

LU aus Technischer Chemie (CHE.161UF)

Polymerverarbeitung Laborkurs virtuell

Sommersemester (SS) 2022

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Institut für Chemie und Technologie Biobasierter Systeme
(IBIOSYS)
Technische Universität Graz

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- 2.3.2. Herstellung von Zugprüfstäben durch UV-Vernetzung von PDMS

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- 2.4.2. Quarzkristall-Mikrowaage mit Dissipation (QCM-D): Theorie und Anwendungsbeispiele

0. Allgemeine Informationen

0.1. Lernziele

- Methoden der Polymerverarbeitung kennen
- Die Viskosität von Polymerlösungen und Schmelzen erklären können
- Polymerlösungen / Gele herstellen können
- Polymere durch Extrusion auf einem 3D Drucker verarbeiten können
- Polymere zu Fasern verspinnen können
- Silikone durch UV-Licht vernetzen können
- Mechanische Zugprüfung kennen

0.2. Lernunterlagen und Termine

- Laborskriptum zur Übung – ICTM webpage
 - <https://www.tugraz.at/institute/ictm/education/bach-chem/>
- Termine - alle Webex – link wird vorab gesendet (**im Fall einer Quarantäne**)
 - **Vorbesprechung: 24.02.2021, 14:45-15:45**
 - **Laborübung Feb 13 – 18 Uhr (siehe Unterlagen Prof. Robert Saf)**
 - Aktive Diskussion des theoretischen Hintergrunds
 - Kommentierte Videos der praktischen Laborarbeit
- Bücher
 - Baird, Donald G. Polymer Processing. Wiley Professional, Reference & Trade (Wiley K&L), 2014.
 - *Ed. Fakirov Handbook of Condensation Thermoplastic Elastomer*. WILEY-VCH: Weinheim, Germany, 2005.

0.3. Beurteilung

- Pro Übung werden 10 Punkte vergeben
 - Eingangskolloquium (mündlich online) (**Skriptum ansehen!**)
 - Arbeit im Labor (virtuell aktive Teilnahme an Diskussion)
 - Protokoll – Übersicht zu den Experimenten u. Literatur
 - Nachbesprechung der Protokolle
- Protokolle bis SPÄTESTENS eine Woche nach der Übung!
- Linearer Notenschlüssel (max. 100 Punkte, ≥ 50 Punkte für ‚Genügend‘)

0.4. Kolloquiumsfragen

F1: Welche Möglichkeiten der Verarbeitung von Polymerschmelzen kennen Sie, und wie unterscheiden sich diese?

F2: Eine Schmelze von hochmolekularem Polyethylen wird mit einem Zweischaubenextruder im Spritzguss verarbeitet. Ändert sich die dynamische Viskosität der Schmelze, wenn die Drehzahl des Extruders bei gleicher Temperatur erhöht wird? Wie wird ein solches Verhalten genannt?

F3: Wie und woraus stellt die Kunststoffindustrie PET Getränkeflaschen her? Wird PET auch als Textilfaser verwendet?

F4: Wie wird das Polymer Hydroxyethyl cellulose (HEC) chemisch hergestellt? Wozu wird es im Alltag verwendet?

F5: Welche Arten der generativen Fertigung kennen Sie? Was unterscheidet diese?

F6: Was sind thermoplastische Elastomere? Wie erklärt man sich Ihre Eigenschaften?

F7: Was ist die Thiol-ene Reaktion? Wozu kann sie verwendet werden?

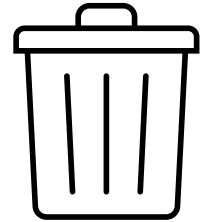
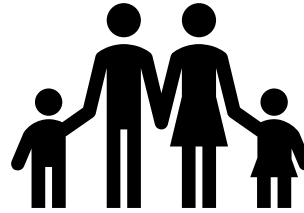
F8: Welche Spinnverfahren für Fasern kennen Sie und was unterscheidet diese?

0.5. Protokoll

- Zusammenfassung der durchgeführten Experimente (2-4 Seiten)
- Verwenden Sie die Daten zu den Zugprüfversuchen aus dem per email gesendeten Excel sheet für das Protokoll:
 - **2.1.2 3D Druck von Thermoplasten (Sample Thermoplastisches Elastomer und ester)**
 - 2.3. Gießen und Härten von Silikonen (Sample Silikon)
 - **2.4.1 Herstellung und Hydrolyse von Trimethylsilylcellulose (TMSC) Filme zu Cellulose Filme**
 - **2.4.2. Quarzkristall-Mikrowaage mit Dissipation (QCM-D): Theorie und Anwendungsbeispiele**
- Wählen Sie selbst ein Unterkapitel aus einer der folgenden Publikation und fügen Sie eine kurze Zusammenfassung (1-2 Seiten) dieses Kapitels ins Protokoll ein
 - Lim, K. S.; Galarraga, J. H.; Cui, X.; Lindberg, G. C. J.; Burdick, J. A.; Woodfield, T. B. F., Fundamentals and Applications of Photo-Cross-Linking in Bioprinting. *Chemical Reviews* **2020**.
 - Schaffner, M.; Faber, J. A.; Pianegonda, L.; Rühls, P. A.; Coulter, F.; Studart, A. R., 3D printing of robotic soft actuators with programmable bioinspired architectures. *Nature Communications* **2018**, 9 (1), 878.

1.1. Warum Polymerverarbeitung?

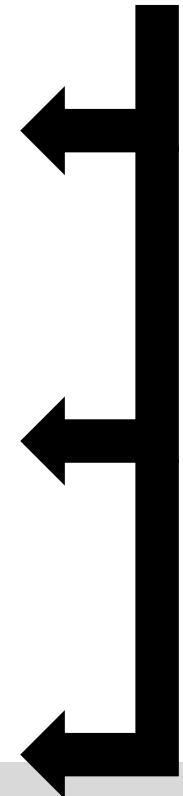
Form
Funktion
Gebrauchswert
Nutzen/Schaden?



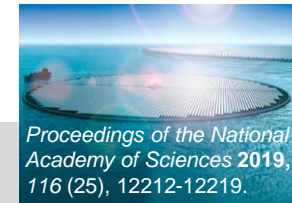
Polymerverarbeitung



Chemische Synthese



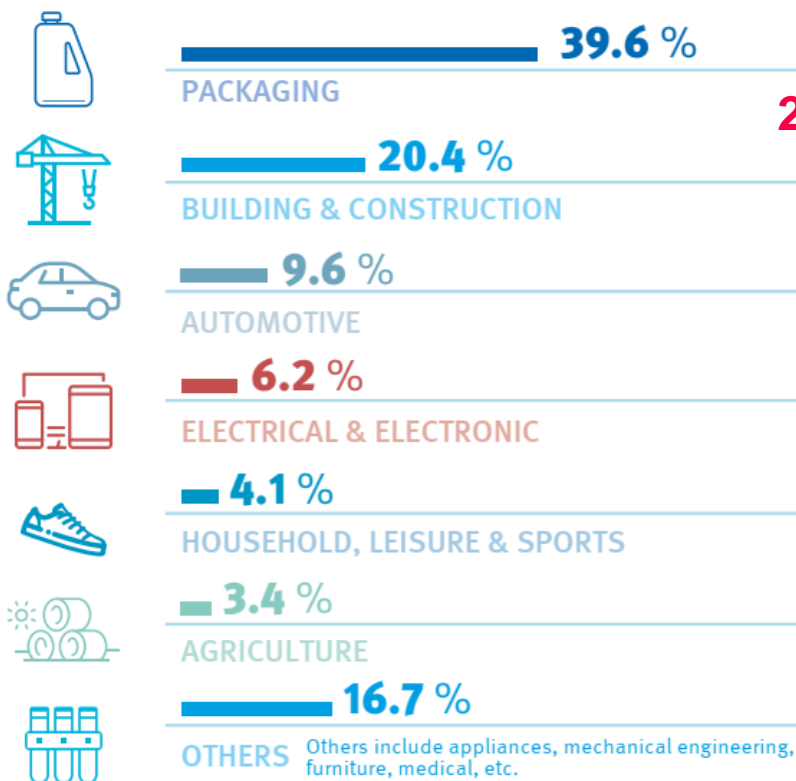
Rohstoffextraktion



PLASTICS DEMAND BY SEGMENT 2019

Distribution of European (EU28+NO/CH) plastics converters demand by segment in 2019. Packaging and building & construction by far represent the largest end-use markets. The third biggest end-use market is the automotive industry.

SOURCE: PlasticsEurope Market Research Group (PEMRG) and Conversio Market & Strategy GmbH



250 g / person / day

50.7 Million tonnes
Total European plastics converters demand



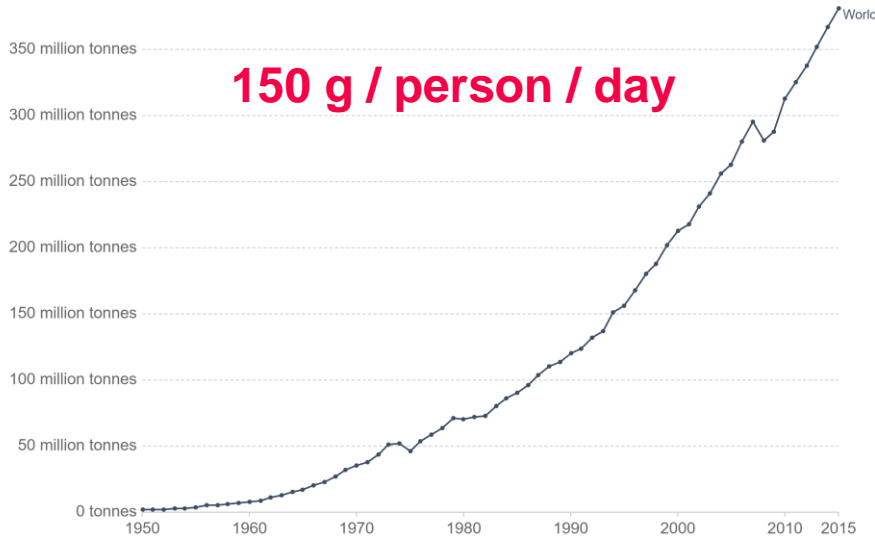
3 kg / person / day

In 2018, total imports of **crude oil** to the **EU** amounted to **512.5 million tonnes**

<https://ec.europa.eu/eurostat/statistics-explained/pdfscache/43212.pdf>

Global plastics production, 1950 to 2015

Annual global polymer resin and fiber production (plastic production), measured in metric tonnes per year.



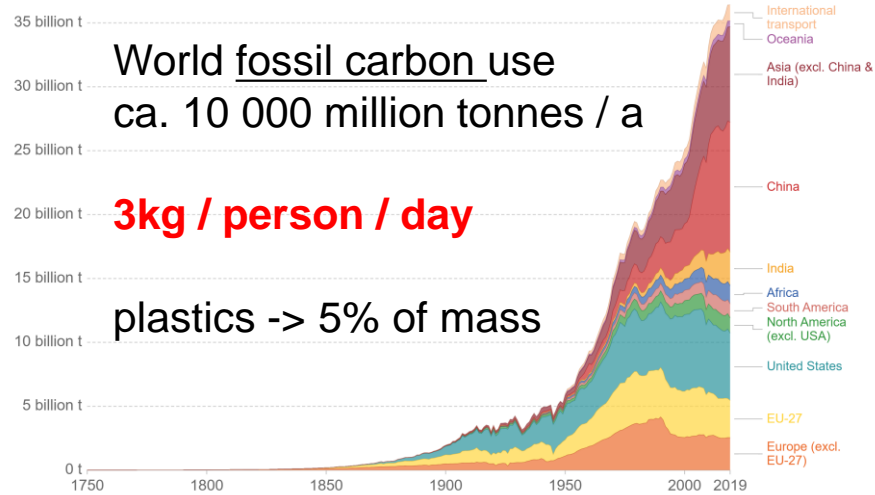
150 g / person / day

Source: Geyer et al. (2017)

CC BY

Annual total CO₂ emissions, by world region

This measures CO₂ emissions from fossil fuels and cement production only – land use change is not included.



World fossil carbon use
ca. 10 000 million tonnes / a

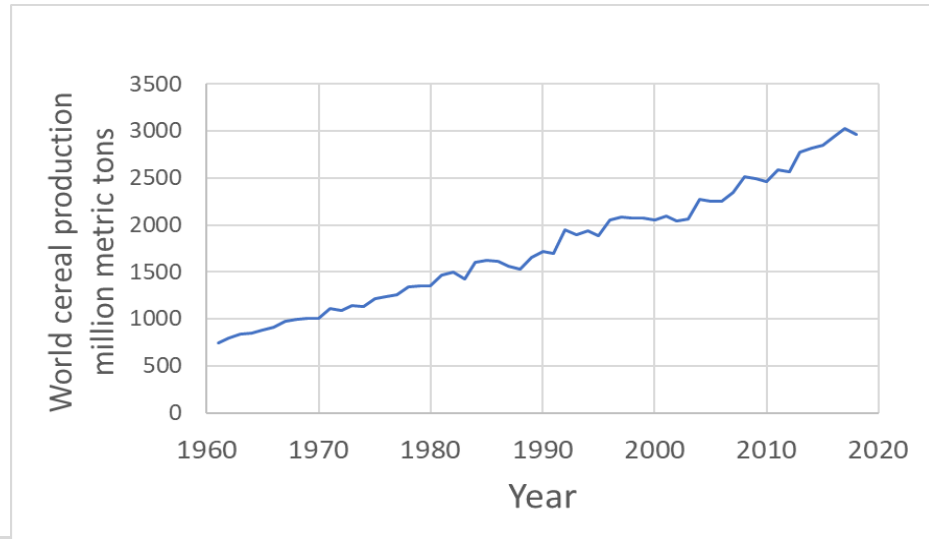
3kg / person / day

plastics -> 5% of mass

Source: Our World in Data based on the Global Carbon Project

Note: 'Statistical differences' included in the GCP dataset is not included here.

OurWorldInData.org/co2-and-other-greenhouse-gas-emissions • CC BY



World cereal production

wheat, rice, maize....

ca. 3000 million tonnes / a

1kg / person / day

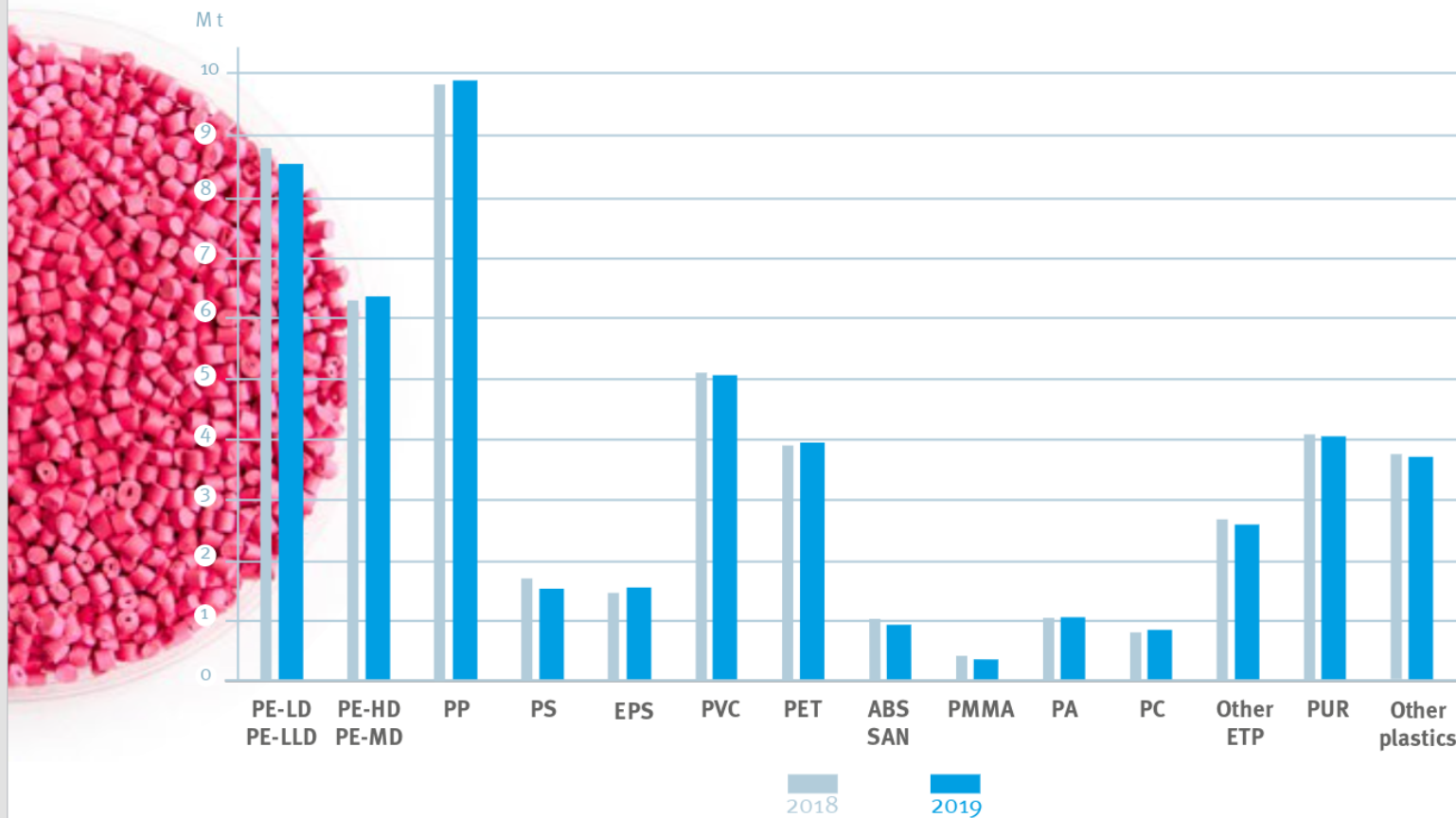
biobased ;-)



SOURCE: PlasticsEurope
Market Research Group
(PEMRG) and Conversio
Market & Strategy GmbH

PLASTICS DEMAND BY RESIN TYPE 2019

Distribution of European (EU28+NO/CH) plastics converters demand by resin type in 2019.
Leading polymers are the polyolefins (PE & PP).

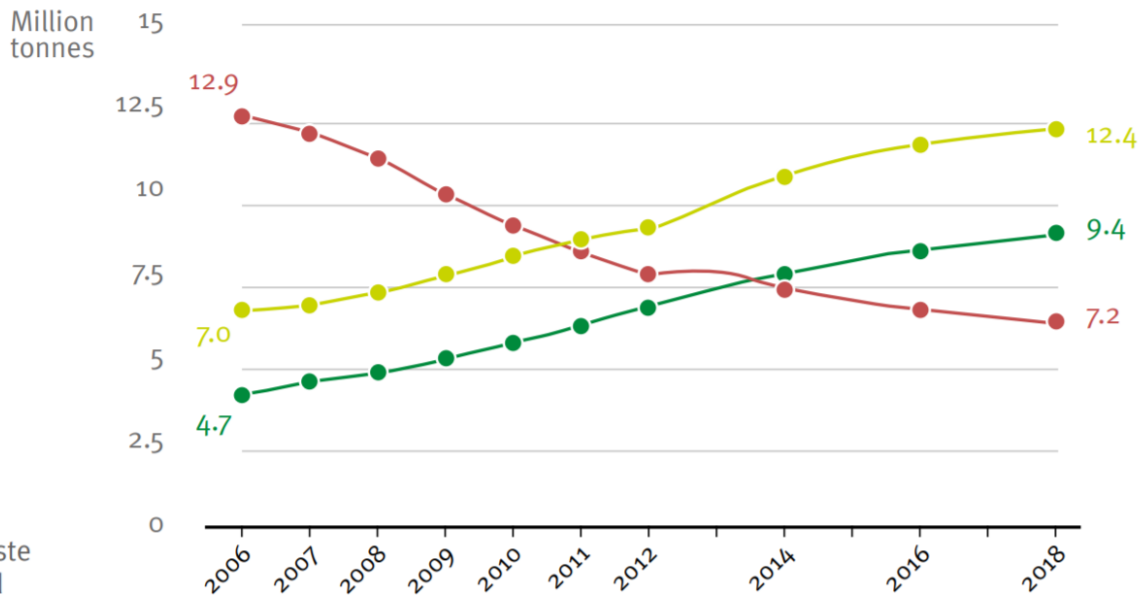
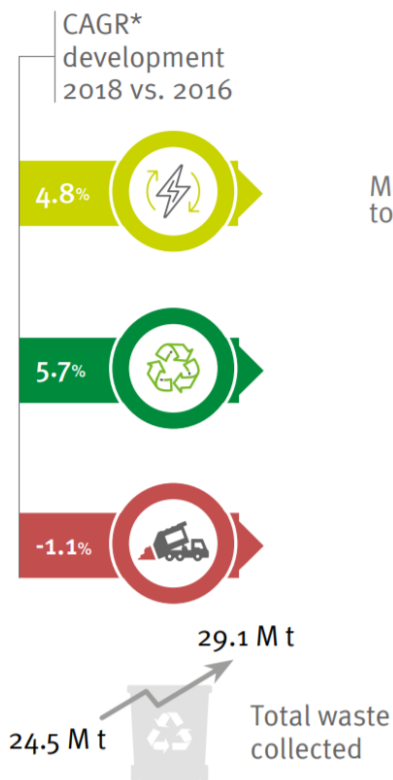
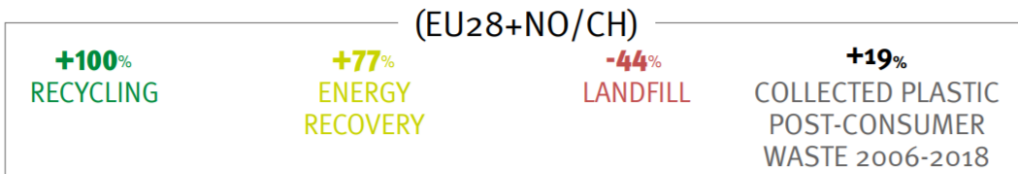


SOURCE: Conversio Market & Strategy GmbH
 *CAGR: Compound Annual Growth Rate is the mean annual growth rate over a specific period of time

SINCE 2006, THE AMOUNT OF PLASTIC WASTE SENT TO RECYCLING HAS DOUBLED

However, 25% of plastic post-consumer waste was still sent to landfill in 2018.

2006-2018 evolution of plastic post-consumer waste treatment (EU28+NO/CH)

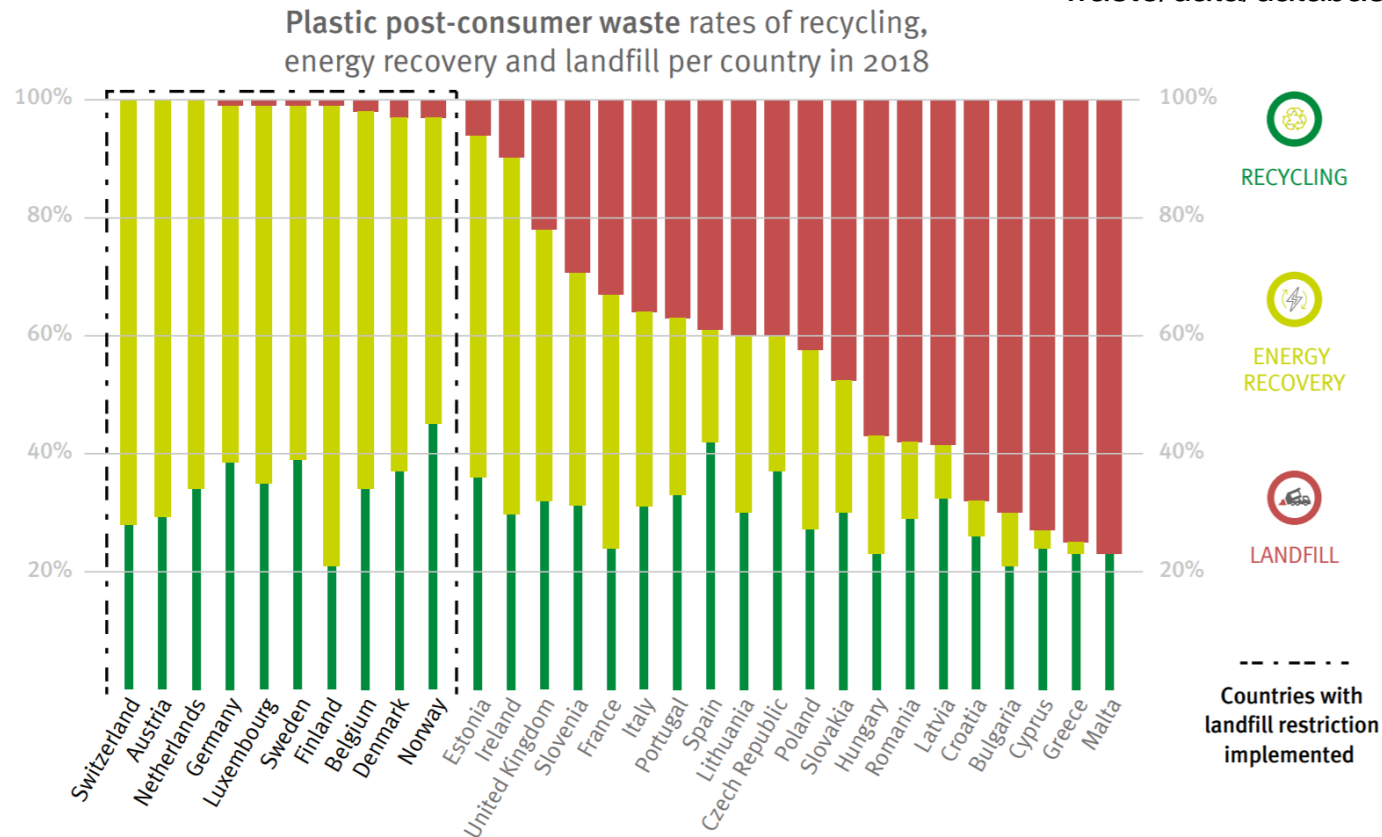


ZERO LANDFILLING IS NEEDED TO ACHIEVE THE CIRCULAR ECONOMY OF PLASTICS

Countries with landfill restrictions of recyclable and recoverable waste have, on average, higher recycling rates of plastic post-consumer waste.

SOURCE: Conversio Market & Strategy GmbH

<https://ec.europa.eu/eurostat/web/waste/data/database>



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<http://www.awvspittal.at/der-aww/muellverbrennung-arnoldstein>

<https://www.wienenergie.at/ueber-uns/unternehmen/energie-klimaschutz/energieerzeugung/abfallverwertungsanlagen/>

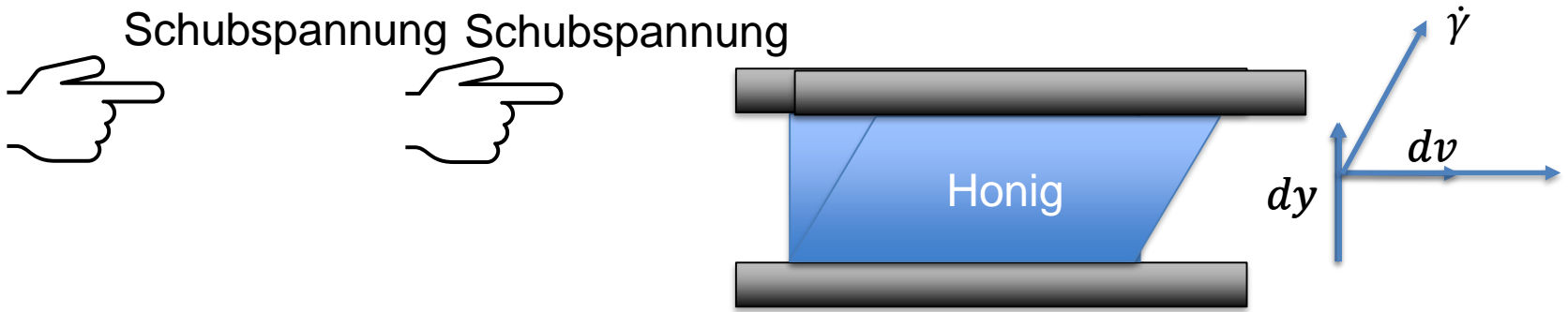
https://ec.europa.eu/environment/news/plastic-waste-shipments-new-eu-rules-importing-and-exporting-plastic-waste-2020-12-22_en

„In 2019, the EU exported 1.5 million tonnes of plastic waste, mostly to Turkey and Asian countries such as Malaysia, Indonesia, Vietnam, India and China.“

1.2. Viskosität von Polymerlösungen und Schmelzen „Gesetz“ von Newton

Schubspannung $\tau = \frac{\text{Kraft}}{\text{Fläche}} = \frac{F}{A}$ (Pascal; N/m²)

Schergeschwindigkeit $\dot{\gamma} = \frac{dv}{dy}$ ($\frac{1}{\text{sec}}$)



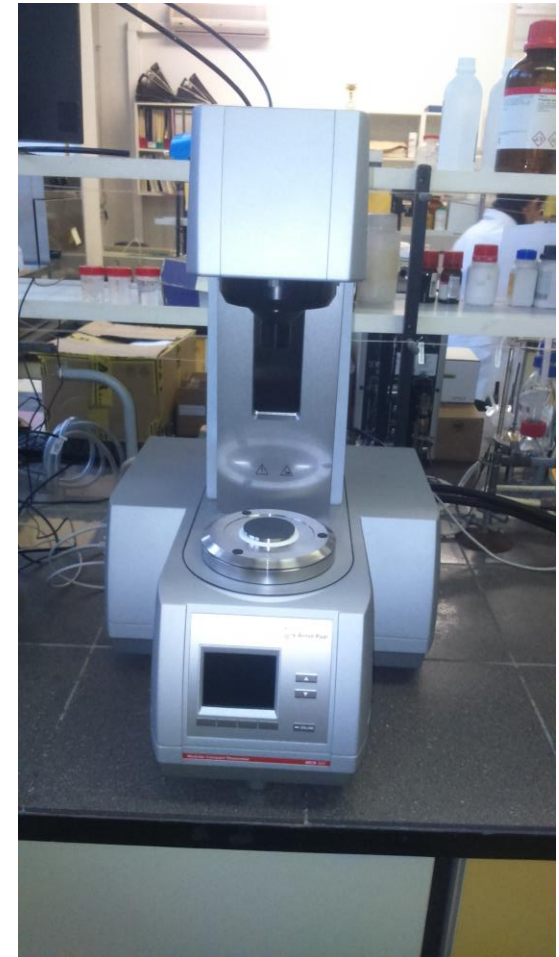
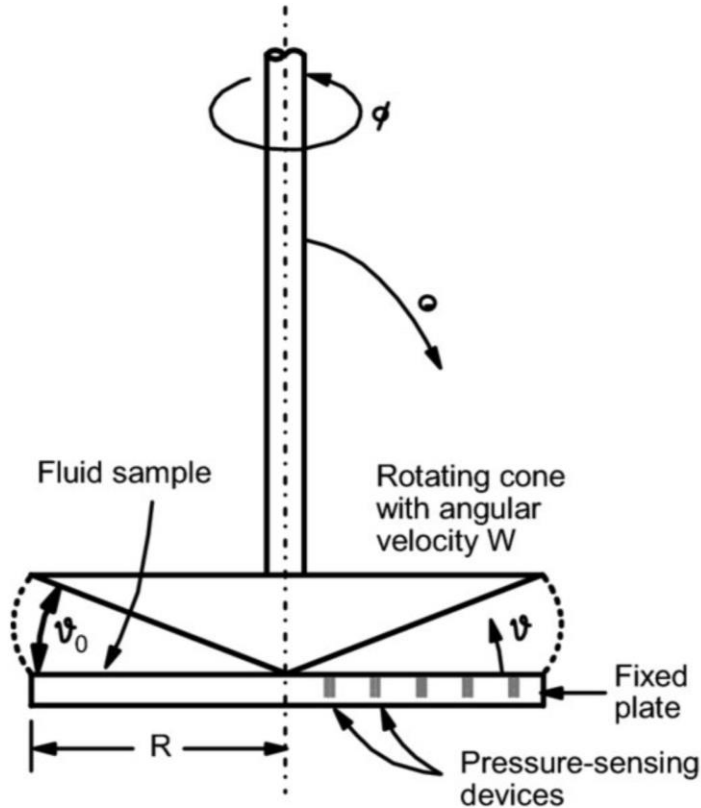
$\frac{\tau}{\dot{\gamma}} = \text{proportional} = \text{dynamische Viskosität } \eta (\text{Pa s})$

η (Glycerin): ~ 1400 mPa s η (H₂O): ~ 1 mPa s

andere gebräuchliche Einheit: 1 cP (centiPoise) = 1 mPas

Messung der Viskosität - Kegel Platte Rheometer

<https://www.anton-paar.com>

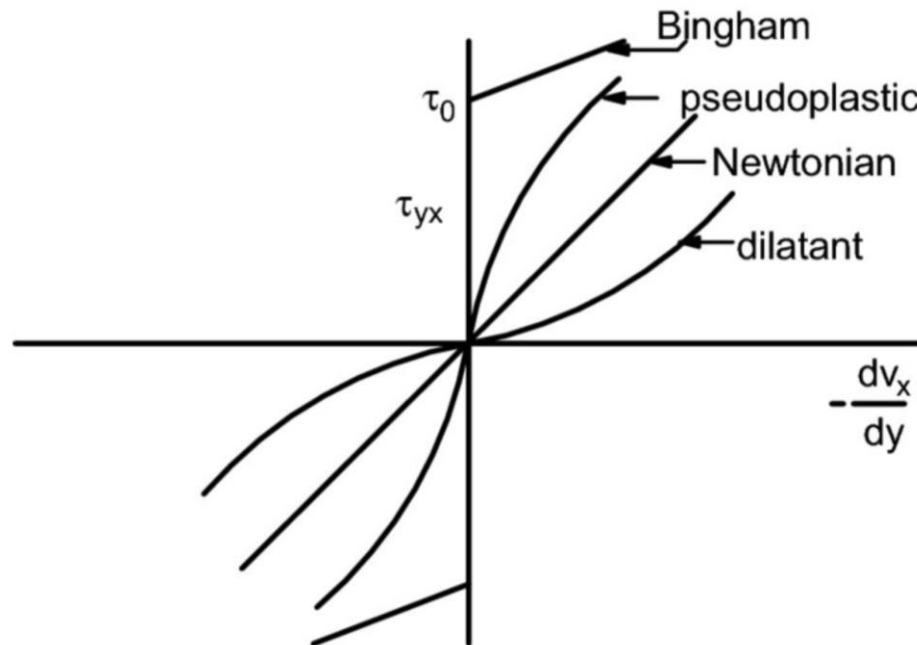


Nicht – Newtonsche Fluide

$\frac{\tau}{\dot{\gamma}}$ = *proportional* = *dynamische Viskosität* η (Pa s)

$\frac{\tau}{\dot{\gamma}}$ ist nicht immer linear -> non Newtonian viscosity

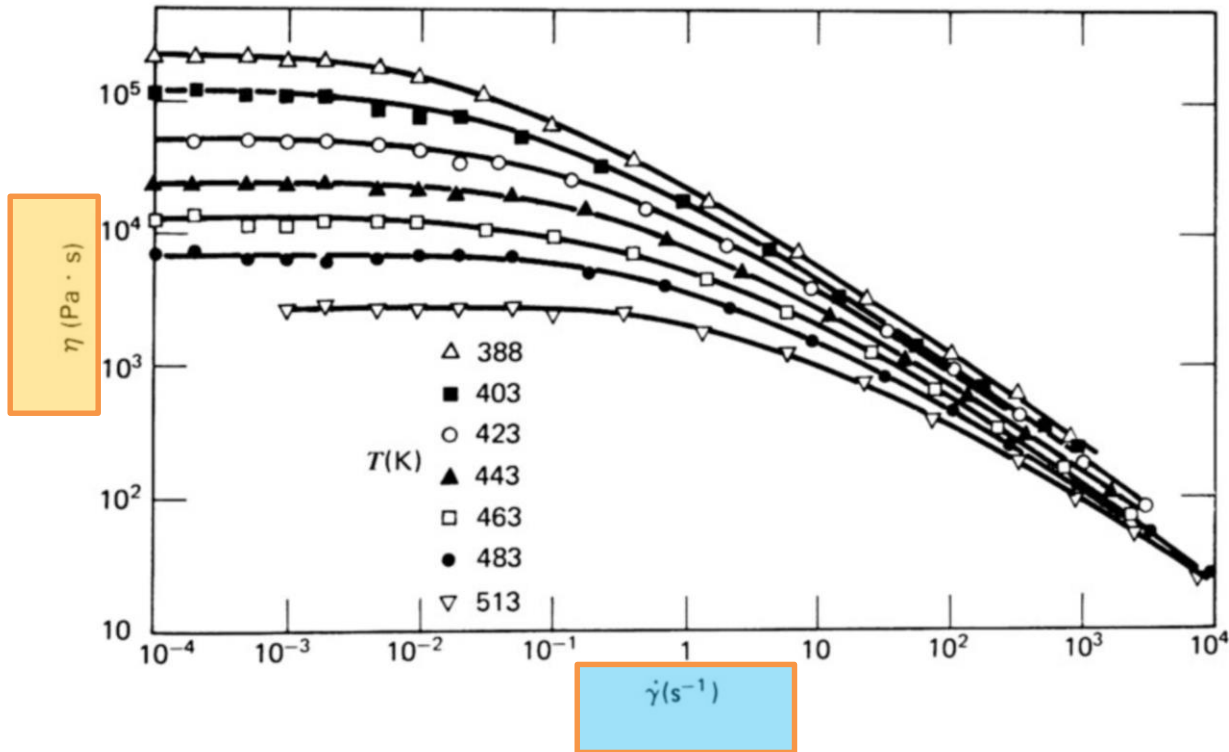
Non-Newtonian Viscosity



Polymerschmelzen

Non-Newtonian viscosity of a low density polyethylene (LDPE) melt

dynamische Viskosität η (Pa·s)



Schergeschwindigkeit $\dot{\gamma}$

1.3. Wichtige Verfahren der Polymerverarbeitung

1.3.1. Extrusion

1.3.2. Spritzguss

1.3.3. Blasformen

1.3.4. Kompressionsformen

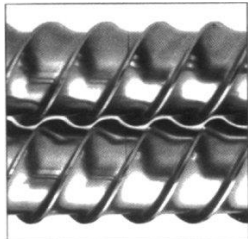
1.3.5. Faserspinnen

1.3.6. Generative Verfahren „3D Druck“ (Additive Manufacturing)

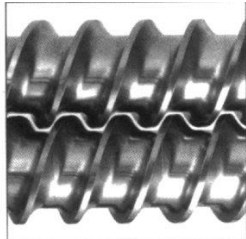
**1.3.7. Addendum: Spin coating von Polymeren –
Dünnschichten für die Elektronik**

1.3.8. Polymerschäume und Membranen

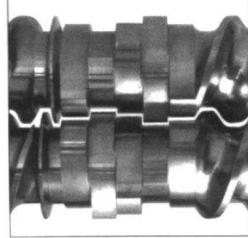
1.3.1. Extrusion



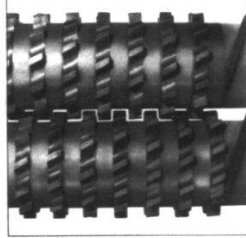
Pushing flight profiles, triple-flighted



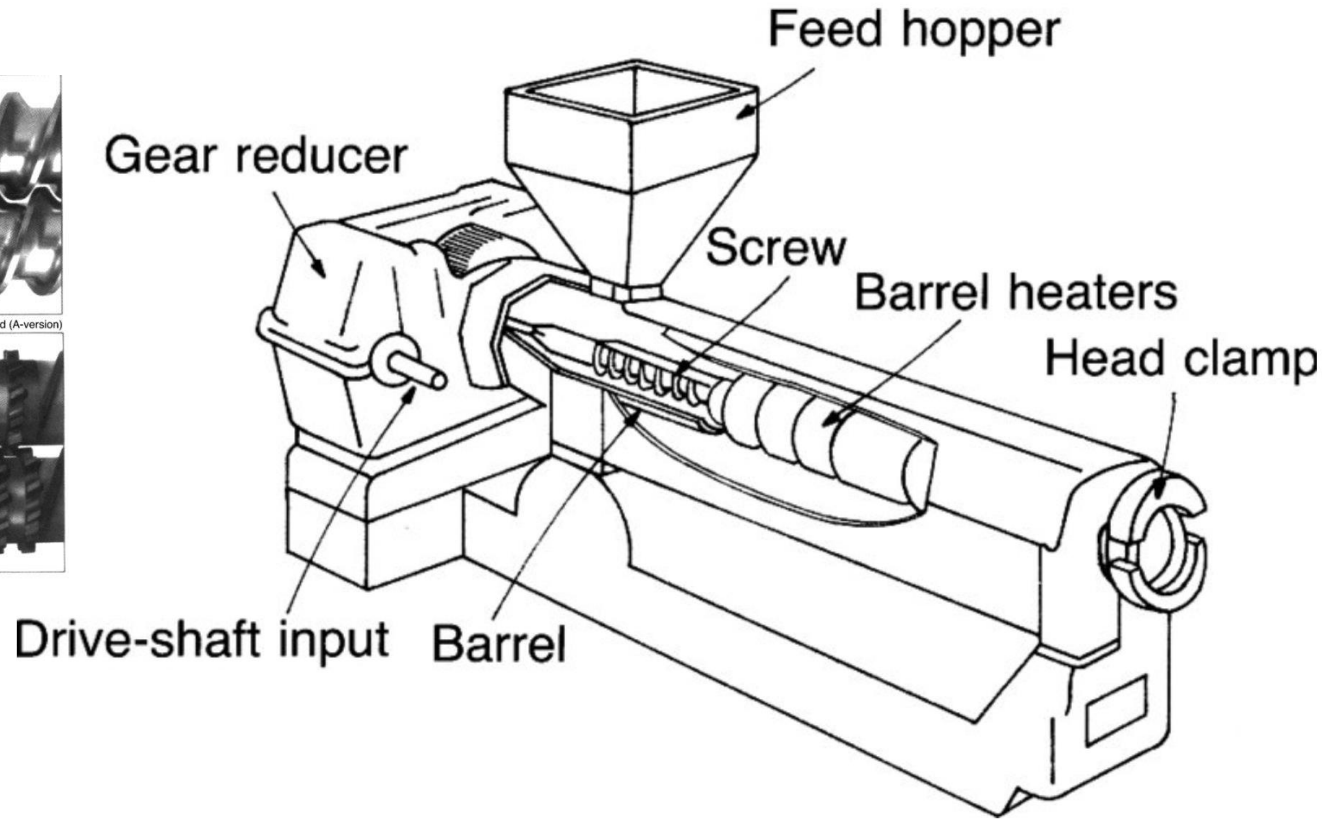
Pushing flight profiles, double-flighted (A-version)



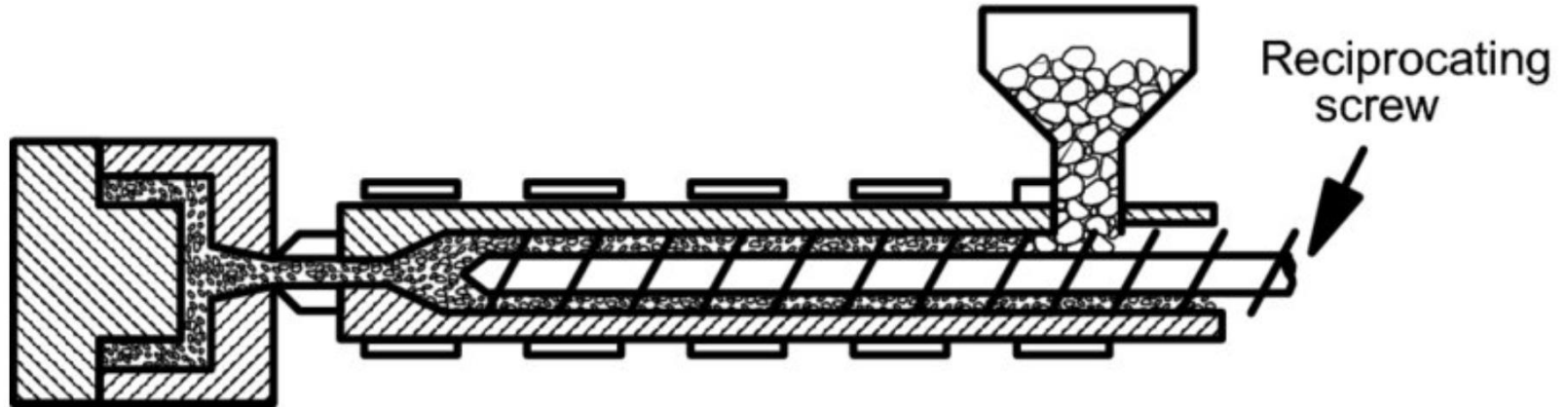
Kneading block



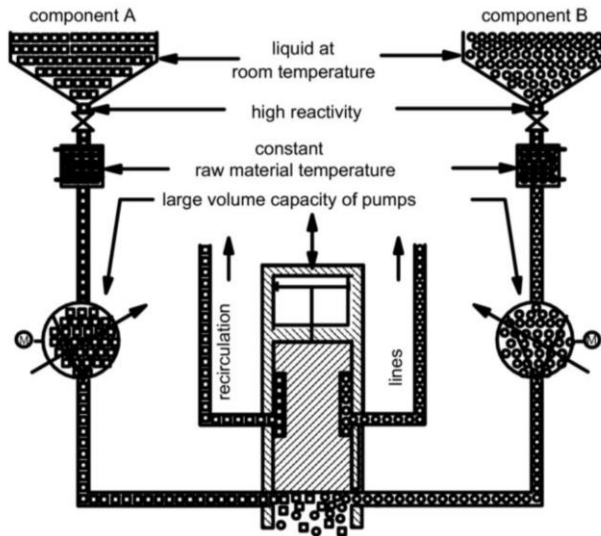
Mixing elements



1.3.2. Spritzgießen

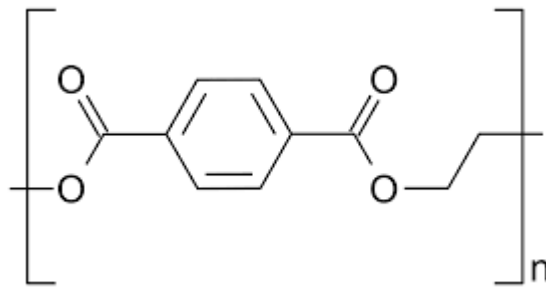


Reaktions-spritzgießen (RIM)



1.3.3. Blasformen (blow molding)

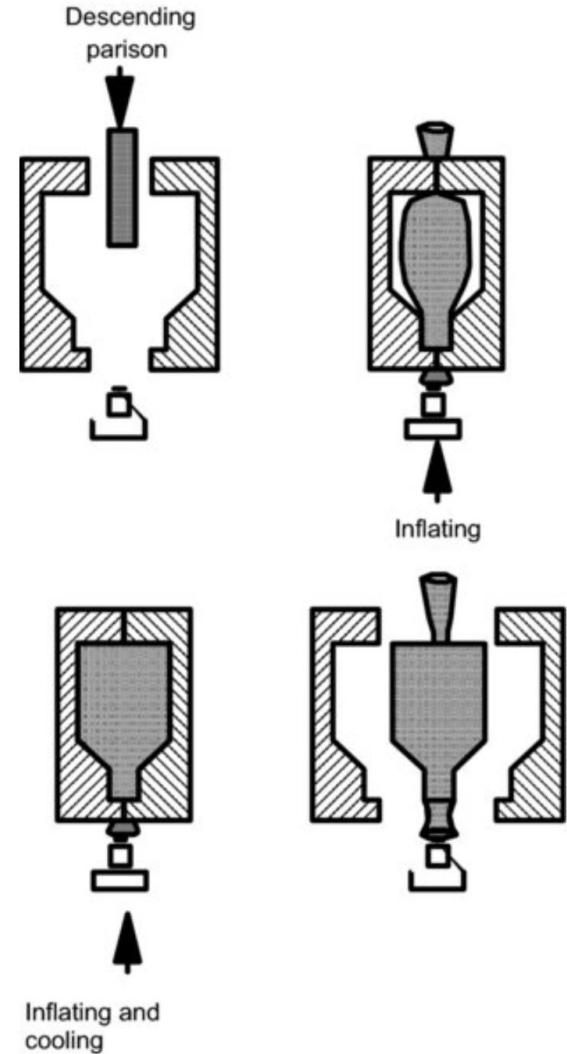
P. Nistico, Polymer Testing, Volume 90, October 2020, 106707



Polyethyleneterephthalate (PET)

Tg: 70-80° C

Tm: 245-265° C

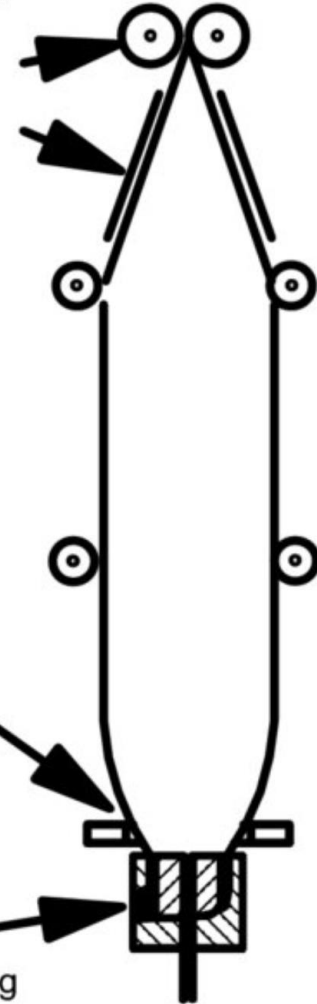


Film blowing (bags etc.)



Surface properties:

frictional and
triboelectric
phenomena

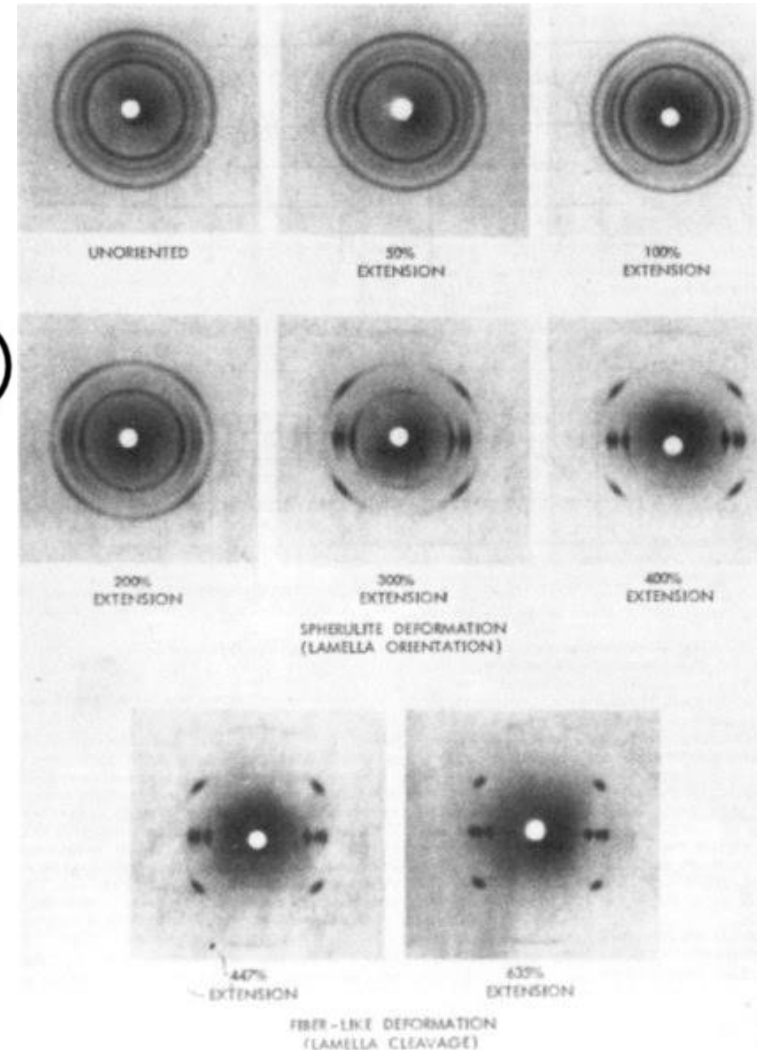
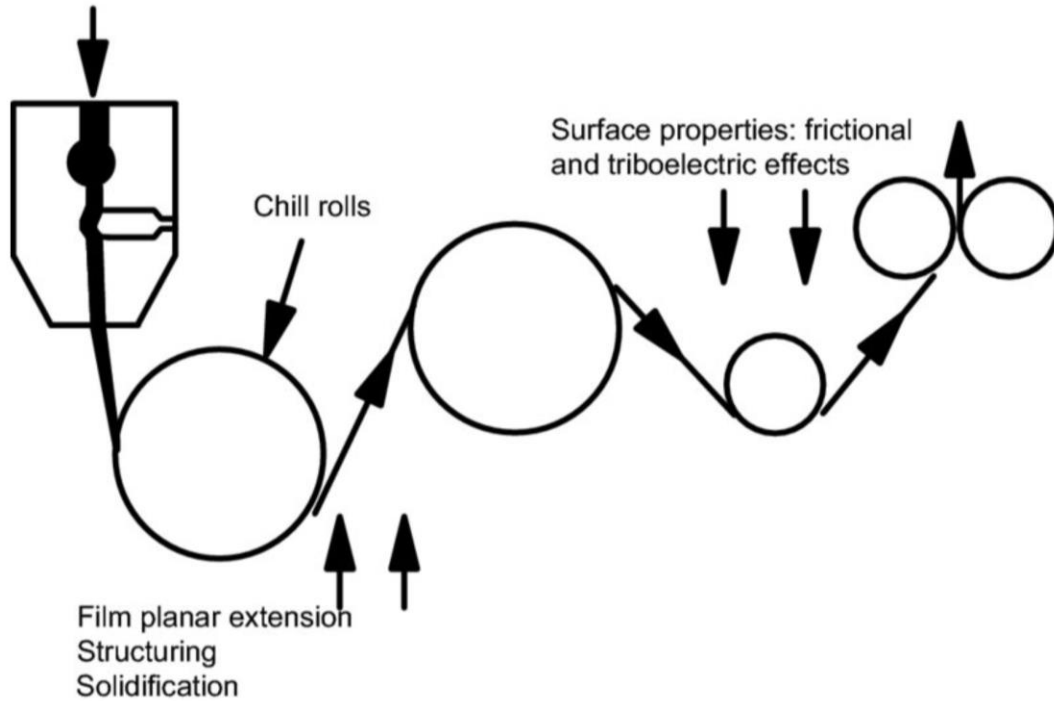


Film blowing
Structuring
Solidification

Tubular die forming

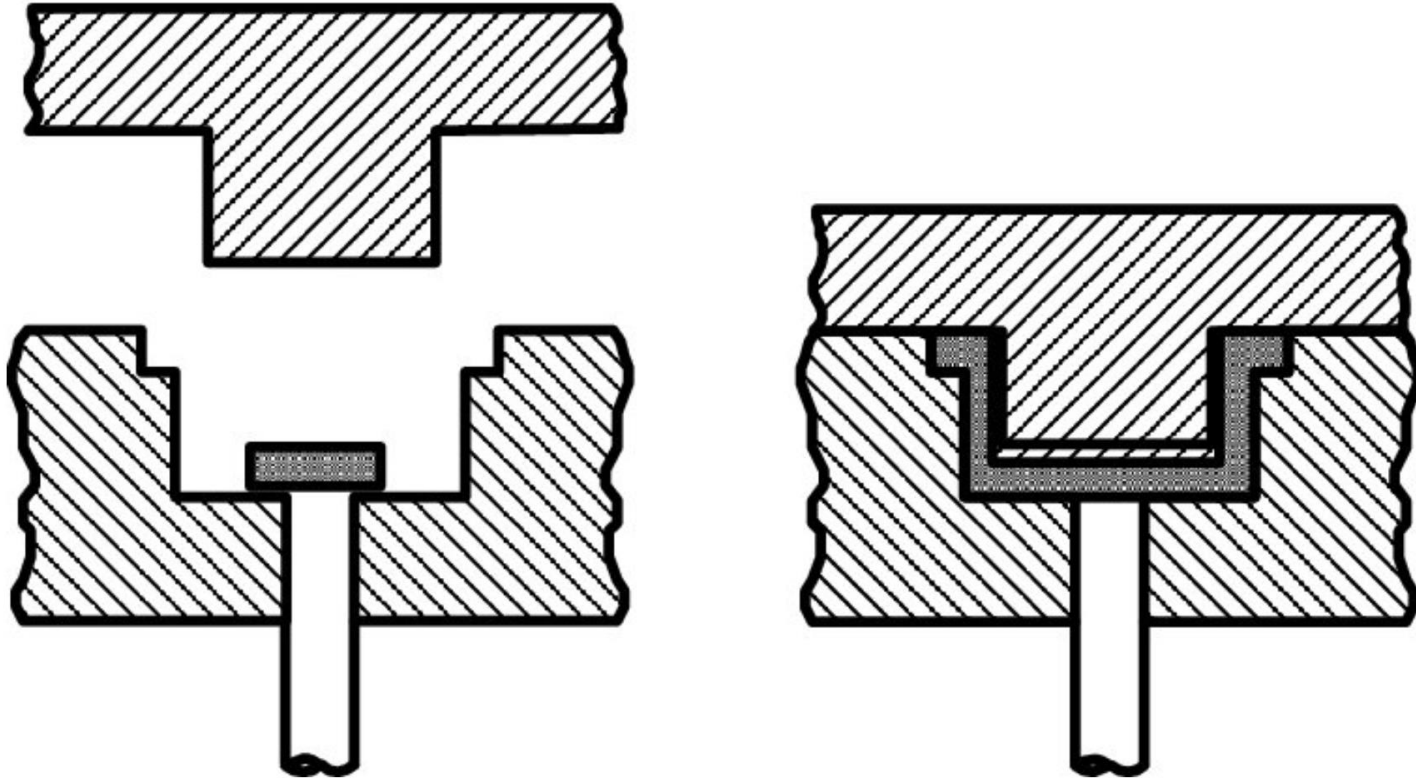
From Wagner, J. R., 10 - Blown Film, Cast Film, and Lamination Processes. In *Multilayer Flexible Packaging (Second Edition)*, Wagner, J. R., Ed. William Andrew Publishing: 2016; pp 137-145.

Filmextrusion



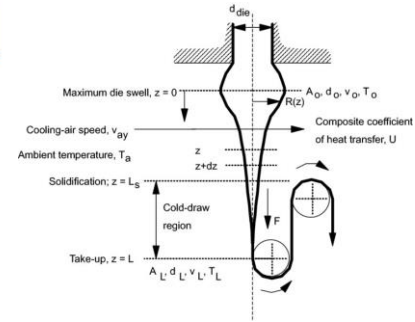
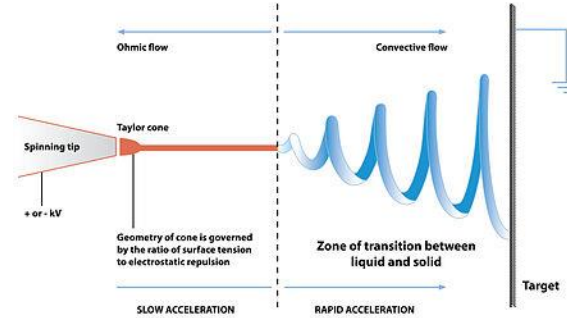
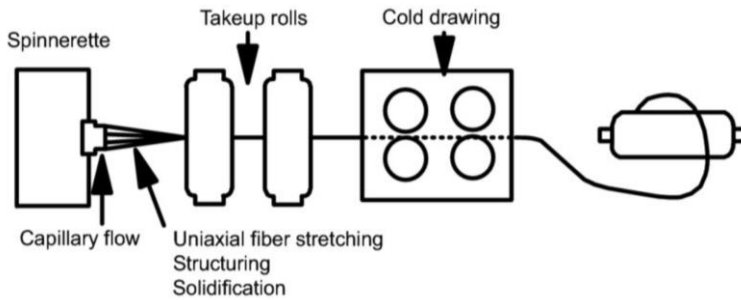
Effect of isotactic polypropylene film extension on the wide-angle X-ray diffraction patterns. From: Baird, Donald G. Polymer Processing. Wiley Professional, Reference & Trade (Wiley K&L), 2014.

1.3.4. Kompressionsformen



1.3.5. Faserspinnen

Melt spinning

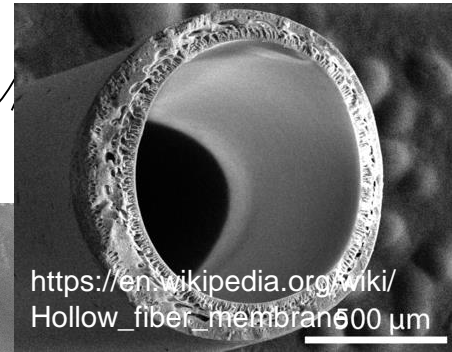
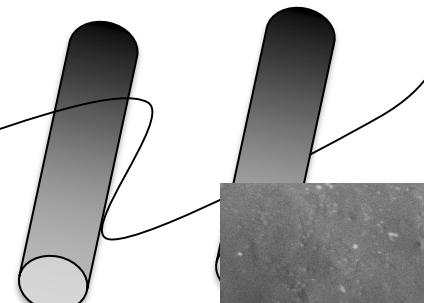


<https://en.wikipedia.org/wiki/Electrospinning>

Wet spinning

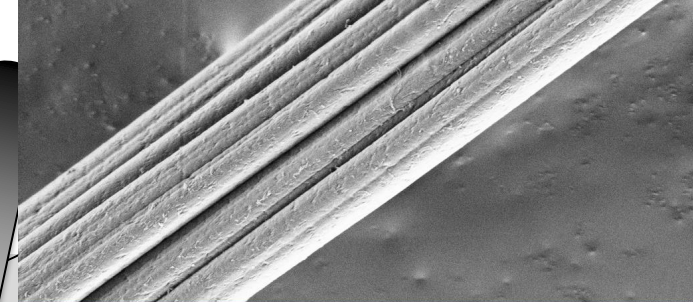
Polymer
lösung

Spinnbad
Polymer
unlöslich



Dry spinning

Polymerlösung
Lösungsmittel
verdampfbar



1.3.6. Generative Verfahren „3D Druck“ (Additive Manufacturing)

Vat Photopolymerization

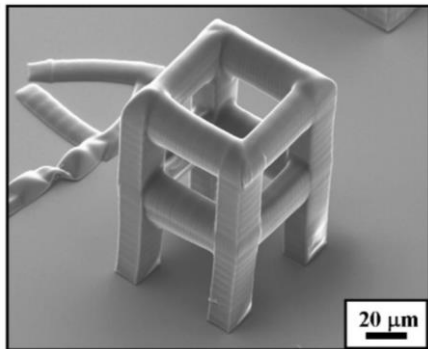
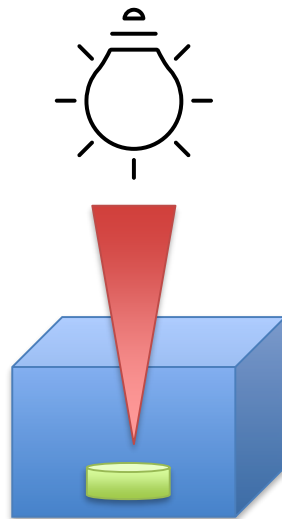


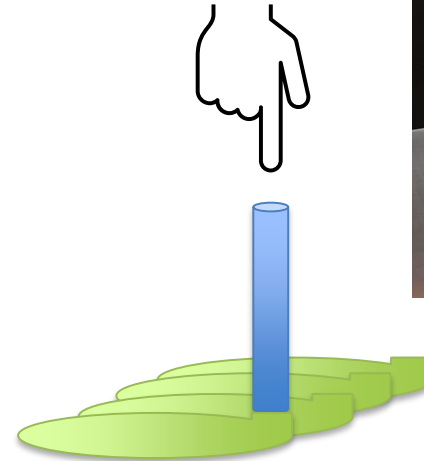
Figure 4 – SEM image of a three-dimensional microstructure fabricated by TPP.

<https://www.newport.com/>



Flüssigharz polymerisiert unter Licht in XYZ Richtung

Material Extrusion

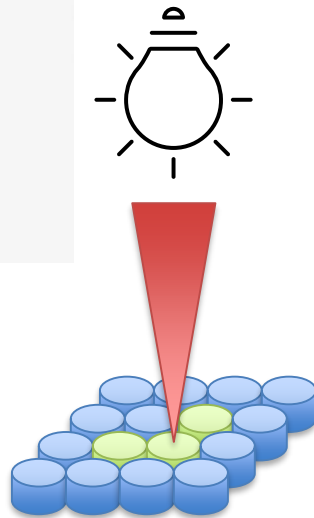
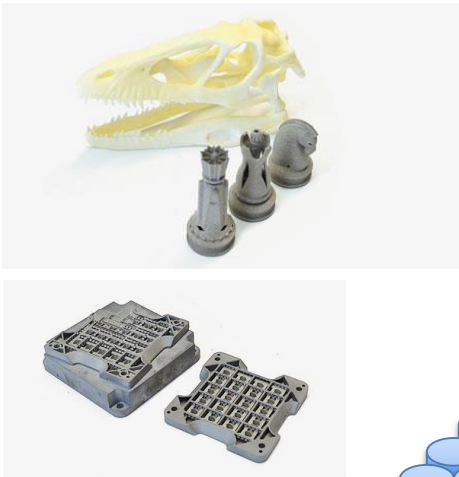


Material wird durch Kraft in XYZ extrudiert

<https://www.stratasys.com/de>

1.3.6. Generative Verfahren „3D Druck“ (Additive Manufacturing)

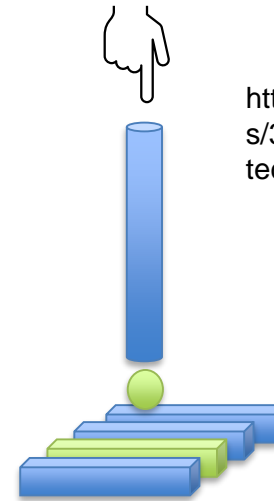
Powder Bed Fusion



<https://www.rpd.at/>

Feste Partikel verbinden sich durch Hitze in XY Richtung. Eine frische Pulverschicht wird nach jedem Schritt aufgetragen

Material and Binder Jetting



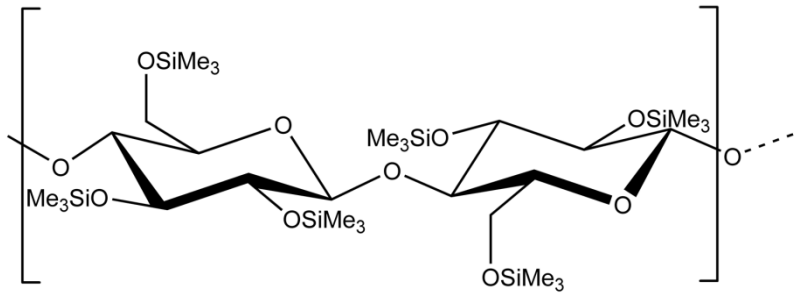
<https://www8.hp.com/us/en/printers/3d-printers/products/multi-jet-technology.html>



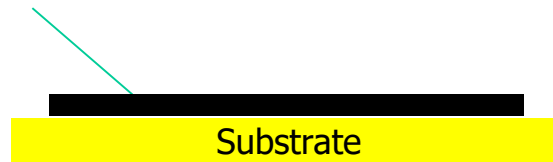
Material wird durch die Auftragung von Reaktiver Tinte gebunden und/oder UV-Licht gehärtet. Multi-jets möglich.

Andere Methoden: sheet lamination

1.3.7 Spin coating (process) of 2D trimethylsilyl cellulose polymer films

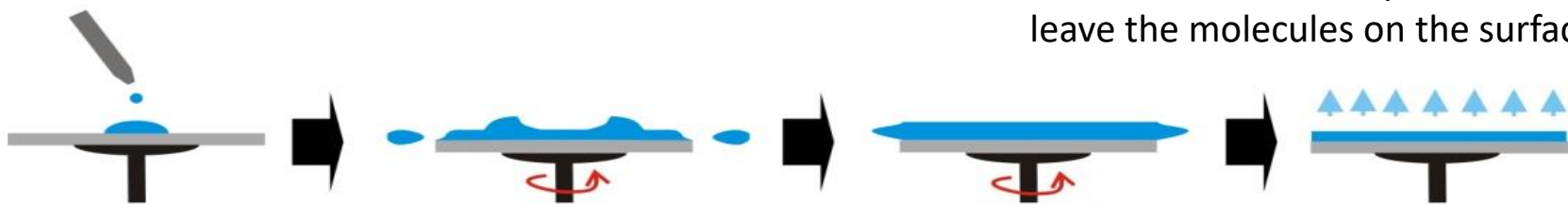


TMSC thin films

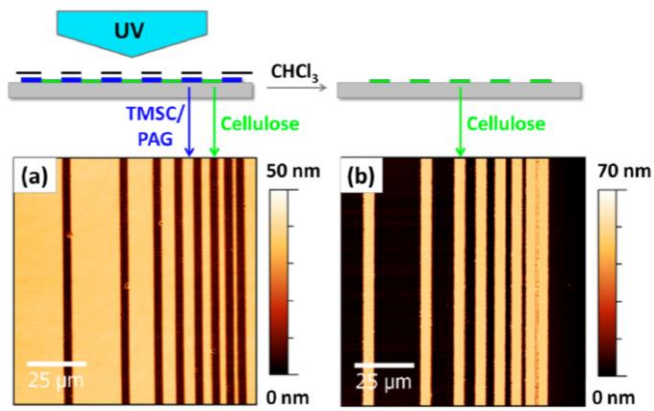
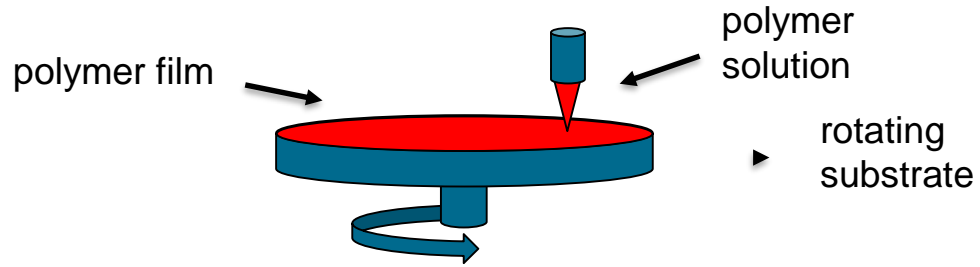


Example of spin coating a polymer molecule in solution using a static dispense.

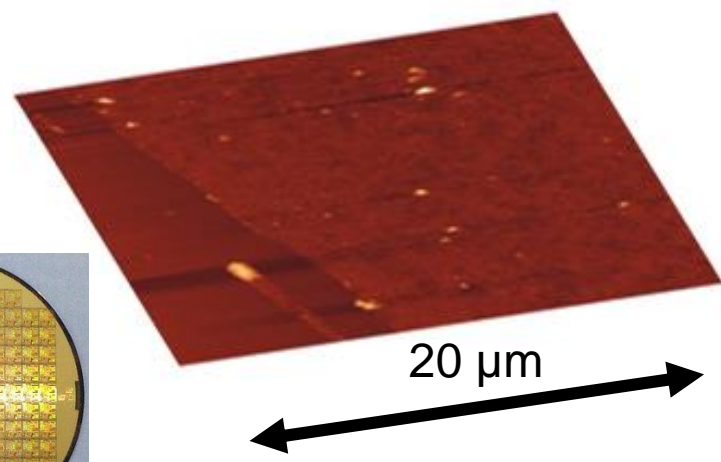
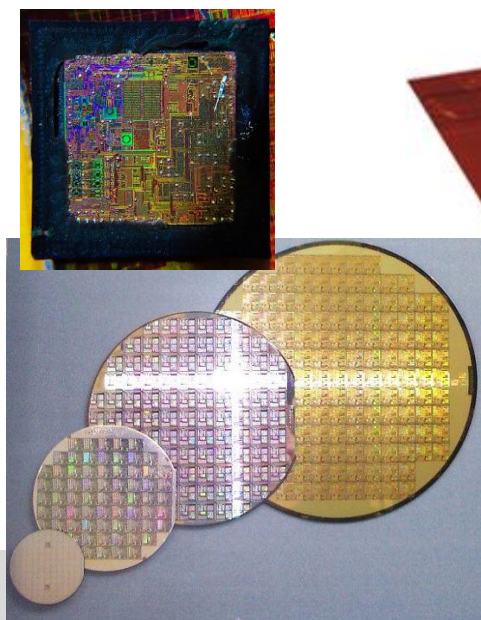
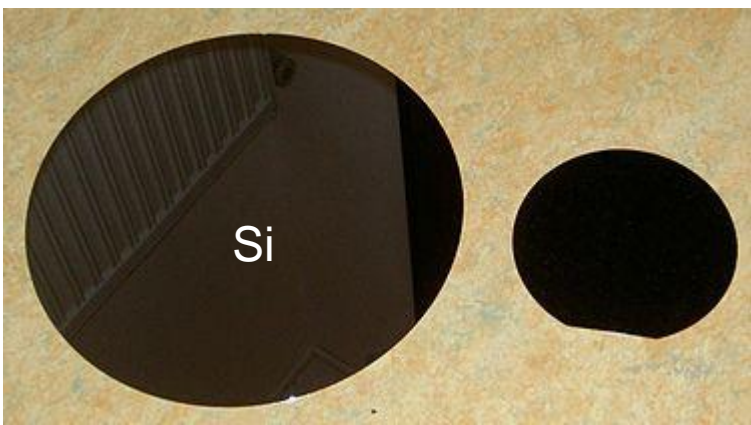
1. Dissolved or dispersed polymers in a suitable solvent is deposited on the substrate (e.g. silicon or gold).
2. Then the substrate is rotated at high speed and the majority of the liquid/solvent is flung off the side.
3. The coating thins at a rate that depends on the velocity at which the wafer is spinning and the viscosity of the fluid.
4. Before the film fully dries to just leave the molecules on the surface.



Spin coating von Polymeren – Dünnschichten für die Elektronik



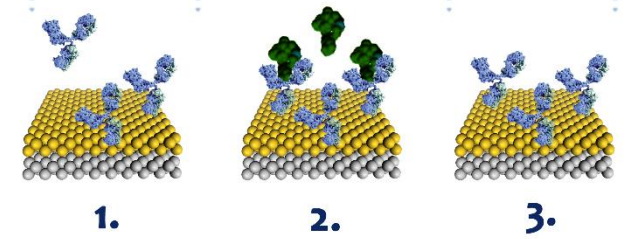
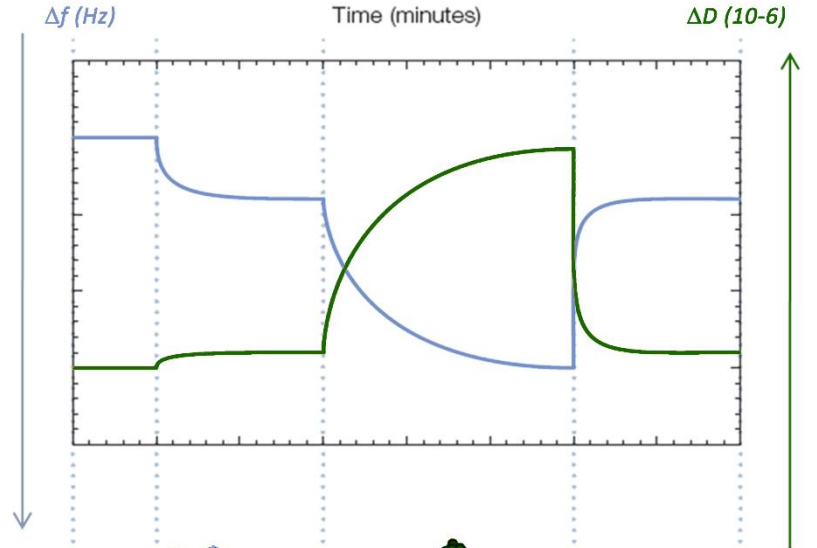
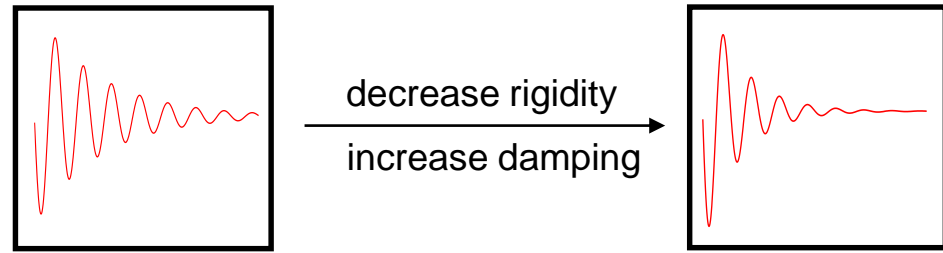
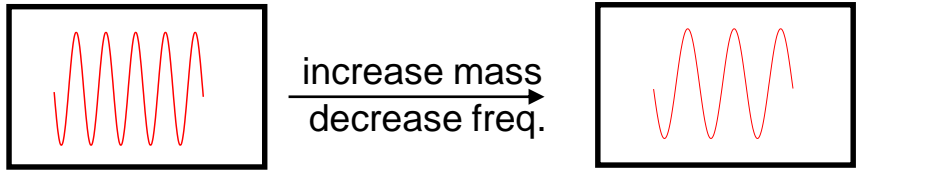
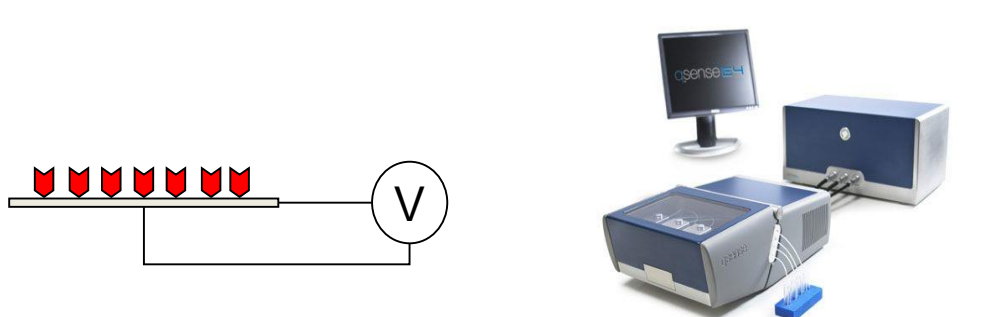
Mohan et al. *J. Colloid Interface Sci.* **2011**, 358, 604-610
 Kargl et al. *Nordic Pulp and Paper Research Journal*, **2015**, 1, 6-13
 Wolfberger et al. *Molecules* **2014**.



Images from
[https://en.wikipedia.org/wiki/Wafer_\(electronics\)](https://en.wikipedia.org/wiki/Wafer_(electronics))
[https://en.wikipedia.org/wiki/Die_\(integrated_circuit\)](https://en.wikipedia.org/wiki/Die_(integrated_circuit))

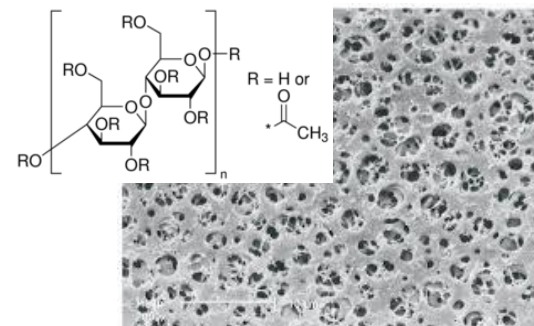
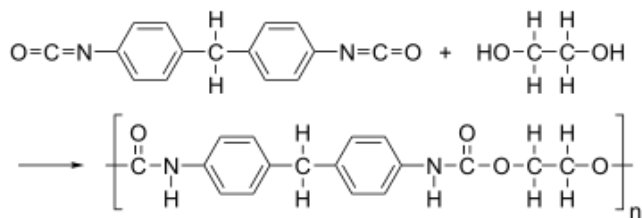
1.3.8 Applications for 2D thin polymeric films

The Quartz Crystal Microbalance QCM-D



- QCM-D Measures **wet mass, viscoelastic properties**
- Change of oscillators eigen frequency

1.3.9. Polymerschäume und Membranen

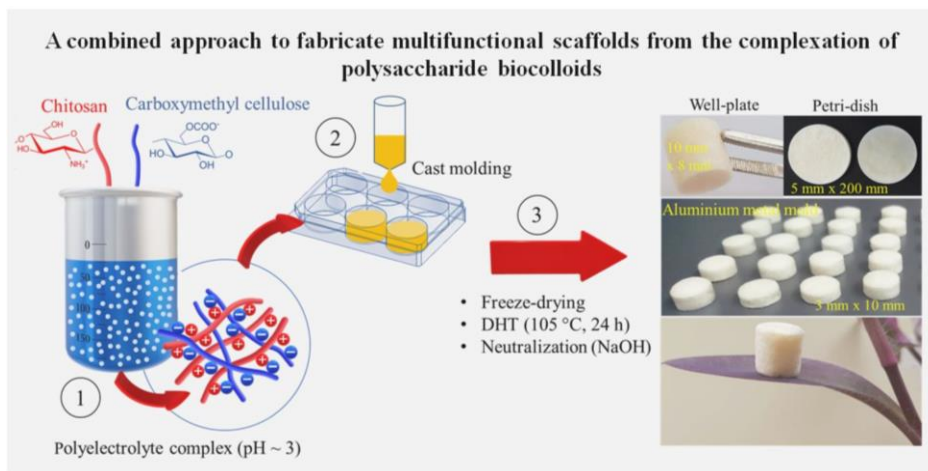


<https://www.fishersci.se/shop/products/sartorius-ca-membrane-filters-27/10709671>

Polyurethanschäume

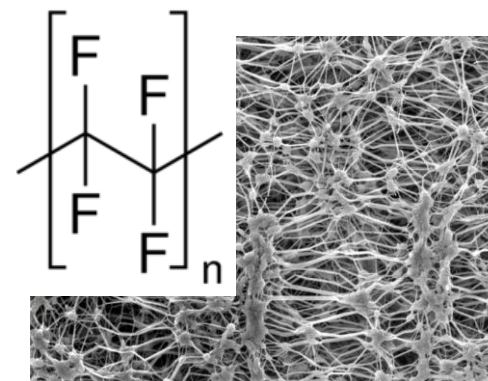
Gasentwicklung durch CO₂ Bildung

Isocyanate reagieren mit Wasser zu CO₂ und Aminen



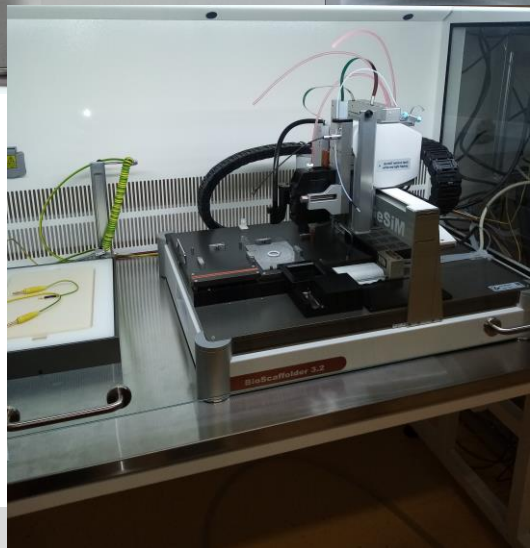
Foams by freeze drying

Štiglic et al., ACS Applied Materials & Interfaces, 2021 submitted

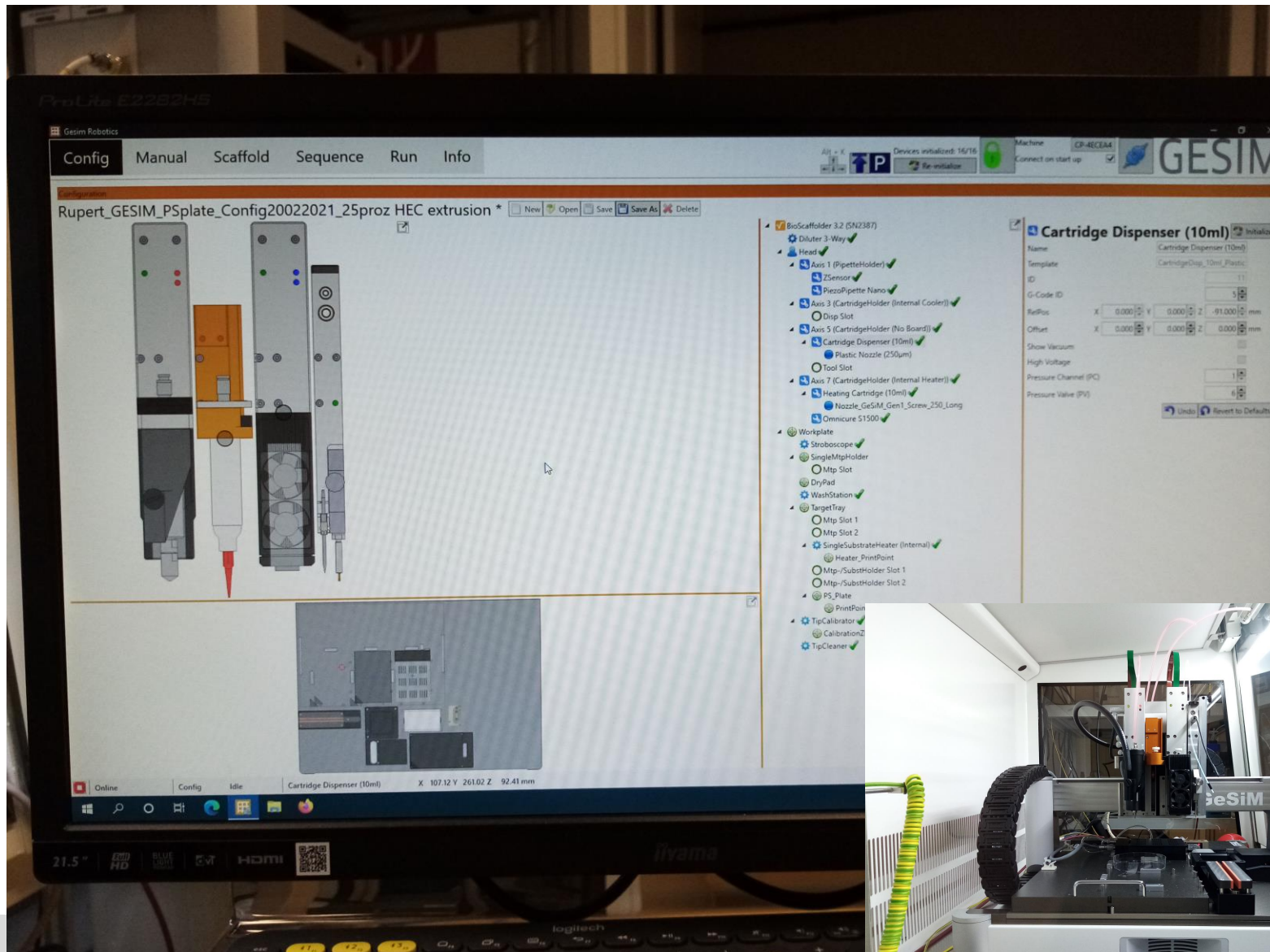


<https://www.gore-tex.com/>

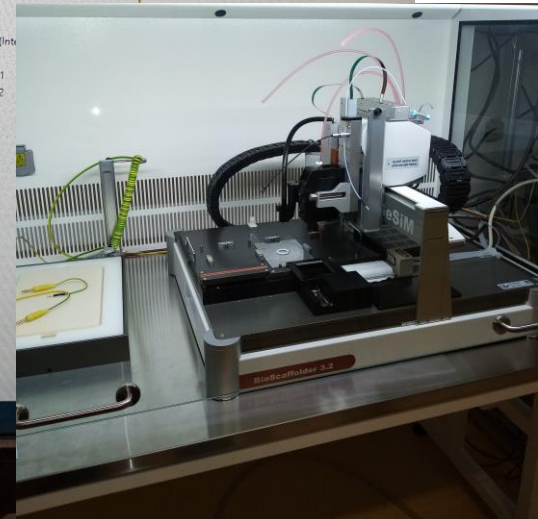
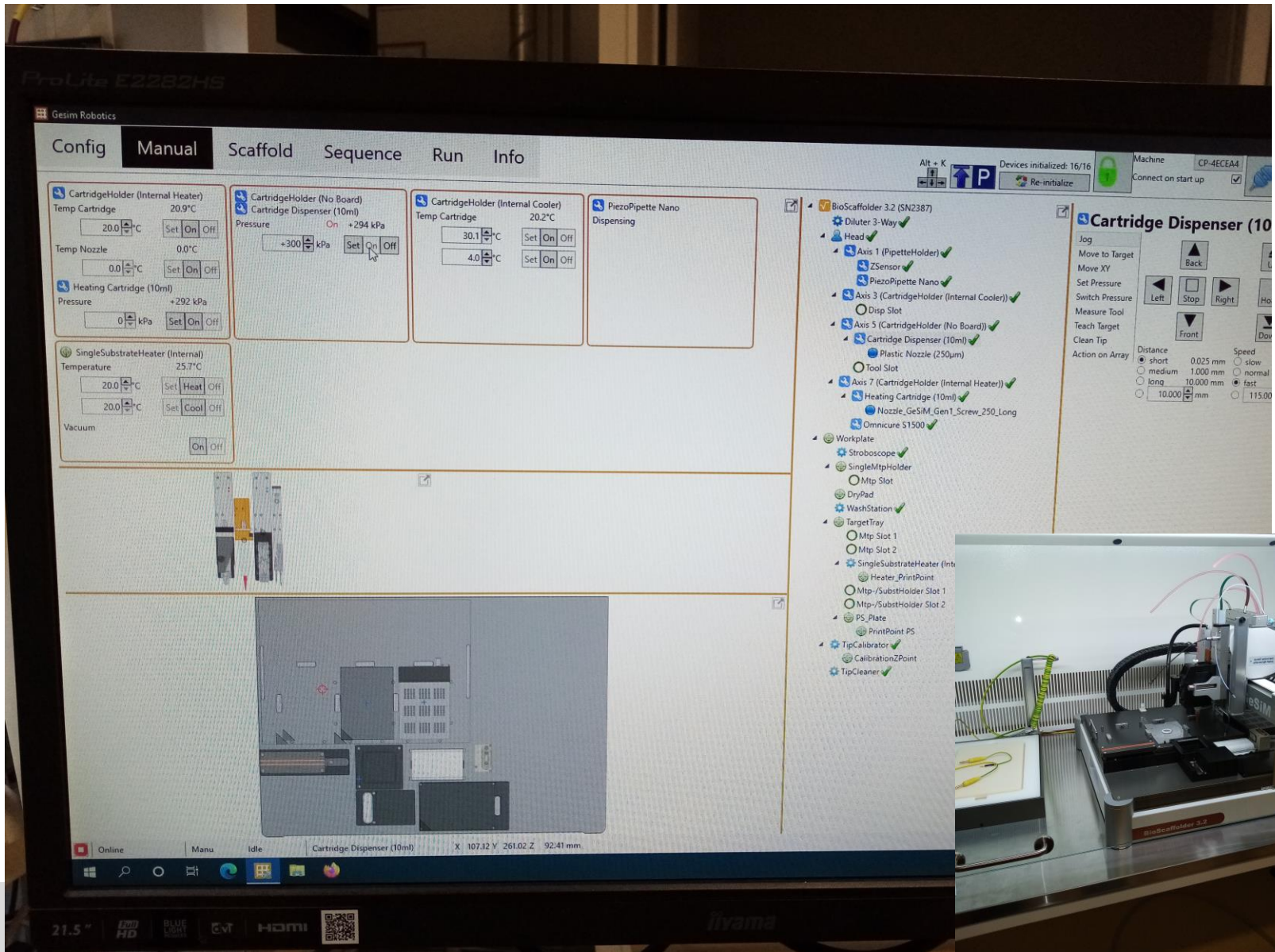
2. Praktische Laborarbeit



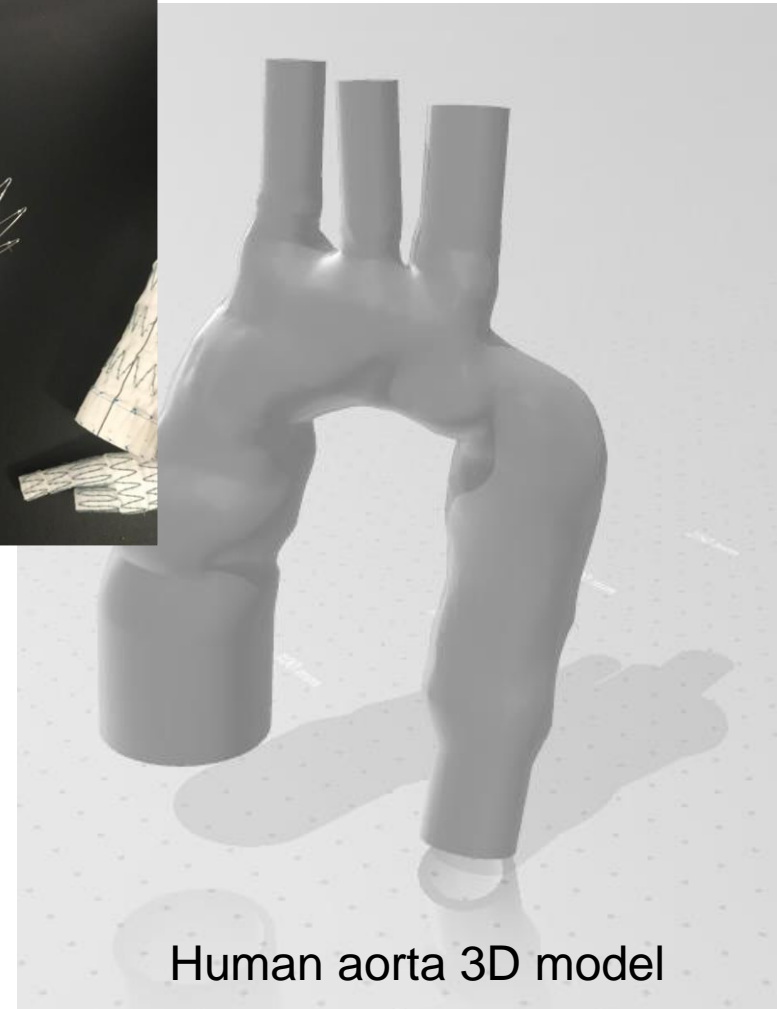
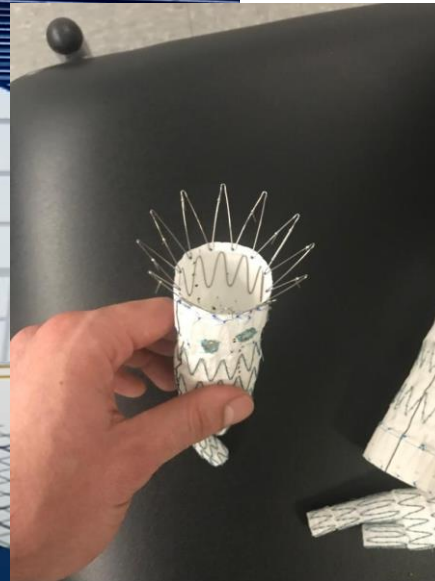
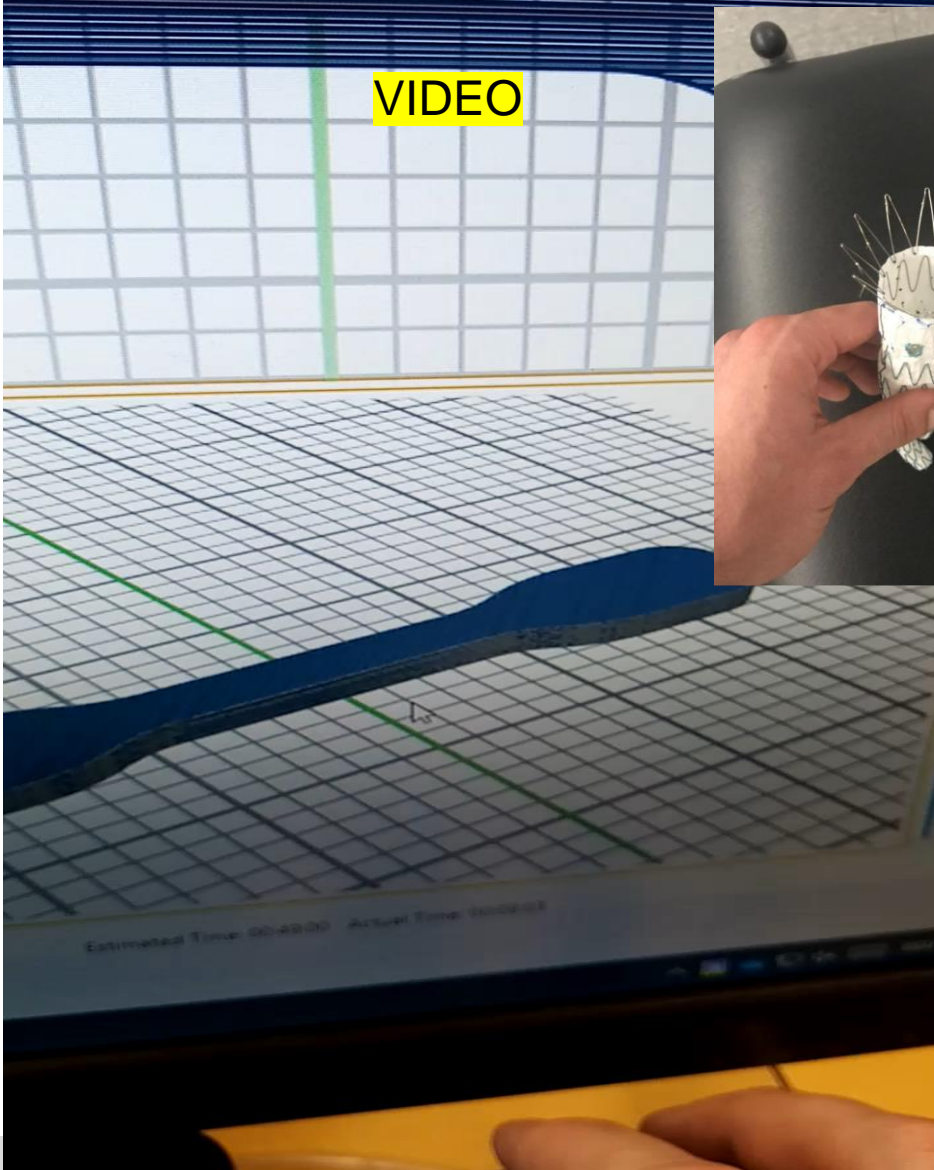
2.1.1. Übersicht 3D Drucker



2.1.1. Übersicht 3D Drucker



2.1.1. Übersicht 3D Drucker



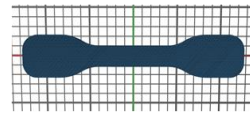
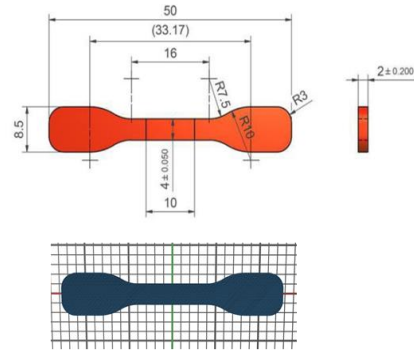
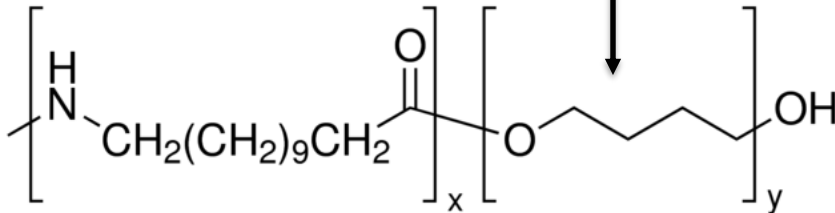
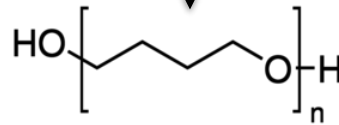
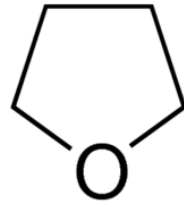
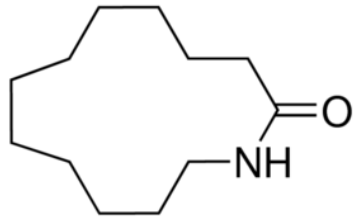
2.1. 3D Druck von Thermoplasten

2.1.2. Thermoplastische Elastomere

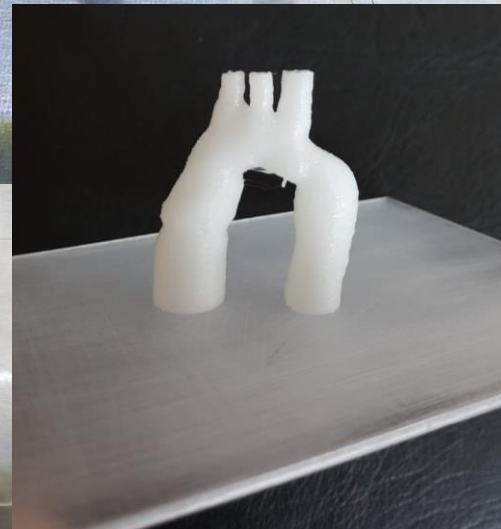
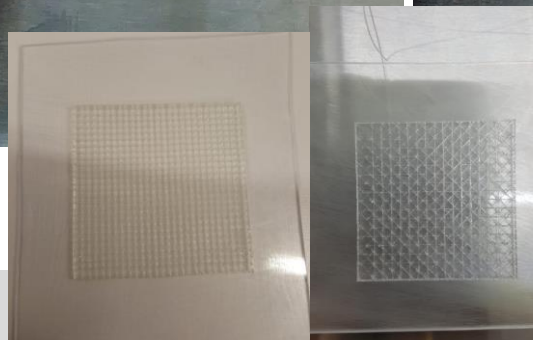
$T_m: 148^\circ \text{C}$

Verwendung: Sportartikel, Schläuche

Monomere

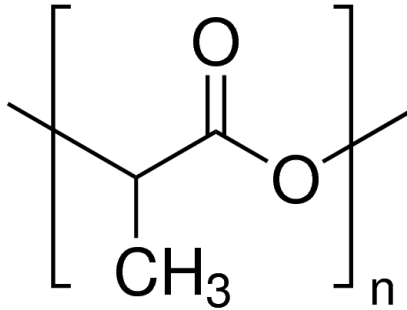


Polylauryllactam-*block*-polytetrahydrofuran

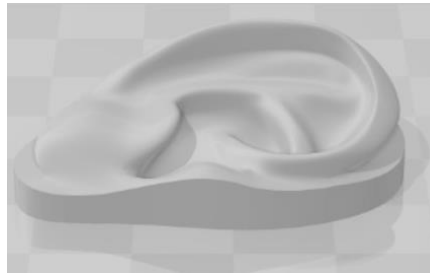
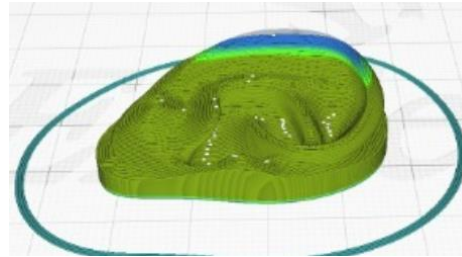


Herstellung eines 3D-gedruckten Ohrs unter Verwendung von Polylactid

VIDEO



Polylactid



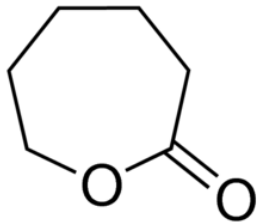
Druckparameter optimiert für den 3D-Druck von Ohrmodellen mit Polylactid

Material	PLA
Düse	0.4 mm
Schichthöhe	0.2 mm
Strichstärke	0.4
Wandnummer	4
Füllung	40%
Füllung Muster	kubisch
Düsentemperatur	205 °C
Betttemperatur	50 °C
Geschwindigkeit	50 mm/s

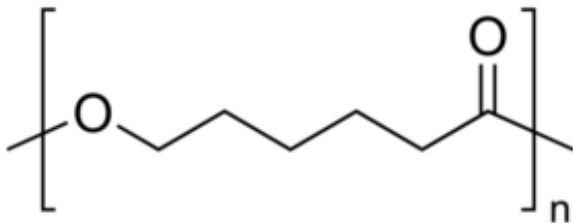


2.2. Spinnen von Polymerfasern

2.2.1. Schmelzspinnen von Polycaprolacton (PCL)



Monomere

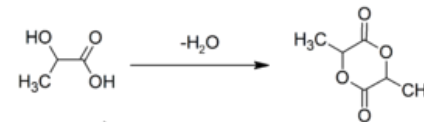
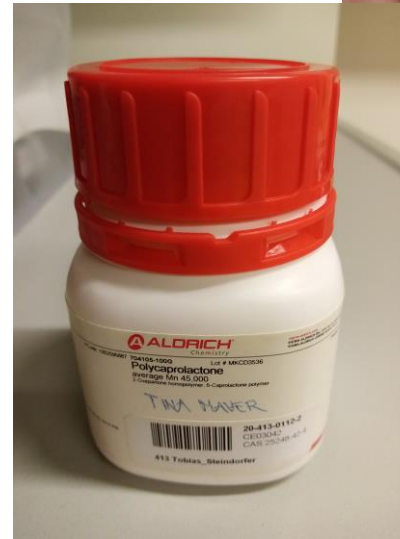


T_m: 60° C

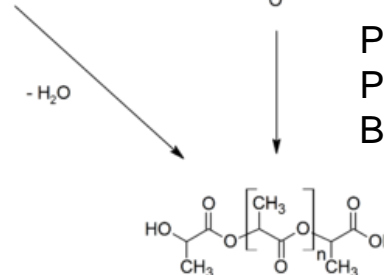
M_n: 45 kg / mol

Biologisch abbaubar

Verwendung: Polymerblends, Biomedizin

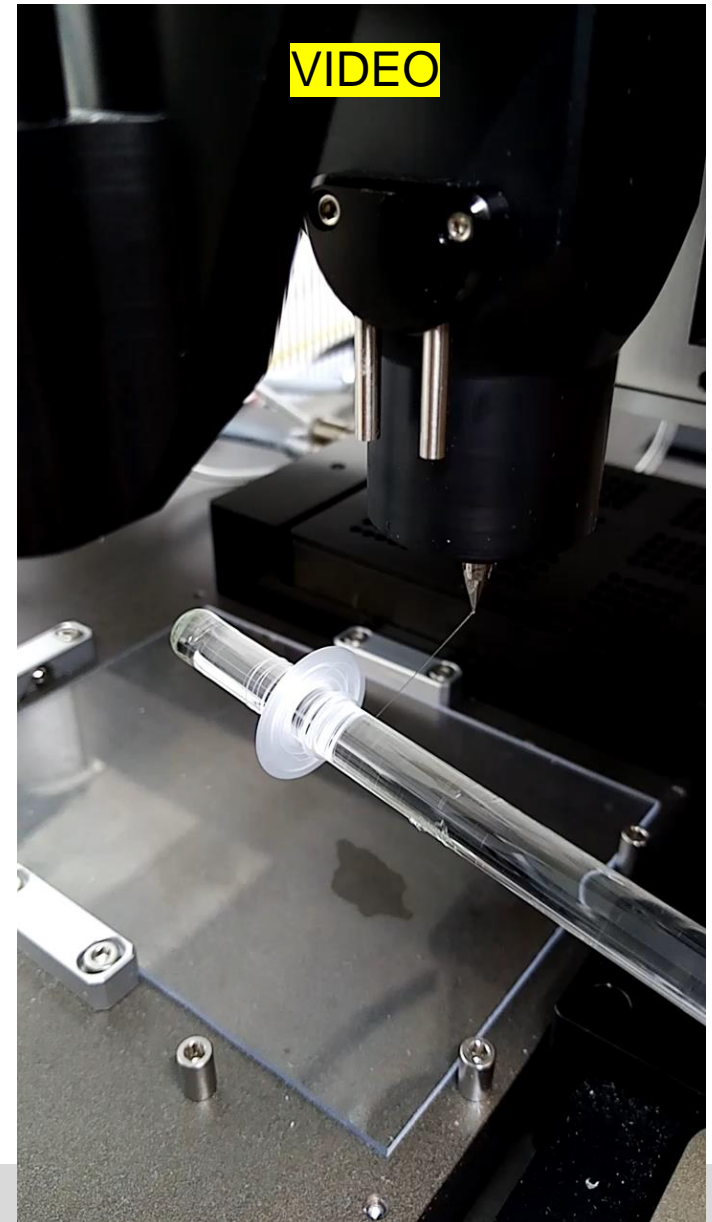
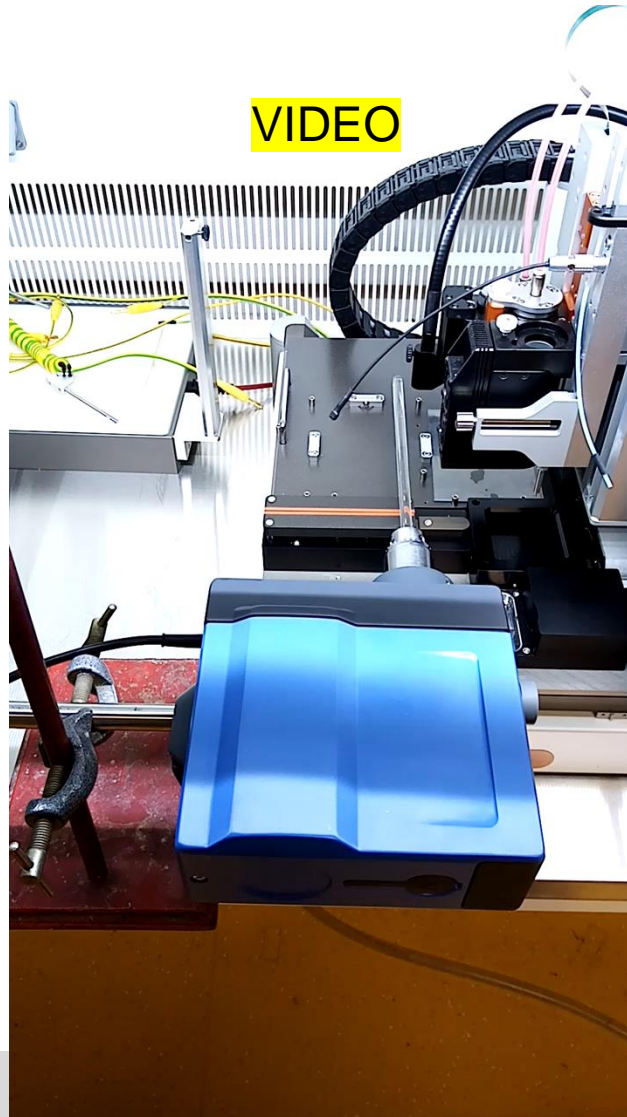
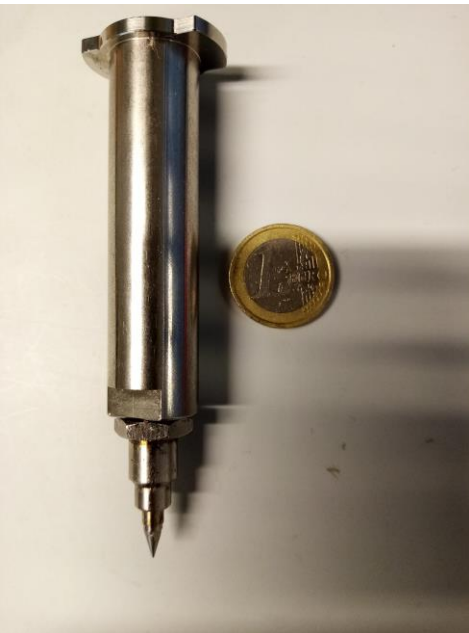


PLA
Polylactic acid
Biodegradable polyester



2.2. Spinnen von Polymerfasern

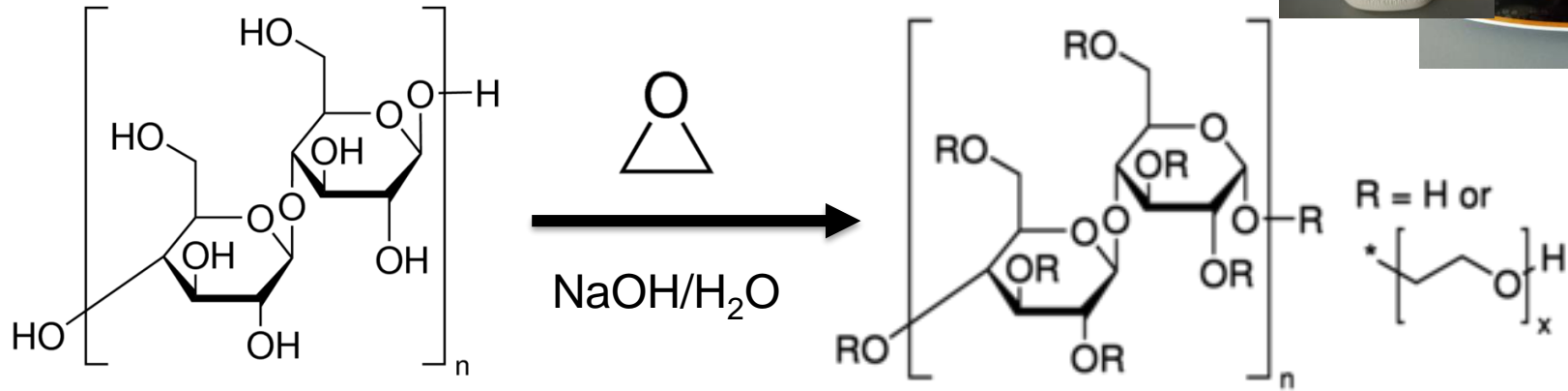
2.2.2. Schmelzspinnen von PCL



2.2. Spinnen von Polymerfasern

2.2.3. Nassspinnen von Hydroxyethylcellulose (HEC)

HEC hergestellt durch Reaktion von Cellulose mit Ethylenoxid



Wasserlöslicher Celluloseether

Mw: 250 kg / mol

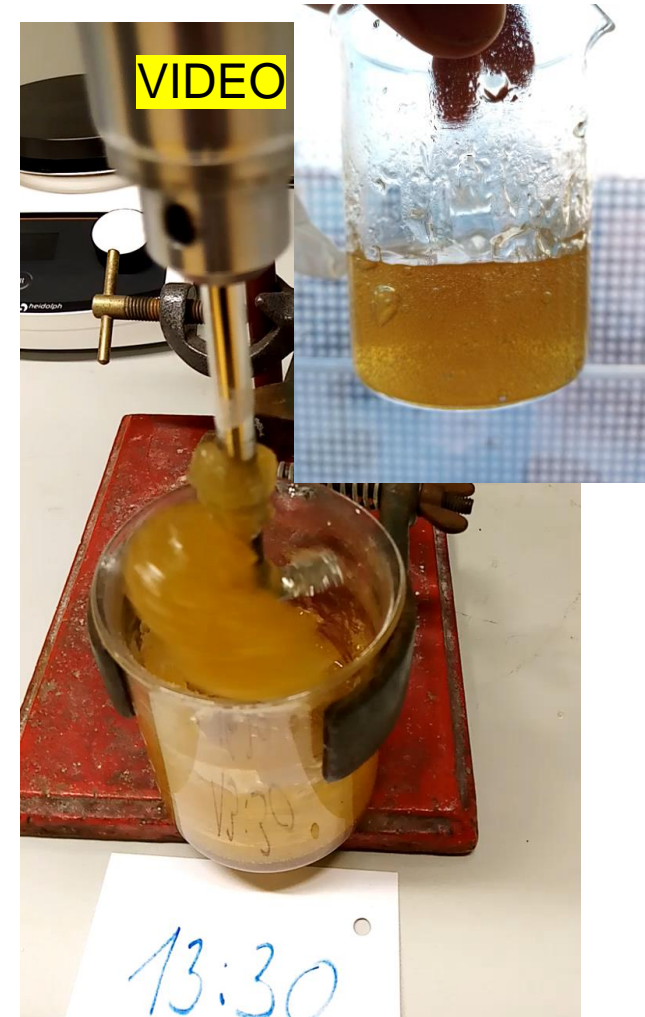
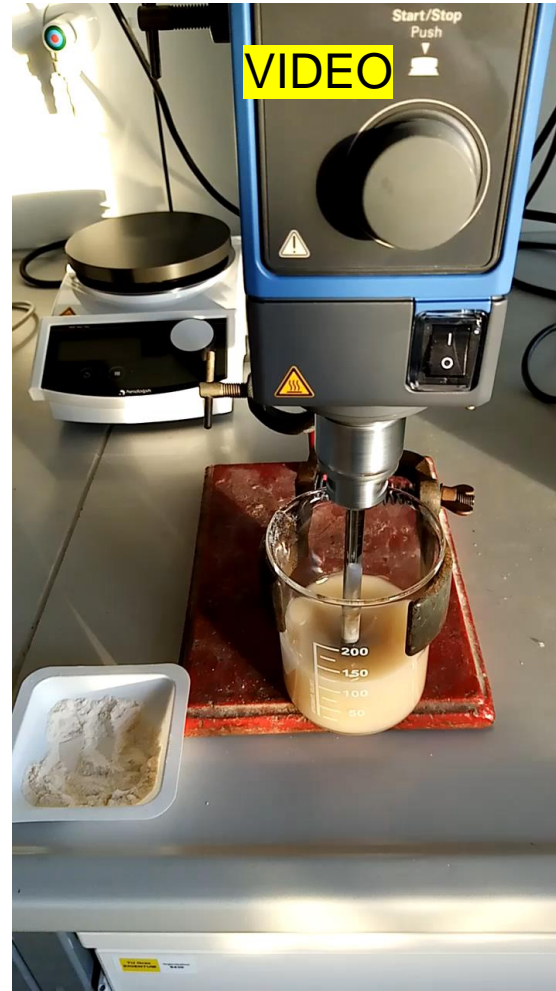
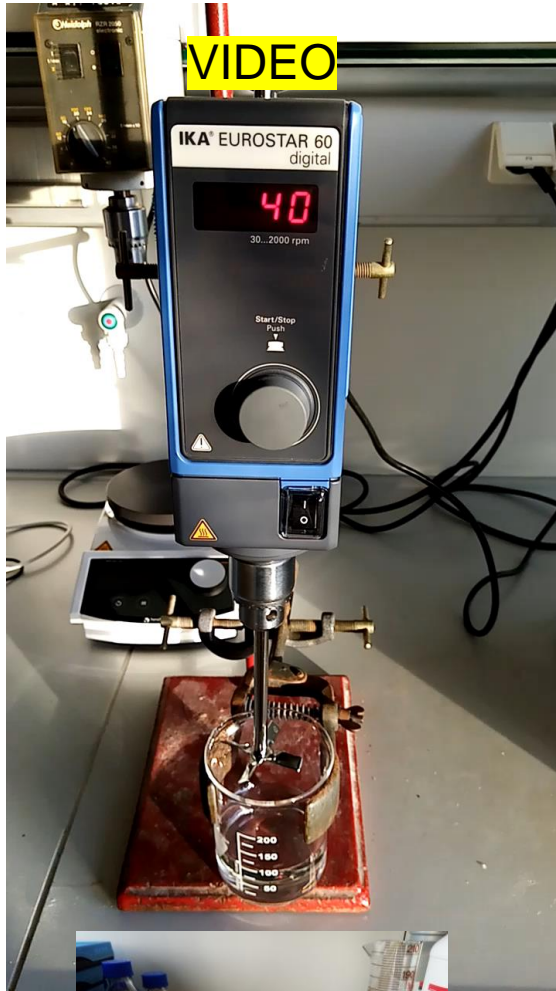
Dynamische Viskosität: abhängig von Mw: 300 - 400 mPas, c = 2%; Water at 25° C

Verwendung: Verdickungs- und Verarbeitungshilfsmittel Mörtel/Kleber/Putze/Ölförderung

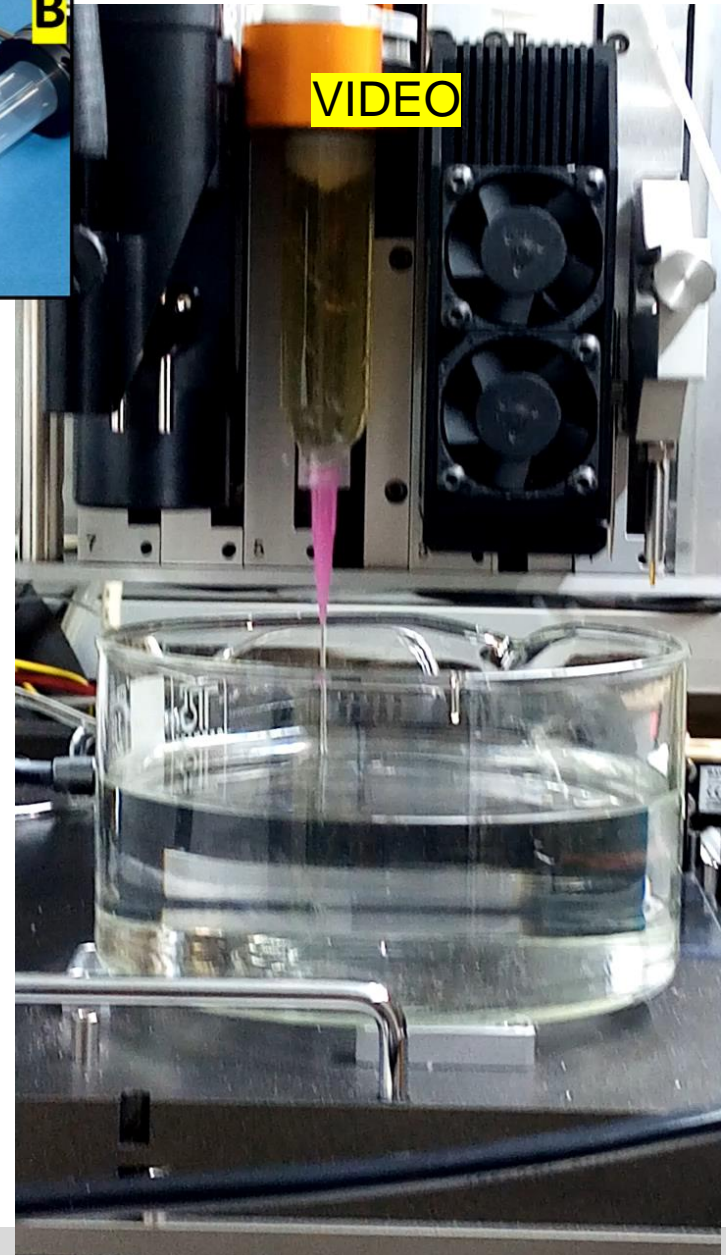
Rel. leicht biologisch abbaubar

Teilw. biobasiert

2.2.3. Nassspinnen von Hydroxyethylcellulose (HEC)

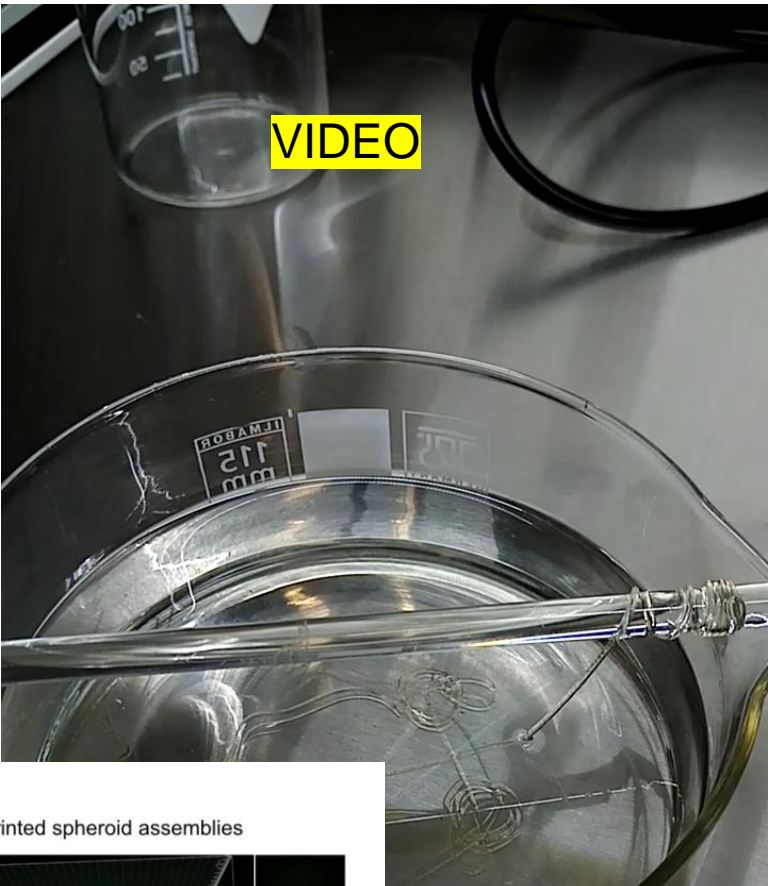


Herstellung: Einwaage HEC: 25 g, 100 ml Wasser
 Pulver langsam unter rühren zugeben (nicht Wasser zu Pulver)
 Ca. 3 -5 h rühren bis transparent



3D Druck: Abfüllen der HEC Lösung in 10 ml Druckpatrone (250 micrometer Nozzle).
 Spinnbad: 500 ml EtOH_{techn.}

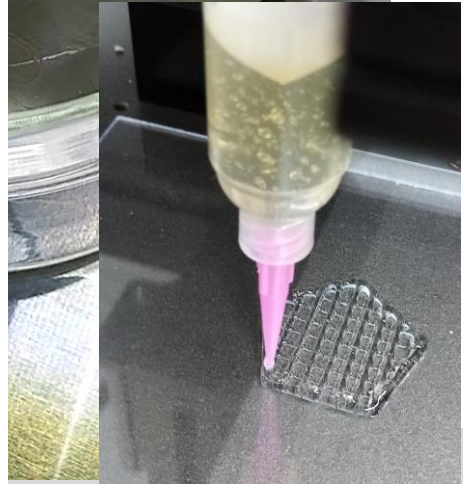
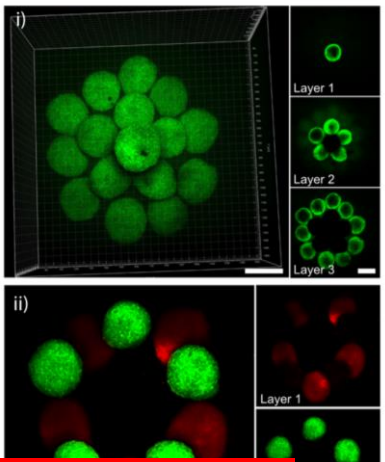
VIDEO



VIDEO

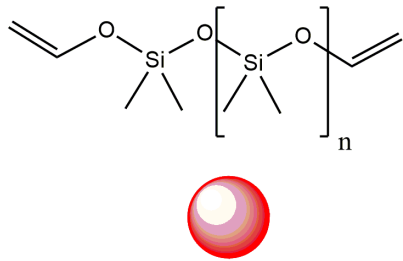


C
3D printed spheroid assemblies

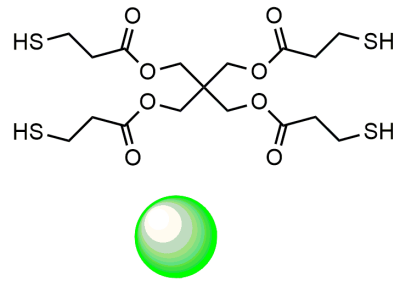


2.3. Gießen und Härten von Silikonen

2.3.1. Polydimethylsiloxan (PDMS) und die Thiol-ene Reaktion



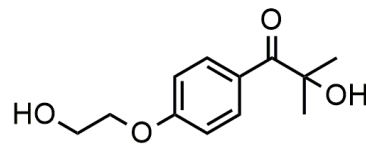
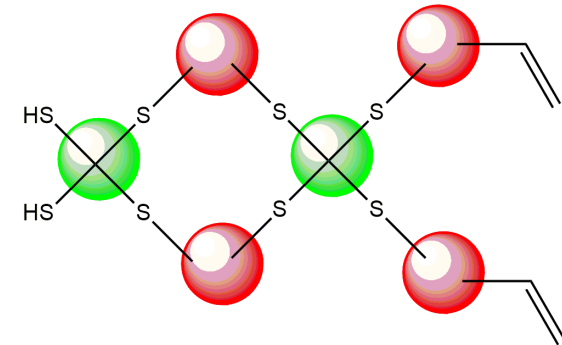
Polydimethylsiloxan
PDMS



Pentaerythrit-tetrakis-(3-mercapto-propionat)
PTMP

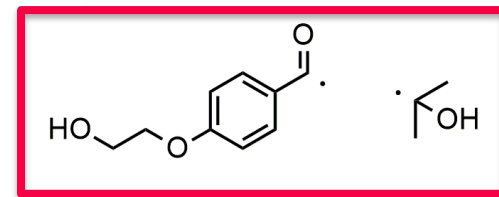
UV-Licht

Radikalbildner

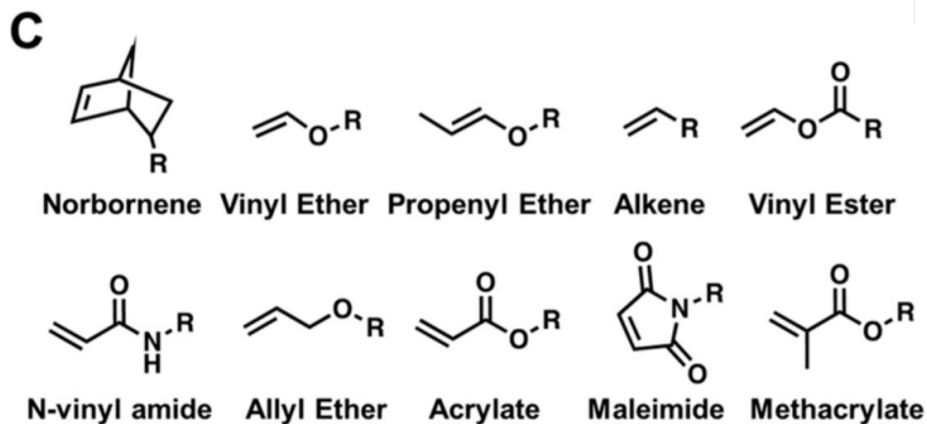
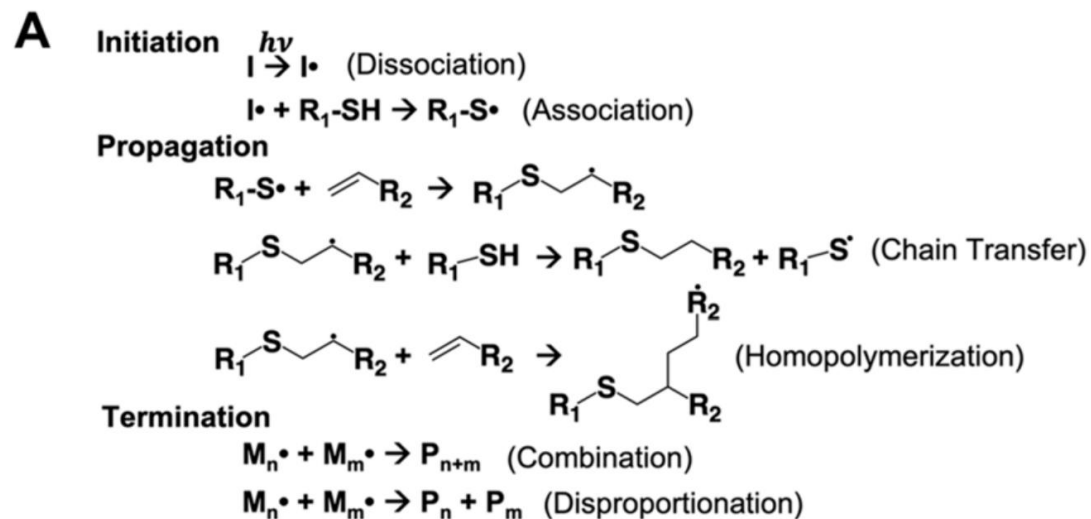


α -Hydroxy-4-(2-hydroxyethoxy)- α -methylpropiophenon
HMP

UV-Licht



Thiol-ene Reaktionen

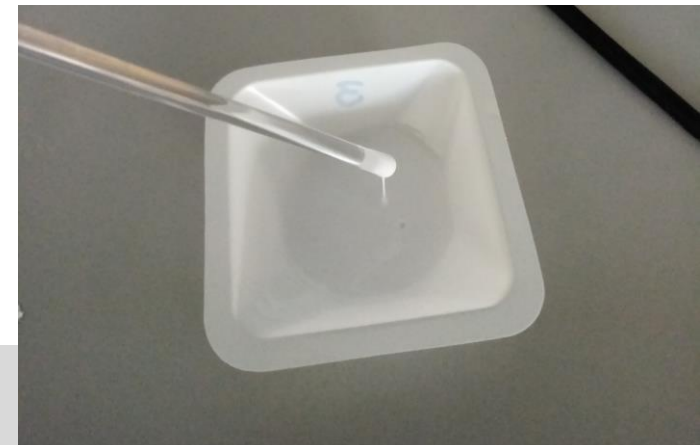


2.3.2. Herstellung von Zugprüfstäben durch UV-Vernetzung von PDMS



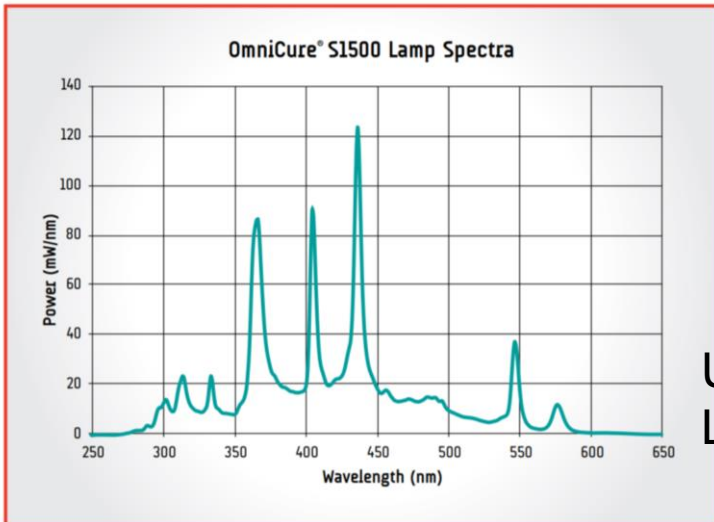
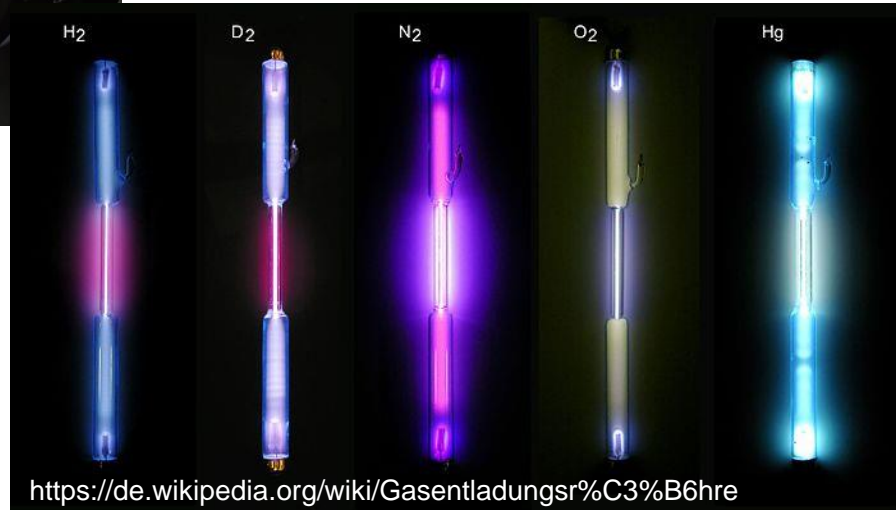
1. Mischung PTMP (1,44g) + HMP (0,17g)
2. 1. zu PDMS geben

PDMS	PTMP + HMP Mischung
4g	0.2g
4g	1.0g



UV-Vernetzung

<https://www.excelitas.com/product/omnicure-e-s1500-spot-uv-curing-system>



UV-A Irradiance: up to 10W/cm²
Lamp power: 200 W

VIDEO

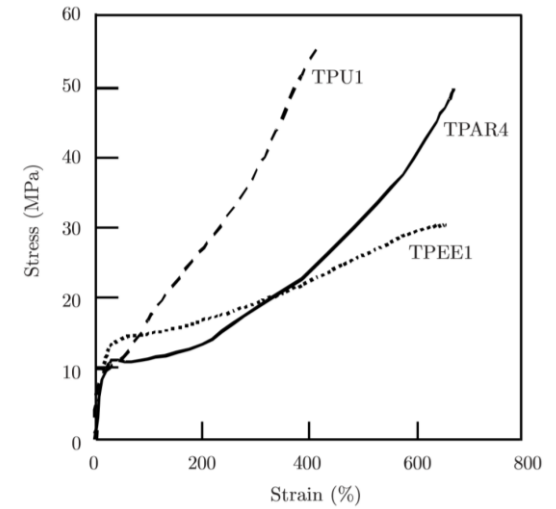
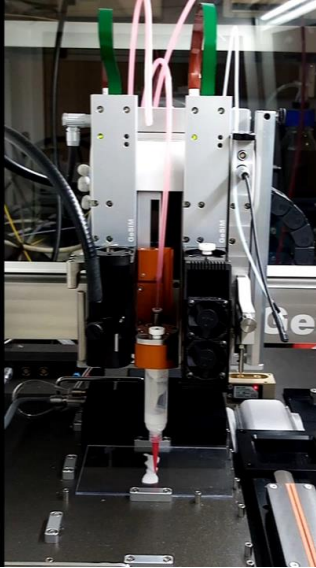
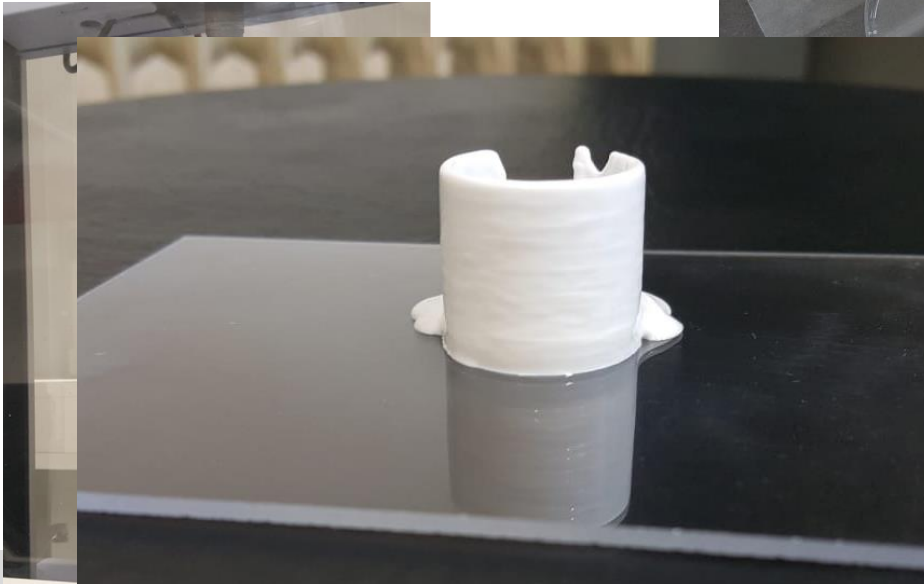
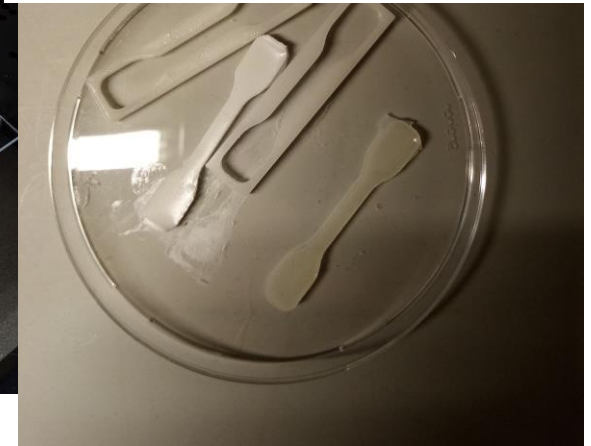


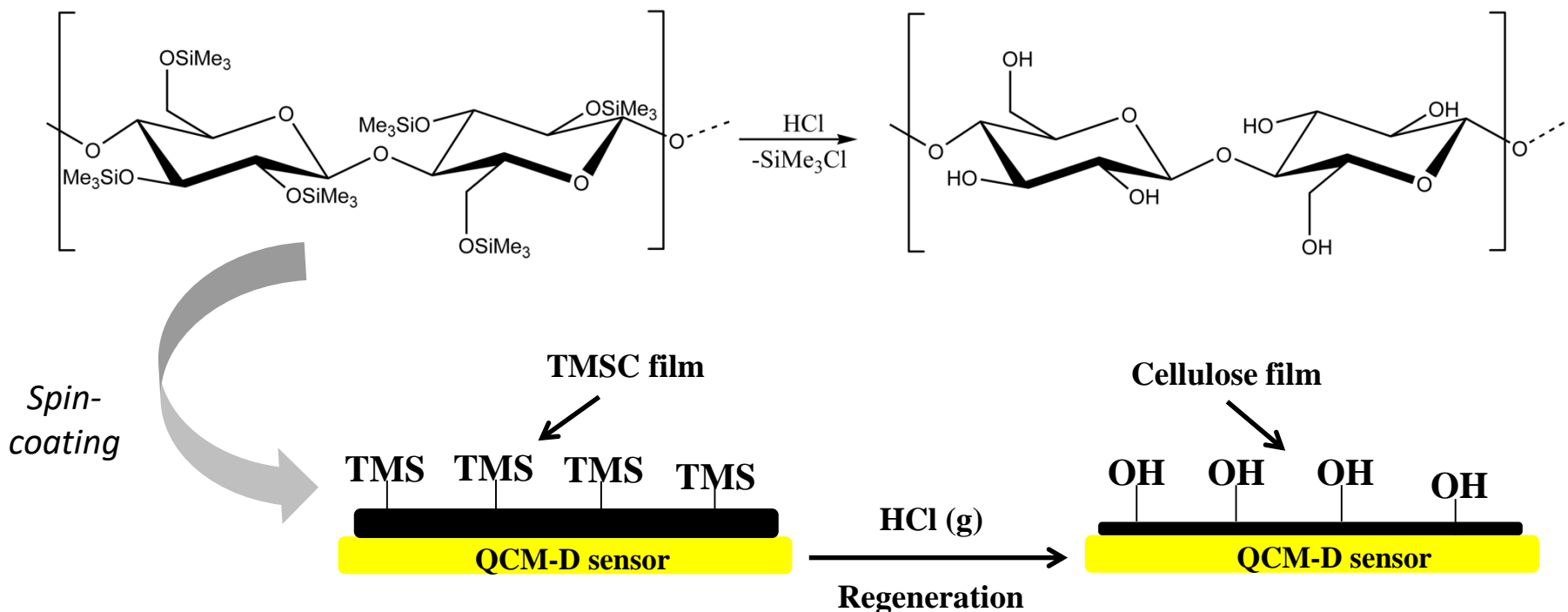
Figure 14. Stress-strain curves of TPEs



g am 3D Drucker
für Zugprüfung werden gedruckt
wird gegossen und vernetzt
gkeit wird am Zugprüfgerät gemessen



- Spin coating of trimethylsilyl cellulose (TMSC) on matrices like Si-wafer and Au-layer
- Regeneration of cellulose via vapors of HCl
- Films are regenerated for 12 minute

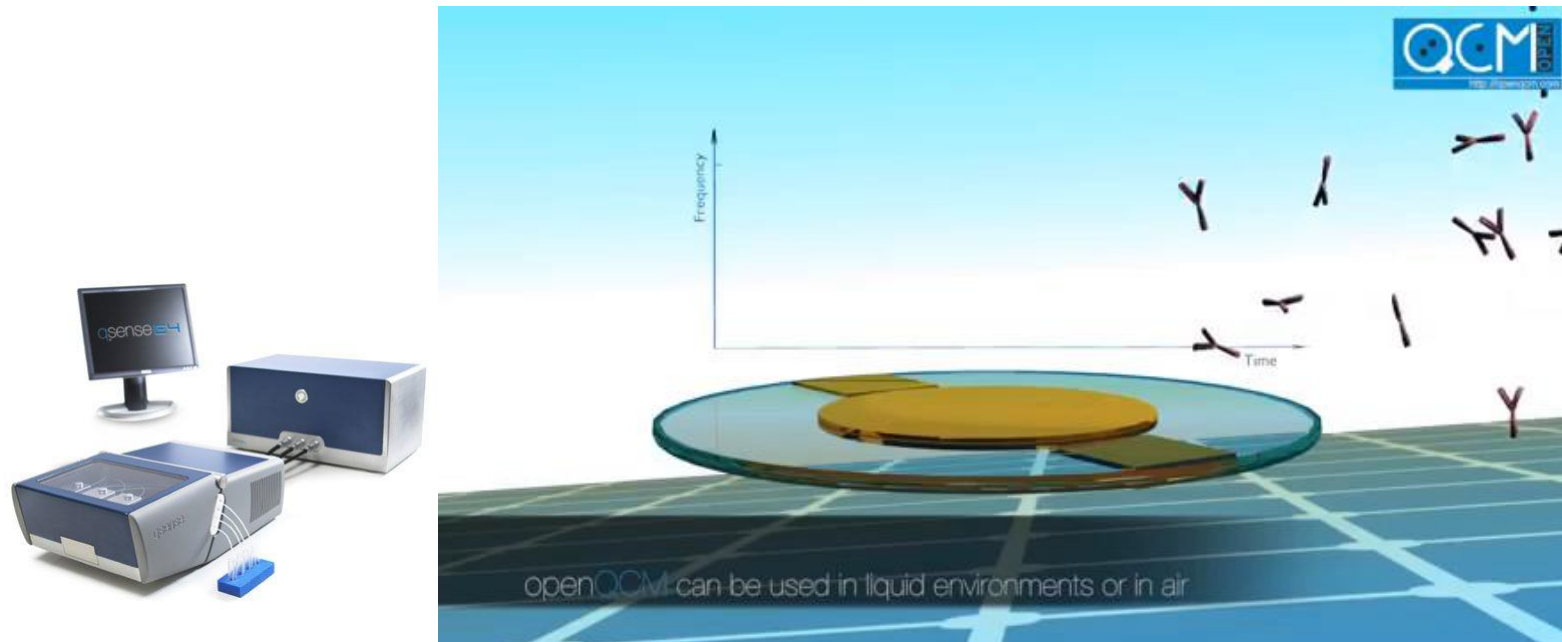
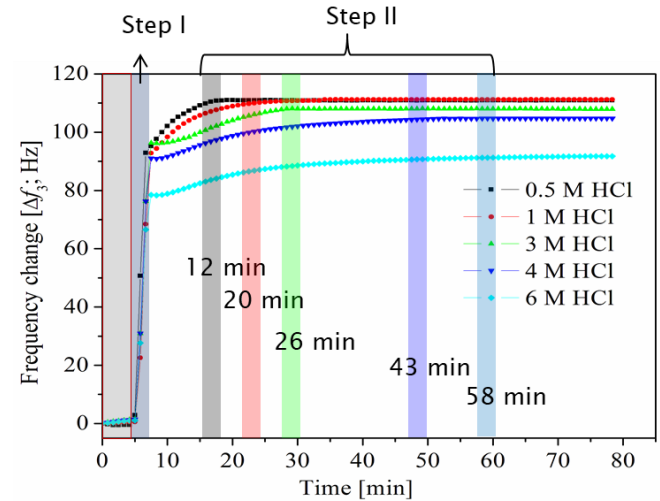
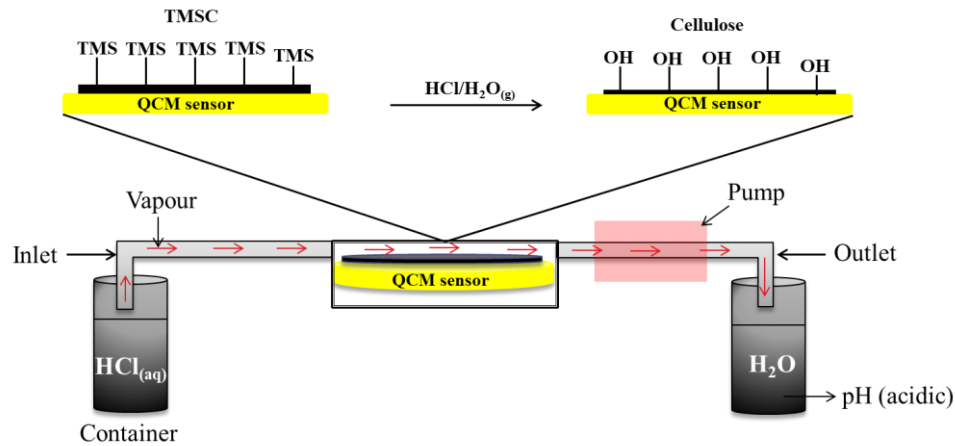


• DS_{silyl} : 2.8, soluble in toluene

layer thickness: ca. **65 nm**,
static water contact angle: **94°**

12 minutes of exposure to HCl(g):

neat cellulose, **d~30 nm**,
static water contact angle **24°**



Viel Erfolg!