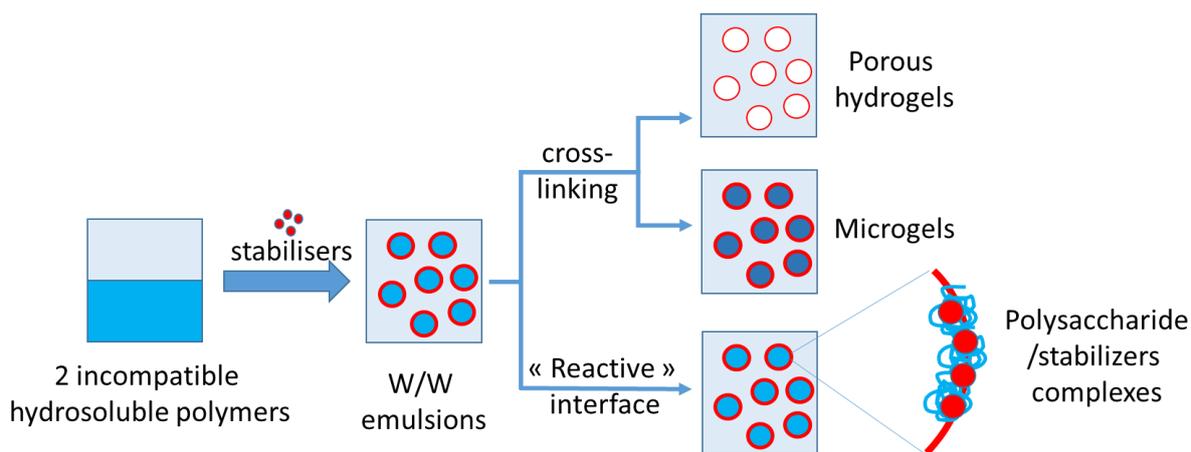


Figure 1 : Various potentials of water in water emulsions based on polysaccharides

[1] Nguyen B.T., Nicolai T., Benyahia L. *Langmuir*, 29, 10658–10664 2013.

[2] Peddireddy K. R., Nicolai T., Benyahia L., Capron I. *ACS Macro Letters*, 5 (3), 283-286, 2016

[3] Tea L., Nicolai T., Renou F. *Langmuir*, 35 (27), 9029-9036, 2019

[4] de Freitas, R. A., Nicolai T., Chassenieux C., Benyahia L. *Langmuir* 32 (5), 1227-1232, 2016.



XYLOGLUCAN AND CELLULOSE NANOCRYSTALS THERMORESPONSIVE HYDROGELS: GELATION MECHANISM AND FUNCTIONAL PROPERTIES

Géraldine Rangel^a, Christophe Chassenieux^b, Bernard Cathala^a

a Biopolymers, Interactions et assemblages INRAE Nantes, France

b Institut des Molécules et Matériaux du Mans, Le Mans, France

* Bernard.cathala@inrae.fr

Nanocellulose are a class of biobased nanoparticles encompassing nanocrystals (CNC) and nanofibers (CNF); the first are stiff nanorods while the second are flexible and semi crystalline. For decades, they have been used in many applications due to their excellent mechanical properties, biocompatibility and broad functionalization possibilities. Xyloglucan (XG) is one of the hemicelluloses whose interaction with cellulose has been extensively studied and used for materials elaboration. Adsorption of XG onto cellulose surfaces is now understood as an entropic process that can be modulated by kinetic effects.^{1,2} The properties of the final nanocellulose/XG network can therefore be adjusted by controlling the XG/nanocellulose ratio and concentrations. Nanocellulose and xyloglucan mixtures therefore represent systems of choice to both gain understanding on mixtures of biobased nanoparticle/polymer and to develop new innovative materials from renewable resources. Indeed, polymer-nanoparticle self-assembly is a simple route to control the dispersion of nanoparticle and rheological properties of nanoparticles dispersion but also to design tunable materials, such as hydrogels, without the need for complex synthetic chemistry approaches. XG/CNC Hydrogels were formulated by mixing solutions of XG and cellulose nanocrystals. Then the impact of XG/CNC ratio and concentrations were investigated using a triphasic diagram. We were able to differentiate between liquid systems, viscous liquids, gels. We also demonstrated the occurrence of a reversible thermal transition at certain XG/CNC ration. Hydrogel were further concentrated by osmotic dehydration to investigate their functional properties at high solid content. Hydrogels display high mechanical strength and recover instantaneously their properties after breakage making them efficient materials for moldability or 3D printing. Additionally, all these results make it possible to describe formation mechanisms of hydrogels and features that rule their properties.

1. Dammak, A.; Quemener, B.; Bonnin, E.; Alvarado, C.; Bouchet, B.; Villares, A.; Moreau, C.; Cathala, B., Exploring Architecture of Xyloglucan Cellulose Nanocrystal Complexes through Enzyme Susceptibility at Different Adsorption Regimes. *Biomacromolecules* **2015**, *16*, (2), 589-596.
2. Villares, A.; Moreau, C.; Dammak, A.; Capron, I.; Cathala, B., Kinetic aspects of the adsorption of xyloglucan onto cellulose nanocrystals. *Soft Matter* **2015**, *11*, (32), 6472-6481.



CELLULOSE-ALGINATE HYDROGELS FOR WATER DESALINATION INSPIRED BY THE STRUCTURE AND FUNCTION OF PLANTS

Katsuya KOMIYAMA^{*a}, Corentin ESCHENBRENNER^a, Ahmed HAMRAOUI^a, Clémence SICARD^b, Francisco M. FERNANDES^a

^a Sorbonne Université, UMR 7574, Laboratoire de Chimie de la Matière Condensée de Paris, 75005, Paris, France

^b Université de Versailles Saint-Quentin-en Yvelines, UMR 8180, L'Institut Lavoisier de Versailles, 78035, Versailles, France

* katsuya.komiyama@sorbonne-universite.fr

Plants have attracted enormous attention as biomimetic models because of their remarkable combination of mechanical strength and lightweight. The hierarchical cellular structure of highly-oriented cellulose fibrils in the matrix (hemicellulose and lignin) is largely responsible for such properties in plant tissues. Beyond the structural aspects, plants perform a myriad of functions. In particular, liquid transport between the roots and the leaves is inspiring to design new desalination devices. The driving force behind this function is transpiration, which determines water transport from the roots through the stems' macropores (xylem) up to the surface of its leaves, driven by sunlight. One of the consequences of transpiration is the separation of the water from its solutes. Especially, plants like mangroves, willows and reeds are able to generate clean water from seawater and wastewater through the solar power as a sole inexhaustible energy source.

Here we propose an analogous system able to reproduce the functions and structure of the plant stem and leaves, ultimately capable of water desalination via sun-powered evaporation. The isotropic hydrogels corresponding to the "stem" were obtained by ice templating, a materials processing technique that enables the formation of aligned macropores by precisely controlling ice growth in solutions and/or suspensions [1, 2]. By freezing oxidized cellulose dispersion in alginate matrix and stabilizing them through ion-crosslinking, we aim at reproducing the vascular structure and function of the plant stem. Furthermore, buckypapers (carbon-clay black paper-like material) were prepared to act as artificial "leaves" by vacuum filtration [3], and placed on top of the anisotropic hydrogels. Because buckypapers have excellent photo-thermal properties, they accelerate the capillary liquid transport behavior of the hydrogels in the presence of the artificial solar light.

Herein, we will discuss the influence of the alginate moiety on the mechanical properties and morphologies of cellulose-based hydrogels through compression tests and SEM. Besides, we will describe the role of ice growth speed on the morphology (pore size and pore shape) of cellulose-based hydrogels, on the capillary transport properties. Finally, we will report the assembly of the buckypaper as "leaves" and alginate/oxidized cellulose hydrogel as "stem", which demonstrated excellent desalination properties in the presence of the salt water under the light irradiation.

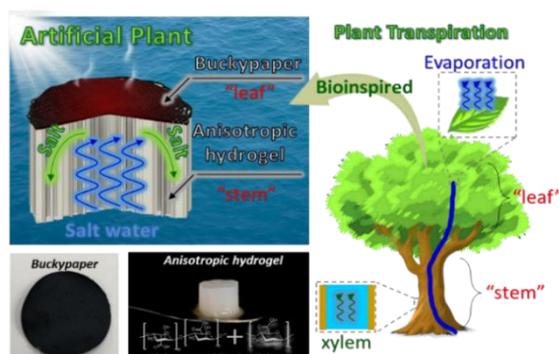


Fig.1 Working principle of cellulose-alginate macroporous hydrogels and their similarity to native plants

[1] Qin et al., *J. Mater. Chem. B*, 9, 2221-2232, 2021, [2] Christoph et al., *Macromol. Biosci.* 16:182-187, 2016, [3] Fernandes et al., *Carbon*, 72, 296-303, 2014



NOVEL CARBOHYDRATE-BINDING PROTEINS: CBM92 AND THEIR HYDROGEL-FORMING ABILITIES

Meng-Shu Hao^a, Scott Mazurkewich^{b,c}, He Li^a, Srijani Saha^a, Salla Koskela^a, Johan Larsbrink^{b,c}, Qi Zhou^{a,c}, Lauren S McKee^{a,c}

^a *Division of Glycoscience, Department of Chemistry, KTH Royal Institute of Technology, AlbaNova University Centre, 106 91 Stockholm, Sweden*

^b *Division of Industrial Biotechnology, Department of Biology and Biological Engineering, Chalmers University of Technology, Gothenburg, Sweden*

^c *Wallenberg Wood Science Center, Teknikringen 56-58, 100 44 Stockholm, Sweden*

* mengshu@kth.se

Carbohydrate-binding modules (CBMs) are primarily associated with carbohydrate-active enzymes (CAZymes) and possess non-catalytic carbohydrate-binding activity. Twelve CBM92 domains, which we have recombinantly produced and characterized from 5 phylogenetically diverse species, preferentially bind to β -1,6-glucans, despite the variety of predicted substrates for enzymes connected to CBM92 domains. We also analyzed five variant forms of a CBM92 domain, generated by site-directed mutagenesis at the proposed binding sites, to better understand ligand binding abilities. Our findings suggest that CBM92 represents a new family of CBMs with multivalent binding sites, each with varying affinities for ligand.

We demonstrated that CBM92 can form a three-dimensional hydrogel network with branched polysaccharides consisting of a linear β -1,3-glucan backbone and single glucose units attached via β -1,6-linkage (Swedish patent application No. 21208133.5). The hydrogel formation occurs rapidly at room temperature through a simple mixing process, requiring no chemical modifications or solvents other than water. We propose that this sustainable hydrogel has potential industrial applications, particularly for direct human body use in cosmetic and medical settings.



INVESTIGATION OF MOLDABLE PHYSICAL CHITIN HYDROGELS AND THEIR APPLICATIONS

Kaku Y.^{*a}, Fujisawa S.^a, Saito T.^a, Isobe N.^b

^a *Laboratory of Pulp and Paper Science, The University of Tokyo, Japan*

^b *Biogeochemistry Research Center, Japan Agency for Marine-Earth Science and Technology, Japan*

* yutokaku@g.ecc.u-tokyo.ac.jp

Polysaccharides are useful gelating materials in the food science and medical fields. Polysaccharide-based hydrogels are generally classified as physical gels in which cross-linking points are formed by molecular entanglement or crystallization. They are obtained by dissolving polysaccharides in water or organic solvents and insolubilizing them by changing temperature or immersing them into a coagulation bath.

Hydrogels made of chitin, an abundant marine biomass, are expected to be useful especially in the medical field to take advantage of its bioactivity. However, its insolubility in general solvents makes it difficult to prepare chitin-based physical hydrogels in arbitrary shapes. For this, one possible approach was the *N*-acetylation of chitosan: once dissolved chitosan was acetylated back to chitin, leading to the gelation [1]. Although several studies have reported the kinetics of the chitin hydrogels, the mechanical properties on a bulk scale were poorly understood. This is because chitin undergoes gelation immediately after acetylation and loses fluidity, making it difficult to prepare a shaped gel with the strength necessary for the handling during mechanical tests. Recently, a facile process to obtain a moldable physical chitin hydrogel was developed by slowing down the acetylation [2]. Here, by exploiting the moldability, a unique feature of the chitin hydrogel, swelling and shrinking behavior by controlling the degree of acetylation [3], was investigated from the mechanical perspective.

Chitosan powder was dissolved in acid methanol-water mixture, and acetylated by adding acetic anhydride (Ac_2O) while stirring at -12°C . The solution was poured into a mold and left at room temperature to allow gelation, followed by washing with water to obtain a chitin hydrogel. Through this method, a volume-controlled, highly transparent chitin hydrogel with various solid concentration from 0.21 to 6.4 wt%, was successfully prepared by changing the degree of acetylation (Figure 1). The swelling/shrinking behavior of the chitin hydrogels was driven by the osmotic pressure derived from the cation charge of the amino groups. X-ray diffraction confirmed that the gel backbone is made of crystalline α -chitin, regardless of solid concentration. Thanks to their moldability, compressional mechanical tests on the obtained chitin hydrogels were successfully conducted, and the results showed a wide range of mechanical properties (compressive Young's modulus : from 4 to 310 kPa) depending on the solid concentrations. These previously-unnoticed characteristics will place the chitin hydrogel in the next-generation bio-derived smart soft materials.

[1] Hirano S., Ohe Y. & Ono H., *Carbohydrate Research*, 47, 315-320, 1976.

[2] Isobe N., Tsudome M., Kusumi R., Wada M., Uematsu K., Okada S. & Deguchi S., *ACS Applied Polymer Materials*, 2, 1656-1663, 2020.

[3] Laurent V., Nathalie Z. & Alain D., *Carbohydrate Research*, 326, 295-304, 2000.

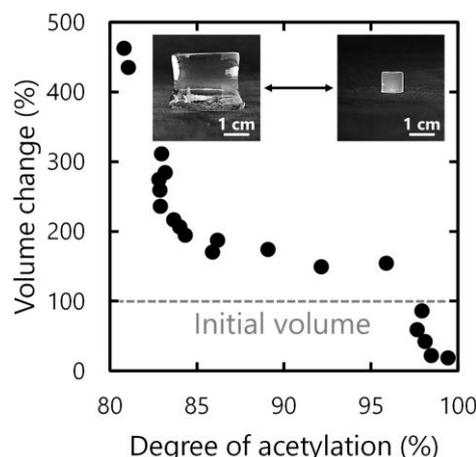


Figure 1 : Volume change of chitin hydrogel by controlling degree of acetylation



GELATION OF CELLULOSE IN AQUEOUS ALKALINE SOLUTIONS BY CO₂

Naserifar Sh. ^{*a,b}, Karna N. ^c, Kozlowski A. ^d, Bernin. D ^a, Hasani M. ^{a,b}

^a Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden

^b Wallenberg Wood Science Center, Chalmers University of technology, 412 96 Gothenburg, Sweden

^c MembramProTec, 59840 Vimmerby, Sweden

^d RISE research institute, 431 53 Mölndal, Sweden

* shirinn@chalmers.se

Cellulose as the most abundant biopolymer on earth is an invaluable sustainable component with a wide range of applications in textiles, packaging materials, membranes, etc. However, in order to be able to utilize cellulose, its processing is a prerequisite. One way to process cellulose is its dissolution followed by coagulation which results in its properties changes. These changes provide opportunities to shape cellulose into different forms for versatile applications. To date, a lot of efforts have been made to develop a number of solvents as well as coagulating media towards cellulose processing.

In my research, we have been investigating quaternary ammonium hydroxides specifically aqueous morpholinium hydroxides as potential solvents for cellulose. In this particular study, CO₂ was used to coagulate cellulose dissolved in benzyltriethylammonium hydroxide (Triton B), *N,N*-dimethylmorpholinium hydroxide and *N*-butyl-*N*-methylmorpholinium hydroxide and the coagulation process as well as the yielded gels were investigated. This study is particularly interesting because CO₂ can be used as an alternative regeneration agent to yield cellulose gels with potential application in the industry such as in textiles, sponges, films, etc. Using CO₂ as a coagulating agent is a sustainable replacement for the commonly coagulant solvents being used such as alcohols. Besides, gels with different properties can be obtained using different dissolution media that would fit for specific applications.

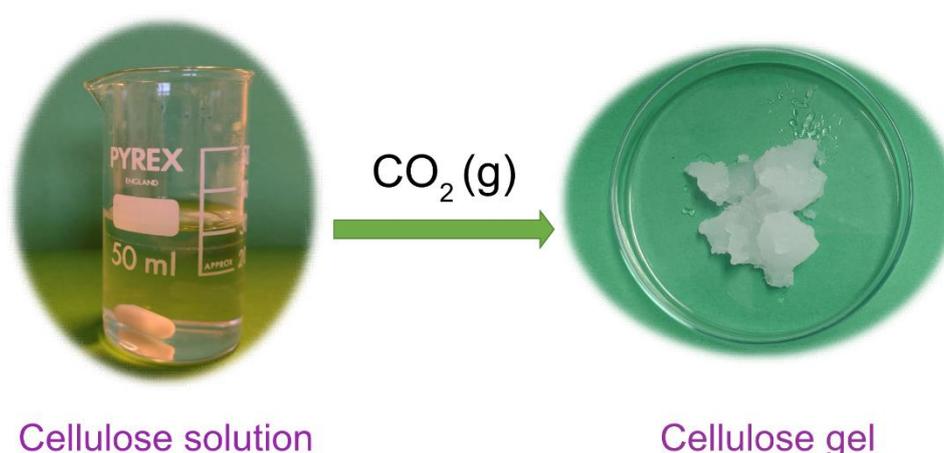


Figure 1 : Cellulose gelation using CO₂ (g)



ELABORATION OF BIO-BASED SUPERABSORBENT HYDROGELS INCORPORATING DIALDEHYDE CELLULOSE EXTRACTED FROM BANANA TREE FIBERS

Boussif Y. ^{*a-b} Cathala B.^a Kaddami H.^b Moreau C.^a Belachemi L.M.^b

^a UR1268 BIA, INRAE, 44300, Nantes, France

^b IMED, Cadi ayyad university, Morocco

*yassineboussif01@gmail.com

Superabsorbent polymers (SAPs) based on bio-sourced polymers are currently a subject of great interest as a biodegradable alternative to substitute SAPs that are entirely synthetic, notably those based on petroleum sources (acrylic and acrylamide). In this context, we focus on synthesizing new hybrid SAP systems based on cellulose and a copolymer of acrylic acid and itaconic acid.

In this study, bleached pulp extracted from banana tree fibers was chemically modified via sodium periodate oxidation to obtain dialdehyde cellulose (DAC) fibers. DAC fibers were characterized (oxidation degree and particle size). They were then incorporated in composites composed of a copolymer of acrylic acid (AA) and itaconic acid (IA) crosslinked by N, N'-methylenebisacrylamide (MBA) and initiated by potassium persulfate (KPS) under controlled experimental conditions (Figure 1). Superabsorbent composites from various compositions (1-10% of fibers) were studied and analyzed using FT-IR, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The swelling characteristics of these novel materials were studied by evaluating their equilibrium absorption capacity in distilled water and a 0.9% NaCl solution. As a result, the maximum water absorption capacities of DAC-g-(AA-co-IA) in distilled water was $1300 \text{ g}\cdot\text{g}^{-1}$ with an amount of 20 wt% biobased materials.

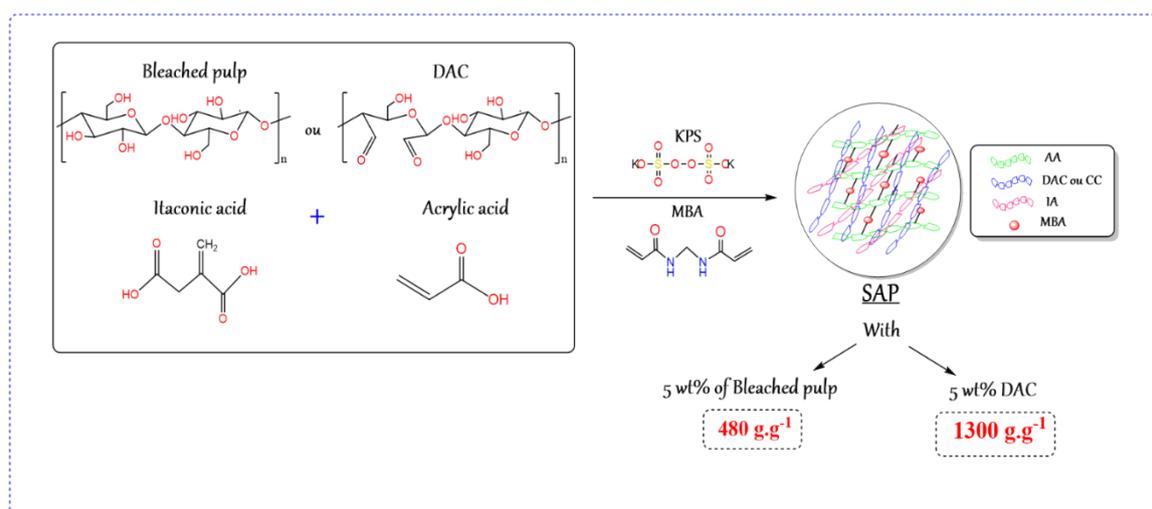


Figure 1: The general process for access of BioSAPs from DACs, itaconic acid and acrylic acid

STARCH AEROGELS AND AEROGEL-LIKE XEROGELS

Fangxin Zou, Tatiana Budtova*

Mines Paris, PSL University, Centre for material forming (CEMEF), UMR CNRS 7635, CS 10207, 06904 Sophia Antipolis, France

* Tatiana.Budtova@minesparis.psl.eu

Aerogels are low-density open-pores nanostructured materials with very high specific surface area, above 100 m²/g. In 2022 IUPAC named aerogels among “Ten Emerging Technologies in Chemistry”. Bio-aerogels are a new class of aerogels developed in the 21st century. The potential applications of bio-aerogels span from thermal and acoustic insulation to life science, energy and electrochemistry. To make bio-aerogels from polysaccharide solutions or gels, drying with supercritical CO₂ is used to avoid pores collapse during drying. Freeze-drying usually leads to pores which are replicas of grown ice crystals, i.e. to material with low density and low surface area. Despite that low- or high-pressure technology are used in industrial processes, one of the challenging goals in bio-aerogel research is to avoid such expensive drying steps.

In this work, different starches were dissolved and materials in different forms – hydrogels, alcogels, aerogels and low-vacuum dried materials (named xerogels) – were designed and tested as carriers of a model drug, theophylline. The influence of starch amylose/amylopectin ratio, concentration in solution, retrogradation time and drying method (supercritical CO₂ drying for aerogels, low-vacuum drying for xerogels) on materials' density, specific surface area and morphology was investigated. Starch alcogels were loaded with theophylline via impregnation; loading capacity and efficiency of alcogels, aerogels and xerogels were determined, and release of the drug from xerogels and aerogels evaluated.

Two remarkable phenomena were obtained: 1) low-vacuum drying method resulted in aerogel-like materials, i.e. xerogels were with low density and specific surface area above 100 m²/g, and 2) starch alcogels were adsorbing theophylline from ethanol resulting in loading efficiency as high as 250 % [1]. The results obtained show a new pathway in making aerogel-like polysaccharide materials without drying in supercritical conditions.

Acknowledgements

Authors are grateful to Roquette for sponsoring the work and providing starches, to Pierre Ilbizian (PERSEE, MINES Paris) for drying with supercritical CO₂ and to Suzanne Jacomet (CEMEF, MINES Paris) for SEM imaging.

[1] Fangxin Zou and Tatiana Budtova, *ACS Sustainable Chem. Eng.* 11, 5617–5625 (2023)



CO-POLYMERIC AEROGELS FROM CELLULOSE BIOMASS AS HETEROGENEOUS CATALYSTS FOR ORGANIC REACTIONS

Nicastro G. ^{*a}, Riva L. ^a, Battocchio C. ^b, Punta C. ^a, Sacchetti A. ^a,

^a Department of Chemistry, Materials and Chemical Engineering, “Giulio Natta”,
Politecnico di Milano, via Luigi Mancinelli 7, 20131, Milano, Italia;

^b Department of Science, Università degli Studi Roma Tre, Viale Guglielmo Marconi, 446,
00146 Roma, Italia

* gloria.nicastro@polimi.it

Increasing concerns related to global environmental degradation necessitate the investigation of new and safe materials for the development of sustainable processes. In this context, cellulose has attracted increasing interest as a suitable building block. [1] Additionally, heterogeneous catalysis perfectly fits into the more relevant than ever circular economy perspective owing to its reusability and recyclability.

Herein, we present a highly porous cellulose-based nanosponge (CNS) composed of TEMPO-oxidized cellulose nanofibers (TOCNF) thermally cross-linked with branched polyethyleneimine (bPEI) and citric acid. CNSs have been deeply characterized, proving their intrinsic micro- and nano-porosity [2].

Given the basicity of the aerogels, amino-catalyzed reactions, such as the Henry and Knoevenagel reactions, were chosen as the model of study. [3] Once the catalytic efficiency of the CNSs was proven, a new class of catalysts was prepared. Previous studies had shown the excellent ability of CNS to absorb transition metal ions from contaminated water as, the alkylamino moieties of bPEI can chelate heavy metals [4]. Thus, the combination of these two features led to the selective loading of metals by exploiting CNSs as active supports of transition metals.

By selecting the metal ion, it is possible to catalyze different reactions, while obtaining high yields, such as aromatic acetal formation from carbonyl compounds with Cu(II) and Zn(II) on CNS [5], or Suzuki cross-coupling reaction with Pd(II)-loaded CNSs. [6]

Recyclability of heterogeneous catalysts is a key point in material development. Reusability tests were performed for all the analyzed reactions, demonstrating the efficiency of the catalysts for several reaction cycles. This feature is one of the advantages of heterogeneous catalysis over homogeneous one. [3-6]

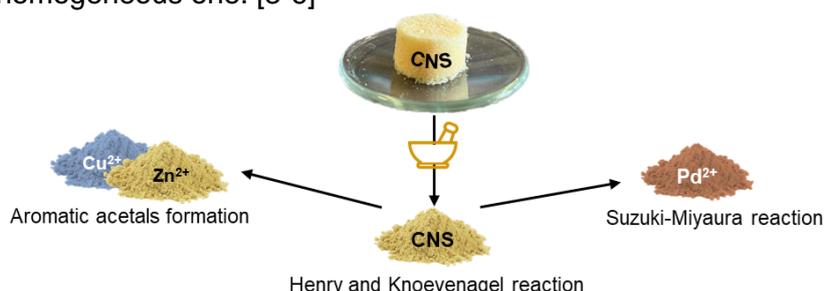


Figure 4 Cellulose nanosponges

[1] Nagarajan K. J., Ramanujam N. R., Sanjay M. R., Siengchin S., Surya Rajan B., Sathick Basha K., Madhu P. & Raghav, G. R., *Polymer Composites*, 42, 1588–1630, 2021

[2] Paladini G., Venuti V., Almásy L., Melone L., Crupi V., Majolino D., Pastori N., Fiorati A. & Punta C., *Cellulose*, 26, 9005–9019, 2019.

[3] Riva L., Punta C. & Sacchetti A., *ChemCatChem*, 12, 6214–6222, 2020.

[4] Fiorati A., Grassi G., Graziano A., Liberatori G., Pastori N., Melone L., Bonciani L., Pontorno L., Punta C. & Corsi I., *J. Clean. Prod.*, 246, 119009, 2020.

[5] Riva L., Lotito A.D., Punta C. & Sacchetti A., *Gels*, 8(1), 54, 2022.

[6] Riva L., Nicastro G., Liu M., Battocchio C., Punta C. & Sacchetti A. *Gels*, 8, 789, 2022



3D PRINTED CARBOXYMETHYL CELLULOSE BASED AEROGELS AND COMPARATION WITH “BULK” AEROGELS

Sujie Yu*, Romain Castellani, Anselmo Pereira, Rudy Valette, Tatiana Budtova

Center for Materials Forming (CEMEF), MINES Paris-PSL, UMR CNRS 7635, 06904 Sophia Antipolis, France

* sujie.yu@minesparis.psl.eu

Bio-aerogels are new materials based on natural polymers, polysaccharides¹. They are nanostructured, lightweight and display high internal pores' surface area, making them very promising for biomedical applications, in particular, in the field of wound healing. To adapt bio-aerogels for use as wound dressings, complex shapes are often needed ; 3D printing is a tool able to make these shapes on-demand, making it well fitted to this purpose. Carboxymethyl cellulose (CMC) is an appealing polymer and has been widely used as wound healing material, thanks to its biocompatibility, water solubility, and rather low cost. However, practically nothing is known about CMC 3D printed aerogels. Therefore, this work aims to show the feasibility of 3D printed neat CMC aerogels. Here, CMC solution (“inks”) with five different polymer concentrations (1, 3, 5, 6 and 7 wt%) were used and their rheological properties, filament deposition mechanisms and shape “stabilisation” (20 layers can be obtained) were studied to evaluate their printability. The results showed that CMC concentration below 5 wt% did not present suitable characteristics to keep shape fidelity after printing. The experimental work was accompanied by modelling in order to understand and predict the printability, using rheological parameters. Aerogels were obtained by non-solvent-induced phase separation applied on printed gels followed by drying with supercritical CO₂. Density, porosity, specific surface area and morphology were evaluated. All CMC aerogels were low-density porous materials with specific surface area around 150 m²/g. In summary, we demonstrated the feasibility of making 3D printed aerogels based on CMC, which opens the prospects in using them in biomedical applications.

Reference:

[1] T. BUDTOVA, *Cellulose*, 26, 81–121, 2019

Acknowledgements:

The China Scholarship Council (CSC) is gratefully acknowledged for funding of this project. We thank Julien Jaxel (PERSEE, Mines Paris,PSL, France) for supercritical drying, Frederic Georgi (CEMEF, Mines Paris, PSL) for help with SEM imaging and IFF for providing CMC samples.



IMPACT OF NON-SOLVENT INDUCED PHASE SEPARATION ON CELLULOSE AEROGEL MORPHOLOGY

Loris G.^{*a}, Gurikov P.^b, Budtova T.^a

^a*MINES Paris, PSL University, Center for Material Forming (CEMEF), UMR CBRS 7635, CS 10206, 06 904 Sophia Antipolis, France*

^b*Laboratory for Development and Modelling of Novel Nanoporous Materials, Hamburg University of Technology, Germany*

*loris.gelas@minesparis.psl.eu

Aerogels from biomass, especially from polysaccharides, are of great interest due their good mechanical properties, general biocompatibility, biodegradability, and chemical tailorability for specific applications (adsorption of drug or pollutant, hydrophobization, crosslinking, catalyst substrate, among others).

Except the case of nanocellulose, cellulose aerogels are fabricated from a homogeneous cellulose solution. As solvents of cellulose are highly polar compounds, which are able to disturb the dense hydrogen bond network of native cellulose, they are not miscible with supercritical CO₂, making direct supercritical drying not possible. It is thus necessary to exchange this solvent by another solvent, which is miscible with CO₂. This solvent, in turn, is a non-solvent for cellulose leading to local coagulation of cellulose and phase separation into polymer rich and polymer lean phases (surface of interactions between cellulose and non-solvent is minimized).

The non-solvent induced phase separation is expected to a large extent determine the morphology of the cellulose porous network obtained after supercritical drying. As the solvent exchange cannot be performed immediately, mass transport properties of both solvent and non-solvent (diffusion coefficients, their densities), play an important role. It is also known that other parameters (affinity of the solvent and non-solvent towards cellulose, their miscibility, cellulose concentration and process temperature), influence network morphology, [1]–[3]. Overall, the parameter space is very large and remains largely unexplored.

In this work, we made first attempts at systematically analyze the impact of the non-solvents and their sequence on the properties of aerogels made from cellulose dissolved in aqueous sodium hydroxide. Coagulation kinetics and shrinkage during non-solvent induced phase separation was evaluated and corelated with aerogel morphology, density, specific surface area and cellulose crystallinity.

Acknowledgements: Thank you to French national research agency for funding the project: Phase transitions in bio-gels: towards structure/properties control of bio-aerogels and of responsive biomaterials (Bio-Gel). We are thankful to Julien Jaxel (PERSEE) for supercritical drying, Gabriel Monge for XRD measurements and Anja Hajnal (TUHH) for the following of coagulation kinetic. I would also like to thank COST action AERoGELS: Advanced Engineering and Research of aeroGels for Environment and Life Sciences (CA18125) for funding the visit of TUHH in Hamburg and to use their equipment P.G. gratefully acknowledges support for this research from the German Research Foundation (DFG) under the project GU 1842/6-1.

[1] G. R. Guillen, Y. Pan, M. Li, et E. M. V. Hoek, *Ind. Eng. Chem. Res.*, vol. 50, n° 7, p. 3798-3817, 2011

[2] R. Gavillon et T. Budtova, *Biomacromolecules*, vol. 8, n° 2, p. 424-432, 2007

[3] P. Gurikov, R. S. P., J. S. Griffin, S. A. Steiner, et I. Smirnova, *Ind. Eng. Chem. Res.*, vol. 58, n° 40, p. 18590-18600, 2019



THE STRUCTURE OF MICELLES CONTROLS THE RHEOLOGICAL AND MECHANICAL PROPERTIES OF CELLULOSE ETHER-BASED HYDROGELS AND CRYOGELS

Denise F. S. Petri^{a,*}

^a *Institute of Chemistry, University of São Paulo, Brazil*

* dfsp@usp.br

Hydrogels and cryogels containing hydroxypropyl methylcellulose (HPMC), bis (2-ethylhexyl) sodium sulfosuccinate (AOT, two C8 chains and sulfosuccinate head group) and sodium dodecyl sulfate (SDS, one C12 chain and sulfate head group) at different concentrations were investigated using small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM), rheological measurements, and compressive tests. SDS micelles bound to the HPMC chains building “bead necklaces”, increasing considerably the storage modulus G' values of the hydrogels and the compressive modulus E values of the corresponding cryogels. The dangling SDS micelles promoted multiple junction points among the HPMC chains. AOT micelles and HPMC chains did not form “bead necklaces”. Although AOT increased the G' values of the hydrogels, the resulting cryogels were softer than pure HPMC cryogels. The AOT micelles are probably embedded between HPMC chains. The AOT short double chains rendered softness and low friction to the cryogel cell walls. This work demonstrated that the structure of the surfactant tail can tune the rheological behavior of HPMC hydrogels and hence the microstructure of the resulting cryogels.

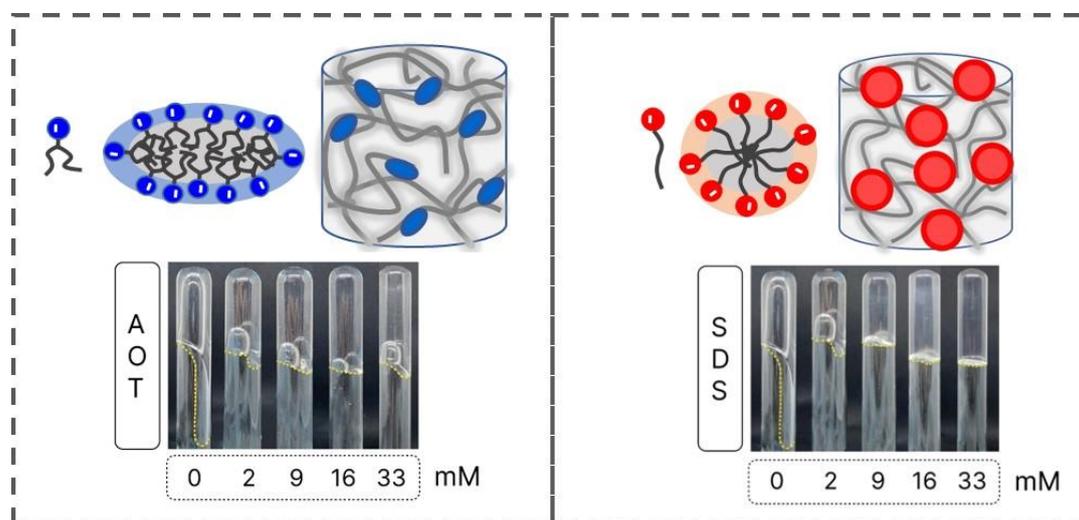


Figure 1 : Schematic representation of the AOT and SDS micelles in the HPMC hydrogels along with the photographs of the corresponding hydrogels



STRETCHABLE HYDROGELS FROM THE CONTROLLED POLYELECTROLYTE ASSOCIATION OF POLYSACCHARIDES

Balima M.^a, Sudre G.^{*a}, Montembault A.^a

^a Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, F-69622 Villeurbanne Cédex, FR

*guillaume.sudre@univ-lyon1.fr

Chitosan (CS) and hyaluronic acid (HA) are two oppositely charged naturally occurring polyelectrolyte polysaccharides with interesting biological properties. They can interact through polyelectrolyte complexation in aqueous solutions, and even form hydrogels without requiring external crosslinkers or chemical modification. The materials are obtained by decreasing the salt concentration of homogeneous solution mixtures of HA and CS containing an excess of NaCl. The presence of salts screens the electrostatic interactions and their progressive removal by dialysis allows to control the self-assembly of the polysaccharides.[1] When HA is the host (larger molar mass) in excess and CS is the guest, highly stretchable hydrogels can be obtained when the pH of the dialysis bath is close to the pKa of HA (~2.9).[2]

In this work, we study the formation of hydrogels with CS (high molar mass and high degree of acetylation) as the host and HA (low molar mass) as the guest at pH close to the pKa of CS (pH ~ 7). Dialysis was performed against sodium acetate (AcONa) solutions of various concentrations for several days. First, we obtained very soft gels at 10⁻¹ M of sodium acetate. Then, at 10⁻² M of sodium acetate, by solely varying the charge molar ratio $r_{-/+}$ corresponding to the ratio of $n_-(HA)/n_+(CS)$, either solutions or stretchable hydrogels were obtained (figure 1). Our results highlight the influence of extrinsic parameters (e.g. pH, ionic strength, $r_{-/+}$) on the conformation and the self-assembly of the polyelectrolytes, and thus, the mechanical properties of the resulting materials.

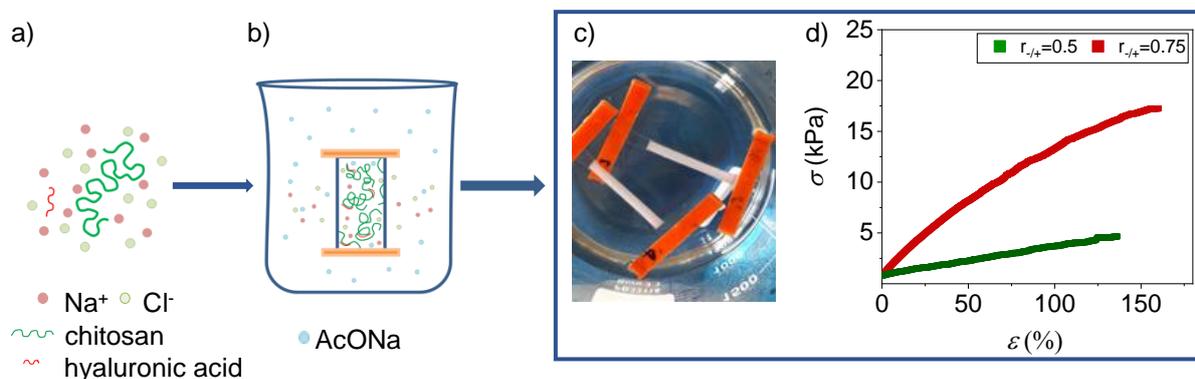


Figure 1: Formation of stretchable CS/HA hydrogels from the polyelectrolyte associations. (a) Preparation of homogenous mixture of CS/HA with an excess of NaCl. (b) Desalting of the mixture by dialysing against AcONa at neutral pH. (c) Formation of the hydrogels after few days of dialysis. (d) Stress-strain curves at 10 mm/min of the hydrogels at $r_{-/+}$ of 0.5 and 0.75.

References

- [1] Costalat, M., David, L. & Delair, T., *Carbohydrate Polymers*, 102, 717–726, 2014
 [2] Lalevée, G., David, L., Montembault, A., Blanchard, K., Meadows, J., Malaise, S., Crépet, A., Grillo, I., Morfin, I., Delair, T. & Sudre, G., *Soft Matter*, 13, 6594–6605, 2017.



TAILORED NANOCELLULOSE-BASED HYDROGELS PREPARED BY OSMOTIC DEHYDRATION

Guccini V. ^{*a}, Arumughan V. ^a, Attallah N. ^a, Mihhels K. ^a, Maloney T. ^a, Kontturi E. ^a

^a Department of Bioproducts and Biosystems, Aalto University, Finland

* valentina.guccini@aalto.fi

Nanocellulose-based hydrogels can be tuned over a wide range of physical-chemical properties without compromising their structural integrity, thanks to the nanocelluloses' water affinity and dynamics coupled with excellent mechanical properties and chemical versatility [1]. This makes them ideal matrices for cell and microbial cultures as in biomedical applications and photosynthetic cell factories for example [2]. In this respect, their gas-fluid transport (thus the porosity) is crucial to ensure biological viability. Recently Guccini et al. [3] described the use of osmotic dehydration to prepare cellulose nanofibers' hydrogels with fine-tuned porosity, following and quantifying for the first time their porosity directly in the wet state over a wide range of solid contents (from 0.7 to 12 wt%). Herein, we present a range of nanocellulose-based hydrogels (both nanofibres and nanocrystals) prepared by osmotic dehydration with different pore size distributions and surface areas. Their porosity has been characterized directly in their native and wet state by thermoporosimetry, excluding the possibility of artefacts induced by drying. Furthermore, we correlate the porosity with their gas-fluid transport using fluorescence recovery after photobleaching (FRAP). The hydrogels have been used as matrices to host photosynthetic cells, showing excellent performance in terms of cell viability and mechanical properties over 30 days. Our study contributes to the fundamental understanding of nanocellulose hydrogels and accelerates their use in applications involving cells and microbial cultures or as a material platform for the preparation of porous materials such as foams.

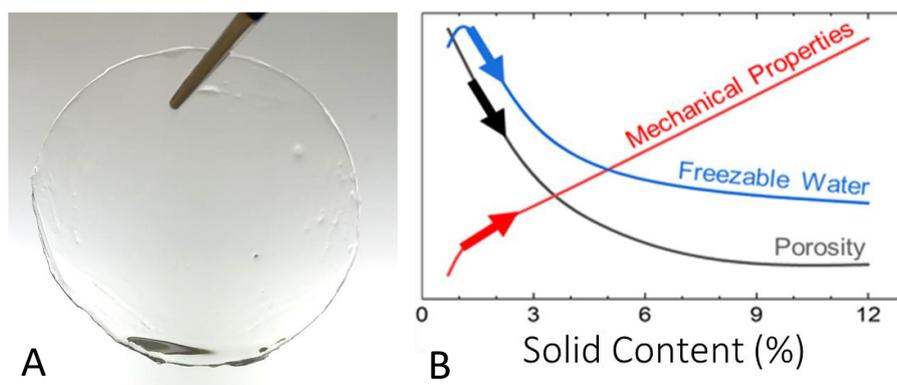


Figure 1: (A) typical appearance of a cellulose nanofibers' hydrogel and (B) the effect of the hydrogel's solid content on mechanical properties, freezable water and porosity.

- [1] Solhi L., Guccini V., Heise K., Solala I., Niinivaara E., Xu W., Mihhels K., Kröger M., Meng Z., Wohler J., Tao H., Cranston E. D., Kontturi E., Chem. Rev. 123, 1925-2015, 2023
 [2] Heise K., Kontturi E., Allahverdiyeva Y., Tammelin T., Linder M. B., Nonappa, Olli Ikkala O., Adv. Mater. 33, 2004349, 2021
 [3] Guccini V., Phiri J., Trifol J., Rissanen V., Mousavi S. M., Vapaavuori J., Tammelin T., Maloney T., Eero Kontturi E., ACS Appl. Polym. Mater. 4, 24-28, 2023



PRODUCTION OF VARIOUS HYBRID BIO-BASED GEL INK MATERIALS MADE OF POLYMER GRAFTED NANOCELLULOSE, SUITABLE FOR 3D PRINTING APPLICATION

Jiang X., Dalloul F., Barba E., Mietner B., Navarro J.R.G.*

Institute of Wood Science, University Hamburg, Germany

* Julien.navarro@uni-hamburg.de

The use of biodegradable and renewable material resources, which can replace petroleum-based products, to produce performant functional materials are one of the greatest challenges for a future sustainable society. Within this philosophy, bio-based polymers such as nanocellulose have attracted considerable attention. However, nanocellulose needs further chemical surface modification to be considered as suitable ink material in specific applications or for being processed through 3D gel-printing.

This talk will focus on the opportunity and the advantages of modifying the CNF surface chemically through the selective grafting and cross-linking of numerous polymers on its surface, with and without the presence of inorganic nanoparticles. The grafting of those specific entities onto the CNF surface not only affect the behavior of the CNF in suspension, but allows also to introduce numerous new properties before being processed through 3D-printing^{1,2,3}. In this talk, several gel-ink examples with various properties (luminescent, self-healing, anti-microbial) will be presented and their ability to be 3D printed will be shown.

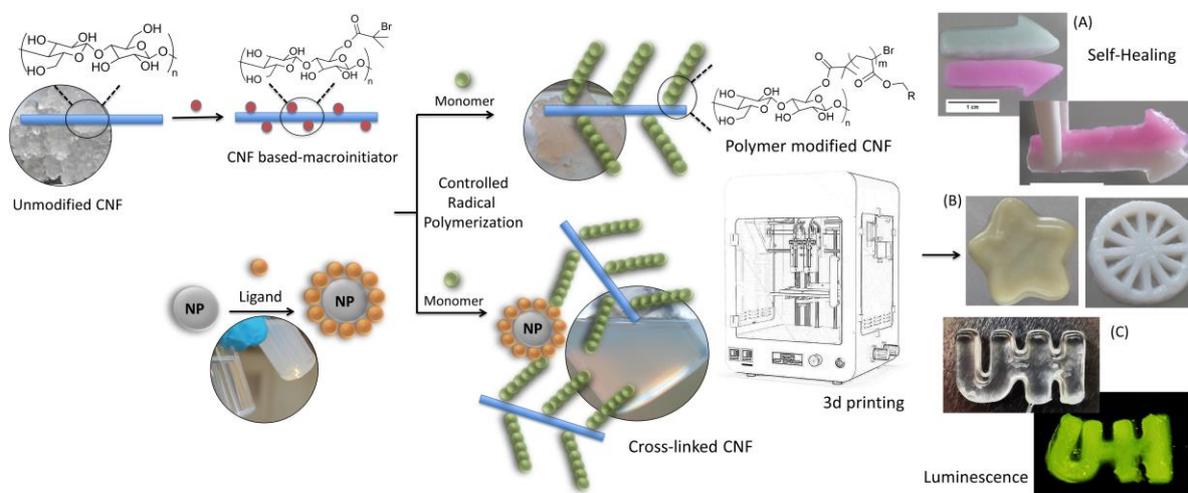


Figure 1: Schematic representation of the CNF hybrid gel synthesis and some 3D printed object with (a) Self-healing, (b) Anti-microbial and (c) Luminescence properties.

[1] Jiang, X.; Mietner, J. B.; Navarro, J. R. G., *Cellulose* **2023**, No. 0123456789.

[2] Jiang, X.; Mietner, J. B.; Harder, C.; Komban, R.; Chen, S.; Strelow, C.; Sazama, U.; Fröba, M.; Gimmler, C.; Müller-Buschbaum, P.; Roth, S. V.; Navarro, J. R. G., *ACS Appl. Mater. Interfaces* **2023**, 15 (4)

[3] Dalloul F.; Mietner, J. B.; Navarro, J. R. G., *ACS Appl. Polym. Mater.* **2023**, accepted



NANOCELLULOSE AS STABILIZER FOR STORABLE EMULSIONS OF DITHIZONE/CHLOROFORM IN WATER, AND THEIR RESPONSE TO MERCURY(II) IONS

Aguado R.J. ^{*a,b}, Mazega A. ^{a,b}, Fiol N. ^b, Tarrés Q. ^{a,b}, Marc Delgado-Aguilar ^{a,b}

^a LEPAMAP-PRODIS Research Group, University of Girona, Spain

^b Department of Chemical and Agricultural Engineering and Agrifood Technology, University of Girona, Spain

* roberto.aguado@udg.edu

Despite the long tradition of using dithizone (DTZ) for colorimetric heavy metal detection, its worrisome stability issues and the common requirement to use it in aqueous systems have not met a satisfactory solution yet. Briefly put, DTZ can be long-term stored if dissolved in dry or acidified chloroform, but this limits its range of applications. Likewise, it can be dissolved in alkaline aqueous solutions, but then it must be used immediately after preparation (Figure 1a). This communication aims to overcome this limitation by means of nanocellulose-stabilized emulsions.

With anionic cellulose nanofibers as Pickering stabilizer, we attained DTZ-containing emulsions with high physical and chemical stability. These emulsions had at least 95 wt% water and 0.1–0.8 vol% acetic acid conforming the continuous phase, while dispersed droplets of diameter $<1 \mu\text{m}$ consisted of a 3 wt% solution of DTZ in chloroform. The solvation shell was computed by molecular dynamics, suggesting that chloroform slightly reduces the dihedral angle of the solute. Concentrations of nanofibers over 0.2 wt% attained apparently homogeneous mixtures, avoiding coalescence. Besides, the rate of degradation of DTZ in the nanocellulose-stabilized emulsion was roughly as slow as in a DTZ/chloroform solution (without water), achieving higher chemical stability than in toluene or acetonitrile (Figure 1a, 1b). Finally, nanocellulose-stabilized DTZ emulsions are readily and immediately responsive towards mercury(II) in water, as displayed in Figure 1c. Anionic nanofibers even decreased interferences from other ions, including cadmium(II) and lead(II) [2].

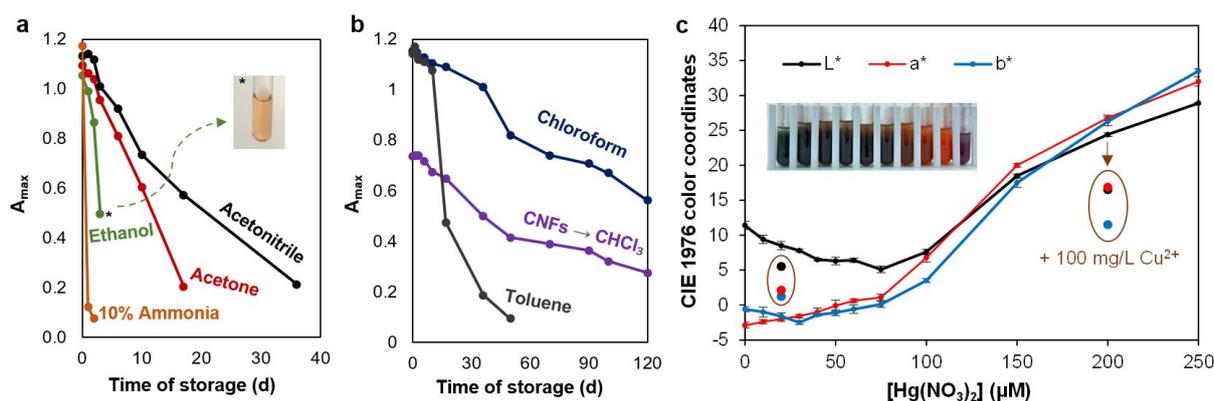


Figure 1 : Chemical stability of DTZ in different solvents (a, b) and colorimetric response towards mercury(II) nitrate of nanocellulose-stabilized Pickering emulsions.

[1] Von Eschwege K.G., Conradie J., Kuhn, A., *J. Phys. Chem. A*, 115, 14637–14646, 2011.

[2] Aguado R.J., Mazega A., Fiol N., Tarrés Q., Mutjé P., Delgado-Aguilar M., *ACS Appl. Mater. Interfaces*, 15, 12580–12589, 2023.



DEVELOPMENT OF BIO-BASED AMBIENT-DRIED AEROGELS WITH PH CONTROLLABLE SURFACE CHARGE FOR VERSATILE WATER PURIFICATION

Zhaleh Atoufi ^{*a}, Per A. Larsson ^a, Lars Wågberg ^{a,b}

^aDepartment of Fiber and Polymer Technology, KTH Royal Institute of Technology, Sweden.

^bWallenberg Wood Science Center (WWSC), KTH Royal Institute of Technology, Sweden

*Zhaato@kth.se

Water contamination with synthetic dyes and heavy metals has become one of the most acute environmental problems in recent decades. Aerogels, owing to their ultralight highly porous structure and often high specific surface area, are considered as promising adsorbents for water purification. However, the preparation of aerogels from low-cost renewable resources via energy efficient and green processes is challenging. In this study, bio-based aerogel-like adsorbents based on dialdehyde carboxymethylated cellulose nanofibrils (DA-C-CNFs) and amyloid nanofibrils (ANFs) were prepared via a freeze-linking methodology which facilitated the formation of a highly porous structure at ambient conditions without the need of highly energy and time-consuming techniques such as freeze-drying. In this procedure, controlled mixtures of DA-C-CNFs and ANFs were frozen in a kitchen freezer (-18°). During the freezing, the growth of ice crystals packed DA-C-CNFs and ANFs into thin lamellae between the ice crystals forcing the fibrils into close contact with each other allowing the aldehyde groups on the cellulose backbone to form hemiacetal bonds with hydroxyls, most likely on other CNFs, hence crosslinking the entire structure and physically locking the ANFs into the structure due to the entanglements and non-covalent interactions. The frozen network was then thawed, solvent exchange to acetone and ambient dried.

The resulting aerogels exhibited low densities (18-28 kg.m⁻³), high mechanical robustness in both the dry and the wet state, and a highly porous structure. Moreover, owing to the amphoteric nature of ANFs, the hybrid aerogels represented a pH tunable surface charge which enabled them to interact with both cationic and anionic contaminants. The effect of pH on the adsorption of cationic (methylene blue and Pb(II)) and anionic (brilliant blue, congo red, and Cr(VI)) model contaminants was investigated. Moreover, to further investigate the interaction between the hybrid aerogel and model contaminants, Langmuir and Freundlich models were employed showing that the adsorption best could be described by the Langmuir model and the Langmuir saturation adsorption capacity of the aerogel was calculated to be 68, 79, and 42 mg.g⁻¹ for brilliant blue, Pb(II), and Cr(VI), respectively. An analysis of the kinetics of adsorption of brilliant blue to the hybrid aerogels revealed that the adsorption is a diffusion limited process which leads to an apparent second-order adsorption behaviour. Furthermore, the reusability of the aerogels was tested over three cycles of adsorption and desorption and the aerogels maintained 97 and 96% of their adsorption capacity for MB and Pb(II) as cationic model contaminants and 89 and 80% of their initial adsorption capacity for Cr(VI) and BB as anionic model contaminants. Finally, the selectivity of aerogel for Pb(II) in the presence of calcium and magnesium as common ions present in, for example, lakes was tested and the aerogels showed remarkable selectivity for Pb(II). Overall, using renewable materials and the energy-efficient fabrication procedures, along with structural robustness, versatile adsorption behavior (anionic and cationic speciation), reusability, and remarkable selectivity for Pb(II), makes hybrid DA-C-CNF/ANF aerogels promising adsorbents for water remediation.



FUNGAL CHITOSAN IN PICKERING EMULSION: PROMISING FULLY EMULSIFIED SYSTEM FOR TOPICAL APPLICATION

ASDRUBAL Aurélie^a, HUCHER Nicolas^a 1, PICARD Céline^a

^a *Université Le Havre Normandie, Normandie Univ, URCOM UR 3221, F-76600 Le Havre, France*

* email of presenting author: aurelie.asdrubal@univ-lehavre.fr

The interest in Pickering Emulsions is increasing thanks to the extreme stability against destabilization phenomenon [1]¹ and to their eco-friendly and non-toxic behavior with a reasonable choice of particles. Some polysaccharide stabilizers have been used in O/W Pickering emulsions like cellulose and chitin. Fungal chitosan (linear polysaccharide composed of D-glucosamine and N-acetyl-D-glucosamine units) is a choice of interest thanks to its biodegradable, biocompatible, and non-toxic properties [2]².... Chitosan is used in the pharmaceutical, food, and cosmetic field as a drug and bioactive delivery system, and to stabilize Pickering emulsions.

In this study the intrinsic properties of the selected chitosan particle permit to obtain a stable emulsion defined by the capacity of the particle to anchor at the interface and stabilize an emulsion over time against coalescence, as well as against common reversible destabilization phenomena (creaming, coalescence, flocculation).

Our chitosan particles show an ability to decrease the interfacial tension of oil against water with physical modifications and specific formulation process. Scanning electron microscopy images show the anchoring of the particle at the interface. Moreover, the arrangement of the particle in the bulk insures the stability of the emulsions against reversible destabilization phenomena.

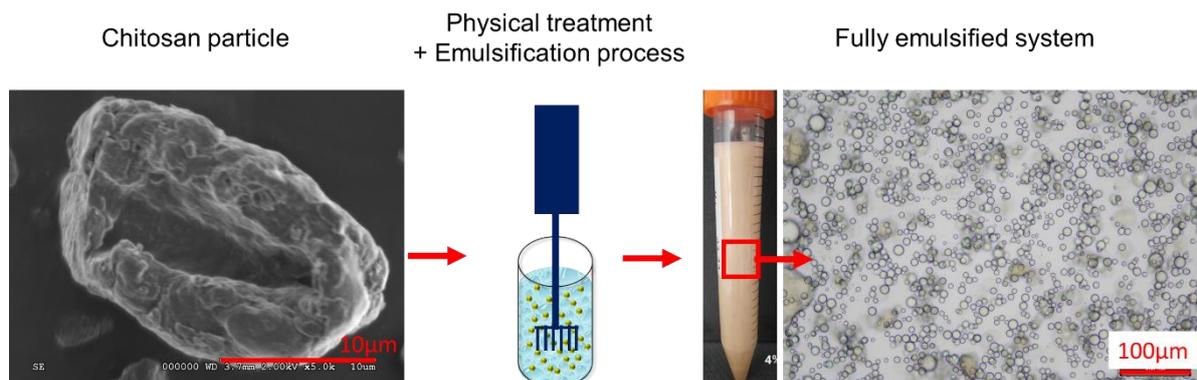


Figure 1 : from left to right - Particles of fungal chitosan (Scanning Electron Microscopy), physical treatment, fully emulsified system (Optical microscopy)

1 B. P. Binks and T. S. Horozov, Eds., *Colloidal Particles at Liquid Interfaces*, Cambridge University Press, Cambridge, 2006.

2 A. Sharkawy, M. F. Barreiro and A. E. Rodrigues, *Carbohydrate Polymers*, 2020, 250, 116885.



DEVELOPMENT OF POROUS DICARBOXYMETHYL CELLULOSE ADSORPTIVE MEMBRANES

Gago D.^{*a}, Arfaoui Rim^b, Gonzalez-Ortiz Danae^c, Pochat-Bohatier Céline^c, Souza V.^d, Fuciños P.^d, Pastrana L.^d, Chagas R.^e, Ferreira L. M.^a, Coelho I.^a

^aLAQV-REQUIMTE, Departamento de Química, NOVA School of Science and Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal. ^bFaculty of Sciences of Tunis, University of Tunis El Manar, Tunis, Tunisia. ^cInstitut Européen des Membranes, IEM UMR-5635, ENCSM, CNRS, University of Montpellier, Place Eugene Bataillon, 34095, Montpellier, France. ^dInternational Iberian Nanotechnology Laboratory (INL), Av. Mestre José Veiga s/n, 4715-330 Braga, Portugal. ^eFood4Sustainability-Associação para a Inovação no Alimento Sustentável, Centro Empresarial de Idanha-a-Nova, Zona Industrial, 6060-182 Idanha-a-Nova, Portugal.

* dx.gago@campus.fct.unl.pt

Increasing environmental awareness and restrictions have led to the replacement of petroleum-derived products for bio-based materials. Simultaneously, membrane technology may improve process sustainability by lowering the carbon footprint. Cellulose derived materials have appealing physico-chemical characteristics and their high availability contributes to lower process costs. [1,2]

Dicarboxymethyl cellulose (DCMC) is a recently developed polymer produced by heterogeneous etherification of cellulose [3]. The application of this polymer in methylene blue removal from aqueous solutions [4], protein adsorption [5] and white wine stabilization [5] has already been successfully demonstrated. Developing adsorptive membranes with this interesting adsorbent material can contribute to the selectivity and reversibility of the process.

DCMC with a DS above 0.5 is water soluble, but insoluble in countless organic solvents. This presents a unique challenge in the development of DCMC membranes. DCMC membranes were prepared by phase inversion or freeze drying, in which the dope solution consisted of DCMC aqueous solutions or Pickering emulsions. Membranes prepared with DCMC, montmorillonite (MMT) and castor oil and monoliths produced via freeze drying (Fig. 1) were porous prior to crosslinking. Studies on the influence of the crosslinking methods on pore size and overall membrane morphology are underway. Future work will focus on the optimization of the membranes, followed by characterization and evaluation for filtration/adsorption processes.

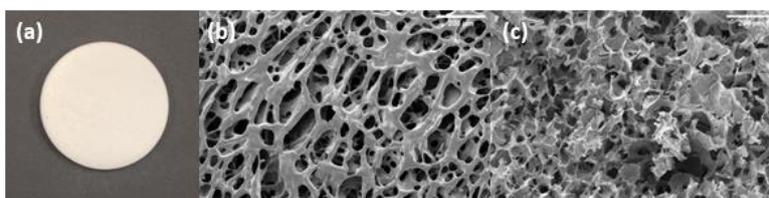


Figure 1. (a) Digital photo and SEM micrographs of a DCMC monolith (b) top view (surface) and (c) cross-section.

- [1] Tomietto, P.; Russo, F.; Galiano, F.; Loulergue, P.; Salerno, S.; Paugam, L.; Audic, J.-L.; De Bartolo, L.; Figoli, A. *Journal of Membrane Science*, 643, 120061, 2022.
 [2] Choi, S.M.; Rao, K.M.; Zo, S.M.; Shin, E.J.; Han, S.S. *Polymers*, 14, 1080, 2022.
 [3] Chagas, R.; Gericke, M.; Ferreira, R.B.; Heinze, T.; Ferreira, L.M. *Cellulose*, 27, 1965-1974, 2020.
 [4] Gago, D., Chagas, R., Ferreira, L.M., Velizarov, S., Coelho, I. *Membranes*, 10, 2020.
 [5] Gago, D.; Corvo, M.C.; Chagas, R.; Ferreira, L.M.; Coelho, I. *Polymers*, 14, 5122, 2022.



CHITOSAN-BASED HYDROGELS: INFLUENCE OF CROSSLINKING STRATEGY ON RHEOLOGICAL PROPERTIES

Dutertre F. ^{*a}, Roas Escalona N. ^a, Delair T. ^a, Becquart F. ^a

^a Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, F-42023 Saint-Étienne Cédex 2, France

* fabien.dutertre@univ-st-etienne.fr

The thiol-ene click chemistry is a versatile methodology widely used to form bio-hydrogel by crosslinking polysaccharides. In this opportunity, chitosan-based macrogels were prepared through thiol-ene reactions. First, the chitosan (CS) was functionalized with a vinyl group (CS-ene) or thiol groups (CS-SH). Then, two crosslinking strategies (photochemically and thermochemically activated) were compared: (1) CS-ene with CS-SH and (2) CS-ene cross-linked with di(ethylene glycol)-bis(thiol) (dEG-(SH)₂).

The first strategy, where the crosslinking reaction occurs between two functionalized macromolecules and intra-chains crosslinking reactions are avoided (“no loop”), leads to the formation of weak gels. In this case, rheology displays a critical gel point ($G' \approx G'' \approx \omega^{0.5}$) and the cross-linking density estimated by NMR slightly depends on the substitution degree of pentenoate-modified CS. The second strategy, where the functionalized chitosan (CS-ene) is crosslinked by reaction with a small di-thiol molecule (dEG-(SH)₂), provided stronger gels with a faster diffusion of the dEG-(SH)₂ during the network formation, which strengthen the gel modulus. The last strategy is the most efficient methodology for the macrogel synthesis, despite that the “loop” formation cannot be fully avoided. Finally, both methodologies were transposed at the microscale through inverse emulsion to attempt to synthesize chitosan-based microgel.

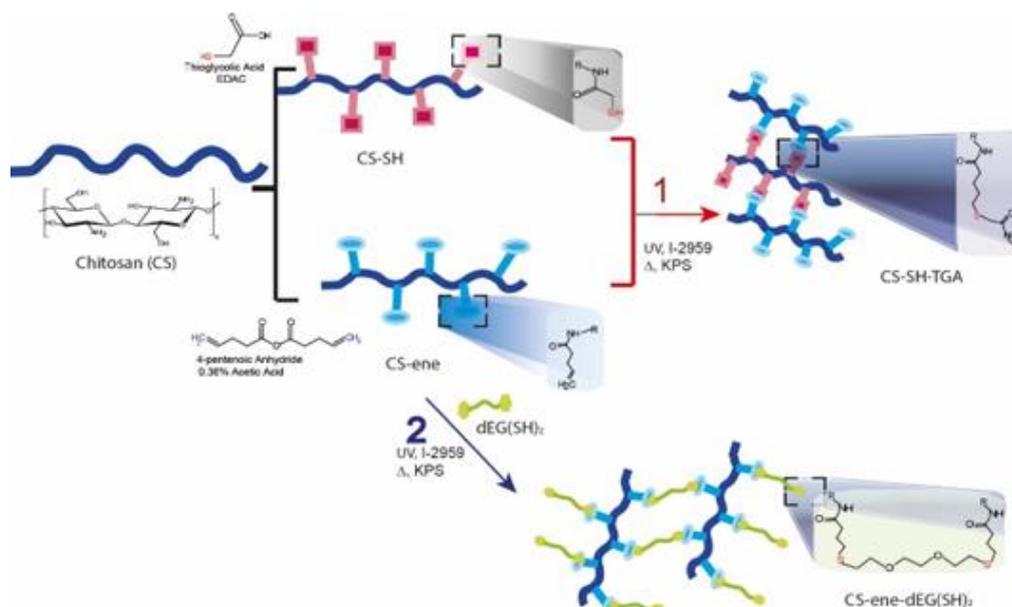


Figure 1 : Scheme of chitosan functionalization by-thioglycolic acid (CS-SH) and pentenoic anhydride (CS-ene); and thiol-ene reaction with strategy 1 (CS-ene and CS-SH) and strategy 2 (CS-ene and dEG(SH)₂).



PREPARATION AND CHARACTERIZATION OF HYALURONIC ACID-NANOCHITIN CAPSULES FOR DRUG DELIVERY APPLICATIONS

Laurianne Legay^{*a}, Milad Kamkar^{b,c}, Sytze Buwalda^a, Orlando J. Rojas^b, Tatiana Budtova^a

^a MINES Paris, PSL Research University, Center for Materials Forming (CEMEF), UMR CNRS 7635, CS 10207, 06904 Sophia Antipolis, France

^b Bioproducts Institute (BPI), Departments of Chemical and Biological Engineering, Chemistry and Wood Science, The University of British Columbia (UBC), Vancouver, British Columbia, Canada

^c University of Waterloo, Department of Chemical Engineering, Waterloo, Ontario, Canada

* laurianne.legay@minesparis.psl.eu

Hyaluronic acid (HA) and chitin (Ch) are biodegradable, biocompatible and bioactive polymers that are very attractive for biomedical applications.^{1,2} Capsules for drug delivery were prepared from hyaluronic acid (HA) and nanochitin (nCh), two oppositely charged natural polysaccharides. Capsule formation occurred thanks to interfacial assembly and complexation after injection of one aqueous phase into another, avoiding the use of any, potentially toxic, crosslinking agents. The interactions between HA and nCh were evidenced by FTIR spectroscopy. The resistance of the capsule membrane against degradation was demonstrated by immersion in aqueous solutions containing e.g. salts, acetic acid or NaOH. SEM revealed that the capsule is porous, suggesting that this capsule can be used as controlled-release drug delivery system. The release kinetics of different model compounds from the capsules could be tuned via preparation parameters such as the initial polymer concentration. These robust HA-nCh capsules, obtained by simply mixing the two polymers, are promising biomaterials with potential in drug delivery applications.



Figure 1. Example of a HA-nCh capsule.

ACKNOWLEDGEMENTS

The authors thank the French National Research Agency (ANR, project 3D-AER-HYAL) and the France-Canada Research Fund for financial support. We are also grateful to the following persons from the BPI (UBC, Canada): Xiaoya Su for her help in conductimetric titration of nanochitin fibers, Yi Lu for his help in AFM characterization of nanochitin fibers and Xuetong Shi for her help in FTIR spectroscopy.

[1] Bai, L.; Liu, L.; Esquivel, M.; Tardy, B. L.; Huan, S.; Niu, X.; Liu, S.; Yang, G.; Fan, Y.; Rojas, O. J. Nanochitin: Chemistry, Structure, Assembly, and Applications. *Chem. Rev.* **2022**, 122,13, 11604-11674. <https://doi.org/10.1021/acs.chemrev.2c00125>.

[2] Balazs, E. A. Viscoelastic Properties of Hyaluronan and Its Therapeutic Use. In *Chemistry and biology of Hyaluronan*, 1st ed.; Garg, G. G., Hales, C. A., Eds.; Elsevier Ltd.: Amsterdam, The Netherlands, **2004**; p 415.



TEGYLATED PHENOTHIAZINE-CHITOSAN BASED FRAMEWORKS FOR MERCURY RECOVERY

Sandu Cibotaru*, Daniela Ailincai, Bianca-Iustina Andreica, Luminita Marin

“Petru Poni” Institute of Macromolecular Chemistry, Gr. Ghica Voda Alley, 41A, 700487 Iasi, Romania

* cibotaru.sandu@icmpp.ro

The release of heavy metals into the environment is a major global concern, severely impacting human and animal health [1]. The impact of heavy metals on the environment is significant and can include effects on ecosystems, such as the degradation of soil quality and the reduction of biodiversity. Among these toxic metals, mercury is especially dangerous because it easily sublimates, contaminates the air, and deposits in the waters and soil, being a constant pollution source [2]. In living organisms, mercury denatures proteins, killing cells, including the neurons [3].

The recovery of mercury from the environment is a complex and challenging process. That's why, our attention was focused on the development of new solid materials based on TEGylated phenothiazine and chitosan, with a high capacity to recover mercury ions from aqueous solutions. They were prepared by hydrogelation of chitosan with a formyl derivative of TEGylated phenothiazine, followed by lyophilization. Their structural and supramolecular characterization was carried out by ¹H-NMR and FTIR spectroscopy, as well as X-ray diffraction and polarized light microscopy. Their morphology was investigated by scanning electron microscopy and their photophysical behavior was examined by UV/Vis spectroscopy. Swelling evaluation in different aqueous media indicated the key role played by the supramolecular organization for their hydrolytic stability. Mercury recovery experiments and the analysis of the resulting materials by X-ray diffraction and FTIR spectroscopy showed a high ability of the studied materials to bind mercury ions by coordination with the sulfur atom of phenothiazine, imine linkage, and amine units of chitosan.

- [1] Wu, D.; Sedgwick, A.C.; Gunnlaugsson, T.; Akkaya, E.U.; Yoon, J.; James, T.D. Fluorescent Chemosensors: The Past, Present and Future. *Chem. Soc. Rev.* 46, 7105–7123, 2017.
- [2] Bodnar, D.; Burlibasa, L.; Varlan, C.; Marcov, N.; Georgescu, S.; Marcov, C. Mercury, Biocompatibility and Its Impact on Environment. *Metal Int.* 14, 95–100, 2009
- [3] Dórea, J.G. Integrating Experimental (In Vitro and In Vivo) Neurotoxicity Studies of Low-Dose Thimerosal Relevant to Vaccines. *Neurochem. Res.* 36, 927–938, 2011.

Acknowledgments: This work was supported by a grant from the Romanian Ministry of Education and Research, CNCS—UEFISCDI, project number PCE2/2021 within PNCDI III.



SOMETHING FROM THE TWO WORLDS: CELLULOSE HOSTING METAL CATIONS

Spiliopoulos, P.^a, Spirk, S.^b, Kádár, R.^c, Nypelö T. ^{*a,d}

^a Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Sweden

^b Institute of Bioproducts and Paper Technology, Graz University of Technology, Austria

^c Department of Industrial and Materials Science, Chalmers University of Technology, Sweden

^d Department of Bioproducts and Biosystems, Aalto University, Finland

* tiina.nypelo@chalmers.se, tiina.nypelo@aalto.fi

Utility of sulfate esters in cellulose is typically seen to be in controlling water solubility or in the case of cellulose nanoparticles, to provide stability due to repulsive ionic interactions between the charged particles. Choice of the sulfate group counterion further tunes the particle interactions. For example, use of Na⁺ avoids irreversible aggregation upon drying. However, there inevitably are more properties that can be evoked with the choice of the counterion. We have introduced various counter cations to the sulfate half ester group on cellulose nanocrystals via ion exchange and demonstrate exchange rates up to 89%. As go-to cations, the alkali metals, Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺, [1] and as more exotique alternatives selected lanthanides, Eu³⁺, Gd³⁺, Dy³⁺, were investigated. Within the alkali metal cation series, the cations with higher atomic numbers, *i.e.*, larger ion sizes, generally tended to form stronger viscoelastic gels. The choice of the cation is potentially able to modulate the assembly of the particles in the suspension in static and dynamic (flow) states, and these findings will be discussed. We will also discuss what does it take to study the particle arrangements in these suspension systems. [2,3] The lanthanide cations were also succesfully introduced although with lower inclusion levels than the alkali metal cations. They transformed the viscous liquid-like systems to gel-like systems and Eu³⁺ equipped the cellulose with luminescence and Gd³⁺ with efficiently shortened MRI relaxation time. However, Dy³⁺ inclusion failed to provide any functionality. The sulfate esters on cellulose seem to be good hosts for several kinds of metal cations. However, there is a gap in knowledge regarding the mechanism of the exchange as well as the effect of the coordination environment on the properties and some of these items will be discussed.

[1] Petschacher P, Ghanbari R, Sampl C, Wiltsche H, Kádár R, Spirk S, Nypelö, T. *Nanomaterials*. 2022;12(18):3131.

[2] Kádár R, Fazilati M, Nypelö T. *Cellulose*. 2020;27(4):2003-14.

[3] Kádár R, Spirk S, Nypelö T. *ACS Nano*. 2021;15(5):7931–45.



INTERDISCIPLINARY CHARACTERIZATION OF NANOCELLULOSE- AND ALGINATE-BASED HYDROGELS FOR SOLID-STATE PHOTOSYNTHETIC CELL FACTORIES

Levä T.*^a, Rissanen V.^a, Nikkanen L.^b, Siitonen V.^b, Heilala M.^c, Phiri J.^d, Maloney T.C.^d, Kosourov S.^b, Allahverdiyeva Y.^b, Mäkelä M.^a, Tammelin T.^a

^a VTT Technical Research Centre of Finland Ltd, Finland

^b Molecular Plant Biology, Department of Life Technologies, University of Turku, Finland

^c Department of Applied Physics, Aalto University, Finland

^d Department of Bioproducts and Biosystems, Aalto University, Finland

* tuukka.leva@vtt.fi

Solid-state photosynthetic cell factories (SSPCFs), where photosynthetic microbes are immobilized in biocompatible hydrogel matrices from alginate or TEMPO-oxidized cellulose nanofibrils (TCNF), showcase potential for efficient and sustainable production of a variety of chemicals like biofuels [1] and polymer precursors [2]. However, both the cells and the matrix affect the performance of SSPCFs, which necessitates interdisciplinary methods to develop and tune them according to the requirements of a specific product or operational condition. We studied the structure, mass transfer and operative durability of TCNF- and alginate-based hydrogel matrices by combining multivariate rheological data analyses with investigation of porosity via thermoporosimetry and scanning electron microscopy, and by monitoring the O₂ and CO₂ fluxes of immobilized photosynthetic cells with membrane-inlet mass spectrometry. With Ca²⁺-ions as the primary crosslinker for all matrices, we showed that the TCNF-based matrices resist shear deformation and yielding better than the alginate matrix, although the alginate matrix has higher rigidity and solid-like properties at rest. We also observed highest porosity for TCNF matrices with small addition of alginate or polyvinyl alcohol, and we showed that the mechanical behaviour and porosity of the matrices were reflected in their photosynthetic gas exchange rates over time. Overall, this work established an experimental toolbox for exploring the dynamic properties of the hydrogel matrices that can be tailored according to the needs of the SSPCF being developed.

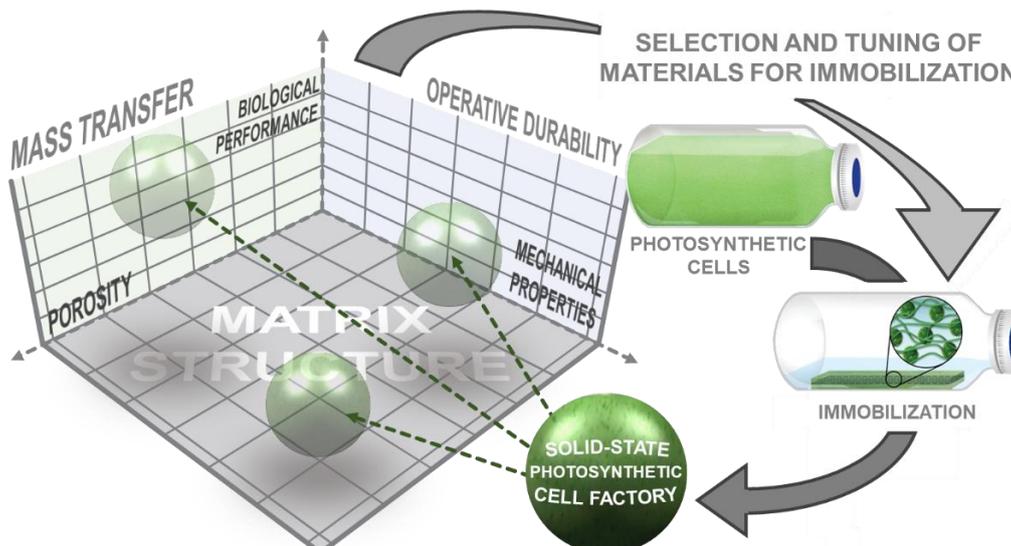


Figure 1. The key dimensions for tailoring the materials during SSPCF development.

[1] Jämsä, M., Kosourov, S., Rissanen, V., Hakalahti, M., Pere, J., Ketoja, J. A., Tammelin, T. & Allahverdiyeva, Y., *J. Mater. Chem. A*, 14, 5825–5835, 2018.

[2] Rissanen, V., Vajravel, S., Kosourov, S., Arola, S., Kontturi, E., Allahverdiyeva, Y. & Tammelin, T., *Green Chem.*, 10, 3715–3724, 2021.



PICKERING EMULSIONS AND HYDROPHOBIZED FILMS OF AMPHIPHILIC CELLULOSE NANOFIBERS SYNTHESIZED USING RING-OPENING ESTERIFICATION IN DEEP EUTECTIC SOLVENT

Qasim U.*^a, Suopajarvi T.^a, Sirvio J.^a, Liimatainen H.^a

^aFibre and Particle Engineering Research Unit, University of Oulu, Oulu, Finland

*Umair.Qasim@oulu.fi

Herein, a dual-functioning deep eutectic solvent (DES) system based on triethylmethylammonium chloride and imidazole was harnessed as a swelling agent and reaction media for the ring-opening esterification of cellulose with n-octyl succinic anhydride (OSA). The esterified cellulose, synthesized using three different OSA-to-anhydroglucose unit molar ratios (0.5:1, 1:1, and 1.5:1), was further converted into amphiphilic cellulose nanofibers (ACNFs) with a degree of substitution (DS) of 0.41–1.13. The ACNFs possessed a lateral dimension of 2.42–18.00 nm and displayed surface activity due to the balance of hydrophobic and hydrophilic characteristics. The ACNFs made stable aqueous dispersions; however, the instability index of ACNF-3 (0.51) was higher than ACNF-1 (0.29) and ACNF-2 (0.33), which was attributed to the high DS-induced hydrophobicity, causing the instability in water. The amphiphilic nature of ACNFs promoted their performance as stabilizers in oil-in-water Pickering emulsions with an average droplet size of 4.85–5.48 μm . Self-standing films of ACNFs showed high contact angles of 97.48°–114.12°, while their mechanical properties (tensile strength of 115 MPA) were inversely related to DS. ACNFs were also used as a coating for fruits to improve their shelf life. Coatings improved their shelf life by decreasing oxygen contact and moisture loss.

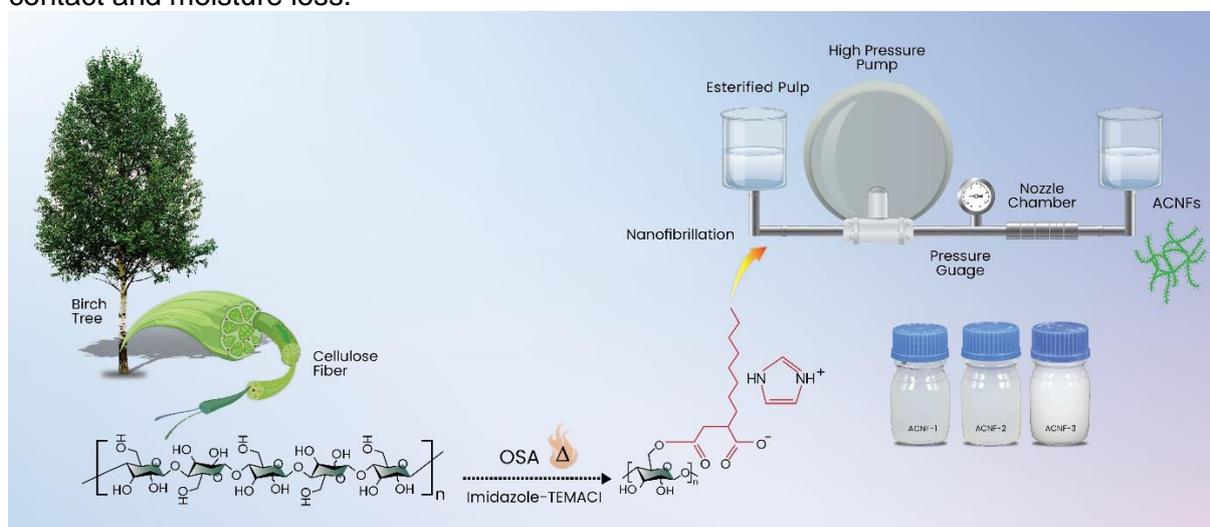


Figure. Graphical illustration of Synthesis of esterified cellulose nanofibers through the ring-opening esterification of cellulose pulp with n-octyl succinic anhydride in the deep eutectic solvent



Session 5 Poster



KEVLAR NANOFIBROUS AEROGEL-BASED TANDEM CLOAK ENABLES HIGHLY EFFICIENT THERMAL CAMOUFLAGE

Liu C. ^{*ab}, Lyu J.^c, Xiong Y.^b, Zhang X.^c, Liimatainen H.^a

^a Fiber and Particle Engineering Research Unit, University of Oulu, Finland

^b Department of Chemistry, Zhejiang Sci-Tech University, China

^c Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, China

* chenming.liu@oulu.fi

The control of thermal emission has played a significant role in various emerging fields including energy conversion, infrared sensing, thermal imaging, etc., however, long-term and highly-efficient thermal camouflage for hot object under sunlight is still a giant challenge. Herein, an Kevlar aerogel-based tandem cloak for long-term thermal emission inhibition was proposed, which composed of Janus top layer, isotropic middle layer, and Janus bottom layer. The top layer was fabricated by sputtering silver (Ag) on one-side of un-patterned Kevlar nanofibrous aerogel film (Ag|KNA), demonstrating low thermal emissivity (0.12) and high optical reflectivity (0.87). The middle layer, as an optional and thickness-adjustable layer, was realized by incorporating of phase change paraffin wax (PW) into KNA film (KNA/PW), showing phase change enthalpy of 162 J·g⁻¹. The bottom layer was fabricated by sputtering Ag on one patterned side of the KNA film (PKNA|Ag), illustrating high thermal reflectivity (0.94) and high thermal resistance (10.42 K·W⁻¹). Then flexible tandem cloak was constructed via stacking these aerogel-based top, middle and bottom layers in sequence, showing high-efficiency hiding of thermo-model targets under heating and sunshining simultaneously. This work provides a promising strategy for designing more practical tandem cloak for emerging applications.

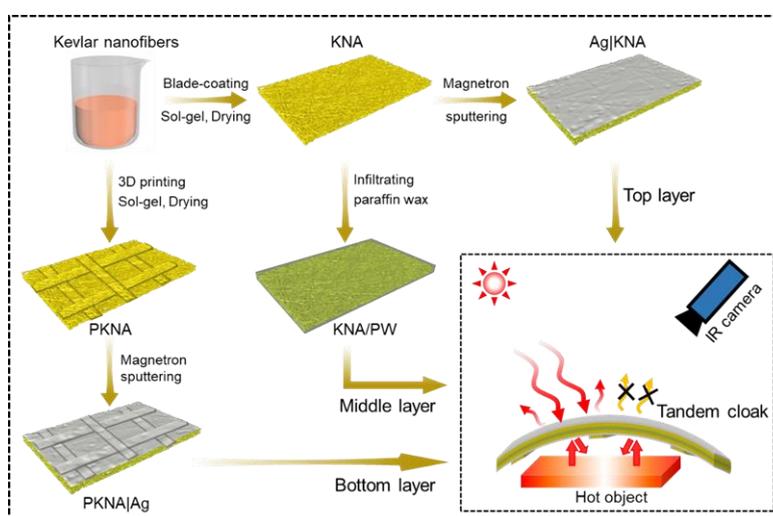


Figure 1 : Fabrication strategies of the Ag|KNA film, the KNA/PW film and the PKNA|Ag film, respectively. These films have served as top layer, middle layer, and bottom layer to construct a tandem cloak for long-term thermal emission inhibition.

[1] Hong S., Shin S. & Chen R., *Adv. Funct. Mater.*, 11,1909788, 2020

[2] Hu J., Hu Y., Ye Y. & Shen R., *Chem. Eng. J.*, 1, 139147, 2023

[3] Peng L., Liu D., Cheng S., Zhou S. & Zu M., *Adv. Opt. Mater.*, 23, 1801006, 2018



CARRAGEENANS FROM VERSATILITY ON TEXTURES TO NEW FILM PROPERTIES.

Everaert E.P.^{1*}, Lemoine C.¹, Clio D.², Fournier A.²

¹ Cargill Beauty, Global Innovation, Paris-la-Défense, France, ² Cargill Beauty, R&D, Vilvoorde, Belgium

*Presenting author: emmanuel_everaert@cargill.com

Keywords: Carrageenan, mode-of-action, sustainable sourcing, textures; film; tightening; smoothing.

OBJECTIVE: Review the 3 main types Carrageenan manufacturing and key physico-chemical properties as well as the mechanisms of film forming. The research for natural alternatives to synthetic polymer for a better sourcing and better end of life is highly demanded. This shift will impact the way to formulate but also will bring new benefits to finish products.

METHOD: The 3 types of carrageenan (ι ; κ ; λ types) showed 3 different rheological behaviors. A tertiary diagram experimental plan on these carrageenans was explored to identify the interesting stable area. On a second study, we evaluate the film with pure material and mix on ex-vivo then on in-vivo tests: Quality of film by SEM-FEG, the tightening effect by surface topography and fringe projection; firming film by Dinaskyn and cooling effect by Infra-red camera. The evaluation is completed by sensory test.

RESULTS: The carrageenan allows us to provide transparent, from fluid to classical emulsion to gel-alike mask and even to solid cosmetic like solid bar soap. We proved by rheology and sensory analysis that these natural polymers can replace synthetic polymers on finish products for serum or cream. Moreover, we surprisingly found that the carrageenan film has an excellent smoothing touch; it brings measurable tightening effect on wrinkles depth and on pores surface; It gives firmness to skin and finally cool down skin for a freshness sensation. All the results were confirmed by the expert sensory panel.

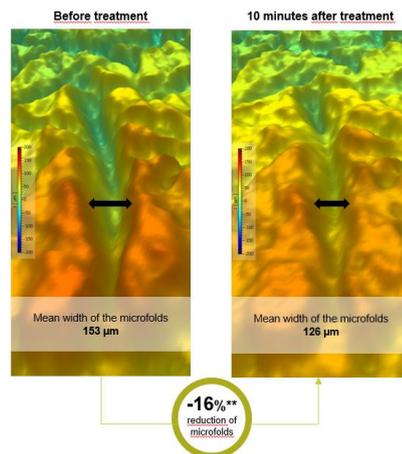


Figure 1. Skin surface topography and tightening effect on skin explant by Polytec TMS-500 light interferometer - Using topography technique. Reduction of width of microfold after application of kappa carrageenan at 1%

CONCLUSIONS: The carrageenan's are sustainable, natural and readily biodegradable. These polymers will be the reference the future of the cosmetic in order to provide a wide range of textures and even replace synthetic carbomers. Providing tightening, smoothing and colling properties, these ingredients will bring additional instant and long lasting value to finish products.



3D PRINTING OF GELATIN-CHITOSAN-GUARGUM-NANOCELLULOSE BIOMATERIAL BIOINK

Manisha Sonthalia ^{*a, b}, Amit Kumar Jaiswal^b

^a School of Bio Sciences and Technology (SBST), VIT, Vellore, 632014, Tamil Nadu, India

^b Centre for Biomaterials, Cellular and Molecular Theranostics (CBCMT), VIT, Vellore, 632014, Tamil Nadu, India

* manisha.sonthalia@vit.ac.in

The usage of 3D printed scaffolds using natural polymers for cell culture is of great demand in tissue engineering. The 3D culture enables researchers to mimic the extracellular matrix *in vitro*. Nanocellulose helps in bioink thickening and show low cytotoxicity. For our research work, this polysaccharide was extracted from banana inflorescences. The aim was to optimize the printing of gelatin, chitosan and guar gum biomaterial with nanocellulose. The printability and rheological properties were characterised. To check the biocompatibility of the 3D printed scaffold, cell viability assay was also performed. The result showed that the optimised printing helped in achieving smooth-flow printing of the given prototype model. This biomaterial bioink can used for 3D bioprinting and cell culture studies based on its low cytotoxicity outcome.

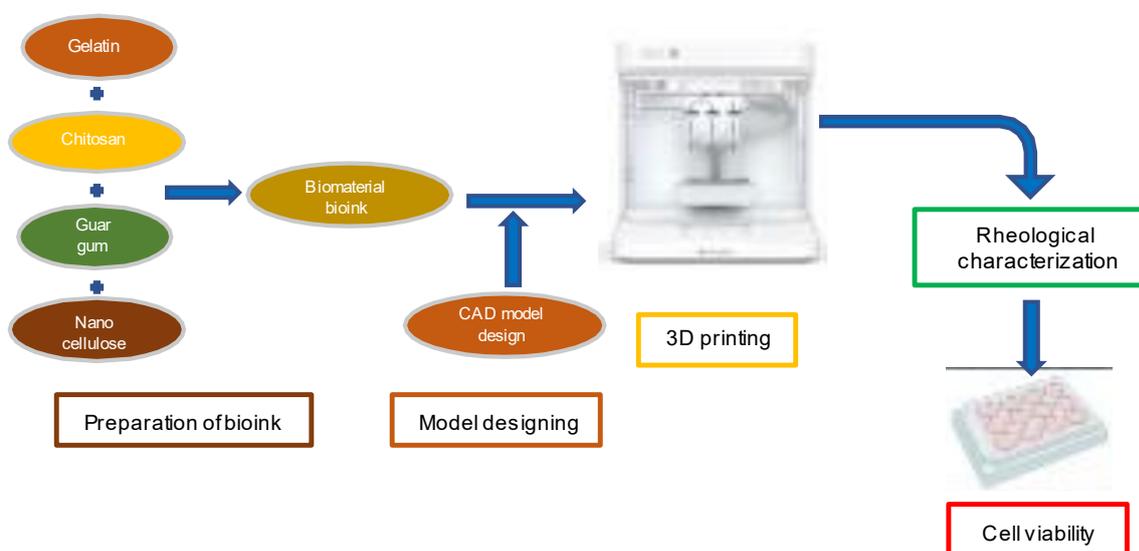


Figure 1 : Schematic representation



CELLULOSE-BASED CRYOGELS FOR OXYGEN RELEASE

Chiaregato C. G.^{*a}, Bernardinelli O. D.^b, Shavandi A.^c, Sabadini E.^d, Petri D. F. S.^a

^a Department of Fundamental Chemistry, Institute of Chemistry, USP, Brazil

^b Department of Physics, UFSCar, Brazil

^c BioMatter Unit, École Polytechnique de Bruxelles, ULB, Belgium

^d Department of Physical Chemistry, Institute of Chemistry, UNICAMP, Brazil

* camichiaregato@usp.br

The interactions between water molecules and cryogels prepared with hydroxypropyl methylcellulose (HPMC), a cellulose ether with hydrophobic methyl groups (DS) and hydrophilic hydroxypropyl groups (MS), in the presence and absence of commercial CaO₂ microparticles were investigated using kinetics experiments, structural and morphological characterization and Time-Domain Nuclear Magnetic Resonance (TDNMR). Cryogels were prepared by freezing, during 24h, and freeze-drying the gel precursor made of HPMC, with different proportions of DS and MS on its chain, containing citric acid as crosslinker and sodium hypophosphite as catalyst, followed by oven heating for esterification reaction. The effect of DS and MS of HPMC on the swelling kinetics and contact angle were studied. FTIR spectra showed absence of new bends and no shift in the principal bands, meaning that only physical interactions occurred. SEM images showed that only the presence of CaO₂ changed the morphology of the cryogels, making the cell walls rougher and heterogeneous, Fig.1 (a and b). For TDNMR, most water molecules presented transverse relaxation time t_2 typical of intermediate water and a small population of more tightly bound water. HPMC cryogels with DS of 1.9 (MS = 0.25) exhibited slow swelling rate ($0.519 \pm 0.053 \text{ g}_{\text{water}}/(\text{g}\cdot\text{s})$) and high contact angle value ($85.250^\circ \pm 0.004^\circ$), whereas those with DS of 0.75 (MS = 1.5) presented fast swelling rate ($7.29 \pm 0.92 \text{ g}_{\text{water}}/(\text{g}\cdot\text{s})$) and low contact angle ($73.5^\circ \pm 2.8^\circ$), Fig. 1 (c). The initial rate (V_0), calculated from the kinetics of O₂ release, was slower for all cryogels compared with pure CaO₂, avoiding burst release. The slowest release of O₂ was observed for CaO₂ in HPMC with the highest DS (1.9), due to the slow swelling rate, Fig. 1 (d). These findings are important for applications where tuning of swelling kinetics is critical, such as in biomedical devices or wastewater treatment.

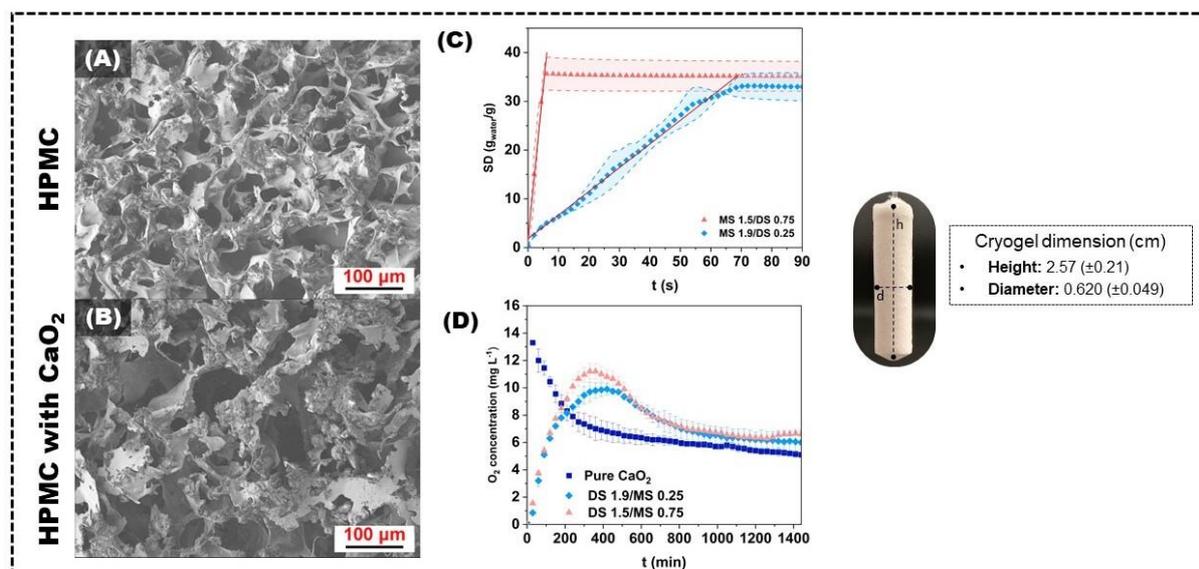


Figure 1. SEM images of (A) HPMC; (B) HPMC with CaO₂; (C) Mean values of swelling degree; (D) Kinetics of O₂ release



LIGNOCELLULOSIC MATERIALS AS EFFICIENT DEMULSIFIERS OF INDUSTRIAL LITHIUM GREASE PRODUCTION WASTE

Daiana M. F. Sandrini^{1,*}, Laíse M. Furtado¹, Denise F. S. Petri¹

¹Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes 748, 05508-000, São Paulo, Brazil

*daianamf@usp.br

In this work, the demulsification of an O/W emulsion waste from a lithium grease manufacturer was successfully achieved by low-cost bio-based filters. The filters were composed of two layers: (i) A top layer of ethanol (70% v/v) treated ground kapok fibers (KF) from the *Ceiba Speciosa* tree, and (ii) a xerogel at the bottom, which was based on sugarcane bagasse microparticles (BG, 83%) hydroxypropyl methylcellulose (HPMC, 16%), and polydopamine (PDA, 1%), as shown in Figure 1a. For comparison, KF, BG, HPMC and PDA were combined to prepare one layer filter (KF-BG). PDA and citric acid promoted the efficient interparticle adhesion and mechanical stability; whereas HPMC yielded plasticity to mold the filters in the desired shape. The filters were characterized by FTIR, SEM, and TGA. The milky O/W emulsion permeated the filters mounted in a column. The outlet was less milky and permeated the same filter five times consecutively, when the filtrate was transparent (Figure 1b), in both types of filters. Measurements of conductivity, pH, UV-vis, TGA and ICP-OES of the filtrates and original O/W emulsion indicated that the demulsification is driven by an ion-exchange between the Li⁺ ions and the protons belonging to the BG carboxylic acid groups in the 1st run, in the subsequent runs, the oil phase is complete adsorbed on the KF, enabling the complete separation.

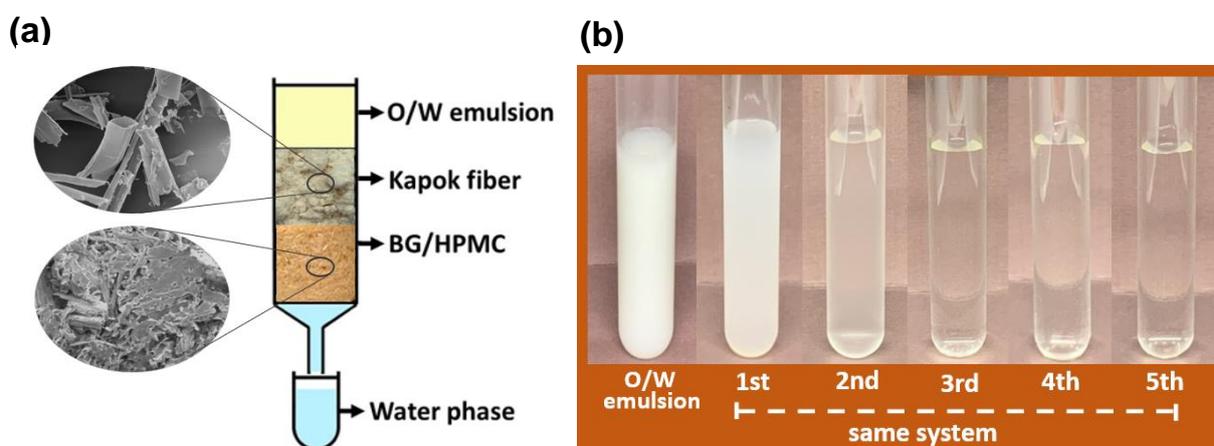


Figure 1.(a) Schematic representation of the KF and BG/HPMC filtration system and (b) photographs of the original O/W emulsion and of the filtrate after each run with the same filter. After the 5th run, the filtrate contained only the water phase.



DEVELOPMENT OF A MULTILAYER CELLULOSIC MATERIAL BASED ON CELLULOSE FOAM AND PAPER FOR WATER VAPOR BARRIER SHIFT CONCEPT IN PACKAGING.

*René Romero. ^{*a}, Fiona Pichon ^a, Stephane Dufreney, Isabelle Desloges ^a, Jérémie Viguié ^a, Julien Bras^a.*

^a Univ. Grenoble Alpes, CNRS, Grenoble INP, LGP2, 38000 Grenoble, FRANCE

*rene.romero-lezama@grenoble-inp.fr

Nowadays, new legislations in Europe as the directive on single-use plastics suggest to develop new sustainable packaging solutions limiting fossil-based materials. Thus, cellulose-based packaging materials seem to have potential for this new sustainable transition of the packaging industry, due to their bio-based character, high availability and recyclability. Developing high-performance cellulosic packaging becomes an important step to increase the shelf life and preserve the quality of different type of products and then limit use of plastics. High humidity atmospheres usually are a problem for some food, textiles and electronics products. Thus, protection from humidity is an important parameter to control when packaging is exposed to high variations of moisture. In this case, cellulosic materials are not enough water vapor barrier and petrol-based plastic films are often used in excess (overpacking) to avoid any issue. Upgrading cellulosic packaging by developing new multilayer structures is a viable way to obtain new performant properties for moisture protection. This study proposes an innovative material based on a multilayer structure of cellulose foam and barrier papers. The main goal is to develop a packaging material to protect products from humidity by using the barrier shift approach. This is based on the absorption capacity of the cellulose foam layer and the barrier capacity of the paper to control the final moisture level inside the packaging atmosphere. Firstly, cellulose foams are prepared by wet foaming process using softwood fibers and a surfactant as blow agent followed of oven drying. Once their morphology is characterized, the absorption and transfer kinetic capacity of water vapor are measured through the cellulose foam with or without polysaccharides additives such as Hydroxypropylmethylcellulose (HPMC), Carboxymethyl cellulose (CMC), xyloglucan, alginate or starch inside the foam matrix. Techniques such as Dynamic Vapor Sorption (DVS), are proposed to study the water vapor absorption capacity at different relative humidity (50-90%) of the various materials. Promising results are obtained when adding alginate by increasing water vapor adsorption cellulose foam. Then the assembling and the characterization of the structure cellulose foam/barrier paper is performed and the determination of the barrier shift character measured. The barrier shift capacity is determined by analyzing the moisture transfer kinetic using a technique developed in our laboratory and with a similar technique to the water vapor transmission rate measurement. Moreover, the moisture effect on the mechanical properties is analyzed by compression and three-point flexural test. Preliminary results are promising and the presence of the foam limit the penetration of the water vapor inside the packaging. Up to our knowledge, this is the first time such approach using various polysaccharides inside cellulosic foams is proposed as a solution to limit water vapor penetration inside secondary packaging reducing the quantity of plastic films used for moisture protection.



PROMISING POTENTIAL OF BIO-SOURCED AMPHIPHILIC XANTHAN AS AN EMULSIFIER IN O/W DISPERSIONS

About Did M.*, Gore E., Grisel M.

Normandie Univ, UNILEHAVRE, FR 3038 CNRS, URCOM, 25 rue Philippe Lebon, BP 1123, 76063 Le Havre cedex, France

*mira.abou-dib@univ-lehavre.fr

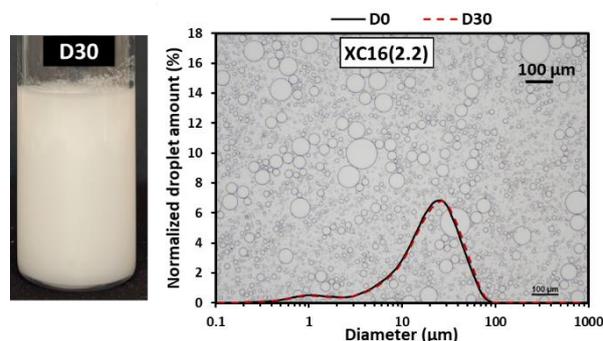
Among others, amphiphilic modified polysaccharides represent one of the green solutions to replace conventional surfactants [1], the latter being controversial because of their harmful toxicological and environmental impacts [2]. The enthusiasm for the exploitation of polysaccharides is explained by several advantages including availability, biodegradability, non-toxicity and low cost [3]; another advantage is their potential for chemical modification which allows them to acquire outstanding physicochemical properties. In the present project, xanthan polysaccharide was hydrophobically modified following the principles of green chemistry in order to enhance its interfacial properties in addition to its remarkable inherent thickening and viscosifying capacities.

A series of xanthan derivatives was first prepared through green esterification using alkenyl succinic anhydrides varying from alkyl chain length as grafting agents [4]; then corresponding chemical and physicochemical properties were characterized [5] and finally their emulsion stabilization ability was investigated by preparing oil-in-water emulsions without adding any conventional surfactant.

Results obtained on both macroscopic and microscopic scale as illustrated on Figure 1 allowed evidencing that amphiphilic xanthan (AX) owns high emulsifying potential when compared to pristine xanthan (PX), this later being known for its poor interfacial properties as a non-absorbing polymer [6]. In addition, the mechanisms responsible for AX based emulsions stabilization and destabilization were investigated through deep microstructure stability monitoring over time by Static Multiple Light Scattering, thus highlighting the effects of both the grafting rate and alkyl chain length.

This work clearly demonstrates the promising and effective emulsifying capacities for such new-brand bio-sourced amphiphilic xanthan to get stable oil-in-water emulsions of promising potential for industrial applications.

Figure 1: Photographs and optical microscopy image at D30 and droplet size distribution at D0 and D30 of the Oil-in-Water dispersion emulsified by amphiphilic xanthan



- [1] Landoll L. M., Journal of Polymer Science: Polymer Chemistry Edition 1982, 20, 443–455.
 [2] Olkowska E., Polkowska Ž. and Namieśnik J., Chemical Reviews, 2011, 111, 5667–5700.
 [3] Barclay T. G., Day C. M., Petrovsky N. and Garg S., Carbohydrate Polymers, 2019, 221, 94–112.
 [4] Abou Dib M., Hucher N., Gore E., and Grisel M., Carbohydrate Polymers, 2022, 291, 119548.
 [5] Abou Dib M., Gore E., and Grisel M., Food Hydrocolloids. 138, 2023, 108461.
 [6] Tempio J. S. and Zatz, J. L., Journal of Pharmaceutical Sciences, 1981, 70, 554–558.



THE INFLUENCE OF HEMICELLULOSE CONTENT ON THE SOLUBILITY AND REGENERATION OF BLEACHED SOFTWOOD PULP IN NOVEL IONIC LIQUID

Ahokas P. ^{*a}, Khakalo A.^a, Jaiswal A.^a, Koso T.^a, King A.W.T.^a, Spönla E.^a, Harlin A.^a, Orelma H.^a

^a VTT Technical Research Centre of Finland Ltd., Tietotie 4E, FI-02044 Espoo, Finland

* pauliina.ahokas@vtt.fi

Regenerated cellulose products are increasing research interest as sustainable alternatives to petroleum-based materials, especially in the packaging and textile industries. Most cellulose regeneration studies utilize high-purity dissolving pulps, which are known to possess higher reactivities than the more robust kraft pulps. Therefore, we investigated the influence of hemicellulose content of bleached softwood pulp on its dissolution and regeneration using novel recyclable superbase-based ionic liquid (IL). Cold caustic extraction was used to control the hemicellulose content of pulps, and alkaline hydrogen peroxide treatment was applied to control the molar mass of pulps. Commercial sulphite dissolving grade softwood pulp was used as a reference. Pulp solubilities were examined by optical microscopy and by following dissolution rates and solution qualities via rheological means.

Water was observed to improve the completeness of dissolution. Carbohydrate compositions of pulps and regenerated cellulose were analyzed via liquid-state nuclear magnetic resonance (NMR), and showed good regeneration ability of hemicelluloses within the film. Interestingly, hemicellulose was noticed to enhance the mechanical properties of regenerated cellulose films that were measured by tensile measurements. The pulp treatment methods proposed in the study, allowed fabrication of regenerated cellulose films with enhanced mechanical properties compared to films prepared from commercial reference pulp. Fundamental information about the influence of hemicellulose and water contents in aqueous pulp-IL solutions on the solubility of pulps and characteristics of regenerated films is presented.

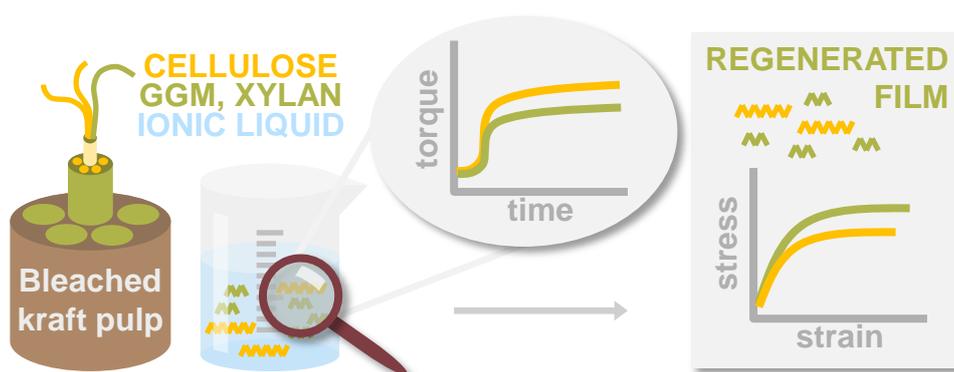


Figure 1 : A schematic representation for the effect of hemicellulose on solution viscosity and mechanical properties of regenerated cellulose films. [1]

[1] Ahokas P., Khakalo A., Jaiswal A., Koso T., King A.W.T., Spönla E., Harlin A. & Orelma H., *Effect of the carbohydrate composition of bleached softwood pulp on its dissolution and regeneration using the ionic liquid*, 2023, Manuscript submitted for publication.



ANTIOXIDANT FILMS AND COATINGS FROM NANOCELLULOSE-STABILIZED EMULSIONS OF THYME ESSENTIAL OIL IN WATER

Aguado R.J. ^{a,b}, Saguer E. ^{a,b}, Fiol N. ^b, Tarrés Q. ^{a,b}, Marc Delgado-Aguilar ^{a,b}

^a LEPAMAP-PRODIS Research Group, University of Girona, Spain

^b Department of Chemical and Agricultural Engineering and Agrifood Technology, University of Girona, Spain

* roberto.aguado@udg.edu

The essential oil in *Thymus vulgaris* (thyme) is rich in thymol, an antioxidant phenolic compound, although the overall beneficial effect of this essential oil likely owes to the synergy between thymol and other components, namely carvacrol and linalool [1]. With an aqueous solubility below 0.1 vol%, stabilizing agents are needed to attain durable emulsions,

This communication presents the stabilization of 10 vol% thyme essential oil in water, using 1 wt% or less of regioselectively oxidized cellulose nanofibers. Emulsions were highly stable, as coalescence was prevented even after 60 days of storage (Figure 1). The role of the nanofibers in the resulting emulsions is not only that of Pickering stabilizer, but they also can act as rheology modifiers, film-forming agents, and binders for paper coating. Films were produced by solvent evaporation and testliner paper was coated with the aforementioned emulsions. To assess the function of these films and paper sheets as natural antioxidant emitters to lipophilic foodstuffs, they were placed in food simulant D1 (ethanol 50 vol%) and the liquid was submitted to the Folin-Ciocalteu test and to 2,2-diphenyl-1-picryl-hydrazyl-hydrate (DPPH) inhibition assays. All in all, they showed significant reducing and antioxidant activity. Moreover, the release rate to air or water was slow enough to store said films and sheets for long times until the emission of the oil components to lipophilic media is forced.

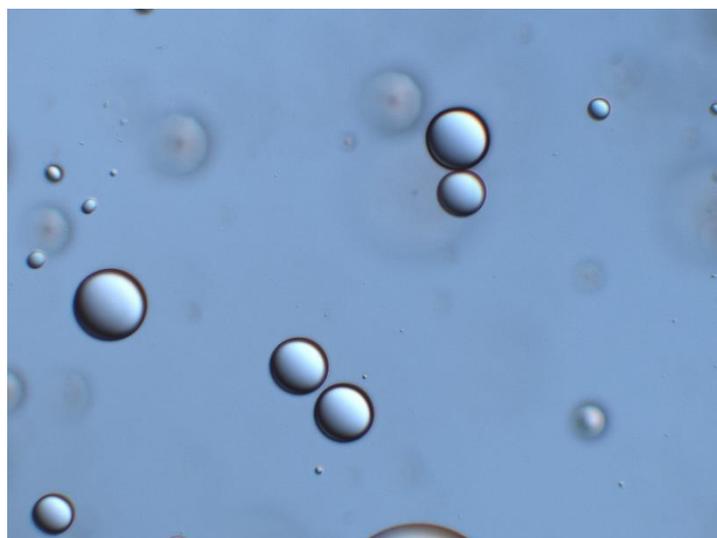


Figure 1 : Optical micrography of a nanocellulose-stabilized emulsion of thyme essential oil in water, showing non-coalescing doublets.

[1] Gavaric N., Mozina S.S., Kladar N., Bozin B., *J. Essent. Oil. Bear Pl.*, 18, 1013–1021, 2015.



RHEOLOGY AND MICROSTRUCTURES OF CONCENTRATED LOW-MOLAR MASS XYLOGLUCAN MIXED WITH CELLULOSE NANOCRYSTALS

Voisin H., Vasse A., Bonnin E., Capron I.

UR1268 BIA, INRAE, Nantes, France

* hugo.voisin@inrae.fr

Whether it comes from nature or from industrial waste, plant biomass constitutes an important renewable resource on Earth. This biomass is mainly composed of polysaccharides present in the plant cell wall, such as cellulose and hemicelluloses, which include xyloglucan (XG). Cellulose nanocrystals (CNC) are nano-sized crystalline particles, while XG is a water-soluble polymer. CNC-XG interactions have already been studied for the elaboration of various biobased materials, such as aerogels, hydrogels or films. In this study, we have elaborated CNC-XG assemblies by focusing on systems with a high concentration of CNC (>60 g/L) and with specially prepared very low-molar mass XG between 20 000 g/mol and 40 000 g/mol. These conditions led to the observation of rich rheological behaviors, depending on the concentration and molar mass of the XG. This difference in behavior is due to the variety of microstructures formed depending on the XG conformation on the CNC surface. All these results provide fascinating insights on the variety of architectures and properties obtained from biobased particles-polymer systems, as well as potential information on the cellulose-XG interactions involved in the plant cell wall.¹

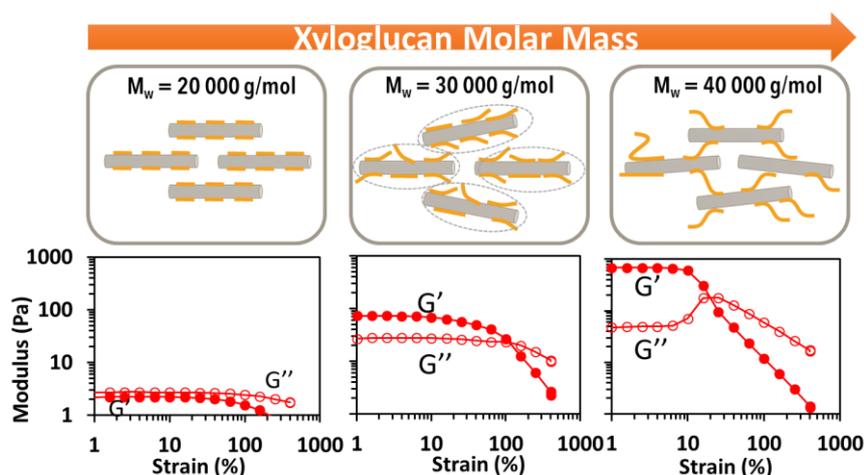


Figure 1: Influence of XG molar mass on the CNC-XG structures and rheology

- (1) Voisin, H.; Vasse, A.; Bonnin, E.; Capron, I. Influence of Low-Molar-Mass Xyloglucans on the Rheological Behavior of Concentrated Cellulose Nanocrystal Suspensions. *Biomacromolecules* **2023**, *24* (1), 358–366. <https://doi.org/10.1021/acs.biomac.2c01172>.



PIPERONYL-IMINO-CHITOSAN HYDROGELS AS PLATFORM FOR DRUG DELIVERY APPLICATIONS

Ailincăi D.^{*a}, Rosca I.^a, Marin L.^a

^a Polycondensation and Thermostable Polymers, "Petru Poni" Institute of Macromolecular Chemistry, Romania

*ailincăi.daniela@icmpp.ro

Infections caused by microorganisms have been always a serious problem related to human healthcare, being considered by World Health Organization a global health priority. Among microorganisms, *Candida* is one of the most opportunistic and virulent one, the infections caused by *Candida* being a cause of mortality worldwide, especially in the case of immunocompromised patients. Its virulence is given by the ability to change its morphology from yeast to biofilm, which is far more resistant [1]. The present study reports the obtaining and characterization of new hydrogels and drug delivery systems (DDSs) based on piperonyl-imino-chitosan derivatives and Amphotericin B antifungal drug. The hydrogels were synthesized by the acid condensation of chitosan amino groups with the aldehyde group of piperonal monoaldehyde, followed by the self-assembling of the obtained derivatives due to hydrophobic/hydrophilic segregation, while the drug delivery systems were obtained by the *in situ* hydrogelation of chitosan with piperonal in the presence of Amphotericin B [2].

The hydrogels and the DDSs were characterized from the structural point of view by FTIR spectroscopy and NMR spectroscopy, which revealed the success of the imination even in the presence of the drug. The supramolecular architecture of the systems was evaluated by polarized optical microscopy and wide-angle X-ray diffraction, demonstrating the high degree of ordering of the obtained systems at supramolecular level, along with the homogenous encapsulation of the drug into the hydrogels. The characteristics of the systems were further investigated in the view of their applications, demonstrating their biodegradability, their high swelling ability and last but not least their ability to release the antifungal drug in a sustained manner. The evaluation of the antifungal activity of the DDSs was done *in vitro* by the Kirby Bauer method, and very good results were obtained, revealing the high potential of these materials to be used for the treatment of different types of *Candidiasis*.



Figure 1. The activity of the samples against *Candida parapsilosis*

Selective references:

1. Lopes J.P., Lionakis M., Virulence, 13, 89-121, 2022
2. Ailincăi D., Rosca I., Polymers, 15, 753, 2023

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PCE2/2021 within PNCDI III.



NANOCHITIN-JAMMED BICONTINUOUS EMULSIONS

Y. Lu^{*a}, M. Kamkar^{a,b}, S. Guo^a, X. Niu^a, L. Bai^c, O.J. Rojas^{a,d}

^a *Bioproducts Institute, Department of Chemical and Biological Engineering, Department of Chemistry and Department of Wood Science, University of British Columbia, Canada*

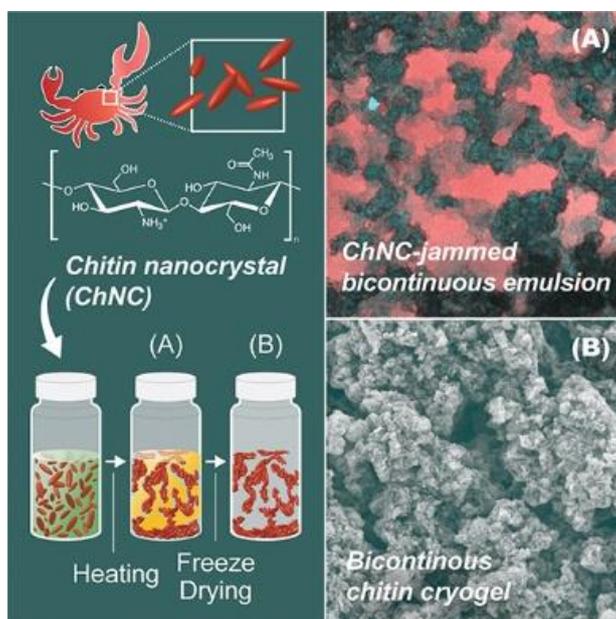
^b *Department of Chemical Engineering, Waterloo Inst. Nanotechnology, University of Waterloo, Canada*

^c *Key Laboratory of Bio-Based Material Science and Technology (Ministry of Education) Northeast Forestry University, China*

^d *Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland*

* yi.lu@ubc.ca

Non-equilibrium multiphase systems were formed by mixing two immiscible phases, leading to bicontinuous emulsions that were used to template cryogels with interconnected, tortuous channels. We use a renewable, rod-like biocolloid (chitin nanocrystals, ChNC) to kinetically arrest bicontinuous morphologies. Specifically, we found that ChNC stabilizes intra-phase jammed bicontinuous systems at ultra-low particle concentrations (as low as 0.6 wt.%), leading to tailorable morphologies. The synergistic effects of ChNC high aspect ratio, intrinsic stiffness, and interparticle interactions produced hydrogelation and, upon drying, led to open channels bearing dual characteristic sizes, suitably integrated into robust bicontinuous ultra-lightweight solids. Overall, we demonstrate the successful formation of ChNC-jammed bicontinuous emulsions and a facile emulsion templating route to synthesize chitin cryogels that form unique super-macroporous networks.



[1] Lu, Y., Kamkar, M., Guo, S., Niu, X., Wan, Z., Xu, J., Su, X., Fan, Y., Bai, L.*, and Rojas, O.J.*, *Small*, In press, 2023



BIOAEROGELS FROM ORANGE JUICE SIDE-STREAMS

Possari L. T.^{*a}, Otoni C. G.^b, Bettini S. H. P.^{a, b}

^a *Federal University of Sao Carlos, Graduate Program in Materials Science and Engineering, Brazil.*

^b *Federal University of Sao Carlos, Department of Materials Engineering, Brazil.*

* lais.possari@estudante.ufscar.br

The orange juice industry generates huge amounts of residues, since 50-60 wt.% of the fruits are turned into by-products during processing. On a global scale, it is estimated that 54 million tons of these side-streams are produced annually. The disposal of such can lead to serious environmental problems, such as groundwater contamination, disturbance of the soil microbiome, and proliferation of pests and diseases. As consequence, they must be properly treated before disposal, leading to increased costs for the industries. When not landfilled, these side-streams are either incinerated or used in slaughter animal feed production. [1] It is desirable, therefore, to upcycle these side-streams into higher-added value applications. Converting them into new and more sustainable materials has been considered as a promising strategy because these residual biomasses are mainly constituted by natural polymers (such as pectin, starch, cellulose, hemicellulose) and also have bioactive substances like flavonoids and limonoids. [2]

Unutilized orange parts, such as peels and residual pulps, are rich in pectin (25-30 wt.% of the dried raw material). [3] Therefore, upcycling orange agro-industrial side-streams into aerogels is promising. In this work, bioaerogels were produced by a simple method that does not require pectin extraction. Aqueous suspensions were prepared with dried and ground orange residues in the presence of citric acid and converted into a pectin-rich liquid phase with dispersed insoluble fibers upon heating and homogenization. The suspensions were then coagulated with ethanol prior to drying with supercritical carbon dioxide (sCO₂). Pectin reference samples were produced for comparison purposes, as well as samples of each individual fraction of which the residual orange biomass is composed – namely: peel, bagasse, and residual pulp (representing 56, 28, and 16 wt.%, respectively). Soluble polysaccharides were quantified gravimetrically after ethanol-induced precipitation and drying, and characterized by Fourier-transform infrared (FTIR) spectroscopy. The rheological behaviors of the suspensions and coagulated gels were evaluated. The morphology of the obtained bioaerogels was assessed by scanning electron microscopy (SEM) and density measurements.

[1] Teigiserova D. A. et al. *Journal of Environmental Management*, 280, 111832, 2021.

[2] Otoni C. G. et al. *Advanced Materials*, 33, 2102520, 2021.

[3] Budtova T. et al. Biorefinery approach for aerogels. *Polymers*, 12, 2279, 2020.



Session 6

Polysaccharide in food and nutrition

Session organizers:

Laura Nyström, Gleb Yakubov, Maija Tenkanen, Caio Otoni

Keynote speaker:

Robert Gilbert

Starch molecular structure and diabetes



STARCH MOLECULAR STRUCTURE AND DIABETES

Gilbert Robert G. ^{*a,b}, Jihui Zhu^{a,b}

^a *College of Agriculture, Yangzhou University, China*

^b *Centre for Nutrition & Food Science, University of Queensland, Australia*

* b.gilbert@uq.edu.au

Starch is a complex branched glucose polymer, and is the largest single component of human food energy. Rice, which is largely starch, is one of the most important foods for the world's people. Steamed white rices that are popular with consumers are usually quick to digest, which is however disadvantageous to metabolic health. However, varieties which are slow to digest are generally regarded as less palatable. Starch molecular structure is a major determinant of both properties. Starch structure includes distinct attributes, such as the chain-length distribution of debranched chains and the size distribution of (unbranched) whole molecules; these are measured with tools familiar to polymer scientists, such as size-exclusion chromatography. While some structural attributes control both properties, it is found that there are some structural features which are significant determinants for one property and not the other. Here, a novel means of using this fact to overcome these competing demands of slow digestibility and acceptable palatability is explored. The chain-length distributions (CLDs) and in vitro digestibility of 98 varieties, and palatabilities of 9 market varieties, were measured using SEC for the CLDs, and human panelists for palatability. The CLDs were parameterized with biosynthesis-based models, one each for amylopectin and for amylose. Four structural features of the CLDs, involving the amounts of short and long chains in various CLD regions, showed significant correlations, with correlation coefficients having opposite signs for both digestibility and palatability, and which thus were the key factors in the conflicting demands of slower digestibility versus acceptable palatability. It was also found that different structural parameters were dominant for digestibility and palatability. Hence optimizing these two separate sets of parameters provides a means of finding an overall set of structural parameters which can be used to give the best combination of lower digestibility and acceptable palatability. Because the genes controlling these CLDs have been established, this can help rice breeders to develop varieties which give the best compromise for simultaneously optimizing both properties.



STARCH HYDROLYSIS BY AMYLASE: A CLOSE LOOK AT THE FIRST-ORDER REACTION RATE CONSTANT

Yuzy Wang^a, Kamal Kansou^{a*}, Jean-Philippe Raï^b, Luc Saulnier^a

^a INRAE, UR1268, Biopolymers, Interactions & Assemblies (BIA), 44316, Nantes, France

^b CSIRO Agriculture and Food, GPO Box 1700, Canberra ACT 2601 Australia.*
kamal.kansou@inrae.fr

The enzymatic hydrolysis of starch, called amylolysis, converts starch into soluble glucans and glucose through the catalytic action of amylolytic enzyme (amylase and amyloglucosidase). It is central in biological processes (human/animal digestion, grain germination) and in industrial processes (malting, bioethanol production). Determining the rate and the extent of the amylolysis has always been an important topic for the research area, especially for its expected role in human nutrition. The typical in-vitro starch digestion assay involves a digestive α -amylase e.g. porcine pancreatic α -amylase. The amylolysis is a heterogeneous reaction, that takes place at the interface between the solid phase (starch) and the liquid phase that conveys the enzyme. Amongst the various models that can describe the amylolysis kinetics, the most popular is the pseudo-first order reaction model usually cast in its integrated form: $X_t = X_\infty (1 - e^{-k t})$. Where t is hydrolysis time, X_t is the instantaneous hydrolysis extent, X_∞ is $X_{t=\infty}$, k is the reaction rate coefficient. The successful fitting of this equation to amylolysis measurements would imply that the reaction rate is proportional to the amount of digestible starch following the coefficient k . k is generally assumed constant in publications, however in practice a time-dependent coefficient can give better fitting results [1]. The determinants for this time-dependency are still ill-known.

This work presents a rigorous characterisation of the time dependency of the reaction rate coefficient for various starch substrates. To this end, we have compiled and analysed the hydrolysis kinetics of two hundred wheat starches and several starchy materials obtained with extrusion, retrogradation and cryo-grinding to produce samples with controlled properties. Our results revealed that the reaction rate coefficient time-dependency can be approximated in a first approach by a simple model (Fig.1). The parameters of this empirical model are clearly affected by substrate characteristics such as the average particle size, the amylose/amylopectin ratio and the crystalline order. It is worth mentioning that the pseudo first-order model is a special case of this generic model. This result can be used to improve the kinetics analysis of in-vitro starch digestion.

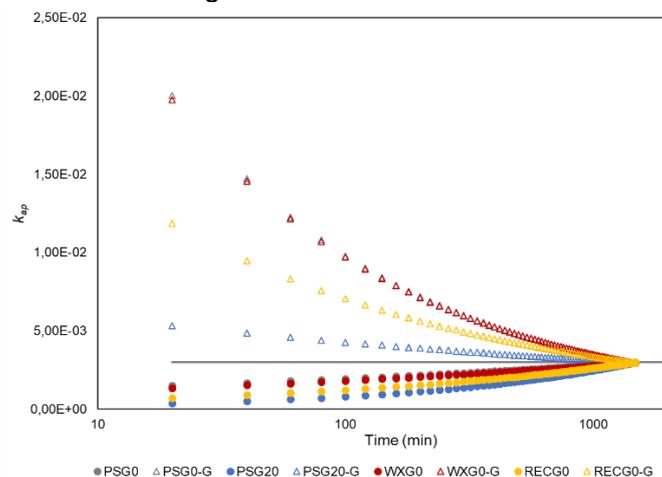


Figure 1 : simple model of the reaction rate coefficient (k_{ap}) over time for different extruded starch samples

[1] Kansou, K., Buléon, A., Gérard, C., & Rolland-Sabaté, A. *Carbohydrate Polymers*, 123, 266–274, 2015.



TOPOCHEMICAL DESIGN OF CELLULOSE-BASED CARRIERS FOR IMMOBILIZATION OF ENDOXYLANASE

De Wever P.^{*a}, De Schepper C.^b, Poleunis C.^c, Delcorte A.^c, Courtin C.M.^b, Fardim P.^a

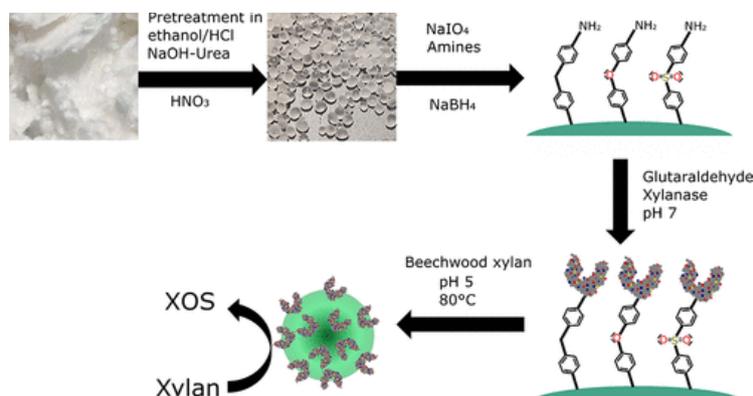
^a Department of Chemical Engineering, Chemical and Biochemical Reactor Engineering and Safety Section, KU Leuven, Belgium

^b Department of Microbial and Molecular Systems, Laboratory of Food Chemistry and Biochemistry & Leuven Food Science and Nutrition Research Centre (LFoRCe), KU Leuven, Belgium

^c Institute of Condensed Matter and Nanosciences, UCLouvain, Belgium

* pieter.dewever@kuleuven.be

Xylooligosaccharides (XOSs) gained much attention for their use in food and animal feed, attributed to their prebiotic function. These short-chained carbohydrates can be enzymatically produced from xylan, one of the most prevalent forms of hemicellulose. In this work, endo-1,4- β -xylanase from *Thermotoga maritima* was immobilized on cellulose-based beads with the goal of producing xylooligosaccharides with degrees of polymerization (DPs) in the range of 4–6 monomeric units. More specifically, the impact of different spacer arms, tethers connecting the enzyme with the particle, on the expressed enzymatic activity and oligosaccharide yield was investigated. After surface functionalization of the cellulose beads, the presence of amines was confirmed with time of flight secondary ion mass spectrometry (TOF-SIMS), and the influence of different spacer arms on xylanase activity was established. Furthermore, XOSs (DPs 2–6) with up to 58.27 mg/g xylan were obtained, which were greatly enriched in longer oligosaccharides. Approximately 80% of these XOSs displayed DPs between 4 and 6. These findings highlight the importance of topochemical engineering of carriers to influence enzyme activity, and the work puts forward an enzymatic system focusing on the production of longer xylooligosaccharides. [1]



[1] De Wever P., De Schepper C., Poleunis C., Delcorte A., Courtin C.M. & Fardim P., *Biomacromolecules*, 24 (1), 132-140, 2023



FUNCTIONALIZATION OF FOOD HYDROCOLLOIDS USING ENZYMES

Frommhagen M.^{*a}, Merz M.^a, Vafeiadi C.^a

^aNestlé Research, Institute of Food Science, Lausanne, Switzerland

*matthias.frommhagen@rd.nestle.com

Currently, hydrocolloids are extensively used in the food industry. These hydrocolloids are a heterogeneous group of long chain polymers, like polysaccharides and proteins, that are characterized by their thickening and gelling behavior in aqueous solutions. Knowledge on how the fine structure of these hydrocolloids drive functionality has already been built through years of research and ingredient development. To achieve such modifications of the rheology of food systems, these hydrocolloids which are naturally present in plants are often chemically extracted and modified to obtain a purified ingredient.

Alternative technologies to minimize the use of these purified hydrocolloids are highly desired by the food industry. Today, food products are being judged by the consumer not only by their sensorial attributes, but also by the ingredients and methods employed for their production [1]. The use of purified ingredients in food products is associated with unfamiliar names on the ingredient list. Therefore, one of the key drivers of the food industry is the development of alternative technologies that lead to clean label products comprising ingredients which are perceived as more natural and familiar by the consumer. Moreover, sustainable development goals of the food industry evoke a strong interest in food production practices including the use of ingredients that are more environmentally friendly.

In this research, we explored the potential of an enzyme-based technology to reduce the use of chemically extracted hydrocolloids, like carbohydrates, in food systems. Therefore, carbohydrates that are intrinsically present in the plant cell wall were modified using fungal and plant-derived carbohydrate-active enzymes. The latter were identified and characterized in commercially available enzyme preparations. Based on these findings, tailor-made enzymes were expressed to study in a greater detail their mode of action and impact on the techno-functional properties of carbohydrates.

In conclusion, the modification of hydrocolloids using enzymes has the potential to contribute to the development of more sustainable technologies that enable industry to offer more natural and, therefore, clean label food products to the consumer.

[1] Varela, P., & Fiszman, S. M. (2013). Exploring consumers' knowledge and perceptions of hydrocolloids used as food additives and ingredients. *Food Hydrocolloids*, 30(1), 477-484.



AN NMR APPROACH TO FOLLOW THE STRUCTURAL MODIFICATION OF NATIVE APPLE PECTIN DURING DIGESTION

Clara Comuzzi*, Marilisa Alongi, Umberto Lanza, and Lara Manzocco

*Department of Agricultural, Food, Environmental and Animal Sciences, University of Udine,
Via delle Scienze 206, I-33100 Udine, Italy*

* clara.comuzzi@uniud.it

Dietary fiber (DF) is involved in many biological functions. These can be attributed not only to the native polymers but also to the oligomers formed during metabolic events. Since DF bioactivity is mainly carried out at the intestinal level, understanding if and to what extent modifications can occur during its journey throughout the gastrointestinal tract is crucial to correlate biological functions with DF composition and structural characteristics. Here an NMR approach to qualitatively and semi-quantitatively follow the degradation pathway of a bioactive polysaccharide under simulated gastrointestinal conditions is proposed. The method was applied to pursue the gastrointestinal fate of *Golden Delicious* apple pectin contained in apple tissues characterized by different levels of mechanical disintegration, *i.e.*, intact pulp, puree, and homogenate. Experiments were also performed on model systems of native pectin extracted from the fruit. One and two-dimensional NMR experiments (^1H , ^{13}C , COSY, HSQC, TOCSY, HSQC-TOCSY, HMBC, and NOESY) were collected to gain insight into the structural modification of the heteropolysaccharide as affected by different gastrointestinal parameters (*i.e.*, pH, bile salts, enzymes). The results indicated that the extent of pectin degradation was influenced by the intensity of mechanical disintegration of the vegetable matrix. Results also suggest a crucial role of upper gastrointestinal parameters in inducing pectin degradative reactions.



STUDIES ON THE FORMATION OF EXOPOLYSACCHARIDES IN FERMENTED BEVERAGES

Hassler, V.^{*a}, Brand, N.^a, Messerschmidt, R.^a, Wefers, D.^a

^a *Institute of Chemistry, Food Chemistry – Functional Food, Martin-Luther-University Halle-Wittenberg, Germany*

* verena.hassler@chemie.uni-halle.de

Fermented beverages such as water kefir and kombucha enjoy great popularity, because consumers prefer “natural” and homemade food. These beverages are produced by fermenting sucrose-containing formulations with microorganisms (mainly lactic and acetic acid bacteria). The respective organisms are known to produce potentially prebiotic exopolysaccharides via glucan- or fructansucrases. However, little is known about the biopolymers formed or the enzymes involved into polysaccharide production, therefore, these aspects were investigated in detail.

To analyze the exopolysaccharide formation in kombucha, green and black tea kombucha were prepared using starter cultures of different manufacturers. The polysaccharide fraction was then isolated and characterized using various analytical approaches. Acid hydrolysis and subsequent quantification of the monosaccharides showed that fructans were predominantly produced during the fermentation. The analysis of the linkage types by methylation analysis, the analysis of enzymatically produced oligosaccharides, and one- and two-dimensional NMR spectroscopy showed that the produced fructans were levans. Depending on the type of starter culture and the cultivation medium, the levans showed a different degree of branching and a varying concentration in the beverage.

It has already been demonstrated that water kefir contains mainly dextrans and that the isolated microorganisms produce different types of dextrans [1,2]. For example, *Leuconostoc (Lc.) citreum* TMW 2.1194 forms a complex dextran with a high portion of branches at position O4 and O3. However, it wasn't possible to explain the high degree of branching at position O3 with the of the four previously characterized glucansucrases from this organism. Further investigations led to the identification of another glucansucrase in the genome that could be responsible for the insertion of side chains. This enzyme was produced recombinantly and used to modify enzymatically produced α -glucans. In various co-incubations an increased degree of branching at position O3 was observed. Thus, the fermentative production of dextrans by *Lc. citreum* TMW 2.1194 occurs via two different glucansucrases.

Overall, fermented beverages represent a source of different potentially prebiotic exopolysaccharides and the microbial exopolysaccharide production may contribute to the postulated health-promoting properties of kombucha and water kefir.

[1] Fels, L., Jakob, F., Vogel, R. F. & Wefers, D., *Carbohydrate Polymers*, 189, 296–303, 2018

[2] Münkler, F., Bechtner, J., Eckel, V., Fischer, A., Herbi, F., Jakob, F. & Wefers, D., *Journal of Agricultural and Food Chemistry*, 67, 6856–6866, 2019



CORRELATING PHYSICOCHEMICAL PROPERTIES OF PEA POLYSACCHARIDES TO THEIR *IN VITRO* FAECAL FERMENTATION

Karlsson J.^a, Lopez-Sanchez P.^b, Marques T.^c, Krona A.^d, Ström A.^a

^a Division of Applied Chemistry, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Sweden.

^b Food Technology, Dept Analytical Chemistry, Nutrition and Food Science, University of Santiago de Compostela, Campus Lugo, Spain.

^c Faculty of Health and Medicine, School of Medical Sciences, Örebro University.

^d RISE Research Institute of Sweden, Agriculture and Food, Sweden

* jakkarl@chalmers.se

A healthy and sustainable diet includes plant-based or plant-derived proteins and intake of dietary fibre. Field pea (*Pisum Sativum* L.) consists of 20-30% protein and 15-25% dietary fibres, making peas interesting due to its high nutritional values. Another aspect is the possibility to grow peas in temperate climates, which is not possible for e.g., soy. We aim to characterize the physicochemical properties of pea polysaccharides as a function of thermal processing and correlate them to their microbial fermentation products after batch *in vitro* fermentation with human faecal microbiota.

Chemical composition of pea polysaccharides was examined through hydrolysis of fibres followed by monosaccharide analysis. In addition, starch and uronic acid content was determined. Rheological properties, such as viscosity, storage- and loss modulus were performed at different temperature to understand the behaviour of the polysaccharide suspensions. Confocal laser scanning microscopy (CLSM) and light microscopy (Figure 1) was used to identify swelling of pea polysaccharides after thermal processing, as well as visualising the microstructure of the fibre. Future studies include *in vitro* faecal fermentation of pea polysaccharide-protein blends.



Figure 1. Light microscopy image of pea hull polysaccharide before *in vitro* faecal fermentation. Scale bar 50 μ m.



PLASTICIZED, GREASEPROOF, AND TRANSPARENT FOOD PACKAGING BIOPLASTICS FROM CHITIN-RICH WASTES

Guzman-Puyol S. ^{*a}, Benítez JJ.^b, Giacomo Tedeschi^c, Yandira Morales^d, Dolores Fernández-Ortuño^d, Athanassia Athanassiou^c, Heredia-Guerrero JA.^a

^a Instituto de Hortofruticultura Subtropical y Mediterránea "La Mayora" (IHSM, UMA-CSIC), Bulevar Louis Pasteur 49, 29010, Malaga, Spain.

^b Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, Calle Americo Vespucio 49, Isla de la Cartuja, Sevilla 41092, Spain.

^c Smart Materials, Istituto Italiano di Tecnologia, Via Morego, 30, Genova, 16163, Italy.

^d Instituto de Hortofruticultura Subtropical y Mediterránea "La Mayora", Universidad de Málaga-Consejo Superior de Investigaciones Científicas (IHSM, UMA-CSIC), Departamento de Microbiología, Bulevar Louis Pasteur 49, 29010, Malaga, Spain.

* susana.guzman@csic.es

Conventional petroleum-based plastics are one of the most widely used materials in the world. Food packaging accounts as the largest end-use market, with ~40% of the global production. However, production and disposal of petroleum-based plastics have significant environmental impacts. In this sense, bioplastics constitute a promising alternative for the substitution of petroleum-based food packaging materials. Conversion of food wastes into bioplastics is a practice that is gaining interest in the last years. In particular, the seafood industry generates ~25 million tons of wastes globally, being mainly composed by chitin, a highly-ordered, intractable polymer insoluble in most of the common solvents.

In this work, we report the fabrication of transparent, robust, and biodegradable bioplastics from chitin and glycerol as a plasticizer by using a mixture of trifluoroacetic acid (TFA) and trifluoroacetic anhydride as a common solvent. First, the effect of the solvents on the chemical and thermal properties and crystallinity of chitin was studied, revealing an amorphous structure, as determined by X-ray diffraction, Figure 1A,B. Second, the role of glycerol on the final properties of the bioplastics was systematically investigated and compared to other natural and synthetic polysaccharides. In particular, the incorporation of glycerol modified the mechanical properties by inducing a plasticizer effect, Figure 1C, and improved the transparency. In addition, hydrodynamic and barrier properties were determined by contact angle and water vapor and oxygen transmission rates, respectively, revealing typical values of other polysaccharides. These bioplastics also presented an excellent greaseproof behavior and overall migration values in compliance with the European regulation as well as antifungal properties against *Botrytis cinerea* and high biodegradation rates in seawater. In view of the results, the potential use of these bioplastics as food packaging materials is suggested.

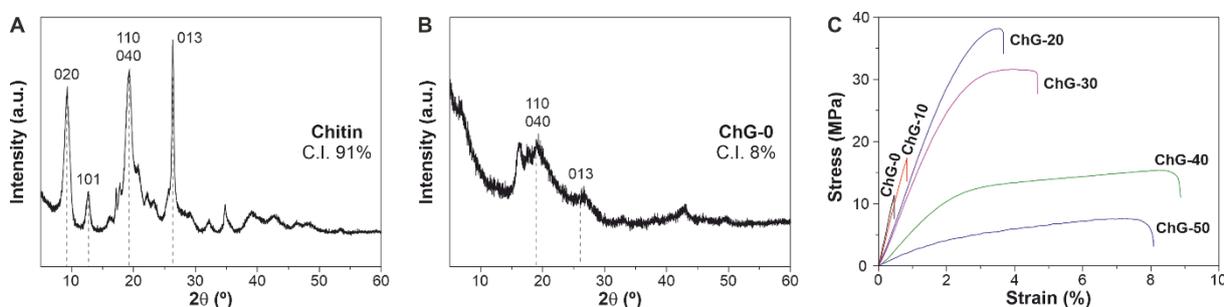


Figure 1. A,B, X-ray diffraction curves of chitin before and after the acidic treatment, respectively. C, stress-strain curves of chitin-glycerol films.



CARRAGEENAN-BASED ACTIVE AND INTELLIGENT PACKAGING FILM INTEGRATED WITH TiO₂-DOPED CARBON DOTS AND SWEET POTATO ANTHOCYANIN

Riahi Z. ^{*a,b}, Kim JT. ^{a,b}

^a Department of Food and Nutrition, Kyung Hee University, Republic of Korea

^b BioNanocomposite Research Center, Kyung Hee University, Republic of Korea

* Zohreh.riahi95@gmail.com

Multifunctional smart nanocomposite indicator films were fabricated using carrageenan (CAR) and sweet potato anthocyanin (SPA) combined with TiO₂-doped sweet potato-derived carbon dots (TSP-CDs). The synthesized TSP-CDs exhibited potent antibacterial activity against *L. monocytogenes*, *S. aureus*, *S. enterica*, and *E. coli* and high antioxidant efficacy against ABTS and DPPH radicals (~100% at 100 µg/mL). The addition of anthocyanin and 1,3 wt% TSP-CDs donated antioxidant and antimicrobial capabilities to the polymer matrix and improved its physicochemical and UV-blocking characteristics. The carrageenan-based indicator film showed discoloration from red to brown according to pH 2-12 adjustments. As an indicator of spoilage, the designed nanocomposite film was used for shrimp packaging, and a visual color change from red (for fresh shrimp) to brown (for spoiled shrimp) was observed concurrently with a rise in total volatile basic nitrogen and a change in the pH of the packaged sample during the storage. Active and intelligent nanocomposite indicator film based on CAR/SPA/TSP-CDs is expected to be applied as multifunctional smart packaging materials that can display food quality changes, maintain quality, and extend the shelf life of packaged foods.

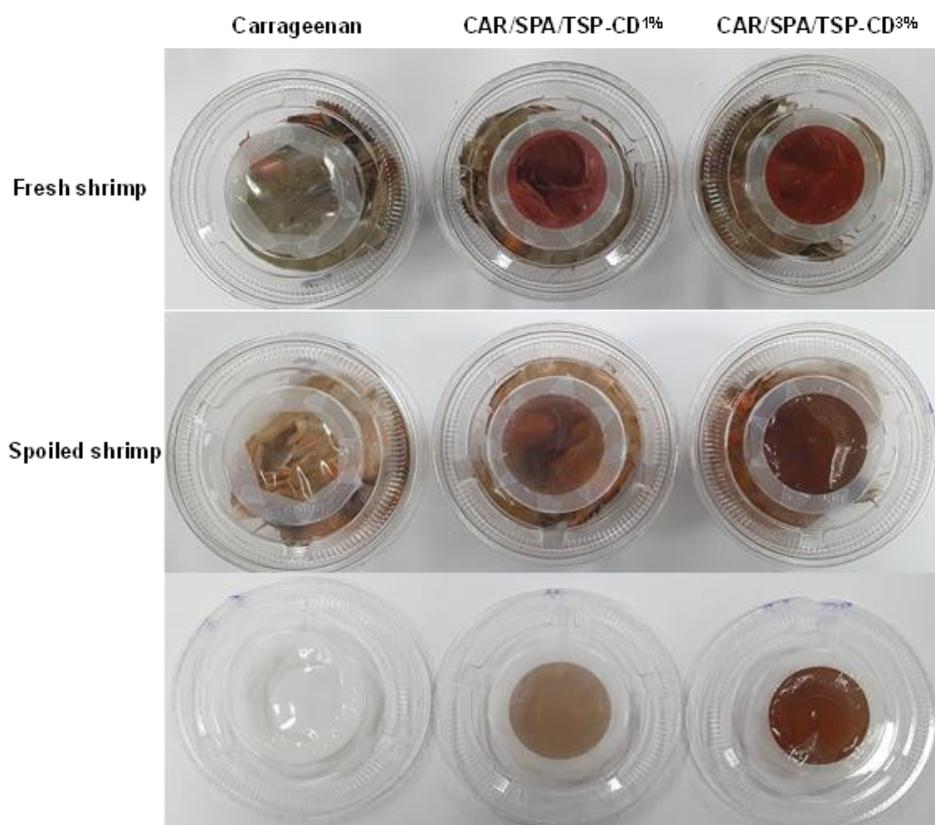


Figure 1: Shrimp freshness monitoring by CAR/SPA/TSP-CDs indicator film.



STRUCTURE CHARACTERIZATION AND LIPID-LOWERING ACTIVITY OF A HOMOGENEOUS HETEROPOLYSACCHARIDE FROM SWEET TEA (*RUBUS SUAVISSMUS S. LEE*)

Jingxuan Jia ^{*a,b,c}, Yi Xiong ^{a,b}, Xiaoyi Li ^{b,c}, Jiayu Wang ^{a,b}, Wenchen Yu ^{a,b}, Weihong Lu ^{b,c}

^a School of Chemistry and Chemical Engineering, Harbin Institute of Technology, China

^b Institute of Extreme Environment Nutrition and Protection, Harbin Institute of Technology, China

^c School of Medicine and Health, Harbin Institute of Technology, China

* 22b925092@stu.hit.edu.cn

Sweet tea (*Rubus Suavissimus S. Lee*) is consumed as herbal tea in southwestern China, which has multiple functions such as relieving cough, alleviating allergic responses, and clearing away heat. Here we report the structure and lipid-lowering activity of a sweet tea polysaccharide (STP-60a). STP-60a is a homogeneous heteropolysaccharide with a molecular weight of 9.16×10^4 Da, and composed of rhamnose, arabinose, glucose, galactose and glucuronic acid. The main backbone of STP-60a consists of β -L-Rhap-(1 \rightarrow , \rightarrow 3)- β -D-Galp-(1 \rightarrow , \rightarrow 4)- β -D-Glcp-UA-(1 \rightarrow , \rightarrow 3,6)- β -D-Galp-(1 \rightarrow , \rightarrow 6)- β -D-Galp-(1 \rightarrow , \rightarrow 3)-4-OAc- β -L-Arap-(1 \rightarrow , \rightarrow 3)- α -L-Araf-(1 \rightarrow and \rightarrow 3)- α -D-Glcp-(1 \rightarrow . Using *Caenorhabditis elegans* (*C. elegans*) in a high-sugar diet as a model, we found that STP-60a significantly reduced the fat accumulation in the intestine of *C. elegans*, and extensively affected lipolysis, fatty acid synthesis and β -oxidation processes. This research provides a new direction for the development and utilization of sweet tea, and lays a solid foundation for the promotion of sweet tea polysaccharides as a lipid-lowering food ingredient.

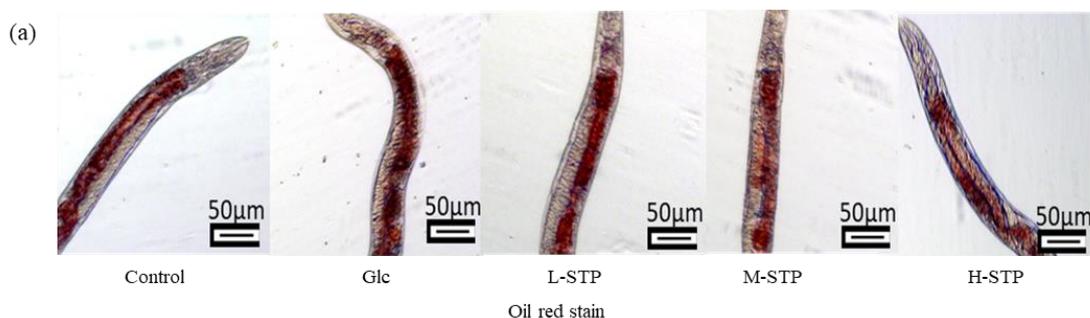


Figure 1 : The effect of STP-60a on intestinal fat content of nematodes fed a high-sugar diet
— Representative images of oil red stain



FORMULATIONS BASED ON PULLULAN AND A DERIVATIVE AS COATING MATERIAL FOR THE FOOD SECTOR

Hernandez-Tenorio F. ^{*a}, Giraldo-Estrada C. ^a

^a *Environmental Processes Research Group, Universidad EAFIT, Medellín-Colombia*

* fehernandt@eafit.edu.co

The waste generated annually due to postharvest spoilage of fruits and vegetables is a situation that causes food safety concerns. Therefore, the use of naturally occurring coating materials such as pullulan (PU) is required to extend the shelf life of these foods. PU is an exopolysaccharide with the potential to be chemically modified, which makes it possible to induce new characteristics such as solubility, thermal properties, among others [1]. In consequence, the aim of this work was to develop formulations based on PU and its derivatives as coating material with application in the food sector. For this purpose, PU was produced from *Aureobasidium pullulans* ATCC 15233, and modified such as carboxymethylpullulan (CMP) by etherification reaction (Figure 1), under three different degrees of substitution (DS). Characterization was performed by infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), and thermogravimetric analysis (TGA). In addition, the contact angles, opacity, and mechanical properties of the formulated films were quantified. The PU and CMP-based coating were performed on strawberries and goldenberries (*Physalis peruviana*). The FT-IR and NMR spectra of PU showed signals similar to the standard, and for CMP signals corresponding to the formation of carboxymethyl groups were found. TGA showed that carboxymethylation decreased the decomposition temperature (T_d) of PU (238.84 °C). Furthermore, it was found that carboxymethylation decreased the opacity of PU films ($3.09 \pm 0.10 \text{ mm}^{-1}$). On the other hand, the contact angle decreased with increasing DS in CMP and values were lower compared to PU ($71.34 \pm 0.47^\circ$). The mechanical properties tensile strength and elongation at break of CMP films increased compared to PU films. The CMP-based coating prolonged the shelf life of strawberries and goldenberries compared to the control.

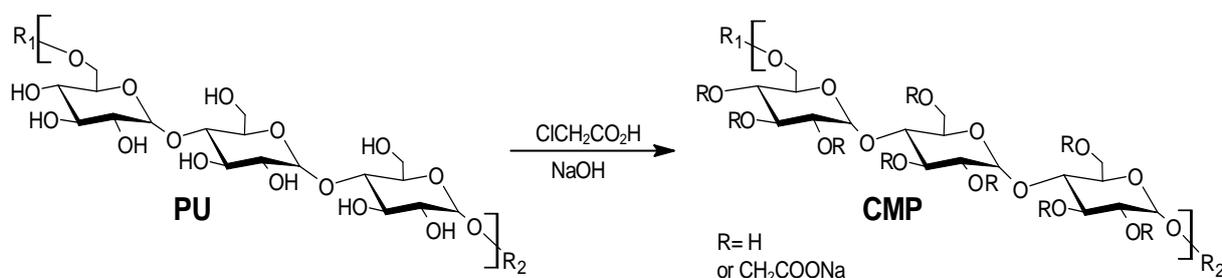


Figure 1. PU etherification reaction.

- [1] F. Hernandez-Tenorio and C. Giraldo-Estrada, "Characterization and chemical modification of pullulan produced from a submerged culture of *Aureobasidium pullulans* ATCC 15233," *Polym Test*, vol. 114, p. 107686, 2022, doi: 10.1016/j.polymertesting.2022.107686.



TIME-DEPENDENT CHANGES IN THE FINE STRUCTURE OF STRUCTURALLY DIFFERENT PECTINS IN *IN VITRO* FERMENTATION STUDIES WITH HUMAN INTESTINAL BACTERIA

Bender, C. ^{*a}, Stoll, D. ^b, Huch, M. ^b, Keller, J. ^a, Kulling S. ^b, Bunzel, M. ^a

^a *Institute of Applied Biosciences, Department of Food Chemistry and Phytochemistry, Karlsruhe Institute of Technology, Germany*

^b *Federal Research Institute of Nutrition and Food, Department of Safety and Quality of Fruit and Vegetables, Max Rubner-Institut, Germany*

* caroline.bender@kit.edu

Due to the growing interest in a health-conscious diet, pectins are becoming increasingly important as dietary fiber. In the course of human digestion, pectins reach the large intestine almost unmodified, where they are fermented by colonic microorganisms. Previous studies on pectin fermentation were largely limited to the analysis of short-chain fatty acids as fermentation end products or changes in the composition of the microbiota during fermentation. Here, the focus was on structural changes in the fine structure of different pectin domains (especially homogalacturonan neutral type I rhamnogalacturonan (RG I) side chains, and RG I backbone) during *in vitro* fermentation.

For this purpose, mildly extracted pectins that were rich in RG I side chains as well as commercial, galacturonic acid-rich pectins, both from different raw materials (citrus, apple and sugar beet), were structurally characterized (including monosaccharide composition (HPAEC-PAD), glycosidic linkage analysis (GC-MS/FID), degree of methylation and acetylation (¹H-NMR), and molecular weight distribution (HPSEC-RI/MALLS)). Pectins were incubated *in vitro* with human fecal suspensions for different time periods (10 min – 48 h). In order to draw conclusions about changes in the fine structure, carbohydrate components of the fermentation mixtures were separated into oligo- and polysaccharides by ethanol precipitation. The residual polysaccharide structures were analyzed with respect to both monosaccharide and glycosidic linkage composition, whereas the structures of oligo- and monomeric intermediate cleavage products were elucidated using HPAEC-PAD/MS and UHPLC-MS².

The neutral RG I side-chains of all studied pectins were rapidly metabolized. Concerning the fine structure, an initial debranching of arabinans and a reduction of the chain length of type I arabinogalactans was observed. In the further course of fermentation, metabolization of the homogalacturonan backbone followed by the RG I backbone was detected, with this order being largely independent of the pectin studied. The observed fermentation kinetics suggest that the different structural units of pectins are fermented in different sections of the colon.



INFLUENCE OF AMYLOSE AND AMYLOPECTIN MOLECULAR STRUCTURE ON SELF-ASSEMBLY AND WHEAT BREAD-STALING

Spotti M. J.^a, Franco M.^b, Moldin^c, Henriksson T.^c, Martinez M. M.^{*a}

^a Center for Innovative Food (CiFOOD), Department of Food Science, Aarhus University, AgroFood Park 48, Aarhus N 8200, Denmark.

^b Food Technology Area, College of Agricultural Engineering, University of Valladolid, Avda. Madrid, 34004, Palencia, Spain.

^c Lantmännen ek för, Box 30192, SE-104 25 Stockholm, Sweden.

* mm@food.au.dk

The measurement of the increase in crumb hardening is the most widely set indicator of staling. Despite the lack of consensus regarding the staling mechanisms, starch retrogradation and moisture loss are known to be major contributors. Here, we aimed to understand starch molecular targets that could result in baked goods with extended self-life. Specifically, the fine starch structure of 36 wheat varieties with different crop seasonality (winter and spring) and type of use (feed or baking) was investigated and correlated to their assembly during retrogradation using a hydrogel model system. The molecular weight (MW) of amylopectin (AP) and amylose (AM), as well as their chain length distribution, was investigated by HPSEC-MALS-RI. The hardening of starch hydrogels over time was significantly lower for spring-baking varieties, which possessed significantly higher protein content, MW AP, AM content together with longer amylose chains than the rest of wheat categories. Spring-baking varieties also showed longer populations of short AP chains. Principal component analysis showed that gel hardening (ΔG) was inversely correlated to MWAP, protein content, AM content and ratio of long to short AP chains. Spring varieties showed significantly lower retrogradation enthalpies (as measured by DSC) than winter ones, which aligned to the lower gel hardening and was explained by the higher MW AP and/or longer AM. To evaluate if these results can be correlated to bread systems, 3 winter-baking and 3 spring-baking lines were selected for bread-making. Spring lines required a higher amount of hydration to reach the same torque in Mixolab tests and presented lower bread staling (hardening) than winter counterparts, which was attributed to their molecular features and to their higher capacity to retain water over time (LF-NMR). This work provides biosynthetic markers for breeders and defines in planta modifications that could result in slow-retrograding and high yielding wheat varieties.



CHEMICAL, TECHNOLOGICAL AND BIOLOGICAL FEATURES OF AN EXOPOLYSACCHARIDE FROM *LEUCONOSTOC MESENEROIDES*

Bisson G.*^a, Comuzzi C.^a, Melchior S.^a, Calligaris S.^a, Zanocco M.^b, Andreatta F.^b, Marino M.^a

^aDepartment of Agricultural Food Environmental and Animal Science, University of Udine, Italy

^b Polytechnic Department of Engineering and Architecture, University of Udine, Italy

bisson.giulia@spes.uniud.it

Microbial exopolysaccharides (EPS) from lactic acid bacteria have received great interest in both the industrial and research fields, due to their technological properties (e.g., water binding capacity, stabilizers, ...) and biological activities (e.g., antimicrobial, antioxidant, ...) [1,2]. For this reason, the research of new EPS with peculiar technological properties and biological activity is of great interest. In this study, chemical characteristics, technological properties, and antimicrobial activity of an EPS (EPS_O) from a *Leuconostoc mesenteroides* strain of dairy origin were investigated. One- and two-dimensional NMR, DOSY and FT-IR revealed that EPS_O was a high molecular weight dextran (about 10^8 Da) with a very compact appearance, as evidenced by SEM. EPS_O was characterized by high water- and oil-holding capacity (784 and 496% respectively) and high solubility in water (about 99%). The thermal stability of EPS_O was also investigated by DSC analysis revealing the melting peak at 147 °C and the Tg at 83 °C. When EPS_O (50 mg/mL) was put in contact with water cold gelation occurred resulting in a weak gel as confirmed by rheological analysis. Antimicrobial activity of EPS_O was also investigated against *Escherichia coli*, *Enterococcus faecium*, *Staphylococcus aureus*, *Salmonella enterica* and *Listeria monocytogenes* through the observation of the turbidimetric growth kinetics. EPS_O displayed significant activity on *L. monocytogenes* decreasing the cell concentration at the end of the growth. All these characteristics could highlight the potential use of EPS_O as a promising ingredient to improve food characteristics and bioactivities.

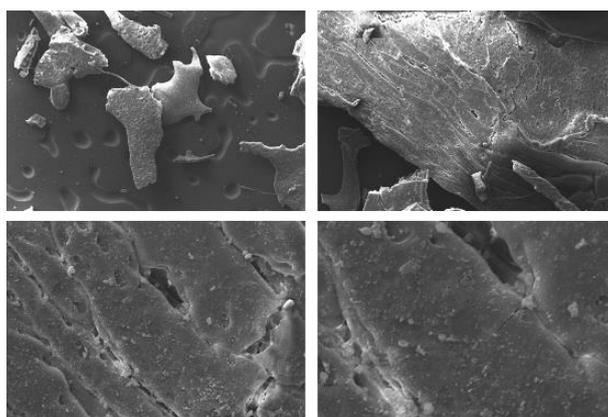


Figure 1. SEM images of EPS_O at different magnifications (up to 2000x)

[1] Korcz E. & Varga L., *Trends in Food Science and Technology*, 110, 375-384, 2021.

[2] Zhou Y., Cui Y. & Qu X. *Carbohydrate Polymers*, 207, 317-332, 2019.



INSIGHTS OF BACTERIAL CELLULOSE NANOFIBERS' BIOINTERACTION USING *C. ELEGANS* AS A MODEL

Muñoz-Juan, A. ^{*a}, Benseny-Cases, N. ^b, Laromaine, A. ^a

^a Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Campus UAB, Spain

^b Universitat Autònoma de Barcelona, Biophysics Unit/Center for Biophysical Studies, Department of Biochemistry and Molecular Biology, Faculty of Medicine, Avinguda de Can Domènech, 08193, Cerdanyola del Vallès, Spain

* amunoz@icmab.es

Dietary fibers are being investigated for increasing the poor fiber content of the current modern diets^[1]. New sources have been discovered, such as the use of bacteria or algae^[2] for producing cellulose. The safety and effects of these fibers should be evaluated before incorporating them into new products. Bacterial cellulose (BC), produced by gram-negative bacteria, has been proposed recently as a food additive^[3], claiming the beneficial lipid-lowering effect of this fiber. Some studies have evaluated the safety of BC and BC nanofibers (BNCf) in *in vitro* and *in vivo* models^{[4],[5]}, using different concentrations and treatment duration. Despite BNCf being claimed to be biocompatible material, there are still some doubts about its interaction with biological systems

Here, we evaluated BNCf in the simple model *Caenorhabditis elegans* (*C. elegans*) to assess the effect of these fibers on the organism's well-being focusing on lipid metabolism. This model shares 60-80% of genetic homology with humans, and regarding lipid metabolism, approximately 70% of genes involved in this pathway are homologous to mammals^[6]. Worms were exposed to different BNCf concentrations, and survival rate and body length were evaluated. Life span and reproduction effects, difficult to measure in other models, were also recorded, taking advantage of the fast life of ~3 days and ~3 weeks of life span. BNCf does not produce any detrimental effect but slightly reduces body length. Going deeper into the evaluation, a lipid-lowering effect of these fibers was observed using different colorimetric techniques and μ FTIR- with Synchrotron radiation.

This project reflects the evaluation of BNCf on the *C. elegans* model and adds new information about the lipid-lowering effect related to these fibers.

References

- [1] F. Branca *et al.*, *BMJ*, 364 :l296, 24-29,2019
- [2] Y. W. Chen, V. Lee, C. Juan, & S.-M. Phang, *Carbohydr Polym*, 151, 1210–1219, 2016
- [3] L. Marchetti, B. Muzzio, P. Cerrutti, S. C. Andrés, & A. N. Califano, *Food Structure*, 14, 52–59, 2017.
- [4] A. C. Rodrigues *et al.*, *Environ Sci Nano*, 10, 781-799, 2023
- [5] S. Moreira *et al.*, *Toxicol Lett*, vol. 189(3), 235–241, 2009,
- [6] L. An, X. Fu, J. Chen, & J. Ma, *Int. J. Mol. Sci.*, 24(2), 1173, 2023.

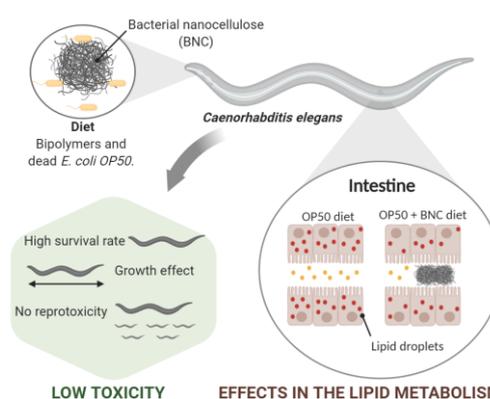


Figure 5. Graphical abstract of the project.

THE EXOPOLYSACCHARIDES OF A MEDICINAL FUNGUS CS-HK1: ANTI-INFLAMMATORY ACTIVITY, MECHANISM OF ACTION AND STRUCTURE CHARACTERIZATION

Wu J.Y. *, ZHU Y.Y., GU F.T.

Research Institute for Future Food, Department of Food Science and Nutrition, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

(* Email: jian-yong.wu@polyu.edu.hk)

Edible fungi or mushrooms have been widely used in healthy foods and nutraceuticals. Polysaccharides are major active components of edible fungi with notable antitumor, immunomodulatory, anti-inflammatory and many other activities. Cs-HK1 is a fungus strain originated from the Chinese caterpillar fungus, a well-known medicinal fungus in traditional Chinese medicine. Cs-HK1 mycelial fermentation has been developed and applied for mass production of mycelial biomass and exopolysaccharides (EPS). The Cs-HK1 EPS have shown significant anti-inflammatory activity in both cell culture and animal models, inhibiting lipopolysaccharide (LPS)-induced gut epithelial tissue injury and pro-inflammatory factors including NO, TNF- α and IL-1 β . Two possible mechanisms for the anti-inflammatory effects of EPS have been detected, the blockage of the toll-like receptor (TLR) mediated proinflammatory signal pathway and the modulation of gut microbiota. A highly-active exopolysaccharide (EPS) fraction, EPS-LM, was isolated from the lower molecular weight (MW) fraction of EPS and then purified by column chromatography. EPS-LM was composed of mannose, glucose and galactose residues at 3.9:6.9:1 mole ratio with an average MW of 360 kDa. It had a main chain of [6)- β -D-Glcp-(1 \rightarrow 4)- α -D-Manp-(1 \rightarrow 4)- α -D-Glcp-(1)₂ \rightarrow 3,6)- α -D-Glcp-(1 \rightarrow 3)- α -D-Manp-(1 \rightarrow 4)- α -D-Glcp-(1)₂, which was branched at the O-3 position of 3,6)- α -D-Glcp -(1 \rightarrow with β -D-Galf-(1 \rightarrow side chains (~8% degree of branching). EPS -LM produced by Cs-HK1 mycelial fermentation is a promising candidate for anti-inflammation therapy.

[1] Li L.Q., ... Wu J.Y. *International Journal of Molecular Sciences*, 22(5): 1–13, Art. 2450, 2021,

Li L.Q., ...Wu JY*, *International Journal of Biological Macromolecules* 149:1042-1050, 2020.



COMPOSITES NANOFIBERS BASED ON QUATERNIZED CHITOSAN FOR FOOD PACKAGING

Andreica B.-I.^{a*}, Rosca I.^a, Marin L.^a

^a “Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania

* andreica.bianca@icmpp.ro

Chitosan and its quaternized derivative are two biopolymers that have been exhaustively studied for various applications of contemporary interest [1]. While both biopolymers have been shown to have excellent properties, such as biodegradability, low toxicity, antioxidant activity, quaternized chitosan has been found to possess better antimicrobial properties [2]. This makes it particularly useful in the design of active packaging materials that can help to extend the shelf life of food products, a topic not very exploited yet.

In this context, the goal of this study was the development of fiber mats containing chitosan, quaternized chitosan, vanillin and poly(ethylene oxide) in different ratios. The selection of each component was deliberate, aiming to achieve nanofibers that meet all the necessary criteria for materials used in food packaging.

The structural characterization of the nanofibers by FTIR and NMR spectroscopy showed the formation of imine bonds between the amine groups of chitosan/quaternized chitosan and the aldehyde group of vanillin, while thermogravimetric analysis revealed a strong and stable network of H-bonds between the components, resulting in good thermal stability suitable for food packaging applications. SEM microscopy revealed entangled continuous nanofibers, with no defects or beads, and a mean diameter of around 140 nm. The mechanical properties of the nanofibers were found to be comparable or even higher than those of other materials designed for the same application, due to the presence of quaternized chitosan which improved the fiber mats' strength and elasticity.

The evaluation of the antioxidant activity in solution and in solid state revealed high scavenging activity of the fibers, which is important for preserving food freshness for a longer time. The study evaluated also the ability of the fibers to release vanillin in food simulants media, demonstrating that the aldehyde's release is controlled by its removal from the media, and also the fibers are able to rapidly absorb water while maintaining their integrity. Tested on *E. coli*, *S. aureus* and *C. albicans*, the fibers with a high content of quaternized chitosan and moderate quantity of vanillin were able to destroy up to 90% of the microbial cells. A preservation experiment assessed on raspberries as model fruits revealed that the fibers were able to extend the freshness of the fruits up to 7 days, better than the commercial packaging. Moreover, the fibers completely degraded in soil in 7 weeks, complying therefore to the current trend of designing biodegradable materials.

In conclusion, the rational design of choosing the above-mentioned specific components for the development of composite fiber mats met the initial expectations. The nanofibers showed excellent properties for food packaging applications, such as strong antioxidant and antimicrobial properties, and effectively preserved the quality of the fruits, with the added benefit of being biodegradable.

Acknowledgment: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE2020-2717, within PNCDI III, no. PCE 2/2021 and from the project H2020-MSCA-RISE-2019, SWORD-DLV-873123.

[1] Florez M., Guerra-Rodriguez E., Cazon P., & Vasquez M., *Food Hydrocolloids*, 124, 2022

[2] Andreica B.-I., Anisie A., Rosca I., Sandu A.-I., Pasca A. S., Mititelu-Tartau L. & Marin L., *Carbohydrate Polymers*, 302, 2023



EFFECT OF AN INULIN-TYPE FRUCTAN FROM *PLATYCODON GRANDIFLORUM* ON THE INTESTINAL MICROBIOTA IN RATS EXPOSED TO PM2.5

Weihong Lu ^{*b,c}, Wenchen Yu ^{a,b,c}, Junwen Wang ^{a,b,c}, Jiangfei Li ^{a,b,c}, Mengnan Liu ^{a,b,c},
Jingxuan Jia ^{a,b,c}

^a School of Chemistry and Chemical Engineering, Harbin Institute of Technology, China
^b Institute of Extreme Environment Nutrition and Protection, Harbin Institute of Technology, China

^c School of Medicine and Health, Harbin Institute of Technology, China

* LuWeihongABC@outlook.com

In this study, PGPI-1-a with a molecular weight of 12.1 kDa was isolated and purified from the roots of *Platycodon grandiflorum* through hot water extraction, ethanol precipitation, and column chromatography purification. Monosaccharide composition analysis and NMR spectra confirmed that PGPI-1-a was an inulin-type fructan containing (2→1)-linked β-D-fructofuranose (Fru) and a terminal α-D-glucopyranose (Glc). PGPI-1-a was semi-crystalline in nature, with a crystallinity of 53.6%. PM2.5 exposure significantly increased the relative abundance of Peptoniphilaceae_[G-2] and Lachnospiraceae_[G-2], while the intervention of PGPI-1-a decreased their relative abundance. In addition, PGPI-1-a treatment remarkably promoted the growth and proliferation of *Butyrivibrio* that is a butyric acid-producing genus. This study suggested that PGPI-1-a could improve the imbalance of intestinal microbiota in rats caused by PM2.5 exposure to a certain extent, thereby might reduce the risk of some diseases caused by PM2.5 exposure.

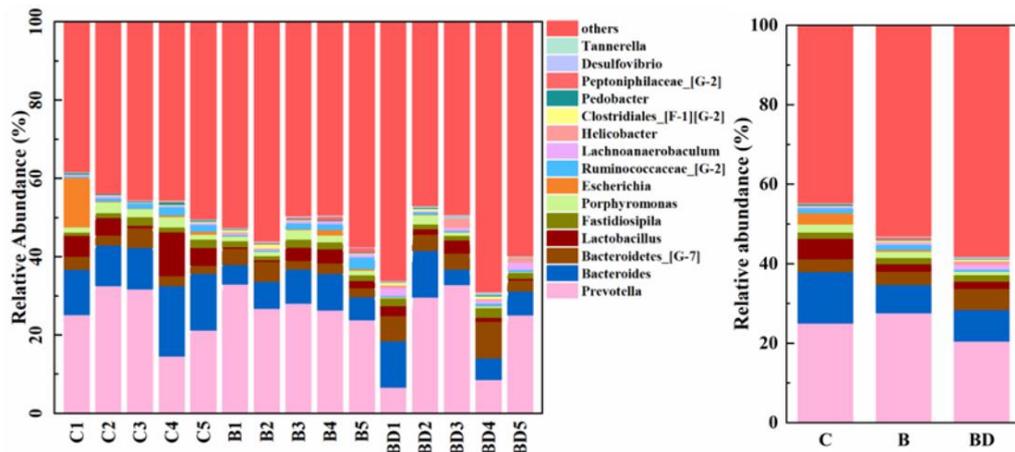


Figure 1 : Species distribution of rat gut microbiota at the genus level in control group (C), PM2.5 exposure group (B) and PGPI-1-a intervention group (BD)



WOOD INSPIRED BIOBASED NANOCOMPOSITE FILMS FOR ACTIVE PACKAGING

José M. Silva^{*a}, C. Vilela^a, Mara G. Freire^a, Armando J. D. Silvestre^a, P.C. Branco^b, João Martins^c, Carmen S. R. Freire^a

^a CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal

^b RAIZ – Instituto de Investigação da Floresta e Papel, 3800-783 Eixo, Aveiro, Portugal

^c Celbi SA – Celulose Beira Industrial (Celbi) S.A, 3081-853 Figueira da Foz, Portugal

* E-mail: jose.miguel.silva@ua.pt

The widespread use of petroleum-based single use plastics, such as food packaging films or trash bags has increased dramatically in the past few decades, leading to serious environmental problems due to their nonbiodegradability and wide spread in the environment¹. As consumers become more environmentally conscious, the demand for biobased and biodegradable materials is growing, leading to a shift from common petroleum-based plastics to more sustainable materials. In this sense, active biobased packaging emerge as a sustainable and eco-friendly alternative solutions, that can help to improve the safety, quality and shelf-life of the packaged foods, while contributing to the reduction of waste^{2,3}.

On this basis, the goal of the current work was to prepare functional wood inspired biopolymeric nanocomposite films by solvent casting suspensions containing beechwood xylans, nanofibrillated cellulose and lignosulfonates (magnesium or sodium salts), that exhibit good antioxidant and UV blocking properties and improved mechanical performance.

In order to demonstrate their potential for application in active packaging, the optical properties, antioxidant activity, mechanical performance, thermal stability, and moisture uptake capacity of the obtained biobased films were assessed. All films presented good homogeneity, translucency, and thermal stability up to 153 °C allowing for common sterilization procedures. The films showed good mechanical properties (Young's modulus = 1.08 – 3.79 GPa and tensile strengths at break up = 12.75 – 14.02 MPa), antioxidant capacity (DPPH scavenging = 71.57 – 82.40 %) and UV protection (transmittances \leq 18.6 % (200 – 400 nm)). These results, show the potential of using low-cost and eco-friendly resources for the development of sustainable active food packaging materials.

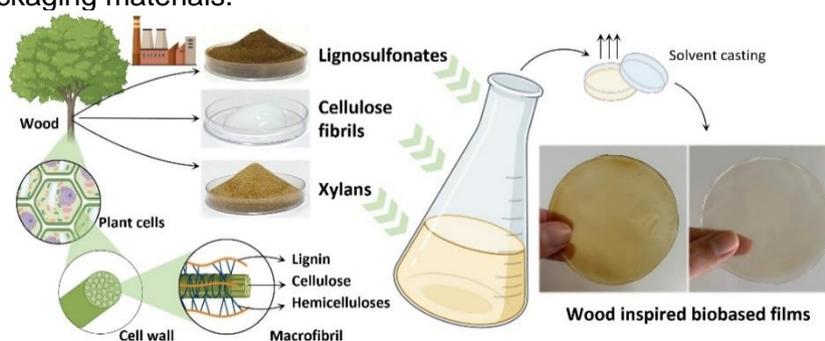


Figure 1: Schematic illustration of the preparation of the films

- [1] Fiorentino, G., Ripa, M. & Ulgiati, S. *Biofuels, Bioprod. Biorefining*, 1, 195–214, 2017.
- [2] Vilela, C. *et al. Trends Food Sci. Technol.*, October, 212–222, 2018.
- [3] Shi, J. *et al. Carbohydr. Polym.*, February Part B, 1–11, 2023.

This work was developed within the scope of the projects CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 and LA/P/0006/2020, financed by national funds through the FCT/MECTES (PIDDAC). The authors would also like to acknowledge Celbi – Celulose da Beira Industrial, SA and The Navigator Company for funding the PhD scholarship.



TOWARDS GUT MICROBIOTA-ORIENTED FOOD: INVESTIGATIONS OF DIETARY POLYSACCHARIDES

Huizi Tan*, Wenqi Huang, Linlin Fan, Quanyong Wu, Qianhuang Xiao, Shaoping Nie

State Key Laboratory of Food Science and Technology, China-Canada Joint Laboratory of Food Science and Technology (Nanchang), Nanchang University, China

* huizi.tan@ncu.edu.cn

Considerable evidence describing the beneficial effects of various food-derived complex polysaccharides, including metabolic modulation, inflammation amelioration, and immunity strengthening. However, polysaccharides properties as well as personal features greatly impact the outcomes of interventions, which elicited concerns that how to achieve the rational selection and effective supplementation of polysaccharides[1].

The human gut is heavily colonized with microorganisms, which can degrade and be shaped by dietary bioactives[2]. Advanced research is expanding our understanding of the physiological functions of gut microbiota and beyond to the health of the gastrointestinal tract. Distinct microbiota phenotypes potentially mediate the heterogeneous host responses to food polysaccharides, which may be the key to unlocking the mystery of the differential functionalities of polysaccharides.

In this study, an *in vitro* artificial colon model and *in vivo* animal models have been established to mimic healthy status, acute colitis, or dysbiosis induced by a high-fat diet and low-dose antibiotics [3,4,5]. The interactions of gut microbiota under each condition and pectin with multiple degrees of esterification were analyzed. Meanwhile, the associated physiological outcomes were studied. These results may provide evidence for the further development of gut microbiota-oriented polysaccharides-based food.

[1] Tan H & Nie S. *FEMS Microbiology Reviews*, 45, fuaa065, 1-18, 2021.

[2] Tan H & Nie S. *Trends in Food Science and Technology*, 106: 171-181, 2020.

[3] Qian X, Huang W, Wu Q, et al. *Food Function*, DOI: 10.1039/D2FO03966D, 2023.

[4] Wu Q, Fan L, Tan H, et al. *Applied Microbiology and Biotechnology*, 106, 3707-3720, 2022.

[5] Huang W, Fang Q, Fan L, et al. *eFood*, 3, e5, 1-11, 2022



CHITOLIGOSACCHARIDES HYPOCHOLESTEROLEMIC ACTIVITY: RELEVANCE OF IONIC AND NON-IONIC INTERACTIONS

Coreta-Gomes, F.,^{a, b,*} Moreno, M.,^b Nunes, C.,^c Coimbra, M.A.^a

^a LAQV-REQUIMTE, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

^b Coimbra Chemistry Centre - Institute of Molecular Sciences (CQC-IMS), Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

^c CICECO-Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193, Aveiro, Portugal

* filipecoreta@ua.pt

Several polysaccharides have been described to have hypocholesterolemic potential.[1-3] Chitooligosaccharides are positively charged and their cholesterol reducing properties are usually linked with their capacity to sequester the negatively charged bile salts, through ionic interactions. The decrease on the bile salt content enables the decrease of cholesterol solubility [2,4] leading to its precipitation and excretion. Yet, at physiological conditions, chitooligosaccharides are mostly uncharged, which emphasizes that other type of interactions may play a role on the interaction with bile salts. In this work, the bile salt sequestration and cholesterol accessibility of chitooligosaccharides sample with an average degree of polymerization of 10 and 90 % deacetylation was studied.

Chitooligosaccharides were shown to sequester bile salts to a similar extent as the cationic resin colestipol (pharmacologic drug), both decreasing cholesterol accessibility as measured by NMR (pH 7.4). A decrease in the ionic strength leads to an increase in the binding capacity of chitooligosaccharides, in agreement with the involvement of ionic interactions. However, a decrease on pH to 6.4 does not significantly increase chitooligosaccharide bile salt sequestration, although its degree of ionization was increased. This substantiates the involvement of non-ionic interactions, which was further supported by a) NMR chemical shift analysis; b) electrophoretic mobility attained for the bile salt- chitooligosaccharide aggregates at high bile salt concentrations.

These results highlight that in the intestinal physiological range of pH (6.4 – 7.4) chitooligosaccharides both ionic and non-ionic character are relevant structural features for enhancing sequestration of bile salts and promoting the decrease of cholesterol accessibility. This knowledge can be used to optimize polysaccharides hypocholesterolemic properties and should be considered in the development of innovative hypocholesterolemic food ingredients based on carbohydrates.

Acknowledgments: to Fundação para a Ciência e a Tecnologia (FCT)/MCTES, namely the support to the research units LAQV-REQUIMTE (UIDB/50006/2020) including Filipe Coreta-Gomes research contract; and also supported by the project PTDC/QUI-OUT/29373/2017 through national funds (OE), and co-financed by the FEDER by the Operational Program of Competitiveness and Internationalization (POCI), within the PT2020 Partnership Agreement. NMR data was collected at the UC-NMR facility which is supported in part by FEDER – European Regional Development Fund through the COMPETE Programme (Operational Programme for Competitiveness) and by National Funds through FCT through grants RECI/QEQ-QFI/0168/2012, CENTRO-07-CT62-FEDER-002012, and also through support to Rede Nacional de Ressonância Magnética Nuclear (RNRMN) and to Coimbra Chemistry Centre through grant UID/QUI/00313/2019.

- [1] I. M. V. Silva, F. Machado, M. J. Moreno, C. Nunes, M. A. Coimbra, and F. Coreta-Gomes, *Molecules*, vol. 26, no. 15, p. 4559, Jul. 2021.
- [2] F. M. Coreta-Gomes *et al.*, *Nutrients*, vol. 12, no. 2, p. 437, Feb. 2020.
- [3] C. L. Pires, I. M. V. Silva, M. A. Coimbra, M. J. Moreno, and F. Coreta-Gomes, *Foods*, vol. 11, no. 19, p. 2935, Sep. 2022.
- [4] A. S. P. Moreira *et al.*, *Mar. Drugs*, vol. 21, no. 3, 2023.



RED CHICORY LEAF DIETARY FIBER ALLEVIATIVE DSS-INDUCED COLITIS VIA ENHANCING THE INTESTINAL BARRIER AND REGULATING THE GUT MICROBIOTA

Chunhua Chen ^{*a}, Xiaojun Huang ^a, Yadong Zhong ^a, Han Huang ^a, Xinyi Mu ^a, Hui Wang ^a, Shaoping Nie ^a

^a State Key Laboratory of Food Science and Technology, China-Canada Joint Lab of Food Science and Technology (Nanchang), Key Laboratory of Bioactive Polysaccharides of Jiangxi Province, Nanchang University, China

* E-mail address: chenchunhuach@163.com

Inflammatory bowel disease (IBD) is a chronic idiopathic inflammation of the gastrointestinal tract. Its incidence is increasing rapidly and has become a global health issue. Red chicory (*Cichorium intybus* L.) is a biennial or perennial root plant from the *Cichorium* genus, Asteraceae family, and has been shown to exert beneficial effect on alleviating inflammation and regulating gut microbiota. However, there are few reports on the intervention of red chicory leaf dietary fiber in the treatment of colitis. This study extracted soluble (SDF), insoluble (IDF) and total dietary fiber (TDF) from red chicory leaf, and investigate the protective effect of red chicory leaf different dietary fiber on dextran sodium sulfate (DSS)-induced ulcerative colitis in mice. The result showed that red chicory leaf insoluble and total dietary fiber can promote the expression of tight junction proteins ZO-1, Occludin and Claudin-1, and maintain the integrity of the intestinal barrier function. However, red chicory leaf soluble dietary fiber had limited effect and only significantly increased the expression of ZO-1. β -diversity result showed that the gut microbiota of colitis mice changed after red chicory leaf dietary fiber intervention. Furthermore, red chicory leaf dietary fiber remodeled the gut microbiota by accelerating the proliferation of beneficial bacteria *Ruminococcus* and inhibiting pathogenic bacteria *Sutterella*. Thus, Red chicory leaf dietary fiber has the potential to be a functional food against colitis.

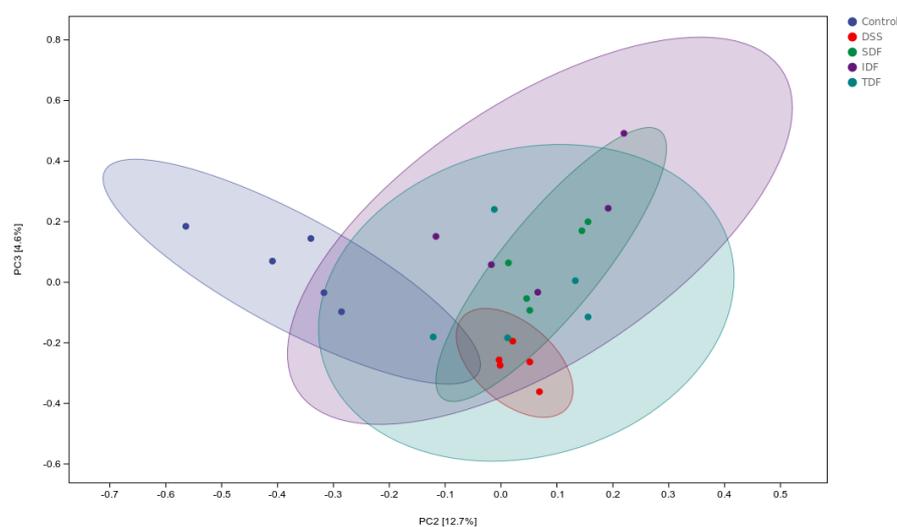


Figure 1 : β -diversity of gut microbiota



Session 6 Poster



POLYSACCHARIDE-BASED SELF-ASSEMBLED SMART HYDROGEL FOR IN VITRO DELIVERY OF CO-ENCAPSULATED PROBIOTICS AND FOLIC ACID

Nandita Srivastava^{*ab}, Richa^a, Anirban Roy Choudhury^a

^a Biochemical Engineering Research & Process Development Centre (BERPDC), Institute of Microbial Technology (IMTECH), Council of Scientific and Industrial Research (CSIR), Sector 39A, Chandigarh 160036, India.

^b Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India

*Presenting author

Email: nansri2501@imtech.res.in

Abstract

The biologically active platforms such as hydrogels are three-dimensional hydrophilic porous structures capable of supporting bioactive components attachment to their surface. They can serve as cargos for sustainable and controlled delivery of compounds to the site of action through reversible sol-gel transitions. Hence, developing novel hydrogel materials with smart or intelligent properties that can undergo structural and volume changes by responding to external triggers is vital. Therefore, we have fabricated a self-assembled, stimuli-responsive, novel tri-composite polysaccharide-based hydrogel of chitosan, gellan, and κ-carrageenan devoid of toxic chemical cross-linkers. A polysaccharide-based composite hydrogel can overcome problems associated with individual polysaccharide gels, such as mechanical strength and stability. Although there are several reports on encapsulating probiotics and bioactive compounds, however maintaining the viability of loaded probiotics, folate stability, and their bioavailability is still challenging. We utilized tri-composite hydrogel to facilitate the co-encapsulation of folate (vitamin B9) and probiotic spores. Its co-encapsulation with folate, while increasing the nutritional value of the system, also helps to maintain viability of spores. The studies on hydrogel revealed that it possessed remarkable encapsulation efficiency and exhibited sustainable release. The release rate studies at different pH suggested maximum release in alkaline conditions, correlating with release *in vitro* in the simulated intestinal phase. Moreover, microscopic and FE-SEM analyses depicted the conversion and colonization of bacterial spores to vegetative cells in the intestinal phase. This study paves the way to develop a single green matrix for co-encapsulating various functional foods with controlled delivery at the targeted site.



COATING TECHNOLOGIES FOR PLA USING NATURAL EXTRACTS AND POLYSACCHARIDES FOR THE DEVELOPMENT OF ACTIVE PACKAGING CONCEPT

Lidija Fras Zemljič^{a*}, Tjaša Kraševac Glaser^a, Tanja Labohar^a, Mojca Škerget^b,

Maja Čolnik^b, Sonja Smole Možina^c

^aUniversity of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterization of Polymers and Processing of Polymers materials, Smetanova 17, SI-2000 Maribor, Slovenia

^bUniversity of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory for Separation Processes and Product Design, Smetanova 17, SI-2000 Maribor, Slovenia

^cDepartment of Food Science and Technology, Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, 1000 Ljubljana, Slovenia

* lidija.fras@um.si

Eco-innovative and functional food packaging is increasingly becoming a strategic goal for the European food sector and market [1-2], encouraging the development of new concepts.

Based on coatings of natural extracts and polysaccharides, we have developed various coatings for PLA as active packaging, aiming to achieve properties such as active functionality, i.e. antioxidant, antimicrobial as well as biodegradability. The coatings were prepared as a colloidal solution and applied to PLA films by different methods, namely spraying, rolling, dipping, impregnation, and green supercritical fluid technology. The performance of the different methods was evaluated in terms of stability and useful properties such as wettability, oxygen permeability, antioxidant and antimicrobial properties by physicochemical analysis and bioactivity. We found that in all methods, the natural extracts and polysaccharide systems contribute to the desired functionalities as a layer-by-layer coating. The immersion method and the supercritical fluid technology were found to be the most optimal in terms of efficiency. Among them, the immersion method was the most efficient as well as environmentally and economically acceptable technology. The synergistic effect of the two active ingredients used, polysaccharides and polyphenols, resulted in excellent antioxidant (and antimicrobial) performance of the functionalized films. We improved the wettability of the material, reducing the likelihood of condensation occurring and thus of rapid spoilage, and avoided poorer transparency. We have also significantly reduced oxygen permeability, which prevents oxidative spoilage of food. Through ecological (LCA) and economic (LCC) analysis, we have confirmed that the dipping method is the most environmentally and cost optimal method to apply the coating to PLA film. All the listed properties of the functionalized films indicate a great potential for their use in packaging to extend the shelf life of food products.

REFERENCES:

- [1] "The Environmental Impact of Food Packaging - FoodPrint," GRACE Communications Foundation, Aug. 10, 2018. <https://foodprint.org/issues/the-environmental-impact-of-food-packaging/> (accessed Nov. 28, 2022).
- [2] S. Yildirim et al., "Active Packaging Applications for Food," *Comprehensive Reviews in Food Science and Food Safety*, vol. 17, no. 1. Blackwell Publishing Inc., pp. 165–199, Jan. 01, 2018. doi: 10.1111/1541-4337.12322.



ACTIVE FOOD PACKAGING CONCEPT FOR POLYPROPYLENE BASED ON BILAYER COATINGS OF CHITOSAN AND PLANT EXTRACT FORMULATIONS

Kaloper S.^a, Plohl O.^a, Finšgar M.^b, Smole Možina S.^c, Vesel A.^d, Šimat V.^e, Zemljič Fras L.*^a

^a Laboratory for Characterization and Processing of Polymers, Faculty of Mechanical Engineering, University of Maribor, Slovenia

^b Laboratory for Analytical Chemistry and Industrial Analysis, Faculty of Chemistry and Chemical Engineering, University of Maribor, Slovenia

^c Department of Food Science and Technology, Biotechnical faculty, University of Ljubljana, Slovenia

^d Department of Surface Engineering and Optoelectronics, Jožef Stefan Institute, Slovenia

^e University Department of Marine Studies, University of Split, Croatia

* lidija.fras@um.si

Polysaccharides that have an abundance of functional groups, good film-forming properties and exhibit antimicrobial potency have risen in interest as coatings, individually or in combination with other antimicrobial or antioxidative agents, for the development of active food packaging to prevent food spoilage and food-borne diseases. In this study, we improved the functionality of polypropylene (PP) food films with natural bilayer coatings. The first layer was a coating of primary (CH) or quaternary chitosan (QCH), and the second layer was a coating of a natural extract - either juniper needles (*Juniperus oxycedrus*; JUN) or blackberry leaves (*Rubus fruticosus*; BBL), extracted from agro-food by-products from traditional Croatian agro-productions. PP films were activated with UV-ozone and subsequently coated with different combinations of coatings to obtain data on the effect of each layer in bilayer formulations. The deposition of the coatings on the surface was confirmed and their composition, as well as morphology, were studied by gravimetry, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM), respectively. The surface contact angle (SCA), as an important food packaging parameter, was measured and compared with uncoated PP films (PP-NA/A) (Figure 1). The functionalized films were investigated for their antioxidative (AOP) and antimicrobial potential (AMP) by the ABTS assay and on bacteria *S. aureus* and *E. coli*, respectively. The results showed the successful formation of bilayer coatings on PP films, a pronounced decrease in SCA and a significant increase in AOP with the application of BBL and JUN extracts as second layer. QCH, BBL and JUN exhibited excellent AMP as mono- and bilayers against *S. aureus*, while CH as monolayer exhibited no AMP, however the addition of BBL and JUN enhanced it. In the case of *E. coli*, excellent AMP was observed only for the QCH monolayer, whereas no AMP was observed for the samples coated with extracts.

PP-NA $\alpha=72^\circ \pm 3^\circ$	PP-A $\alpha=64.1^\circ \pm 0.6^\circ$	PP + 2%CH $\alpha=74^\circ \pm 2^\circ$	PP + 2%QCH $\alpha=59^\circ \pm 2^\circ$
PP-A $\alpha=64.1^\circ \pm 0.6^\circ$	PP-BBL $\alpha=20^\circ \pm 3^\circ$	PP + 2%CH + BBL $\alpha=10.3^\circ \pm 0.7^\circ$	PP + 2%QCH + BBL $\alpha=30^\circ \pm 4^\circ$
PP-A $\alpha=64.1^\circ \pm 0.6^\circ$	PP-JUN $\alpha=9^\circ \pm 3^\circ$	PP + 2%CH + JUN $\alpha=10^\circ \pm 1^\circ$	PP + 2%QCH + JUN $\alpha=30^\circ \pm 1^\circ$

Figure 1: SCAs [α°] of untreated (PP-NA) and activated PP film (PP-A), followed by different coatings, applied individually or by bilayer application.



SULFUR QUANTUM DOTS ADDED ACTIVE PACKAGING/COATING FORMULATIONS BASED ON SEAWEED-DERIVED POLYSACCHARIDES FOR FOOD PRESERVATION

Ruchir Priyadarshi*, Zohreh Riahi, Jong-Whan Rhim

BioNanocomposite Research Centre, Department of Food and Nutrition, Kyung Hee University, 26 Kyungheedaero Dongdaemun-gu, Seoul 02447, Republic of Korea

* ruchirpriyadarshi16@gmail.com

Non-biodegradable plastic-based waste accumulation in the environment and food wastage due to spoilage are two massive problems all the world's economies face. Although these problems seem mutually unrelated, the development of sustainable, biodegradable active food packaging materials has emerged as a common solution to these problems. To this end, this work attempts to develop food packaging and coating solutions using biodegradable seaweed-based polysaccharides - alginate and carrageenan. Seaweeds are one of the most abundant renewable resources on earth. These sustainable polysaccharides are biodegradable, safe, edible, and show excellent film/coat formation, making them suitable for this application. Furthermore, sulfur quantum dots (SQDs) have been used as multifunctional nanofillers imparting polysaccharides with antioxidant, antimicrobial, and UV-blocking properties. SQDs are also sustainable and value-added active materials derived from sublimed sulfur waste produced in humongous amounts by the petrochemical industries during petroleum refining. Hence, this work presents Alginate/SQD formulation to coat food wrapping and packaging grade paper. Alginate is cross-linkable by bivalent metal ions such as Ca^{2+} , making the paper moisture-resistant. On the other hand, Carrageenan/SQD was used as a direct coating on food items, such as fresh produce, to prevent them against microbial contamination, oxidation, and UV-mediated spoilage. Since carrageenan is readily water soluble, the carrageenan/SQD coating is washable, and the coated fruits and vegetables can be rinsed with water to remove the coating before consuming them. Both alginate and carrageenan possess an excellent ability to carry and release active components, such as SQDs, in a controlled manner. Both formulations exhibited an excellent ability to enhance the shelf life of packed/coated food products while showing excellent biodegradation in soil under ambient conditions, simultaneously addressing environmental and food safety issues.

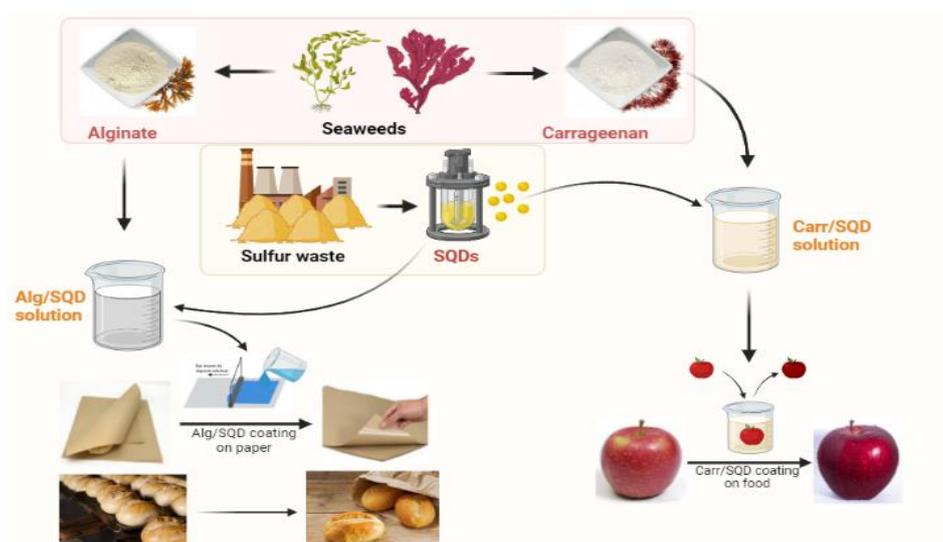


Figure 1. Sustainable multifunctional coating and packaging solutions were developed for preserving food products using the value-addition of naturally renewable seaweed and sublimed sulfur waste.



GLYCOPROANTHOCYANIDINS FROM WESTERN RED CEDAR BARK AS FUNCTIONAL INGREDIENTS IN FOOD

Bautista G.F.M.^{*ab}, Musl O.^a, Rosenau T.^e, Potthast A.^e, Rojas O.J.^{a-d}

^a *Bioproducts Institute, University of British Columbia, Canada*

^b *Department of Chemistry, University of British Columbia, Canada*

^c *Department of Chemical and Biological Engineering, University of British Columbia, Canada*

^d *Department of Wood Science, University of British Columbia, Canada*

^e *Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences, Austria*

* email of presenting author: gmbautista@chem.ubc.ca

Thermal processing of food improves aroma, texture, and storage stability. Unfortunately, Advanced Glycation End-products (AGEs, also known as glycotoxins¹) are simultaneously formed during this process in a chain of non-enzymatic reactions commonly referred to as the Maillard reaction. AGEs in food are typically reduced by changing processing conditions or lowering the amount of carbohydrates, lipids, and proteins in food. However, these changes in the food formulation greatly affect food flavor and texture, ultimately affecting its marketability. In this study, we propose the use of glycoproanthocyanidins in food to inhibit advanced glycation processes.

Glycoproanthocyanidins (GPs) are complexes of polysaccharides and proanthocyanidins that can be accessed from Western Red Cedar (WRC) bark by hot water extraction (5.58%, oven-dried basis). Monosaccharide analysis after hydrolysis of the GPs showed that glucose is the most abundant monosaccharide at 72%, while arabinose, rhamnose, fucose, galactose, xylose, mannose, galacturonic acid, and 4-O-methylglucuronic acid cumulatively account for less than 15% of the monosaccharides. Proanthocyanidins bound to the polysaccharides were detected visually after oxidative depolymerization of the extract in dilute acid. WRC bark GPs show good thermal stability ($T_{\text{degradation}} = 317\text{ }^{\circ}\text{C}$), and are applicable in wide range of food thermal processes. Aqueous dispersions of WRC bark GPs were colloidally stable (centrifugation at 20130g for 2 hours), with particles having a mean hydrodynamic size of $165 \pm 39\text{ nm}$, a ζ -potential of -18 mV ($\text{pH} = 6.89$), and an intrinsic viscosity ($[\eta]_0$) of 0.07 mL/mg . Based on DPPH radical-scavenging assay, WRC bark GPs exert antioxidant activity, which shows their potential as AGE inhibitors and as food preservatives against spoilage. In addition, WRC bark GPs have appreciable surface activity (48 mN/m at 4 mg/mL vs air), making them advantageous over conventional food emulsifiers because of their added health benefits. These newly reported colloidally stable glycoproanthocyanidins from Western Red Cedar bark are expected to open new opportunities for formulating foods with a variety of functional properties and health benefits.

[1] Chen, G. Dietary N-epsilon-carboxymethyllysine as for a major glycotoxin in foods: A review. *Comprehensive Reviews in Food Science and Food Safety* **20**, 4931–4949 (2021).



STRUCTURAL ANALYSIS AND ATTENUATES HYPERURICEMIC NEPHROPATHY OF DEXTRAN FROM THE *IMPERATA CYLINDRICA* BEAUV. VAR. MAJOR (NEES) C. E. HUBB.

Wenchen Yu ^{*a,b,c}, Mengnan Liu ^{a,b,c}, Jiangfei Li ^{a,b,c}, Junwen Wang ^{a,b,c}, Jingxuan Jia ^{a,b,c}, Weihong Lu ^{b,c},

^a School of Chemistry and Chemical Engineering, Harbin Institute of Technology, China
^b Institute of Extreme Environment Nutrition and Protection, Harbin Institute of Technology, China
^c School of Medicine and Health, Harbin Institute of Technology, China

* yuwenchen1117@hotmail.com

We isolated two new polysaccharides from *Imperata cylindrica*, named ICPC-a and ICPC-b, through hot water extraction, decolorization, ethanol graded precision, and DEAE-52 purification. The activities of ICPC-a and ICPC-b were evaluated by XOD inhibition experiments. The results showed that *Imperata cylindrica* polysaccharides had certain XOD inhibitory activity, and the inhibitory effect of ICPC-a on XOD was significantly stronger than that of ICPC-b. ICPC-a was purified with Sephadex G-100 column and analyzed the structure by GC-MS, FT-IR, NMR. The results showed that ICPC-a was a novel neutral polysaccharide with a molecular weight of 45 kDa, which was composed of α -D-1,3-Glcp and α -D-1,6-Glcp. X-ray diffraction analysis confirmed its amorphous nature, and scanning electron microscopy revealed a layered morphology. ICPC-a significantly reduced apoptosis and improved fibrosis in HK-2 cells (human renal tubular epithelial cells) induced by uric acid. The purpose of this study is to provide scientific basis for the development and utilization of polysaccharides from *Imperata cylindrica*.

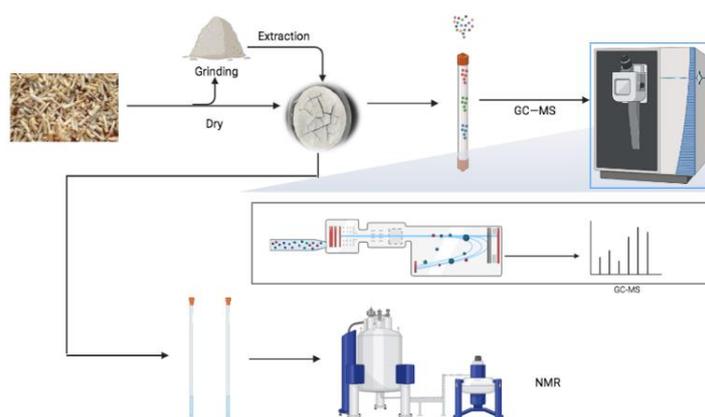


Figure 1 : Isolation, extraction and purification of polysaccharides



Session 7

Polysaccharides in medical and pharmaceutical applications

Session organizers:

Rupert Kargl, Carmen Freire, Pietro Matricardi, Sylvia Collic-Jouault, Wu Jiang-Yong

Keynote speaker:

Shaoping Nie - ~~withdrawn~~

Prospects for the Relationship of the Structure of Bioactive Polysaccharides and Their Multifunctional Effects

Petra Kotzbeck

Bacterial nanocellulose and its implications in wound healing and skin regeneration

Nicola Tirelli

Knowns and unknowns in hyaluronic acid interactions with ITS main receptor (CD44)



BACTERIAL NANOCELLULOSE AND ITS IMPLICATIONS IN WOUND HEALING AND SKIN REGENERATION

Kotzbeck, P. ^{*a,b}, Hofmann, E. ^{a,b}, Hecker, A ^{a,b}, Mohr, G ^d, Funk, M.^e, Bernadelli de Matos, I.^c, Geissler-Holzer, JCJ. ^{a,b}, Kamolz, LP. ^{a,b}

^a Medical University Graz, Research Unit for Tissue Regeneration, Repair and Reconstruction, Division for Plastic, Aesthetic and Reconstructive Surgery, Graz, Austria

^b JOANNEUM RESEARCH Forschungsgesellschaft mbH, COREMED –Centre of Regenerative and Precision Medicine, Graz, Austria

^c Fraunhofer Institute for Silicate Research ISC, Translational Center Regenerative Therapies, Würzburg, Germany

^d JOANNEUM RESEARCH Forschungsgesellschaft mbH, MATERIALS – Institute for Surface Technologies and Photonics, Graz, Austria

^e EVOMEDIS GmbH, Graz, Austria

* petra.kotzbeck@medunigraz.at

Wound healing is a complex physiological process that can be significantly improved by innovative biomaterials. Polysaccharides, with their biocompatibility and diverse properties, have emerged as promising candidates for wound dressing materials. Polysaccharide-based materials, such as alginate, bacterial nanocellulose (BNC), and hyaluronic acid, offer diverse advantages in wound coverage and wound healing. Alginate provides a versatile and easy-to-use option, while BNC and hyaluronic acid offer unique properties that can actively enhance tissue regeneration. Moreover, the functionalization of BNC opens up exciting possibilities for customizing wound dressings to meet the specific needs of patients and optimize the wound healing process.

To achieve the full potential of BNC for wound healing, functionalization is crucial. By incorporating antimicrobial agents, bioactive molecules or even pH sensitive dyes into BNC matrices, these materials can be modified to address specific wound healing challenges. For instance, the inclusion of antimicrobial agents such as antiseptics can mitigate the risk of infection, a common complication in chronic wounds or burn wounds. Further, pH dyes can be cross-linked to BNC to achieve a wound dressing that indicates pH changes and can serve also as diagnostic tool to monitor potential pathological changes during wound healing. To study the drug delivery of antiseptics, BNC was loaded with four different clinically used antiseptic solutions. The antibacterial activity and antiseptic concentration were measured in punch biopsies of the loaded BNC at different time points. To monitor the pH value, BNC was chemically functionalized with the indicator dye GJM-534. To investigate the temporal resolution, circular pH donors with different pH values were used.

We were able to show that clinically relevant antiseptic concentrations could be achieved within BNC that leads to effective inhibition of bacterial growth. We also found that BNC was effectively functionalized with indicator dye, that was reactive to a wide range of different pH values. The combination of antiseptics with BNC proved to be an efficient approach to combat bacterial infections. Further, functionalization with pH indicators would potentially allow pH monitoring during the wound healing process. Both modifications of BNC represent clinically viable approaches to improve the wound healing and wound monitoring and help many patients with chronic wounds and burn wounds.



KNOWN AND UNKNOWN IN HYALURONIC ACID INTERACTIONS WITH ITS MAIN RECEPTOR (CD44)

Tirelli N. *

Laboratory of Polymers and Biomaterials, Italian Institute of Technology, Genova, Italy

* Nicola.tirelli@iit.it

Hyaluronic acid (HA) is both a naturally occurring extracellular matrix component (ECM) and a popular biomaterial. From a regulatory point of view, HA has traditionally been regarded as a medical device, in that its mode of action e.g. as a dermal filler or in the 'viscosupplementation' of arthritic joints was typically believed to be based on its physical properties (rheology, osmotic pressure).

HA, however, has a rather rich list of interaction partners, which range from cell surface receptors such as CD44 or the cognate HARE to ECM proteoglycans such as aggrecans; the presence of these interactions, which e.g. control the cellular uptake of HA [1,2] or modulate the ECM mechanical properties make it difficult to discuss the HA role in purely physical terms.

A major consequence of this point is that it may become difficult to foresee how broad the definition of HA can be stretched: in drug delivery or regenerative medicine, HA is generally derivatized, which may be sufficient to alter the HA-receptor interactions. A threshold probably exists, above which chemical changes weaken so much both affinity and avidity (HA can cluster several receptors on its chain) to dramatically alter biological performances; this begs the question whether one should still be calling 'HA' a chemical entity that is hardly recognized by HA receptors?

This presentation will first review the 'ontology' of HA (focusing on an often neglected parameter such as chain rigidity) and of its receptors (which interactions control them and whether there is a role for macromolecular rigidity). We will then move to a detailed analysis of how even rather simple chemical modifications may have dramatic effects on both physical parameters (e.g. coil expansion) and biological interactions (e.g. the kinetics of HA internalization in cells)..

[1] Rios de la Rosa J.M. et al., *Advanced Healthcare Materials*, 8, 1901182, 2019.

[2] V. Quagliariello et al. *Biomaterials Advances*, 130, 112475, 2021.



HYALURONAN-CHOLESTEROL NANOGELS FOR ENHANCING THE OCULAR DELIVERY OF THERAPEUTICS

N. Zoratto^a, L. Forcina^b, L. Mosca^c, A. Musarò^b, C. Di Meo^a, P. Matricardi^{a*}

^a Department of Drug Chemistry and Technologies, Sapienza University of Rome, Italy

^b DAHFMO-Unit, Sapienza University of Rome, Italy

^c Department of Biochemical Sciences, Sapienza University of Rome, Italy

* pietro.matricardi@uniroma1.it

Topical drug delivery is widely used to treat both anterior and posterior segment diseases affecting the ocular tissues, and eye drops are the most common method for drug administration. [1] Although topical instillation is patient-compliant, its application still faces several challenges due to the anatomical and physiological barriers of the eye, which hinder drug penetration. Hence, less than 5% of topically applied therapeutics reach the intraocular tissues. [2] Cornea is the main mechanical and chemical barrier limiting the diffusion of the hydrophilic and most of the hydrophobic drugs into the anterior eye camera. Consequently, the use of nanocarriers with appropriate particle sizes and bioadhesive properties may represent an efficient strategy to topically treat several ocular disorders. [3] Moreover, nanoparticles composed of natural polymers show the additional advantage of being usually mucoadhesive, non-toxic, biocompatible, and biodegradable. Among the natural polymers, hyaluronic acid (HA), represents a good candidate for the preparation of nanoparticles. HA naturally occurs in the human body and high concentrations can be found in the eyes, where it is located in both corneal endothelium and epithelium, thanks to its interaction with the CD44 receptors of cells. Moreover, an enhanced expression of CD44 receptors was observed on the epithelium of corneas with inflammation and allograft rejection. As a result, HA is widely used in ophthalmology for the treatment of dry eye disease as well as in the formulation of eye drops as a viscosifying agent. [4] We already developed amphiphilic hyaluronan-cholesterol nanogels (HA-CH NHs) for drug delivery applications. [5,6] Grafting cholesterol (CH) moieties to the HA chains allowed the polymer to assemble spontaneously in aqueous environment thus forming NHs, composed of internal hydrophobic cholesterol domains interspersed within a hydrophilic environment of HA chains. Such HA-CH-based NHs were able to efficiently entrap both hydrophobic and hydrophilic drugs. Compared to other polysaccharide-based NHs intended for ocular drug delivery, the HA-CH NHs prepared for the present work show the further advantage of an easy-fast preparation procedure (sterile and drug-loaded NHs are formed in a single step by autoclaving process), which is amenable to their scale-up production as eye-drops. Specifically, in this work, the bioadhesive properties of NHs were investigated *ex-vivo*, confirming that NHs are able to interact with corneal components, being retained on porcine corneas. Then, both hydrophobic (dexamethasone and piroxicam) and hydrophilic (tobramycin and diclofenac) drugs were successfully loaded into NHs. *Ex-vivo* experiments showed that the entrapment of hydrophobic therapeutics into NHs results in different transcorneal drug permeation, which is limited by the water solubility of the drug. In contrast, the delivery of hydrophilic drugs is highly enhanced by NHs. The obtained results suggest that NHs formulations can improve the ocular bioavailability of the instilled drugs, thus opening the route for the application of HA-based NHs in the treatment of both anterior and posterior eye segment diseases.

[1] Janagam, D. R., et al., *Advanced Drug Delivery Reviews*, 122, 31-64, 2017

[2] Omerović, N. et al., *Application of Nanoparticles in Ocular Drug Delivery Systems*. Health and Technology (Berl)., (2020) 1-18

[3] Cuggino, J. C. et al., *Journal of Controlled Release*, 307, 221-246, 2019

[4] Dubashynskaya, N., et al., *Pharmaceutics*, 12, 22, 2020

[5] Di Meo, C. et al., *Pharmaceutics*, 10, 213, 2018

[6] Montanari, E., et al., *Advanced Healthcare Materials*, 7, 1701483, 2018



CHITOSAN-BLOCK-DEXTRAN COPOLYSACCHARIDES FOR NUCLEIC ACID DELIVERY

Courtecuisse E.^{*a}, Christensen B.E.^b, Schatz C.^a

^a *Laboratoire de Chimie des Polymères Organiques (LCPO), Université de Bordeaux, France*

^b *NOBIPOL - Department of Biotechnology and Food Science, NTNU, Trondheim, Norway*

* ecourtecuis@enscbp.fr

Block copolymers containing polysaccharides are increasingly considered for their sustainability, biodegradability, and biological properties. A first achievement was performed in the late 2000s and early 2010s with the design of hybrid copolymer structures containing a polysaccharide block associated to a synthetic one. This coincided with the advent of the click chemistry based on the Huisgen 1,3-dipolar cycloaddition which has been widely applied to the copolymer field. It seems now rather obvious that the next step would consist in synthesizing copolymers exclusively made of polysaccharides, i.e block copolysaccharides. In this context, it is relevant to use a click chemistry approach specific of the reducing end of polysaccharides [1]. Here, we propose difunctional linkers based on hydrazide or oxyamine groups that could perfectly meet this objective. Advantages of these linkers include their very good reactivity with the reducing end at room temperature both in terms of yield and reaction rate, their water-solubility, the easy removal of excess product and their commercial availability. In our case, the block copolysaccharides chosen are composed of chitosan and dextran. Dextran is a PEG-like polysaccharide and chitosan is a bio-sourced, positively charged polymer with interesting biological and physicochemical properties such as its low toxicity, its antimicrobial properties and last but not least its complexing properties with nucleic acids [2].

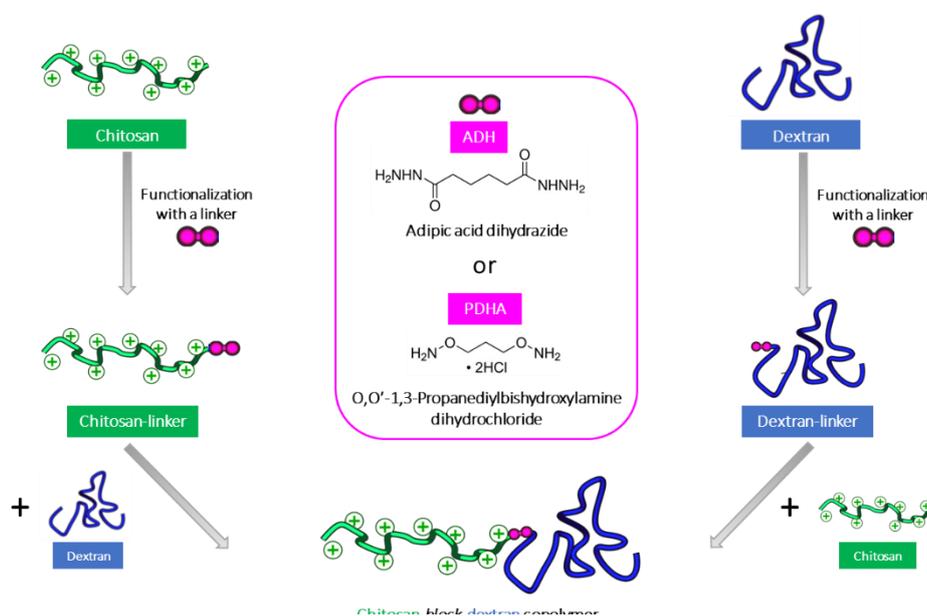


Figure 1. General scheme of the two main synthesis routes to obtain chitosan-block-dextran copolysaccharides

[1] Amalie Solberg, Ingrid V Mo, Line Aa Omtvedt, Berit L Strand, Finn L Aachmann, Christophe Schatz, Bjørn E Christensen, *Click chemistry for block polysaccharides with dihydrazide and dioxyamine linkers - A review*. *Carbohydr Polym* **2022**, 278, 118840

[2] Tim Delas, Formulation and stabilization of colloidal polyelectrolyte complexes of chitosan and siRNA, thesis, University of Bordeaux, **2021**



ALGINATE ESTERS AS NOVEL MULTIFUNCTIONAL EXCIPIENTS FOR TABLET FORMULATION: STRUCTURE-FUNCTION RELATIONSHIP

Sanchez-Ballester N.M. ^{*a,b}

^a ICGM, University of Montpellier, CNRS, ENSCM, Montpellier, France

^b Department of Pharmacy, Nîmes University Hospital, Nîmes, France

* noelia.sanchez-ballester@umontpellier.com

Tablets remain the solid dosage form of choice for administering medicines to patients. They have a number of advantages over other dosage forms, such as ease of administration, improved patient experience and the ability to modify the release of the active pharmaceutical ingredient. However, tablets also present some challenges as they have to be designed according to specific criteria (hardness, disintegration, dissolution and physico-chemical stability) that are essential to ensure that the drug actually reaches the patient. [1]

A topic presenting increase interest in pharmaceutical research is the development of directly compressible excipients displaying multifunctional properties for tablet's production. [2] Multifunctional excipients are attractive as they combine two or more functionalities through a single ingredient, have high intrinsic functional performance to increase the batch size and loading of the active ingredient and excellent performance characteristics.

In this context, alginic acid and its salts appear to be an excellent choice for the development of value-added materials for tableting and drug delivery applications due to their abundance, biodegradability and non-toxicity. These materials are versatile in their applications; while alginate salts have been used as sustained release matrices, alginic acid has interesting properties as a disintegration-promoting excipient in tablets designed for immediate drug release. [3] However, despite their proven interest, the use of these materials continues to be limited due to certain drawbacks such as uncontrolled swelling properties, low tablet hardness and poor powder flow.

Our recent work demonstrates that an effective way to improve these drawbacks is the use of methyl alginate esters as excipients for the manufacture of tablets by direct compression. These easily prepared materials exhibit better flow and compressibility than native alginate, resulting in tablets with tensile strength comparable to microcrystalline cellulose (MCC). They act as multifunctional excipients (disintegrant, binder, etc.), with drug release time controlled by the degree of methylation. [4] Furthermore, they show less impact of moisture conditions than MCC widely used in the pharmaceutical industry for tablet production. [5] These findings suggest that alginate esters can also act as moisture-scavenger's excipients without losing their functional properties and reducing the degradation of moisture-sensitive drugs. Thus, this presentation will describe the work done on the development of these alginate derivatives as a cheaper and easier candidate replacement for co-processed commercial excipients.

[1] Augsburger L.L. & Hoag S.W., *Pharmaceutical Dosage Forms – Tablets*, 3rd Ed. Taylor and Francis Group, 2008; [2] Saha S. & Shahiwala A.F., *Expert Opin Drug Deliv*, 2009, 6(2), 197-208, 2009; [3] Sanchez-Ballester N.M., Bataille B., et al., *Carbohydrate Polymers*, 270, 118399, 2021; [4] Sanchez-Ballester N.M., Bataille B., et al., *Carbohydrate polymers*, 240, 116280, 2020; [5] Sanchez-Ballester N.M., Trens P., et al., *Carbohydrate Polymers*, 297, 120063, 2022.



PREPARATION AND CHARACTERIZATION OF WOOD NANOFIBER HYDROGELS AS WOUND DRESSINGS

Bas Y. ^{*a}, Hanna K. ^b, Sotra Z. ^b, Zattarin E. ^c, Junker J. P. E. ^b, Rakar J. ^b,
Aili D. ^c, Berglund L. ^a, Oksman K. ^{a,d}

^a *Wood and Bionanocomposites, Luleå University of Technology, Sweden*

^b *Experimental Plastic Surgery and Center for Disaster Medicine and Traumatology, Linköping University, Sweden*

^c *Laboratory of Molecular Materials, Linköping University, Sweden*

^d *Department of Mechanical & Industrial Engineering (MIE), University of Toronto, Canada*

* yagmur.bas@ltu.se

Chronic and non-healing wounds consume immense resources for healthcare systems. Innovative materials have the potential to improve wound management. Ideally, wound dressings should be non-toxic and mechanically stable barriers covering wounds in a "see-through" fashion, while absorbing wound exudates, and providing a moist environment to accelerate re-epithelialization. TEMPO oxidized cellulose nanofibers (TO-CNFs) are charged and forms networks suitable for use in wound dressings due to their biocompatibility, high absorption ability and transparency. [1] Conventionally, preparation of TO-CNFs requires pulping and bleaching of wood followed by oxidation of the bleached pulp, that is a multi-step processing requiring several set-ups and washings. This project focuses on direct utilization of wood to develop wound dressings. Herein, CNFs were obtained from direct TEMPO mediated oxidation (TO) of softwood (SW) and hardwood (HW), followed by fibrillation in a microfluidizer. Obtained nanofibers assembled into self-standing networks via vacuum filtration only by means of interfibrillar interactions, which can be used as dressings. Materials were investigated from a structure-property relationship by examination of oxidized wood fibers, detection of nanofiber size and morphology, evaluation of mechanical, thermal, water absorption properties and cytocompatibility of the networks. Degree of oxidation was 0.48 ± 0.11 and 0.40 ± 0.07 mmol/g for TO of SW and HW, respectively, where nanofibers with widths smaller than 10 nm were obtained from both wood species after fibrillation. The nanofiber networks were transparent, exhibited excellent water absorption abilities (~ 2500 wt%), and good mechanical properties with ultimate tensile strengths of 210 ± 60 and 190 ± 30 kPa in hydrogel state, for SW and HW, respectively. The networks did not show detrimental effects on proliferation of human fibroblast cells and exhibited comparable properties to networks derived from similar fibrillation processing of commercial TEMPO oxidized pulp, which was used as a reference material. Preparation of biocompatible and sustainable materials meeting the needs of advanced dressings directly from wood, the most abundant source of cellulose, with a single step treatment is valuable from both environmental and economic perspectives.

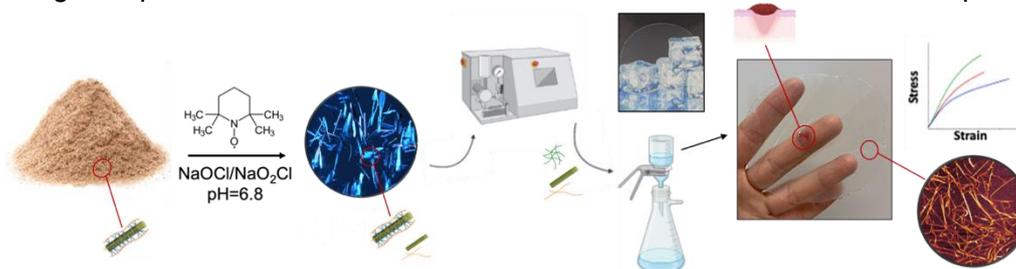


Figure 1: Scheme of direct oxidation and processing of wood for CNF wound dressings.

[1] Squinca P., Berglund L., Hanna K., Rakar J., Junker J., Khalaf H., Farinas C.S., & Oksman K., *Biomacromolecules*, 22, 3202-3215, 2021



ENCAPSULATION OF COSMETIC ACTIVES BY COMPLEX COACERVATION: THE POTENTIAL OF FUNGAL CHITOSAN

Delaporte A.^{a*}, Paraskevopoulou A.^b, Grisel M.^a, Gore E.^a

^aURCOM EA 3221 INC3M-CNRS-FR 3038, Université Le Havre Normandie, France

^bLaboratory of Food Chemistry and Technology, School of Chemistry, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece

* adeline.delaporte@doct.univ-lehavre.fr

Natural biologically active compounds, such as vitamins, polyphenols, and essential oils, are commonly used in topical delivery systems due to their diverse qualities, including antioxidant, anti-aging, regenerative, and anti-inflammatory effects [1,2]. However, many limitations such as low solubility, restricted skin penetration, sensitivity to environmental parameters, and chemical instability often impact the efficacy of these compounds, thereby reducing the efficiency of the formulation, and representing potential risks to consumers.

Complex coacervation, a physicochemical method of encapsulation involving two polymers of opposite charges self-assembling through electrostatic interactions, appears as a promising technique to overcome these limitations. This technique enables high loading capacities and high encapsulation efficiencies; therefore, it represents an excellent approach to improve the oxidative stability and controlled release behavior of biologically active compounds [3].

This study focuses on the potential of **fungal chitosan (FC)**, a cationic polysaccharide issued from fungal sources, which was combined with **gum Arabic (GA)** to ensure **fully vegetal encapsulation** of biologically active ingredients by complex coacervation. Thus, FC-GA coacervates were successfully elaborated and physicochemical properties such as viscoelasticity, yield and encapsulation efficiency were explored, further highlighting the suitability of fungal chitosan as an innovative encapsulation ingredient. The potential of FC in cosmetic applications extends beyond its encapsulation capacities as it brings **multiple bioactive properties** such as antimicrobial, anti-inflammatory, and wound healing properties which can further enhance the efficacy of topical delivery systems [4]. Its fully vegetal nature also makes it a **sustainable and eco-friendly** choice for encapsulation in cosmetic and skincare formulations [5].

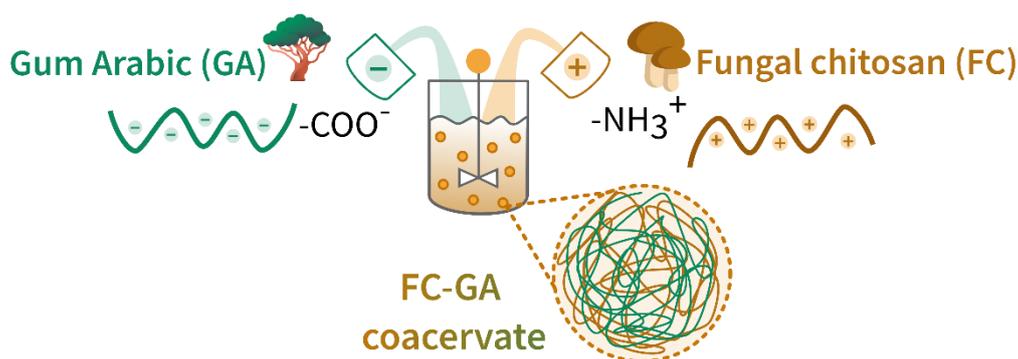


Figure 6 : Schematic representation of FC-GA coacervation

- [1] S. SILVA, M. FERREIRA, A.S. OLIVEIRA, C. MAGALHÃES, M.E. SOUSA, M. PINTO, J.M. SOUSA LOBO, AND I.F. ALMEIDA, *INT J COSMET SCI*, 4, 378–386, 2019.
- [2] H.T. HOANG, J.-Y. MOON, AND Y.-C. LEE, *COSMETICS*, 4, 106, 2021.
- [3] Y.P. TIMILSENA, T.O. AKANBI, N. KHALID, B. ADHIKARI, AND C.J. BARROW, *INTERNATIONAL JOURNAL OF BIOLOGICAL MACROMOLECULES*, 1276–1286, 2019.
- [4] T. HUQ, A. KHAN, D. BROWN, N. DHAYAGUDE, Z. HE, AND Y. NI, *JOURNAL OF BIORESOURCES AND BIOPRODUCTS*, 2, 85–98, 2022.
- [5] V. GHORMADE, E.K. PATHAN, AND M.V. DESHPANDE, *INTERNATIONAL JOURNAL OF BIOLOGICAL MACROMOLECULES*, 1415–1421, 2017.



HYDROGEL LOADED 3D PRINTED BONE GRAFT FOR RECONSTRUCTION OF THE SEGMENTAL BONE DEFECT

Jaiswal A.K. ^{*a}

Centre for Biomaterials Cellular and Molecular Theranostics (CBCMT)
Vellore Institute of Technology (VIT) Vellore, Tamilnadu, India

*amitj@vit.ac.in

One of the three triads, scaffolds, is crucial to tissue engineering as it acts as a temporary matrix to help cells develop and replace missing components. These scaffolds would promote cellular adhesion, proliferation, and differentiation in both *in vitro* and *in vivo* conditions. Hydrogels are such materials that act as a 3D matrix for populating cells and loading bioactive molecules. Although they help in cell proliferation and act as a carrier of bioactive molecules, they lack the mechanical strength required for their application in bone tissue engineering in particular for the reconstruction of long bone defects [1]. Hence, to overcome this limitation, we have designed and fabricated a polydopamine-coated polycaprolactone-based 3D printed construct to provide the required mechanical strength. To facilitate the growth of cells and provide a cellular microenvironment, natural polymer-based composite hydrogels made of chitosan-gelatin-chondroitin sulfate have been embedded in this construct, thereby obtaining a hybrid construct. The hydrogel prepared was analyzed for various physicochemical, mechanical and biological properties through diverse characterization techniques. The presence of functional groups was determined by FTIR analysis. The hydrogels prepared were then determined for their swelling ability, degradation property and drug release properties. It has also been analyzed for its microstructure through SEM analysis. These results meet the requirement for the hydrogels and thus were taken further for biological characterization. Hydrogels were then cultured with mesenchymal stem cells following intra-hydrogel culture. Then the osteogenic potential in the presence of hydrogel was determined through various assays such as alizarin red assay and alkaline phosphatase assay. The composite hydrogel also has VEGF as a component which assists in angiogenesis. The release profile of the growth factor was also determined and was found to have a sustained release. Thus, the hydrogel obtained will be loaded onto the 3D-printed construct and taken further for *in vivo* analysis on a rabbit tibia model to analyze the neo-bone formation through micro-computed tomography and histological studies.

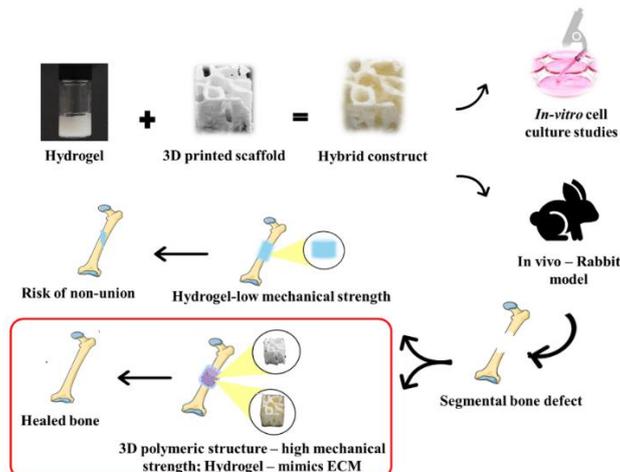


Figure 1: Work plan schematic of 3D printed-hydrogel loaded hybrid construct for reconstruction of segmental bone defects

[1] Xue, X., Hu, Y., Deng, Y. H., Su, J., *Advanced Functional Materials*, 19, 2009432, 2021



CELL ACTIVITIES ON VISCOELASTIC SUBSTRATES SHOW AN ELASTIC ENERGY THRESHOLD AND CORRELATE WITH THE LINEAR ELASTIC ENERGY LOSS IN THE STRAIN-SOFTENING REGION

Francesco Piazza^{1*}, Pasquale Sacco¹, Eleonora Marsich² and Ivan Donati¹

¹ *Department of Life Sciences, University of Trieste, Via Licio Giorgieri 5, I-34127 Trieste, Italy*

² *Department of Medicine, Surgery and Health Sciences, University of Trieste, Piazza dell'Ospitale 1, I-34129 Trieste, Italy*

* francesco.piazza2@phd.units.it

Extracellular matrix (ECM) owns complex mechanical milieu characterized by non-linear, plastic and viscoelastic behaviour. Cells are able to perceive this biophysical milieu and convert the resulting external mechanical forces into intracellular biochemical signals through a process called mechanotransduction [1,2]. Stiffness and viscoelasticity (in terms of stress relaxation or loss tangent) are the key mechanical features that play a role in the mechanosensing process of the cell [3,4]. Recently, energy-sensing of viscoelastic substrates has been shown to be an important controller of cellular activities, modulating mechanical transmission and transduction processes [5,6,7,8].

In this contribution, I will present the characterization and application of viscoelastic agarose-based hydrogels as ECM substrates endowed with fine-tune elastic energy. Furthermore, I will show how the cell response in 2D cell cultures conditions is steered by the energy-sensing process. Oscillatory mechanical stimulation on this set of materials reveals a linear stress-strain response of the substrates followed by a softening behaviour, typical trait of some biological tissues. Rheological data together with cell adhesion tests reveal the existence of a threshold value for elastic energy ($\sim 0.15 \text{ J/m}^3$) above which cell adhesion is impaired. Below this threshold, a correlation is found between the number of cells adhering to the substrate and the theoretical elastic energy loss calculated up to the maximum deformation that hydrogels can withstand under oscillatory shear. This elastic energy loss affects the formation of the focal adhesion points and the resulting ability of the cell to remodel the underlying matrix. In summary, this contribution remark the importance of the energy-sensing process of cell in the development of viscoelastic substrates to be used as ECM-like model.

- [1] B. D. Hoffman *et al.*, *Nature* 2011, 475, 7356.
- [2] O. Chaudhuri *et al.*, *Nature* 2020, 584, 7822.
- [3] S. Kumar *et al.*, *Biophys J* 2006, 90, 10.
- [4] O. Chaudhuri *et al.*, *Nat Mater* 2016, 15, 3.
- [5] P. Sacco *et al.*, *Adv Funct Mater* 2020, 30, 31.
- [6] P. Sacco *et al.*, *Adv Funct Mater* 2022, 32, 29.
- [7] Natalie Török *et al.* Research Square, 10 October 2022
- [8] Carla Huerta-López *et al.*, bioRxiv, 2022.11.16.516826



BIO-BASED UV FILTERS-FUNCTIONALIZED POLYSACCHARIDES FOR COSMETICS

Samalens F. ^{*a,b,c,d}, Berthomieu P. ^d, Billon L. ^{a,c}, Fernandes S. ^{a,b}

^a *Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, France*

^b *MANTA: Marine Materials Research Group, Universite de Pau et des Pays de l'Adour, E2S UPPA, France*

^c *Bio-inspired Materials Group: Functionalities & Self-assembly, Universite de Pau et des Pays de l'Adour, E2S UPPA, France.*

^d *Les Laboratoires de Biarritz, France*

* Email: fsamalens@univ-pau.fr / f.samalens@laboratoires-biarritz.com

Polysaccharides are extensively employed in cosmetic products as emulsifiers, thickening agents or moisturizing agents, and have important properties namely biocompatibility, biodegradability, antimicrobial activity, among others. Also, due to their physicochemical properties, polysaccharides are apt to chemoenzymatic and physical modifications to improve their intrinsic properties. Although polysaccharides are currently omnipresent in cosmetic products, very few research have been done towards their potential use in formulations for ultraviolet (UV) radiation protection.

Currently available sunscreens, that contain mainly synthetic organic or inorganic UV-filters, can cause detrimental effect on human health and marine habitats. Find out new environmentally friendly UV-filters is a major challenge in the 21st century. In this context, polysaccharides could be used to tackle this challenge, by replacing and/or enhancing the properties of current UV-filters.

This work aimed at elaborating UV absorbing materials based on the grafting of Mycosporine-like amino acids (MAAs) on marine oligosaccharides and polysaccharides. MAAs are biomolecules present in algae that have antioxidant properties and highly absorb UV light which make them good candidates to be used in the field of cosmetics. [1] MAAs have been grafted to Agarose, a polysaccharide also extracted from algae, and oligo-Agarose using green approaches. The Agarose-MAAs conjugates obtained exhibit good absorption in the UV range as well as photostability, film forming, antioxidant, UV-absorbing and gelling properties. These materials could be incorporated in emulsions, forming new and bio-sourced sunscreen.

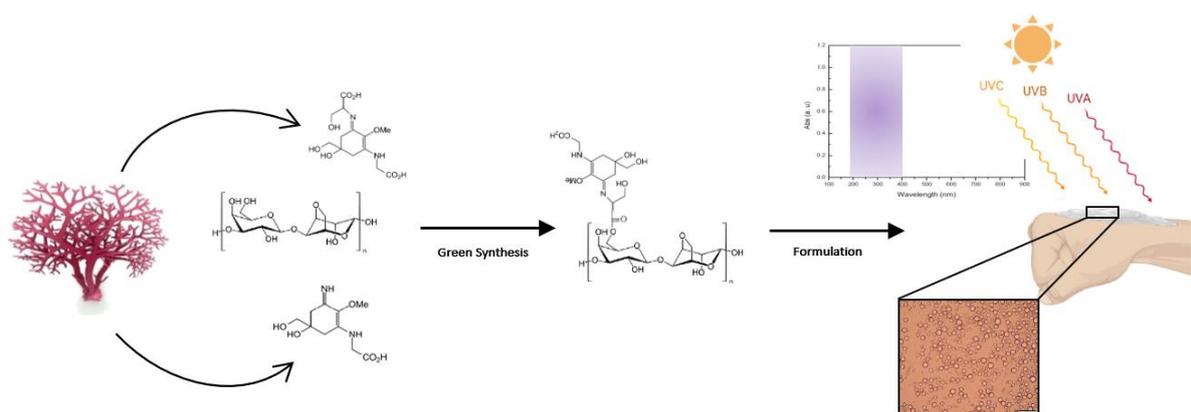


Figure 1 : Schematic representation of the formulation of bio-sourced sunscreen based on the green synthesis of Agarose-MAAs conjugates.

[1] Fernandes S., Alonso-Varona A., Palomares T., Zubillaga V., Labidi J., & Bulone V., *ACS Applied Materials & Interfaces*, 7, 16558-16564, 2015



3D PRINTING AND CHARACTERIZATION OF VASCULAR MODELS FROM POLYSACCARIDES

Lackner F.^{*a}, Šurina P.^a, Fink J.^b, Kotzbeck P.^b, Stana J.^c, Grab M.^d, Tsilimparis N.^c,
Mohan T.^a, Kargl R.^a, Stana Kleinschek K.^a

^a Institute for Chemistry and Technology of Biobased Systems (IBioSys), Graz University of Technology, Austria

^b Coremed, Joanneum Research, Austria

^c Department of Vascular Surgery, Ludwig Maximilians University, Germany

^d Department of Cardiac Surgery, Ludwig Maximilians University, Germany

*lackner@tugraz.at

Biological systems found in nature exhibit highly complex hierarchically ordered 3D structures with many degrees of organization and functionalization to achieve their unique mechanical and biological properties. The superior mechanical strength toughness of these naturally evolved composites originates from precise orientation of reinforcing fibers or particles such as the Bouligand chitin fiber structure found in crabs or lobsters. While living organisms grow these anisotropic reinforcement architectures, the fiber alignment in polymer processing and especially 3D printing requires external forces such as shear force, electric – or magnetic fields and is often limited to specific scenarios.[1] Herein we present the research results of our 3D printing experiments to create anisotropic structures from a nanofibrillated cellulose/alginate nanocomposite. The homogeneous bio-ink received from mixing of the biopolymers and CaCO₃ nanoparticles with tailor-made stirrers could be processed with an extrusion-based 3D printer, allowing in-situ fiber alignment to produce scaffolds with anisotropic properties. The subsequent crosslinking with weak acids additionally enables the precise control of mechanical properties within one single printing process, to create sophisticated structures with tuneable properties.[2] Various tubes with different fiber alignment patterns could be 3D printed to demonstrate the anisotropic and water-resistant behavior of our material. Further the material was characterized to assess important biomedical parameters like cell compatibility, nutrient diffusion and controlled degradability.

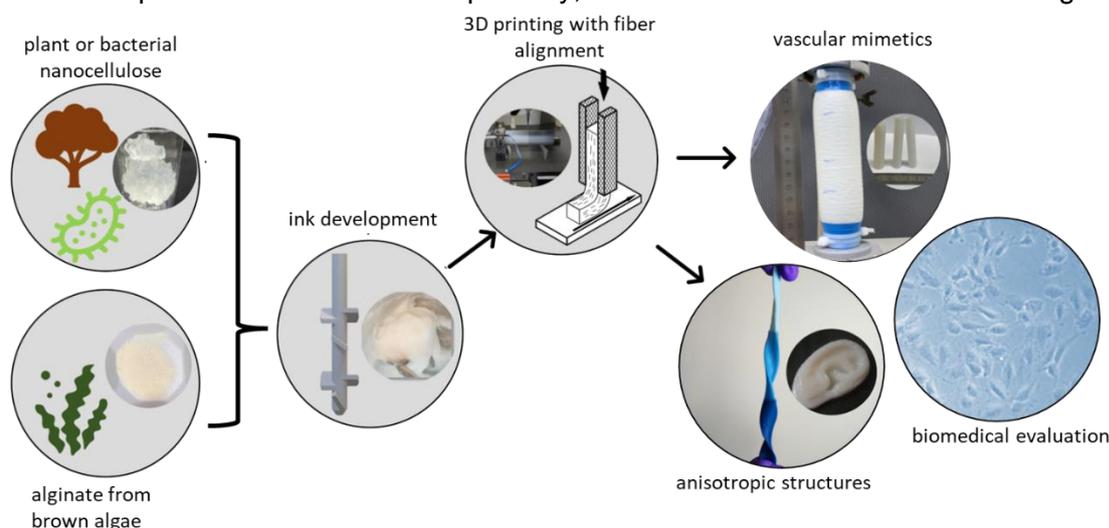


Figure 1 : Overview workflow

[1] Y. Yang, Z. Chen, X. Song, Z. Zhang, J. Zhang, K. K. Shung, Q. Zhou, Y. Chen, *Adv. Mater.*, 29, 1605750, 2017

[2] F. Lackner, I. Knechtl, M. Novak, C. Nagaraj, A. Dobaj Štiglic, R. Kargl, A. Olschewski, K. Stana Kleinschek, T. Mohan, *Adv. Mater. Technol.*, 2201708, 2023



FULLY CHARACTERIZED FATTY ACID CELLULOSE ESTERS (FACES) AS STARTING RAW MATERIAL FOR BIOMATERIALS, ADDITIVES AND ELECTRONICS SUPPORT APPLICATIONS

Joly N., Martin P.

Unité Transformations & Agroressources - ULR7519, UniLasalle, Univ. Artois, F-62408
Béthune, France

NICOLAS.JOLY@UNIV-ARTOIS.FR

Concerning fatty acylation of cellulose, a lot of studies, including ours [1], are dedicated to the characterization of mechanical and/or thermal and/or structural properties of Fatty Acid Cellulose Esters (FACES) [2], according to degree of substitution (DS) and fatty chain length [3]. These works are almost complete, now great deals are focussed on Synthesis processes and on the investigations on the potential applications of such bio-based materials. Interested in thermoplastic and hydrophobic FACE materials, our purpose sums up almost 15 years of our research work, and deals with the fully characterization of FACES, especially the structure-property relationship, and study of their potential applications. FACES with both various degrees of substitution (from DS = 1.7 to 3) and side chain length were obtained by grafting aliphatic fatty acid chlorides (from C10 to C16) onto cellulose, under homogeneous conditions (LiCl/DMAc as solvent). These FACES were characterized by classical methods such as Fourier Transformed InfraRed (FTIR) and Nuclear Magnetic Resonance of Proton (^1H NMR) spectroscopies, as well as Wide Angle X-ray Scattering (WAXS), Differential Scanning Calorimetry (DSC), mechanical analyses, and other physical properties (Hydrophobicity). Results have shown that all samples displayed a layered structure as described in Figure 1, whatever the alkyl chains length and the DS are. Plasticizing effect of the alkyl chains was less pronounced as the DS decreased, improving their ability to crystallize. Regarding the mechanical behavior and the chemical resistance, similar results were observed whatever the DS is.

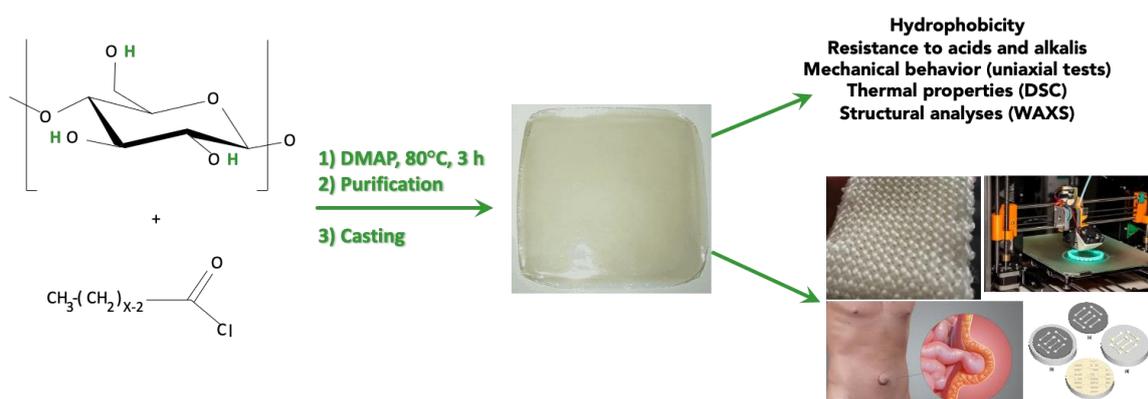


Figure 1. Synthesis and potential applications FACES.

Various applications were accordingly considered for these FACES such as chemical bottle coatings, or acid or base protection films. Some of them confirmed, as biomaterial for abdominal hernia sheets, as hydrophobic additive to improve properties of commercial biopolymers, as support for flexible support for microelectronics, or for 3D-printing applications.

REFERENCES

1. Duchatel-Crépy, L., Joly, N., Martin, P., Marin, A., Tahon, J.-F., Lefebvre, J.-M., Gaucher, V. *Carbohydrate Polymers*, **2020**, 234, 115912
2. Vaca-Garcia, C., Gozzelino, G., Glasser, W.G., Borredon, M.E. *Journal of Polymer Science: Part B: Polymer Physics*. **2003**, 41, 281-288
3. Peydecastaing, J., Vaca-Garcia, C., Borredon, E. *Cellulose*. **2011**, 18, 1023-1031.



POLYSACCHARIDE-BASED BIOHYBRID NANOFIBERS FOR WOUND HEALING APPLICATIONS

Fardim, P*. ^a, Shiny, J.P. ^b, Devi, M.V. ^{b,c}, Felciya, S.J.G. ^{b,c}, Ramanathan, G. ^{a,b}, Tiruchirapalli U. ^b

^a Department of Chemical Engineering, Chemical and Biochemical Reactor Engineering and Safety, KU Leuven, Celestijnenlaan 200F, Leuven 3001, Belgium

^b Biological Materials Laboratory, CSIR-Central Leather Research Institute (CLRI), Adyar, Chennai, India

^c Department of Leather Technology, (Housed at CSIR-Central Leather Research Institute), Alagappa College of Technology, Anna University, Chennai-600020

* pedro.fardim@kuleuven.be Twitter: @Chemenghealth

The protective layer of the body, the skin is often prone to damage due to several factors like trauma, accidents, stress, and hazardous exposure. This requires the skin to regenerate itself which is a finely regulated process. To hasten the process and prevent further damage, the dressing material is of prime importance. Herein, we fabricated poly-3-hydroxybutyric acid (P)-sodium alginate (S)-(core-shell) nanofibrous matrix as protective scaffold for the skin tissue regeneration in excision wound model. The arginine (A) and layered double hydroxides-bacitracin (LB) were incorporated into the core and shell of the nanofibrous matrix using co-axial electrospinning. The core-shell nanofibers assist in the synergistic, controlled delivery of L-arginine, and bacitracin with major role in the protein synthesis, cell signaling and infection control at wound site respectively. In vitro biocompatibility was confirmed by testing on dermal fibroblasts. Furthermore, in vivo studies revealed the synergistic effect of both the components in active healing of wounds. The biochemical, histochemical and immunohistochemical studies reveal that the arginine loaded scaffold aided cellular migration and proliferation. These results suggest that the simultaneous existence of the drug bacitracin-nano clay complex and L-arginine in the shell and core respectively has conferred interesting dynamic properties to the scaffold towards wound healing [1].

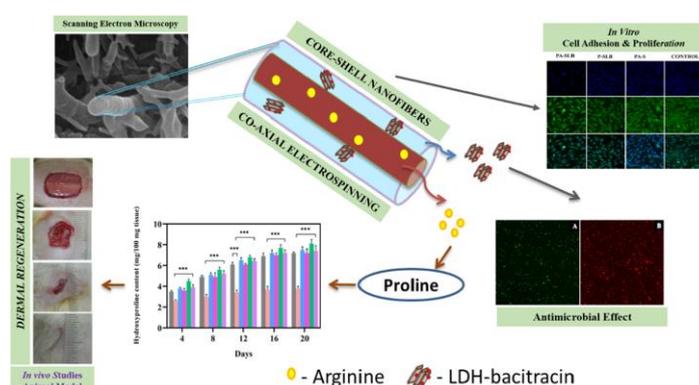


Figure 1 : In vitro and In vivo evaluation of polysaccharide-based biohybrids for wound healing

[1] Punalur John Shiny, Mohan Vimala Devi, Sekar Jeyakumar Grace Felciya, Giriprasath Ramanathan, Pedro Fardim, Uma Tiruchirapalli Sivagnanam, *International Journal of Biological Macromolecules*, 168, 46-58, 2021

CHARACTERIZATION OF CELL-BIOMATERIAL ADHESION FORCES THAT INFLUENCE 3D CELL CULTURE

Polez R.T. ^{a,b}, Huynh N. ^a, Pridgeon C.S. ^{a,b},
Valle-Delgado J.J. ^a, Harjumäki R. ^b, Österberg M. ^a

^a *Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland*

^b *Drug Research Program, Division of Pharmaceutical Biosciences, Faculty of Pharmacy, University of Helsinki, Finland*

* roberta.teixeirapolez@aalto.fi

Biomaterials, such as cellulose, offer advantages in 3D cell culture by mimicking natural cell environments. To further optimize 3D cell culture and explore new potential materials, it is essential to gain a deeper, quantitative knowledge on cell-biomaterial and cell-cell interactions. Herein, atomic force microscopy (AFM)-based techniques, especially single cell force spectroscopy (SCFS) and colloidal probe microscopy (CPM), were utilized to measure cell-cell and cell-biomaterial adhesion forces, and the results were correlated with experimental observations in 3D cell cultures. Two types of cell lines –human liver cancer cells HepG2 and human induced pluripotent stem cells iPS(IMR90)-4–, and 2 types of biomaterials –cellulose nanofibrils (CNF) and Matrigel– were studied in this work. The results showed that within 72 hours, both cell types formed rounded spheroids in CNF-embedded cultures. However, when embedded in Matrigel, the cells produced aggregates with a loose, non-spheroidal morphology. Interestingly, the adhesion force and energy between individual HepG2 cells were larger than between HepG2 cells and CNF. In the case of iPS(IMR90)-4 cells, the cell-Matrigel adhesion was found to be stronger than cell-CNF and cell-cell adhesion. These findings suggest that well-defined spheroids are formed when the cell-cell adhesion is stronger than the cell-material adhesion, as is the case for 3D cell cultures in CNF hydrogels. On the contrary, cell aggregates different from spheroids are formed when the cell-material adhesion prevails over the cell-cell adhesion. Understanding these adhesion mechanisms can optimize 3D cell cultures for *in vitro* drug development and regulatory studies, reducing reliance on animal testing and, consequently, making drug screening more ethical, efficient, and relevant to human physiology. This aligns with the recent elimination of the requirement for animal testing by the US Food and Drug Administration (FDA) in drug development.



ENDOTHELIALIZATION OF POLYCAPROLACTONE SCAFFOLDS WITH HYALURONIC ACID - PEPTIDE CONJUGATES

Mohan T.*^a, Gürer F.^b, Lackner F.^a, Gradišnik L.^c, Maver U.^c, Kargl R.^a, Stana Kleinschek K.^a

^aInstitute for Chemistry and Technology of Biobased System (IBioSys), Graz University of Technology, Stremayrgasse 9, Graz 8010, Austria

^bLaboratory for Characterisation and Processing of Polymers, Faculty of Mechanical Engineering, University of Maribor, Smetanova Ulica 17, 2000 Maribor, Slovenia
^cInstitute of Biomedical Sciences, Faculty of Medicine, University of Maribor, Taborska Ulica 8, 2000 Maribor, Slovenia

* tamilselvan.mohan@tugraz.at

Surface modification of vascular grafts with bioactive molecules can effectively improve the hemocompatibility of artificial vascular grafts and thus prevent thrombosis. However, these modified surfaces may be excessively hydrophilic or hydrophobic, limiting the initial adhesion of vascular endothelial cells and the formation of a confluent endothelial layer^[1]. Therefore, improving the endothelialization of these grafts by chemical modification with polysaccharide-peptide conjugates is attracting increasing interest. In this work, we report a one-step aqueous method for the synthesis of isolated and purified hyaluronic acid (HA)- amino acids or -peptide conjugates. Glycine methyl ester (Gly-OMe), diglycine methyl ester (DiGly-OMe), and tryglycine ethyl ester (TriGly-OEt) as model compounds for cell-adhesive peptides were conjugated to HA using carbodiimide in water at ambient conditions^[2]. The conjugates were oxidized using periodate oxidation to provide additional aldehyde functionality to the backbone of HA^[3]. In addition to extensive structural, solubility and charge analysis, these modified conjugates were chemically immobilized onto the aminolyzed polycaprolactone scaffold surfaces using Schiff's base reaction. The PCL surfaces modified with HA -amino acids or -peptide conjugates showed excellent biocompatibility and endothelial cell growth when incubated at increasing time points. The modular approach proposed in this work can be used not only to modify the backbone of polysaccharides with peptides, but also to develop or mimic the structural properties of various types of proteoglycans and develop new types of synthetic vascular grafts.

[1] Ren, X., Feng, Y., Guo, J., Wang, H., Li, Q., Yang, J., Hao, X., Lv, J., Ma, N., and Li, W. *Chemical Society Reviews*, **44**, 5680-5742, 2015.

[2] Pandit, A.H., Mazumdar, N., and Ahmad, S. *International Journal of Biological Macromolecules* **137**, 853-869, 2019.

[3] Gürer, F., Kargl, R., Bračič, M., Makuc, D., Thonhofer, M., Plavec, J., Mohan, T., and Kleinschek, K.S. *Carbohydrate Polymers* **267**, 118226, 2021.



STRATEGIES FOR LOADING LYOTROPIC LIQUID CRYSTALS WITHIN HYDROGELS: THE CASE OF CUBOSOMES AND BACTERIAL CELLULOSE TOWARDS CONTROLLED CARGO RELEASE

Villalva D.^a, Otoni C.*^b, Loh W.^a

^a *Institute of Chemistry, UNICAMP, Brazil*

^b *Department of Materials Engineering, UFSCar, Brazil*

* caio.otoni@ufscar.br

Among its different sources, cellulose is produced by some bacterial strains as a highly entangled and hydrated mat at the air/static culture medium interface. The low solid content of such a rather mechanically robust hydrogel enables loading molecules and particles within the interfibrillar space, with hydrophilic entities being of inherently easier loading in the aqueous compartments. We herein put forward the concept of loading bacterial cellulose hydrogels with both hydrophilic and hydrophobic molecules, in turn entrapped within cubosomes, dispersions of lyotropic liquid crystalline nanostructures bearing a bicontinuous cubic reverse arrangement. We synthesized ca. 200-nm-big cubosomes using phytantriol and the block copolymer Pluronic® F-127. This host (cubosome)/guest (model drug/dye) approach was validated here with fluorescein as a hydrophilic dye, Nile red as a hydrophobic dye, and sodium diclofenac as a model drug and. For the cubosomes themselves to serve as guests hosted by the bacterial cellulose mat, we put forward both *in situ* and *ex situ* strategies to entrap the nanostructures into the hydrated network. The BC membrane was produced in Hestrin-Schramm (HS) medium by *Komagataeibacter xylinus* cells. We propose an *in situ* immobilization protocol, by producing bacterial cellulose in cubosome-containing HS medium, as well as an *ex situ* protocol, via freeze-drying of the wet membranes followed by their reswelling in a cubosome dispersion. Also, the *in situ* strategy has been extended to biofabricated 3D capsules in addition to flat membranes. Small-angle X-ray scattering (SAXS), high-resolution confocal microscopy, and cryogenic transmission electron microscopy (cryo-TEM) confirmed the persistence of the internal cubic bicontinuous structure and that the cubosomes were evenly spread over the BC membranes in both methods. We hypothesize two mechanisms for sodium diclofenac delivery from BC membranes, namely: (i) sustained release of the cubosome-entrapped diclofenac and (ii) cubosome leaching from the biocellulose membranes. Finally, an external sodium alginate shell is proposed as a protecting, pH-responsive layer to control both mechanisms in a colon-targeted fashion. Altogether, this presentation will offer an overview of these and other efforts to promote the use of cubosome-loaded bacterial cellulose membranes for biomedical applications, mainly drug delivery for skin therapies for the flat membranes and colon-targeted delivery in the case of the alginate-coated biofabricated capsules.

Acknowledgements: FAPESP (grant no. 2021/12071-6), CNPq (grant no. 304753/2022-0), and CAPES (Finance Code 001).



DEVELOPMENT OF ALL-CELLULOSE BIOINKS FOR 3D BIOPRINTING APPLICATIONS

João P. F. Carvalho ^{a*}, Nicole S. Lameirinhas ^a, Maria C. Teixeira ^a, Jorge L. Luís ^{a,b}, Helena Oliveira ^c, José M. Oliveira ^{a,b}, Carla Vilela ^a, Carmen S. R. Freire ^a

^a CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

^b EMaRT Group - Emerging: Materials, Research, Technology, School of Design, Management and Production Technologies Northern Aveiro, University of Aveiro, 3720-511 Oliveira de Azeméis, Portugal

^c Department of Biology & CESAM, University of Aveiro, 3810-193 Aveiro, Portugal

* joao.pedro.carvalho@ua.pt

The biofabrication of living tissue constructs by 3D bioprinting is achieved through the layer-by-layer deposition of cell-laden biomaterials (bioinks), originating living three-dimensional structures with potential to be used for different biomedical applications like tissue engineering, drug development and testing, and as models of disease. The bioinks must possess suitable properties to be bioprinted and result in constructs with high shape fidelity, while also constituting an appropriate matrix for cells to remain viable and to prosper. Understandably, the success of the 3D bioprinting process is often dependent on the overall performance of the available bioinks. Therefore, the development and availability of bioinks with high performance is crucial to boost the progress of this field. In this sense, the present work describes the development of novel all-cellulose hydrogel bioinks based on the combination of a cellulose derivative, namely carboxymethylcellulose, with nanofibrillated cellulose. The impact of the addition of various contents of nanofibrillated cellulose in the properties of the inks' formulations (i.e., the rheological features) and of the final crosslinked hydrogels (i.e., degradation rate in different media, mechanical properties, and viscoelastic behaviour) is thoroughly explored. The crosslinking of the formulations with different ionic crosslinkers, and in various concentrations, was also investigated. Furthermore, the cytotoxic impact of the developed formulations against living cells is evaluated for up to 48 h. After the optimization of the 3D printing parameters (namely printing speed, pressure, and nozzle diameter), the bioprinting of the corresponding cell-laden bioinks was carried out, leading to the biofabrication of complex living structures with defined shape and size, and high cell viabilities after 1, 3 and 7 days post bioprinting.

Acknowledgments: This work was developed within the scope of the projects CICECO-Aveiro Institute of Materials (UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020) and CESAM (UIDP/50017/2020 & UIDB/50017/2020 & LA/P/0094/2020), financed by national funds through the FCT/MEC (PIDDAC), and financially supported by the project I&D "NANOBIINKS - Engineering bio-based nanofibers for the development of high-performance nanostructured bioinks for 3-D bioprinting, CENTRO-01-0145-FEDER-031289"- funded by the Operational Program of the Center Region, in its FEDER/FNR component, and by national funds (OE), through FCT/MCTES. FCT is acknowledged for the doctoral grant to J.P.F.C (2020.09018.BD) and N.S.L. (SFRH/BD/140229/2018) and the research contracts under Scientific Employment Stimulus to C.S.R.F. (CEECIND/00464/2017), C.V. (CEECIND/00263/2018 and 2021.01571.CEECIND) and H.O. (CEECIND/04050/2017).



SOLARSAFE – LIGHT-MEDIATED SELF-STERILIZING CELLULOSIC HYBRID MATERIAL

Daniel Langerreiter*^[a], Katariina Solin^[b], Mireia Jorda Redondo^[c], Roger Bresoli Obach^[c],
Santi Nonell Marrugat^[c], Mauri A. Kostianen^[a], Eduardo Anaya Plaza^[a]

^[a]Department of Bioproducts and Biosystems Aalto University 02150 Espoo, Finland

^[b]VTT Technical Research Centre of Finland Ltd., Functional Cellulose FI-02044 Espoo, Finland

^[c]Department of Applied and Analytical Chemistry Institut Químic de Sarrià Universitat Ramon Llul Barcelona, Catalunya 08007, Spain

*daniel.langerreiter@aalto.fi

Introduction:

Photodynamic inactivation (PDI) has gathered growing attention, due to the therapeutical advantages to tackle the increase of microbial antibiotic resistance. This technology is based in the light-mediated generation of reactive oxygen species mediated by a photosensitizer. Furthermore, singlet oxygen generation gives the opportunity for killing multi-resistant bacteria. Organic dyes like phthalocyanines, toluidine blue or porphyrins are among the widely used molecules with this property.

The aim of SolarSafe is the development of a self-sterilizing, yet biodegradable, single use materials for hygiene areas in regions of crisis and disaster. The photoactivity of cellulose-phthalocyanine hybrids have been already explored by our research group.¹ To prevent migration of phthalocyanine by contact, the photosensitizer is covalently bond directly on cellulose nanofibers (CNF).

For covalently coupling between the CNF, and photosensitizer EDC/s-NHS chemistry is used. As a control, the photosensitizer was mixed with CNFs and through the charge of the material physically adsorbed. Each step for both samples is followed by thorough characterization like IR, SPR, UV-Vis and AFM. The accessibility, singlet oxygen generation and quality of the photosensitizer were measured with laser flash photolysis and time-resolved near-infrared phosphorescence. The photodynamic inactivation was done at 630nm and with a sun simulator.

References:

1. Anaya-Plaza, E. *et al.* Photoantimicrobial Biohybrids by Supramolecular Immobilization of Cationic Phthalocyanines onto Cellulose Nanocrystals. *Chem. - A Eur. J.* **23**, 4320–4326 (2017).

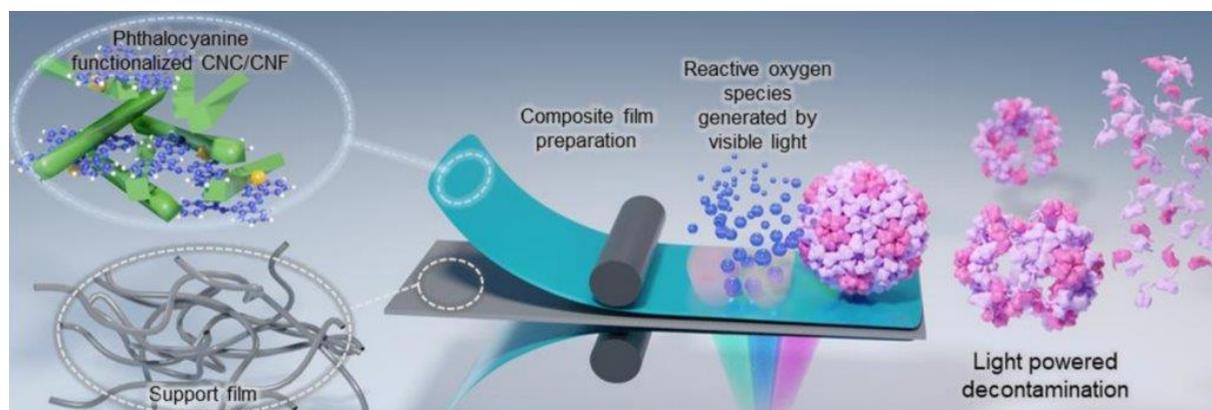


Figure 7: The aim is to create through covalently linked photosensitizer a self-sterilizing cellulose hybrid material.



NANOGELES OF POLYSACCHARIDES WITH ANTIOXIDANT AND ANTIBACTERIAL ACTIVITIES FOR DRUG DELIVERY

Dulong V. ^{*a}, Thébault P.^a, Labat B.^a, Picton L.^a, Le Cerf D.^a

^a *Polymers, Biopolymers, Surfaces, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, PBS, 76000 Rouen, France*

* virginie.dulong@univ-rouen.fr

The complexation of polyanions with polycations can spontaneously form nanogels having interesting properties for applications in drug delivery [1] [2] [3]. In this study, nanogels have been elaborated by the complexation of polysaccharides functionalized or not with a phenolic compound having an antioxidant activity [4]. Chitosan (CHIT) has been chosen as the polycation and carboxymethylpullulan (CMP) or hyaluronic acid (HA) grafted with aminoguaiacol (with different grafting degrees) as the polyanions (CMP-G, HA-G). The charge ratio between polyanion and polycation ($R_c=R^-/R^+$) has been varied from 0.1 to 5 to elaborate the PECs and find the conditions giving the best results in terms of size (D_h) and polydispersity (PDI). The presence of the aminoguaiacol moieties (which are hydrophobic) on CMP or HA has led to a better stability (in different media) of the corresponding PECs with some differences between PECs based on CMP-G or based on HA-G. Moreover, the analyses of the PECs by fluorescence spectroscopy in the presence of pyrene (hydrophobic probe) have shown the formation of hydrophobic clusters in the PECs. These clusters can be used to encapsulate hydrophobic molecules of interest (curcumin, diclofenac). The antioxidant properties of PECs have been evaluated by the DPPH method. Their antibacterial properties have been assessed against *Staphylococcus aureus* and the cytotoxicity has been studied with fibroblast cells.

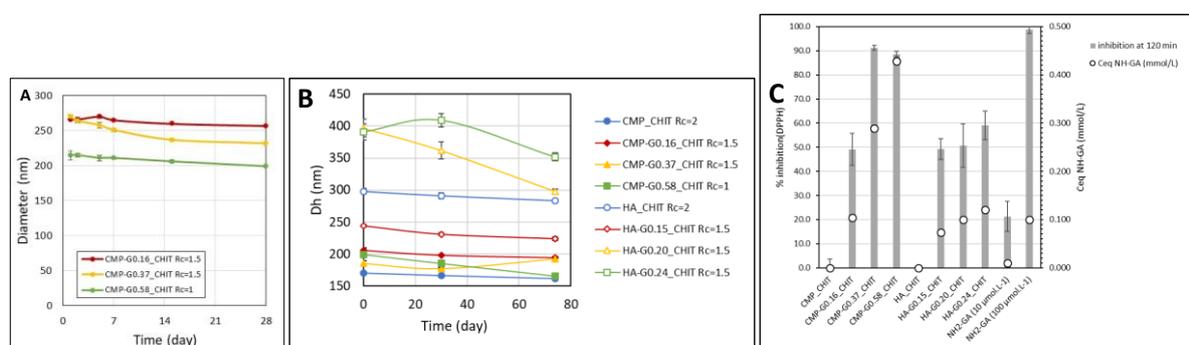


Figure 1: Stability of PECs (A) in PBS (B) in water; (C) Inhibition (%) of DPPH radical (50 $\mu\text{mol.L}^{-1}$) by CMP_CHIT and CMP-G_CHIT PECs and by HA_CHIT and HA-G_CHIT at 0.25 g.L^{-1} in water/ethanol (50/50 V/V)

- [1] H. V. Le, D. Le Cerf, *Small*. 18, 2204283, 2022.
- [2] H. V. Le, V. Dulong, L. Picton, D. Le Cerf, *Colloids Surfaces A*. 629, 127485, 2021.
- [3] H. V. Le, V. Dulong, L. Picton, D. Le Cerf, *Carbohydr. Polym.* 292, 119711, 2022.
- [4] M.C. Kouassi, P. Thébault, C. Rihouey, E. Dé, B. Labat, L. Picton, V. Dulong, *Biomacromolecules*. 18, 3238–3251, 2017.



NANOFIBERS BASED ON QUATERNIZED CHITOSAN AS BIOABSORBABLE WOUND DRESSINGS

Marin L.^a, Anisiei A.^a, Andreica B.I.^a, Mititelu-Tartau L.^b, Coman C.^b, Bilyy R.^c, Bila G.^c, Rosca I.^a, Sandu A.I.^a, Amler E.^d

^a "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

^b "Grigore T. Popa" University of Medicine and Pharmacy, Iasi, Romania

^c Lectinotest R&D, Mechamichna Str 2, 79022, Ukraine

^d Research and Development Department Inocure, Prague, Czech Republic

* lmarin@icmpp.ro

Background: Quaternary chitosan (QC) based fibers have emerged as promising biomaterials for tissue engineering, wound healing and hygiene related textiles, but their in vivo application is restricted by the lack of biodegradability of the synthetic polymers used as co-spinning agents. To overcome this issue, we designed and prepared via electrospinning fully biodegradable chitosan/QC nanofibers, using PEO as sacrificial additive.

Methods: The composition and morphology of the fiber mats were confirmed by FTIR and NMR spectroscopy, TGA, X-ray diffraction, and POM and SEM microscopy. Their properties required for in vivo application, such as behavior in moisture media (dynamic vapor sorption, swelling and enzymatic degradation tests), muco- and bio-adhesiveness, mechanical properties and antimicrobial activity were measured. The in vitro biocompatibility on normal human dermal fibroblasts was investigated in line with standards for biomedical devices and in vivo acute toxicity and biocompatibility was assessed by monitoring hematological, biochemical and immunological profile on Wistar rats. Wound closure and healing was studied on burn wound healing models in rats.

Results: The combination of chitosan with its QC derivative into nanofibers enabled high swelling ability and fluid exchange, biodegradability rate controlled by the QC content and pH of media, muco- and bio-adhesive character, mechanical properties similar to skin tissue, strong antimicrobial activity and in vitro and in vivo biocompatibility. Moreover, their subcutaneous implantation in rats revealed in vivo biodegradation and lack of toxicity. As a proof of concept, the fiber mats application on burn wound healing models in rats showed wound closure and active healing, with fully restoration of epithelia.

Conclusions: The use of PEO as electrospinning and sacrificial additive, is a straight pathway to the obtaining of biodegradable chitosan/QC nanofibers suitable for wound healing.

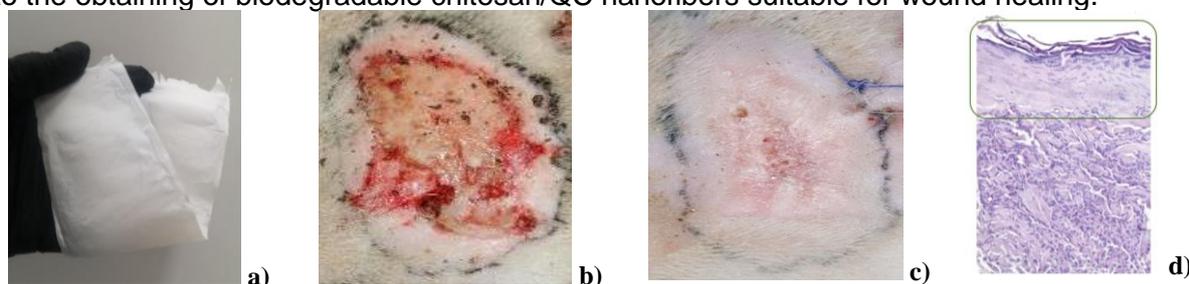


Figure 1. Image of a) chitosan/QC nanofiber mat; the wound a) before and c) after application of the nanofibers mat; d) the histology image of the healed wound showing almost total restoration of the epidermis after 22 days.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PCE2/2021 within PNCDI III and from the European Commission through the project H2020-MSCA-RISE-2019, SWORD- DLV-873123.



DEVELOPMENT OF GUAR GUM-BASED HYDROGELS WITH POTENTIAL APPLICATION AS WOUND DRESSINGS

Canafístula, F. V^a, Oliveira, M.X.^a, de Azevedo Neto, A.C.^a, Marinho Filho, J.D.B^b, Silva, D.A.^c, Araujo, A.J.^b, Sa, R.E.^b, Araujo, A.R.^c, Ribeiro, F.O.S.^c e Paula, R. C. M^a, Feitosa, J.P. A^{a*}

^a Polymer Laboratory, Federal University of Ceará, Brazil.

^b Cell Culture Laboratory of the Delta, Federal University of Delta of Parnaíba, Brazil,

^c Research Center on Biodiversity and Biotechnology, Federal University of Delta of Parnaíba, Brazil.

* judith@dqi.ufc.br

Wound healing of the skin remains a significant clinical problem because of its susceptibility to inflammation and infection. Hydrogel dressings are promising materials, as they have a three-dimensional structure, maintain ideal moisture, absorb exudate and do not cause discomfort to the patient during dressing changes [1].

Hydrogels obtained via crosslinking by the Schiff's base reaction were prepared from guar gum (GG) and gelatin (GEL). Galactomannan was degraded to increase solubility, oxidized with sodium periodate in three different degrees (20, 50 and 80%) and characterized. The hydrogels were prepared by mixing their precursors (GGOX and GEL) in different proportions (v/v) of GGOX/GEL (20:80, 30:70 and 40:60).

The hydrogels were characterized by gelling time, FTIR, rheology, SEM, swelling and degradation. The toxicity of the hydrogels, as well as their starting materials, were evaluated in L929 cells. Antibacterial activity was analyzed against *S. aureus*, *S. aureus* MRSA and *S. epidermidis*. The cross-linking reaction of the hydrogels was confirmed by FTIR. The G' modulus values were 849, 817 and 549 Pa for the ratios 20/80, 30/70 and 40/60, respectively. All gels exhibited interconnected porous structures with different pore sizes dependent on the GG_{ox}/GEL ratio.

The degree of swelling increases as the oxidized gum content increases, due to the decrease in the crosslinking density. This effect was more pronounced in the 40:60 ratio, which showed a swelling degree at equilibrium of 5 g of liquid/g of gel, a value 1.5 and 2 times greater than the swelling rate of the 20:80 and 30:70 formulations, respectively. In addition, the 40:60 hydrogel showed a lower degradation rate, presenting 10% of its initial weight on the 28th day of the incubation process. The 20:80 and 30:70 gels completely degraded on the 3rd and 14th day, respectively.

Hydrogels do not show toxicity. All hydrogels showed > 90% inhibitory potential for the Gram-positive bacteria used in the study, with greater potential against the methicillin/oxacillin-resistant bacteria *S. aureus* MRSA. GG_{ox}80/GEL hydrogels showed good mechanical properties, adequate swelling rate, appropriate degradation time and excellent antibacterial properties, in addition to cell viability. All these characteristics indicate that the hydrogel has the potential to be used in future biomedical applications in the area of dressings and/or tissue engineering.

Acknowledgments: FINEP (CV.01.22.0174.00), CAPES ((Finance Code 001, PROEX 23038.000509/2020-82), CNPq, MCTIC/CNPq (INCT/Polysaccharide #406973/2022-9), FUNCAP.

[1] NGUYEN, H. M.; LE, T. T. N.; NGUYEN, A. T.; LE, H. N. T.; PHAM, T. T. RSC Advances, v. 13, p. 5509-5528, 2023.



CHITOSAN NANOFIBERS FOR BURN HEALING APPLICATIONS

Ailincai D.*^a, Cibotaru S.^a, Anisiei A.^a, Rosca I.^a, Mititelu-Tartau L.^b, Marin L.^a

^a *Polycondensation and Thermostable Polymers, "Petru Poni" Institute of Macromolecular Chemistry, Romania*

^b *"Grigore T. Popa" University of Medicine and Pharmacy, Iasi, Romania*

*ailincai.daniela@icmpp.ro

Burn injuries occur when the skin or other tissues in the body are exposed to extreme heat, chemicals, electricity, or radiation. They can range from mild to severe and can have a significant impact on a person's physical and psychological well-being. These types of injuries are often painful and can cause scarring, disfigurement, and in severe cases, can be life-threatening, especially when they are accompanied by infection with several microorganisms [1]. Therefore, the development of materials with a rational design, meeting the requirements for burn healing applications represents a significant challenge and an important research topic.

Within this framework, the study presents new composite materials based on non-woven mesoporous fiber mat of chitosan loaded with norfloxacin and coated with an antifungal monoaldehyde, 2-formylphenylboronic acid. The systems were thought as biomaterials able to prevent infections by creating a barrier against bacterial and fungal strains and to be biodegradable, in order to avoid the trauma caused by the debridement of the bandage post-treatment.

The chemical structure of the obtained systems was evaluated by NMR and FTIR spectroscopy demonstrating the drug's presence and also the success of the imination reaction between chitosan and the monoaldehyde. The morphology of the obtained systems was investigated using POM, SEM and AFM techniques, indicating an uniform distribution of the drug into the nanofibers. The encapsulation degree and the drug release kinetics were investigated by UV-VIS spectroscopy, while the *in vitro* biodegradability of the systems was monitored in the presence of lysozyme, at different values of the pH, correlated with the variation of the pH during the wound healing process. The antimicrobial activity of the systems was tested *in vitro* by the Kirby-Bauer method, leading to high values of the diameters of the inhibition zones. Moreover, the biocompatibility of the designed systems was evaluated both *in vitro* and *in vivo* indicating the biosafety of the obtained materials. Last but not least, the wound healing ability, evaluated on second/third-degree burn model in rats, by monitoring the decrease of the wound size and by histological analysis at different times, revealed the high potential presented by these materials, their presence favoring the wound healing and improving the skin quality.

Selective references:

1. Brusselaers N., Monstrey S., Vogelaers D., *Critical Care*, 14, R188, 2010.
2. D'Abbondanza J. A., Shahrokhi S., *Surgery Infection*, 22 (1), 58-64, 2021.
3. Anisiei A., Rosca I., Sandu A.I., Bele A., Cheng X., Marin, L., *Pharmaceutics*, 14(1), 117, 2022

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PCE2/2021 within PNCDI III and from the European Commission through the project H2020-MSCA-RISE-2019, SWORD- DLV-873123.



RHIZOBIAL SUCCINOGLYCAN-BASED HYDROGELS FOR STIMULI-RESPONSIVE DRUG DELIVERY

Yohan Kim^{a*} and Seunho Jung^{a,b}

^a Department of Bioscience and Biotechnology & ^b Department of System Biotechnology, Microbial Carbohydrate Resource Bank (MCRB), Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, South Korea

* shsks1@hanmail.net

Succinoglycan (SG) is an extracellular polysaccharide (EPS) from soil microorganisms, *Sinorhizobium* and *Agrobacterium* species. SG contains non-carbohydrate substituents, such as pyruvate, succinate, and acetate groups, in repeating octasaccharide unit consisting of seven glucose residues and one galactose residue [1]. Since the physical properties of SG are constant even under high temperature, shear rate, and salt condition, SG is generally used in commercial products such as pharmaceuticals, fertilizer formulations and cosmetics, which can be used as a thickener, stabilizer, gelling agent, and emulsifier [2]. In addition, recent study reported antibacterial activity of SG by activating the MAPK/IL-6 pathway [3].

In our studies, the rheological and physiological properties of SG were used as a material for stimuli-responsive smart hydrogels, suggesting potential for various applications such as cell culture, regenerative medicine, tissue engineering, and drug delivery systems.

We prepared chitosan (CS) based multifunctional hydrogels using oxidized succinoglycan (OSG) with a semi-dissolving acidified sol-gel transition method [4]. OSG cross-linked CS hydrogels (OSG/CS) was prepared by aldehyde-amine Schiff-base reaction. OSG/CS physically showed increased thermal stability, enhanced mechanical strength, excellent self-healing properties. In addition, OSG/CS showed antibacterial effect, pH-controlled drug release pattern, and cell viability.

In addition, we fabricated temperature/pH-responsive hydrogels based on succinoglycan/poly(N-isopropylacrylamide) with improved mechanical and swelling properties [5]. The fabricated SG/PNIPAM (SGPN) hydrogels showed improved thermal stability and compressive stress improved up to 8-fold than PNIPAM gel. Since, the swelling ratio of SGPN hydrogels decreased with increasing temperature, SGPN hydrogels performed a temperature/pH-responsive drug release for 5-fluorouracil.

The rheological analysis confirmed that the Fe³⁺-coordinated succinoglycan (Fe³⁺-SG) hydrogel revealed that the Fe³⁺ cations that coordinated with succinoglycan were converted to Fe²⁺ by a reducing agent and visible light, promoting a gel-sol conversion [6]. The Fe³⁺-SG hydrogel was then successfully used for controlled drug delivery based on gel-sol conversion in the presence of reducing agents and visible light.

As a result, the SG-based hydrogel can effectively release drugs in response to various stimuli (pH/temperature/oxidation-reduction/light), suggesting various application possibilities as biomaterials.

[1] Simsek, S., Wood, K., & Reuhs, B. L. (2013). *Journal of bacteriology*, 195(9), 2032-2038, 2013.

[2] Bakhtiyari, M., Moosavi-Nasab, M., & Askari, H. *Food Hydrocolloids*, 45, 18-29, 2015.

[3] Wu, Z., Cheng, Y., Yang, Y., Gao, Y., Sun, X., Wang, L., . . . Xu, X. *International journal of biological macromolecules*, 150, 802-813, 2020.

[4] Kim, Y., Hu, Y., Jeong, J. P., & Jung, S. *Carbohydrate Polymers*, 284, 119195, 2022.

[5] Hu, Y., Kim, Y., Jeong, J. P., Park, S., Shin, Y., Hong, I. K., . . . & Jung, S. *European Polymer Journal*, 174, 111308, 2022.

[6] Hu, Y., Jeong, D., Kim, Y., Kim, S., & Jung, S. *Polymers*, 12(4), 977, 2020.



DEVELOPMENT OF ANTIOXIDANT WOUND DRESSINGS BASED ON FUNCTIONALIZED AND CROSSLINKED CHITOSAN

C. Ciarlantini^{a*}, E. Lacolla^a, I. Francolini^a, A. Piozzi^a

^aChemistry Department, University La Sapienza, Piazzale Aldo Moro 5, 00185 Rome, Italy

*Clarissa.ciarlantini@uniroma1.it

Tissue engineering is an interdisciplinary field that develops new methods to enhance the regeneration of damaged tissues. Skin tissue engineering takes advantage of principles of engineering, biology and chemistry for manufacturing dressings that can promote the regeneration of injured skin. Polysaccharides such as hyaluronic acid, alginate and chitosan have appropriate biological properties to be used as wound dressings [1]. Furthermore, the presence of functional groups in their backbone makes them easily modifiable both by chemical reactions and physical interactions with different molecules, allowing the development of materials with better antibacterial and/or anti-inflammatory activity. In the present work, innovative dressings based on modified chitosan were developed using the solvent casting technique. In particular, chitosan (CS), characterized by good antimicrobial activity [2] but poor dimensional stability in physiological environment, was first modified with glycidymethacrylate (GMA) and glycerol (GLY) and then with ethylene glycol dimethacrylate (EGDMA). GMA was introduced into the polysaccharide to have a functionality (double bond) to be exploited in the subsequent crosslinking reaction with EGDMA, while GLY was taken into consideration to provide a good degree of elasticity to polymer films, which must be able to adapt to the skin. To evaluate the effect of GLY on the mechanical properties of the developed matrices, the films were obtained by varying the glycerol concentration (10, 20 and 30% w/v). For all samples, at each concentration of GLY, an increase in the elongation at break and in the dimensional stability in aqueous environment was observed, accompanied however by a considerable decrease in the elastic modulus. The matrices were then subjected to chemical crosslinking using EGDMA in order to create bridges between the GMA-modified CS chains. To evaluate how the cross-linking process affected the elasticity of the films, three different concentrations of EGDMA (0.05-0.1-0.5 mM) were tested for the same reaction time (5 min). The crosslinked matrices showed a significant increase in the value of the elastic modulus, but only in the case of the lowest EDGMA concentration the matrices maintained an elongation at break suitable for the development of dressings. With the aim of avoiding possible inflammatory reactions during the healing phase, the films were functionalized with 3,4 hydroxycinnamic acid (HCAF), an antioxidant capable of limiting the phenomenon of oxidative stress [3]. The introduction of the antioxidant into the films was carried out both by covalent bonding between CS amino groups and the ortho position of the catechol ring, using laccase as catalyst, and imbibition. In both cases the introduction of HCAF molecules increased the antioxidant properties and the elastic modulus of the films. Biological tests are underway to verify the possible application of these systems in skin tissue engineering.

[1] Sahana, T.G., Rekha, P.D., «Biopolymers: Applications in wound healing and skin tissue engineering». *Mol Biol Rep*, vol. 45, pp. 2857–2867, 2018.

[2] D. d. B. O. B. G. A. Rejane C. Goy, «A Review of the Antimicrobial Activity of Chitosan,» *Polímeros: Ciência e Tecnologia*, vol. 19, n. 3, pp. 241-247, 2009.

[3] Tarique Hussain, Bie Tan, Yulong Yin, Francois Blachier, Myrlene C. B. Tossou, Najma Rahu, "Oxidative Stress and Inflammation: What Polyphenols Can Do for Us?", *Oxidative Medicine and Cellular Longevity*, vol. 2016, pp. 1-9, 2016.



MULTIFUNCTIONAL NANOFIBER-HYDROGEL SANDWICH-LIKE SYSTEM FOR INFECTION CONTROL IN CHRONIC WOUNDS

Lara C. Ribeiro^{a,b}, Ana R. M. Ribeiro^a, Marta O. Teixeira^a, Carla Silva^b and Helena P. Felgueiras^{a,*}

^a Centre for Textile Science and Technology (2C2T), University of Minho, Portugal

^b Centre of Biological Engineering (CEB), University of Minho, Portugal

* helena.felgueiras@2c2t.uminho.pt

Nowadays, chronic wounds (CW) are described as a global health problem. Typically, these wounds are characterized by defective cell matrices, high microbial concentration, dysregulated moisture, and uncoordinated, self-sustained inflammation. Considering conventional dressings present a passive action against microorganisms, new interactive and bioactive structures based on hydrogels and nanofibers (resemblance with extracellular matrix) have been explored [1,2]. Here, a multifunctional sandwich-like system was proposed and examined for its potential in fighting CW infections. The scaffolding system was made of three layers: (outer) nanofibrous mat of polycaprolactone (PCL) working as a barrier for preventing other microorganisms and impurities from reaching the wound bed; (middle) sodium alginate (SA) hydrogel loaded with the antimicrobial agents polyethylenimine (PEI) and ceftazidime (CEF) for maintaining a moisture environment, absorbing exudates and liberating the antimicrobial payload in a paced manner (synergistic profiles); and (inner) a second nanofibrous mat composed of PCL and polyethylene glycol (PEG) for facilitated cell integration and recognition, reduced hydrophobicity and complementary antimicrobial effects.

Antimicrobial examinations of PEI, CEF and PEG were conducted against the most prevalent bacteria in CW, *Staphylococcus aureus* and *Pseudomonas aeruginosa*, using the broth micro-dilution assay (determination of minimum inhibitory concentration or MIC), followed by the checkboard test. MICs were established at 64 and 32 µg/mL for PEI and CEF, respectively, and 256 mg/mL for PEG against the two bacteria, with synergisms being detected between the three compounds (FICI < 0.5). PCL was prepared at 14% w/v in chloroform/dimethylformamide (CHF/DMF) at 90/10% v/v (1 h at 50°C). It was used alone (outer layer) or modified with PEG (inner layer) at MIC and processed in the form of nanofibrous mats via electrospinning (12 kV, 0.7 mL/h, 17 cm, 18G). On its turn, the hydrogel was obtained by solvent casting-phase inversion method using a 2% w/v SA aqueous solution and a coagulation bath of 2% w/v CaCl₂. Again, PEI and CEF were loaded at MIC. The sandwich-like system was generated by pouring the hydrogel solution onto a casting mold lined with the inner layer and depositing the outer layer at the top of the viscous solution. After a few minutes of intimate contact, the casting solution was added and 1 h afterwards the scaffolding system was ready and totally detached from the mold. Presence of all components in the system was confirmed by Fourier-transform infrared spectroscopy. Thermal gravimetry and calorimetry analyses established the influence of the antimicrobial additives on the polymers' thermal stability. Hydration capacity was averaged at > 200% of the sample's weight, and degradation experiments reported a loss in mass of ≈20% after 28 days of incubation (biodegradable profile). Controlled release of the antimicrobial agents was examined up to 72 h, revealing a paced liberation of the hydrogel-entrapped molecules. Antimicrobial testing determined the high efficiency of the scaffold (> 99% elimination of both *S. aureus* and *P. aeruginosa* bacteria). Cell viability examinations are currently ongoing to confirm the safety of the system. Adhesion experiments using porcine skin determined the scaffold's ability to be detached without great mechanical effort. Overall, data reports the effectiveness of this sandwich-like system for potential applications in CW care.

[1] Ribeiro A.R.M., Teixeira M.A., Pereira-Lima S.M.M.A., Costa S.P.G. & Felgueiras H.P., *Tekstil ve Muhendis*, 128, 308-314, 2022.

[2] Teixeira M.O., Antunes J.C. & Felgueiras H.P., *Antibiotics*, 3, 1-34, 2021



GLUCOMANNANS INITIATE A MULTI-PATHWAY SYNERGISTIC IMMUNE RESPONSE BASED ON THE RECOGNITION OF INNATE IMMUNE RECEPTORS

Xiaojun Huang*, Mingzhi Li, Nie Shaoping

State Key Laboratory of Food Science and Technology, China-Canada Joint Lab of Food Science and Technology (Nanchang), Nanchang University, China

*huangxiaojun0617@163.com

In recent years, frequent evidence of interaction between different structural polysaccharides and Toll-like receptor (TLR) or C-type lectin receptor (CLR) has pushed. Polysaccharide is reported to be involved in the regulation of the innate immune system through innate immune receptors. In this study, three different structural glucomannans (GMs), including Konjac glucomannan (KGM), Aloe vera gel polysaccharide (AGP), Dendrobium officinale polysaccharide (DOP), were selected to study their possible mechanism in initiate innate immune response.

In vivo study in cyclophosphamide (CTX) mice proved the three GMs significantly improve the immunity from both the cellular and humoral immune functions. The enhancement of cellular immune function was demonstrated by increasing the total number of circulating lymphocytes in the blood, stimulating the secretion of various cytokines in the spleen regulating the ratio of CD4+ and CD8+ T cell subsets in the spleen, and upregulating the expression of key nuclear transcription factor T-bet in Th1-type T cells. The stimulation of humoral immune function was manifested by the upregulation of plasma cell differentiation gene XBP-1 to promote immunoglobulin production.

Detailed study on RAW264.7 macrophage cell line demonstrated that GMs enhanced all immune functions of macrophages, includes the proliferation, endocytosis, and uptake of antigens by macrophages. The further mechanism study was completed by the combined use of molecular expression, activity inhibition, gene knockdown, and molecular docking. The receptor inhibitor screen showed that TLR4 and MD2 activity deficiency significantly blocked the secretion of various inflammatory mediators by GM-stimulated macrophages. GMs also promoted the formation of TLR4-MD2 dimer on the cell surface. In addition, silencing of the mannose receptor (MR) also significantly blocked glucomannans from elevating the secretion of various inflammatory mediators and the phosphorylation level of NF- κ B in the nucleus. The molecular docking results showed that the glucomannans repeat unit (Aloe oligosaccharide, oligo-AGP) exhibit optimal binding stability to TLR4-MD2 dimer, followed by the C-type lectin-like domain 4 (CTLD4) binding stability to MR.

The above results provided the hypothesis: GMs can be recognized by the cell surface CD14-TLR4-MD2 recognition cascade in cooperation with MR, and synergistically promotes intracellular multi-pathway signaling to further enhance inflammatory activation.



SULFATED POLYSACCHARIDES FROM MARINE RESOURCES AS VALUABLE COMPOUNDS FOR BIOMEDICAL APPLICATIONS

Ferreira A. S.^a, Moreira A. S. P.^a, Gomes F. C.^a, Coimbra M. A.^a, Nunes C.^{b*}

^a LAQV-REQUIMTE, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

^b CICECO-Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193, Aveiro, Portugal

* claudianunes@ua.pt

Polysaccharides from marine environments emerge as a new class of renewable and functional molecules. The sulfated polysaccharides present in marine environments have a high potential due to their physical and biological properties. These polysaccharides resemble the chemical and biological properties of mammalian glycosaminoglycans and have received a growing interest for application in biomedical areas [1]. Besides their use as natural drugs (anticoagulant and anticancer), they have been proposed for tissue engineering, immobilization of biomolecules, and coating of biomedical devices, contributing to the bioactivity of the materials. Nevertheless, the structural characterization of these polysaccharides and the relation with the biological properties is still very limited. This knowledge is regarded as a major boost to assess their valorisation.

The approach of this work was the structural analysis of the polysaccharides from different marine seaweed and microalgae. The immunostimulatory and hypocholesterolemic activities of the purified polysaccharides were assessed to identify their potential application.

The polysaccharides from brown seaweed (*Saccharina latissima*) and different microalgae species (*Nannochloropsis oculata*, *Chlorella vulgaris*, and *Porphyridium purpureum*) were extracted with hot water and fractionated by ethanol precipitation and/or by anion-exchange chromatography. The fucose-containing sulfated polysaccharides (FCSP) from brown seaweed were rich in uronic acids, fucose, and galactose [2]. *N. oculata* water-soluble polysaccharides are constituted by mixed-linked ($\beta 1 \rightarrow 3$, $\beta 1 \rightarrow 4$)-glucans, ($\alpha 1 \rightarrow 3$)-, ($\alpha 1 \rightarrow 4$)-mannans, and anionic sulfated heterorhamnans [3]. Besides starch, the most abundant polysaccharide, *C. vulgaris* produces an exopolysaccharide, a sulfated galactan [4]. *P. purpureum* is rich in floridean starch and has the ability to excrete high amounts of sulfated polysaccharides, namely a glucuronoglucogalactoxylan [5].

The FCSP from brown seaweed, the soluble polysaccharides of *N. oculata* and the exopolysaccharides from *C. vulgaris* and *P. purpureum* revealed to stimulate murine B-lymphocytes *in vitro*, being the sulfate esters relevant for this activity. In addition, FCSP from brown seaweed showed the capacity to sequester cholesterol. This opens a great potential for using the marine environment as a source of sulfated polysaccharides that can be used for biomedical applications.

Acknowledgments: The authors thank to the financial support of CICECO (UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020), and LAQV-REQUIMTE (UIDB/50006/2020, UIDP/50006/2020) financed by national funds through the FCT/MEC (PIDDAC). This work is part of project "Pacto da Bioeconomia Azul" (C644915664-00000026) supported by PRR and the Next Generation EU European Funds. A. S. P. Moreira, and F. C. Gomes thank the research contract funded by LAQV-REQUIMTE (UIDB/50006/2020). C. Nunes thanks Portuguese national funds (OE), through FCT, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19 (REF. 049-88-ARH/2018).

References:

- [1] Silva T.H. *et al.*, *Biomatter*, 2, 278-289, 2012.
- [2] Moreira A. S. P. *et al.*, *Marine Drugs*, 21, 3, 2023.
- [3] Pandeirada C. *et al.*, *Carbohydrate Polymers*, 222, 114962, 2019.
- [4] Ferreira A. S. *et al.* *Algal Research*, 45, 101757, 2020.
- [5] Ferreira A. S. *et al.* *Algal Research*, 59, 102439, 2021.



SILANIZED MODIFIED-BACTERIAL CELLULOSE AS PROMISING CELL CULTURE PLATFORM

Vitória Maria Medalha Colturato^{*a}, Amanda Maria Claro^a, Nayara Cavichioli do Amaral^a,
Marina de Lima Fontes^a, Hernane da Silva Barud^a

^a *University of Araraquara - UNIARA, Rua Carlos Gomes 1217, 14801-340 Araraquara, SP, Brazil*

* vmmcolturato@uniara.edu.br/hsbarud@uniara.edu.br

Bacterial cellulose (BC) can be excreted by the bacterium *Komagataeibacter rhaeticus* and consists of a three-dimensional structure, formed by nanofibers randomly arranged with less than 100 nm in width and diameter ranging from 2 to 4 nm, and it has been considered as paper-like material and therefore, a suitable support for cell culture since it resembles the extracellular matrix (MEC). Due to the presence of hydroxyl (OH) groups on the BC surface, it is possible to carry out a variety of chemical modifications. In this sense, the aim of this study aiming at the functionalization of the BC surface, based on the silanization reaction, followed by the immobilization of different cell lines in order to evaluate the adhesion, proliferation, cytotoxicity, and healing potential of the materials.

The produced platforms were functionalized with $-(\text{CH}_2)_7\text{CH}_3$, $-(\text{CH}_2)_2\text{CH}_3$, $-\text{NH}_2$, $-\text{SH}$ groups (Figure 1) and then structurally characterized by vibrational spectroscopy in the infrared region by attenuated total reflectance (FTIR-ATR), thermal properties were determined by Thermogravimetric Analysis (TG/DTG), the surface wettability of the BC-based platforms was determined by measuring the contact angle, and their morphologies was analyzed by high-resolution scanning electron microscopy. In short, the research work revealed that the chemical modification methodology used was effective for the groups $-(\text{CH}_2)_7\text{CH}_3$, $-\text{NH}_2$, and $-\text{SH}$. The in vitro cell assays allowed evaluation that the native and modified BC platforms revealed promising cell culture properties and became a target for future studies.

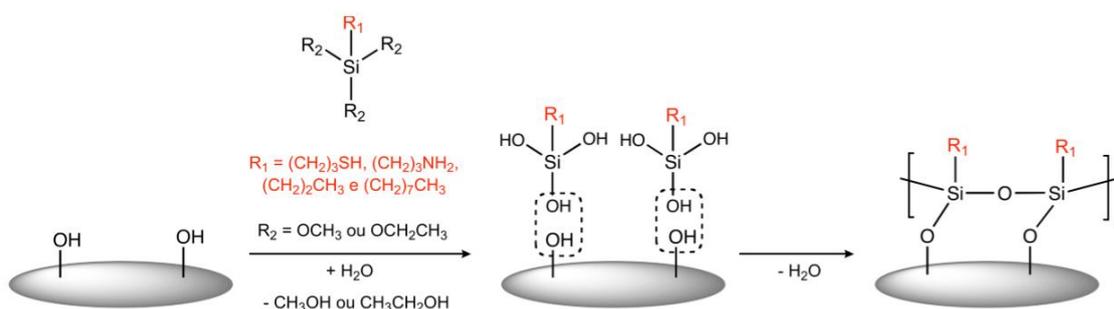


Figure 1: Schematic reaction of the preparation of the silanized modified bacterial cellulose.



Session 7 Poster



MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HYDRATED LAUROYL-HYALURONAN FILMS

Mrázek J. ^{*a}, Sita J. ^a, Ondreáš F. ^a, Chmelař J. ^a

^a *Contipro a.s.; 561 02 Dolní Dobrouč 401, Czechia*

* mrazek@contipro.com

Introduction: Hyaluronic acid derivatives such as lauroyl-hyaluronan (LHA) can serve as biomaterials for various medical applications. Here we present self-supporting films of LHA prepared by solution drying. We explored the relationship between the drying parameters, film mechanical properties and its microstructure, both in dry state and after hydration. Characteristics such as swelling or mechanical resilience will determine the macroscopic properties of potential products (e.g., wound dressings), while the structure and toughness on the micro-scale will influence cell interaction with the film [1].

Experimental: Films from LHA with various degree of substitution were prepared in a custom-built apparatus [2]. The Nile Red dye was mixed in the starting solution of LHA in water/2-propanol. Hydrated film samples were imaged on a laser confocal microscope. Films were characterized by swelling measurements, tensile testing and nanoindentation.

Results: Despite the LHA films appeared non-porous when dry, a distinct microstructure was revealed after hydration (Fig.1). Depending on the drying conditions, Bénard-Marangoni convection may develop in the solution [3]. These convective flows were imprinted in the microstructure and could be studied in three dimensions. Films dried in ambient air swelled preferentially by increasing thickness while film area remained constant even at high swelling ratios (>3000 %). In contrast, slow drying without convective flows led to more isotropic swelling. Tensile testing showed that the elastic modulus of hydrated films correlated with the degree of LHA substitution. Nanoindentation probes were able to map mechanical properties on the micro-scale, with the local modulus variations reflecting the film microstructure. It can thus be expected that cells will perceive the film as an inhomogeneous material and, consequently, the microstructural parameters could be important characteristics of the film. Overall, our results suggest that the properties of LHA films can be optimized for individual applications by varying the drying conditions and LHA substitution.

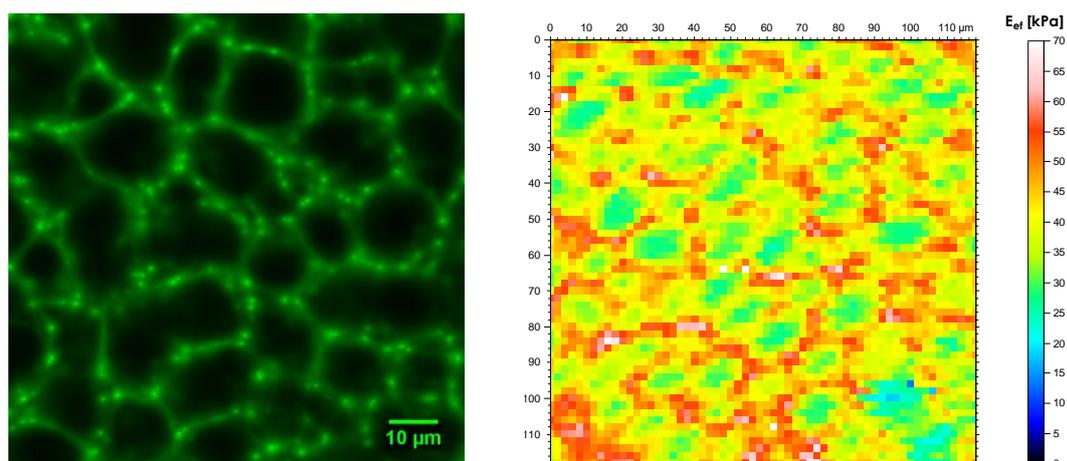


Fig. 1 Microstructure of the hydrated LHA film and a map of film local elastic modulus (right).

[1] Lehká K, Starigazdová J, Mrázek J, et al., *Carbohydrate Polymers*, 310, 120701, 2023

[2] Chmelař J, Mrázek J, Hermannová M, et al. *Carbohydrate Polymers*, 224, 115162, 2019

[3] Chmelař J, Mrázek J, Dušánková M, et al. *Macromol. Chem. Phys.*1800515, 2019



MACHINE LEARNING-BASED MONOSACCHARIDE PROFILING FOR TISSUE-SPECIFIC CLASSIFICATION OF WOLFIPORIA EXTENSA SAMPLES

Hsiung S. ^{*a}, Deng S. ^b, Li J. ^c, Liaw C. ^d, Huang S. ^e, Wang C. ^b, Hsieh S. Y. Y. ^{a,f}

^a Hsieh Lab, Taipei Medical University, Taiwan

^b Wang Lab, Taipei Medical University, Taiwan

^c Li Lab, Shanghai Normal University, China

^d Liaw Lab, Taipei Medical University, Taiwan

^e Huang Lab, Academia Sinica, Taiwan

^f Hsieh Lab, KTH Royal Institute of Technology, Sweden

* D301110009@tmu.edu.tw

Machine learning (ML) involves utilizing a computer program to induce a model through the use of training data. This approach has become increasingly prevalent in bioinformatics applications, particularly in clinical decision-making processes and diagnostic procedures. Our study investigated the performance of eight different algorithms - linear discriminant analysis (LDA), logistic regression (LR), *k*-nearest neighbor (KNN), random forest (RF), gradient boosting machine (GBM), support vector machine (SVM), Naïve Bayes classifier (NB), and artificial neural network (ANN) - in classifying and predicting the monosaccharide composition and proportion of four tissue types in *Wolfiporia extensa*. Our aim was to develop a reliable predictor/classifier for quality control of selective Chinese herbal medicines.

All models we examined demonstrated exemplary performance in terms of area under the curve (AUC) evaluation, with scores above 0.8. Five models achieved exceptional results in classifying the four tissue types, with an AUC score exceeding 0.9. Additionally, seven of the models (excluding ANN) were reliable predictive models for classifying three tissue types, with an AUC score over 0.8 and cross-validation (CV) score over 0.7. Our model predictors surpassed the single LDA plotting method and demonstrated that ML methods can perform better than traditional regression techniques, particularly when dealing with large sample sizes.

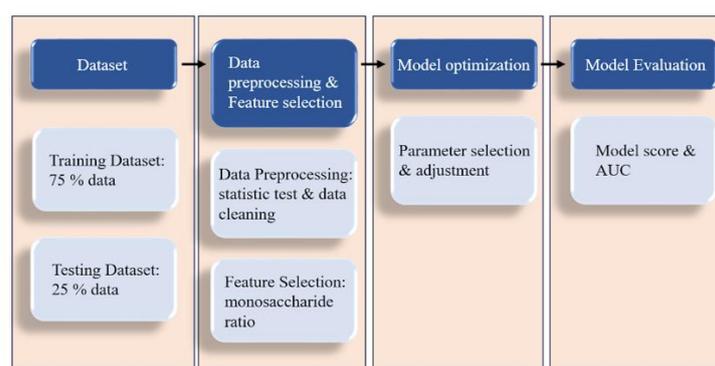


Figure 1 : Modeling procedure: Splitting datasets, preprocessing data, selecting features, optimizing model, and evaluating model



PREPARATION, CHARACTERIZATION OF HYALURONAN/ZINC OXIDE NANOCOMPOSITE-BASED MEMBRANE

Abdel-Rahman R.M. ^{*a}, Abdel-Mohsen A.M. ^{a,b}

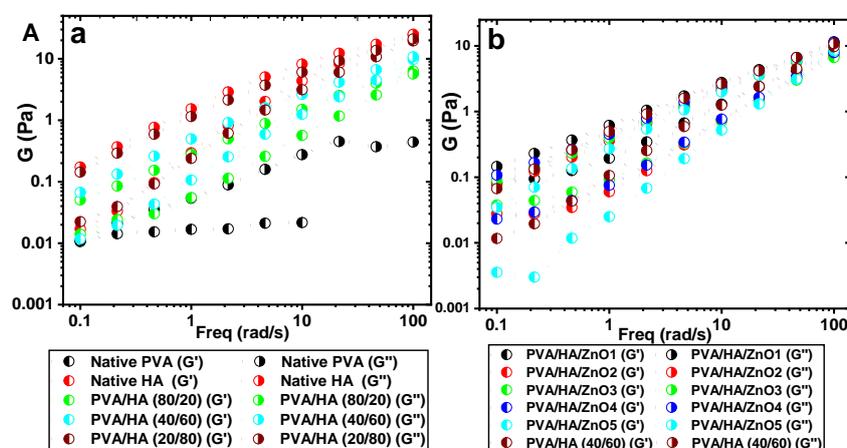
^a Institute of Macromolecular Chemistry, Czech Academy of Sciences, Czech Republic

^b CEITEC-Central European Institute of Technology, Brno University of Technology, Czech Republic

* radwan@imc.cas.cz

Abstract

The use of hyaluronic acid and zinc oxide nanoparticles in the preparation of an antibacterial wound dressing is an innovative approach that addresses the limitations of traditional wound dressings. The incorporation of ZnO-NPs provides the nanocomposite membrane with antibacterial properties, while the HA/PVA matrix ensures good mechanical properties and swelling ability. Successfully we prepared an antibacterial wound dressing using hyaluronic acid (HA) as a reducing and stabilizing agent, and incorporated zinc oxide nanoparticles (ZnO-NPs) via in situ synthesis¹. The resulting hybrid nanostructure of ZnO-NPs and HA/PVA matrix demonstrated good mechanical properties and high swelling capacity, with the ability to absorb exudates from wounds. The uniform spherical shape of ZnO-NPs (50 ± 10 nm) was evenly distributed throughout the HA/PVA matrix, and prevented the NPs from dropping off the PVA/HA network, thereby minimizing the potential toxicity of NPs. Additionally, the hybrid nanostructure formed by the interaction between the ZnO-NPs and the HA/PVA matrix minimizes the toxicity of the NPs and allows for the attachment and growth of normal human dermal fibroblasts and human primary osteogenic sarcoma.



References:

[1] Abdel-Rahman R.M. & Abdel-Mohsen A.M. ACS Applied Polymer Materials, 4, 7723–7738, 2022.

Acknowledgments:

This work was supported by LUAUS23004 Inter-Excellence Grant from MEYS CR is greatly appreciated.



POLYSACCHARIDE BASED STIMULI RESPONSIVE SMART WOUND DRESSINGS WITH CONTROLLED ANTI-INFLAMMATORY DRUG RELEASE

Elveren B. ^{*a}, Kurečič M. ^a

^a *Laboratory for Characterization and Processing of Polymers, Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia*

* beste.elveren@um.si

Smart materials are materials that can interact with their environment, sense, and react to the conditions or environment change with the help of built-in sensors and/or stimuli-responsive agents.[1] Polymer science enabled researchers to explore all aspects of smart material development. Smart materials hold several characteristics such as sensing, healing, and responding to their environment. Halochromic polymers are responsive to pH change in their environment. Furthermore, it is known, that the pH value within the wound milieu directly and indirectly influences all biochemical reactions taking place in the process of wound healing. [2] It has been proven that the surface pH of a wound plays an important role in wound healing as it helps control infection and increase antimicrobial activity, oxygen release, angiogenesis, protease activity, and bacterial toxicity.[3]

In this study, a polysaccharide based responsive smart material with controlled drug release, by using electrospinning technique, was developed, which allowed the formation of responsive nanofibers with rapid visual detection of pH change in the wound bed, along with anti-inflammatory activity. Responsiveness of the nanofibers were achieved by integration of different halochromic dyes [bromocresol green (BCG), bromothymol blue (BTB) and thymol blue (TB)] to obtain a range of pH values. Produced smart materials were characterized according to their morphological and chemical properties. To tackle the problem of leaching of the dyes, a complexing agent; poly-diallyldimethylammonium chloride (PDADMAC) was used and the formation of complexation was analyzed using pH-potentiometric titration and Quartz Crystal Microbalance with Dissipation (QCM-D), and time of flight secondary ion mass spectroscopy (ToF-SIMS) techniques. Additionally, release tests were performed to prove that the leaching of the halochromic dyes is reduced significantly up to 99%. Furthermore, the responsiveness of the nanofibers was investigated by exposing the nanofibers to different buffer solutions with pH values 4, 7 and 10. The color change of the nanofibers were analyzed using the CIE Lab system while a visual color shift was observed according to the dye characteristics. Lastly, diclofenac (DFC), an anti-inflammatory drug molecule, was integrated to the system and drug release studies were performed by using Franz diffusion cells. A controlled release of DFC to the wound bed was achieved and quantitative evaluations were done.

References

1. Mostafalu, P.; Amugothu, S.; Tamayol, A.; Bagherifard, S.; Akbari, M.; Dokmeci, M.R.; Khademhosseini, A.; Sonkusale, S. Smart flexible wound dressing with wireless drug delivery. In Proceedings of 2015 IEEE Biomedical Circuits and Systems Conference (BioCAS), 22-24 Oct. 2015; pp. 1-4.
2. Pakolpakçıl, A.; Karaca, E.; Becerir, B. Investigation of a Natural pH-Indicator Dye for Nanofibrous Wound Dressings. *IOP Conference Series: Materials Science and Engineering* **2018**, *460*, 012020, doi:<https://doi.org/10.1088/1757-899X/460/1/012020>.
3. Bazbouz, M.B.; Tronci, G. Two-layer Electrospun System Enabling Wound Exudate Management and Visual Infection Response. *Sensors (Basel, Switzerland)* **2019**, *19*, doi:<https://doi.org/10.3390/s19050991>



ADVANCED SURFACE AND PROCESSING TECHNIQUES FOR THE DESIGN OF MULTIFUNCTIONAL 2D AND 3D POLYMERIC MATERIALS

Mohan T.^a, Lackner F.^a, Šurina P.^a, Steindorfer T.^{a*}, Kargl R.^a, Kleinschek Stana K.^a

^a*Institute of Chemistry and Technology of Biobased System (IBioSys), Graz University of Technology, Austria.*

*tobias.steindorfer@tugraz.at

The design of functional 2D and 3D materials with specific properties is an active research area with many potential applications in regenerative medicine and tissue engineering (TE). For example, 3D scaffolds can be used for reconstruction and restoration of various anatomical defects of complex organs and functional tissues[1]. The biomaterial scaffold enables attachment, proliferation and migration of cells, transport of body fluids and reconstruction of bones, nerves, vessels, etc., while providing a platform for defect reconstruction[2]. Scaffolds with all these challenging properties can be fabricated by combining biodegradable polymers and advanced 3D bioprinting technology, which can produce customized scaffolds with high structural complexity and design flexibility for soft (e.g., cartilage) and hard (e.g., bone) tissue engineering applications[3]. On the other hand, the complex 3D scaffold geometries pose an analytical challenge in TE. Most analytical techniques require suspension or flat-surface geometries (e.g., spin coated thin solid polymer films) to which biological molecules (e.g., cells, enzymes, or bacteria) can be attached, grown, and characterized. In such cases, the solid-liquid interaction or adsorption kinetics between biological samples and polymer surfaces can be monitored and quantified in situ using surface sensitive techniques such as quartz crystal microbalance with dissipation (QCM-D), while the latter technique can also be used to monitor solid-vapor interactions[4].

In this work, an overview of the current state of the art of 3D printing technologies such as VAT -polymerization (or resin-based) and direct-ink writing (extrusion) and their potential applications in the field of TE will be given. In addition, the application of QCM-D to understand the interaction of DNA, enzymes, platelets, or vapors with the surfaces of biodegradable polymers such as cellulose and polycaprolactone will be presented in detail. Insights from these advanced surface analysis and bulk techniques should be highly complementary and useful for creating novel functional coatings and complex 3D geometries that could be used in medicine or other high-end engineering applications in general.

[1] Chan B. P., and K. W. Leong., *European Spine Journal*, 17, 467-479, 2008

[2]Mohan T., Maver., Štiglic A. D., Kleinschek K.S., Kargl R, in *Fundamental Biomaterials:Polymers*,105-141, 2018

[3]Lackner F., Liu H., Štiglic A.D., Bračič M., Kargl R., Nidetzky B., Mohan T., Kleinschek K.S., *ACS Applied Bio Materials*, 12, 5728–5740, 2022

[4]Kargl R., Vorraber V., Ribitsch V., Köstler S., Kleinschek K.S., Mohan., *Biosensors and Bioelectronics*, 68, 437-441, 2015



SIMPLE »THIOL-CLICK« ROUTE TO STABLE BIOPOLYMER-BASED ANTIFOULING COATINGS ON POLYDIMETHYLSILOXANE

Kuzmič K.*^a, Bračič M.^a, Vesel A.^b, Makuc D.^c, Pušnik Črešnar K.^{a,d}, Mohan T.^{a,e}

^a *Laboratory for Characterization and Processing of Polymers, University of Maribor – Faculty of Mechanical Engineering, Maribor, Slovenia*

^b *Department of Surface Engineering, Jožef Stefan Institute, Ljubljana, Slovenia.*

^c *Slovenian NMR Centre, National Institute of Chemistry, Ljubljana, Slovenia*

^d *Faculty of Polymer Technology, Slovenj Gradec, Slovenia*

^e *Institute of Chemistry and Technology of Biobased System (IBioSys), Graz University of Technology, Graz, Austria*

* katja.kuzmic@um.si

Biofouling is a significant issue in the medical industry, especially for implants and medical implants made of synthetic polymers. This is due to the hydrophobic nature of the polymeric surfaces (e.g. PDMS: polydimethylsiloxane), which encourages the adhesion and proliferation of unwanted cells and proteins. Surface coatings have been proposed as one of the potential solutions to address this problem [1]. Various synthetic or bio-based origins coating materials have been developed based on their biocompatibility and biodegradability. However, achieving good stability of these coatings remains a challenge, particularly due to the inert, hydrophobic nature of PDMS surfaces [2]. This paper presents a simple and efficient method for the development of stable biopolymer-based coatings on PDMS surfaces using a "thiol-click" approach. In this approach, the UV-ozone-treated PDMS surface was first functionalized with self-polymerized mussel-inspired polydopamine, which provides a hydrophilic surface for the subsequent covalent coupling of thiolated chitosan derivatives by dip-coating. Two thiolated chitosan derivatives: carboxymethyl chitosan and trimethyl chitosan (quaternary chitosan) were investigated with respect to coating efficacy and stability. The resulting coating exhibits excellent stability and resistance to protein fouling, demonstrating its potential application in the development of medical devices. The study also highlights the importance of surface functionalization of highly hydrophobic PDMS-based implants to achieve stable coatings and the potential of bio-based coatings as a promising solution to biofouling.

[1] X. Li, L. Sun, P. Zhang, & Y. Wang, *Coatings*, vol. 11, no. 3, p. 294, 2021

[2] H. Zhang & M. Chiao, *Journal of Medical and Biological Engineering*, vol. 35, no. 2, pp. 143-155, 2015



THE EFFECT OF THE DEGREE OF SUBSTITUTION AND MOLECULAR WEIGHT ON ANTIMICROBIAL ACTIVITY OF CHITOSAN DERIVATIVES

Másson M.^{*a}, Rathinam S.^a, Nagy V.^a, Amani A.^a

^a Faculty of Pharmaceutical Sciences, University of Iceland, Iceland.

* mmasson@hi.is

Chitosan and its derivatives have attracted significant interest as antimicrobial agents due to their broad-spectrum activity against bacteria, fungi, and viruses. While the antimicrobial activity of chitosan has been known for several decades, recent research has focused on investigating the structure-activity relationship of chitosan derivatives. In particular, the degree of substitution (DS) and molecular weight (Mw) of chitosan derivatives have been shown to have a significant impact on their antimicrobial activity [1]

Several chitosan derivatives, including carboxymethyl chitosan (CMC), *N,N,N*-trimethyl chitosan (TMC), *N*-(2-hydroxyl), propyl-3-trimethyl ammonium chitosan chloride (HTCC) and hydroxypropyl chitosan (HPC), have been investigated as antimicrobial agents. Studies have shown that cationic derivatives such as TMC and HTCC exhibit stronger antimicrobial activity than other derivatives. The mechanism of action of chitosan and its derivatives against microorganisms involves the disruption of the cell membrane, although other targets such as intracellular nucleic acids, surface proteins, and lipopolysaccharides have also been suggested.

Studies have shown that the degree of substitution (DS) of chitosan derivatives can significantly affect their antimicrobial activity. For instance, TMC [2] and *N*-quandylated chitosan [3] exhibit a positive relationship between DS and activity against certain microorganisms, such as *S. aureus*, MRSA, and *P. aeruginosa* at pH 7.2. Conversely, a negative relationship between DS and antibacterial activity has been observed for the hydroxypropyl group in HPC [4] and HTCC against *S. aureus* at pH 5.5 and *E. coli* at pH 5.5 and 7.2.

In addition to DS, the molecular weight (Mw) of chitosan derivatives has been shown to play a critical role in their antimicrobial activity. Studies have shown that the effect of Mw on activity varies depending on the microorganism, and there is no clear consensus on the relationship between Mw and activity. However, a closer look at the published data reveals that many studies have shown that the activity will increase with Mw when the molecular weight is low until critical molecular weight for activity (CMW) is reached, beyond which the activity does not change. For TMC, the CMW was found to be around 20 KD. [5] Similar relationships can be observed for other chitosan derivatives. [6,7]

In conclusion, the degree of substitution and molecular weight are crucial factors that affect the antimicrobial activity of chitosan derivatives. Understanding the structure-activity relationship of chitosan derivatives is essential for optimizing their use in various applications such as plant protection, food preservation, wound treatment, and water purification. Further studies are needed to elucidate the precise mechanisms of action of chitosan derivatives and to identify the optimal DS and Mw for specific applications

[1] Másson, M. Antimicrobial Properties of Chitosan and Its Derivatives. In: Jayakumar, R., Prabakaran, M. (eds) Chitosan for Biomaterials III. Advances in Polymer Science, vol 287. Springer, 131-168, 2021

[3] Sahariah P. et. al., *Carbohydrate Polymers*, 127, 407-417, 2015

[4] Rathinam S. et al. *Int. J. Biol. Macromol.* 165, 1686-1693, 2020

[5] Sahariah P. et al. *Int. J. Mol. Sci.* 20.

[6] Kulikov S.N. et al. , *Eur. J. Med. Chem.*, 74,169-178, 2014

[7] Omura et. al. *Biocontr. Sci.*, 8, 25 – 30, 2003



PREPARATION OF COLLAGEN-CELLULOSE SCAFFOLDS FOR TISSUE ENGINEERING WITH CONTROLLED MECHANICAL PROPERTIES AND LONG-TERM STABILITY

Dobaj Štiglic A. ^{*a,1}, Bračič M. ^{a,1}, Kargl R. ^{a,b,1}, Stana Kleinschek K. ^{b,c,1}, Mohan T. ^{a,b,1}

^a *Laboratory for Characterisation and Processing of Polymers, University of Maribor, Slovenia*

^b *Institute of Chemistry and Technology of Biobased System (IBioSys), Graz University of Technology, Austria*

^c *Institute of Automation, University of Maribor, Slovenia*

¹ *Members of the European Polysaccharide Network of Excellence (EPNOE)*

* andreja.stiglic@um.si

Over the last decade, tissue engineering (TE) has made significant progress by utilizing three-dimensional (3D) scaffolds as supportive biomaterials, as they closely mimic the natural hierarchical structure and organization of the extracellular matrix (ECM). For use in TE, the 3D scaffold must possess specific characteristics, including biocompatibility, biodegradability, porosity, mechanical stability, and the ability to support cell attachment and growth. Despite decades of research in developing novel scaffolds, challenges still remain in terms of their production and optimization for specific human tissue.

In this study, we prepared a four-component ink system, from nanocellulose, carboxymethyl cellulose, ECM-based collagen and organic crosslinker, citric acid, which showed suitable shear-thinning behavior and printability. The optimized inks were used for the preparation of scaffolds in the following way: (i) direct-ink-writing 3D printing, (ii) freeze-drying, (iii) dehydrothermal-heat treatment and (iv) acid-neutralization. The elevated temperature (120°C) used during the heat treatment process caused crosslinking between the ink components through ester bonds, resulting in dimensionally and mechanically stable scaffolds. We analyzed the crosslinked scaffolds in terms of their morphology, porosity, chemical structure, swelling, and degradation in both dry and wet states. We investigated the compressive strength, elastic modulus, stability, shape recovery and biocompatibility of the scaffolds as a function of collagen concentration. Prepared scaffolds have huge potential for various *in vitro* and *in vivo* TE applications, such as cartilage TE [1].

[1] Dobaj Štiglic A., Mohan T., *iScience*, 25, 1-23, 2022



QUATERNIZED CHITOSAN NANOFIBERS FOR BONE REGENERATION

Anisiei Alexandru, Andrei Bejan, Sandu Cibotaru*, Luminita Marin

“Petru Poni” Institute of Macromolecular Chemistry, Gr. Ghica Voda Alley, 41A, 700487 Iasi, Romania

* cibotaru.sandu@icmpp.ro

Bone diseases have a major impact on the population, affecting more than 300 million people in the last years, according to World Health Organization (WHO). In this view, bone regeneration is essential to restore the normal function of bones and prevent complications, but their reconstruction is a complex process [1]. One of the best methods used to improve bone regeneration is by providing the necessary minerals directly to the affected part of the tissue and releasing it in a controlled manner. One of the best sources is hydroxyapatite (HA) which is the main mineral component of natural bone and has been shown to promote bone regeneration. The combination of chitosan nanofibers and HA has been shown to promote bone regeneration [2]. The chitosan nanofibers provide a high surfaces area for cell attachment and proliferation while hydroxyapatite provides a mineral component necessary for bone regeneration [3].

In this context, in this work we propose the use of new materials based on chitosan/quaternized chitosan loaded with hydroxyapatite in order to use them as scaffolds for bone regeneration. The advantages brought by the quaternized chitosan are the improved water solubility, antimicrobial activity and bio adhesivity, which can favor the scaffold attachment and the release in a sustained manner of the minerals.

The chemical structure of the obtained systems was assessed using NMR and FTIR spectroscopy, which demonstrated the presence of hydroxyapatite and also the quaternized moiety on chitosan. The morphology and supramolecular organization of the studied composite materials were investigated using POM, SEM and XRD techniques, indicating the uniform distribution of the mineral in the scaffold. The investigation of the thermogravimetric and mechanical properties indicated an increasing of degradation temperature and an increasing in stiffness respectively, pointing for the strong intermolecular forces between composite components.

Furthermore, the swelling properties, *in vitro* biodegradability, mucoadhesiveness, and biocompatibility, and *ex vivo* bioadhesivity were determined, and the results showed the propensity of these materials for application as scaffolds for bone regeneration.

- [1] Dimitriou, R., Jones, E., McGonagle, D. et al. Bone regeneration: current concepts and future directions. *BMC Med* 9, 66, 2011;
- [2] Van Hong Thien, D., Hsiao, S.W., Ho, M.H. et al. Electrospun chitosan/hydroxyapatite nanofibers for bone tissue engineering. *J Mater Sci* 48, 1640–1645 (2013);
- [3] Huanhuan L., Hongju P., Yan W., Can Z., Youzhi C., Guowei X., Qin L., Xiao C., Junfeng J., Yanzhong Z., Hong W. Ou Y., The promotion of bone regeneration by nanofibrous hydroxyapatite/chitosan scaffolds by effects on integrin-BMP/Smad signaling pathway in BMSCs, *Biomaterials*, 34,18, 4404-4417, 2013;

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PCE2/2021 within PNCDI III and from the European Commission through the project H2020-MSCA-RISE-2019, SWORD- DLV-873123.



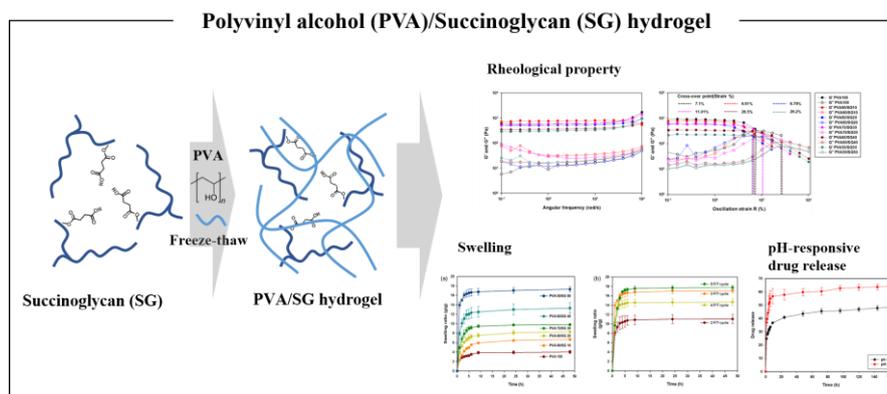
PROPERTIES AND CHARACTERISTICS AND pH-RESPONSIVE DRUG DELIVERY OF FREEZE-THAWED POLYVINYL ALCOHOL/SUCCINOGLYCAN HYDROGELS

Jae-pil Jeong ^{a*}, Yohan Kim^a, and Seunho Jung ^{a,b}

^a Department of Bioscience and Biotechnology & ^b Department of System Biotechnology, Microbial Carbohydrate Resource Bank (MCRB), Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, South Korea

* bruce171525@gmail.com

Polyvinyl alcohol (PVA) has been widely applied in the biomedical field due to its hydrophilicity, non-toxicity and chemical resistance. However, due to the disadvantage of lack of swelling ability, PVA hydrogels are often blended with other polymers such as polyacrylamides and polysaccharides [1]. Succinoglycan (SG) is an anionic water-soluble exopolysaccharide produced by soil bacteria as one of the bacterial exopolysaccharides. SG has been widely used in cosmetic and non-food industries. Recently, a new approach using succinoglycan as a drug delivery system has been reported [2]. In this study, a hydrogel composed of PVA and SG was prepared by freeze-thaw method. First, the hydrogel composition and freeze-thaw cycles were adjusted to optimize the swelling ratio and rheological properties. The swelling ratio of the hydrogel tended to increase as the concentration of SG increased. The G' and G'' values versus oscillation strain of hydrogels explained about the elasticity of the PVA/SG hydrogels increased as the SG content increased. It was explained that SG imparted elasticity to the hydrogels on a rigid PVA hydrogel network with little elasticity. This phenomenon was also investigated from changes in morphology and pore size with a scanning electron microscope. The highest swelling ratio was measured at 17.18 g/g in deionized water. The optimal condition for the PVA/SG hydrogel was selected as PVA50/SG50 based on the swelling ratio and rheology measurement after 5 freeze-thaw cycles. The characteristics of the selected hydrogel were confirmed by fourier transform infrared spectroscopy, X-ray diffraction, and thermogravimetric analysis. Using 5-fluorouracil (5-FU) as a model drug, the applicability of the PVA/SG hydrogel as a drug carrier was confirmed under various pH conditions. The amount of 5-FU finally released was measured to be 48.8% at pH 1.2 and 64.5% at pH 7.4, showing a differential drug release pattern according to pH. PVA/SG hydrogel was suggested as one of the useful hydrogels for pH-responsive drug delivery systems with improved mechanical properties.



[1] Wang, M., Bai, J., Shao, K., Tang, W., Zhao, X., Lin, D., *International Journal of Polymer Science*, 1-16, 2021

[2] Kim, Y., Hu, Y., Jeong, J. P., & Jung, S., *Carbohydrate Polymers*, 284, 119195, 2022



NEW SYNERGISM BETWEEN NATIVE CELLULOSE AND BIOMOLECULES

Mehling M. ^{*a}, Kritharis A.^b, Lu Y.^a, Yadav V.^b, Rojas, O.^a

^a *Biobased Colloids and Materials, University of British Columbia, Canada*

^b *Biofoundry, University of British Columbia, Canada*

* mmehling@student.ubc.ca

We propose a universal and solvent-free method to immobilize biomolecules onto cellulose. Biomolecule immobilization is important to many technologies and processes that rely on the catalysis, detection, or signalling capabilities of these molecules. For example, rapid antigen tests rely on immobilized antibodies, a type of protein, to offer at-home or clinical diagnostics safely and reliably. The continuous production of many pharmaceuticals, cosmetics, textiles, and foods relies on immobilized enzymes for bioprocessing. Synthetic substrates such as nitrocellulose, polyester, epoxies, and other thermoplastics are used to support biomolecule immobilization because they demonstrate high stability and can natively participate in covalent interactions. However, such materials oppose efforts to reduce the global dependence on fossil carbon, are often not amenable to re-use, and demonstrate poor biodegradability.

Cellulose films, particularly ones synthesized by bacteria, are highly pure, biocompatible, stable in aqueous environments, and are biodegradable and compostable. These key characteristics have allowed cellulose to become a common substrate in biomedical implants and sutures. However, the polymer's chemical inertness presents a challenge for biomolecule linking: how can proteins or nucleic acid probes attach to cellulose to advance its material capabilities?

Current efforts to make cellulose amenable to covalent linking require subjecting the polymer to hydrolysis or oxidation reactions with solvents noted to pose environmental harm. Nature offers a better solution. Many organisms that decompose cellulosic mass contain protein complexes with cellulose binding domains, which can uniquely bind to native cellulose. We have engineered novel protein complexes synthesized in *Escherichia coli* that feature a cellulose binding domain and a biotin binding site. We hypothesize that only a brief incubation (<2 minutes) is needed for these protein complexes to form a monolayer coating on cellulose substrates. After doing so, any biomolecule fused with biotin (vitamin B7) can bind to the substrate spontaneously, yet reversibly. Biotin can attach to nearly any biomolecule through conjugation with a biologically expressed AviTag™ sequence or through a biotinylation reaction for which a diversity of commercial kits are available. Given the universality of biotinylation, our linking system is poised to allow a wide range of proteins and nucleic acid probes to adhere onto native cellulose.

This work witnesses a new synergism between polymers and biomolecules that can help realize material composites suitable for tissue engineering or *in vivo* diagnostics. This method can also help synthesize fully biobased, biocompatible, and biodegradable alternatives to current bioprocessing scaffolds or diagnostic devices that plague landfills and contribute to the demand for fossil carbon.



DESIGN, PREPARATION, CHARACTERIZATION AND EVALUATION OF THE TARGETING ABILITY OF PEG/HYALURONIC ACID-PHOSPHOLIPID CONJUGATE MIXED MICELLES

Bincoletto V.^a, Andreana I.^a, Pulignano C.^a, Kopecka J.^b, Riganti C.^b, Stella B.^a,
Matricardi P.^c, Arpicco S.^{*a}

^a Department of Drug Science and Technology, University of Torino, Italy

^b Department of Oncology, University of Torino, Italy

^c Department of Drug Chemistry and Technologies, "Sapienza", University of Roma, Italy

* silvia.arpicco@unito.it

Hyaluronic acid (HA) is an anionic glycosaminoglycan that receives particular attention for its interesting targeting ability properties being its receptor, CD44, overexpressed on different solid (colon, ovarian, breast, lung, pancreatic) tumors [1]. We previously prepared conjugates (HA_{4.8}-DPPE or HA_{14.8}-DPPE) obtained by linking HA with two different molecular weights (4800 and 14800 Da) to an aminated phospholipid (1,2-dipalmitoyl-*sn*-glycero-3-phosphoethanolamine, DPPE) by reductive amination [2].

In this work, we explored the applicability of PEG-DSPE/HA-DPPE mixed micelles as delivery systems "tailored" for CD44-positive cancer cells. The obtained micelles were characterized in terms of critical micelle concentration with pyrene as a fluorescent probe, morphology using FESEM analyses, and physico-chemical characteristics (mean size and Z potential). Micelles showed a spherical shape, a uniform size distribution, and a negative Z potential value.

The targeting ability of HA_{4.8}-DPPE or HA_{14.8}-DPPE containing mixed micelles was evaluated on two pancreatic cancer cell lines with high (Panc-1) and low (Capan-1) CD44 expression and compared to that of PEG-DSPE micelles. To this aim, the cellular uptake of fluorescently labeled micelles and the intracellular accumulation of the fluorophore was measured by flow cytometry analysis. The results showed that the uptake of HA_{4.8}-DPPE or HA_{14.8}-DPPE containing mixed micelles was significantly higher in Panc-1 cells and no differences in the uptake between mixed and PEG-DSPE micelles were detected in poorly expressing Capan-1 cells, suggesting that the entrance of HA-conjugated formulations is likely receptor-mediated. The *in vitro* experiments showed no toxicity on both cancer cell lines.

Taken together, these results suggest that PEG/HA-DPPE mixed micelles could be considered a promising carrier for the selective delivery of hydrophobic anticancer compounds.

[1] Choi, K.Y., Chung, H., Min, K.H., Yoon, H.Y., Kim, K., Park, J.H., Kwon, I.C. & Jeong, S.Y., *Biomaterials*, 31, 106–114, 2010.

[2] Arpicco, S., Lerda, C., Dalla Pozza, E., Costanzo, C., Tsapis, N., Stella, B., et al. *European Journal of Pharmaceutics and Biopharmaceutics*, 85, 373–380, 2013.



HYALURONAN-ESTRADIOL NANOGELS AS POTENTIAL DRUG CARRIERS TO TARGET ER+ BREAST CANCER CELL LINE

Paoletti L. ^{*a}, Zoratto N.^a, Benvenuto M.^{b,c}, Nardozi, D.^d, Angiolini V.^d, Mancini P.^d, Masuelli, L.^d, Bei, R.^c, Frajese G. V.^e, Arpicco S.^f, Matricardi, P.^a, Nalli, M.^a, Di Meo, C.^a

^a Department of Drug Chemistry and Technologies, Sapienza University of Rome, Italy

^b Saint Camillus International, University of Health and Medical Sciences, Italy

^c Department of Clinical Sciences and Translational Medicine, University of Rome "Tor Vergata", Italy

^d Department of Experimental Medicine, Sapienza University of Rome, Italy

^e Department of Sports Science, Human and Health, University of Rome 'Foro Italico', Italy

^f Department of Drug Science and Technology, University of Turin, Italy

* luca.paoletti@uniroma1.it

The delivery of bioactive molecules to the target site has attracted increasing attention over the past three decades as a turning point in the treatment of several diseases [1]. In this regard, polysaccharide-based nanoparticles offer benefits in terms of high loading efficiency, rapid drug release rates and good targeting ability through the easy functionalization of the polymeric backbones [2,3]. Finally, small molecules, peptides, proteins, and nucleic acids can be loaded into nanoparticle systems, which can be functionalized on the surface to actively deliver the cargo to cells that have receptors capable of selectively recognizing the ligand [4].

In this light, an innovative hyaluronan-based nano-delivery system is proposed for the active targeting towards ER+ breast cancer. Hyaluronic acid (HA), an endogenous and bioactive anionic polysaccharide, was functionalized with estradiol (ES), a sexual hormone involved in the development of some hormone-dependent tumors, to give an amphiphilic derivative (HA-ES) able to spontaneously self-assemble in water to form soft nanoparticles or nanogels (ES-NHs). ES-NHs ability to entrap hydrophobic molecules was also investigated, by loading curcumin (CUR) and docetaxel (DTX), both able to inhibit the growth of ER+ breast cancer. The formulations were studied for their capability to inhibit the growth of the MCF-7 cell line, thus evaluating their efficacy and potential as a selective drug delivery system, and internalization assays were performed to follow the cell distribution of the nanosystems.

Ours results demonstrate that both ES-NHs/CUR and ES-NHs/DTX inhibit MCF-7 cell growth, with ES-NHs/DTX effect higher than that of free DTX. Internalization of fluorescent-labeled ES-NHs shows a rapid intracellular uptake, assuming a receptor-dependent targeting.

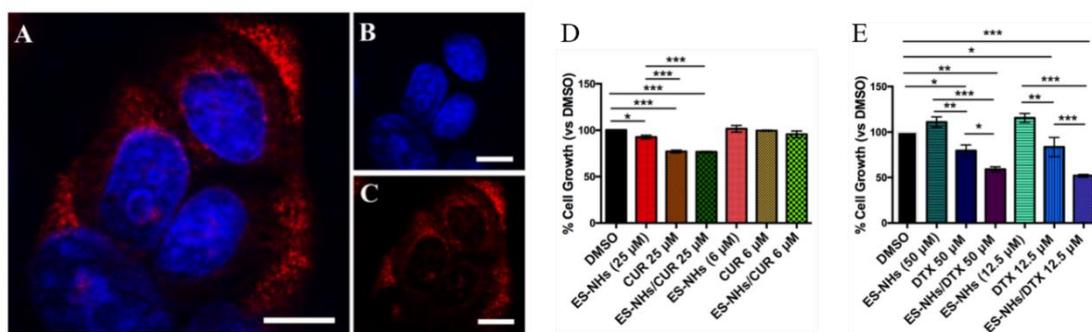


Figure 1 : Internalization analysis of MCF-7 cells incubated with fluorescent ES-NHs : A) merge, B) DAPI, C) ES-NHs ; Effect of D) ES-NHs/CUR and E) ES-NHs/DTX formulation on MCF-7 cell line.

[1] Mazdaei M. et al., *British Journal of Pharmacy*, 7(1), 1-13, 2022

[2] Plucinski A. et al. *Journal of Materials Chemistry B*, 9(35), 7030-62, 2021

[3] Zoratto N. et al. *Pharmaceutics*, 13(11), 1781, 2021

[4] Sanità G. et al. *Frontiers in Molecular Biosciences*, 7, 587012, 2020



POLYMER CROSS-LINKING COLON-TARGETED ENCAPSULATION STRATEGY ENABLES TO IMPROVE OXIDATIVE STABILITY OF PUFA-RICH OILS

Joanna Wojciechowska^{*a}, Aleksandra J. Dyba^{b,c}, Małgorzata Błochowiak^a, Anna Prescha^a, Karol P. Nartowski^{c,d}

^a Department of Dietetics and Bromatology, Wrocław Medical University, Poland

^b Institute of Pharmacy, University of Innsbruck, Austria

^c Department of Drug Form Technology, Wrocław Medical University, Poland

^d School of Pharmacy, University of East Anglia, Norwich, United Kingdom

*email of presenting author: joa.wojciechowska@student.umw.edu.pl

Linseed (LSO), pomegranate seed (PSO) and black currant seed (BCSO) oils are rich in polyunsaturated fatty acids (PUFA) that exhibit anti-inflammatory and immunomodulatory properties, but also are highly prone to oxidation [1]. Polyelectrolyte complexes of Na/Ca alginate are used here to form a capsule shell using the polymer cross-linking strategy with additional chitosan coating. The objective of this study was to create a colon-specific delivery system for preserving the oxidative stability of PUFA.

The encapsulation process was conducted according to Peniche et al. with modifications [2]. The final homogenized formulation contained 5% Na alginate aqueous solution and 20% LSO/PSO/BCSO. Emulsion viscosity, mean diameter of the dispersed phase and stability under processing conditions were evaluated. The emulsions were found stable during the processing time. DLS analysis allowed to distinguish two populations of different size dispersed particles. The optimal conditions for capsule synthesis were identified and the resulting formulation was utilized to carry out drug loading experiments with FFA and QRC. The capsule size during the drying process was monitored at ambient conditions. The final products were stored at RT in a desiccator until further analysis.

DSC and TGA analysis were used to evaluate the oxidative stability of the encapsulated oils. SEM was used to assess the morphology and surface of the capsules. The chemical composition of the fresh and enclosed oils was identified using GC-MS. Simulated digestion process was also conducted and the total amount of the released oil and encapsulation efficiency were determined. The effectiveness of oil encapsulation, chitosan-coating process and drug encapsulation were verified using FTIR. Dried capsules exhibited a narrow size distribution from $1,57 \pm 0,06$ mm (LSO) to $1,63 \pm 0,07$ mm (PSO). Oil content in capsules varied from 62 (LSO) to 72% (PSO). FTIR spectroscopy results allowed to confirm oil encapsulation and effectiveness of chitosan-coating process as well as drug loading. Isothermal DSC analysis at 120°C demonstrated that fresh oils have undergone oxidative changes, while capsules showed no sign of degradation for 12 hours. Encapsulation of PUFA-rich oils into alginate-based polymer capsules was proven successful during the study. Oil-loaded chitosan-coated alginate capsules may be used as potential carriers for drugs or nutraceuticals.



Figure 1. The encapsulation process and examination of the obtained capsules

[1] Boroushaki et al. *Int J Pharm Sci Res*, **7**, 430–42 (2016).

[2] Peniche et al. *Food Hydrocoll*, **18**, 865–71 (2004).

DOXURUBICIN-GALACTOMANNAN COPOLYMER NANOCONJUGATES FOR POTENTIAL CANCER TREATMENT

Laís R. M. Lima L. R. M.^a, Silva M. F. S^b., Ribeiro F. O. S.^c, Pessoa C.^b, Silva, D.A.^c, Feitosa J. P.A.^a, Paula H.C.B.^a, Araújo, G.S.^d, Marinho Filho J.D.B^d, Araújo A.J.^d, de Paula R. C. M. ^{a*}

^a Polymer Laboratory, Federal University of Ceará, Brazil.

^b Experimental Oncology Laboratory - Federal University of Ceará, Brazil;

^c Research Center on Biodiversity and Biotechnology, Federal University of Delta of Parnaíba, Brazil.

^d Cell Culture Laboratory of the Delta, Federal University of Delta of Parnaíba, Brazil.
rpaula@dqoi.ufc.br

Nanoconjugate prodrugs are formed by a stimuli responsive covalent bonds of desired drug with other molecules such as antibodies, peptides, polymers, inorganic nanoparticles, or another drug [1,2]. Nanoconjugate prodrugs are stable during extracellular transport and respond to changes in the targeted cell microenvironments, enabling a drug-controlled release or drug activation at the site.

The present work uses the Schiff's base covalent bond, which respond to pH variation, to synthesise galactomannan (GM) copolymers with poly-(N-isopropylacrylamide) (PNIPAm) and also produced the nanoconjugates with doxorubicin (DOX). The reactions used, as starting materials, the oxidized galactomannan (extracted from *Delonix regia* seeds) with a degree of oxidation of 25.6% and the amine poly-(N-isopropylacrylamide) (PNIPAm-NH₂) with molar mass of 2.3×10^4 g/mol. Copolymers formed were used to form nanoconjugate prodrugs with doxorubicin (DOX), an anti-cancer drug.

The synthesis of copolymers and nanoconjugate prodrugs were confirmed by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) and the analyses of dynamic light scattering (DLS) and confirms that both systems were thermal and pH dual-responsive. The copolymer without DOX (CP) showed critical aggregation concentration ($0.115 \mu\text{g/mL}$) and particle size (236 nm) higher than the copolymer with Dox (CP-DOX), respectively $0.086 \mu\text{g/mL}$ and 180 nm. Copolymers also showed a response to pH variation, with particles at pH 5.0 being greater than at pH 7.4, probably due to hydrolysis of the imine bond. A higher percentage of doxorubicin was released at pH 5.0 (100%) at 96 h, compared to physiological pH = 7.4 (60%), confirming a pH-sensitive release profile. The *in vitro* cytotoxicity assay demonstrated that the nanoconjugate (CP-DOX) can inhibit cancer cell proliferation (B16F10- melanoma cancer; HCT-116- human colorectal cancer and MCF-7- human breast cancer) and promote reduced cytotoxicity in non-tumor cells (L929- murine fibroblast non-cancer cells). Therefore, CP-DOX nanoconjugates exhibited potential as selective delivery of doxorubicin in tumour cells.

Acknowledgments: FINEP (CV.01.22.0174.00), CAPES ((Finance Code 001, PROEX 23038.000509/2020-82), CNPq, MCTIC/CNPq (INCT/ Polysaccharide #406973/2022-9), FUNCAP (MLC-0191-000153.01.00/22).

[1] Ding C., Chen C., Zeng X., Chen H., Zhao Y. ACS Nano. 16, 13513-1355, 2022.

[2] Zhao B., Chen S., Hong Y., Jia L., Zhou Y., He X., Wang Y., Tian Z., Yang Z., Gao D., Pharmaceutics. 14, 1522, 2022



PHYSICO-CHEMICAL AND BIOLOGICAL CHARACTERIZATION OF SYNTHETIC AND EGGSHELL DERIVED NANOHYDROXYAPATITE/CARBOXYMETHYL CHITOSAN COMPOSITES FOR PULP-DENTIN REGENERATION

Saravana Karthikeyan B.^{*a}, Mahalaxmi S.^a, Madhana Madhubala M.^a, Rajkumar G.^b, Dhivya V.^b, Kishen A.^c, Srinivasan N.^d

^aDepartment of Conservative Dentistry and Endodontics, SRM Dental College, Ramapuram, SRM Institute of Science and Technology, Chennai, India

^bDepartment of Physics, Easwari Engineering College, Ramapuram, Chennai, India,

^c Faculty of Dentistry, University of Toronto, Ontario, Canada

^dHamad Dental Centre, Doha, Qatar

*skmcdc2006@gmail.com; saravanb@srmist.edu.in

It is well documented in literature that a combination of polymeric materials with bioceramics for scaffold applications will aid in achieving an optimal balance between bioactivity and mechanical properties.¹ There is a plethora of studies pertaining to bone tissue regeneration using chitosan/hydroxyapatite-based scaffolds.^{1, 2} More recently, our team also explored the feasibility of nanohydroxyapatite (nHA)/carboxymethyl chitosan (CMC) composite scaffolds for dentin regeneration.^{3,4} But, there are no literature evidence comparing the biomineralization abilities of synthetically and biogenically derived nHA incorporated CMC scaffolds. Hence, the aim of the present investigation is to analyze the physico-chemical characterization of CMC scaffolds incorporated with synthetic and egg shell derived nHA and to comparatively evaluate their odontogenic potentials on cultured human dental pulp stem cells (DPSCs). Commercially available synthetic nano-hydroxyapatite (SnHA) and chitosan were procured. CMC was prepared from chitosan extract and egg shell derived nano-hydroxyapatite (EnHA) was synthesized from egg biowastes. Then, the composite scaffolds, namely, SnHA-CMC and EnHA-CMC were prepared using freeze drying technique. The prepared biomaterials were characterized by SEM-EDX, FT-IR, XRD and TEM analytic methods. Then, the scaffolds were loaded onto cultured DPSCs to assess the cell viability by MTT assay whereas the angiogenic and odontogenic differentiation potentials were evaluated by VEGF and DSPP gene expressions by flow cytometry and RT-qPCR methods at 7, 14 and 21 days respectively. Data were statistically analyzed using Kruskal-Wallis and Friedman's Two-way ANOVA tests with a significance level set at $p < 0.05$.

Synthesized EnHA comprised of crystals ranging from 20-50 nm with spherulite morphology and 1.67 Ca/P molar ratio. The ultrastructure of the scaffolds revealed a highly interconnected porous microstructure with pore diameter ranging between 60-200 μm while the chemical characterization displayed specific functional groups of both HA and CMC. Both the test scaffolds supported cell viability with enhanced VEGF and DSPP expression levels on DPSCs at the tested time intervals. However, EnHA-CMC significantly upregulated VEGF and DSPP levels when compared to SnHA-CMC following 21 days of interaction ($p > 0.05$).

Both SnHA-CMC and EnHA-CMC scaffolds in 1:5 w/w proportions displayed favorable porous microstructure with increased cell viability as well as upregulated angiogenic and odontogenic specific gene expressions on cultured DPSCs. Further, the odontogenic differentiation abilities of 1:5 w/w EnHA-CMC were significantly better than that of SnHA-CMC and may serve as a promising scaffold for dentin-pulp regeneration.

1. Maji S., et al. Carbohydr Polym, 189, 115–25, 2018.
2. Budiraharjo, et al. J Colloid Interface Sci, 366, 224-32, 2012.
3. Baskar K., et al. Int Endod J, 55, 89-102, 2022.
4. Gurucharan I., et al., Int Endod J, 26, 486-501, 2023.



DEVELOPMENT OF CROSSLINKING PROCESS FOR THE BIOPOLYMER CHITOSAN USING FUROIC ACID FOR BIOMEDICAL APPLICATIONS

Maria Lazaridou ^{1,2}, Dimitrios N.Bikiaris ¹, Rupert Kargl ²

¹ *Laboratory of Chemistry and Technology of Polymers and Dyes, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*

² *Institute for Chemistry and Technology of Biobased System, Graz University of Technology, 8010 Graz, Austria*

Abstract

Environmental issues, regarding the consumption of petroleum-based products, raise serious efforts to employ alternative materials from natural resources. As a result, more attention has been recently paid to polysaccharides as polymeric renewable materials. Among others, chitosan, the deacetylated form of chitin, is a naturally occurring polymer that is abundant in nature, specifically in the shells of arthropods, the cell walls of bacteria and algae. Due to its good physicochemical properties and unique biological properties, chitosan finds applications in many industries, including the medical, food, chemical, cosmetics, water treatment, metal extraction and recovery, biochemical, and biomedical engineering industries. Furthermore, chitosan has two functional groups that allow its modification with several monomers ameliorating its properties such as solubility and viscosity. Aromatic five-membered heterocyclic compounds, like 2-furoic acid, are commonly encountered in natural products and active pharmaceutical molecules, showing enhanced antioxidant activity. It is also derived from the oxidation of the furfural which valorization as a biomass product remains one of the main objectives of FUR4SUSTAIN Cost Action. In detail, 2-furoic acid contains a carboxylic group which could react with the amino group of chitosan molecule leading to an amide bond between them. This bond is expected to alter the properties of chitosan inducing the formation of a three-dimensional network. The aim of this study was the investigation of the mechanism of the reaction taking part and also the physicochemical characterization of the new biomaterial in order to further process its potential use in biomedical applications.

Acknowledgment: This work is supported by COST Action- FUR4Sustain- European Network of FURan-based chemicals and materials FOR a Sustainable development, CA18220, supported by COST (European Cooperation in Science and Technology)



ACTIVITY OF CHITOSAN-SODIUM USNATE NANO-ASSEMBLIES AGAINST OSTEOSARCOMA 143B CELLS

Benedetta Brugnoli^a, Alessia Mariano^b, Beatrice Simonis^{a,c}, Cecilia Bombelli^c, Simona Sennato^d, Antonella Piozzi^a, Vincenzo Taresco^e, Veeren M. Chauhan^f, Steven M. Howdle^e, Anna Scotto d'Abusco^b, Iolanda Francolini^a

^{a,b}Department of Chemistry, Sapienza University of Rome, P.le A. Moro, 5, 00185, Rome, Italy;

^cCNR-Institute for Biological Systems (ISB), Secondary Office of Rome-Reaction Mechanisms c/o Chemistry Department, Sapienza University, Rome, Italy;

^dCNR-Institute of Complex Systems (ISC)- Sapienza c/o Physics Department, Sapienza University, Rome, Italy;

^eDepartment of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK;

^fSchool of Pharmacy, Boots Science Building, University of Nottingham, Nottingham NG7 2RD, UK

*benedetta.brugnoli@uniroma1.it

Osteosarcoma (OS) is the most common primary malignant bone cancer disease in pediatric and adolescent patients. Chemotherapy remains the main therapeutic strategy against OS but, unfortunately, causes alterations in cellular growth not only in cancerous cells but also in healthy ones [1]. Drug encapsulation in polymer nanoparticles is a strategy commonly employed to mitigate inconvenience associated with toxic drugs, including poor solubility and systemic toxicity [2].

In this study, chitosan (CS) nanoparticles (NPs) were investigated as carriers for the anticancer drug sodium usnate (NaU). Self-assembled CS NPs were obtained by ionotropic gelation and loaded with NaU, without the use of organic solvents or surfactants. A high drug encapsulation efficiency was obtained thanks to the establishment of drug/polymer ionic interactions. Hepatotoxicity of free and encapsulated drug was evaluated against HepG2 cells. The efficacy of the formulations against osteosarcoma 143B cells was investigated by both cell viability assay and evaluation of the Maspin protein production, a tumor suppressor agent. A significant reduction in NaU hepatotoxicity when encapsulated in CS NPs compared to free NaU was evidenced and, for the first time, a relevant synergistic activity of CS and NaU in promoting Maspin stimulation in 143B cells was found. The safety of NaU-loaded CS NPs observed in in vivo biocompatibility tests on nematodes further validates these systems as suitable nano-formulations to deliver toxic anticancer agents.

[1] Li, S., Zhang, H., Liu, J., & Shang, G. *Journal of cancer research and clinical oncology*, 2023

[2] Francolini, I., Taresco, V., Crisante, F., Martinelli, A., D'Ilario, L., & Piozzi, A. *International journal of molecular sciences*, 14(4), 7356–7369, 2013



Session 8

Composites, textiles and fiber network structures

Session organizers:

Nicolas LeMoigne, Avinash Manian, Ulrich Hirn, Tadahisa Iwata, Jörg Müssig

Keynote speakers:

Kristiina Oksman

Bio-based nanomaterials and their use in composites

Robert Pelton

Analyzing polymer adsorption isothermes on porous wood pulp fibers



BIO-BASED NANOMATERIALS AND THEIR USE IN COMPOSITES

Oksman K.*^a

^a *Wood and Bionanocomposites, Luleå University of Technology, Sweden*

* Kristiina.Oksman@ltu.se

This presentation is about processing, structure and properties of polysaccharide nanomaterials and their biocomposites. Our interest is to isolate the nanomaterials using energy-efficient and scalable processes and achieve high yields and find new functions based on nanomaterials natural composition or structure. As example brown algae is consisting of cellulose and alginate, the alginate phase is shown to facilitate the isolation process of the cellulose nanofibers and act as a natural binder between the nanofibers as well as a natural fire retardant [1]. The other example is chitin nanocrystals which have been studied as an additive on PLA and it has shown to act as antibacterial and anti-static agent as well as reinforcement for the polymer in the nanocomposites [2].

The processing of bionanocomposites has been focused on solvent casting and some other laboratory scale methods, however we are interested to use processed which can be upscaled [3,4]. We have developed an extrusion process where the nanomaterial is fed into the extruder as a liquid suspension and this process can lead to good dispersion of the nanomaterial if compared with processes where the nanomaterials dried before the blending with the polymer [3,4]. The dispersion of the nanomaterial is critical and we have shown that if the nanomaterials are well dispersed, they can increase the polymer properties already in very low concentrations and in addition if the nanomaterials can be oriented in the composite, they will further increase the reinforcing effect [5,6]. Drawing of PLA chitin nanocomposites resulted in increased strength and toughness of the composites as shown in the Figure 1. [6]. Another process which is interesting is to use the nanofiber network as a preform in resin infusion process [7]. Nanofiber networks are very stiff and strong but also very dense with low permeability. We have worked with preform development which could allow a common vacuum infusion of a thermoset resin into the network [7].

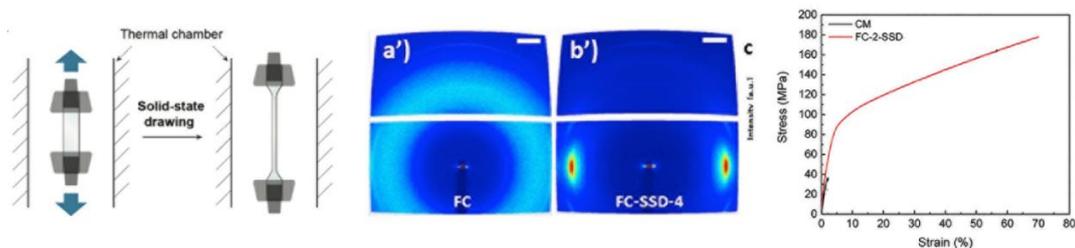


Figure 1. Solid-state drawing of PLA nanocomposites, orientation of the structure and effect on mechanical properties.

- [1] Berglund L., Nissilä T., Sivaraman D., Komulainen O., Telkki V-V. & Oksman K., *ACS Applied Mater Interfaces*, 13, 29, 34899, 2021.
- [2] Herrera N., Roch H., Salaberria AM., Pino MA., Labidi J., Fernandes SCM., Radic D., Leiva A. & Oksman K. *Materials Design* 92, 846-852, 2016.
- [3] Oksman K., Mathew A.P., Bondeson D., Kvien I., *Composites Science and Technology* 66, 2776-2784, 2006.
- [4] Patel MK., Zacccone M., De Brauwer L., Nair R., Monti M., Martinez-Nogues V., Frache A & Oksman K, *Polymers*, 14, 23, 5104, 2022,
- [5] Singh A.A. Geng S., Herrera N., Oksman K., *Composites Part A*, 104, 101-107, 2018.
- [6] Singh S., Patel M., Geng S., Teleman A., Schwendemann D., Maspoch ML, & Oksman K. *Nanomaterials* 11, 3308, 2021
- [7] Nissilä T., Wei J., Geng S., Teleman A. & Oksman K., *Nanomaterials* 11, 2, 490, 2021.



ANALYZING POLYMER ADSORPTION ISOTHERMS ON POROUS WOOD PULP FIBERS

Pelton R. ^{*a}, Karami A. ^a

^a Department of Chemical Engineering, McMaster University, Canada

* peltonrh@mcmaster.ca

The adsorption of cationic water-soluble polymers onto negatively charged wood pulp fibers is an important component of papermaking technologies. The literature contains many examples of adsorption isotherms for polymers, with narrow molecular weight distributions. Such measurements have been used to make estimates of fiber wall pores sizes or the density of charged groups on external fiber surfaces. This contribution summarizes the information that can be extracted from isotherms involving polymers with broad molecular weight and/or compositional distributions, typical of polymers used in papermaking. The most useful parameter is the y-axis intercept, Γ_1 , which measures the maximum capacity of fibers to fully adsorb all added polymer. For a given fiber type, the magnitude of Γ_1 is dictated by the presence, but not the concentration, of the highest molecular weight fraction of the polymer. By contrast, the maximum content of the adsorbed polymer, Γ_{\max} , is linked to the lowest molecular weight fraction of the adsorbing polymer. Presented is a model predicting the saturated content of adsorbed polymer on the external fiber surfaces and other parameters as functions of experimental values for Γ_{\max} , Γ_1 and the slope of the isotherm approaching the intercept. Whereas many authors emphasize Γ_{\max} , when interpreting adsorption data, we propose that Γ_1 provides more useful information.

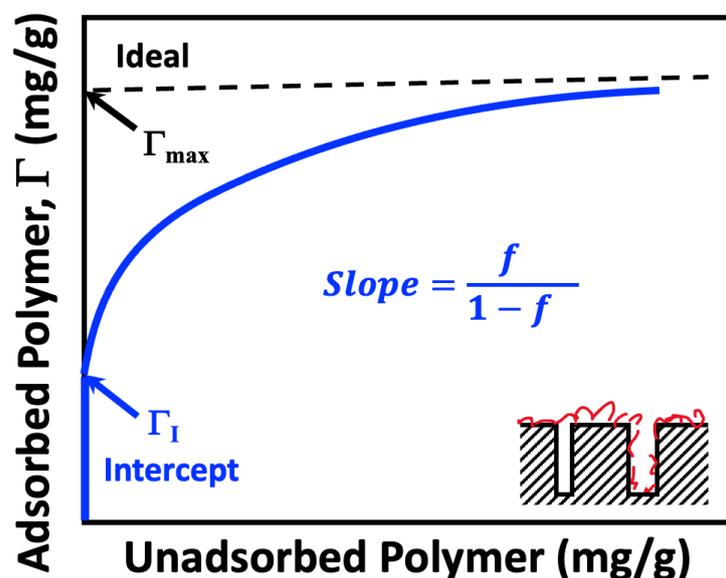


Figure 1 A typical adsorption isotherm where f is the fraction of added polymer that adsorbs at a given polymer dose.



CELLULOSE FOAM FILMS WITH IMPROVED WATER TOLERANCE FUNCTIONALIZED WITH WILLOW BARK EXTRACT

Lohtander-Piispa T. ^{*a}, Ngoc H^b., Hjelt T. ^a, Gestranus M. ^a, Österberg M. ^b, Arola S. ^a

^a *Biomass Processing and Products, VTT Technical Research Centre of Finland Ltd., Finland*

^b *Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland*

* tia.lohtander-piispa@vtt.fi

The demand for renewable materials to replace fossil-based packaging materials is constantly increasing. Abundant, renewable, and recyclable cellulose-based materials have been identified as promising alternatives to plastic. The one major drawback limiting the use of lignocellulosic biopolymers is their hygroscopicity and dimensional instability. In this work, we produced self-standing, lightweight cellulosic foam films from high-consistency nanocellulose with improved water tolerance and dimensional stability. Functionalization of the foam films was achieved by the addition of alkyl ketene dimer (AKD) and willow bark extract (WBE). AKD and WBE showed a synergistic effect in improving the hydrophobicity and water tolerance of the foam films as AKD was found to hydrophobize the surfaces of both cellulose nanofibers and polyphenolic WBE oligomers.

The dry foam films showed moderate conformability and bendability, and WBE was proven to improve the strength of the films. Bark extractives, including WBE, typically contain valuable bioactive polyphenolic components. Herein, we aimed to harness the bioactive properties of WBE to the foam structure and the results of antioxidant and ultraviolet protection factor tests verified that the bioactivity was successfully brought to the foam films. The achieved water tolerance and bioactivity combined with a straightforward and scalable process enable new opportunities to utilize biodegradable cellulosic foams as insulating coatings and layers in multilayer structures, for instance, in active packaging applications.

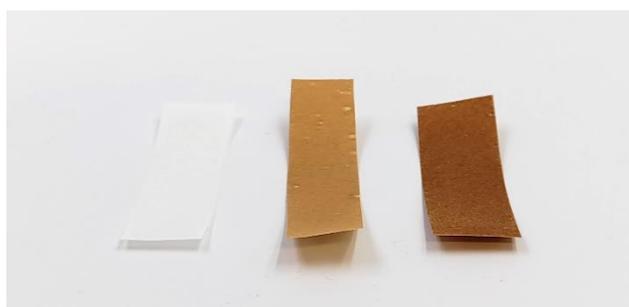


Figure 1. The foam films with improved water tolerance and functionalized with varying willow bark extract content.

[1] Lohtander T., et al. Bioactive foam films from cellulose and willow bark extract with improved water tolerance. *Manuscript under preparation.*



ANIONIC MODIFIED CELLULOSE TEXTILE COATED WITH CONDUCTING POLYMER

Mayer P. ^a, Bechtold T. ^a, Pham T. ^a

^a *Research Institute of Textile Chemistry and Textile Physics, University of Innsbruck, Austria*

* paul.mayer@uibk.ac.at

Due to their semiconductor properties conductive polymers often find application for instance in solar cells, light emitting diodes or thin film transistors. [1]

In order to combine textile with properties of conductive polymers, they have been coated onto textiles by different techniques such as dipcoating, vapor coating, electrochemical coating and in situ solution polymerization. [2]

In this study, a pretreatment of the textile surface before the coating step is presented in order to improve the electric conductivity of the textile-conductive polymer composite. By modifying the surface of textiles with anionic functionalities an ionic bond between the (cationic) polyelectrolyte nature of conducting polymers and the modified textile is formed.

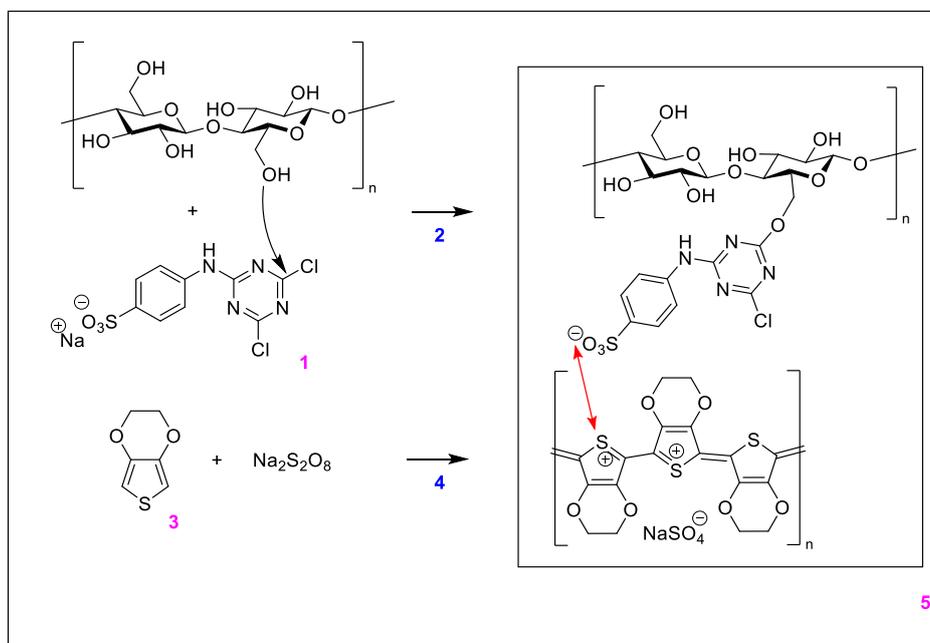


Figure 1: Schematic representation of the experimental steps

The anionizing agent sodium 4-((4,6-dichloro-1,3,5-triazin-2-yl)amino)benzenesulfonate **1** is anchored **2** in the cellulose textile. 3,4-ethylenedioxythiophene **3** is then polymerized **4** on the surface of the pretreated cellulose textile in aqueous environment. A black electrically conductive coating of poly(3,4-ethylenedioxythiophene) is formed on the surface of the modified cellulose textile **5**.

The anchoring of the anionic sulfonate group to the cellulose textile improves the electric conductivity of the poly(3,4-ethylenedioxythiophene) coated cellulose textiles compared to untreated cellulose textile.

[1] Guo X., Facchetti A., Nature materials, 19 (9), 922-928, 2020

[2] Allison L.; Hoxie, S. & Andrew T. L., Chem. Commun., 53 (53), 7182–7193, 2017



FROM INDUSTRY 4.0 TO RESEARCH 4.0. A MODULAR APPROACH FOR THE DEVELOPMENT OF CELLULOSIC FIBRES

Canga Rodríguez J. ^{*a}, Müller-Probandt S. ^a

^a DIENES Apparatebau GmbH, Germany

* j.canga@dienes.net

Biobased fibre products pose a big technological challenge as growing demands on the varying quality of recycled feedstock and the achievement of a consistent fibre performance require a continuous development and optimisation of both technology and production parameters. Research 4.0 aims to enable researchers working on their development optimally supported by the system. As already mentioned, research work in the field of biobased fibres is characterised by a high degree of adaptation needs. Research facilities must be able to be adapted after initial experiments and the knowledge gained thereby. All necessary adjustments are made under the conditions of a highly complex manufacturing process, which is determined by many parameters. Summarised it results in the following requirements for the flexibility of modular research facilities:

- INTEGRATION: Easy integration of new production modules
- SCALABILITY: Easy replacement of production modules with modified specifications
- FLEXIBILITY: Easy modification of production steps' positioning within the production line
- HIGH PERFORMANCE: Intelligent production modules synchronized by a master process control level
- ANALYTICS: Continuous monitoring and evaluation of process parameters

A reliable development of new innovative biobased fibres demands an efficient, systematic and, in part, self-optimising experimental working system, which must be intelligent in gathering data from the process and flexible in enabling the rearrangement of the process. Applying the principles of Research 4.0, each module of a plant represents a production step and is equipped with a PLC to control itself and to organise in association with other modules within the line. The control hierarchy has an intelligent modular structure that configures itself according to the arrangement of each single module given by the hardware and the interfaces within the system. Moreover, all production parameters can be permanently visualised and recorded, enabling a complete traceability of the process.

This paper will present the implementation of Research 4.0 as a tool for the development of a product from the idea to its practical implementation implementation based on a modular conceptual approach which ensures the required flexibility for the complete validation process from the first lab trials up to an industrial scale production line: principle → process → product → production.



Figure 1 : Example of a Research 4.0 modular pilot plant for developing cellulosic based multifilament yarns



VISCOSE PROCESS - OFTEN ALREADY PRONOUNCED DEAD AND STILL VERY MUCH ALIVE

Röder T. ^{*a}

^a Lenzing AG, Werkstraße 2, 4860 Lenzing, Austria

* t.roeder@lenzing.com

To shape native cellulose like wood or cotton one needs to dissolve cellulose first. This means to break the strong hydrogen bonds in between the cellulose chains and to replace those by interactions with a direct/complexing solvent or by derivatization of the cellulose OH-groups.

In 1892 a patent written by C.F. Cross, E.J. Bevan, and C. Beadle described a derivatization process of cellulose with sodium hydroxide and CS₂ to cellulose xanthogenate – the viscose process. Lenzing has been producing Viscose, the first generation of cellulose fibers, for more than 85 years now.

The knowledge it has acquired in Viscose production is reflected in the superb quality of LENZING™ ECOVERO™, which nowadays sets the standard for the textile industry. The well established man-made cellulose fibers viscose (staple fibers, tyre cord, filament), modal (staple fibers) and lyocell (staple fibers, filament) are compared with other regenerated cellulose fibers regarding their structure-property-relationships. Crystallinity, orientation, cross section and working capacity are important parameters for further processing into textiles and nonwovens.

The different manufacturing processes are discussed in terms of their degrees of freedom and their possibilities.

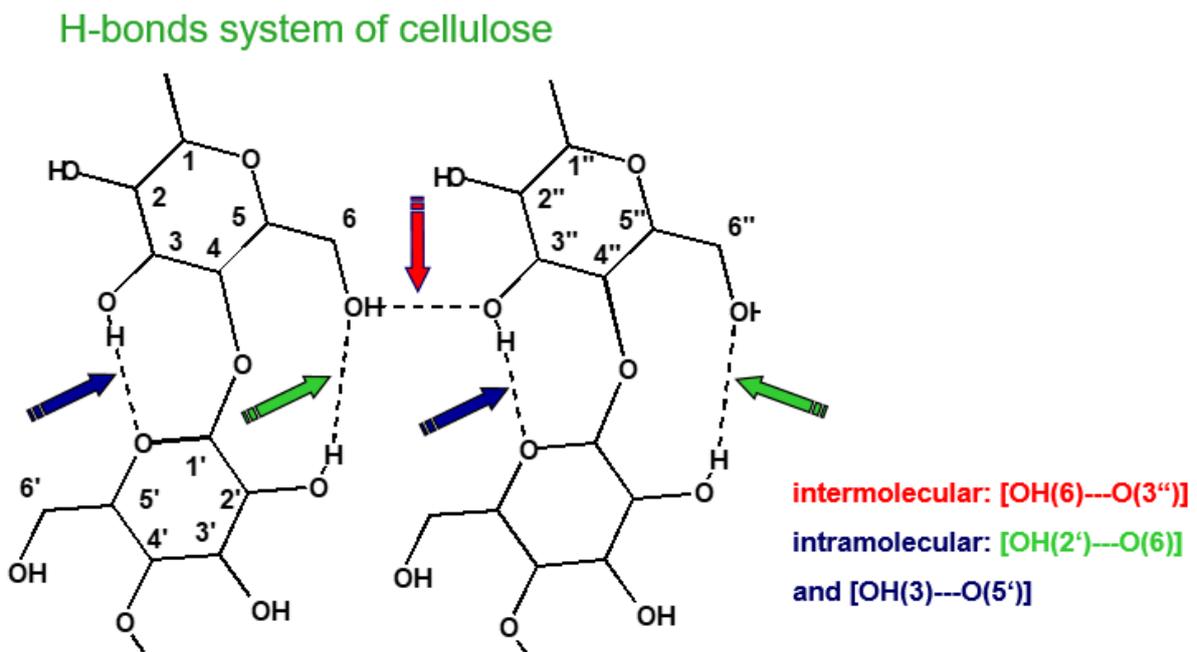


Figure 1 : Hydrogen bond system of cellulose



TOPOGRAPHICAL DISTRIBUTION OF FUNCTIONAL GROUPS IN CELLULOSE FIBERS AFTER HETEROGENEOUS CARBOXYMETHYLATION

Bogner P.^{*}, Manian A.P., Bechtold, T., Pham T.

Research Institute of Textile Chemistry and Textile Physics, University of Innsbruck, Austria

* paul.bogner@uibk.ac.at

Carboxymethyl cellulose attracts interest as a substitute for acrylate-polymer based absorbents in hygiene products or as binding agents for pollutants in wastewater remediation [1-3]. A primary concern is mechanical stability of the system, to prevent displacement of the polymer from its intended location and for ensuring robust performance. Multiple options are available to address it. One is to deposit and fix the polymer on a carrier. Another is to spin fibers from a dope of carboxymethylated cellulose into fibrous networks. A third is to assemble cellulose fibers into networks followed by carboxymethylation under heterogeneous conditions. In heterogeneous carboxymethylation, apart from reaction conditions, the fiber supramolecular structure and morphology may dictate the degree of substitution and topographical distribution of functional groups, and thus influence performance of the final product.

We report on results of our investigations into the influence of fiber supramolecular structure and morphology on the degree of substitution in heterogeneous carboxymethylation of cellulose fibers. Cellulosic fibers were carboxymethylated at different temperatures from aqueous media of different compositions after and without alkali activation. The resulting products were analyzed with different methods to determine the degree of substitution (back titration, conductometric titration, FTIR spectroscopy), and correlated with their binding propensity and water retention. We observed differences in performance between fibers with the same degree of substitution, which may be attributed to differences in the topological distribution of functional groups. Further evidence to confirm changes in substitution topology is being sought with a combination Atomic Force Microscopy-Infrared spectroscopy mapping of the products.



Figure 1: Carboxymethylated fibers embedded in epoxy resin

[1] Chen J., Wu J., Raffa P., Picchioni F., Koning C. E., *Progress in Polymer Science*, 125, 101475, 2022

[2] Wang Z., Jiang Y., Mao L., Mao S., Deng M., Liang X., *Cellulose*, 30 (6), 3611-3623, 2023

[3] Wang J., Liu M., Duan C., Sun J., Xu Y., *Carbohydrate Polymers*, 206, 837-843, 2019



PARTIAL WELDING OF CELLULOSE FIBERS AS STRUCTURAL MATERIAL

Yizhou Sang, Yeedo Chun, Tianyu Guo, Xun Niu, Orlando J. Rojas*

*Bioproducts Institute, Department of Chemical and Biological Engineering,
Department of Chemistry and Department of Wood Science, University of British
Columbia, 2360, East Mall, Vancouver, BC V6T 1Z3, Canada.*

* orlando.rojas@ubc.ca

Renewable and sustainable wood can be used to produce eco-friendly material to which can not only ensure a gradual transition from petroleum-based economy to sugar-based economy but also alleviate the environment pollution.

We report a two-step processing strategy to convert the cellulose fibers into strong material through molecular soldering and welding technology. After obtaining the cellulose network from pulping and papermaking process, we partially weld the material through selective fiber dissolution and in situ regeneration. The approach concentrates the cellulose solution at the interphases between the fibers and regenerates the cellulose in situ with appropriate solvent allowing the formation of strong bonds at the molecular level. This strategy provides an approach to make structural material with high strength and flexibility directly from wood fibers.



ELECTROKINETIC AND SORPTION PROPERTIES OF PLASMA TREATED JUTE FABRICS

Kostic M.^{*a}, Milosevic M.^a, Obradovic B.^b, Ivanovska A.^c, Korica M.^c, Kuraica M.^b, SvircevZ.^{d,e}

^aFaculty of Technology and Metallurgy, University of Belgrade, Serbia

^bFaculty of Physics, University of Belgrade, Serbia

^cInnovation Center of the Faculty of Technology and Metallurgy, University of Belgrade, Serbia

^dFaculty of Sciences, University of Novi Sad, Serbia

^eFaculty of Science and Engineering, Åbo Akademi University, Finland

*kostic@tmf.bg.ac.rs

Jute fibers are characterized by a complex layered structure with the presence of a hydrophobic surface outer layer consisting of a mixture of waxes and fats. This outer layer is responsible for fibers' low sorption properties. In this work, raw jute fabric was subjected to atmospheric pressure dielectric barrier discharge (DBD) under different conditions (150 Hz and 15.2 kV, vs. 300 Hz and 12.6 kV, air as working gas, constant time of 120 s) to remove the mentioned hydrophobic layer. Changes in the surface chemistry of DBD modified jute fabrics were monitored by ATR-FTIR spectroscopy and measurement of the electrokinetic properties, while the fabric sorption properties were evaluated by measuring the wetting time and capillarity. Special attention was given to the aging effect investigated up to fourteen days after plasma treatment.

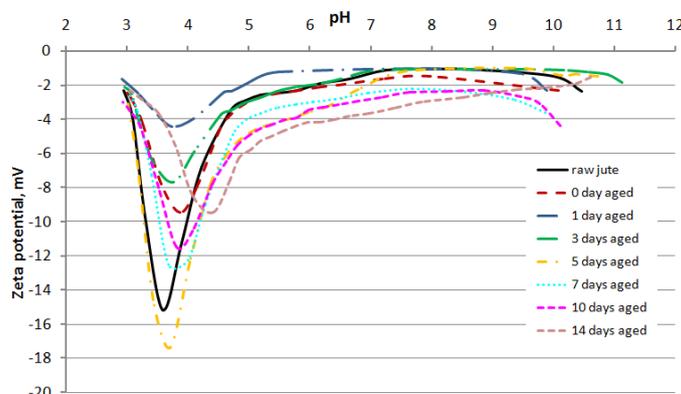


Figure 1 : Zeta potential of DBD treated jute fabrics as a function of pH and aging time

The obtained results reveal that the measurement of the electrokinetic properties could be used to follow changes in the surface chemistry of DBD treated jute fabrics due to the post-plasma reactions (Fig. 1) and confirm the significance of aging effects in natural cellulose fibers' functionalization using plasma. Although the changes in the fabric surface chemistry were more pronounced for fabric treated with a higher DBD frequency DBD, a lower frequency DBD treatment resulted in better sorption properties. Both DBD treatments and aging decreased wetting time from 145.9 ± 6.0 s for raw jute fabric down to 1.2 ± 0.1 s for a lower frequency DBD treated fabric after 7 days of aging. Independently on the applied DBD treatment conditions, the jute fabrics' capillarity was significantly improved; i.e., their capillary height increased from 87 mm for the raw jute fabrics up to 138 mm and 120 mm for a lower and higher frequency DBD treated fabrics, respectively.

Acknowledgments: This research was funded by the Science Fund of the Republic of Serbia (#7726976), Integrated Strategy for Rehabilitation of Disturbed Land Surfaces and Control of Air Pollution -RECAP.



LOW-LEVEL CATIONIZATION OF COTTON AS POSSIBLE ROUTE TO SALT FREE REACTIVE DYEING

Netzer F.^a, Seemork K.^b, Bechtold T.^a, Manian A. P.^a, Pham T.^a

^a *Research Institute of Textile Chemistry and Textile Physics, Universität Innsbruck, Austria*

^b *Department of Textile Science, Kasetsart University, Thailand*

* felix.netzer@uibk.ac.at

The conventional dyeing of cellulose fibres including cotton as its most prominent representative consumes large amounts of inorganic electrolytes and fresh water, resulting in high salinity and coloured wastewater. These effluents can cause serious environmental pollution and pose a potential threat to living organisms. In order to make reactive dyeing more sustainable, different approaches are pursued, including the cationization of cellulose fibres. The use of cationic fibres enables salt free dyeing and thus helps to reduce wastewater.

According to state of the art, cationization of cellulosic fibres often used an amount of about 30 - 100 g/L of cationic modifier, resulting in high levels of cationization. While salt free reactive dyeing is possible, non-uniform dyeing and shading are observed. As far as chemical balancing is concerned, the elimination of salt loads is covered by the generous use of cationic modifiers.

In our work [1] we report on a novel approach of low level cationization of cotton fabrics with a cationic group content ranging from 5 to 79 mmol/kg. The cationization was carried out with 3-Chloro-2-hydroxypropyl-*N,N,N*-trimethylammonium chloride (CHPTAC) in a cold-pad-batch procedure. Salt free reactive dyeing of modified cotton fabrics was performed in exhaust dyeing experiments using Reactive Blue 19. It was demonstrated that a low cationic group content of 14 mmol/kg is comparable to a conventional dyeing process using a salt load of 50 g/L NaCl.

The optimised cationization procedure allows a reduction of chemical consumption by 90 % compared to recently published literature and demonstrates a new approach for the elimination of salt loads during reactive dyeing.

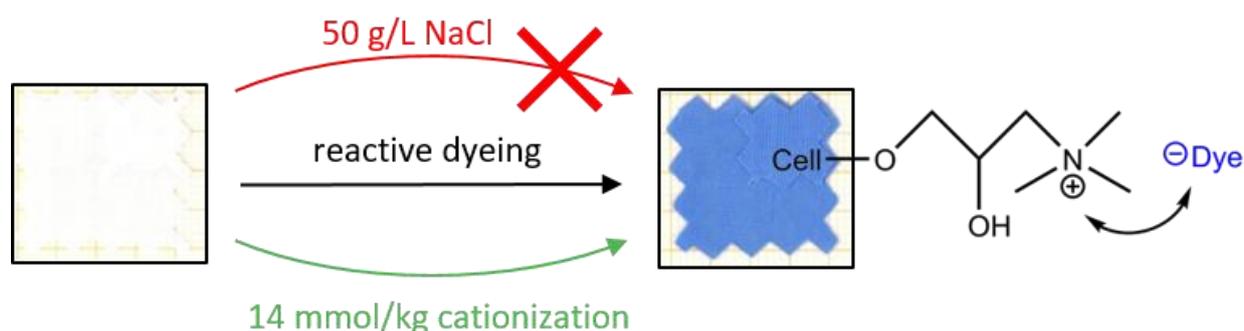


Figure 1 : Salt free reactive dyeing of low-level cationized cotton fabrics.

[1] Setthayanond, J., Netzer, F., Seemork, K. et al., *Cellulose*, <https://doi.org/10.1007/s10570-023-05136-5>, 2023



HYDROPHILIC MODIFICATION OF CELLULOSIC SUBSTRATES BY CARBOXYMETHYLATED STARCH COMPOSITING

Wurm F. ^{*a}, Kozich M.^b, Mann K.-J.^b, Seidl B.^b, Tung P.^a, Bechtold T.^a

^a *Universität Innsbruck, Research Institute of Textile Chemistry and Textile Physics, Hoehsterstrasse 73, 6850 Dornbirn, Austria; Universität Innsbruck, Innrain 52, 6020 Innsbruck, Austria*

^b *Agrana Research & Innovation Center GmbH, Josef-Reither-Straße 21–23, 3430 Tulln, Austria*

* florian.wurm@uibk.ac.at

The transition to bio-based and bio-degradable products includes the substitution of petrol-based, and mostly non-degradable, hydrophilic polymers in hygiene and sanitary products. One possible approach is the combination of a hydrophilic biopolymer, e.g. carboxymethylated starch, in combination with a cellulosic substrate. The hydrophilic polymer can be cross-linked onto the substrate for fixation, as for non-dissolution in fluids. Swell-able and water-absorbing composites, supported by cellulosic structure, can thus be prepared. Such a hydrophilic modification can be applied to various textile structures. The hydrophilic biopolymer preparations can be used in printing, for coating as for infiltration of textile structures. The swelling magnitude of the hydrophilic structures can be tuned by its polymer concentration, the degree of substitution (D_s) of the monomer as the degree of applied cross-linking.

Carboxymethylated starches, with different D_s , were used to prepare gelatinized starch dispersions/solutions. These were either stencil-printed on cellulosic fabrics or used for, single as multi-filament, fibre coating. A peristaltic pump was used to ascertain a defined drawing speed in fibre coating. Depending on the viscosity of the starch preparations surface coating and infiltration of the cellulose was present. To counteract starch loss in aqueous media, cross-linking of these polymers by citric acid was included in the composite formation. The amount of cross-linker was modified to assess the opposite effects of starch loss in swelling media and swelling extent restriction.

So produced fibre and fabric composites were characterised using microscopy, swelling magnitudes in water and by dynamic vapour sorption properties. The elution of un-cross-linked citric acid using HPLC was quantified. One set of composite fibres was subjected to a fine wash, and subsequent swelling properties were determined. As anticipatable, the swelling ability of starches with a higher D_s is superior to lower substituted starches. However, due to water solubility, these are also easier lost in swelling media. Accordingly, extensive cross-linking hinders swelling magnitude. Confining the swelling magnitude by cross-linking, such composites can be partially washable, with minor starch loss.

The approach is rather simple and applicable by the textile industry. Common textile processes can be used to produce such composites or modify textile products. This possibly facilitates its introduction in existing production processes. Furthermore, cellulosic substrates can be substituted by other bio-degradable fabrics and fibres. However, care must be given to the cross-linking approach, which might not work as readily with non-cellulosic substrates.

Limitation to the approach are the imminent lower swelling magnitude compared to petrol-based absorber, as the competitiveness compared to direct carboxymethylation of cellulose substrates. Finally, using an edible component for non-food applications has to be factored in.



DEVELOPMENT OF 100% BIO-BASED AND BIODEGRADABLE WOMEN'S SANITARY NAPKINS FROM LIGNIN-RICH FIBERS

Sillard C.^a, Marietti N.^a, Deville M.^a, Cossus L.^a, Vigié J.^a, Charlier Q.^a, Desloges I.^a, Peyroux R.^b.

^aUniversité Grenoble Alpes, Grenoble INP, CNRS UMR 5518, LGP2, Grenoble, France

^bUniversité Grenoble Alpes, Grenoble INP, CNRS UMR 5522, 3SR, Grenoble, France

*cecile.sillard@lgp2.grenoble-inp.fr

The female population is continuing to increase, thereby leading to the growth of the feminine hygiene products market. The global market is valued at USD 34,535.63 million in 2021 and is expected to grow at a CAGR of 4.81% during the forecast period (2022-2027). Conventional women's sanitary napkins are composed of approximately 50% cellulosic products, 6% petroleum-based superabsorbents, and 36% polymers like PP, PET, or PE. These products are neither recyclable nor biodegradable, which raises concerns regarding their end-of-life and environmental impact. Additionally, accessibility to these products varies widely depending on the societal and economic context, particularly in less developed countries.

The LGP2 laboratory is working on the development of sustainable and cost-effective solutions for feminine hygiene protection. Its objective is to provide an alternative to current products that is biodegradable, made from renewable resources, technologically simple, and affordable. Our strategy involves using a single raw material to create **a specific fibrous structure for each component of the multilayer structure**. This involves employing straightforward processing steps to produce a final napkin consisting of three elements that exhibit different properties and fulfill distinct roles:

- A veil that is in contact with the body and needs to be soft and absorbent, which is accomplished by creating a **less tightly bonded fiber mat**.
- A pad that must absorb body fluids, which is achieved by making an **ultra-porous cellulose foam** [1].
- A waterproof paper that also provides mechanical strength to the product, which is obtained by forming a **high-density barrier paper** by thermo or ultrasonic pressing the fiber mat.

In this context, the present study describes the various stages involved in the preparation of the three elements, starting from bamboo pulp obtained by thermomechanical treatment. The resulting materials properties will be evaluated and compared with the performance of commercially available products using dedicated methods. The study will focus on the relationship between the structures and microstructures obtained and the final performance of the materials in terms of fluid absorbency, retention, mechanical strength as well as flexibility.

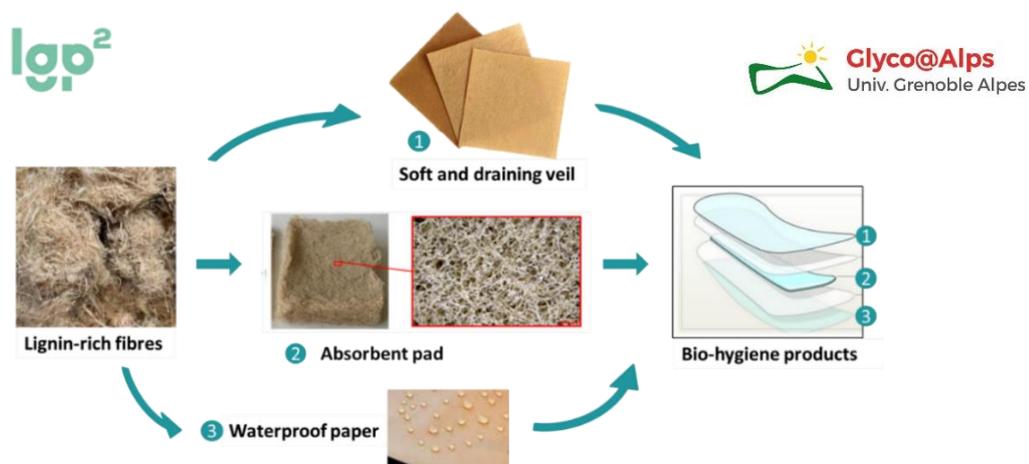


Figure 1: LGP2 strategy to obtain bio-based sanitary napkin starting from a single raw material.

[1] Hjelt, T. Jukka A. Ketoja, J.A., Kiiskinen, H., Koponen, A., I., and Pääkkonen, E. (2022) Foam forming of fiber products: a review. *J Dispers Sci Technol.*, Vol. 43, NO. 10, 1462–149



FLAX SHIVES AS REINFORCEMENTS FOR INJECTION MOLDED BIO-BASED COMPOSITES

Nour El Dein A.^{*a,b,c}, Barbulée A.^c, Gamond O.^d, Le Moigne N.^b, Pucci M.^a, Caro A.S.^a

^a LMGC, IMT Mines Ales, Univ Montpellier, CNRS, Ales, France

^b Polymers Composites and Hybrids (PCH), IMT Mines Ales, Ales, France

^c DEPESTELE, Teillage Vandecandelaere, 5 rue de l'Eglise, 14540 Bourguébus, France

^d AG PLAST, Route de Matafelon, 01460 Nurieux-Volognat, France

* ali-al-hadi.nour-el-dein@mines-ales.fr

Flax shive is the main by-product of flax fiber production. It represents about 50% of the weight of the dry flax stem. Its low price (around 100 €/t) and its very low bulk density (100 to 140 kg/m³) attracts its use as an alternative bio-based filler in bio-composite materials. Recent studies [1] have shown a significant effect of flax shives granulometry on the tensile properties of the composite. Therefore, this study aims to further investigate the influence of the size and shape distributions of flax shives on the mechanical behavior of the composite and interpret the results through microstructural analysis. Different fractions were prepared by grinding and sieving to obtain these particle sizes: less than 200 µm, 200-500 µm, 500-800 µm and 800-1600 µm. Flax shive / polypropylene (PP) composites were prepared using twin-screw extrusion and injection molding with fiber weight fractions of 10%, 20%, 30%, and 40%. Maleic anhydride grafted polypropylene (MAPP) was used as a compatibilizer with an optimized ratio. Figure 1a presents the tensile properties of the resulting composites, revealing that flax shives sieved between 200 and 500 µm provide the optimal tensile properties. Microstructure analysis showed that better fiber dispersion and higher interfacial area (shown in Figure 1b) are obtained for composites reinforced with low fiber granulometry. The aspect ratio of the particles was determined after solvent extraction of flax shives from the composite. X-ray tomography (shown in Figure 1c) provided additional data regarding the orientation and the distribution of the flax shives in the composite. Microstructural data were then used to predict the mechanical behavior of the composites and estimate the Young's modulus of the flax shive through both Mori-Tanaka analytical model and finite element analysis.

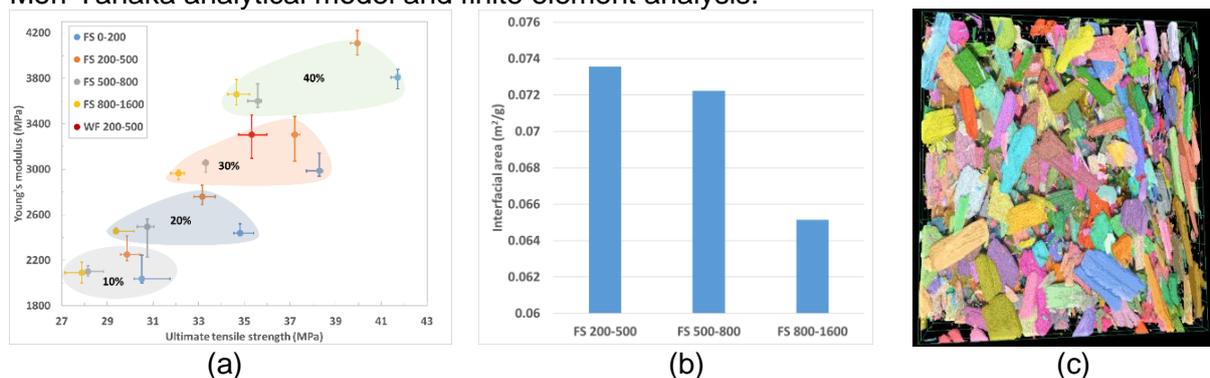


Figure 1: (a) Ashby diagram for the Young's Modulus versus ultimate tensile strength for flax shive (FS) and wood flour (WF) reinforced PP composite at different fiber weight fractions and initial particle sizes. (b) Interfacial area measured using X-ray tomography images for composite reinforced with 30% in weight of flax shive. (c) X-ray tomography for PP composite reinforced with 10% in weight of FS 200-500 µm after segmentation.

Acknowledgements:

The authors thank the French Agency for Ecological transition "ADEME" for funding ProActif project.

[1] Nuez L., Beaugrand J., Shah D.U., Mayer-Laigle C., Bourmaud A., D'arras P. & Baley C., *Industrial crops and products*, 148, 112324, 2020



MODIFICATION OF WRAPPED FLAX ROVINGS WITH TANNINS MOLECULES FOR THE DEVELOPMENT OF FABRICS FOR COMPOSITE APPLICATIONS

K. Tilouche-Guerdelli¹, C. Lacoste¹, D. Perrin¹, P. Ouagne², J. Tirillò³, F. Sarasini³, X. Gabrion⁴, V. Placet⁴, A. Bergeret¹

¹ *Polymers Composites and Hybrids (PCH), IMT Mines Ales, Ales, France*

² *The production engineering laboratory (LGP), INP-ENIT, Tarbes, France*

³ *Department of Chemical Engineering Materials Environment, Sapienza-Università di Roma, Roma, Italy*

⁴ *FEMTO-ST, CNRS/UFC/ENSMM/UTBM, Besançon, France*

Contact: Anne.Bergeret@mines-ales.fr; Speaker: Khouloud.Tilouche@mines-ales.fr

CONTEXT Currently, composite materials are made from synthetic reinforcing materials such as glass, carbon and aramid fibers. However, the growing awareness of environmental impact has led to the development of composite materials based on lignocellulosic fibers such as flax. These biocomposites are attractive alternatives due to their low density, excellent specific mechanical properties, low cost, and environmental benefits. However, their use is limited due to their poor thermal and mechanical performance as well as their moisture absorption. Current research focuses on the development of specific surface treatments for lignocellulosic fibers to improve the thermal stability and fiber/matrix interfacial adhesion of the resulting composites. Among the different surface functionalization strategies for plant fibers, chemical treatments are the most used, although only a few of them involve biobased molecules.

AIM AND METHODOLOGY The objective of this study is to chemically modify wrapped flax rovings with biobased molecules such as condensed tannins using a dedicated impregnation line. A comparison was carried out with a non-bio-based molecule widely used for glass fibers and more recently lignocellulosic fibers, namely an aminosilane. Plain and satin fabrics were woven using these treated wrapped rovings with a manual loom device for shaping bioepoxy/flax fabric biocomposites by thermocompression.

RESULTS

Mid Infrared spectroscopy (FT-IR) analyses allowed to observe the presence of grafted molecules on the surface of the fibers after treatment. The results of the tensile tests of the wrapped flax rovings and of the elaborated flax fabrics showed an increase of the tenacity following the various surface treatments. It was observed that the tensile strength of composite materials stepped up significantly with chemical treatment, due to an increase in interfacial adhesion between the fiber and the matrix, which was proven by scanning electron microscopy (SEM). The porosity of different composites was investigated by X-ray tomography in order to better understand the results obtained. The influence of the weave pattern on the properties of the resulting materials at different scales was also studied.

KEYWORDS Lignocellulosic, wrapped rovings, flax, bio-based molecules, tannins, impregnation line, surface treatments, biocomposite, epoxy/flax interface



THE ROLE OF POLYSACCHARIDES IN PREVENTION OF ACIDIC DEGRADATION OF CELLULOSE-BASED PAPER ARTEFACTS

Bračič M.^a, Malešič J.^b, Brunčko M.^a, Bračič D.^a, Mohan T.^{a,c}

^a *Laboratory for Characterization and Processing of Polymers University of Maribor, Slovenia*

^b *National and University Library, Slovenia.*

^c *Institute for the Protection of Cultural Heritage of Slovenia, Slovenia*

^c *Institute of Chemistry and Technology of Biobased System (IBioSys), Graz University of Technology, Graz, Austria*

* matej.bracic@um.si

Degradation of paper artifacts is a cause for great concern as the information about our cultural heritage needs to be preserved in its original form for a core of valid reasons like national, political, legal, historical, economic, scientific, and emotional.[1] Degradation of paper is caused by physical, chemical and biological factors. Endogenous factors, e.g., pH value of the paper, are crucial determinants for paper degradation and its longevity.[1] Paper acidity arising from the addition of aluminum sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (alum), as a sizing agent in the final stages of papermaking from the mid-19th century until the final decades of the 20th century, is generally accepted as a main cause of paper degradation. Consequentially, enormous effort and financial resources are put into development of special deacidification treatments to preserve paper artifacts. The potential for such treatments is huge in Slovenia alone, as 230 km of bookshelves full of archival material exist and $\approx 80\%$ of it was produced after 1830. In this work, the role of cellulose in preparation of non-aqueous colloidal dispersions of alkaline particles and their role in preserving the mechanical integrity of compromised paper artefacts is presented. The stability and particle size in the colloidal dispersions of alkaline particles are evaluated by DLS and turbidimetry. Successful application of the dispersions on model paper artefact is evaluated by chemical analysis (FTIR) and penetration depth using SEM/EDX of paper cross-sections. Neutralisation of the paper's acidity and the added alkaline reserve are determined by standard methods and new protocols for pH measurement and alkaline reserve determination. Finally, the visual appearance of the paper artefacts is evaluated by UV-VIS spectroscopy.

New perspectives of using functional polysaccharides to achieve multifunctionality of speciality treatments for acidic paper artefacts will briefly be presented as well.

1.Strlič, M. & Kolar, J. (National and university library, 2005)



COLORED TEXTILE WASTE AS CELLULOSE SOURCE FOR MANUFACTURED FIBERS

Hummel M.*^a, Nygren Nicole A.^a, Schlapp-Hackl I.^a

^a Department of Bioproducts and Biosystems, Aalto University, Finland

* michael.hummel@aalto.fi

The overconsumption of textiles during the past three decades has led to continuously growing amounts of textile waste which pose environmental threats on multiple levels. However, discarded textiles have meanwhile also been recognized as important and plentiful material resource. Cellulosic fibers, foremost cotton but also manufactured cellulose fibers (MCFs) can be turned into a dissolving-pulp like feedstock for the production of new MCFs. [1,2] This is an opportunity to introduce circularity into a currently mostly linear textile economy. However, textile waste is a multi-material mix of different fibers and additives such as dyes and finishes. Pretreatment procedures are thus needed to separate the fibers and remove undesired components.[3] Currently, this includes bleaching protocols to arrive at a white substrate. Evidently, thereafter spun fibers need to undergo a dyeing process again.

Herein we present strategies to recycle dyed cellulose waste to produce *in situ* dyed fibers. The recyclability of VAT, reactive and disperse dyes is evaluated and compared. Further, we disclose strategies to produce spin-dyed fibers can be recycled without any loss in the dye intensity.

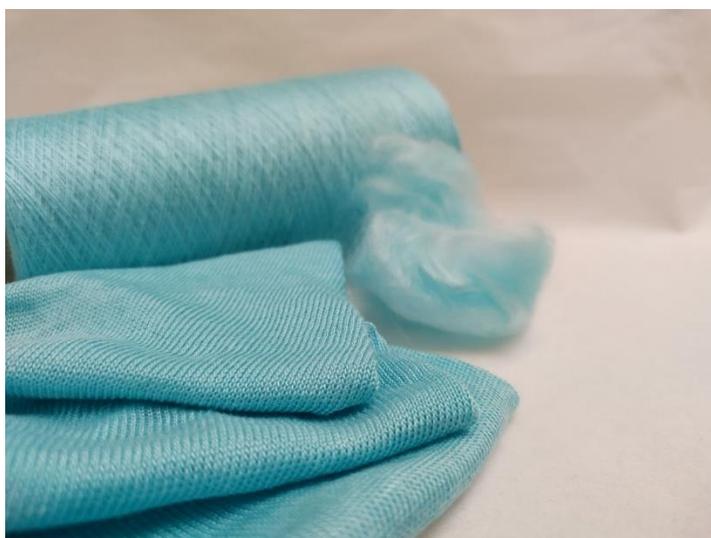


Figure 1: Spun-dyed fibers, yarn and fabrics for to enable a circular textile economy.

[1] Asaadi S., Hummel M., Hellstén S., Ma Y., Michud A. & Sixta H. *ChemSusChem* 9, 3250–3258, 2016

[2] Haslinger S., Hummel M., Anghelescu-Hakala A., Määttänen M. & Sixta, H. *Waste Manage.* 97, 88-96, 2019

[3] Haslinger S., Hietala S., Hummel M., Maunu S.L. & Sixta, H. *Carbohydr. Polym.* 207, 11-16, 2019



HIGH-VELOCITY STRETCHING OF RENEWABLE POLYMER BLENDS

Mautner A.^{*a,b}, Eichelter J.^{b,c}, Wilhelm H.^c, Bismarck A.^{b,d}

^a *BioPlastics Technology, Institute of Environmental Biotechnology, IFA Tulln, University of Natural Resources and Life Sciences (BOKU), Austria*

^b *Polymer and Composite Engineering (PaCE) group, Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Austria*

^c *Laboratory of Polymer Engineering (LKT-TGM), Austria*

^d *Department of Chemical Engineering, Imperial College London, UK*

* andreas.mautner@boku.ac.at

Environmental pollution caused by plastic waste and concerns regarding the emission of greenhouse or toxic gases during incineration or landfilling of plastic waste results in increased interest in biodegradable polymers produced from renewable resources. However, the industrial use of renewable polymers is often limited by their costs and less favourable physical and mechanical properties compared to conventional synthetic polymers. This holds even more for polymers used in strength dominated applications, for instance films, tapes, and textiles, e.g. weaves for flexible intermediate bulk containers, also called “BigBags”. In particular, the poor stretchability of renewable polymers is disadvantageous for packaging applications, in which stretching is key to achieve the required mechanical performance. [1]

Here, we investigated blending of various renewable polymer grades in various amounts that can be utilized in high-speed stretching, commonly applied in the industrial production of polymer tapes. Stretching at velocities of up to 800 mm/s, similar to industrial production of non-degradable synthetic polymers, allows for achieving much higher strength and stiffness as compared to conventional stretching at low velocity regularly performed in laboratory scale. This was enabled by using a custom-made setup installed on an injection molding machine and making use of the high opening-velocity of the device. The influence of the type and amounts of the various renewable polymers onto the stretchability as well as mechanical properties, in particular Young’s modulus and yield stress, of the prepared composites was evaluated.

Renewable polymer blends based on TPS, PBAT, and PLA with high stretchability as well as high modulus and yield stress of stretched tapes comparable to high-density polyethylene (PE-HD) and isotactic polypropylene were identified. Particularly high stretchability (up to 380%) was facilitated with TPS-PBAT tapes whereas comparably high moduli (up to 5 GPa) and yield stresses (up to 160 MPa) of stretched tapes were obtained for mixtures of different PLA grades resulting in moduli exceeding that of PE-HD. A balance of these properties approaching those of synthetic polymers was achieved with PLA-PBAT blends (stretchability: 340%, modulus: 4.5 GPa, yield stress: 120 MPa).

[1] Eichelter J., Wilhelm H., Mautner A., Fahrngruber B., Schafner E., Eder A., Kozich M & Bismarck A., *Journal of Polymers and the Environment*, 29, 3509-3524, 2021



UPGRADING WHEAT STRAW TO HIGH-PERFORMANCE BINDERLESS BOARDS

Neudecker F. ^{*a}, Veigel S. ^a, Gindl-Altmutter W. ^a

^a *Institute of Wood Technology and Renewable Materials, Department of Material Sciences and Process Engineering, BOKU - University of Natural Resources and Life Sciences, Vienna, Konrad-Lorenz-Strasse 24, 3430 Tulln, Austria*

* felix.neudecker@boku.ac.at

To transform our current fossil-based into a modern bio-based economy, new utilization concepts for the available biomaterials are required. Here, the material use of underutilized agricultural by-products like wheat straw offers considerable potential. Nature has optimized the structure of straw towards the ability to transfer the grain ear load and withstand external forces such as wind. This is accompanied by excellent strength properties, which the straw receives due to its fibrous structure. Due to the high-performance structure, the question arises whether it is more reasonable to utilize the structure of the straw in an engineering material than to disassemble the bio composite for biorefinery or to burn it directly without material utilization.

In the scope of our research, a straightforward biotechnological approach was adopted to upgrade wheat straw to high-performance fibreboards without the use of binding agents. For this purpose, as shown in Figure 1, straw was first converted into fibres using a mild semi-chemical pulping process. The fibres were then exposed to natural water retting for various periods of time. The treated fibres were finally hot-pressed into fibreboards following a wet process. Detailed analysis and sequencing revealed the microorganisms involved and showed that generated xylanase interacted with the fibres. On the one hand, this improved the drainability of the fibres and thus the processability, bringing the process closer to industrial implementation. On the other hand, the biotreatment improved the self-bonding properties of the straw fibres, increasing both the mechanical properties and water resistance. Here, an 8-day biotreatment proved to be optimal and resulted in impressive flexural strengths of 64 MPa, flexural moduli of 6.8 GPa and internal bond of 1.1 MPa. While the properties partially reached the level of the top performers of binderless fibreboards made of straw, this approach offers above all the possibility of boards manufactured more efficiently and simply.

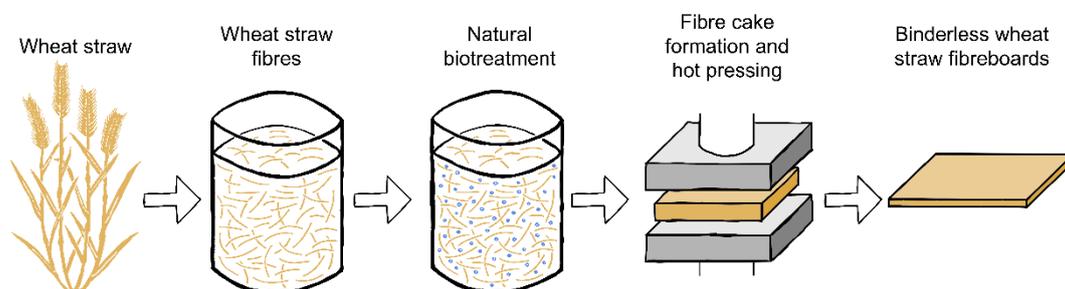


Figure 1: Schematic illustration showing the production of binderless fibreboards from wheat straw



EFFECT OF ENZYME HYDROLYSIS INCUBATION CONDITIONS ON MECHANICAL PULP FIBRE MORPHOLOGY

Frias de Albuquerque M.^{a,c}, Trajano H.^{a,c}, Stoeber B.^{b,c}, Olson J.^{b,c}

^a *Department of Chemical and Biological Engineering, University of British Columbia, Canada*

^b *Department of Mechanical Engineering, University of British Columbia, Canada*

^c *Energy Reduction in Mechanical Pulping Phase 3*

Microfibrillated cellulose (MFC) has been extensively studied as a material that holds promise as reinforcing agent in the papermaking industry and the manufacture of bioresource-based composites. These microfibrils are mechanically resistant, biodegradable, and present a high surface area, which allows them to form strongly interconnected networks. However, producing MFC through mechanical pulp refining requires high specific energy, and, as such, the process calls for an additional fibre treatment to facilitate fibrillation. Enzyme hydrolysis of the fibre's chemical components is a potential method for aiding cell wall delamination and generating microfibrils with desirable structure and aspect ratio. The most commonly used enzyme for this end is endoglucanase, which promotes the cleavage of internal bonds in the cellulose structure. For better performance, endoglucanases are often combined with other enzyme types, such as exoglucanase, xylanase or mannanase. However, the enzymatic hydrolysis of mechanical pulp is very complex due to the substrate's heterogeneous nature and the enzymes' sensitivity to reaction environment conditions. Furthermore, the literature still poorly describes the combined effect of enzyme hydrolysis and mechanical refining on MFC properties.

Hence, a systematic study was performed on the effect of hydrolysis conditions of mechanical pulp by cellulases on fibre quality. First, bleached chemi-thermomechanical pulp fibres were pretreated with cellulases at different dosages and incubation conditions. Then, fibres were subjected to refining at the PFI mill for 10,000 revolutions. The resulting fibres were characterized through conductivity, sedimentation tests, morphology analysis, and scanning electron microscopy. Finally, paper handsheets were produced, and mechanical properties were measured according to standard protocols. Combining enzyme hydrolysis with low-energy refining of mechanical pulp is expected to sustainably generate fibrils with tailored properties for potential applications in various sectors, such as packaging reinforcement, films, and coatings.



BARRIER PERFORMANCE OF POLYSACCHARIDE-COATED PAPER AND BOARD AS A FUNCTION OF THE COATING METHOD AND SUBSTRATE PROPERTIES

Mayerhofer, A.^a, Bauer, W.*^a, Mandlez, D.^a, Kopacic, S.*^a

^a *Institute of Bioproducts and Paper Technology (BPTI), Graz University of Technology, Austria*

* wolfgang.bauer@tugraz.at

Paper and board are well-established materials in packaging applications due to their easy recycling and biodegradability. Because of the hydrophilic and porous behaviour of paper, however, modifications are necessary to achieve the required barrier properties against gases, aromas, water, grease and oil necessary in e.g. packaging of food.

In conventional packaging these barrier properties are often achieved by the application of layers made from non-renewable materials such as plastic or metal films. However, these composite materials pose a significant problem for the environment and for the recyclability of fibre-based packaging materials. Naturally occurring polysaccharides, such as alginate, chitosan, nano- and microfibrillated cellulose, have shown to be good oxygen and oil barriers. The application of these materials onto paper substrates, however, poses several challenges to standard paper coating equipment because of the difference in rheological properties compared to conventional paper coating materials. For instance, biopolymers usually have a significantly higher viscosity already at low solids content.

This contribution presents our approach to investigate the principle suitability of a polysaccharide or any other biopolymer for barrier coating applications on paper. Furthermore, two different application methods are compared with respect to the resulting barrier properties of the coated papers: 1.) the application using a conventional film press, a standard coating unit in the paper industry, and 2.) the application with a purpose-built spray coating unit developed for biopolymer coatings. Additionally, the different biopolymers were applied onto different commercial base papers consisting of either virgin or recycled fiber materials to also examine the influence of both coating material and substrate properties on the resulting barrier performance, such as oxygen transmission rate, water vapour transmission rate, grease resistance and mineral oil migration and permeation.

The results will provide insights on how to best apply biopolymer-based barrier coatings in the paper and board industry and will highlight the advantages and limitations of these application methods. Furthermore, novel findings regarding the interaction between biopolymer, substrate and coating method for the desired packaging applications will be presented.

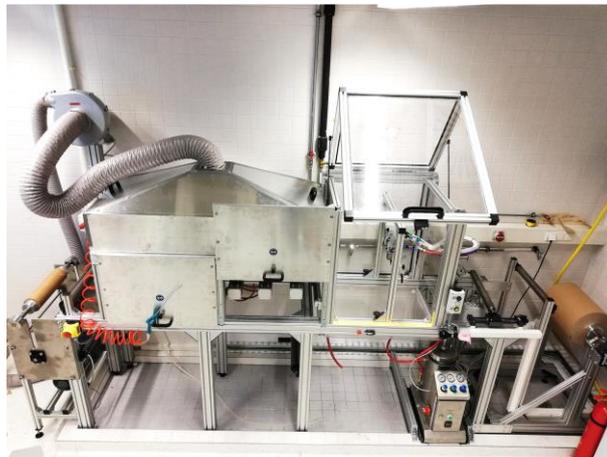


Figure 1 : Purpose-built spray coating unit at BPTI, TU Graz



FUNCTIONAL POLYSACCHARIDES TO TAILOR FUNCTIONAL PAPER FOR IMPROVED AND NEW APPLICATIONS

Biesalski, M.

*Laboratory for Macromolecular Chemistry and Paper Chemistry,
Technical University of Darmstadt, Germany*

markus.biesalski@tu-darmstadt.de

Paper has been known for thousands of years for its unique profile of properties. Despite its classical applications as print, packaging and hygiene paper, it has been in focus for several years in very challenging areas, e.g. in lateral flow tests (LFT), light-weight construction materials (e.g. as a honeycomb core in door leaves or shelves), as well as most recently in paper-based packaging as well as paper-based soft robotics. In this talk I will introduce our recent efforts in understanding and tailoring paper properties by controlled functionalization of the fiber and paper-sheet interfaces with macromolecules, including those derived from polysaccharides. Examples progress from the use of functional wax-polysaccharide coatings [1] to modulate barrier properties to cross-linking of polymers with paper fibers to introduce wet-strength properties[2-4] in a sustainable fashion and the spatial control of interfacial attachment of polymers inside paper to gain 4D paper-based actuators [5].

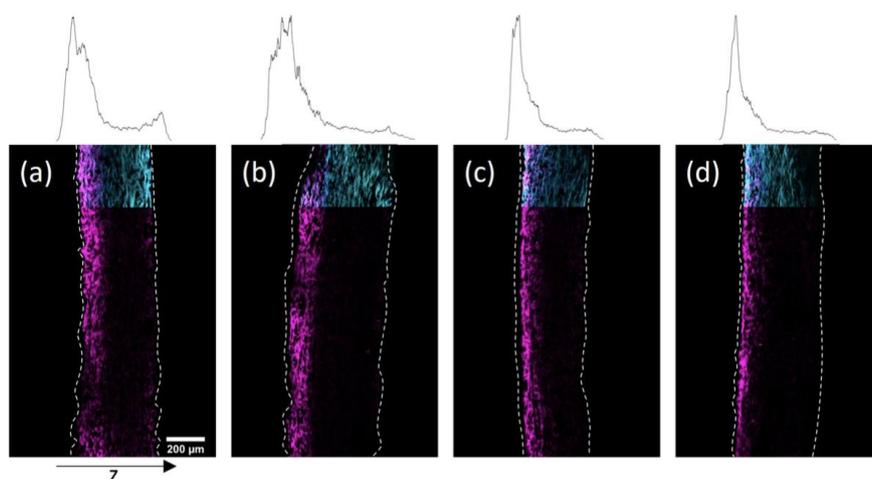


Figure: Maximum one figure or table (adapted from [5])

- [1] Cordt, C., Geißler, A., Biesalski, M., *Adv. Mater. Interf.* 200125 (2020)
- [2] Seelinger, D., Trosien, S., Nau, M., Biesalski, M., *Carbohydr. Polym.*, 117458 (2021).
- [3] Schölch, S., Schäfer, J.L., Meckel, T., Brandstetter, T., Biesalski, M., Rühle, J., *Biomacromolecules* 22(7), 2864-2873 (2021).
- [4] Schäfer, J.L., Schölch, S., Meckel, T., Brandstetter, T., Stockert, A.R., Rühle, J., Biesalski, M., *Cellulose*, 28, 5775-5791, (2021).
- [5] Schäfer, J.L., Meckel, T., Poppinga, S., Biesalski, M., *Biomimetics* 28, 5775-5791 (2023).



IMPROVING MELT DISPERSION OF CELLULOSIC FILLERS IN POLY(BUTYLENE ADIPATE-CO-TEREPHTHALATE): BENEFITS OF STARCH

Keskes M. ^{a,b}, Desse M. ^{*a}, Jaziri M. ^b, Carrot C. ^a

^a Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, F-42023 SAINT-ETIENNE Cédex 2, France

^b Laboratoire Electrochimie et Environnement, ENIS, Université de Sfax, Sfax 3038, Tunisie

* melinda.desse@univ-st-etienne.fr

Dispersion in the melt of cellulosic fillers (cellulose microfibrils, MFC) in a polymer matrix is a difficult issue to tackle when considering the production of composites. A proper dispersion is a key parameter to ensure good mechanical properties of the obtained material. This study aims at improving dispersion in a polyester matrix, poly(butylene adipate-co-terephthalate) (PBAT). The efficiency of various methods has been tested : oxidization of the hydroxyl groups responsible for agglomeration of the fillers, change of freeze-drying medium to induce steric hindrance and hence reduce the formation of hydrogen bonds and finally the addition of a third component, chemically similar to cellulose, to promote dispersion. If the two first methods have proven inefficient, the addition of starch has led to enhanced mechanical properties, both in the solid and the molten state, through increased starch/cellulose interactions. Further investigations have led to using PBAT containing 15% thermoplastic starch (TPS), commercially available (Marter-Bi, MB). In this case, the starch is plasticized and previously dispersed in the matrix. Microscopic observations were performed on the composites based on MB or neat PBAT. Tensile tests and dynamic mechanical analysis in the solid and molten state have been performed. Results showed a strong interaction between TPS and cellulose (Figure 1), leading to adhesion between the components of the composites.

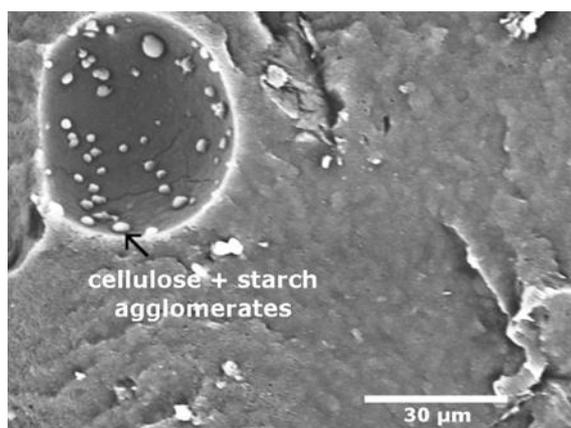


Figure 1: Microscopic observations of MB (PBAT + 15% TPS) with 5%-wt MFC



ULTRA-LIGHTWEIGHT FOAMED INSULATION PANELS MADE OF OIL PALM TRUNK FIBRES

Lukmanul Hakim Zaini ^{*ab}, Wolfgang Gindl-Altmutter^a, Axel Solt-Rindler^c, Christoph Preimesberger^c, Christian Hansmann^c, Stefan Veigel^a

^a *Institute of Wood Technology and Renewable Materials, Department of Material Sciences and Process Engineering, University of Natural Resources and Life Sciences, Vienna (BOKU), Austria*

^b *Department of Forest Products, Faculty of Forestry and Environment, IPB University, Bogor, Indonesia*

^c *Wood K plus – Competence Centre for Wood Composites and Wood Chemistry, Tulln, Austria.*

* lukmanhz@apps.ipb.ac.id

Abstract

Foam technology has been largely applied on insulation building application but mostly from inorganic material. The environmental awareness and more sustainable as well as environmentally friendly technologies encourage the use of renewable resources. Oil palm trunk (OPT) is a suitable raw material for the preparation of insulation board due to its relatively high fiber content, low cost, and abundant availability as a by-product of palm oil production. This research focuses on developing a thermally insulating material from utilizing foaming agent and oil palm trunk fibers which will be used in building applications. The effects of surfactant (1%, 2% and 3% of polysorbate (T80)), wheat gluten (5%, 10% and 15%), oil palm trunk fibers, and fire retardant on the properties of the resulting board was investigated. In comparison to the reference, there was a trend that increased surfactant content resulted in higher thermal conductivity and lower density. On the other hand, the trend was not obvious within different wheat gluten content which was showed higher thermal conductivity after 10% concentration but declined after adding 15% content of wheat gluten while using fire retardant seems affecting thermal conductivity in positive manner. Compression properties mostly determined by wheat gluten content which is also has a role as a binder instead of foaming agent only, while fire retardant did not show significant effect to this mechanical characteristic.

Keywords

foam; fire retardant; insulation; fibers; oil palm trunk



MADE IN CHITIN: THE POTENTIAL OF FUNGAL YARNS IN THE FASHION INDUSTRY

Kathrin Weiland^a, Anne Zhao¹, Mitchell Jones^b & Alexander Bismarck^{a,c*}

^a *Institute of Material Chemistry and Research, Polymer and Composite Engineering (PaCE) Group, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090, Vienna, Austria*

^b *Institute of Materials Science and Technology, Faculty of Mechanical and Industrial Engineering, Technische Universität Wien, 1060 Vienna, Austria*

^c *Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.*

*Corresponding author. Email address: alexander.bismarck@univie.ac.at (A. Bismarck).

Fungi-based textiles and leather substitutes rapidly gained attention due to their biodegradability and unique properties, and represent a promising sustainable alternative to synthetic materials and bovine leather [1]. However, the scope of fungi-derived textiles is severely restricted by the fact that the end product is in the shape of a sheet rather than a yarn limiting their applicability and efficiency in garment production. Processing fungal biopolymers into yarns can overcome this problem by increasing scalability and cost efficiency, and therefore holds great potential for expanding the scope of fungal biopolymers in the fashion industry. This study investigated the development and characterisation of fibers based on chitin, the structural biopolymer found in fungal cell walls [2]. Inspired by the Shifu technique of paper yarn production, the yarns are prepared by producing fungal biofilms that are thinly sliced and rolled into continuous threads [3]. Physical and mechanical properties as well as water absorption behavior were characterised. Scanning Electron Microscopy (SEM) imaging, Dynamic Vapor Sorption (DVS) and mechanical tests were characterisations.

The resulting fungal yarns showed promising mechanical and physical properties, with tenacity and elastic modulus reaching or even exceeding the values of commercial cellulose paper yarns. The developed process shows the feasibility to produce low-cost, environmentally friendly and biodegradable fungal yarns with mechanical properties, potentially suitable for applications in the fashion industry.

[1] Jones M., Gandia A., John S. & Bismarck A., *Nature Sustainability*, 4, 9, 2021

[2] Gandia A., Van den Brandhof J., Appels F. & Jones M., *Trends in Biotechnology*, 39, 1322, 2021

[3] Chummun, J. & Rosunee S., *RJTA*, 16, 93, 2012



NEW HYBRID ALGINATE-SILICA AEROGEL FILMS

Niemeyer P.*^a, Milow B.^a

^a German Aerospace Center, Institute of Materials Research, Department of Aerogels and Aerogel Composites, Germany

* philipp.niemeyer@dlr.de

Silica aerogels already show good thermal insulation performance, but they are usually brittle, which particularly with thin films leads to poor handling. Various combinations of a silica aerogel phase and a strengthening biopolymer phase have been reported in the literature, but these are difficult to scale up.[1, 2]

In this work, highly scalable processes were developed for the fabrication of mechanically stable hybrid silica-aerogel films. The particle composite material consisting of silica aerogel granules embedded in an alginate aerogel matrix enables bending radii of 10 mm. Scanning electron microscopy studies show that the superhydrophobic silica phase connects perfectly with the fibrillar alginate aerogel phase, see Figure 1.

Films of a thickness of 750 μm with a volume ratio of silica aerogel to alginate aerogel of 1:1 were produced. The composite material is perfectly scalable from laboratory to large-scale production with manufacturing methods already established in the market.

Due to the low average pore size of 14nm, which is mainly dominated by the silica phase, the measured thermal conductivity at 0°C is $0.018 \text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$ and increases to $0.023 \text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$ at 80°C.

In the presentation, we will look at the manufacturing process and discuss the properties of the composite material based on applications.

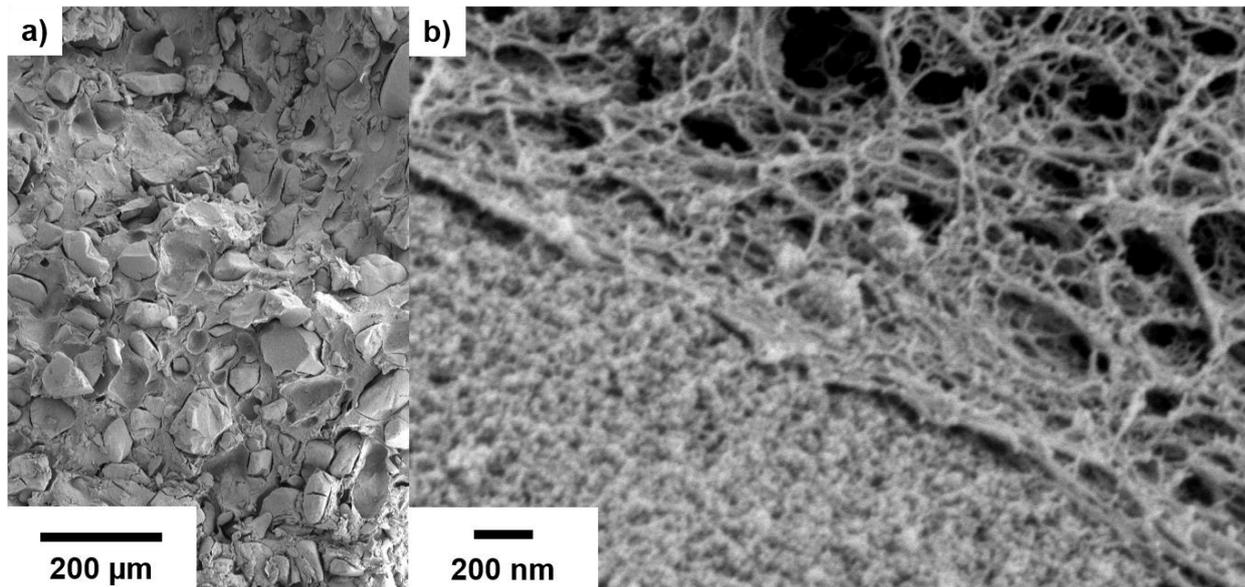


Figure 1 : Scanning electron micrograph; a) silica aerogel particles dispersed in alginate aerogel matrix, b) interface of silica and alginate aerogel phases.

[1] Demilecamps A., Beauger C., Hildenbrand C., Rigacci A. & Budtova T., *Carbohydr Polym.*, 122, 293-300, 2015

[2] Horvat G., Pantić M., Knez Ž. & Novak Z., *Sci Rep*, 9, 1-10, 2019



EXPLORING THE ANISOTROPY OF CELLULOSIC FIBERS

Czibula C.*^{a,b}, Koski K. J.^b, Hirn U.^a

^a Institute of Bioproducts and Paper Technology, Graz University of Technology, Austria

^b Department of Chemistry, University of California Davis, USA

* caterina.czibula@tugraz.at

Cellulose is the most abundant biopolymer and its products such as paper, tissue, and paper board are necessities for our daily life. With the biobased industrial sector gaining importance, the demand for cellulosic materials is increasing further.

However, a lot of the influencing parameters on the final product's properties are unknown. Especially figuring out the interplay between the single fiber and the fiber network level is challenging. One reason is that single fibers are complicated to investigate. They exhibit a complex hierarchical structure and have anisotropic properties which depend on moisture content. Furthermore, the geometry of such fibers is , with a diameter of about 20-50 μm and a limited length of 2-5 mm, making them difficult to handle in conventional testing methods. Tensile testing is the main technique to investigate single fiber behavior. Besides high scattering and the need for fixation on a sample holder, it yields only properties in one fiber direction. With atomic force microscopy and nanoindentation, the testing of more fiber directions is possible, however, tedious and error-prone [1].

Here, Brillouin light scattering spectroscopy comes into play as a technique which enables the measurement of the whole elastic stiffness tensor in a non-contact manner. Using laser light to probe phonons in different directions and assuming a crystal geometry like hexagonal for fibrous materials [2] enables the determination of the elastic constants in the GHz regime (Fig. 1). In this talk, first results of such investigations will be presented for cellulosic fibers such as flax and pulp fibers and comparisons to mechanical testing will be drawn.

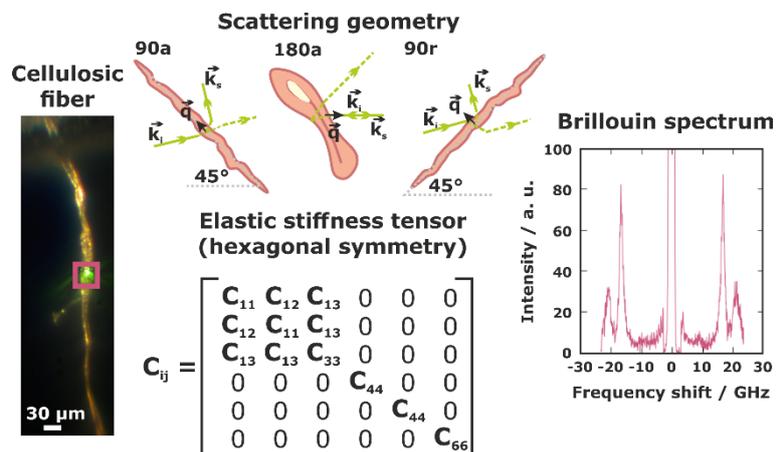


Figure 1 : Experimental procedure of Brillouin measurements for elastic stiffness tensor determination: The laser beam is hitting a cellulosic (pulp) fiber and the scattered light within the square is collected to obtain a Brillouin spectra in different scattering geometries. A hexagonal symmetry is commonly assumed for the elastic stiffness tensor of fibrous materials.

[1] C. Czibula, A. Brandberg et al., *Sci. Rep.*, Vol. 11, 22411, 2021

[2] K. J. Koski et al., *Nat. Mat.*, Vol. 12, p. 262-267, 2013



Session 8 Poster



WATER DISPERSABILITY OF PAPERS– BALANCING MATERIAL STRENGTH AND DISPERSIBILITY

Andrea Christine Pfennich^a, Elisabeth Anna Schoeffmann^a, Herfried Lammer^a, Ulrich Hirn^b

^a *Wood K Plus - Competence Center for Wood Composites and Wood Chemistry, Altenberger Straße 69, 4040 Linz, Austria*

^b *Graz University of Technology; Institute of Bioproducts and Paper Technology, Inffeldgasse 23, 8010 Graz, Austria*

* Presenting author's e-mail address: a.pfennich@wood-kplus.at

ABSTRACT:

Water- dispersability of papers is useful in various applications as it disintegrates into its fibers after usage, and also is a fully biodegradable material. In this work, we have first introduced a test for the disintegration performance of different paper grades. Based on that disintegration and comprehensive statistical analysis we have performed a quantitative analysis on the technological and physical mechanisms responsible for a good paper dispersibility in water.

Regarding technological parameters for paper production, we identified lignin content, degree of refining and addition of starch as relevant factors reducing paper dispersibility. Addition of a debonding agent, a surfactant, was not found to be effective here.

In order to clarify the physical mechanisms governing paper disintegration behavior we analyzed paper properties related to mechanical strength and water uptake. We found a strong correlation between wet- and dry tensile strength of paper, both of which were highly affecting the dispersibility. Water uptake in the network, or water uptake into the fibers (WRV), or fiber wetting (contact angle) were not, or only very moderately, related to paper dispersibility. The only water absorption related paper property correlated to the disintegration results was liquid penetration speed measured with ultrasonic testing.

We are concluding that the same mechanisms that are creating dry strength – high density and strong fiber-fiber bonding – are also responsible for a bad disintegration behavior. Principal component analysis revealed that paper strength and water penetration speed are not governed by different latent variables but instead are all strongly associated with the first principal component. This suggests that the same mechanisms are responsible for reduction of water penetration speed and wet/dry strength. A future solution of the problem might thus be to decouple network strength and water penetration, e.g. by identifying suitable additives that impart bonding strength to the network without reducing the access of water to break the fiber-fiber bonds.



BIOCOMPATIBILITY OF NANOFIBROUS CELLULOSE PREPARED BY WET-TYPE ELECTROSPINNING

Pauliukaitytė I.^a, Čiužas D.^{a,b}, Petrikaitė V.^b, Bulota M.^a, Krugly E.^a, Martuzevičius D.^a

^aDepartment of Environmental Technology, Kaunas University of Technology, Kaunas, Lithuania

^bLaboratory of Drug Targets Histopathology, Lithuanian University of Health Sciences, Kaunas, Lithuania

*ingrida.pauliukaityte@ktu.edu

In recent years, there has been a lot of interest in the production of cellulose structures with superior characteristics. The fabrication of regenerated nanofibrous cellulose from ionic liquid (ILs) solutions is among such production methods [1]. Such cellulose fibres are highly sought-after in the biomedical field because of its biodegradability, biocompatibility, and large surface area [2].

The present research demonstrates a successful dissolution of cellulose by means of IL 1-butyl-3-methylimidazolium acetate (BMIMAc), combined with dimethyl sulfoxide (DMSO) as a co-solvent. The resulting solution was electrospun using a wet-type electrospinning apparatus and the smooth cellulose matrix consisting of nanofibres were obtained. The addition of a co-solvent during the solution preparation stage led to the generation of solutions that demonstrated enhanced uniformity, reduced viscosity, and increased electrical conductivity. As a consequence of that, the electrospinning process and the morphology of nanofibrous matrix were improved.

The research determined that the most favorable proportion of solvent/co-solvent is 1:1. Under these circumstances the resulting electrospun cellulose matrices exhibit smooth structure and comprise cylinder type fibres. The inclusion of the co-solvent did not result in chemical alterations of cellulose.

The fibrous matrix subjected to *in vitro* cytotoxicity assay using mouse fibroblast L929 and cell proliferation tests using human triple-negative breast cancer MDA-MB-231 cell lines. The results showed that the regenerated cellulose matrix did not possess significant cytotoxicity, and supported cell growth during 7 day period. Such results encourage the exploration of cellulose matrices for a further research and potential applications in biomedical fields.

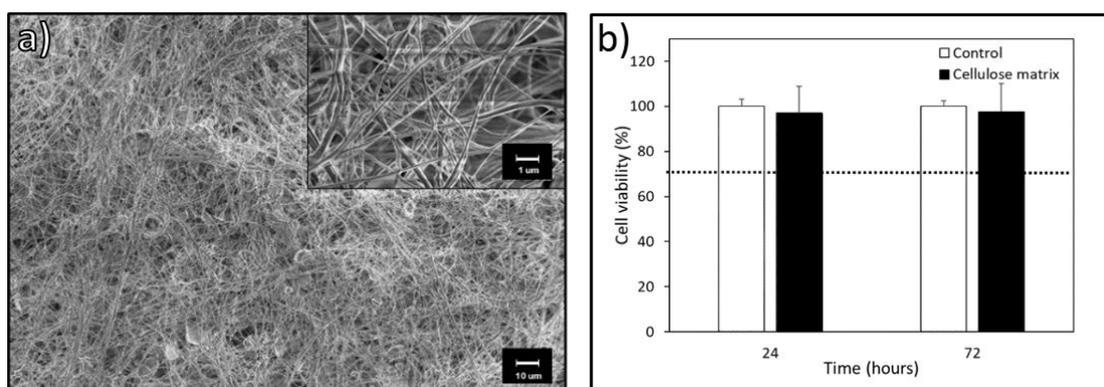


Figure 1. a) SEM image of electrospun cellulose sample with 1:1 BMIMAc:DMSO ratio b) Viability comparison of L929 Cells between Control and Cellulose Matrix Samples

[1] Ciuzas, Darius, et al. "Electrospun cellulose fibers from ionic liquid: Practical implications toward robust morphology." *Journal of Applied Polymer Science* 139.3 (2022): 51525.

[2] Verma, Chandrabhan, et al. "Dissolution of cellulose in ionic liquids and their mixed cosolvents: A review." *Sustainable Chemistry and Pharmacy* 13 (2019): 100162.



PLA FIBERS PRODUCED BY SOLUTION BLOW-SPINNING MODIFIED WITH CURCUMIN AND LIGNIN CARBON DOTS: EVALUATION OF ANTIMICROBIAL ACTIVITY

Rossi P. F.^{*a,b}, Marangon C. A.^b, Santos D. M.^b, Correa D. S.^b, Oréface R. L.^a

^a Department of Metallurgical and Materials Engineering, Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, MG, Brazil

^b Nanotechnology National Laboratory for Agriculture (LNNA), Embrapa Instrumentação, São Carlos, SP, Brazil

* patriciafrossi@gmail.com

In recent years, lignin has become a subject of great relevance in research due to its abundance, low cost and sustainable nature. Besides, investigation on methods to produce carbon dots from lignin by low cost routes has also aroused interest once they can be surface functionalized with polar functional groups, making them suitable to be conjugated with biomolecules for biological applications [1]. In this study, lignin carbon dots (LCdots) obtained by hydrothermal synthesis were employed to modify microfibers of polylactic acid (PLA)/curcumin produced by solution blow spinning (digital image shown in Fig. 1a) aiming at application in wound dressings. These mats exhibit LCdots-like characteristics, such as photoluminescence, and biocompatibility, while curcumin provides them antioxidant, anti-inflammatory and antibacterial properties, which are key for the treatment of skin injuries [2]. Scanning electron microscopy (SEM) indicated that microfibers without defects and randomly oriented could be obtained (Fig. 1b). The antibacterial potential of the developed fibrous mats was evaluated against *Pseudomonas aeruginosa* ATCC 27853 and *Staphylococcus aureus* ATCC 25923, two pathogenic bacteria frequently associated with infections. The results demonstrated the ability of PLA fibrous mats combined with LCdots and curcumin to inhibit the growth and activity of these bacteria (Fig. 1c) upon contact, making it a promising approach for developing wound dressings that can prevent infections while helping to accelerate the skin healing process.

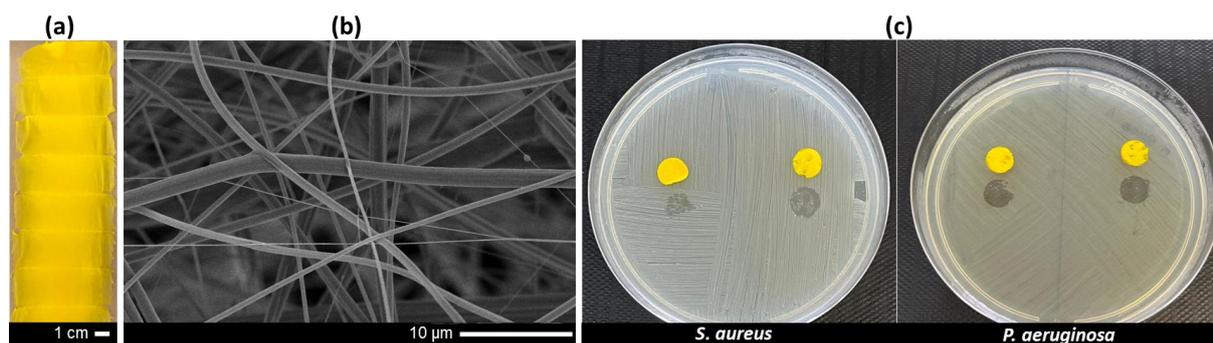


Figure 1: (a) Fibrous membrane of polylactic acid (PLA) modified with Lcdots and Curcumin, (b) SEM images and (c) Inhibition halo against *S. aureus* and *P. aeruginosa*.

[1] Liu W. et. al., Industrial Crops & Products, vol. 171, 113963, 2021.

[2] Chagas P. A. M. et. al., Reactive and Functional Polymers, vol. 163, 104889, 2021.



EFFECT OF PROCESSING ON PARTICLE DISPERSION AND RHEOLOGICAL BEHAVIOUR OF CNC REINFORCED POLYVINYL ALCOHOL NANOCOMPOSITES

Bugaut M. ^{*a}, Taguet A. ^a, Le Moigne N. ^a, Heuzey M.-C. ^b

^a *Polymers Composites and Hybrids (PCH), IMT Mines Alès, France*

^b *Chemical Engineering, CREPEC, Polytechnique Montréal, Canada*

* mathieu.bugaut@mines-ales.fr

Cellulose nanomaterials (CNMs), such as cellulose nanocrystals (CNCs), are expected to play a major role in the current environmental and societal transition towards a larger use of bio-based products. They demonstrate a great potential as sustainable and high-performance fillers for the development of materials with tunable rheological, thermo-mechanical, optical and barrier properties [1]. Currently they are mainly used in paper manufacturing, packaging, membranes and bioengineering.

As other nanoparticles, the dispersion of CNMs in thermoplastic polymers remain a huge challenge for the development of polymer nanocomposites. Several approaches have been studied to improve their dispersion and the mechanical properties of the nanocomposites, by using solvent and melt based processes (Figure 1a) with various thermoplastic polymers as well as physico-chemical and processing aids [2], [3]. In this work, a comparative study is made of these different processes applied to polyvinyl alcohol (PVA)/CNC formulations, starting from “classical” processes, such as melt extrusion and solvent casting, to more innovative ones, such as wet compounding. The impact of the processing route on the dispersion of CNCs in PVA is discussed, in particular through rheological analyses performed on PVA/CNC suspensions (Figure 1b) and molten PVA/CNC composites.

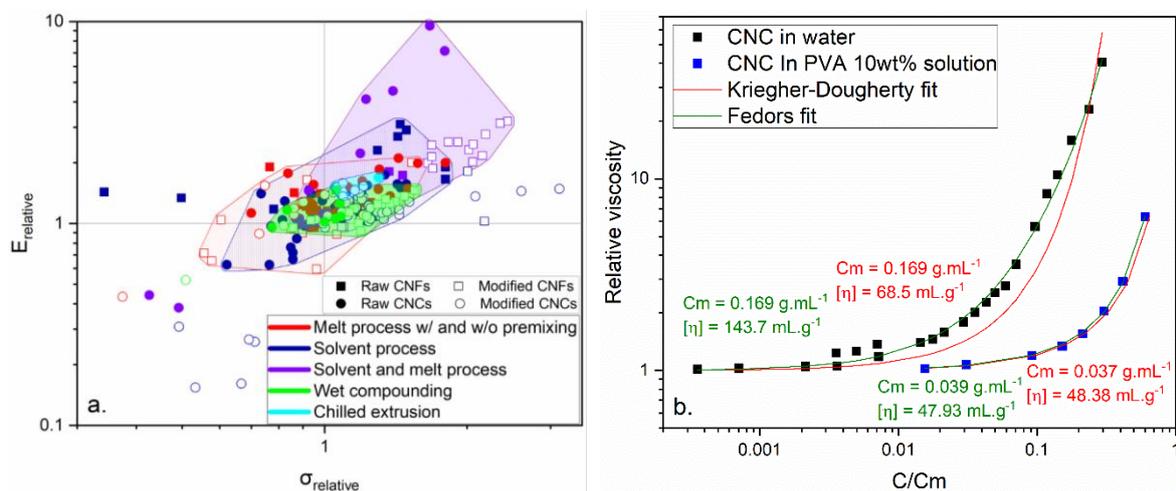


Figure 1 : (a.) Ashby diagram with relative Young's modulus versus relative yield strength : effect of processing method [3]; (b.) Influence of the CNC dispersion on the relative viscosity of different dispersing media (water and PVA/water solution).

- [1] T. Li *et al.*, “Developing fibrillated cellulose as a sustainable technological material,” *Nature*, vol. 590, no. 7844. Nature Research, pp. 47–56, Feb. 04, 2021. doi: 10.1038/s41586-020-03167-7.
- [2] X. Ma, Y. Wang, Y. Shen, J. Huang, A. Dufresne, and N. Lin, “6 Current Status of Nanocellulose-Based Nanocomposites,” Wiley, 2019. doi: 10.1002/9783527807437.ch6.
- [3] G. Banvillet, M. Bugaut, E. Doineau, A. Taguet, N. Le Moigne, and Orlando J. Rojas, “Advances in the production of cellulose nanomaterials and their use in engineering,” *In press, Springer nature*.



EXPLORING THE PARTIAL DISSOLUTION OF CELLULOSE FIBERS IN IONIC LIQUID

Alexa Scheer^{*1}, Lukas Pachernegg¹, Stefan Spirk¹

¹ *Institute of Bioproducts and Paper Technology, Graz University of Technology, Inffeldgasse 23, 8010 Graz, Austria*

*a.scheer@tugraz.at

A key focus in biopolymer research and across a broad spectrum of industries is the dissolution of cellulose, which is considered essential for unlocking its full utilization potential. Ionic liquids, a class of salts that exhibit liquid properties at ambient temperatures, possess the ability to dissolve cellulose fibers. The formation of regenerated cellulose can be achieved by subsequently rinsing the dissolved fibers with anti-solvents. [1] However, the partial dissolution of fibers and precipitation of the solubilized components to form a network of regenerated cellulose and residual fibers, e.g. to densify paper, represents a field with limited existing research. Here we demonstrate the interaction between the ionic liquid 1-Ethyl-3-methylimidazoliumacrylate (EMIM-ACR) and paper fibers. Through microscopic imaging of individual fibers immersed in varying concentrations of EMIM-ACR, the influence of water content on the dissolution power of the ionic liquid was demonstrated. Distinct structures of regenerated cellulose were obtained by rinsing fiber bundles with either ethanol or water after immersion in ionic liquid at 80°C. Additionally, paper samples were immersed in EMIM-ACR for varying durations at 80°C, rinsed with water, and pressure dried. The formation of regenerated cellulose was confirmed by infinite focus microscopy. A significant compaction was determined with the measurement of air permeability using the Bendtsen and Gurley method. Our findings demonstrate the potential of using EMIM-ACR to create networks of regenerated cellulose and residual fibers by partial dissolution. The densification achieved by closing the fiber interstices via the presence of precipitated cellulose could be a promising approach for enhancing the density of paper.

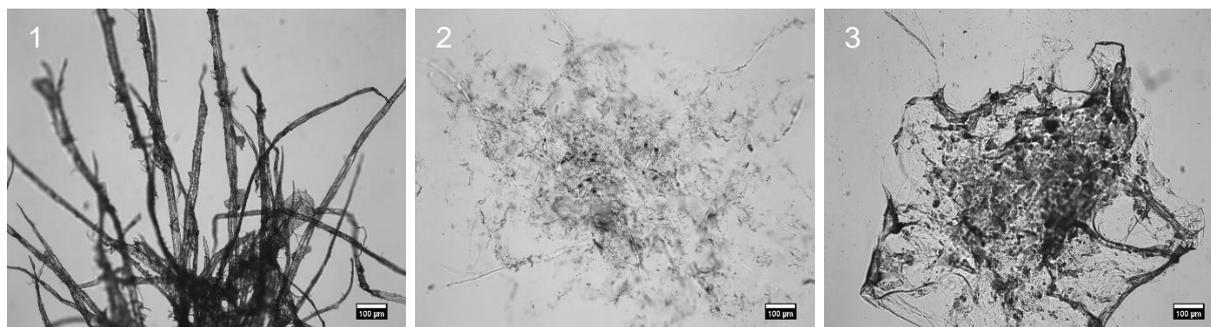


Figure 1 : (1) original fibers, (2) partially dissolved fibers in EMIM-ACR after 1 min at 80°C, (3) regenerated cellulose – fiber network after rinsing with deionized water

[1] S. Taokaew and W. Kriangkrai, "Recent Progress in Processing Cellulose Using Ionic Liquids as Solvents," *Polysaccharides*, vol. 3, no. 4, pp. 671–691, Oct. 2022



PREPARATION OF CELLULOSE ACETATE-CHITOSAN FILMS USING SOLUTION BLOW SPINNING

Moshfeghi Far N.^a, Kramar A.^{*a,b}, González-Benito J.^{a,b}

^a *Department of Material Science and Engineering and Chemical Engineering, Universidad Carlos III de Madrid UC3M, Spain*

^b *Álvaro Alonso Barba Institute of Chemistry and Materials Technology, UC3M, Spain*

* akramar@ing.uc3m.es

In this work, cellulose acetate (CA) and chitosan (CS) composites in the form of films using solution blow spinning (SBS) are studied. CA and CS as biopolymers, have excellent properties, being eco-friendly, biodegradable, and biocompatible, which makes them potential materials for food packaging. The solution blow spinning device used in this work was developed by the Group of Polymer Composite Materials and Interphases of the UC3M [1].

Several concentrations of chitosan (2.5%, 5%, and 7.5%) are considered for the preparation of composites with a matrix of cellulose acetate. The influence of chitosan content on the porosity, wettability (Table 1), and morphology of the SBS materials was investigated. It was found that addition of chitosan decreases the porosity of composite films and significantly increases water contact angle, which can be beneficial for potential food packaging applications.

Table 1. Water contact angles on the produced CA/CS composite films.

Sample	CA	CA/CS (2.5%)	CA/CS (5%)	CA/CS (7.5%)
Wt% of CS	0.0	2.5	5.0	7.5
Water contact angle				
	$82^\circ \pm 0.5$	$88.5^\circ \pm 0.7$	$94.6^\circ \pm 1$	$99^\circ \pm 0.8$

[1] Domínguez J.E., Olivos E., Vázquez C., Rivera J.M., Hernández-Cortés R., & González-Benito J., *HardwareX*, vol. 10, p. e00218, 2021.



EFFECT OF CURING TEMPERATURE ON PHYTIC ACID CROSS-LINKING TO CELLULOSE

Orzan E. ^{*a}, Spirk S. ^b Nypelö T. ^{a,c}

^a Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Kemivägen 10, 412 96 Gothenburg, Sweden

^b Institute of Bioproducts and Paper Technology, Graz University of Technology, Inffeldgasse 23, 8010 Graz, Austria

^c Department of Bioproducts and Biosystems, Aalto University, Vuorimiehentie 1, FI-00076 Aalto, Finland

* orzan@chalmers.se

The transition to using non-toxic bio-based compounds in the field of materials chemistry has inspired the use of phytic acid, a multifunctional polyphosphate, for the development of novel flame-retardant materials. Covalent cross-linking of phytic acid to fabrics and cellulose has traditionally required the addition of other compounds, yet a recent green alternative involves a hot pressing or curing step after impregnation of the substrate. Here, we elucidate the effect curing temperature has on the resulting cross-linked structure formed between phytic acid and cellulose fibers. Solid-state NMR and FTIR analysis indicated the successful phosphorylation of phytic acid with cellulose and with itself to form various structures. The cross-linking mechanism was further found to promote the retention of flame-retardant properties on washed substrates. Dehydration mechanisms at elevated curing temperatures was found to significantly promote the cross-linking degree yet also causes degradation of the phytate structure. This work provides the fundamental knowledge necessary to progress the application of hot pressing and curing temperatures towards the green cross-linking of phytic acid to OH group containing substrates.

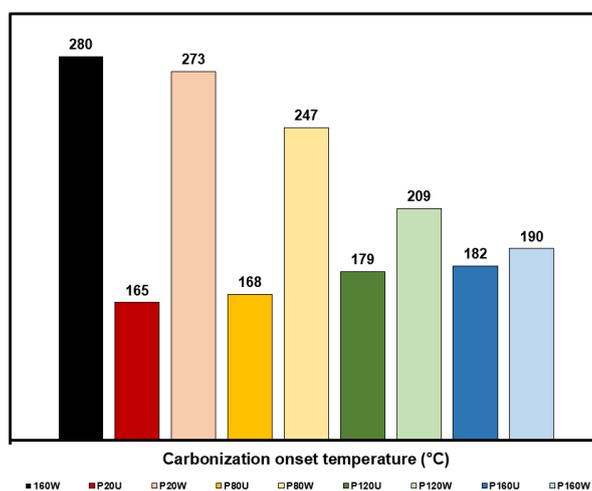


Figure 1 : Carbonization onset temperature of phytic acid doped cellulose filters analysed by TGA. On the labels, P represents 5 wt% of phytic acid added, U or W represent unwashed or washed filters, and the number represents the curing temperature.



TOWARDS NEW SOLVENTS FOR LYOCELL – A COMPARISON OF [MTBDH][ACO] AND ITS SUCCESSOR [MTBNH][ACO]

Sturm M.^{*a,b}, Kosan B.^a, Kilpeläinen I.^b

^a *Thüringisches Institut für Textil- und Kunststoff-Forschung Rudolstadt e.V., Germany*

^b *University of Helsinki, Finland*

* sturm@titk.de

The Lyocell process features direct cellulose dissolution without derivatization prior to fibre spinning. The classic solvent for Lyocell is N-methylmorpholine-N-oxide (NMMO). However, the down side of NMMO solutions is that they can undergo thermal runaway reactions. A group of ionic liquids, could replace NMMO, thus removing the problem of runaway reactions / this problem. These molten salts have very low vapor pressures and due to the high number of anion-cation combinations, their physical properties such as melting point, viscosity, acid-base ratio and toxicity can be tuned, making them "tailor-made solvents". The challenge with the latest ILs is their propensity for hydrolysis. Therefore, when an IL is selected for an industrial application, a comparison based on hydrolytic stability is the first aspect to consider. A thorough comparison along an entire Lyocell processing chain was performed for two of the most recent examples of IIs originating from superbases.

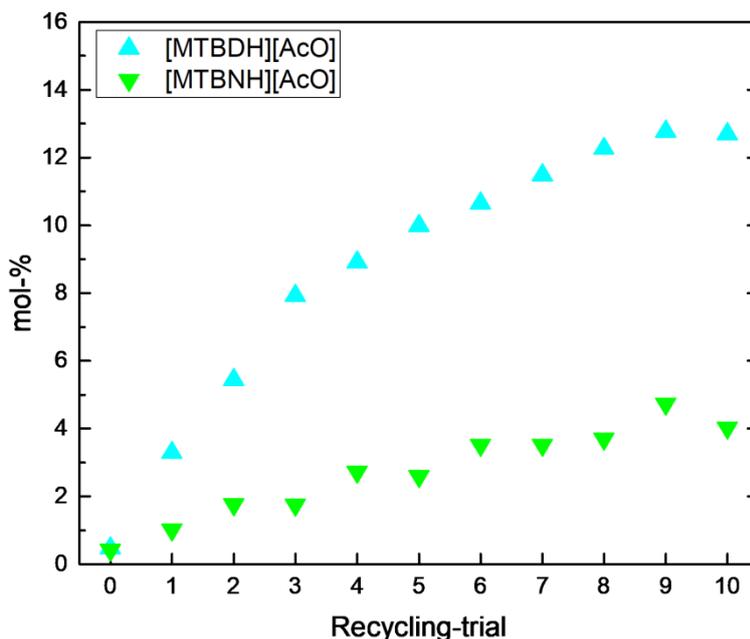


Figure 1 : Comparison of hydrolysis behaviour of the two ionic liquids during the recycling series.



Session 9

Interactions of plant cell wall polymers

Session organizers:

Tiina Nypelö, Chunlin Xu, Johnny Beaugrand

Keynote speakers:

Paul Dupree

Polysaccharide structure influences the interactions with lignin and cellulose in plant cell walls

Herman Höfte

Polymer interactions underlying plant cell wall assembly



POLYSACCHARIDE STRUCTURE INFLUENCES THE INTERACTIONS WITH LIGNIN AND CELLULOSE IN PLANT CELL WALLS

Paul Dupree

The Department of Biochemistry, University of Cambridge, UK

pd101@cam.ac.uk

Plant cell wall polysaccharide structures determine their biophysical properties, utility in applications and digestibility by enzymes. The structure also influences their interactions in the plant cell wall, and hence, for example, affects the way feedstocks are processed for preparation of polysaccharides and dietary fibres can be accessed in food and feed.

To study the assembly of the plant cell wall, my research group has discovered biosynthetic enzymes that are important for synthesis of glucuronoarabinoxylans and galactoglucomannans in plants. By manipulating these pathways in model plants and crop plants, we can investigate how the structure of the polysaccharides influences the incorporation of the polysaccharides in the cell wall. Using biochemical fractionation, enzyme accessibility and solid state NMR, we can assess the changes in cell wall assembly. We can show that polysaccharide structure influences the way the polysaccharides crosslink to lignin, and interact with cellulose fibrils. The information may allow strategies to improve the breeding and processing of plant materials for easier extraction or development of plant hemicellulose polysaccharides with altered properties.



POLYMER INTERACTIONS UNDERLYING PLANT CELL WALL ASSEMBLY

Herman Höfte

Université Paris-Saclay, INRAE, AgroParisTech, Institut Jean-Pierre Bourgin (IJPB), 78000, Versailles, France.

* hermanus.hofte@inrae.fr

The utilization of plant biomass in the emerging bioeconomy will be facilitated by a better understanding of its architecture at different scales going from polymer, cell wall assembly, cell, organ and plant. To understand how the diversity of natural polymers can be exploited it is important to study their structure-function relationship, in particular the rules that govern their interactions.

Cell walls of growing cells are unique polymer assemblies with remarkable mechanical properties. How polymers produced at different cellular locations (cellulose at plasma membrane, matrix polymers in Golgi apparatus) assemble into a strong and expandable network remains poorly understood.

I will first discuss recent insights into how the extracellular matrix of animals and plants can be structured at a mesoscale by the modification of anionic polymers (glycosaminoglycans and pectins respectively) and their interaction with polysaccharide-binding proteins. I will illustrate this by showing how a cell wall associated peptide-receptor complex drives the dehydration and mesoscale patterning of the cell wall through its interaction with polyanionic pectins.

I finally will discuss how the study of cell wall assemblies will be facilitated by new super-resolution imaging technologies combined with the observation of the assembly process in living cells and in biomimetic systems.



NON-CELLULOSIC AND CELLULOSIC CELL WALL POLYMERS INFLUENCE ON FLAX BUNDLES MECHANICAL PROPERTIES

Johnny Beaugrand^{a*}, Maxime Gautreau^a, Sylvie Durand^a, Angeline Paturel^{a,b}, Sophie Le Gall^{a,d}, Loïc Foucat^{a,d}, Xavier Falourd^{a,d}, Bruno Novales^{a,d}, Marie-Christine Raleta, Sylvie Chevallier^e, Antoine Kervoelen^c, Fabienne Guillon^a and Alain Bourmaud^c

^a INRAE, UR BIA, F-44316 Nantes,

^b Université de Lille, UMR-CNRS 8207, UMET, F-59652 Villeneuve d'Ascq, France

^c Univ. Bretagne Sud, UMR CNRS 6027, IRDL, F-56100 Lorient, France

^d INRAE, BIBS facility, PROBE infrastructure, F-44316 Nantes, France

^e Oniris, Nantes Université, CNRS, GEPEA, UMR 6144, F-44000 Nantes, France Affiliation

* johnny.beaugrand@inrae.fr

Fibre bundles are groups of elementary fibres glued together thanks to the middle lamella, and are the main fraction in plant fibre composites. In this study, relationship between the mechanical properties of flax fibre bundles, chemical composition and cellulose structure were investigated. To do so, a sequential biopolymer extraction was implemented. Fibre bundles were first depectinated by oxalate extraction, and then the hemicelluloses were extracted by LiCl/dimethyl sulfoxide (DMSO) and KOH. The oxalate extract consisted of homogalacturonans and type I rhamnogalacturonans, while the LiCl extract was composed mainly of glucomannans and the KOH extract of xyloglucans. The KOH stage resulted in the appearance of cellulose II in flax bundles. The extraction of pectin and hemicelluloses led to the disappearance of the middle lamella concomitant with a decrease in the tensile Young's modulus and maximum strength. Finally, the fibre bundle composition, ultrastructure and mechanical properties are discussed together in view of the thin middle lamella. If many studies have examined the mechanical properties of the secondary wall sublayers [1], few studies are available regarding the weakness points that glue strong individual fibres together. The aim of this research is to fill a gap in the knowledge of the relationships between the biochemical composition of bundles, polymer ultrastructure and mechanical properties on the scale of flax fibre bundles, including the middle lamella.

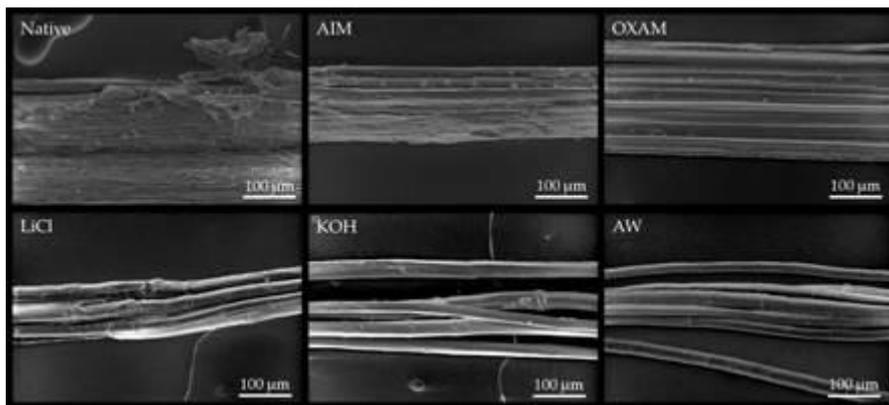


Figure 1 : Fig.1 SEM images of each stage of the sequential extraction (x350)

SEM was applied to the flax fibres bundles to reveal changes induced by the different extraction stages (Figure 1). For native and AIM-treated bundles, the middle lamella is very clearly visible and surrounds the flax fibres within the bundles. As the sequential extraction progresses, the middle lamella is being less visible until it disappears completely

[1] Arnould, O., Siniscalco, D., Bourmaud, A., Le Duigou, A., & Baley, C. (2017). Better insight into the nano-mechanical properties of flax fibre cell walls. *Industrial Crops and Products*, 97, 224-228



THE USE OF SOLID-STATE NMR TO STUDY PLANT CELL WALL POLYSACCHARIDE STRUCTURE AND INTERACTIONS

Rosalie Cresswell^{a*}, Yoshihisa Yoshimi^b, Paul Dupree^b, Ray Dupree^a

^a *The Department of Physics, University of Warwick, UK*

^b *The Department of Biochemistry, University of Cambridge, UK*

* Rosalie.cresswell@warwick.ac.uk

NMR can provide detailed information about structure, conformation, and dynamics of polysaccharides, however in solids this is often limited by the resolution typically obtained in a 1D CP MAS experiment. If ¹³C labelled material is available 2D solid-state NMR can be used to give resolution near that of solution state NMR on native/whole plant samples. Access to a wealth of 2D NMR experiments allows one to obtain unparalleled insight into not only the conformation of polysaccharides in the plant cell wall but also the interactions between cellulose and hemicelluloses such as xylan, glucomannan, as well as arabinoses and xyloglucan etc.

Some examples of our recent work include (i) determining how water influences the structure and properties of the cell wall of softwoods using solid-state NMR which revealed the irreversible changes that occur in the proximity of xylan to cellulose in the oven drying process as well as observing partial solubilisation of the GGM on rehydration of the cell wall.^[1] (ii) Using solid-state NMR to identify several different conformations of mannans in different genetic mutants of *Arabidopsis thaliana*^[2] and (iii) showing how the secondary cell wall of poplar is affected by the incorporation of an additional polymer, callose (β-1-3-glucan). ¹³C solid-state NMR showed that callose was very hydrated and that it aggregates into a triple helical structure. The hydrated channels in the secondary cell wall created by the presence of callose resulted in a decrease in the lignin content, an increase in porosity, and an increase of enzymatic saccharification efficiency with monosaccharide release being > 80 % higher for both glucose and xylose.^[3] We have used solid-state NMR to investigate the structures of a broad range of cellulosic materials such as cellulose nanofibrils, moss, softwood and hardwoods. The information given by such experiments will lead to a deeper understanding, which has evaded us thus far, of the molecular architecture of plant cell walls and of the interactions with the polysaccharides present.

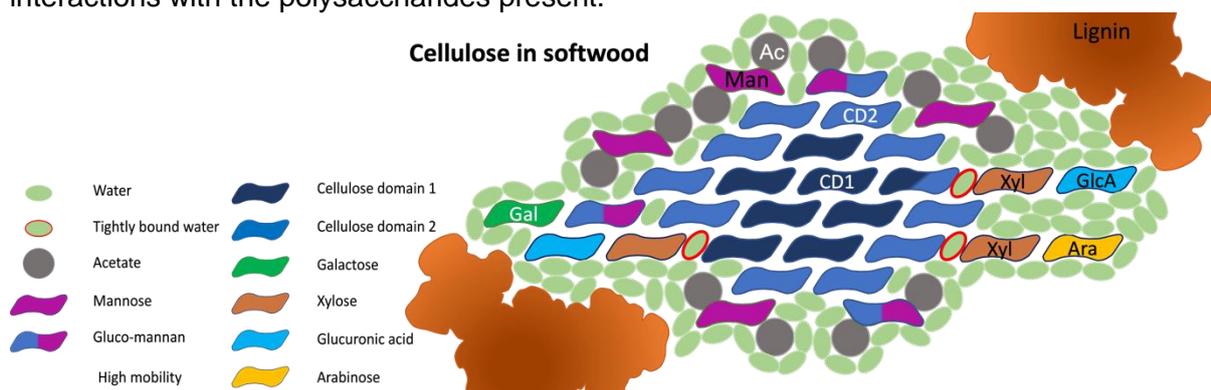


Figure 8: A schematic model of a cellulose microfibril (habitat 2-3-4-4-3-2) of hydrated softwood surrounded by hemicelluloses GGM and xylan with their respective sidechains and lignin. The diagram illustrates all the key interactions of cellulose with the hemicelluloses as interpreted by solid-state NMR spectra and supporting Molecular Dynamics simulations.^[1]

[1] Cresswell R., Dupree R., Brown SP., et al., *Biomacromolecules*, 22(11), 4669-4680, 2021.

[2] Yu L., Yoshimi Y., Cresswell R., et al., *The Plant Cell*, 34(11), 4600-4622, 2022.

[3] Bourdon M., Lyczakowski JJ., Cresswell R., et al. *Nature Plants*, (under review)



IN-SITU MONITORING OF THE ULTRASTRUCTURE AND MECHANICAL PROPERTIES OF FLAX CELL WALLS DURING CONTROLLED HEAT TREATMENT

Elouan Guillou^{a,b}, Loïc Dumazert^c, Célia Caër^d, Alexandre Beigbeder^a, Pierre Ouagne^e, Gwenn Le Saout^f, Johnny Beaugrand^g, Alain Bourmaud^b, Nicolas Le Moigne^{c,*}

^a IPC Laval, Rue Léonard De Vinci, Changé, France

^b Univ. Bretagne Sud, UMR CNRS 6027, IRDL, Lorient, France

^c Polymers Composites and Hybrids (PCH) – IMT Mines Ales, Ales, France

^d ENSTA Bretagne, UMR CNRS 6027, IRDL, Brest, France

^e Laboratoire Génie de Production, LGP, Université de Toulouse, INP-ENIT, Tarbes, France

^f LMGC, IMT Mines Ales, Univ Montpellier, CNRS, Ales, France

^g UR1268 Biopolymères Interactions Assemblages, INRAE, Nantes, France

* nicolas.le-moigne@mines-ales.fr

Plant fibres are increasingly used as reinforcements, especially in thermoplastic composites. Understanding the impact of temperature on the properties of these fibres is an important issue for the manufacturing of high-performance materials with minimal defects. In this work, the structural evolution and mechanical behaviour of flax fibre cell walls were dynamically monitored by temperature-controlled X-ray diffraction and nanoindentation from 25 to 230°C; detailed biochemical analysis was also conducted on fibre samples after each heating step. With increasing temperature up to 230°C, a drop in the local mechanical performance of the flax cell walls was measured. This was associated with a decrease in the packing of the cellulose crystal lattice (increase in d-spacing d_{200}), as well as significant mass losses measured by TGA and changes in the biochemical composition, i.e. non-cellulosic polysaccharides (NCPs) of the middle lamellae but also of the cell walls. This work, which proposes for the first time an *in-situ* investigation of the dynamic temperature evolution of the flax cell wall properties, evidences the reversible behaviour of their crystalline structure (i.e. cellulose) and local mechanical properties after cooling to room temperature, even after exposure to high temperatures. [1]

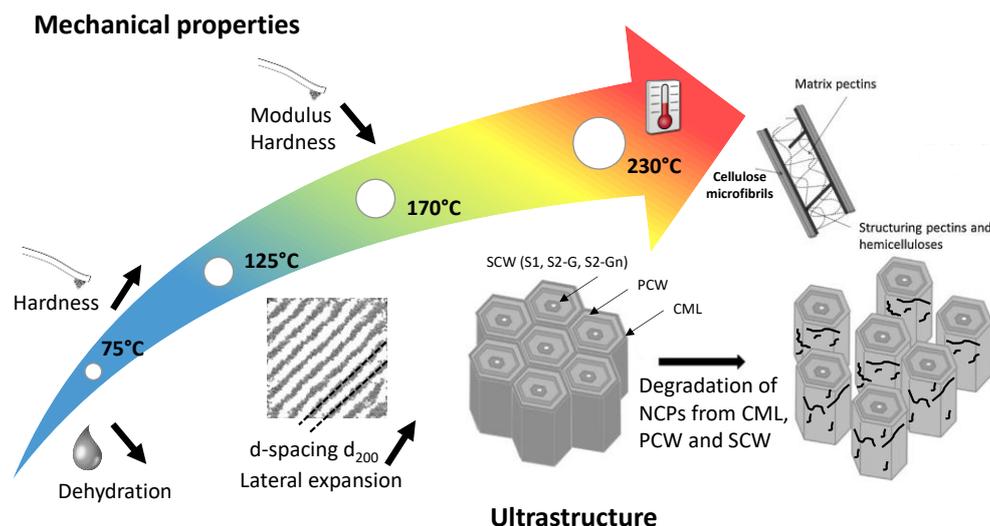


Figure 1 : Main changes in ultrastructure (XRD and biochemical composition) and mechanical properties (nanoindentation) of flax fibres occurring upon heating to 230°C.

[1] Guillou E., Dumazert L., Caër C., Beigbeder A., Ouagne P., Le Saout G., Beaugrand J., Bourmaud A. Le Moigne N., *Carbohydrate Polymers* (under review), available at SSRN 4404621 (2023)



A SCREENING PLATFORM FOR ASSESSING XYLANASE ACTIVITY ON CELLULOSE

Schaubeder J.^a, Orzan, E.^b, Ravn, J.^c, Geijer, C.^c, Nypelö, T.^{c,d}, Spirk, S.^{*a}

^a *Institute of Bioproducts and Paper Technology Graz University of Technology, Austria*

^b *Department of Biology and Biological Engineering, Chalmers University of Technology, Sweden*

^c *Department of Chemistry and Chemical Engineering, and Wallenberg Wood Science Center Chalmers University of Technology, Sweden*

^d *Department of Bioproducts and Biosystems, Aalto University, Finland*

Presenting author: stefan.spirk@tugraz.at

Enzymatic degradation of plant polysaccharide networks is a complex process which involves disrupting an intimate assembly of cellulose and hemicelluloses in fibrous matrices. To mimic this assembly and to elucidate the efficiency of enzymatic degradation in a rapid way, models with physicochemical equivalence to natural systems are needed. Here, we employ xylan-coated cellulose thin films to monitor the hydrolyzing activity of endo-1,4- β -xylanases and related enzymes. Particularly the kinetics of enzyme degradation at surfaces is still a challenging topic as often the classic Michaelis Menten approach does not work to identify the kinetic parameters. In situ surface plasmon resonance spectroscopy (SPRS) is a powerful tool to study interactions at interfaces, and is capable to reveal the underlying kinetic phenomena in xylanase activities. We demonstrate that by using the Hill equation instead of the Michaelis Menten kinetics, we can determine the kinetic constants of enzymatic xylan degradation as a function of different parameters. The experiments were complemented by atomic force microscopy studies to confirm the removal of xylans from the cellulose material. This approach is capable to screen different types of enzymes with nanoscale sensitivity for their interaction potential with cellulose in real time.



BIO-BASED LATEX FROM HEMICELLULOSE

Qiwen Yong ^{a, b}, Martti Toivakka ^a, Chunlin Xu ^{*a}

^a *Laboratory of Natural Materials Technology, Åbo Akademi University, Finland*

^b *College of Chemistry and Chemical Engineering, China West Normal University, China*

* Chunlin.Xu@abo.fi

This is the first time to report a facile strategy to fabricate galactoglucomannan-based latex with highly transparent, hydrophobic, and flexible characteristics by combining etherification with subsequent emulsion polymerization [1]. Hemicellulose is mainly treated as side stream and burnt in black liquor with lignin in forest industry. To achieve economically feasible biorefinery concept, hemicellulose must be utilized in more efficient way than energy production. Here, the allylated galactoglucomannans (A-GGM) and galactoglucomannan-based latexes (GGM-L) were prepared and their chemical structure, substitution degree, molecular weight, conversion rate, particle size and zeta potential were characterized by ATR-FTIR, ¹H NMR, quantitative ¹³C NMR, HP-SEC, HPLC and zeta-sizer nanometer analyzer, respectively. Furthermore, the effects of substitution degree on film surface roughness and homogeneity, water vapor permeability (WVP) and thermal stability were evaluated by AFM, SEM, WVP and TGA, respectively. The optimal GGM-L film exhibited 91.3% transmittance and 0.43% haze, 117° water contact angle, 31.2% elongation at break and 30.9 MPa ultimate tensile stress. The bio-based content of the GGM-L may reach about 99 wt%, which provides a promising avenue for polyolefin-based latex replacement for paper and paperboard applications. [2,3]

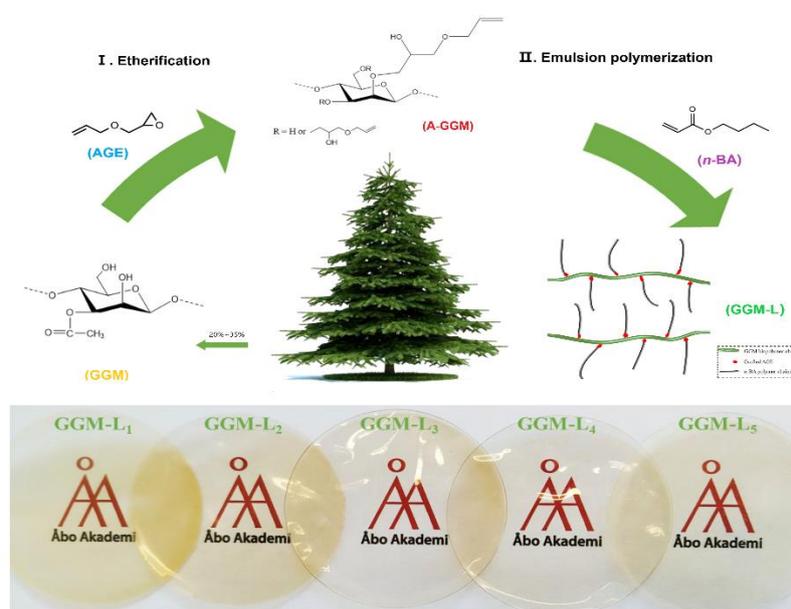


Figure 1: Synthetic route of GGM-L films with high transparency, super hydrophobic and good flexibility

[1] Yong, Q., Xu, J., Wang, L., Tirri, T., Gao, H., Liao, Y., Toivakka, M., & Xu, C., *Carbohydrate Polymers*, 291, 119565, 2022

[2] Liu R., Du J., & Wang H., *Carbohydrate Polymers*, 205, 83-88, 2019

[3] Hardelin L., Bernin D., & Larsson A., *Biomacromolecules*, 5, 1832-1840, 2020



STRUCTURE AND PROPERTIES OF WHEAT BRAN ARABINOXYLANS AND THEIR ETHERIFIED DERIVATIVES FOR THERMOPLASTIC FILM APPLICATIONS

Janewithayapun R. ^{*a}, Cousin F.^b, Hedenqvist M.^c, Larsson A.^a, Ström A.^a

^a Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Kemivägen 10, SE-41296 Gothenburg, Sweden

^b Laboratoire Léon Brillouin, Université Paris-Saclay, UMR 12, CEA-CNRS, 91191 Gif Sur Yvette, France

^c Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

* ratjan@chalmers.se

As part of efforts to develop thermoplastic material from arabinoxylan (AX), an abundant polysaccharide in cereals and grasses, we are attempting to understand the mechanisms with which flexibility can be introduced in these rigid chains. [1] Experimental results show that the thermo-mechanical property of modified AX is also correlated to the starting material property. Scattering experiments using x-rays and neutrons were performed to probe the structure and solution conformations of the starting and modified materials – providing insight on how each material is altered by the modification process.

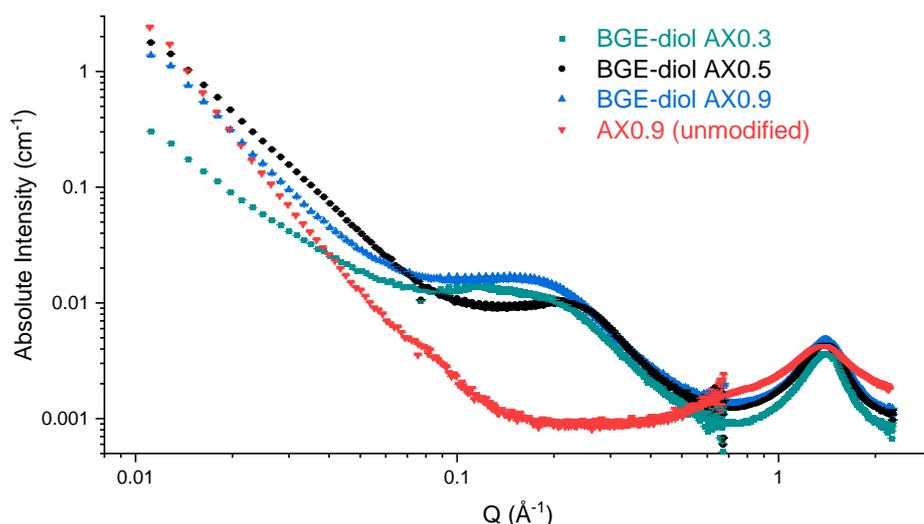


Figure 1 : Merged small and wide-angle x-ray scattering spectra (SWAXS) from films of unmodified arabinoxylan (AX0.9) compared to three modified arabinoxylan films (BGE-diol AX). A clear correlation peak appears after the modification process – indicating the presence of nano-domains within the modified films.

[1] Börjesson, M.; Westman, G.; Larsson, A.; Ström, A., *ACS Applied Polymer Materials*, 1 (6), 1443-1450, 2019.



AN INVESTIGATION OF WOOD BARK AS A PROMISING OF CNF'S RAW MATERIAL

Didik Supriyadi. ^{*a,b}, Wolfgang Gindl-Altmutter^a, Stefan Veigel^a

^a *Institute of Wood Technology and Renewable Materials, Department of Material Sciences and Process Engineering, University of Natural Resources and Life Sciences (BOKU), Austria*

^b *Department of Chemical Engineering, Institut Teknologi Sumatera (ITERA), Indonesia*

* didik.supriyadi@boku.ac.at

The abundant amount of bark from pulp and paper industries is becoming an environmental issue because current methods of bark utilization can not significantly decrease the volume of bark waste. To address this, converting to cellulose nanofibrils (CNF) may be more effective in minimizing the bark and increasing the added value of the bark. In this study, four different raw materials, i.e., spruce wood, poplar wood, spruce bark, and poplar bark, were repeatedly treated with hydrogen peroxide, acetic acid, and sulfuric acid followed by a reaction with a mild concentration of sodium hydroxide solution. The cellulose pulp product was sequential mechanical fibrillated to yield CNF. Characterisation revealed that CNF from bark exhibited comparable results to those derived from wood-based CNF. Therefore, it indicates that bark can be a potential candidate for CNF raw material.



INFLUENCE OF TWIN-SCREW EXTRUSION PRETREATMENT ON THE PROPERTIES OF LIGNOCELLULOSIC-BASED MATERIALS PRODUCED BY UNIAXIAL THERMO-COMPRESSION

Cavaillès J. ^{*a,b}, Vaca-Medina G. ^a, Wu-Tiu-Yen J. ^b, Evon P. ^a, Labonne L. ^a, Peydecastaing J. ^a, Pontalier P.-Y. ^a

^a *Laboratoire de Chimie Agro-industrielle (LCA), Université de Toulouse, INRAE, Toulouse INP, 4 Allée Emile Monso, 31030 Toulouse Cedex 4, France*

^b *eRcane, La Réunion, Sainte-Clotilde, France*

*julie.cavaillès@etu.toulouse-inp.fr

The production of bio-based products from lignocellulosic residues is widely studied [1]. Due to the current environmental issues, the development of green processes is necessary and the twin-screw extrusion is an interesting process for destructuring biomass before transforming it into new bio-based products [2]. The aim of this work was to study the impact of twin-screw extrusion as a pretreatment on the properties of bio-based materials produced by uniaxial thermo-compression with sugarcane bagasse as reference biomass. Extrusion conditions (liquid/solid ratio and three screw profiles with different size of reverse screw elements) were studied in relation to the density, mechanical properties and water resistance of the thermo-compressed materials. All results obtained with extrudates were compared with those obtained from bagasse ground with a 15 mm grid. Thermo-compression experiments were carried out at 200°C, 102 MPa for 10 min. Materials were characterized by three-point bending tests and by immersion in water at 25°C for 24 hours. All materials obtained after the extrusion treatment showed better properties than materials made from ground bagasse with a 15 mm grid. Extrusion pretreatment allowed the bagasse to be destructured and the properties of thermo-compressed materials were improved compared to ground bagasse. For a same L/S ratio, mechanical properties and water resistance for materials were improved by increasing the stress on bagasse using an increasingly sheared screw profile.

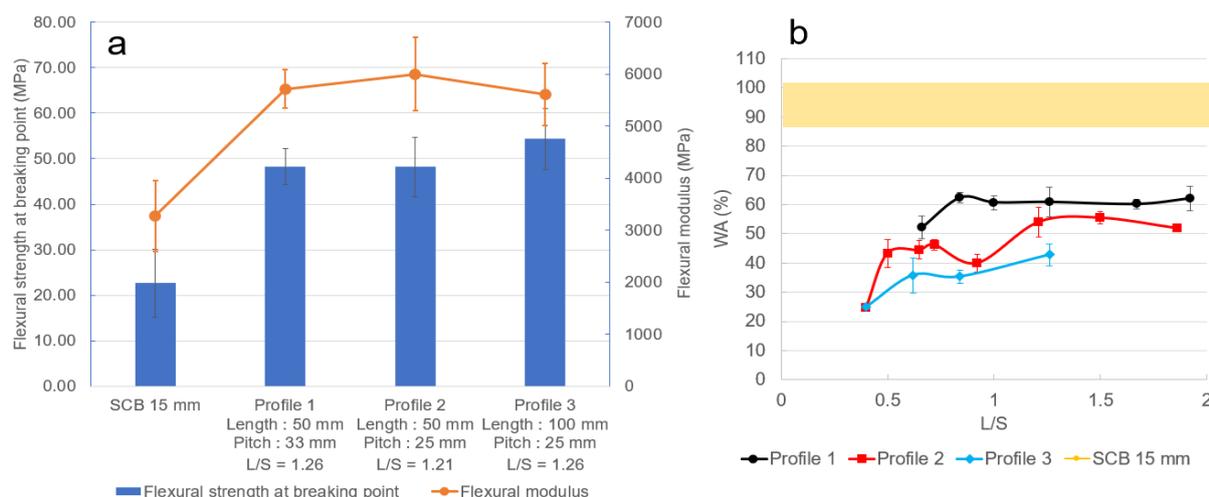


Figure 1: Influence of extrusion pretreatment on the mechanical properties (a) and on the water absorption (WA) of the materials (b)

[1] Tišma M., Bucić-Kojić M. & Planinić M., *Chemical and Biochemical Engineering Quarterly*, 35(2), 139-156, 2021

[2] Zheng J. & Rehmann L., *International journal of molecular sciences*, 15(10), 18967-18984, 2014



MULTIFUNCTIONAL POROUS MATERIALS AND POLYMER COMPOSITES BASED ON ANISOTROPIC PECTIN CRYOGELS

Zou F. ^a, Dong Y. ^{*a}, Li H. ^b, Tewari G.C. ^a, Cucharero J. ^{c, d}, Lokki T. ^c, Vapaavuori J. ^a

^a Multifunctional Materials Design, Department of Chemistry and Materials Science, Aalto University, Finland

^b State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, China

^c Acoustics Lab, Department of Information and Communications Engineering, Aalto University, Finland

^d Lumir Oy, Finland

* yujiao.dong@aalto.fi

Highly aligned porous structures can be observed in the stems of many natural plants. These types of anisotropic constructions endow many functionalities, such as pathways for water and nutrition transmission, enhancement of the mechanical property, and durability. Drawing inspiration from these plants, freeze-casting (or ice-templating), which can be controlled by the ice crystal growth direction, is often used to fabricate anisotropic porous materials, providing an inexpensive, sustainable, and simple process.[1] Pectin, an inexpensive and abundant polysaccharide, which can be extracted from fruits peel and sugar beet pulp, can be employed as a raw materials to fabricate anisotropic porous materials.

Anisotropic pectin cryogels fabricated by freeze-casting exhibit controllable morphology, which can be manipulated by introducing various concentrations of sodium chloride prior to the freezing.[2] As a result, the freeze-casted pectin cryogels have high compression modulus, low thermal conductivity, and excellent sound absorption properties. Moreover, freeze-casted pectin cryogels can be employed as a template to infiltrate polymers into the anisotropic structure, which results in composites with various functions. For instance, we demonstrated optically transparent composites with high transmittance, adjustable haze, high UV blocking ability, and low thermal conductivity by infiltration of poly(methyl methacrylate) (PMMA).[3] Furthermore, blending a phase change material, polyethylene glycol (PEG), into PMMA provides optically transparent composites, which can be utilized in thermal energy storage. Overall, these works highlight the potential of anisotropic pectin cryogels as a more sustainable and environmental-friendly alternative to be utilized in various applications, including optical and energy-efficient applications, as well as sound absorption.

- [1] G. Shao, D. A. H. Hanaor, X. Shen, A. Gurlo, *Adv. Mater.* **2020**, 32.
 [2] F. Zou, J. Cucharero, Y. Dong, P. Kangas, Y. Zhu, J. Kaskirinne, G. C. Tewari, T. Hänninen, T. Lokki, H. Li, J. Vapaavuori, *Chem. Eng. J.* **2023**, 462.
 [3] F. Zou, H. Li, Y. Dong, G. C. Tewari, J. Vapaavuori, *Chem. Eng. J.* **2022**, 439, 135738.



Session 9 Poster



INFLUENCE OF CHEMICAL TREATMENTS ON THE MULTI-SCALE STRUCTURE AND MOLECULAR ORGANISATION OF WHEAT BRAN

Ladd-Parada, M. ^{*a}, Wahlström, N. ^a, Carlsson, J. ^a, Vilaplana, F. ^a

^a *Glycoscience Division, CBH department, KTH, Sweden*

* marlp@kth.se

Wheat bran is one of the major by-products of the wheat processing industry. It is mostly composed of structural polysaccharides (60%), from which arabinoxylan (AX) is the most abundant one representing 20-40% of the total content, alongside proteins and polyphenols [1,2]. AXs have different functional and nutritional properties, such as gelling agents with potential prebiotic and antioxidant effects [3]. However, it is not feasible to extract AXs efficiently via alkaline or subcritical water methods [4] due to the cell wall being highly recalcitrant. From a biochemical perspective, different structural features play a role in this recalcitrance, for example, the degree and pattern of substitution in wheat bran AX and interactions between AX chains via covalent diferulic bridges [5,6]. AX chains are also known to interact with other molecules of the cell wall, such as proteins [7,8] through the presence of tyrosine, lignin via the ferulic acid of the AX chains [9], and other structural polysaccharides like β -glucans and cellulose [10-13].

However, a study of the multiscale structural changes in wheat bran caused by the extraction of AX chemo-enzymatic processing and their relation to cell wall recalcitrance is lacking. Therefore, we aim to understand how the different structural features of wheat bran are related to the cell wall recalcitrance to chemical processing by using biochemical, scattering, and imaging tools.

References

- [1] S Apprich, Ö Tirpanalan, J Hell, M Reisinger, S Böhmdorfer, S Siebenhandl-Ehn, S Novalin & W Kneifel. *LWT - Food Science and Technology* **56**, 222, 2014
- [2] MS Izydorczyk & CG Biliaderis. *Carbohydrate Polymers* **28**, 33, 1995
- [3] AC. Ruthes, A Martínez-Abad, H Tan, V Bulonea, and F Vilaplana *Green Chemistry* **19**, 1919, 2017
- [4] A.C. Ruthes, R.C. Rudjito, J. Rencoret, A. Gutiérrez, J.C. del Río, A. Jiménez-Quero, and F. Vilaplana, *ACS Sustainable Chemistry & Engineering* **8** (18), 7192-7204, 2020
- [5] N Carpita & M McCann. *Biochemistry & Molecular Biology of Plants*, (2000).
- [6] HV Scheller & P Ulvskov. *Annual Review of Plant Biology* **61**, 263, 2010
- [7] M Piber & P Koehler. *Journal of Agricultural and Food Chemistry* **53**, 5276, 2005
- [8] DI Rhodes & BA Stone. *Journal of Cereal Science* **36**, 83, 2002
- [9] A-L Chateigner-Boutin, C Lapierre, C Alvarado, A Yoshinaga, C Barron, B Bouchet, B Bakan, L Saulnier, M-F Devaux, C Girousse & F Guillon. *Plant Science* **276**, 199, 2018
- [10] A Martínez-Abad, J Berglund, G Toriz, P Gatenholm, G Henriksson, M Lindström, J Wohlert & F. Vilaplana. *Plant Physiology*, 2017
- [11] A Martínez-Abad, N Giummarella, M Lawoko & F Vilaplana. *Green Chemistry* **20**, 2534, 2018
- [12] J Berglund, D Mikkelsen, BM Flanagan, S Dhital, S Gaunitz, G Henriksson, ME Lindström, GE Yakubov, MJ Gidley & F Vilaplana. *Nature Communications* **11**, 4692, 2020
- [13] A Martínez-Abad, A Jiménez-Quero, J Wohlert & F Vilaplana. *Green Chemistry* **22**, 3956, 2020



EFFECT ON PAPER PROPERTIES BY ADDING AND REMOVING XYLAN FROM CHEMICAL PULPS

Schaubeder J.^{a,*}, Spirk S.^a, Fliri L.^b, Orzan E.^c, Biegler V.^d, Bakhshi A.^a, Bauer W.^a, Hirn U.^a, Nypelö T.^{b,c}

^a Institute of Bioproducts and Paper Technology, Graz University of Technology, Austria

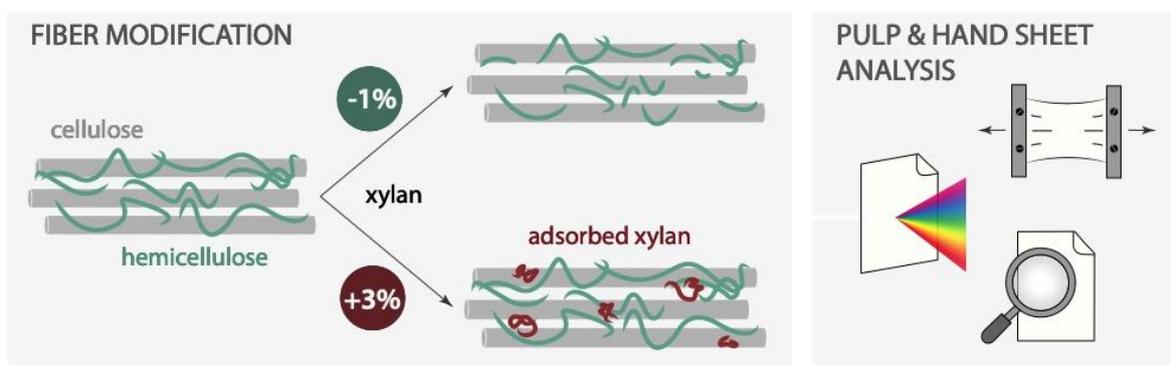
^b Department of Bioproducts and Biosystems, Aalto University, Finland

^c Department of Chemistry and Chemical Engineering, Chalmers University, Sweden

^d Institute for Materials Chemistry and Research, University of Vienna, Austria

* jana.schaubeder@tugraz.at

Xylan, one of the most abundant renewable polymers, is found primarily in the secondary cell wall, which gives plants their support and strength. To take advantage of the reinforcing effect of xylan in papermaking, it is essential to understand the role of xylan in pulp fibers, as it undergoes substantial changes during pulping. Removal and addition of xylan from pulps have been extensively investigated, but few studies have explored the combined effect of xylan adsorption and degradation at the same time, leaving the role of xylan on pulp and paper properties unclear. To address this knowledge gap, we investigated the role of xylan in pulp and paper sheets by (i) partially degrading xylan from refined elemental chlorine free bleached softwood kraft pulp (BSKP) using an endo- β -xylanase and by (ii) adsorbing beechwood xylan onto refined BSKP. Adsorption of 3% xylan resulted in improved fiber-fiber bonding concomitant with an increase in sheet density and a slight increase in mechanical performance. Enzymatic degradation of about 1% xylan from BSKP resulted in lower bond areas and decreased sheet densities. The enzymatic degradation led to a significant weakening of the fiber network in the hand sheets, which cannot be regained by adding xylan to the pulp fibers. These results show that the xylan location in pulps is critical for the resulting properties of paper hand sheets.



INTERACTIONS BETWEEN NEUTRAL SOLUBLE POLYSACCHARIDES AND SMALL MOLECULE: INTERPRETATION BY ISOTHERMAL TITRATION CALORIMETRY

Lupo C. ^{*a}, Boulos S.^a, Nyström L.^a

^a Laboratory of Food Biochemistry, ETH Zurich, Switzerland

* cristina.lupo@hest.ethz.ch

Non-covalent interactions between polysaccharides and small molecules have become a well-studied topic among researchers for many scientific disciplines, and are of interest to various industrial applications in which polysaccharides are involved. These weak associations, including hydrogen bonds, ionic interactions, van der Waals' forces, and hydrophobic interactions, are low in energy and reversible, making the design of a valid detection system particularly challenging [1, 2]. Isothermal titration calorimetry (ITC) is a gold standard method to quantitatively measure the interaction between a macromolecule and a partner molecule. However, most of the ITC studies reported in the literature employ protein-based systems or charged polysaccharides, leaving the molecular mechanism governing the weak associations between neutral soluble polysaccharides and small molecules almost entirely unexplored [3, 4].

In this study, ITC was used to investigate the thermodynamic and kinetic parameters underlying the interaction between hydrolyzed galactomannan (GM_H) and arabinoxylan (AX_H), and mixed linkage cereal β -glucan (BG), and different small molecules, namely gallic acid (GA), sodium gallate (NaGal), sodium ferulate (NaFerul), brilliant blue (BB), patent blue (PB), and lissamine green (LG). Interestingly, no interaction was observed when the polysaccharides were titrated with NaGal and NaFerul, while spontaneous interactions ($\Delta G = \Delta H - T\Delta S < 0$) were measured when all the polysaccharide systems were titrated with GA, LG, PB, and BB. In particular, entropically-driven associations were observed ($\Delta S > 0$), usually related to a combination of hydrophobic, loss of water molecules, and conformational change of the polysaccharide. All these events lead to a favorable effect on the binding energy ($\Delta G < 0$). A negative value of ΔH was measured only when GA was added to GM_H, AX_H, and BG indicating the formation of favorable exothermic interaction between the ligand and the polysaccharide. This favorable enthalpy contribution ($\Delta H < 0$) can be related to the hydrogen type of interaction. Moreover, the dissociation constants (K_d) were on the order of 10^{-6} M, showing that moderate-type associations were formed. A similar binding stoichiometry (n) was calculated when GM and BG interacted with GA, with n (GM) = 0.50 ± 0.03 and n (BG) = 0.45 ± 0.07 , while for arabinoxylan was almost 3 fold higher, n (AX) = 1.50 ± 0.09 , suggesting that, in addition to the molecular weight, the conformation of the polysaccharide in solution, as well as its chemical structure, are additional important parameters that might play a role for the interaction.

In conclusion, this study contributes to bridging the lack of information regarding the mechanism underlying the complexation between soluble neutral polysaccharides and small molecules. In particular, the ITC method helps to better correlate the theoretical description of the interaction with experimental data and, consequently, to optimize the use of these polysaccharides for food and non-food applications.

- 1 Riley, K.E.;Hobza, P. Noncovalent interactions in biochemistry. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2011**, *1*, p. 3-17.
- 2 Rinaudo, M. Non-covalent interactions in polysaccharide systems. *Macromolecular bioscience* **2006**, *6*, p. 590-610.
- 3 Falconer, R.J.;Collins, B.M. Survey of the year 2009: applications of isothermal titration calorimetry. *Journal of molecular recognition* **2011**, *24*, p. 1-16.
- 4 Fernandes, A.;Oliveira, J.;Fonseca, F.;Ferreira-da-Silva, F.;Mateus, N.;Vincken, J.-P.de Freitas, V. Molecular binding between anthocyanins and pectic polysaccharides—Unveiling the role of pectic polysaccharides structure. *Food Hydrocolloids* **2020**, *102*, p. 105625.



MODIFICATIONS OF BACTERIAL CELLULOSE BY IN SITU BIOSYNTHESIS WITH PECTIN AND HEMICELLULOSES

Cybulska J.^{*a}, Cieśla J.^a, Kurzyna-Szklarek M.^a, Szymańska-Chargot M.^a, Pieczywek P.M.^a, Zdunek A.^a

^a Department of Microstructure and Mechanics of Biomaterials, Institute of Agrophysics Polish Academy of Sciences, Doświadczalna 4, 20-290 Lublin, Poland country

* j.cybulska@ipan.lublin.pl

Bacterial cellulose (BC) belongs to the most promising biopolymers due to its purity, cost-effective production, and wide range of possible modifications. BC composites with polysaccharides can be obtained by in situ biosynthesis. The addition of components that naturally occur in plant cell walls, such as water-soluble pectin, arabinan, rhamnogalacturonan I, arabinoxylan, xyloglucan, and glucomannan, to the culture medium, enables stable conjugation of these components to BC. The aim of our study was an examination of the influence of cell wall polysaccharides on the structure and mechanical and thermal properties of BC. Monosaccharide analysis of BC composites with pectin and hemicelluloses showed that these polymers were successfully introduced in the BC network. The amount of glucose in BC composites varied from 73.3 to 82.8 mol%, and the rest were monosaccharides appropriate for used polysaccharides. All polysaccharides caused a decrease in the thermal stability of BC composites, but the impact of pectinic compounds was lesser than hemicelluloses. The fiber and skeleton length and average fiber height of cellulose nanofibers were also reduced when the polysaccharides were added to the culture medium. These modifications influenced the water sorption properties, structure, and crystallinity of BC. Hemicelluloses caused the most pronounced effect on mechanical properties in comparison with pectins. The experiment showed that hemicelluloses influenced the physical properties of BC to a higher degree than pectinic compounds.

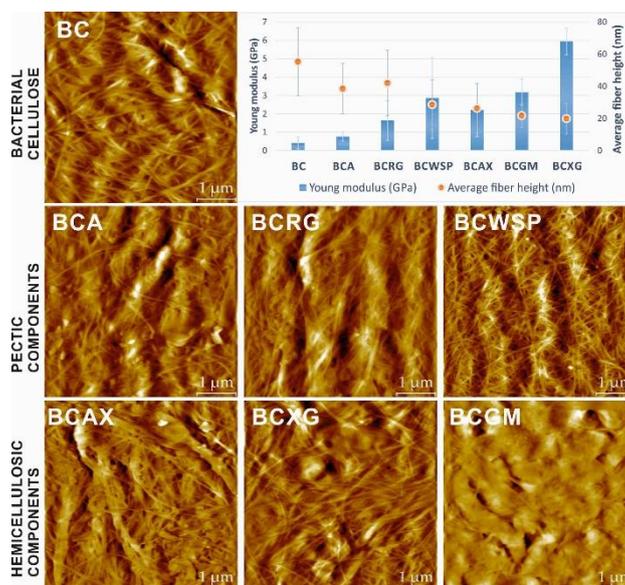


Figure 1: The nanostructure, average fiber height, and Young modulus of bacterial cellulose (BC) composites. BCA- BC + arabinan, BCRG – BC + rhamnogalacturonan, BCWSP- BC + water-soluble pectin, BCAX- BC + arabinoxylan, BCGM – BC + glucomannan, BCXG – BC + arabinoxylan.

This study was supported by the National Science Centre, Poland (Project No. 2020/37/B/NZ9/03159).



FORTIFICATION OF BC-PECTIN CONJUGATES WITH DIVALENT METAL IONS

Kurzyna-Szklarek M., Cybulska J., Szymańska-Chargot M., Zdunek A.

Institute of Agrophysics, Polish Academy of Sciences, Poland

* mkurzyna@ipan.lublin.pl

Bacterial cellulose (BC) extracellularly synthesized by many species of aerobic bacteria is a material with a three-dimensional structure formed by nanofibers of pure and high crystalline cellulose. Due to this unique structure, it can act as a matrix for incorporating other materials that can improve its properties [1].

In this study, the effect of different pectins fractions and divalent ions additives on mechanical, thermal, and structural properties was evaluated. BC composites were produced by *in situ* biosynthesis with different fractions of pectins (water-soluble pectins WSP, diluted alkali-soluble pectins DASP, oxalate soluble pectins OSP) without and with the addition of divalent metal ions (Ca^{2+} , Fe^{2+} , Mg^{2+} , Zn^{2+}).

To obtain information about BC-composites functional groups and the state of bonds in their structure FT-IR spectra were acquired. All spectra show a familiar pattern with characteristic peaks for polysaccharides in the fingerprint region ($1200 - 800 \text{ cm}^{-1}$) and the results are consistent with the literature [2]. To estimate the Young modulus, tangent modulus, stress at break, strain at break, elastic limit, and toughness uniaxial tensile tests were performed. The addition of all pectins fractions was associated with an increase of Young modulus and tangent modulus compared to pure BC. A similar effect was observed for most BC-pectin conjugates with divalent metal ions except for DASP combined with iron. In the BCWSP/Mg variant, the highest increase in elastic limit was noticed in relation to pure BC. In the remaining variants, a similar but lower pronounced effect was observed. During the tensile test, the BCDASP/Fe variant broke at the lowest stresses, while most additives increase the stress at the break of BC-composites. The thermal behavior of produced composites was investigated using differential scanning calorimetry with a scan rate 10 K min^{-1} . The addition of pure pectin fractions caused a slight decrease in thermal degradation temperature, and the lowest value was observed for BCWSP/Mg and BCDASP/Ca. On the contrary, BCOSP/Fe, BCOSP/Mg, and BCOSP/Zn were characterized by the highest thermal stability.

The results indicate that divalent metal ions fortified the mechanical strength of most BC-pectin conjugates. The temperature of thermal degradation of BC was decreased by pectins, but zinc and iron ions prevented this behavior for OSP and WSP. The experiment showed various possibilities for tailoring BC thermal and mechanical properties using specific pectin fractions and divalent metal ions.

[1] Torres F.G., Arroyo J.J., Troncoso O.P. Bacterial cellulose nanocomposites: An all-nano type of material. *Materials Science and Engineering: C*, 98, 1277-1293, 2019

[2] Güzel, M., Akpınar, Ö. Production and Characterization of Bacterial Cellulose from Citrus Peels. *Waste Biomass Valor* 10, 2165–2175, 2019

This study was supported by the National Science Centre, Poland (Project No. 2020/37/B/NZ9/03159).



INTERACTION OF BARLEY β -GLUCAN WITH SMALL MOLECULES STUDIED VIA POLYSACCHARIDE SPIN-LABELLING & PULSE DIPOLAR EPR SPECTROSCOPY

Wu X.^a, Boulos S.*^a, Syryamina V.N.^{a,c}, Yulikov M.^b & Nyström L.^a

^a Laboratory of Food Biochemistry, ETH Zurich, Switzerland

^b Laboratory of Physical Chemistry, ETH Zurich, Switzerland

^c Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of RAS, Novosibirsk, Russia

* samy.boulos@hest.ethz.ch

Interaction studies of polysaccharides with small or large target molecules are of interest in various research fields spanning from nutrition & food science to drug delivery and material sciences. For example, one possible mechanism by which regular intake of soluble dietary fibers (SDFs) may exert their health benefits in reducing risks related to cardiovascular diseases & diabetes is through interaction with certain small molecules during digestion, slowing down or reducing absorption. However, the corresponding interaction mechanisms and structural rearrangements of SDFs at the molecular level are still opaque due to the usually weak binding and the lack of appropriate techniques to determine details of conformational distributions in such weakly organized systems. We present here a toolkit of pulse electron paramagnetic resonance (EPR) techniques to determine these kinds of interactions using stochastically spin-labelled barley β -glucan as SDF[1] binding with various (food) dyes as a model system. Subtle conformational changes of β -glucan were observed by this methodology through detection of multiple details of the local environment of the spin labels. The various food dyes exhibited different binding propensities, which was brought in relation to their pK_a (hydrogen bonding) and planar size (van der Waals/ hydrophobic interactions; Figure 1).[2]

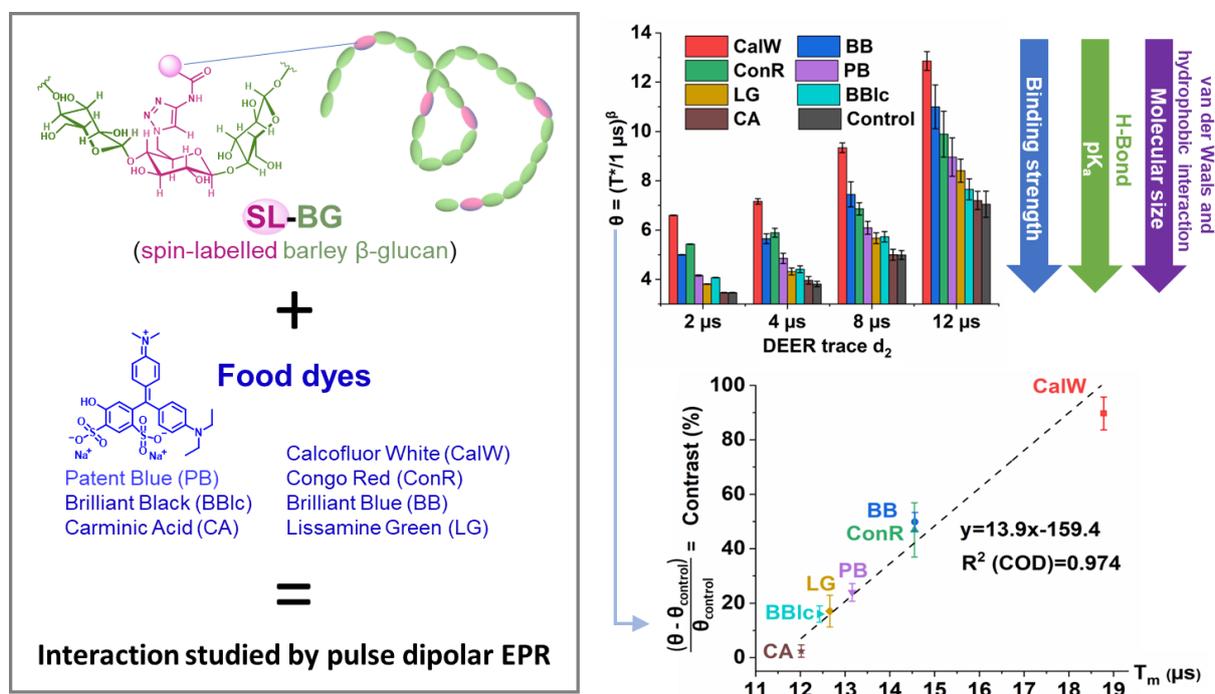


Figure 1: Spin-labelled β -glucan[1] interacting with food dyes (& CaW) and resulting relative binding strengths from double electron-electron resonance (DEER) EPR as example.[2]

[1] Wu X., Boulos S., Yulikov M. & Nyström L., *Carbohydrate Polymers*, 293, 119724, 2022.

[2] Wu X., Boulos S., Syryamina V.N., Nyström L. & Yulikov M., *Carbohydrate Polymers*, 309, 120698, 2023.



PROMISCUITY IN GLYCOSYLTRANSFERASES: EXPLORING THE IN VITRO AND IN VIVO FORMATION OF CHITIN NANOFIBRILS BY BACTERIAL CELLULOSE SYNTHASES

Shamshoum M.^a, Shai N. ^a, Natalio.F ^{a,*}

^a Plant Biodesign Lab, Department of Plant and Environmental Sciences, Weizmann Institute of Science, Israel

* filipe.natalio@weizmann.ac.il

Glycosyltransferases (GTs) play essential roles in various biological processes and exhibit promiscuity in substrate specificity, allowing the synthesis of diverse glycoconjugates, crucial for the adaptation and survival of organisms. Cellulose and chitin synthases are examples of processive GTs involved in cellulose and chitin biosynthesis, respectively. Organisms that produced chitin do not produce cellulose and vice-versa. Recently, we have demonstrated that bacterial cellulose and chitin synthases share highly similar active site architecture despite low global amino acid sequence and 3D structure similarities [1], laying a theoretical framework for experimental validation. Here we demonstrate that recombinant bacterial cellulose synthase from *Rhodobacter sphaeroides* (BscA-BscB) catalyzes the cleavage of uridine diphosphate N-acetylglucosamine (UDP- α -D-GlcNAc), resulting in the formation of chitin nanofibrils in vitro glucose. BscA-BscB has a similar substrate affinity between UDP- α -D-GlcNAc and its natural substrate uridine diphosphate glucose (UDP- α -D-GlcN) but less efficient toward UDP- α -D-GlcNAc. *R. sphaeroides* grown in the presence of UDP- α -D-GlcNAc resulted in the formation of chitin oligomers.

This study highlights the catalytic promiscuity of bacterial cellulose synthase, providing insights into the formation of chitin nanofibrils and expanding our understanding of GTs' functional versatility. The findings contribute to the broader field of glycobiology and have implications for biotechnological applications involving glycoconjugate synthesis.

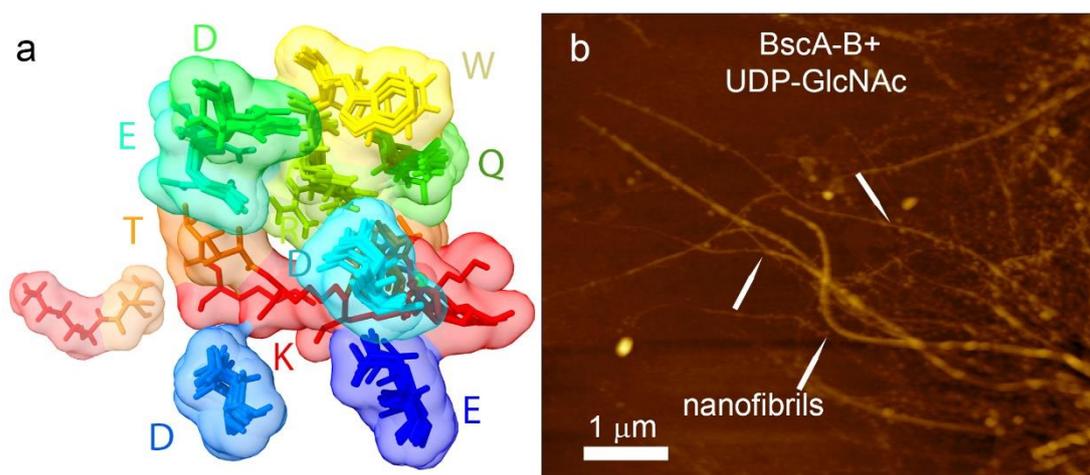


Figure 1 : a, Conservation of bacterial cellulose and chitin active sites [1]. b, atomic force microscopy image of the chitin microfibrils generated by recombinant bacterial cellulose.

1. Shamshoum, M. and F. Natalio, *Conserved active site architecture between bacterial cellulose and chitin synthases*. ChemBioChem, 2023. n/a(n/a): p. e202300388.



Session 10

Polysaccharides in a sustainable and circular economy

Session organizers:

Marco Beaumont, Li Shen, Blaise Tardy, Kristin Syverud, Elisabete Frollini

Keynote speakers:

Herbert Sixta

Novel sustainable wood fractionation process for the production of high-quality products from the separated polysaccharides

Julien Bras

High performance and recyclable cellulosic materials as an alternative solution in packaging within a sustainable and circular economy



HIGH PERFORMANCE AND RECYCLABLE CELLULOSIC MATERIALS AS AN ALTERNATIVE SOLUTION IN PACKAGING WITHIN A SUSTAINABLE AND CIRCULAR ECONOMY

Julien Bras

Univ. Grenoble Alpes, CNRS, Grenoble-INP, LGP2, 38000 Grenoble, FRANCE

Abstract:

Over the past few years, new policies, regulatory frameworks, and standards adopted worldwide enhance the global implementation of the circular economy and the bioeconomy. Especially in Europe, the single use plastic directive from 2018 have completely modified the paradigm in end-user industry which are looking for new sustainable solutions to replace plastics. Applications of bio-based materials in the sustainable packaging industry have then shown strong growth due to these recent legislations consolidated by trends in the consumer market moving toward greener packaging. Within this biobased materials, an excellent candidate for new high performance biobased materials is cellulose, the famous most abundant biobased polymer in earth.

Specifically, adapting cellulose science to traditional field like paper, cardboard or molded cellulose seems to be promising to achieve high performance materials by keeping their end-of life advantages comparing to plastic. This is the main target of the Cellulose Valley which will be shortly introduced. More and more techno-environmental assessments are proposed in our society on this topic and the transition to a bioeconomy have strong influence on the industry, technology development, and fundamental research. The current and future challenges in this topic will be listed

Among solutions, a special focus will be proposed on microfibrillated cellulose (MFC) which brings advantages in strength enhancement, light-weighting and barrier properties. By using MFC, it is possible to reduce the package's total weight, develop films featuring excellent barrier against gases like oxygen and even grease and oil, and at the same time reduce CO2 footprint by replacing aluminum and plastic film in packaging.

In this regard, this keynote will propose solutions or strategies to obtain barrier packaging, light packaging, 3D packaging, transparent packaging, thermosealable packaging by keeping in mind life cycle analysis and end-of life with a specific focus on recyclability in paper streams.

A critical perspective will be included on how these are suitable for defining the sustainability of polysaccharide-based materials and on how to have an impact from academia through working with industry?



NOVEL SUSTAINABLE WOOD FRACTIONATION PROCESS FOR THE PRODUCTION OF HIGH-QUALITY PRODUCTS FROM THE SEPARATED POLYSACCHARIDES

Sixta Herbert^{*a}, Lê Huy Quang^a, Fang Wenwen^a

^a*Department of Biosystems and Bioproducts, Aalto University, Finland*

* herbert.sixta@aalto.fi

Sustainable methods for the fractionation of lignocellulosic feedstocks are essential for the transition from a petroleum-based to a bio-based economy. The commercial Kraft and acid sulfite processes have the disadvantage of using sulfur-containing nucleophiles to initiate selective delignification, resulting in environmentally harmful byproducts. In addition, the Kraft process converts the separated hemicelluloses into a variety of different hydroxycarboxylic acids that cannot be converted into saleable products by commercially viable means.

Two recently developed heteroelement-free pulping processes, the *GVL-Water* and *Steam Explosion-Mild Caustic Extraction (SE-MCE)* processes, are presented as sustainable alternatives that enable selective and efficient separation of polymeric wood constituents and their subsequent conversion into high-value products [1,2].

Using birch wood as a raw material, it is shown how dissolving pulp can be produced from the high-molecular-weight polysaccharide fraction in comparable or better quality than with conventional production methods, and how furfural can be obtained from the C5 hemicellulose fraction at the same time.

In the second part of my talk, I report on the production of loncell fibers from different raw materials. A distinction is made between the use of cellulose I substrates such as pulp, recycled textile waste from natural fibers such as cotton or hemp, and cellulose II substrates such as the recycled loncell fibers, viscose and modal fibers. The interrelationships between the properties of the raw materials and the properties of the fibers made from them are expressed in a structure-property relationship.

[1] Fang W. ; Sixta H. *ChemSusChem*. 8, 73-76, 2015. Lê Huy Qu., Ma Y., Borrega M., Sixta H. *Green Chem.*,18, 5466, 2016. Granatier M., Lê Huy Qu., Gonzalez E-C., Sixta H. *RSC Sustainability*, 1, 97, 2023.

[2] Lê Huy Qu., Sixta H. *Lecture at the Paperweek Canada*, 2023



POLYSACCHARIDES AS ENABLERS OF THE BIOECONOMY IN ARID AREAS

Blaise L. Tardy^{1,2,3*}, M-Hidar A. Al Dali,^{1,2,3*} Luiz G. Greca⁴, Karl Mihhels⁴, Erlantz Lizundia^{5,6}, Ludovic Dumeé^{1,2}, Lourdes Vega^{1,2}

¹ Khalifa University, Department of Chemical Engineering, Abu Dhabi, United Arab Emirates

² Center for Membrane and Advanced Water Technology, Khalifa University, Abu Dhabi, United Arab Emirates

³ Research and Innovation Center on CO₂ and Hydrogen, Khalifa University, Abu Dhabi, United Arab Emirates

⁴ Department of Bioproducts and Biosystems, Aalto University, FI-00076 Aalto, Espoo, Finland

⁵ Life Cycle Thinking Group, Department of Graphic Design and Engineering Projects, Faculty of Engineering in Bilbao, University of the Basque Country (UPV/EHU), 48013, Bilbao, Spain.

⁶ BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.

* blaise.tardy@ku.ac.ae

Biosystems and bioprocesses are typically not connected to arid areas, where the produced biomass and its availability are low. However, there is a large potential for arid areas to become major bioeconomical actors via more localized biomass generation and valorization strategies. A circular bioeconomy in arid area is expected to address important challenges associated to food and (bio)materials supply and, ultimately, to climate and environment. Polysaccharides and particularly lignocellulosics are expected to be central actors. They can be obtained as by- and co-products from the emerging food production in arid area and can synergistically connect into a range of sustainable circular processes, e.g. aiming at the amelioration of arid soils. Herein, we first highlight the established and emerging biomass generation strategies in arid areas (Fig. 1-Top). We then showcase results on valorization of lignocellulosics towards a more prolific agriculture in arid soils (Fig. 1-Bottom). This is exemplified in the context of the United Arab Emirates deserts, where various sand types are composited with such natural polysaccharides (dissolve or as fibers). This results in improved water reponse of the soils as well as a reduction of their Aeolian erosion – critical to prevent spread of desertic areas, i.e. desertification. The impact of polysaccharides is quantified using unconfined compression tests, scanning electron microscopy highlighting the polymeric and fibrous networks, and dynamic vapor sorption measurements to correlate the impact of humidity with the response of the amended sands.

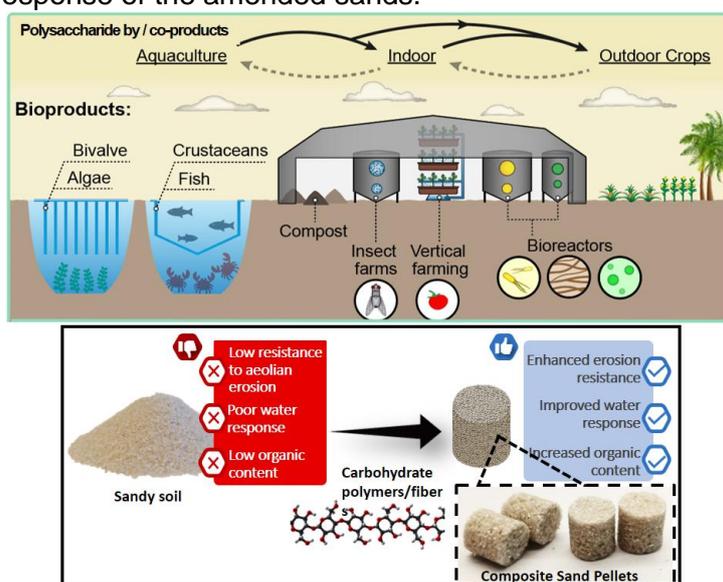


Figure 1 :Top – emerging biomass generation strategies in arid areas and their synergies; Bottom – benefits of polysaccharides as enhancers of sandy soil.

APPROACHING CIRCULARITY WITH PLANT AND MARINE BIOMASS, FIBRILLATED NANOPOLYSACCHARIDES AND BIOMASS RESIDUALS

Rojas O.J.* and collaborators^{a-e}

^a *Bioproducts Institute, University of British Columbia, Canada*

^b *Department of Chemical and Biological Engineering, University of British Columbia, Canada*

^c *Department of Chemistry, University of British Columbia, Canada*

^d *Department of Wood Science, University of British Columbia, Canada*

^e *Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland*

* orlando.rojas@ubc.ca

I introduce the work of the Biobased Colloids and Materials group (BiCMat) using three emblematic cases that highlight the great possibilities of circularity in the bioeconomy based on forest biomass and residuals. First, I discuss a processing route that transforms low-value wood (residual, damaged, decayed, disposed or fractured) into lightweight and strong structural materials. The process involves delignification, combined with partial dissolution and regeneration, to expose cellulose fibrils originally present in the cell walls. The latter form strong hydrogen bonding networks at interphases, leading to a 'healed' wood with a mechanical strength that exceeds that of typical metals and commercial laminated wood. Moreover, recyclability as well as excellent resistance against organic solvents are demonstrated, providing a promising valorization and sustainability pathway for low-value wood [1]. Following similar approaches, I next discuss an option for valorization of biomass, in this case, blueberries pruning residuals and food waste and losses, sourced from agro-forestry operations that can be used to produce added-value products, including platform chemicals and value-added materials [2-3]. Along such examples, I briefly show the premise of new routes for the production of fibrillated cellulose [4-5]. Finally, I give an example of a facile strategy to synthesize all-green SUPs based on chitin nanofibers. The latter are demonstrated for their facile recyclability and biodegradability in natural environments, addressing the limitations of circularity and end of life of non-renewable products [6]. Given the low-cost of the raw materials, their natural micro-structural design and self-adhesion, this presentations show fully sustainable alternatives to products based on nonrenewable carbon.

- [1] Dong *et al.* Low-value wood for sustainable high-performance structural materials. **Nat Sustain** (2022). DOI: 10.1038/s41893-022-00887-8
- [2] Reyes *et al.*, Upcycling agro-industrial blueberry waste into platform chemicals and structured materials for application in marine environments, **Green Chemistry**, 24, 3794–3804 (2022). DOI: 10.1039/D2GC00573E; Direct CO₂ capture by alkali-dissolved cellulose and sequestration in building materials and artificial reef structures, **Advanced Materials**, 2209327 (2023). DOI: 10.1002/adma.202209327
- [3] Otoni *et al.*, The Food-Materials Nexus: Next Generation Bioplastics and Advanced Materials from Agri-Food Residues, **Advanced Materials**, 2102520 (2021). DOI: 10.1002/adma.202102520
- [4] Beaumont *et al.*, Assembling Native Elementary Cellulose Nanofibrils via a Reversible and Regioselective Surface Functionalization, **Journal of the American Chemical Society**, 41, 17040–17046 (2021). DOI: 10.1021/jacs.1c06502
- [5] Beaumont *et al.*, Unique Reactivity of Nanoporous Cellulosic Materials Mediated by Surface-Confined Water, **Nature Communications**, 12, 2513 (2021). DOI: 10.1038/s41467-021-22682-3
- [6] Chen *et al.*, Mildly processed chitin used in one-component drinking straws and single use materials: Strength, biodegradability and recyclability, **Chemical Engineering Journal**, 442, 136173 (2022). DOI: 10.1016/j.cej.2022.136173.



SCLEROTIUM GUM - BIOPOLYMER SHIELD PROTECTION FOR ANTI-POLLUTION

Emmanuel Everaert E.P.J.M.^{1*}, Lemoine C.¹, Clio D.², Le Grand A.¹

¹ Cargill Beauty, Global Innovation, Paris-la-Défense, France,

² Cargill Beauty, R&D, Vilvoorde, Belgium

*Presenting author: emmanuel_everaert@cargill.com

Keywords: Scleroglucan, mode of action, sustainable sourcing, pollution, film forming.

OBJECTIVE:

- 1) Review the Scleroglucan manufacturing and key physico-chemical properties as well as the mechanisms of film forming via triple helix 3D polysaccharides structures.
- 2) Novel benefits properties: The Covid-19 era ushered in a fascination with skin health and increased awareness of the importance of protecting it from external aggressors. Such situation inspired Cargill Beauty to explore the capacity of sclerotium gum to protect the skin from Air pollutants such as particulate matter (most commonly PM2.5 and PM10). To well protect the skin, the film qualities of sclerotium gum need to show high homogeneity coverage and facilitate the cleansing of pollutants.

METHOD: The quality of the film on the skin from sclerotium gum has been assess using a SEM-FEG (Scanning Electron Microscopy-Field Emission Gun) equipment after a single application on the stratum corneum (SC) of a human skin explant.

The efficacy on the ease to rinse PM2.5 after application of the sclerotium has been proven in vitro with a gel at 1% by SEM-FEG coupled with chemical Energy-dispersive X-ray spectroscopy (EDX). Then the results have been confirmed *in vivo*, on the volar forearms of volunteers using environment dust particles, pollen, etc. with a gel formula at 0,6% and 1% by SEM and image analysis.

RESULTS: Scleroglucan is a polysaccharide made by bio-fermentation. It exhibits a very high MW with a nonionic character, making it very suitable & compatible most formulation conditions.

The qualitative analysis shows that 1% of sclerotium gum provided a thin homogeneous film which covers the entire skin surface and creates a shield on top of the skin.

The ease of removability of PM2.5 pollutant from skin explant was evaluated by the amount of particle remaining on skin explant after blowing air and rinsing with water. The skin explant pre-treated with sclerotium gum showed a decrease on the amount of pollutant by 44% ($p < 0,05$).

The validation of the results, *in vivo*, on forearm treated with sclerotium gum at 0.6% or 1% confirm the shield film which help on the removability of the dust. The reduction of environmental test dust compared to the untreated area after cleansing is 87% and 90% for the gels at 1% and 0,6%, respectively (figure 1).



Figure 1 . Example of SEM sample images before cleansing (untreated) versus after cleansing with water treated with 1% and 0.6% ActigumTM CS 11 QD or untreated.

CONCLUSIONS: The sclerotium gum is a high-end rheology modifier with great sensorials. This 100% nature derived biopolymer is part of the best alternatives to synthetic polymer. With these new studies, the sclerotium gum becomes more than a polymer, it acts as a real defense for the skin, creating a biopolymer shield protection from pollution effects.



CONTROLLING THE BIODEGRADABILITY OF PAPER BY SIMPLE SURFACE ACETYLATION

King A. W. T.^{*a}, Koso T.^a, Mahlamäki E.^a, Mäkelä M.^a, Harlin A.^a, Solberg A.^b, Syverud, K.^b, Korpela A.^a

^a VTT The Technical Research Centre of Finland Ltd., Finland

^b RISE-PFI, Norway

* alistair.king@vtt.fi

The European Commission's Single-Use Plastics (SUP) directive and similar legislation worldwide, designed to prevent build-up of micro-nano plastics in our environment, is rather restrictive when it comes to the definition of a SUP. In its current form, any biopolymer which is chemically modified becomes a SUP, after the chemical modification step. This is prompted by heavy lobbying and reports of poor biodegradability of common chemically modified cellulose, such as cellulose acetate. Thus, there is need to refine this legislation, as it is altogether very restrictive for business, without a strong fundamental understanding of the issues and even case-by-case biodegradation or life-cycle studies.

Previously we developed a series of analytics for following the regioselectivity of surface acetylation through gas and liquid phase reaction, with and without catalyst [1]. In this abstract we would like to present our studies into the controlled surface modification of kraft paper and nanopaper. Accurate analytics and a design of experiment approach is used to demonstrate the ability to control biodegradation and further expand the properties of paper towards traditionally fossil-based plastic barriers/materials.

[1] Koso T., *et al.*, *Green Chem.*, 24, 5604, 2022



REPLACEMENT OF FOSSIL-BASED REAGENTS WITH CELLULOSE: ENHANCING MATERIAL PROPERTIES AND CONTRIBUTING TO THE CIRCULAR BIOECONOMY

Frollini E.

University of São Paulo, São Carlos Institute of Chemistry, Macromolecular Materials and Lignocellulosic Fibers Group, São Carlos, São Paulo, Brazil

* elisabete@iqsc.usp.br

By replacing fossil-based raw materials with renewable ones in the synthesis process, we can generate sustainable and environmentally friendly materials. Using cellulose as a substitute for unrenovable reagents may improve material properties while contributing to the circular bioeconomy. In this scenario, the use of cellulose as a polyol in synthesizing polyurethanes has been considered by us in recent years. The chemical reactions occur without the use of any solvents. Castor oil's primary component, ricinoleic acid triglyceride, is utilized as an extra polyol and an effective dispersant for cellulose. Different polyisocyanates have been considered. The reactions occur in molds, under temperature and pressure, with or without reinforcements, forming composites or non-reinforced materials simultaneously with the syntheses. Lignocellulosic mats and/or short fibers have been used as reinforcements. Materials with excellent impact resistance and flexural properties have been formed, expanding the range of possible applications. In another study, the focus is on the syntheses of polyurethanes using the same reagents mentioned, also without solvents, but considering a process that leads to the formation of films simultaneously with the syntheses. Different castor oil/cellulose ratios have been used in the syntheses in this process, and nanocrystalline and nanofibrillated celluloses have also been used as additives. Properties such as tensile and barrier were evaluated, and the results are promising. With an increase in cellulose in the castor oil/cellulose ratio used as a polyol, there was an improvement in properties, sometimes equaling or surpassing the impact of nanocelluloses used as additives. The approach adopted allows for synthesizing with the simultaneous formation of polymeric materials while reducing reliance on non-renewable resources and may lessen the materials' carbon footprint. This promising avenue warrants further exploration and development to optimize its use and benefits. Ongoing research is focused on utilizing acquired knowledge to manufacture cellulose-based materials capable of sorbing and desorbing metals from polluted water. Funding: grant 2020/13703-3, São Paulo Research Foundation (FAPESP).



FATE OF COLORANTS IN RECYCLING OF CELLULOSICS FROM DENIM

Manian, A.P.^{a,*}, Müller, S.^a, Braun, D.E.^b, Pham, T.^a, Bechtold, T.^a

^a *Research Institute of Textile Chemistry and Textile Physics, University of Innsbruck, Hoehsterstrasse 73, 6850 Dornbirn, Austria*

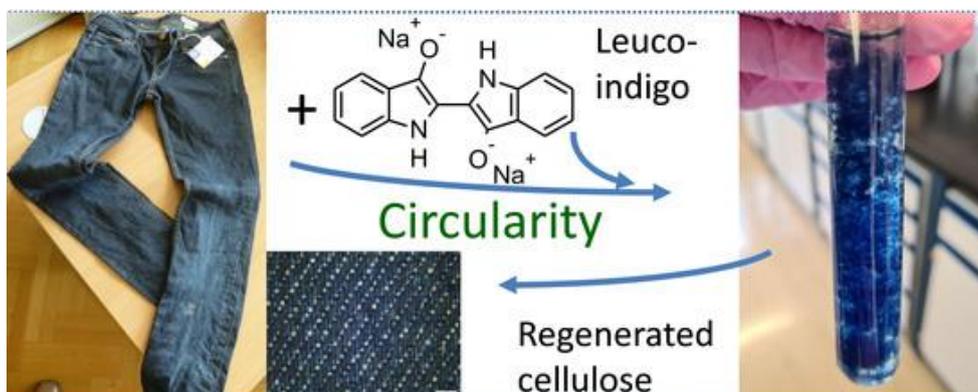
^b *Department of Pharmacy, Pharmaceutical Technology Section, University of Innsbruck, Innrain 52/c, 6020 Innsbruck, Austria*

* avinash.manian@uibk.ac.at

To implement circularity in the textiles and clothing sector, it is necessary to establish fiber-to-fiber recycling i.e. to recover fibers or polymers from discarded textiles for reuse in the construction of new textiles. The intricacy of fiber intertwinement in clothing makes mechanical separation of fibers very difficult if not infeasible, and chemical processes, such as depolymerization/repolymerization or dissolution/regeneration are more effective. In pursuing chemical processes, however, attention is required on the fate and potential impact of textile additives such as colorants.

We present the results of our ongoing investigations into the circularity of cellulosic fibers from denim fabrics. About 2.5 million tonnes of cotton, i.e. 10% of the annual global output, is consumed yearly in the manufacture of denim, and a predominant majority is colored with indigo. The other major colorant, although its use is smaller in proportion, is sulfur black, either alone or in combination with indigo. We investigated the potential of direct dissolution and regeneration of cellulose, dyed with indigo and sulfur black, through the viscose process, which accounts for about 80% of annual output of regenerated cellulosic fibers.

The results show that the colorant persists in the cellulosic mass through the xanthation, dissolution and regeneration of cellulose and there is no measurable leaching of dye from the cellulose into process baths. When dyed and undyed cellulose are mixed together, the colorant is uniformly distributed through the regenerates, and the color may be “topped up” by addition of fresh dye in the cellulose dissolution step. The dye particle size, as estimated with x-ray diffraction, does not appear to exceed the limits necessary for fiber spinning. Thus, when recycling cellulose from waste denim through the viscose process, a prior removal of indigo or sulfur dye may not be required [1].



[1] Manian, A.P.; Müller, S.; Braun, D.E.; Pham, T.; Bechtold, T. Dope Dyeing of Regenerated Cellulose Fibres with Leucoindigo as Base for Circularity of Denim. *Polymers*, 14, 5280, 2022. <https://doi.org/10.3390/polym14235280>



SUGARCANE BAGASSE/POLYDOPAMINE AS MULTIPURPOSE MATERIALS: FROM HEAVY METAL ADSORBENT TO CEMENT-BASED MATERIAL

Mário A.B.S. Nunes¹, Dairon P. Fuentes¹, Pedro V. Oliveira¹, Denise F.S. Petri¹

¹ Institute of Chemistry, University of São Paulo, Brazil

mariobsnunes@gmail.com

In this work sugarcane bagasse (SB) microparticles were coated with polydopamine (PDA) for the removal of Cr(VI) ions, a pollutant. Sugarcane bagasse was rinsed, dried, ground, and sieved. Modifications were made with 2.0 g/L (SB/PDA2) and 4.0 g/L (SB/PDA4) dopamine solutions in Tris-HCl buffer (pH 8.5), under agitation for 4 hours. At the end of the synthesis process, the adsorbent was placed in an oven at 60 °C for 24 hours to evaporate the residual solvent. For the batch adsorption tests, the operational conditions as temperature, initial concentration of adsorbate, pH and time, were investigated. Adsorption capacity, and kinetics adsorption of each of the systems, were evaluated based on the nonlinear adsorption model of Redlich-Peterson; Elovich and Weber models, respectively. Adsorption equilibrium was achieved after 1 hour for both compositions. Thermodynamic analysis showed an endothermic adsorption process. BG/PDA 4.0 g/L bioadsorbents were the most effective, removing up to about 76% of Cr(VI) ions from a solution at 150 mg/L, and pH 2. Column adsorption experiments were performed at a fixed flow rate of 1.5 mL/min and the operational parameters evaluated were adsorbent mass (m_{ads}), initial Cr(VI) solution concentration, and PDA content. The experimental data were fitted to the Thomas model. For a fixed mass amount of adsorbent, q_0 and saturation time were proportionally higher when the concentration of polydopamine was increased from 2 to 4 g/L. For the SB/PDA4 composition, the adsorption capacity (q_0) increased from 197.96 mg/g ($m_{ads} = 50$ mg) to 1417.04 mg/min ($m_{ads} = 500$ mg), with fixed parameters: $C_0 = 150$ mg/L and $v = 1.5$ mL/min. The spent adsorbents were applied to produce a cement-based material, where the leachability, mechanical, and morphological properties were evaluated. Over two months of leaching experiment, the release of Cr(VI) to the water was not observed. Regarding the mechanical properties, the addition of the spent adsorbent to the mortar did not lead to a reduction of the compressive strength. Beyond the high efficiency of SB/PDA4 as adsorbent towards Cr(VI) ions, this work disclosed an effective second use for the spent adsorbents, which is essential to the reduction of a possible secondary contamination.

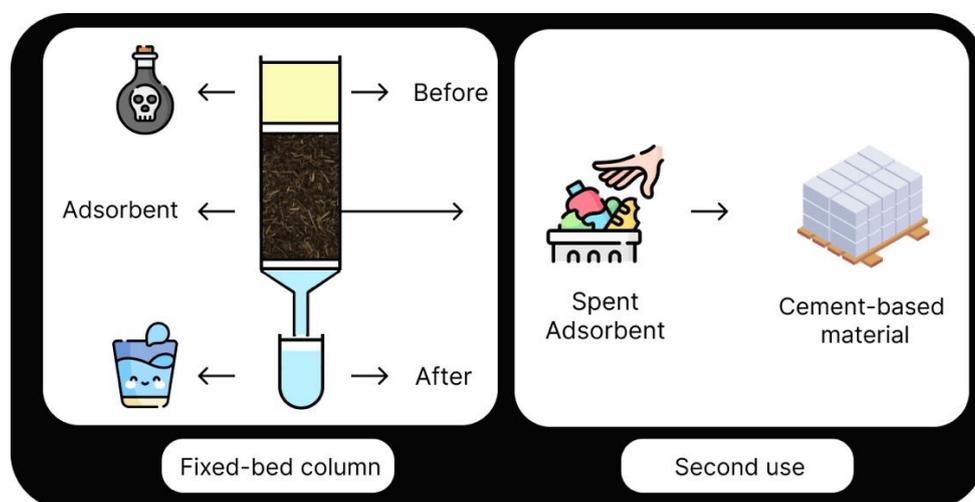


Figure 1 - Multipurpose SB/PDA4: From adsorbent to cement-based material



CLASH OF THE TITANS: PLASTIC VS THE WORLD

M. Kogler ^{*a}, Dimitri D. Deheyn ^b, Kara Wiggin ^b and Sarah-Jeanne Royer ^b

^a *Lenzing AG, Werkstraße 2, 4860 Lenzing, Austria*

^b *Scripps Institution of Oceanography, University of California San Diego, La Jolla, USA*

* m.kogler@lenzing.com

Marine litter is a globally recognized environmental problem of increasing concern. Marine ecosystems worldwide are affected by man-made debris, much of which is plastic. Plastics are ubiquitous in the marine environment. They come from a multitude of sources and are composed of a great variety of polymers and copolymers (e.g. PE, PP, PVC). Plastics can persist for hundreds to thousands of years in marine environment, even longer in the deep sea and polar region due to their high resistance to natural degradation. In the past few years, an increasing number of studies focus on a very particular type of plastic debris: “microplastics”. Microplastics are particles less than 5 mm in size. This kind of debris has been observed within every marine habitat worldwide. Plastics can smother coral reefs, transport invasive species, injure and kill wildlife and even have the potential to transport chemical contaminants, which in turn then may pose a threat to human health. The major sources of microplastics are land-based and it is very difficult to point out the ultimate source of microplastics due to their fragmentation and degradation nature. However, one major source has already been identified: the process of washing clothes. During this fiber fragments are released from garments which will eventually find their way into the oceans.

There have been many scientific reports, which tried to identify and quantify the different types of synthetic particles and fibers found in the marine environment. Plastic pollution has also occupied social media so much that awareness of this topic has been brought up to the forefront of society. Consequently, peoples habits have started to change, policies have begun to shape up towards a single-use plastic-free world, and industry have started to come up with alternatives, more environmentally friendly materials.

In this talk, we want to present a comparative assessment of the physical and chemical degradation of LENZING™ fibers under realistic marine coastal conditions. LENZING™ fibers are produced from the renewable raw material wood, sourced from sustainably managed forests or plantations, feature state-of-the-art, stringently implemented production in line with high quality, environmental and safety standards and they are biodegradable in the natural environment. LENZING™ fibers can therefore contribute to the solution to this problem and help reduce microplastics in our oceans.



DEGRADATION OF THE WHEAT ENDOSPERM MATRIX AND CONSTITUTING BIOPOLYMERS DURING BAKING AND ITS ROLE ON THE PERFORMANCE OF STALE BREAD AS PACKAGING MATERIAL

Guo W.*, Spotti J., Portillo-Perez G., Martinez M.M.

Center for Innovative Food (CiFOOD), Department of Food Science, Aarhus University, Denmark

* wanxiang@food.au.dk

Stale bread is the second type of food waste most generated annually in the world, representing great economic loss along the bread supply chain, as well as great pressure on the environment. Since stale bread is comprised by functional molecules in polymeric form, e.g., starch, gluten, cellulose, and arabinoxylan, we hypothesized that the stale bread matrix has a huge potential for utilization as something of higher value than a mere source of fermentable sugars: as building blocks of future bio-based materials. In this work, we performed a compelling investigation of the molecular structure of starch (SEC-MALS-dRI), water extractable arabinoxylans and the insoluble cell wall residue (SEC-MALS-dRI, HPAEC-PAD, phenolic acid content) and proteins (SDS-PAGE) before and after baking. We also performed an assessment of the creation/disruption of supramolecular arrangements upon baking (DSC, XRD, CLSM, FTIR, FTIR-TGA). Moreover, a film prototype was made from stale bread milled particles (B-film) and compared to the wheat flour counterpart (WF-film) in terms of morphology and mechanical, thermal and barrier properties.

Baking resulted in a great degradation of starch granules and molecules, with Mw decreasing from 42.5×10^7 g/mol to 6.4×10^7 g/mol, and the degree of polymerization of amylose chains from ~1180 to ~447 glucose units. No significant differences were found in the yield and neutral sugar composition of water extractable arabinoxylans, while their Mw was reduced. The yield of insoluble cell wall material increased after baking, which was accompanied by an increase of its protein content, suggesting protein-hemicellulose crosslinking. These results aligned with a higher proportion of bound polyphenols found after baking (61.5% vs 83.5%). Reducing and non-reducing electrophoresis showed proteins aggregation during baking mainly through disulfide bonds. Both wheat flour and stale bread particles were able to result in transparent and cohesive film prototypes, although they displayed different properties. B-film presented significantly lower tensile strength, elastic modulus, and degradation temperature than WF-film. Importantly, B-film presented a significantly higher elongation at break (EB), which was explained by its lower relative crystallinity, degradation of starch molecules (especially amylose), and attractive/segregative interactions between the gluten and the polysaccharide networks as detected by CLMS and FTIR-microscopy. In conclusion, baking wheat flour induced the degradation of polysaccharides and cross-linking of proteins, which enhanced the flexibility of films made from stale bread. Results of this work will be cornerstone to upcycle the stale bread matrix and its constituting biopolymers into high-performing and fully biodegradable packaging materials.



HIERARCHICAL MATERIALS BASED ON NANOCELLULOSE AND POLY(LACTIC ACID)

Manon Guivier^a, Giana Almeida^a, Sandra Domenek^a, Chloé Chevigny^{a,*}

^a *Université Paris-Saclay, INRAE, AgroParisTech, UMR SayFood, Palaiseau, France*

* chloe.chevigny@inrae.fr

Nanocelluloses have shown excellent gas barrier properties which makes them of the highest interest for food packaging applications [1]. However, the nanocelluloses swelling, in presence of water vapor, thwarts their good gas barrier properties [2]. Consequently, the use of nanocelluloses in food packaging, while extremely promising, is still a challenge. A multilayer architecture starting with an hydrophobic layer of poly(lactic acid) (PLA) could be a solution to protect nanocelluloses. Different studies have been devoted to the use of nanocelluloses as fillers in a PLA matrix [3], but here, a new architecture was developed by depositing layers of nanocelluloses on PLA.

The coverage of PLA films by nanocelluloses was achieved by using a first layer of chitosan. The surface organization of the nanocellulose layers was studied by AFM (Fig.1, a, b and c). The cellulose nanocrystals showed orientation (Fig.1a), which was confirmed by FFT treatment of the images. Concerning the food packaging-related properties, dry and wet O₂ barrier properties were studied on films with different nanocelluloses layer thicknesses (see Fig.1d). Results are very promising, with our samples' O₂ permeation several orders of magnitude lower than PLA, and staying so at high humidity (80% RH).

The multilayer architecture is very efficient to obtain highly performing food packaging films and the protection of the nanocellulose layer by PLA allows to keep this performance over a large range of relative humidity [4].

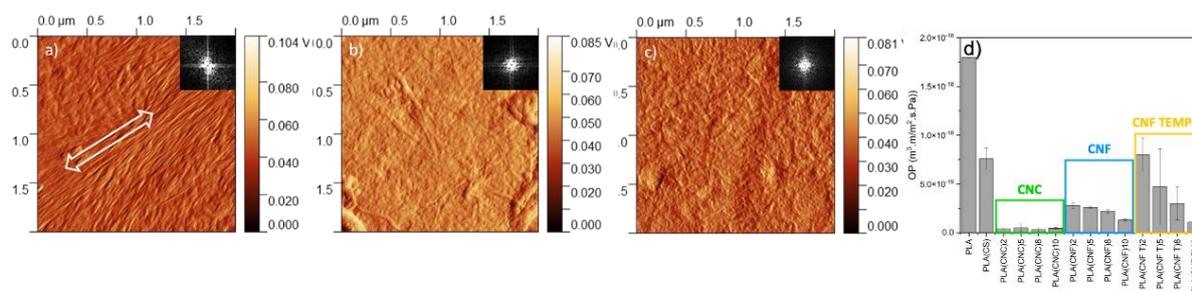


Figure 1 : AFM images of the sample surfaces coated with 10 deposits of CNC (a), CNF (b) and CNF TEMPO (c), and dry Oxygen permeabilities of uncoated and coated-PLA (d).

- [1] S. Belbekhouche *et al.*, "Water sorption behavior and gas barrier properties of cellulose whiskers and microfibrils films," *Carbohydr. Polym.*, vol. 83, no. 4, pp. 1740–1748, 2011.
- [2] A. Liu, A. Walther, O. Ikkala, L. Belova, and L. A. Berglund, "Clay nanopaper with tough cellulose nanofiber matrix for fire retardancy and gas barrier functions," *Biomacromolecules*, vol. 12, no. 3, pp. 633–641, 2011.
- [3] E. Espino-Perez *et al.*, "Designed cellulose nanocrystal surface properties for improving barrier properties in polylactide nanocomposites," *Carbohydr. Polym.*, vol. 183, pp. 267–277, 2018.
- [4] M. Guivier, G. Almeida, S. Domenek, and C. Chevigny, "Resilient high oxygen barrier multilayer films of nanocellulose and polylactide," *Carbohydr. Polym.*, vol. 312, 120761, 2023.



IMPACT OF THERMOMECHANICAL TREATMENT ON DIETARY FIBER POLYSACCHARIDE STRUCTURES OF APPLE POMACES

Trabert A. ^a, Schmid V. ^b, Keller J. ^a, Emin M. A. ^b, Bunzel M. ^{a*}

^a *Institute of Applied Biosciences, Department of Food Chemistry and Phytochemistry, Karlsruhe Institute of Technology, Germany*

^b *Institute of Process Engineering in Life Sciences, Section I: Food Process Engineering, Karlsruhe Institute of Technology, Germany*

* mirko.bunzel@kit.edu

By-products of the food industry, such as apple pomace, are generated in large quantities and are often used only as animal feed or for the extraction of phytochemicals. However, these by-products also contain valuable polymeric ingredients for human nutrition such as dietary fiber polysaccharides. Over the past few years, there has been an increasing interest in the effects of extrusion on dietary fiber to modify the techno-functional properties of by-products and to increase the dietary fiber content of food products.

For this purpose, two different apple pomaces (untreated and enzymatically treated) were treated on different extruders using varying extrusion conditions (water content, screw speed, screw configuration). Depending on these parameters, the materials were exposed to different thermomechanical energy inputs. Analysis of the functional properties demonstrated that extrusion is an effective method to modify the techno-functional properties of both apple pomace and enzymatically treated apple pomace. Thus, water absorption, water solubility, and viscosity can be modified [1,2].

These techno-functional changes are partially due to structural modifications of the dietary fiber constituents. Under the influence of thermomechanical treatment, the amount of soluble dietary fiber increases. At the molecular level, changes in pectic arabinans, neutral side chains of rhamnogalacturonan I, are evident as the analysis of monosaccharides after acidic cleavage shows a decrease in the proportion of arabinose in the pectic polysaccharides. Furthermore, the glycosidic linkage ratios suggest a decrease in substitution in position O-3 of arabinans for both apple pomaces. Application of an enzymatic profiling approach to arabinans using *endo*-arabinanase revealed changes in highly branched arabinan units. Thus, arabinans appear to be particularly labile under thermomechanical stress [1,2]. Also, extrusion affected cellulose crystallinity. However, contrary to our expectations, the proportion of ordered structures (crystalline cellulose) increased with extrusion.

To individually investigate the impact of thermal and mechanical stress (both are applied during extrusion) on the structural changes of pomace polysaccharides, these parameters have to be decoupled. For this purpose, a specialized shear cell (closed cavity rheometer) was used that is able to provide either defined mechanical or thermal treatment conditions close to extrusion conditions. The structures of apple pomace dietary fiber polysaccharides were more susceptible to temperature-based modifications. However, although less pronounced, a mechanical influence - especially in combination with high temperatures - on the structures of pectic polysaccharides was also detected [3].

[1] Schmid V., Trabert A., Schäfer J., Bunzel M., Karbstein, H. P. & Emin M. A., *Foods*, 10, 1-25, 2020

[2] Schmid V., Trabert A., Keller J., Bunzel M., Karbstein, H. P. & Emin M. A., *Foods*, 3, 1-12, 2021

[3] Schmid V., Trabert A., Keller J., Bunzel M., Karbstein, H. P. & Emin M. A., *European Food Research and Technology*, 8, 2109-2122, 2021



HCl GAS ALCOHOLYSIS OF COTTON LINTER FIBERS

Wang Y. ^{*a}, Pääkkönen T.^a, Yousefi N.^a, Kontturi E.^a

^a *Department of Bioproducts and Biosystems, Aalto University, Finland*

* yingfeng.wang@aalto.fi

Alcoholysis of lignocellulose has become an efficient method of conversion because it can significantly increase the solubility of biopolymers and their depolymerization rate, as well as inhibit humin formation and produce valuable platform chemicals, such as alkyl glucosides, xylosides and levulinate.. Here, cotton-based Whatman 1 filter paper samples were first soaked in different alcohols (2-propanol, ethanol, t-butanol and ethylene glycol), and subsequently hydrolyzed by pressurized HCl gas in a gas/solid system. This is contrary to the previous efforts where fibers have usually been directly treated in acidic liquid alcohol. In the meantime, purification of the products was relatively unproblematic from a gas-solid mixture, and a gaseous catalyst was easier to recycle than the aqueous or liquid counterpart. The results lay down a basis for future practical solutions in cellulose hydrolysis where side reactions are controlled, conversion rates are efficient, and the recovery of products and reagents is effortless. [1]

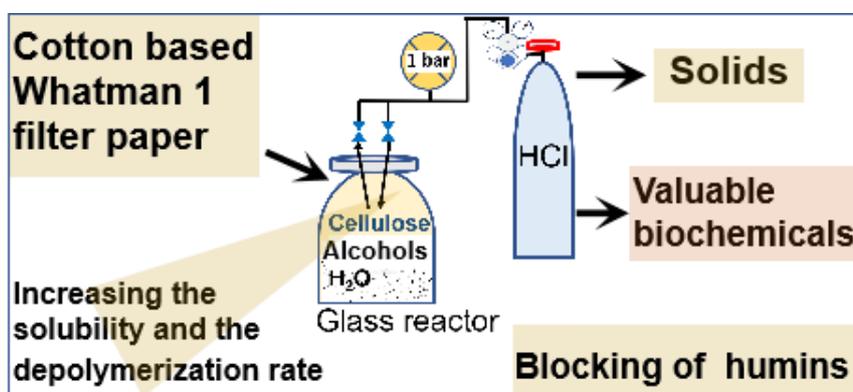


Figure 1 : Concept schematics

[1] Wang Y., Pääkkönen T., Miikki K., H. Maina N., Nieminen K., Zitting A., Penttilä P., Tao H & Kontturi E., *Carbohydrate Polymers*, 302, 2023



CHARACTERIZATION OF ENDO-1,4-GLUCANASES FROM SOFTENING FRUIT FOR ENZYMATIC DEPOLYMERIZATION OF CELLULOSE

Karppinen K.*^a, Edema H.^a, Ashraf M.F.^a, van Steenis F.^a, Jaakola L.^a

^a Department of Arctic and Marine Biology, UiT The Arctic University of Norway, Norway

*katja.karppinen@uit.no

Cellulose is the most abundant organic compound on earth and a major interest as source of biofuels, green chemicals, polymers, and nanomaterials production. However, cellulose is present as part of complex carbohydrate network in plant cell walls, which are recalcitrance for degradation. Biochemical conversion of the plant biomass into sugars via enzymatic hydrolysis is currently the most viable technology, and thus powerful hydrolytic enzyme cocktails are needed to release fermentable sugars from plant cell walls. In contrast to enzymes originating from fungi and bacteria, hydrolytic enzymes and active domains of plant origin are poorly investigated and characterized for their potential for industrial use. Screening new organisms and enzymes gives possibilities to widen the pool of enzymes, including enzyme activities and their binding abilities.

Plants have an ability to efficiently re-arrange and degrade their own cell walls during many developmental processes. One of these processes is soft fruit and berry ripening when rapid loosening and hydrolysis of cell walls in fruit flesh takes place. We have earlier shown that bilberry (*Vaccinium myrtillus*) fruits demonstrate activation of wide variety of cell wall modifying and degrading enzymes during their rapid berry softening stage [1].

In this study, we identified from bilberry four berry-specific glycoside hydrolase family 9 (GH9) cellulases, which were induced during berry ripening and softening. In two of the four cellulases, carbohydrate binding module (CBM) was identified in C-terminus of the protein. The produced recombinant B- and C-type GH9 cellulases were confirmed to exhibit endo-1,4-glucanase activities. Detailed characterization of activities of these GH9 cellulases towards different types of carbohydrate substrates, degradation products, optimal pH and temperature range as well as synergy with other hydrolytic enzymes is ongoing. Cellulases are important targets for improvement and are currently the third largest set of industrial enzymes due to their wide range of applications in various industrial fields, including bioenergy production where their need is increasing [2]. Screening less utilized genome sources opens new possibilities to find and design more substrate-specific and efficient synthetic enzymes towards plant biomass saccharification in the future.

[1] Karppinen K., Tegelberg P., Häggman H. & Jaakola L. *Frontiers in Plant Science* 9, 1259, 2018.

[2] Srivastava N., Shrivastav A., Singh R., Abohashrh M., Srivastava K.R., Irfan S., Srivastava M., Mishra P.K., Gupta V.K. & Thakur V.K. *Journal of Renewable Materials* 9, 615-636, 2021.



A COMPARISON OF POLYSACCHARIDE-BASED FLOCCULANTS FOR TREATING HARMFUL CYANOBACTERIAL BLOOMS

Rao NRH. ^{a,b}, Tyagi S. ^{a,b}, Muylaert K. ^a, Thielemans W. ^b

^a Laboratory of Aquatic Biology, KU Leuven, Belgium

^b Sustainable Materials Laboratory, KU Leuven, Belgium

* naras.hanumanthrao@kuleuven.be

Flocculants are commonly employed in the water treatment field to aggregate individual cyanobacterial cells into larger flocs for easy separation via flotation. Recently, the use of polysaccharides as non-toxic and sustainable flocculants is gaining increased interest. In this study, naturally available chitosan, and cellulose nanocrystals (CNCs) which were extracted from cotton and chemically modified with pyridinium grafts (CNC-PYR) were used to separate the harmful cyanobacteria *Microcystis aeruginosa* from water. The grafting degree of the CNCs was evaluated via elemental analysis, FTIR and XPS and the crystallinity through the WAXS.

The removal efficiency of *M. aeruginosa* increased as the dose of the CNC-PYR flocculant increased, reaching a maximum efficiency of 98% at 4 mg/L. This was in contrast to chitosan which showed no effect on the removal of *M. aeruginosa* at any of the doses (1-50 mg/L) trialled. The performance of the CNC-PYR flocculant was comparable to the synthetic polymer – poly(diallyldimethylammonium chloride) (PDADMAC), which is commonly used in water treatment plants around the world.

Additionally, as the pyridine groups grafted on the CNCs are fluorescent-active, the residual CNC-PYR flocculant in the treated water was tracked, unlike the un-trackable PDADMAC flocculant. This showed that the fate of flocculants can be tracked when using the modified CNC flocculants, which is critical for water treatment plants.

Preliminary investigations also revealed that the acute toxicity (48 h exposure) of the CNC-PYR flocculant was negligible when exposed to *Daphnia*, which is in contrast to the toxic PDADMAC. Overall, the results from this study suggest that modified polysaccharide flocculants such as CNC-PYR promote sustainability due to their efficiency, trackability and low toxicity and have an excellent and a large scope for uptake in water treatment applications.

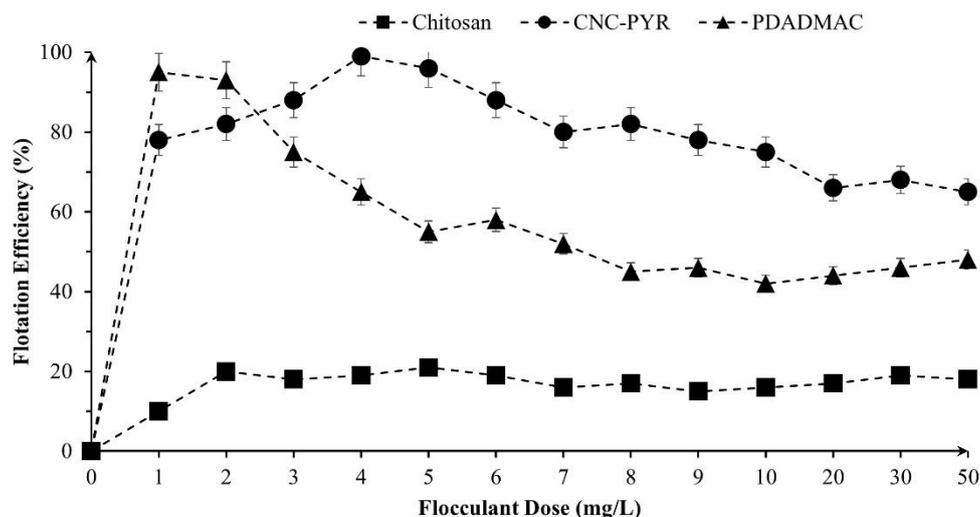


Figure 1 : Removal efficiency of *M. aeruginosa* when trialling different doses of polysaccharide (chitosan, CNC-PYR) and non-polysaccharide (PDADMAC) flocculants.



CHITOSAN-BASED COATINGS FOR THE WATER-PROOFING OF WOOD

Münstermann, N.^a, Weichold, O.^a

^a Schinkelstr. 3, 52062 Aachen, Group of Engineered Polymer Composites, RWTH Aachen, Germany

*muenstermann@ibac.rwth-aachen.de

Wood is one of the oldest building materials and is currently becoming increasingly popular again due to the raised awareness for environmental issues. Wood is hygroscopic and porous, i.e. it not only absorbs moisture from the atmosphere, but also actively and quickly sucks up large amounts of water through the capillary system particularly via the end grain. This leads to dimensional changes, but above all the wood becomes susceptible to rot. As a result, for many applications the wood needs to be protected from moisture. Besides a large number of well-established petrochemical products, there are still some traditional, natural finishes available. The most prominent ones are linseed and tung oil. Both harden in air by autooxidation, due to the large content of linoleic acid. However, to obtain a decent protection, both oils need to be applied in multiple layers and the final coating requires at least several days to harden completely. In addition, an increased use of linseed oil for wood finishes would interfere with the food chain and tung oil is in some publications said to be toxic.

We have recently developed an alternative coating for wood based on chitosan, which can be obtained from food-industry waste. The coating is applied from aqueous solution and adheres nicely on wood surfaces due to the structural similarity of chitosan and cellulose. To prepare the aqueous coating formulation, chitosan is solubilized with itaconic acid. Since itaconic acid is produced in large scale by fermentation of sugars or industrial wastes such as glycerol, the coating chitosan is entirely biobased. Between room temperature and 60 °C, the coating is polymerized to form a water-insoluble film that reliably seals the end grain against liquid water. At 60 °C, polymerization takes place significantly faster without loss of material qualities.



FROM WASTE TO WATTS: UPCYCLING COFFEE AND SUGAR INDUSTRY WASTE FOR SUPERCAPACITORS

Selinger J. ^{*a, b}, Stock S. ^c, Hobisch M. ^a, Schlemmer W. ^a, Egger M. ^a, Meinander K. ^b, Wilson B. ^d, Hummel M. ^b, Spirk S. ^a

^a Institute of Bioproducts and Paper Technology, Graz University of Technology, Austria

^b Department of Bioproducts and Biosystems, Aalto University, Finland

^c Institute of Physics, Montanuniversität Leoben, Austria

^d Department of Chemical and Metallurgical Engineering, Aalto University, Finland

* julian.selinger@tugraz.at

The food producing industry generates tremendous amounts of (poly)saccharide- and extract rich wastes throughout the year. However, those valuable biogenic sources are lacking in comprehensive upcycling opportunities. Herein we investigate the potential of waste/side streams from the sugar- and coffee producing industries with the aim to substitute fossil-based sources in electrochemical applications. The development of renewable energy storage materials is becoming increasingly important as we strive to reduce our reliance on fossil fuels and transition to an eco-friendlier energy system.

We investigated the potential of spent coffee grounds, coffee silver skins, beet pulp, and sugar molasses for the application in supercapacitors, from different angles. All by-products, except molasses, were carbonized and KOH-activated at elevated temperatures to produce activated carbon. The carbons have been extensively characterized (via SEM, TEM, Raman spectroscopy, gas sorption, elemental analysis and XPS). All materials exhibit a pore size distribution favorable for supercapacitors with aqueous electrolytes and high surface areas up to 3700 m²/g. Various capacitance enhancing functional groups were found which provide additional capacitance via faradaic reactions. The activated carbons have been assembled into free standing electrodes. Molasses was used as substrate to produce bacteria derived nanocellulose separators. The chemical stability of the nanocellulose separators was tested, as well as their electrolyte uptake. Spent coffee grounds were, beside using them as precursor for activated carbons, also used to extract redox active caffeic acid. To increase the overall capacitance of the supercapacitor the caffeic acid was mixed with the electrolyte prior testing. Supercapacitors were assembled and the performance was tested by cyclic voltammetry and galvanostatic charge-discharge experiments, using environmentally friendly electrolytes (6M KOH and 1M H₂SO₄).

We achieved capacitances up to 193 F/g in H₂SO₄ and 177 F/g in KOH (at 20 mV/s). By the addition of caffeic acid, we could even boost the capacitance further. The tests of the bacterial cellulose separators showed that we nearly met the capacitance values of conventional glass separators. Overall, our study provides an important insight into the potential of industrial side streams as valuable resources for energy applications from renewable resources. This highlights the need for further innovation in this area to support the transition to a more sustainable and circular economy.



HYBRID BIOPOLYMERIC AEROGELS WITH REDUCED WATER VAPOR SORPTION USING RICE STRAW CELLULOSE COLONIZED BY POLYHYDROXYLAKANOATE-PRODUCING BACTERIA

Cabrera-Villamizar L^a, Campano C^b, Rivero-Buceta V^b, López-Rubio A^a, Fabra MJ^a, Prieto MA.^b

^a Food Safety and Preservation Department, Institute of Agrochemistry and Food Technology (IATA-CSIC), Spain

^b Polymer Biotechnology Group, Biological Research Centre Margarita Salas, Spanish National Research Council (CIB-CSIC), Spain

*la.cabrera10@iata.csic.es

Based on FAO statistics, global rice production accounts for 740 million tons annually. This staple crop generates significant amounts of agricultural residues such as rice straw, with 1-1.5 kg of straw produced for every kilogram of grain harvested [1]. Traditional disposal methods involve leaving the straw in the field or burning it, which leads to the emission of methane and airborne carbon particulate matter. These practices have a negative impact on human health and the environment, making the upcycling of residues an attractive option. Rice straw waste can be processed to deliver value-added products such as paper, composites, absorbent pads, and thermal insulation materials [2]. In this study, aerogels were produced from cellulose extracted from rice straw. To improve the aerogel's properties, they were hydrophobized using a novel strategy that facilitates the interaction between cellulose and polyhydroxyalkanoates (PHA). PHAs are biobased polyesters accumulated in the form of intracellular granules by microorganisms under nutrient-limited conditions and can provide different properties or functionalities to cellulosic materials [3]. In this study, living bacteria with accumulated PHA were used to hydrophobize not only the outer surface of the aerogel but also the fibers within the network. To achieve this, cellulose was first converted into cellulose nanofibers (CNFs) by TEMPO-mediated oxidation and high-pressure homogenization, and, subsequently, freeze-dried. The aerogels were then tested for stability in water. Subsequently, living *Pseudomonas putida* cells with PHA granules colonized the aerogels and the materials were then processed to retain only the PHA granules. The resulting materials were characterized and showed a porous matrix of cellulose nano/microfibers with PHA granules deposited on the fibers inside the aerogel. Additionally, the incorporation of PHA resulted in a reduction in the material's water vapor sorption capacity, which is attributed to the PHA's hydrophobic properties. This method provides an alternative method for cellulose hydrophobization and compatibilization with future prospects for the production of greener materials through a circular economy approach.

[1] Sangon, S., Hunt, A. J., Attard, T. M., Mengchang, P., Ngernyen, Y., & Supanchaiyamat, N., *Journal of cleaner production*, 172, 1128-1139, 2018

[2] Boonterm, M., Sunyadeth, S., Dedpakdee, S., Athichalinthorn, P., Patcharaphun, S., Mungkung, R., & Techapiesanchaorenkij, R., *Journal of Cleaner Production*, 134, 592-599, 2016

[3] Campano, C., Rivero-Buceta, V., Fabra, M. J., & Prieto, M. A. *International journal of biological macromolecules*, 223, 1495-1505, 2022

Aknowledgement to Spanish Ministry of Science and Innovation under the research grant PID2020-112766RB-C21 and PID2020-112766RB-C22, Santiago Grisolia aid of Laura Cabrera-Villamizar (GRISOLIA/2021/050) and the Juan de la Cierva aid of Cristina Campano (FJC2019-040298-I).



AQUATIC PLANTS FROM DANUBE REGION AS URBAN BIOREFINERY FEEDSTOCK

Winter A. ^{*a}, Geiger P. ^a, Gindl-Altmutter W. ^b, Potthast A ^a, Rosenau T ^a, Beaumont M ^a

^a *Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences, Vienna (BOKU), Austria*

^b *Institute of Wood Technology and Renewable Materials, University of Natural Resources and Life Sciences, Vienna (BOKU), Austria*

* armin.winter@boku.ac.at

Aquatic plants (macrophytes) have a huge, yet still untapped potential for bioeconomy applications. In the Old and New Danube ecosystem around Vienna and in the county of Lower Austria, their removal is necessary for ecological and recreational reasons. However, the current practice of composting the 3000 tons of annually removed biomass prevents the further utilization of its components.

The present work focuses on investigating the value-added utilization of *Myriophyllum spicatum*. The chemical composition of the water plant was studied, and its potential use in various material applications was evaluated. The water plant had a high holocellulose content of 45 wt% and 16 wt% of lignin and contained high amounts of proteins and extracts (12 wt% and 15 wt%, respectively). The different fractions of *Myriophyllum spicatum* were investigated for cascading utilization in a biorefinery concept. An alkaline treatment was established to isolate polysaccharide-rich water plant pulp, which was used to produce paper-based materials with a tensile strength of up to 63 MPa. Moreover, extractives and protein-rich fractions were separated and evaluated for material utilization.

Water plants, such as *M. spicatum*, have the potential to replace oil-based and woody materials in bio-based applications. This is particularly relevant in combination with the ecological need to manage waterbody systems, which requires the removal of water plants.



THE CHICORY INULIN PROCESS 2.0

de Roode B.M. ^{*a}, van den Bergh J. ^b, van der Weide P ^c

^a *Manager Innovation, Sensus, The Netherlands*

^b *Senior innovation manager, Cosun Research, Development & Innovation, The Netherlands*

^c *Manager Inicio demoplant, Cosun Research, Development & Innovation, The Netherlands*

* matthew.de.roode@sensus.nl

Inulin from chicory is commercially produced for almost 30 years where the center of production lies in de Belgian/Dutch region. As with most capex-intensive processes changes to the process are often a matter of evolution rather than revolution. Consequently, the resulting inulin products are also mere variants on what is already present on the marketplace.

Fortunately, the need for a drastic change can be induced by market demand. In our case, the strong demand for more sustainable and mildly produced products enabled us to implement a more radical approach to the production of inulin from chicory. Instead of improving the existing situation, we went to the drawing board to design an inulin factory with the knowledge of today. This is not straightforward since chicory contains very bitter tasting components. Thus, a new process should be able to purify inulin in such a way that desired plant components are conserved, but that the bitter taste is removed. In order to tackle this problem, a mild process based on sequential membrane steps was designed. The proof of concept was shown in our demo-facilities where the whole process was operated continuously and repeatably at a scalable size.

The resulting product was certified as organic underlining the revolutionary approach. Moreover, the process showed less capex and opex intensive than the traditional processes, while also carbon emission and gas consumption were reduced. Currently, parts of this new inulin process are introduced parallel to our current process in order to reduce costs in this process as well. Due to this introduction, our process also becomes more flexible for producing inulin types that are processed more sustainably. Moreover, the mild process enables to bring inulin variants to the market that still contain healthy plant components while still tasting great.



RENEWABLE AND ACTIVE 3D PRINTED STARCH-BASED PACKAGES DERIVED FROM POTATO AND COFFEE BYPRODUCTS

Idalina Gonçalves^{a*}, Gabriela de Jesus Campos^a, Beatriz Martins^a, Gonçalo Oliveira^{a,b}, Carolina De Jesus Miranda^c, Matilde Pinho Alves^c, Sofia Gama Silva Gomes^c, Tiago E. P. Gomes^d, Martinho Lima^a, Manuel A. Coimbra^b, Paula Vilarinho^a, Paula Ferreira^a

^a CICECO - Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193 Aveiro, Portugal.

^b LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

^c Júlio Dinis High School, 3880-192 Ovar, Portugal.

^d TEMA - Centre for Mechanical Technology and Automation, Department of Mechanical Engineering, University of Aveiro, 3810 - 193 Aveiro, Portugal.

* idalina@ua.pt

The use and production of biobased and biodegradable packages has been steadily increasing. In this context, the biomass used as feedstocks must be sustainably obtained, with no harm to the environment. Agrifood byproducts are largely produced and often discarded while still containing polysaccharides and other biomolecules of interest to develop biodegradable and active packaging materials. In this work, the feasibility of using starch recovered from potato washing slurries blended with coffee byproducts to develop renewable and active 3D printed starch-based packages was studied. The influence of coffee silverskin (CS) and spent coffee grounds (SCG) on physicochemical, rheological, mechanical, and antioxidant properties of starch-based formulations was studied. Extrudability and 3D printability of the most promising formulations were also assessed.

Starch recovered from potato washing slurries allowed to develop thermoplastic, slightly yellowish, and flexible filaments with 1.75 mm thickness, fitting the marketed 3D printers' requirements. However, the low traction resistance compromised their 3D printing ability. CS and SCG allowed to overcome this drawback, while providing a brownish coloration and antioxidant activity to thermoplastic starch-based filaments. Therefore, despite being wasted, starch-rich agrifood byproducts can be blended with other biomolecules and give place to an ecological and circular strategy for the development of sustainable packages.

Acknowledgments: This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects CICECO - Aveiro Institute of Materials (UIDB/50011/2020 & UIDP/50011/2020 & LA/P/0006/2020), LAQV-REQUIMTE (UIDB/50006/2020), and TEMA (UIDB/00481/2020 & UIDP/00481/2020). FCT is thanked for the Individual Call to Scientific Employment Stimulus (IG, CEECIND/00430/2017), and PhD (GO, SFRH/BD/143191/2019) grants. The authors also acknowledge to POTATOPLASTIC project (POCI-01-0247-FEDER-017938), Isolago – Indústria de Plásticos, S. A., A Saloinha, Lda and FEB – Cafés, S. A. and to Design Factory of Aveiro (DFA).



STARCH BASED HOTMELT ADHESIVES AS BIOBASED ALTERNATIVES TO CONVENTIONAL SYSTEMS

Feldner A. ^{*a}, Kießler B.^a, Mende M.^a, Zahel M.^a

^a *Papiertechnische Stiftung, Germany*

* alexander.feldner@ptspaper.de

The packaging market in Germany is a steadily growing market in which paper products play a central role. In many respects, these claim to be an ecologically sensible alternative to plastic packaging due to their renewable basis and the possibility of multiple recycling. They could underline this claim even more in the future if the adhesives that are mostly indispensable for their production were also based on renewable raw materials. Since the development of thermoplastic starch, there have been efforts to use starch- and carbohydrate-based polymers for hotmelt adhesives. Such products are described in numerous publications and patents. However, they are not yet on the market.

Hotmelt adhesives consist of a composite of several components due to their complex mechanism of action between adhesion and cohesion forces. They are formulated from three basic components, the base polymer, tackifiers (resins) and waxes.

Recent research work in our laboratories has succeeded in synthesising a starch ester *in-situ* in the high consistency range by means of reactive extrusion, which is similar to conventional base polymers such as EVA in terms of thermoplastic and rheological properties. Spectroscopic investigations (FTIR and ¹H-NMR) proved that highly substituted esters were generated, whose thermoplastic character can be proven by DSC measurements. Furthermore, the dynamic viscosities are in the same size range as conventionally used petrochemical polymers.

With the novel bio-based base polymers, it may be possible to substitute petrochemical components in hotmelt adhesives in the future and as a result to provide more sustainable adhesive systems for the paper and packaging industry.



IDENTIFICATION OF HEAT-RESISTANT ENZYMES WITH CARBOHYDRATE BINDING MODULES IN BIOMASS DEGRADATION

He L. ^{*a}, Lova S. ^a, Vasiliki M. ^a, Rasmus G. ^a, Lauren M. ^{a,b}.

^a *Division of Glycoscience, Department of Chemistry, KTH Royal Institute of Technology, Stockholm, Sweden*

^b *Wallenberg Wood Science Centre, KTH Royal Institute of Technology, Stockholm, Sweden*

* he4@kth.se

Promoting energy efficiency and a better quality of life through sustainable consumption and production is crucial in today's high energy world. Biofuels and renewable materials made from lignocellulosic biomass play a key role in the circular sustainable bioeconomy. Thermostable enzymes are efficient catalysts for biofuel production due to their robustness and ability to accelerate reaction rates, improve substrate solubility and penetration, and reduce energy input and contamination risks [1]. However, the high cost of enzymes remains a bottleneck in the process, making it necessary to discover more effective process-stable enzymes to maximize hydrolytic efficiency while minimizing enzyme loading for cost-effectiveness.

Our team is exploring a new family of carbohydrate binding modules (CBM92). These small domains are attached to bacterial glycoside hydrolases that break down complex carbohydrates in plant and microbial biomass. We have found that in some cases these CBMs significantly improve enzyme thermostability by 10-20 °C (Figure 1) and enhance hydrolytic capacity up to three times when applied to complex biomass. These findings suggest that CBM92 domains could play a critical role in improving the efficiency of biomass degradation, which has important implications for the production of biofuels and other bioproducts. To gain a better understanding of how these small modules contribute to enzyme activity and thermostability, we are characterizing multiple types of glycoside hydrolases natively fused with CBM92 domains, assessing their impact on the hydrolysis of, among others, chitin, pustulan, and lichenan.

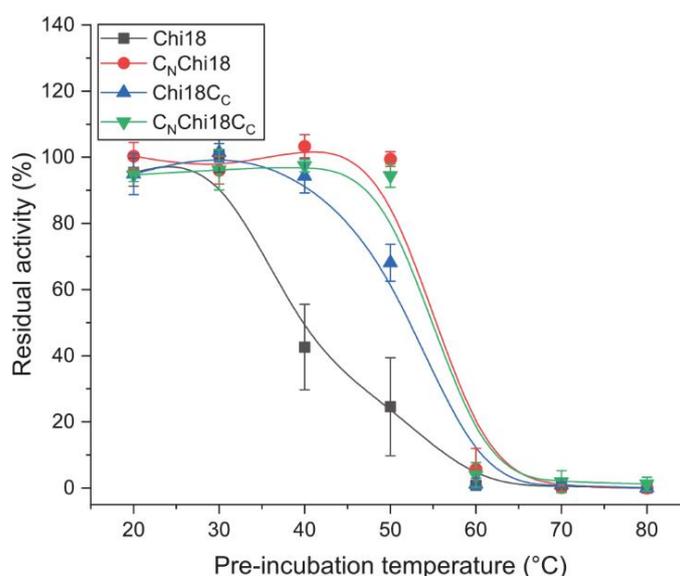


Figure 1 : Thermostability of GH18-containing enzymes

[1] Turnerl P., Mamo G. & Karlsson E.N., *Microb Cell Fact*, 6:9, 2007



WATER-REPELLENT, LOW-DENSITY CELLULOSE-BASED FOAMS: PREPARATION, CHARACTERIZATION, AND BIODEGRADATION

P. Karlsson¹, P. Renström¹, K. Syverud², S. Rodriguez Fabia², H. Edlund³, M. Norgren³, S. Wallstén*¹, P. Westin*¹

¹ MoRe Research Örnsköldsvik AB, SE-891 22 Örnsköldsvik, Sweden,

² RISE PFI, NO-7491 Trondheim, Norway,

³ Mid Sweden University, SE-850 70 Sundsvall, Sweden

*per-oskar.westin@more.se

The demands for alternatives to fossil-based materials for the packaging and building sector is rapidly increasing as new regulations and laws are set. The usage of such materials in low-density applications is increasingly questioned since only a small amount is recycled and a large part ends up in the environment where it has a very long decomposition time and contributes to the emergence of microplastics in our marine eco systems. Alternatives to fossil-based low-density materials has been demonstrated using e.g., starch [1] and cellulose [2] as raw materials. However, challenges remain regarding the process parameters and properties such as strength and water integrity. To fulfil these properties requested by the specification owners, understanding is needed regarding which tools that are available for incorporating wet-integrity and hydrophobicity without causing the wet foam to collapse during the foaming or drying process. It is also of highest importance to have an early understanding of how such materials can be recycled and/or bio-degraded to fit a circular economy.

In this study two different cross-linkers and two different types of hydrophobisers are used to obtain a wet stable and a water repelling low-density material. The wet foams are characterized by measuring the foamability and foam stability and the dry foams are characterized in terms of structure, porosity and degradability. Two demonstrators have been produced based on the most promising material composition and the up-scaling processes of the developed foaming technology to both batch-wise and continuous fabrication of composite foams is underway. Finally, a biodegradation study was conducted and evaluated.



Fig 1. A cellulose-based foam with wet-integrity and hydrophobicity characteristics.



Fig 2. An example of a low-density prototype.

- [1] S. Chaireh, P. Ngasatool, and K. Kaewtatip, "Novel composite foam made from starch and water hyacinth with beeswax coating for food packaging applications," *Int. J. Biol. Macromol.*, vol. 165, pp. 1382–1391, 2020
- [2] C. Qin, M. Yao, Y. Liu, Y. Yang, Y. Zong, and H. Zhao, "MFC/NFC-based foam/aerogel for production of porous materials: Preparation, properties and applications," *Materials (Basel)*, vol. 13, no. 23, pp. 1–21, 2020



ARCHITECTURED PAPERS AND BOARDS BY STARCH-BASED GRID PRINTING: A BIO-INSPIRED, LOW-COST APPROACH TO LIGHTWEIGHT PACKAGING

Turpin C.^{*a}, Viguié J.^a, Reverdy N.^a, Orgéas L.^b, Leroy L.^c, Gourgeon W.^c, Vacher P.^d

^aUniversité Grenoble Alpes, Grenoble INP, CNRS UMR 5518, LGP2, Grenoble, France

^bUniversité Grenoble Alpes, Grenoble INP, CNRS UMR 5522, 3SR, Grenoble, France

^cCentre Technique du Papier (CTP), Grenoble, France

^dUniversité Savoie Mont Blanc, SYMME, Annecy, France

*clement.turpin@lgp2.grenoble-inp.fr

To meet environmental challenges, it is essential to drastically reduce the use of plastics, energy expenditure and the consumption of natural resources. Although paper offers a very interesting bio-based, recyclable and biodegradable alternative to plastic packaging, the paper industry must nevertheless continue its transformation to reduce its consumption of water (10 to 17 m³ per ton of paper), energy (4 to 6 MWh per ton) and wood (3 to 6 ton/ton). LGP2, 3SR and CTP are working on the development of a bio-inspired approach to significantly reduce the weight of packaging while preserving its major function of protecting the product it contains. The panels of the packaging must particularly resist buckling during vertical compression stresses to which it is subjected during storage, transportation, or distribution of products. The buckling resistance of the panels depends directly on the bending stiffness of the material. A very effective solution to increase the bending stiffness-to-weight ratio of a flat structure is to increase the moment of inertia of the section by embossing or forming a network of stiffeners on the surface. This strategy is widely used in nature.

Both "embossed" and "ribbed" structured papers were obtained through 2D printing (industrial screen printing) of patterns from an aqueous starch solution (Fig. 1) [1]. The bending stiffness of a 60 g/m² paper was increased threefold with the addition of only 7 g/m² of starch, achieving a bending stiffness equivalent to that of a 100 g/m² paper, thereby potentially reducing the weight of packaging paper by 35%. However, the underlying mechanisms responsible for the generation of 3D structured relief remain poorly understood. In order to advance our understanding, the kinematic fields on the surface of the paper have been measured by image stereo-correlation during the air-drying of a printed pattern. These data have been used to quantify the shrinkage phenomena along the printed lines and the deformation kinetics of the unprinted areas. They will be utilized to identify the type of loading at the unprinted areas and the boundary conditions along the lines, with the aim of determining whether the phenomenon can be described by a buckling model.

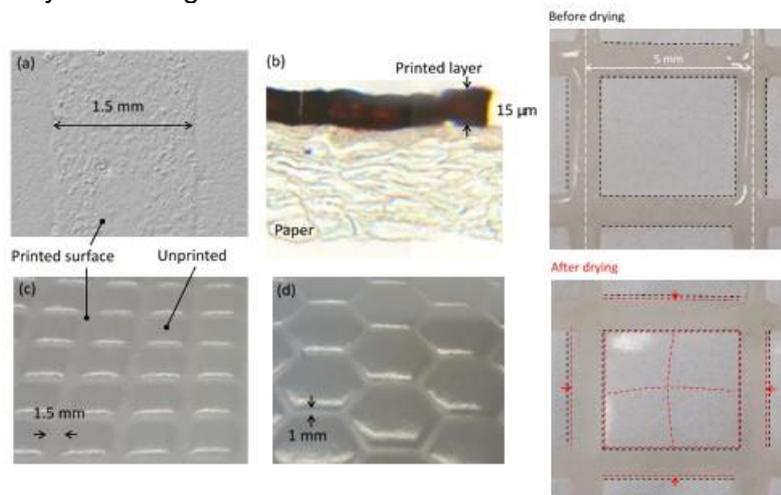


Figure 1: Papers deformed after starch grid printing [1].

[1] Viguié, J., Thalhófer, R., Gourgeon, W., ... & Guérin, D. (2021). Forming architected paper by printing a starch patterned grid: a new low-cost approach for lightweighting packaging. *Cellulose*, 28(10), 6607-6617.



SCREEN-PRINTING OF NANO-FIBRILLATED CELLULOSE FOR AN IMPROVED MOISTURE MANAGEMENT OF FLAME-RESISTANT FABRIC

Tjaša Kolar, Vera Vivod, Vanja Kokol*

^a Faculty of Mechanical Engineering, University of Maribor, Smetanova ul. 17, 2000 Maribor, Slovenia

*vanja.kokol@um.si

Low moisture absorbency of hydrophobically coated flame-resistant (FR) fabrics do not correlate well with the thermo-physiological comfort, i.e. moisture transfer to cool the body and reduce the heat by moisture build-up. In addition, the trend of protective cloths goes in the direction of lighter, environmentally-friendly and user-safe products with an improved performance and wearing comfort, which is difficult to achieve.

In this frame, we were the first to study the effect of screen-printing of different nano-fibrillated cellulose (native, carboxylated, phosphorylated and quarternized) on the fabric surface to meet these requirements and by this also to follow the challenges of sustainability and circularity [1,2]. The micro/nano-cellulose patterning as a function of printing parameters (screen type mesh, pressure of squeegee, and printing speed), and its durability (attachment) after a post-printing of hydrophobic polyacrylate on the same (layer-by-layer) or other side of the fabric will be presented and discussed, thus to maintain one side of the fabric (facing towards the wearer) hydrophilic while keeping the other side (facing outward) hydrophobic. The changing of fabrics properties, abrasion resistance, air permeability and water-vapour resistance, as well as surface wetting and absorbency, will be shown. The synergistic effect of nanocellulose with carbon nanotubes or Al(OH)₃ particles will be presented [3,4].

Acknowledgment: This project has received funding from the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 760601), as well as from the Slovenia Research Agency (Grant agreement No. L2-9249 and research program P2-0424).

[1] Kolar V. Influence of hydroxyethyl and carboxymethyl celluloses on the rheology, water retention and surface tension of water-suspended microfibrillated cellulose. *Cellulose*. 2022, 29(13), 7063–7081.

[2] Kokol V. et al. Screen-printing of microfibrillated cellulose for an improved moisture management, strength and abrasion resistant properties of flame-resistant fabrics. *Cellulose*. 2021, 28, 6663-6678.

[3] Kolar T. & Kokol V. Synergistic effect of screen-printed single-walled carbon nanotubes and phosphorylated cellulose nanofibrils on thermophysiological comfort, thermal/UV resistance, mechanical and electroconductive properties of flame-retardant fabric. *Materials*. 2021, 14(23), 1-23.

[4] Kolar T. et al. Synergistic effect of screen-printed Al(OH)₃Al(OH)₃ nanoparticles and phosphorylated cellulose nanofibrils on the thermophysiological comfort and high-intensive heat protection properties of flame-retardant fabric. *Journal of industrial textiles*. 2022, 51(5), 8267s–8296s.



INVESTIGATION OF PHYSICO-CHEMICAL PROPERTIES OF ISOLATED KERATIN SOLUTION FROM POULTRY FEATHERS BY SUBCRITICAL WATER

Kraševac Glaser T.*^a, Škerget M.^b, Plohl O.^a, Strnad S.^a, Čolnik M.^b, Fras Zemljič L.*^a

^a University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterization of Polymers and Processing of Polymers materials, Smetanova 17, SI-2000 Maribor, Slovenia

^b University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory for Separation Processes and Product Design, Smetanova 17, SI-2000 Maribor, Slovenia

* tjasa.glaser@um.si, lidija.fras@um.si

The use of wool and poultry feather wastes (as renewable sources of biopolymer keratin) has been the subject of numerous research studies due to their high protein content. The biodegradability of keratin, good cell adhesion, and biocompatibility are attracting the interest of researchers as well as consumers and manufacturers. To date, most technologies for recycling keratin from biomass have been harmful, expensive, non-reusable, and difficult to handle [1, 2], generally time consuming, and usually obtained in low yield, with limited solubility, purity, and reduced molecular weights. Nowadays, an innovative technique to recycle protein-based wastes is thermal hydrolysis with water, i.e., hydrothermal processing [3, 4]. Subcritical water, i.e., water at temperatures above 100 °C and elevated pressure, can serve both as a solvent and as a reactant and catalyst in hydrothermal processes due to its specific properties (i.e., lower polarity and higher ionization constant). In the reactions with biomass, it causes the breaking of chemical bonds. However, in order to process the solution obtained, a detailed characterization of this keratin extraction solution must first be performed.

Our goal was to analyze the properties of the keratin solution obtained by hydrothermal degradation of poultry feathers. The solution was analyzed for the following parameters: molecular weight, elemental composition, pH, conductivity, surface tension, turbidity, viscosity, zeta potential and particle size (hydrodynamic diameters). Fourier transform infrared spectroscopy ATR-FTIR confirmed keratin protein structure and indicated its successful isolation. The zeta potential and hydrodynamic diameter were measured as a function of pH to understand the charge behavior, isoelectric point and agglomeration ability as a function of pH. The result for keratin extraction solution showed that macromolecules with an average molecular weight of 9-12 kDa were obtained. Moreover, the solution is a slightly acidic colloidal system with an average particle size of 2.2 μm, which confirmed that it is a suspension. The tendency for the particles to agglomerate was confirmed. The zeta potential was below +/- 30 mV in all pH ranges and the solutions showed amphoteric character.

[1] Sharma S., Gupta A., Brazilian Archives of Biology and Technology, 59, e16150684, 2016

[2] Aluigi A., Corbellini A., Rombaldoni F., Mazzuchetti G., Textile Research Journal, 83(15), p. 1574-1586, 2013

[3] Pahua-Ramos ME, Hernández-Melchor DJ, Camacho-Pérez B., Quezada-Cruz M., BioTechnology: An Indian Journal, 13(6), p. 1-24, 2017

[4] Verdnik A., Čolnik M., Knez Ž., Škerget M., Acta Chimica Slovenica, 68(2), p. 433-440, 2021



UPCYCLING OF PAPER TOWELS – ENZYMATIC SACCHARIFICATION FOR SUSTAINABLE PRODUCTS

Austen D. ^{*a}, Wilharm E. ^a, Patzsch K. ^b, Gebauer I. ^b

^a Ostfalia University of Applied Sciences Wolfenbüttel, Germany

^b Fraunhofer Center for Chemical-Biotechnological Processes CBP Leuna, Germany

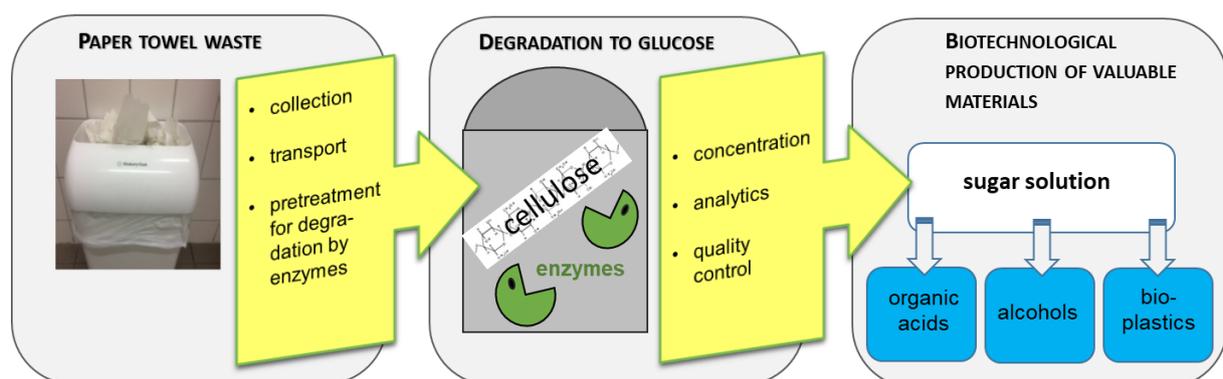
* di.austen@ostfalia.de

The climate crisis and the limited availability of fossil fuels increase the importance of an energy shift and a sustainable, circular economy. Increasingly, the recyclability of waste is required as the basis of a sustainable raw material economy. Cellulosic waste of biogenic origin makes up a large proportion of recyclable waste and is therefore of great importance.

The project Cell2Cell focuses on the material reuse of paper towels, which account for 70 thousand tons of waste per year in public buildings, offices etc in Germany. [1] Currently, the paper towel waste is mainly incinerated with the residual waste. During incineration the cellulose of the paper towels is completely mineralised to CO₂ and released to the atmosphere. Cellulose is composed exclusively of the simple sugar glucose, which can be used as a universal energy and growth substrate for cells and (micro-)organisms for the production of a wide range of biotechnological productions, e.g., alcohols, organic acid, bioplastic and fine chemicals.

During enzymatic break down of cellulose (by cellulases) the carbon backbone remains intact and the release of CO₂ is avoided. We tested different cellulases from filamentous fungi and reached degrees of saccharification of 60 to 80 %. We quantified the degree of saccharification via increase of reducing sugars as well as via the end product glucose using high-performance liquid chromatography.

In a next step several production organisms will be cultivated on the glucose-hydrolysate as sole carbon source. Among those are producers of bioplastic or biofuels, products that are currently produced from oil. If cultivation is successful, a wide range of biotechnological products can be produced from paper towel waste in a climate-neutral way and the process can thus contribute to the waste-based bioeconomy.



Acknowledgements

The German Federal Ministry of Education and Research supports this study financially.

[1] Euromonitor Tissue and Hygiene Research 2017



SACCHARIFICATION OF REJECTS OF PAPER PRODUCTION FOR A CIRCULAR ECONOMY

Klingenberg T.^a, Schleicher M.^{a*}, Wilharm E.^a

^a*Ostfalia University of Applied Sciences Wolfenbüttel, Germany*

*ma.schleicher@ostfalia.de

The transformation of linear product chains to a circular economy is the current challenge in all industrial sectors. Therefore, resource-efficient production is the order of the day in terms of both energy expenditure and material use. The project focuses on rejects in waste paper processing and paper production.

During paper production from the raw material wood and during waste paper processing, short cellulose fibres are produced. In waste paper processing, these are removed from the process with the help of screen sorters. This solid waste is usually referred to as waste paper rejects and, like residual waste, is incinerated and thus removed from the resource cycle.

The raw material wood is largely composed of cellulose, hemicellulose and lignin. From these fractions cellulose not only has the largest share but also the simplest chemical structure. Thus, by means of special enzymes, the cellulases, the linear polysaccharide cellulose can be split into shorter-chain fragments up to the stage of the monomer glucose. The resulting hydrolysis glucose, in turn, can be metabolised as an almost universal carbon and energy substrate by various (micro-)organisms and therefore forms a sought-after fermentation raw material for biotechnological products.

Initial trials show that the cellulose fibres in various rejects of paper production processes can be enzymatically degraded. It is observed that the presence of microorganisms in the waste paper rejects have a negative effect on enzymatic saccharification, as they use the glucose produced for their metabolism. Nevertheless, a degree of saccharification of 44 % could be achieved with the shortest possible saccharification period of 24 hours. With rejects from paper production, a degree of saccharification of up to 63 % could be achieved so far. The optimisation of the saccharification rate and suitability tests of the glucose-hydrolysate against a panel of production microorganisms are currently underway.

Waste paper processing as an example of an already established circular economy process could take on model character for largely closed utilisation cycles in the sense of the bioeconomy through the efficient material reuse of the rejects. In particular, the defossilised economy will focus on the efficient use of complex organic molecules.



CHITOSAN DERIVATIVES FOR WHEAT PROTECTION AGAINST PATHOGENIC FUNGI

Craquelin M.^{*a,b}, Magnin-Robert M.^b, Martin P.^a, Randoux B.^b, Joly N.^a

^aUnité Transformations & Agroressources—ULR7519, UniLasalle, Univ. Artois, F-62408 Béthune, France

^bUnité de Chimie Environnementale et Interactions sur le Vivant (UR 4492), Université du Littoral Côte d'Opale, CS 80699, F-62228 Calais CEDEX

* mathie.craquelin@univ-artois.fr

Chitosan is a well-known natural polymer with diverse biological properties that has been extensively researched in various fields such as medicine, cosmetics, water treatment, biocontrol, and plant biostimulation [1]. It is considered a good candidate for replacing a part of chemical fungicides used in agricultural fields [2]. However, two key parameters, namely the degree of polymerization (DP) and the degree of acetylation (DA), influence the protection conferred by chitosan to plants against pathogens. In addition, chitosan can act as both a biofungicide and an inducer of plant resistance.

Different methods of modifications have been explored to obtain various fractions of chitosans by deacetylation and depolymerization. Deacetylation was typically carried out chemically, with or without the use of ultrasonication [2], while depolymerization was achieved through chemical [4] or enzymatic processes [5]. Deacetylation and depolymerization led to chitooligosaccharides with various DA and DP both determined by titration and GPC, respectively. FTIR-ATR and TGA / DSC analyses were conducted to ensure that the integrity of the polymer is maintained.

Each fraction obtained was tested in controlled conditions for its protective effect on wheat against two phytopathogenic fungi, namely *Blumeria graminis* f.sp. *tritici* and *Zymoseptoria tritici*, responsible for powdery mildew and septoria tritici blotch on aerial parts of wheat, respectively. Their direct antigerminative effect on spores of both fungus species was also assessed *in vitro*.

These tests will allow the selection of the most effective chitosan fractions to protect wheat against both pathogens, and to determine if the protection obtained is associated with a fungistatic or fungicide effect. The fractions that show the most promising potential will be further reworked in order to better characterize them and gain a deeper understanding of their mode of action.

[1] Wang W., Xue C., Mao X., International Journal of Biological Macromolecules, 164, 4532–4546, 2020.

[2] Birolli W. G., Delezuk J. A. de M., Campana-Filho S. P., Applied Acoustics, 103, 239–242, 2016.

[3] El Hadrami A., Adam L. R., El Hadrami I., Daayf F., Marine Drugs, 8, 968–987, 2010.

[4] Lee M.-Y., Var F., Shin-ya Y., Kajiuchi T., Yang J.-W., Process Biochemistry, 34, 493–500, 1999.

[5] Roncal T., Oviedo A., de Armentia I. L., Fernández L., Villarán M. C., Carbohydrate Research, 342, 2750–2756, 2007.



ACETYLATION OF ANHYDROGLUCOSE TO ENHANCE THE HYDROPHOBIC PERFORMANCE OF STALE BREAD AS PACKAGING MATERIAL

Skov., K. B. ^{*a}, Portillo, G. ^a, Martinez M.M. ^a

^aCenter for Innovative Food (CiFOOD), Department of Food Science, Aarhus University, AgroFood Park 48, Aarhus N, 8200, Denmark

[*kbs@food.au.dk](mailto:kbs@food.au.dk)

The distribution scheme of bread favors opportunities for redistribution pathways that are not always viable for mixed waste or microbiologically contaminated fractions. Here, we propose the exploitation of bread waste as a high-performing biopolymer blend for packaging applications by eliminating the shortcomings associated with its high hydrophilicity. To do so, we have successfully modified the primary component of wheat bread, starch, via a sustainable, catalyst-free acetylation reaction using choline chloride/urea deep eutectic solvent as reaction promoter with a reaction time of less than one hour. The degree of substitution of hydroxyl groups by alkanoyl groups was determined by ¹H NMR and ¹³C solid-state NMR. Furthermore, molecular degradation of starch, gluten and water extractable arabinoxylans was investigated by SEC-MALS and glycomic profiling using HPAEC-PAD. Results showed a degree of substitution of between 0.6 and 1.1, which preserves the possibilities for further derivatization reactions. TGA coupled with FTIR revealed additional interactions and degradation of bread macromolecules (e.g., starch and gluten) upon derivatization. The opposite trend between DUMAS and Bradford assays suggested the binding of the solvent to the bread matrix. Finally, the thermal stability of the acetylated bread matrix was investigated using TGA and DSC, with DSC showing a higher onset of glass transition temperature up to 165°C compared to non-modified pure starch (60°C) and modified pure starch (158°C). Our research demonstrates the potential of a catalyst-free acetylation reaction to remove the shortcoming of the stale bread matrix to perform as a biomaterial.



AMPHIPHILIC HEMICELLULOSE AS A STABILIZER IN AQUEOUS DISPERSION COATING

Kvikant M. ^{*a}, Filonenko S ^b, Dax D. ^c, Nick T. ^a, Toivakka M. ^a, Xu C. ^a

^a *Laboratory of Natural Materials Technology, Åbo Akademi University, Henrikinkatu 2, Turku, Finland*

^b *Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, Potsdam, Germany*

^c *Sustainable and Bio-inspired Materials, Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, Potsdam, Germany*

* mkvikant@abo.fi

Dispersants are crucial components in polymer dispersions for a wide range of materials and products, such as packaging and barriers, paints, adhesives, and sealants. However, the use of conventional surfactants as dispersants, poses several challenges in terms of safety and environmental impact, as they often derive from petroleum and are partly not biodegradable. This has led to a need to explore alternative solutions for dispersants that are environmentally safer and more sustainable.¹

This study focuses on the potential of underutilized resources and exploring their value-added applications in various industries. Hemicelluloses have a lot of value-added potential as current forest industry processes, often overlook lignocellulosic components beyond cellulose and are often considered of no more value than their energy value in burning. The present study utilizes galactoglucomannans (GGMs), the major type of hemicellulose found in softwood, which has been identified as a promising material to produce bio-based surfactants.² Furthermore, in this study, suberin is utilized, a complex and wax-like biopolymer consisting of long-chain fatty acids and glycerol. Suberin is predominantly found in the cell walls of certain plant tissues, such as cork and bark and can be derived from waste generated by agricultural industries. The suberin compounds act as a hydrophobic barrier for plants, making them a promising material for use in barrier coatings on fibre-based packaging.³

This study aims to stabilize suberin in an aqueous dispersion coating formulation by utilizing an amphiphilic GGM derivative, grafted with naturally occurring fatty acids. The GGM derivatives have various substitution degrees and fatty acid chain lengths, which determine their physicochemical properties such as the hydrophilic-lipophilic balance and surface tension, critical for controlling their dispersing ability. This study also evaluates the dispersion formulation and stability parameters, including droplet size and charge, surface activity, pH, and temperature. Currently, dispersion coating and oil in water emulsion stability testing using amphiphilic GGM derivatives are ongoing with promising preliminary results.

1. Bhadani, A. *et al.* Current perspective of sustainable surfactants based on renewable building blocks. *Curr. Opin. Colloid Interface Sci.* **45**, 124–135 (2020).
2. Mikkonen, K. S., Xu, C., Berton-Carabin, C. & Schroën, K. Spruce galactoglucomannans in rapeseed oil-in-water emulsions: Efficient stabilization performance and structural partitioning. *Food Hydrocoll.* **52**, 615–624 (2016).
3. Heinämäki, J. *et al.* Suberin fatty acids isolated from outer birch bark improve moisture barrier properties of cellulose ether films intended for tablet coatings. *Int. J. Pharm.* **489**, 91–99 (2015).



CIRCULAR VALORISATION OF INDUSTRIAL ALGAE WASTE STREAMS INTO HIGH-VALUE PRODUCTS TO FOSTER FUTURE SUSTAINABLE BLUE BIOREFINERIES IN EUROPE

Amparo Lopez-Rubio^{*a}, Josep Biosca^a, Eugenia Nuñez^a, Maria José Fabra^a and Antonio Martínez-Abad^a

^a *Food Safety and Preservation Department, Institute of Agrochemistry and Food Technology (IATA-CSIC), Valencia, Spain*

* amparo.lopez@iata.csic.es

Algae biomass is highly underexploited and its efficient utilization is one of the main challenges in current and future EU marine policies towards sustainability. CIRCALGAE will boost the blue bioeconomy by applying an integrated biorefinery concept to valorise the massively produced (over 36 Mt of algae biomass annual world production) and vastly underexploited algae industrial waste streams (which can add up to 95% of the initial biomass) from the main existing sources to date: the phycocolloid production from macroalgae and protein/lipid microalgae industries¹. CIRCALGAE's simple, water-based technologies, will transform these waste streams into value-added ingredients to be used in specific texturized vegan foods, health-promoting food ingredients, protein rich feed, and cosmetic formulations incorporating texturizing or highly bioactive ingredients for topical use. Three blue biorefinery schemes up-scaled to hundreds of kg will be demonstrated throughout CIRCALGAE project. Twelve demonstrator products will be developed by food, feed and cosmetic industry partners validating the great potential of novel algae ingredients in these key sectors. Additionally, two final products will be qualified for market including their studies in consumer acceptance assessments. CIRCALGAE will connect all algae cross-sectional actors, will connect industrial end-user partners with RTOs, technological and consultancy SMEs for the final validation of all health-promoting effects and claims, regulatory aspects and environmental, economic or social impacts, with emphasis in re-shaping the existing marine industrial network by co-creating and co-learning. With a duration of 48 months, a total budget of 10,332,894€, CIRCALGAE is fully in line with the destination "Circular economy and bioeconomy sectors" and further contributes to other key points in the European Green deal and Farm2Fork strategies supporting the role of algae in sustainable food systems.

[1] Araujo, R., Brief on algae biomass production, Lusser, M., Sanchez Lopez, J. and Avraamides, M. editor(s), Publications Office of the European Union (2019), ISBN 978-92-76-12271-5, doi:10.2760/665775.



NANOCELLULOSE PRODUCTION AND APPLICATION IN TISSUE ENGINEERING

Mohan T.^{a*}, Lackner F.^a Šurina P.^{a*}, Steindorfer T.^{a*}, Kargl R.^a, Stana Kleinschek K.^a

^aInstitute of Chemistry and Technology of Biobased System (IBioSys), Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria.

*p.surina@student.tugraz.at

The use of environmentally friendly, renewable, and sustainable biomaterials is becoming increasingly important. This area of research has attracted the interest of academy and industry because such materials are one solution to resource depletion, environmental pollution, global warming, and the energy crisis. Moreover, biopolymers are essential in biomedicine and nutrition. In this context, so called nanocelluloses and other biopolymer-based nanomaterials are considered promising. Those are isolated as nano-particles, very thin fibres, or crystals from ubiquitous renewable biopolymer sources; example cellulosic sources (e.g., wood, algae, bacteria (also polyesters), tunicates). These materials can be sourced from conventional agriculture and forestry, but more importantly, can be obtained through industrial biotechnology in the future. They are biodegradable and combine stiffness with high strength, low thermal expansion, low density, high dimensional stability, and can be modified during and after biosynthesis or processing.

Due to these properties, nano-fibrillated celluloses (NFC) and other nano- biopolymers are expected to appear in various markets soon. These include paper, pulp and packaging, composites, sound and thermal insulation, batteries and fuel cells, sensors, tissue regeneration, 3D printing, drug delivery, cosmetics, and food.

NFC can be produced in larger quantities from biogenic fibres (1 wt%, in 1 liter/hour) using a high-pressure device known as homogenizer as the core technology (GEA Lab Homogenizer Panther 3006, 1.500 bar, **Figure 1**). Pre- and post-treatment equipment for nano-fibre production is followed by characterization/analytcs.

IBioSys at the Graz University of Technology/Austria is already working with NFC for biomedical applications such as 3D printing and tissue regeneration. The procurement of the microfluidizer will allow to produce high quality NFC, and a large variety of other nanoparticles, fibrils and emulsions based on renewable resources. Products and feedstock can be analysed using HPLC/GC. In this presentation, an overview on the GEA homogenizer unit and some potential applications of the produced NFC to create aligned structures [1] and scaffolds for TE will be given.

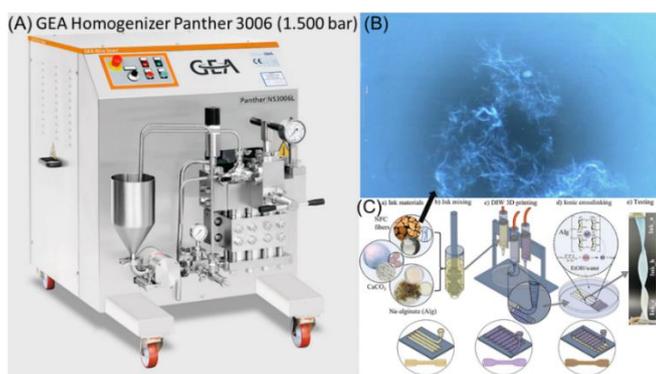


Figure 1. Images of GEA homogenizer and produced nanofibrillated cellulose (B) and application of NFC in 3D printing (C).

- [1] Lackner F., Liu H., Štiglic A.D., Bračić M., Kargl R., Nidetzky B., Mohan T., Kleinschek K.S., *ACS Applied Bio Materials*, DOI: 10.1021/acsabm.2c00763, 2022.



ALL-CELLULOSE SANDWICHES

Debabèche, N. ^{*a}, Wagner, M., Biegler, V., Feist, F., Jiang, Q.^b, Bismarck A. ^a

^a *Institute of Material Chemistry and Research, University of Vienna, Austria*

^b *Vehicle Safety Institute, Technical University of Graz, Austria*

* nesrine.battoul.debabeche@univie.ac.at

Have you ever wondered how to make moulded cellulose pulp foams stronger? Cellulose foams prepared by frothing to introduce air have into pulp suspensions have been reported but these foams are rather weak yet might find promising applications in the construction sector or design space. We will show how to customise such cellulose foams made from wood pulp fibers. Pulp fibres are frothed with surfactants to stabilize the foam and additives to bond the fibres effectively and strengthen the foams. The resulting solid foam after drying is a lightweight high porosity material. We will demonstrate that the mechanical properties of these lightweight materials can be significantly improved using a sandwich approach. We will discuss the design concept and resulting mechanical properties of these novel moulded cellulose materials.



CHEMICAL REACTIVITY OF VERY SWOLLEN CELLULOSE

La Placa A. ^a, Sjöstrand B. ^b, Henriksson G. ^a, Ek M. ^a

^a Wallenberg Wood Science Center, KTH Royal Institute of Technology, Sweden

^b Department of Engineering and Chemical Science, Karlstad University, Sweden

* anlp@kth.se

Cellulose, as the most abundant biopolymer on earth, is an excellent feedstock for a variety of products. However, the intrinsic properties of cellulose, being hydrophobic but also insoluble in water, hinder its potential use in some technical applications. One way to overcome these limitations is to functionalize cellulose via derivatization. Nevertheless, cellulose has rather poor and uneven reactivity due to its crystalline structure and processing can amplify these issues, such as hornification [1].

In this project, highly crystalline cellulose (Avicel) has been dissolved in cold alkali and reprecipitated using acid to form less crystalline and highly swollen cellulose. Previous work by Wang, et al. [2] has shown that such very swollen cellulose is degraded very fast with strong acids or enzymes. Here we aim to use the technique in the making of cellulose derivatives. However, air-drying the precipitated cellulose causes severe hornification, which lowers the reactivity. In this study, we investigate different approaches to hinder hornification, i.e. drying in the presence of glycerol, from acetone, and with freeze-drying (Figure 1). Water retention value (WRV) was investigated as an indirect measurement of the hornification reactivity of the cellulose [3]. In addition, the samples have been carboxymethylated and the degree of substitution (DS) indicates if the samples are more reactive than the crystalline Avicel.

From the results, it is apparent that reprecipitating the cellulose gives a less crystalline and highly swollen cellulose, but that different drying methods give a different degree of hornification and thereby varying reactivity.

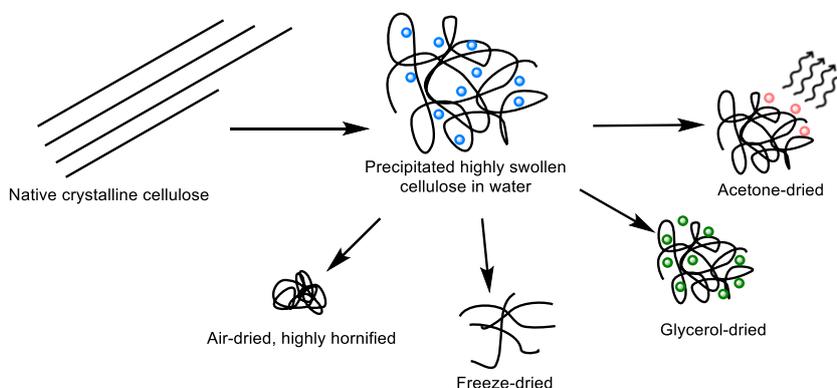


Figure 1: Graphical representation of the cellulose chains after precipitation and different drying methods.

- [1] D. Klemm, *Comprehensive Cellulose Chemistry: Vol. 1: Fundamentals and Analytical Methods*. Vol. 1, 1st ed. ed. Place of publication not identified: John Wiley & Sons Incorporated, 1998.
- [2] Y. Wang, M. E. Lindström, and G. Henriksson, "Mild alkaline treatment activates spruce wood for enzymatic processing: A possible stage in bio-refinery processes," *BioResources*, Article vol. 6, no. 3, pp. 2425-2434, 2011. [Online]. Available: <https://www.scopus.com/inward/record.uri?eid=2-s2.0-80051559058&partnerID=40&md5=516c2cc03938c006820ee4567d0e0732>.
- [3] G. Laivins and A. Scallan, "The mechanism of hornification of wood pulps," *Products of papermaking*, vol. 2, p. 1235, 1993.



MICROFIBRILLATED CELLULOSE (MFC) CRYOGEL INCORPORATED WITH POLY(LACTIC ACID) (PLA) NANOPARTICLES

SUQUISAQUI, A.B.V.^{*a,b}, SILLARD, C.^a, BETTINI, S.H.P.^b, BRAS, J.^a,

^a *Universtité Grenoble Alpes, Grenoble INP LGP2, France*

^b *UFSCAR, Sao Carlos, Brazil*

* ana-beatriz.valim-suquisaqui@grenoble-inp.fr

Plastic consumption has become a significant threat once it is prevenient from fossil source and can take hundreds of years to decompose in the nature. Challenges related to recycling initiatives or the capacity of process recyclable waste may be reasons why the world recycles only 24% of recyclable post-consumer material [1]. As a result, the accumulation of plastic in different environments can result in microplastic pollution, which leads to negative impacts. Within the category of plastic products, polymeric foams are widely used in several applications and although this type of material is technically possible to be recycled, its process presents some challenges in terms of logistics and economics, which can make it not suitable [2]. In this context, the use of biobased and biodegradable materials can be an alternative to conventional plastics. Cellulose, the most abundant renewable polymer on Earth, emerges as an alternative material [3] in which can also be presented as a low density option, in applications as packaging, cushioning, insulation, tissue engineering, among others. Low density cellulose materials can have their morphology influenced by the drying method, including freeze-drying, which will result in the so called cryogels [4]. However, these materials can present some challenges, for instance, the tendency to redisperse and disassemble in water, which is not favorable for applications that is necessary high liquid absorption [3]. Therefore, the aim of this research is to study the properties of MFC cryogels incorporated with PLA nanoparticles.

To produce the MFC cryogels, first a PLA nanoemulsion was prepared by dissolving PLA in dicholoromethane and a biodegradable surfactant in water. Both phases were mixed and ultrasonicated for 2 minutes. Nanoemulsion was heated in water bath at 45°C to allow solvent evaporation. Finally, the resulting nanoemulsion was submitted to 3 cycles of centrifugation to eliminate the surfactant. The cryogels were prepared by mixing MFC at 3 wt%, with PLA nanoparticles in 10 and 20% wt, followed by freezing the samples in liquid nitrogen and drying by freeze-drying for 64h.

Figure 1 presents the MFC cryogel with 10 wt% of PLA nanoparticles. For achieve the objective, samples were analyzed by compression test, vapor absorption and SEM.



Figure 1: MFC cryogels with 10% of PLA nanoparticles.

This research can bring new results and perspectives to the study of low density cellulose based materials once no other example was found in literature using this type of approach.

[1] Wolf, M. J., et al. New Heven, CT: *Yale Center for Environmental Law & Policy*, 2022.

[2] Oliveira, C.T.; Luna, M.M.M.; Campos, L.M.S. *Journal of Cleaner Production*, 235, 562–573, 2019.

[3] de France, K.J.; Hoare, T.; Cranston, E.D. *Chemistry of Materials*. 29, 4609-4631, 2017. [4]

Buchtová, N.; Budtova, T. *Cellulose*. 23, 2585-2595, 2016.



TAILORED NANOCELLULOSE-MICROORGANISM INTERACTION: SWIMMING SUPRAPARTICLES

Eduardo M. Daniél¹, Bruno D. Mattos², Marco Beaumont³, Thomas Rosenau³, Caio G. Otoni⁴, Orlando J. Rojas⁵

¹ *Department of Physics, Federal University of São Carlos (UFSCar), São Carlos, SP, Brazil*

² *Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland*

³ *Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences (BOKU), Vienna, Austria*

⁴ *Graduate Program in Materials Science and Engineering (PPGCEM) & Department of Materials Engineering (DEMa), Federal University of São Carlos (UFSCar), São Carlos, SP, Brazil*

⁵ *BioProducts Institute (BPI), University of British Columbia (UBC), Vancouver, Canada*

Cellulose presents an outstanding renewable building block for materials, in particular, its nanofibrillated form (CNF) that benefits from the high aspect ratio and flexibility merged with the features of mechanical robustness, biodegradability, biocompatibility, and ability to undergo surface modification that is inherent to cellulose. In this contribution, we harnessed these exceptional features of CNF to build materials that ensure the protection and viability of technological yeasts. CNF was used to interlock active *Saccharomyces cerevisiae* cells into quasi-spherical supraparticles produced by drop-cast onto a superhydrophobic PTFE substrate. Mixtures of CNF, silica particles, and yeast yielded porous assemblies, which allowed access to the nutrients required for fermentation and CO₂ production, leading to self-propelled supraparticles with vertical motility tethered to the fermentative process. In this study, the role of silica in the particles was explored to find more eco-friendly and renewable alternatives. In addition, the stability of the supraparticles was increased through functional additives, which enable physical crosslinking reinforcing the particle assembly. Overall, this work highlights the potential of harnessing CNF's unique properties to create innovative and efficient systems for the encapsulation of bioactive compounds to produce microswimmers and to tailor the efficiency of fermentation processes.

Funding: São Paulo Research Foundation (FAPESP; grants no. 2017/07013-1 and 2022/08780-4).

Keywords: cellulose nanofibers, supraparticles, yeasts, microswimmers

