Biomimetische Plasmapolymere zur Funktionalisierung von Papier

– BioPlas4Paper –

Gefördert durch:
Bundesministerium für Ernährung und Landwirtschaft
aufgrund eines Beschlusses des Deutschen Bundestages

FNR
Fachagentur Nachwachsende Rohstoffe e.V.

Amelia Lösch-Zhang [1], Martin Bellmann [3], Dennis M. J. Möck [2], Jörn Appelt [2], Andreas Geißler [1]

THÜNEN

Fraunhofer IST

MACROMOLECULAR AND PAPER CHEMISTRY

PTS

[1] Technical University Darmstadt / Macromolecular Chemistry and Paper Chemistry
[2] Thünen Institute of Wood Research / Bio-based Resources and Materials
[3] Fraunhofer-Institut für Schicht- und Oberflächentechnik IST / Anwendungszentrum für Plasma und Photonic APP

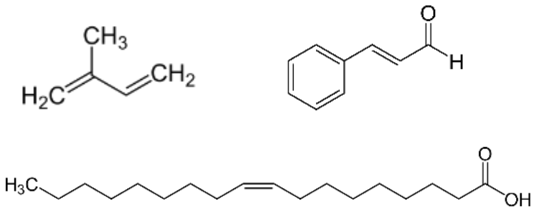
Eckpunkte des Projektes

Laufzeit: 01.05.2021 – 30.04.2024

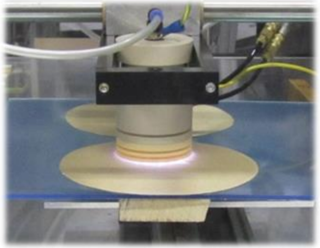
TECHNISCHE UNIVERSITÄT DARMSTADT

Thema:
„Plasmapolymerisation von biogenen Präkursormolekülen auf Papieroberflächen, zur Imitation botanischer Schutzstrategien, als neuartiger Veredlungsansatz um die Performance und Dauerhaftigkeit von Papiererzeugnissen zu erhöhen.“

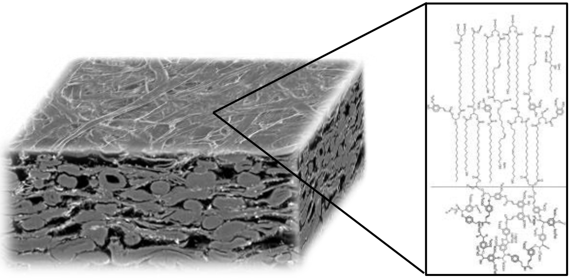
Biogene Präkursoren



PECVD



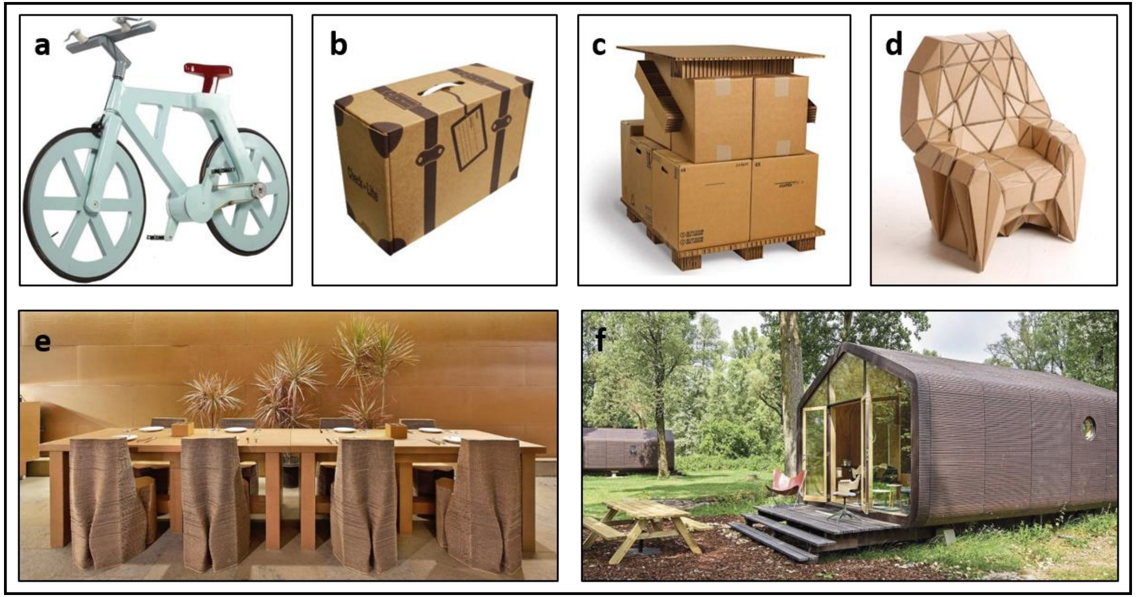
Funktionalisiertes Papier



Forschungseinrichtungen: Fraunhofer IST | THÜNEN | MACROMOLECULAR AND PAPER CHEMISTRY | PTS

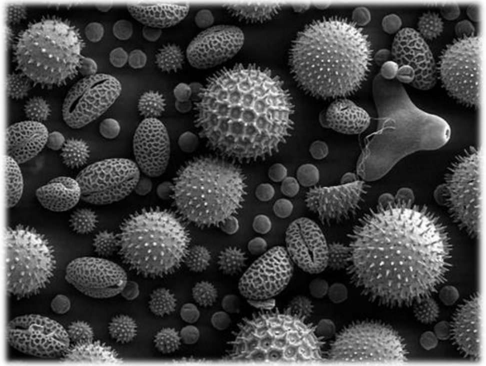
Konstruktionsmaterial – Cellulose

Wood and Fiber Science, 39(2), 2007, pp. 221 – 231



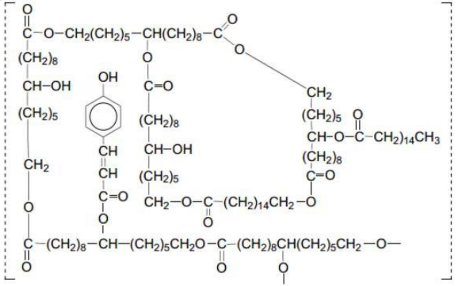
Repräsentative Beispiele papierbasierter Konstruktionsmaterialien in den Anwendungsfeldern Mobilität und Leichtbau (a), Verpackungsmittel (b und c), Möbel und Innenausbau (d und e) sowie Bauwesen (f). [1]

Natürliche Beschichtungsmaterialien

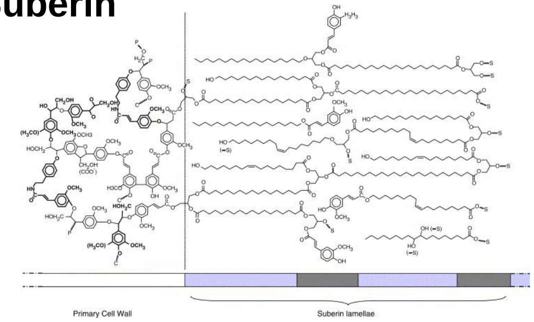


[1]

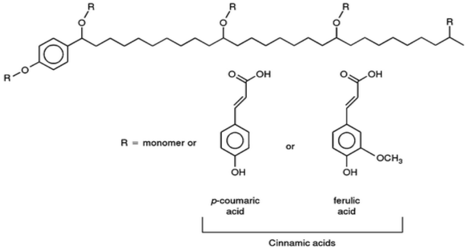
Cutin



Suberin



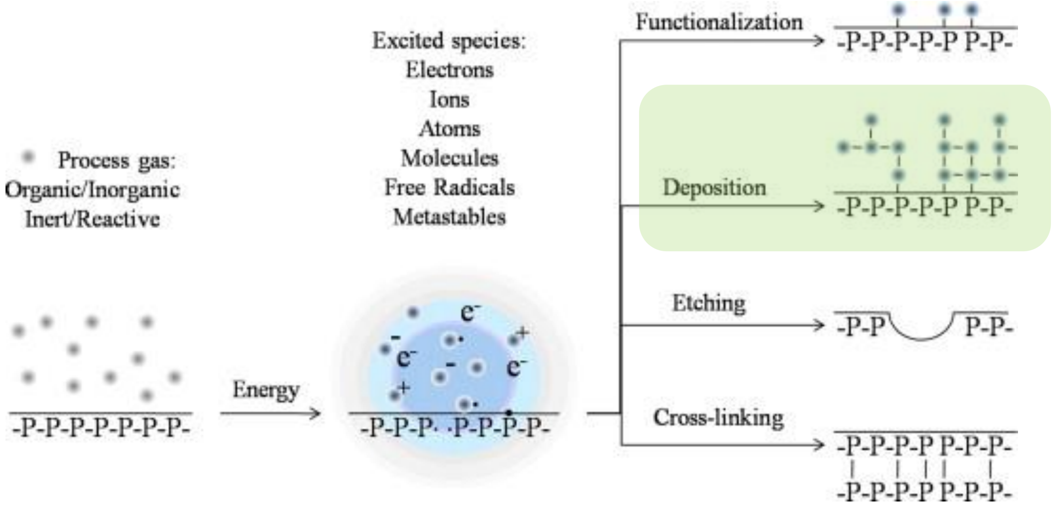
Sporopollenin

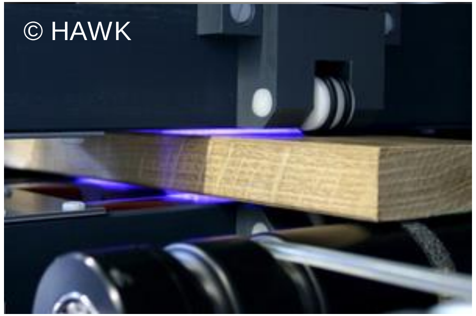


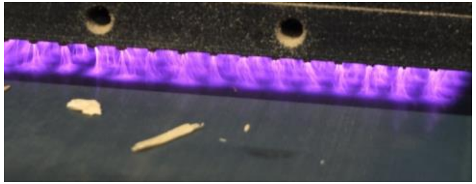
[2]

Plasmapolymerisation

Plasmapolymerisation als Spezialform der *Plasma-enhanced chemical vapor deposition* PECVD.







Plasmapolymerisation: lösungsmittelfrei, sparsam, onlinefähig, in alternierenden Schichten möglich, Applikationsmöglichkeit unlöslicher Polymere, bei RT, keine Trocknung erforderlich, …

Herkömmliche Präkursoren

„Surface fluorination of paper in CF_4-RF plasma environments“

Sahin H.T. et al. *Cellulose* vol. 9, (**2002**) 171–181

„Highly hydrophobic sisal chemithermomechanical pulp (CTMP) paper by fluorotrimethylsilane plasma treatment“

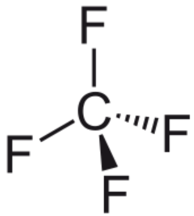
Navarro F. et al. *Cellulose* vol. 10, (**2003**) 411–424

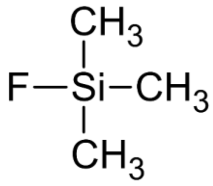
„Paper surface modification by plasma deposition of double layers of organic silicon compounds“

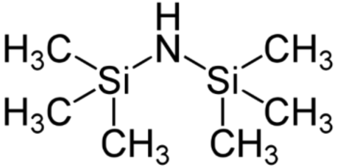
Tan I. H. et al. *J. Mater. Chem*., 11 (**2001**) 1019-1025

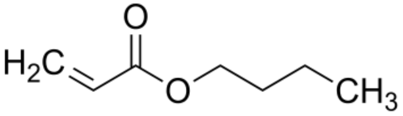
„Plasma-induced polymerization for enhancing paper hydrophobicity“

Song et al. *Carbohydrate Polymers* 92, (**2013**) 928–933

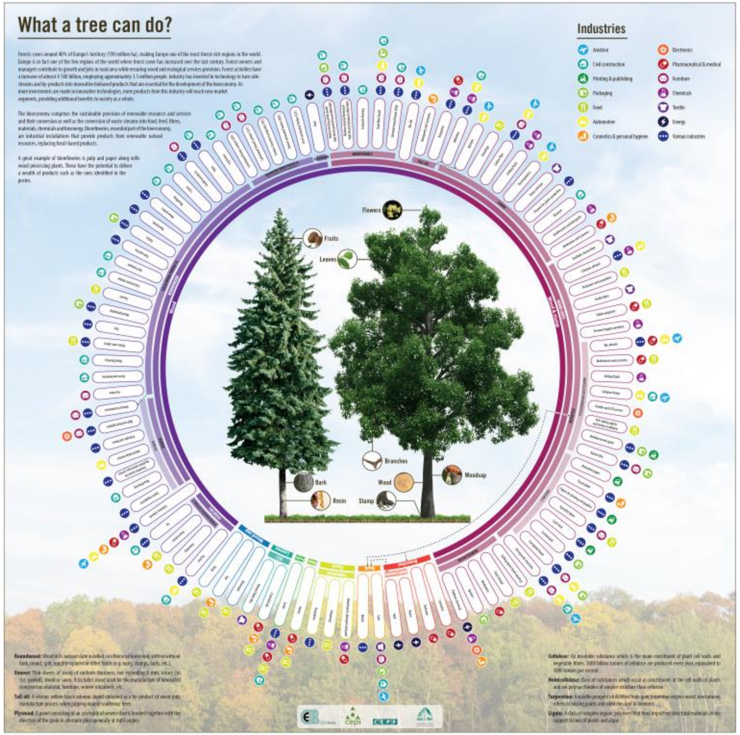








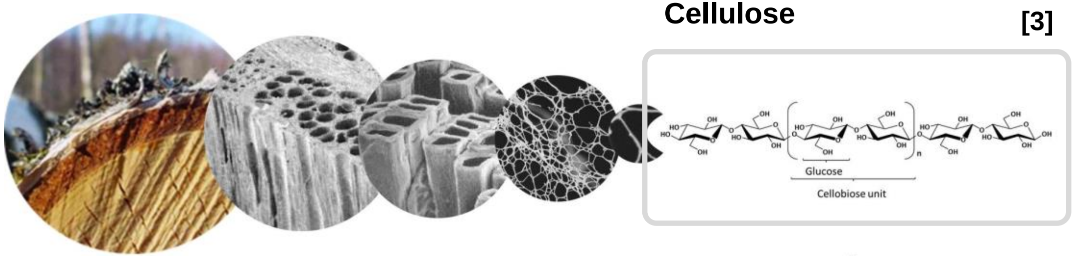
Quellen biogener Präkursoren



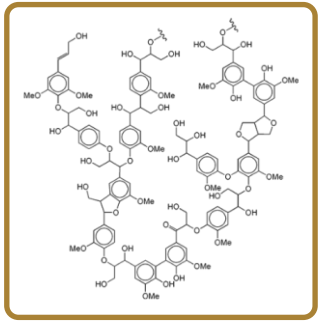
https://www.cepi.org/wp-content/uploads/2021/02/What-a-tree-can-do-final_compressed.pdf

Cellulose

[3]

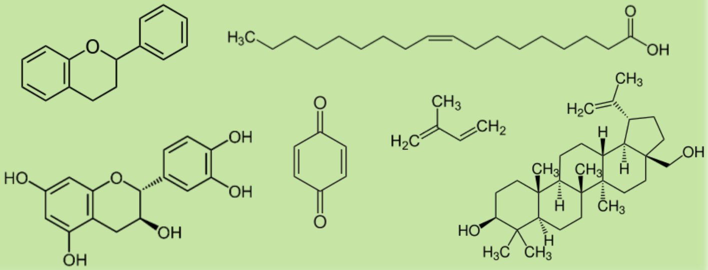


Lignin



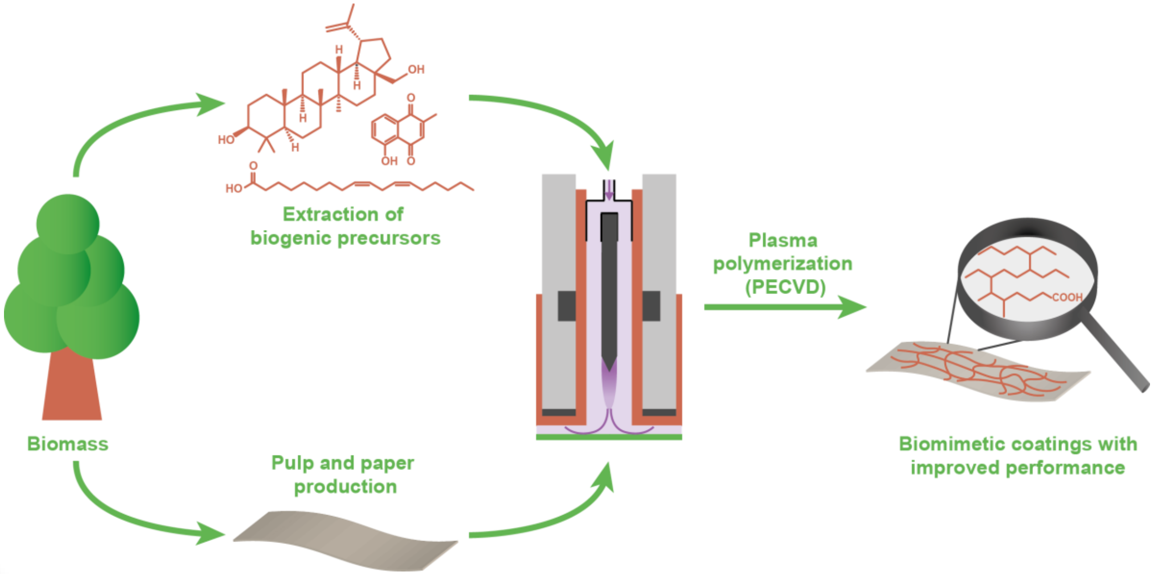
Pflanzliche Extraktstoffe:

Öle, Terpene, Catechine, Flavonoide, Phenole…



Isolation biogener Präkursoren

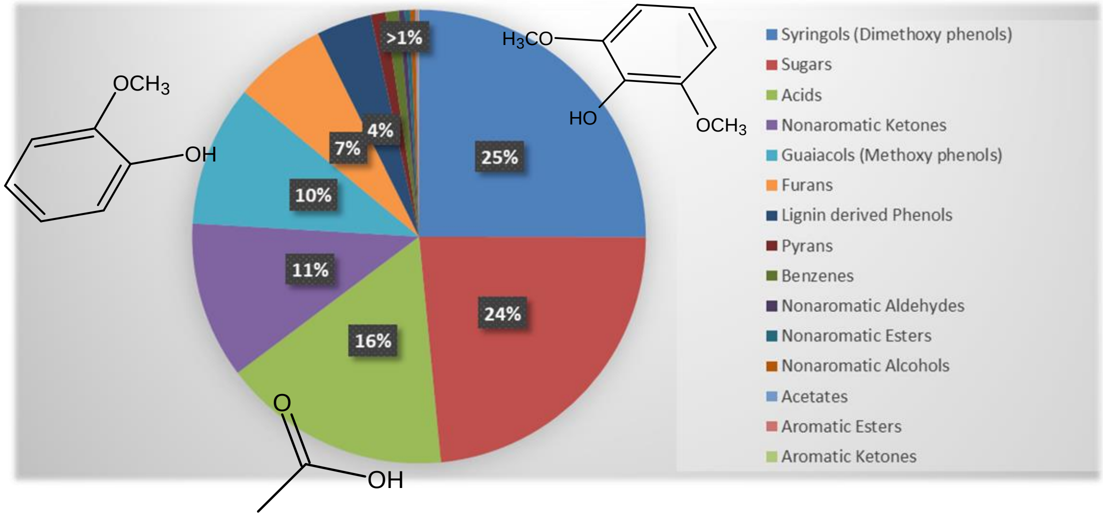
Tallöl, Pyrolyseöl, Rinde, …



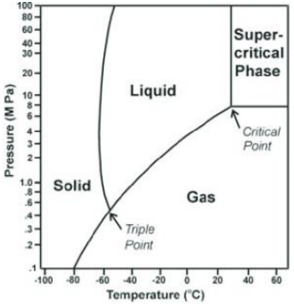
Isolation biogener Präkursoren

Tallöl, Pyrolyseöl, Rinde, …

$scCO_2$-Extraktion von Pyrolyseöl

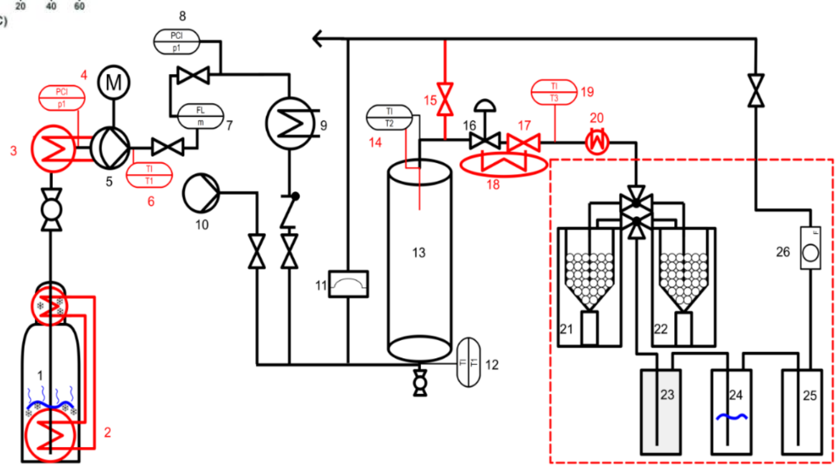


Überkritische CO_2 – Extraktion

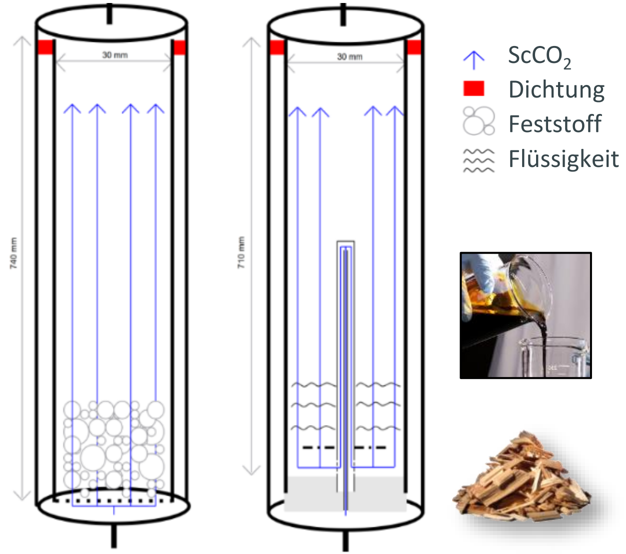


1 CO_2 bottle
2 Water heating
3 Powerful cooler
4, 8 Pressure gauges
5 Cooled high-pressure membrane pump
6,12,14,19 Thermocouples
7 Mass flow meter
9 Preheater
10 Modifier pump
11 Rupture disc
13 Extractor

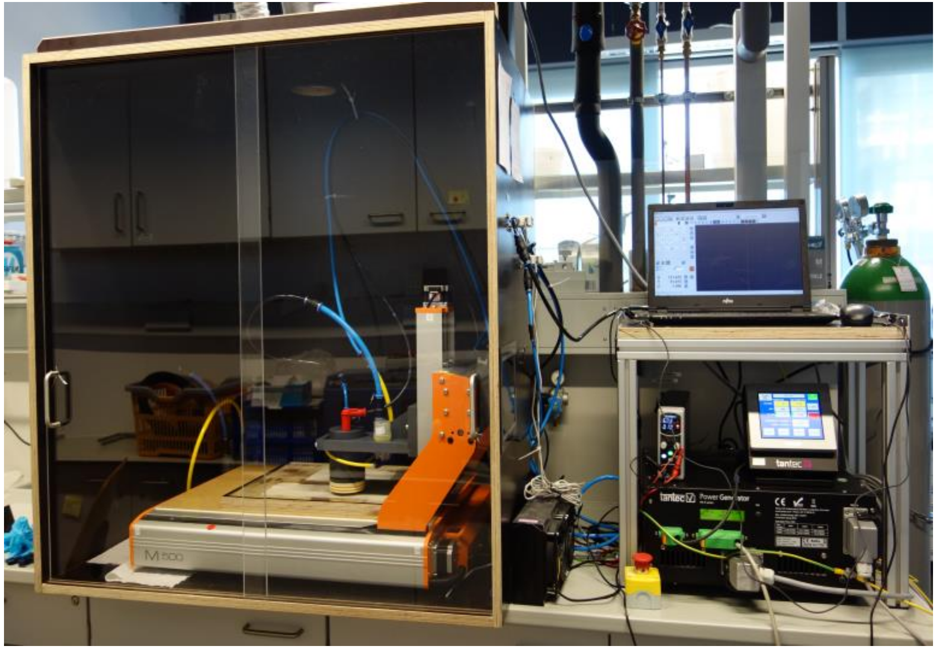
15 Bypass valve
16 Back pressure regulator
17 Proportional overflow valve
18 Adjustable valve heating
20 Cooler for the off-gases
- - - Optimized separation system
21-22. Separators with 2mm glass beads
23. Wash bottle with cotton
24. Wash bottle with water
25. Wash bottle
26 Float-type flow meter

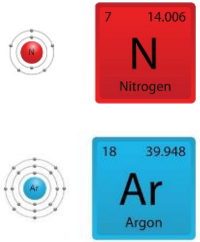


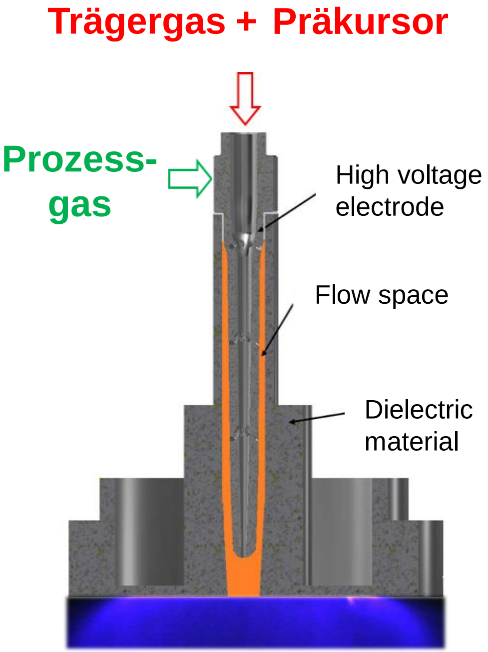
Extraktor



Abscheidung im Labormaßstab

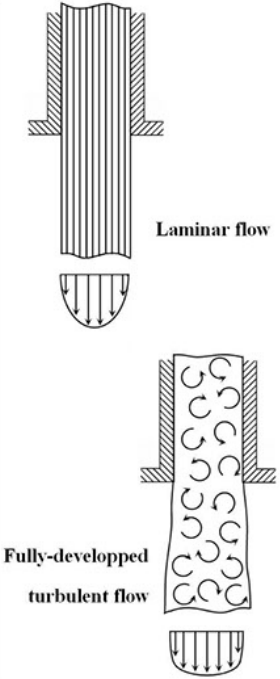


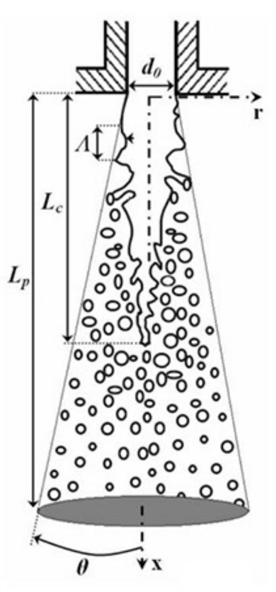




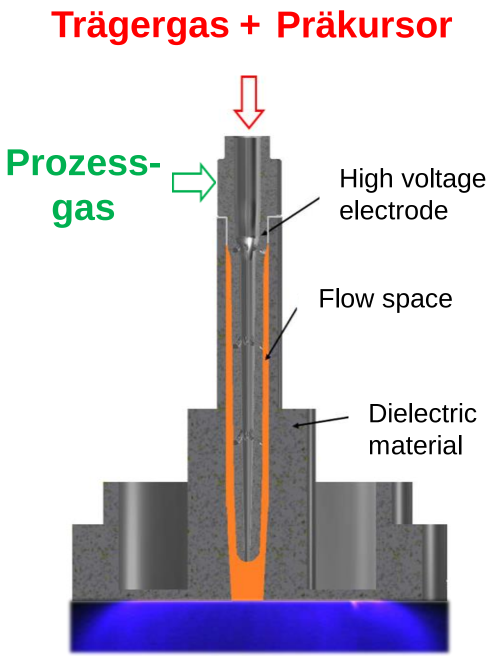
Präkursoreinspeisung

Relevant properties for atomization	
Injected liquid:	- Surface tension - Viscosity - Density
Liquid flow:	- Injection pressure - Velocity - Turbulence in the liquid stream
Ambient gas:	- Gas density - Temperature
Gas flow:	- Absolute velocity - Relative gas-to-liquid velocity - Turbulence in the gas stream
Injector:	- Dimension of the orifice diameter - Internal structure and geometry of the nozzle



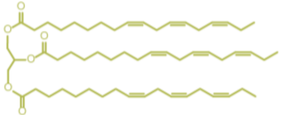
Geometrical aspects and characteristics of sprays	Illustration
- Nozzle flow rate: U_l - Liquid jet or sheet thickness: d_0 - Radial and axial distances: r and x - Length of the liquid core: L_c - Distance of penetration: L_p - Mean drop size: $\overline{D}$ - Drop size distribution: $P(d)$ - Drop number density: N - Radial patternation - Circumferential patternation - Spray angle: θ - Evaporation rate - Wavelength of disturbance: Λ	

[4]



PECVD auf Glas

Test series with Chia Oil:

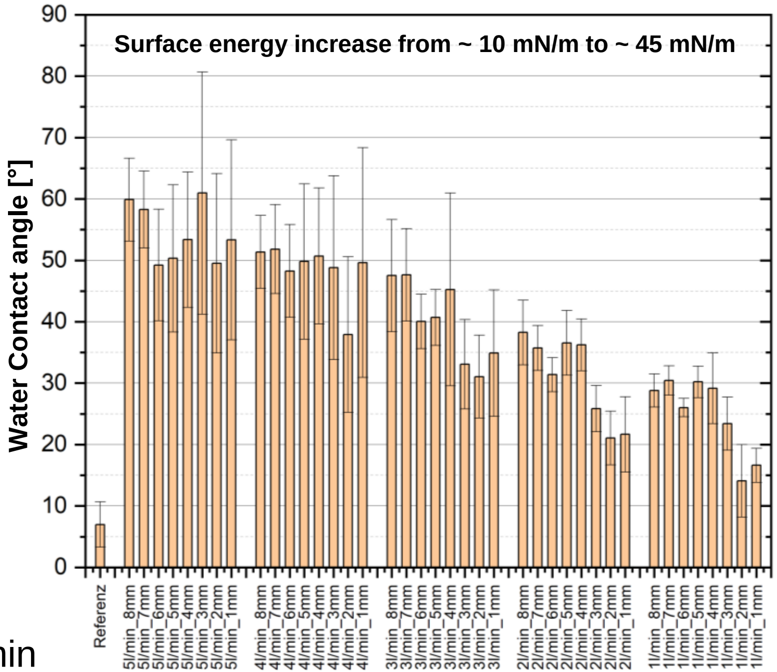


Fixed Parameters:

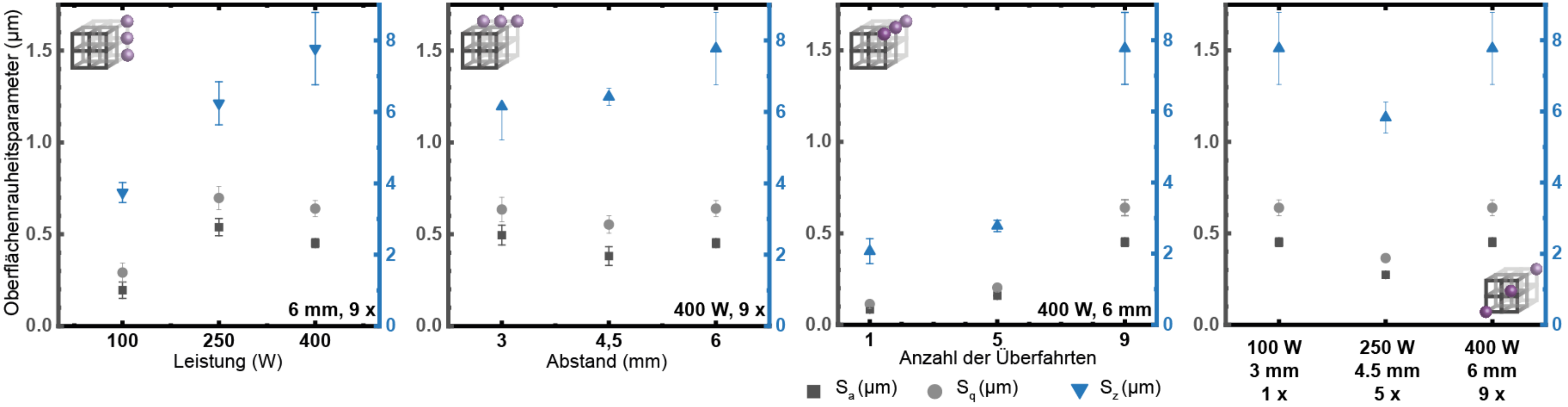
- Velocity: 2 m/min
- Repetitions: 2
- Argon flow: 15 l/min
- Power: 250 W

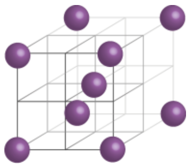
Variable Parameters:

- Distance: 1 – 8 mm
- Nitrogen flow: 1 – 5 l/min



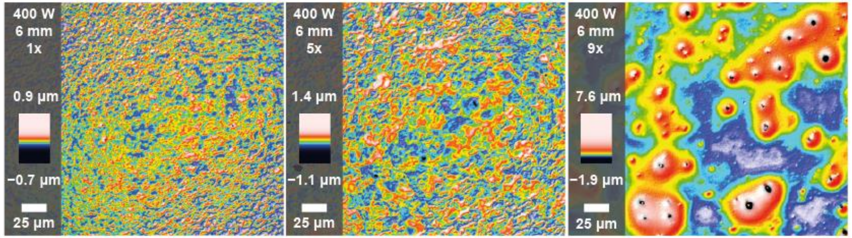
Statistische Versuchsplanung



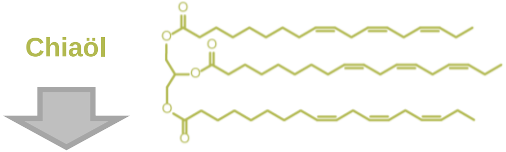


Coating optimization by DOE

- Complete picture accessible
- Reduced number of experiments required
- Parameter influence can be quantified



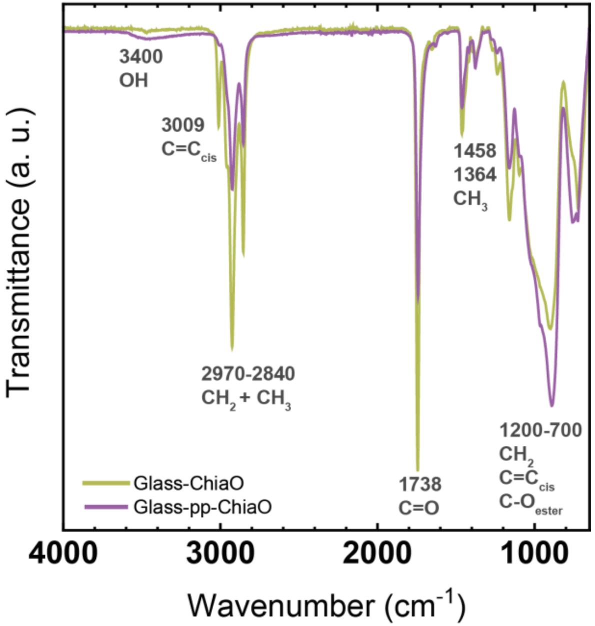
Charakterisierung der Plasmapolymere



Fragestellungen bezüglich:

- Crosslinking (C=C)
- Fragmentierung
- Stickstoffeinbau
- Oxidation
- Alterung

FTIR



PECVD-Beschichtungen auf Papier

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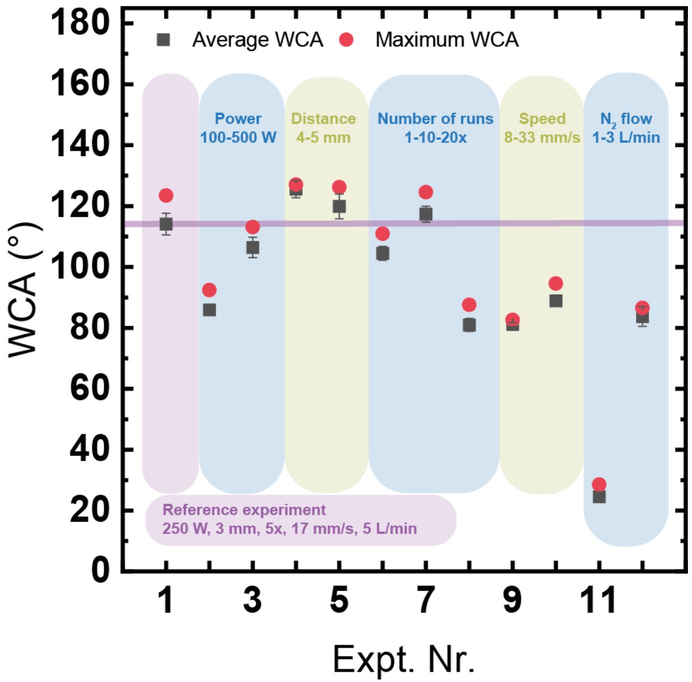
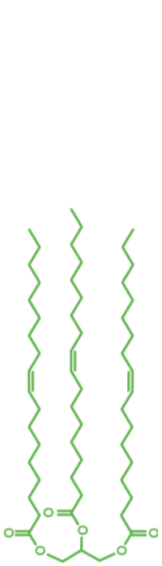
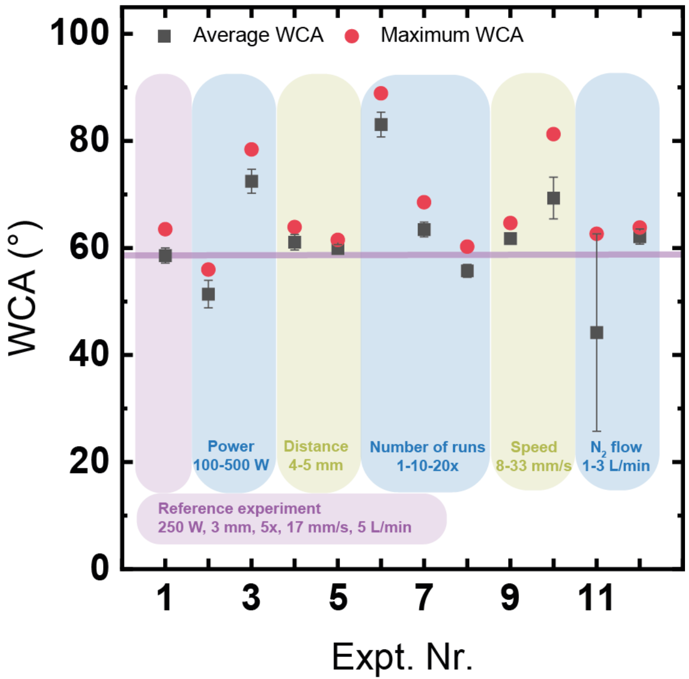
pp(Olive oil) on glassine paper



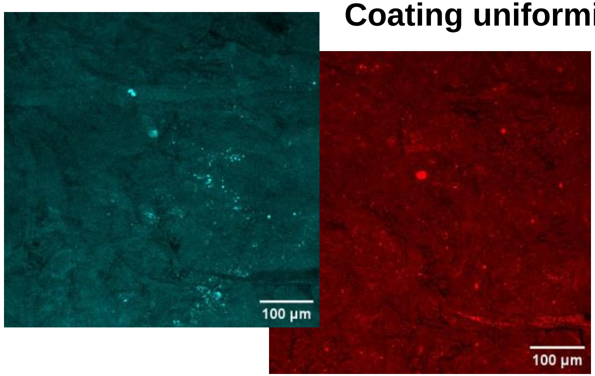


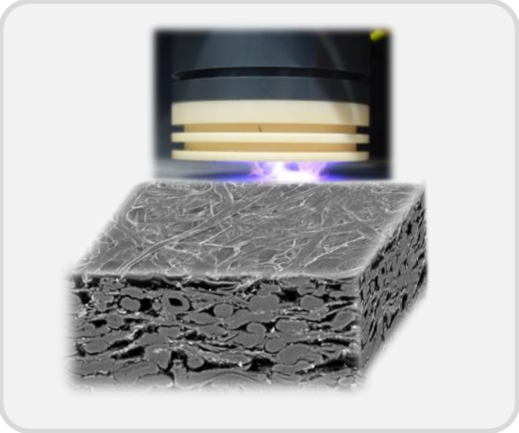
pp(Linoleic acid) on glassine paper



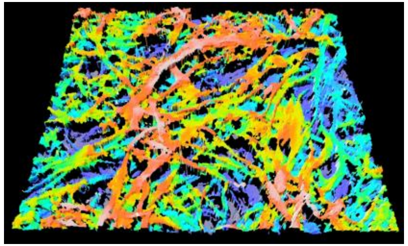
PECVD-Beschichtungen auf Papier

Coating uniformity

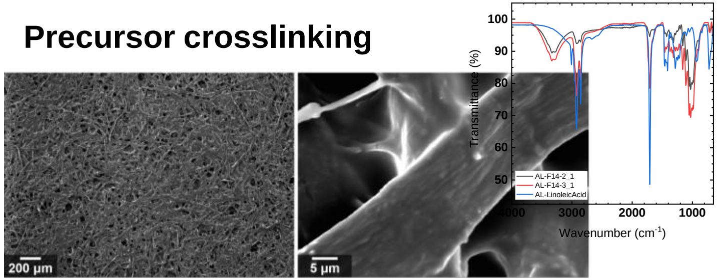




Surface roughness



Precursor crosslinking



Wetting behavior

(119.9 ± 0.6)°

Challenging surface/polymer analysis

- due to low application volumes,
- structure of the paper substrate
- and the covalent bonding of the polymer network to the cellulose

Veröffentlichungen

Bioraffinerietag DBFZ, Leipzig **2022**,

EWLP, Göteborg **2022**,

PTS Conference Biobased Solutions, Dresden **2022**,

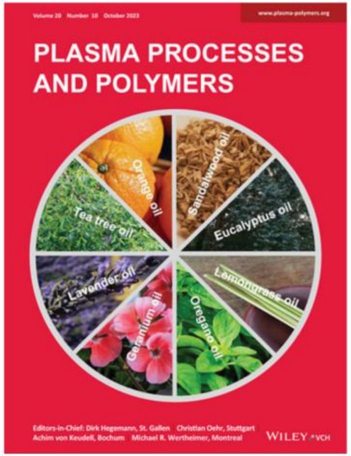
Fachpack, Nürnberg **2022**,

Ligna, Hannover **2023**,

21st ISWFPC, Venedig 07/**2023**

4evergreen Innovations Webinar 26.10.**2023**

…



Loesch-Zhang et al. *MDPI Polymers* **2022** https://doi.org/10.3390/polym14091773

Moeck et al., *The Journal of Supercritical Fluids* **2023** https://doi.org/10.1016/j.supflu.2023.105937

Loesch-Zhang et al. *Plasma Processes and Polymers* **2023** https://doi.org/10.1002/ppap.202300016

Bellmann et al. *Plasma Processes and Polymers* ***2023*** → wird aktuell finalisiert

Vielen Dank für Ihre Aufmerksamkeit

– BioPlas4Paper –

Gefördert durch:

Bundesministerium für Ernährung und Landwirtschaft

aufgrund eines Beschlusses des Deutschen Bundestages

FNR Fachagentur Nachwachsende Rohstoffe e.V.

Amelia Loesch-Zhang

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Andreas Geißler

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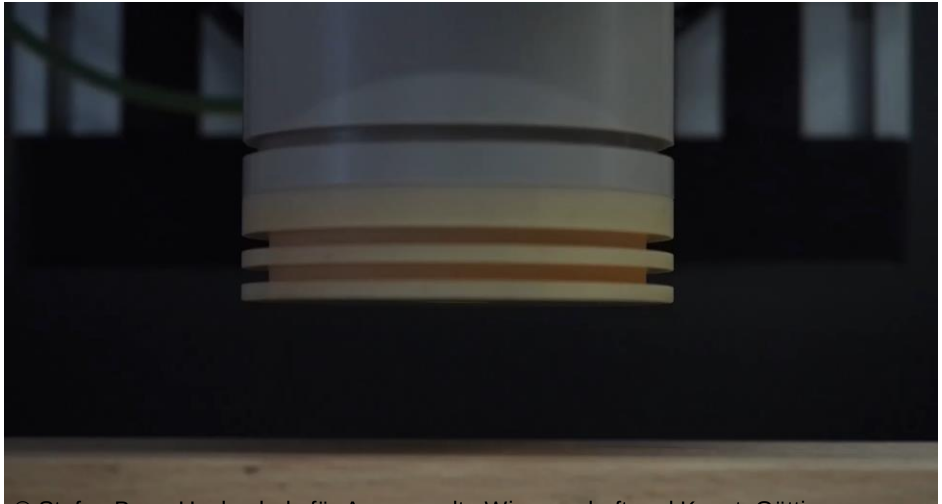

References

[1] https://www.publicdomainpictures.net/en/view-image.php?image=100685&picture=wet-leaves
https://www.dreamstime.com/photos-images/cork-oak-trees-portugal.html
https://svs.gsfc.nasa.gov/10394

[2] Phu et al. Effect of different parameters on extraction performance and tensile properties of cutin membrane from basella alba cuticle. Proceedings of The 2017 International Symposium on Materials Science and Technology. HCMC-Vietnam.
A. Gandini et al. *Prog. Polym. Sci*. 31 (2006) 878–892.
Fadiran O.O. and Meredith J. C. *J. Mater. Chem*. A, 2014, 2, 17031.

[3] https://weidmannfibertechnology.com/wp-content/uploads/2016/12/Aufbau-Holz-neu-1.jpg
Original: Herbert Sixta, Handbook of Pulp, 1, 59, 2006. Patt R. et al., Vom Holz zum Papier, Physik unserer Zeit, 23, 129-136, 1992.

[4] https://spray-imaging.com/spray-description.html

Projektstruktur / Forschungsfragen

TECHNISCHE UNIVERSITÄT DARMSTADT

Industriepartner ⟷ **Forschungseinrichtungen** ⟷ **Unterauftrag**

Industriepartner: Arwed Löseke (Papierverarbeitung und Druckerei GmbH), papair, proFagus (pro Qualität · pro Natur), Felix Schoeller Group (Best Performing Papers. Worldwide.), SIK-Holz (Spielen – Individuell – Kreativ), tantec, THIMM Packaging Systems

Forschungseinrichtungen: Fraunhofer IST, THÜNEN, MACROMOLECULAR AND PAPER CHEMISTRY

Plasmatechnologie:
- Auswahl und Optimierung von Plasmaquellen (Bauformen), Prozessparametern, Trägergasen, Einspeisungsmöglichkeiten von Präkursormolekülen / Monomeren zur Beschichtung / Funktionalisierung poröser, organischer, bahnförmiger Materialien
- Zusammensetzung der Prozessabluft, Anpassung der Prozessparameter

Pflanzenextrakte:
(ggf. Koppelprodukte aus der stofflichen Verwertung?)
- Isolierung (Methodenentwicklung Extraktion) und Charakterisierung der Präkursormoleküle
- Energetische Verwertung?

„biomimetische“ Plasmapolymere:
- Grundlegende Analytik der Polymere, Schichtdickenbestimmung und Visualisierung der Polymere im Papiergefüge,
- Prüfung funktionalisierter Papiere (Bewitterung, gezielte Besiedlung mit Mikroorganismen, Feuchte-, UV-Schutz)
- Nachhaltigkeit → biologische Abbaubarkeit

Unterauftrag: PTS

Papier:
- Charakterisierung der mod. Papiere hinsichtlich optischer und mech. Eigenschaften,
- Rezyklierbarkeit der modifizierten Papiere,
- Emission von Bestandteilen (VOC) aus den Beschichtungen,
- Planungen zur Integration eines Plasmamoduls in die Versuchspapiermaschine

Zeitplan / Arbeitspakete

Laufzeit: 01.05.2021 – 30.04.2024

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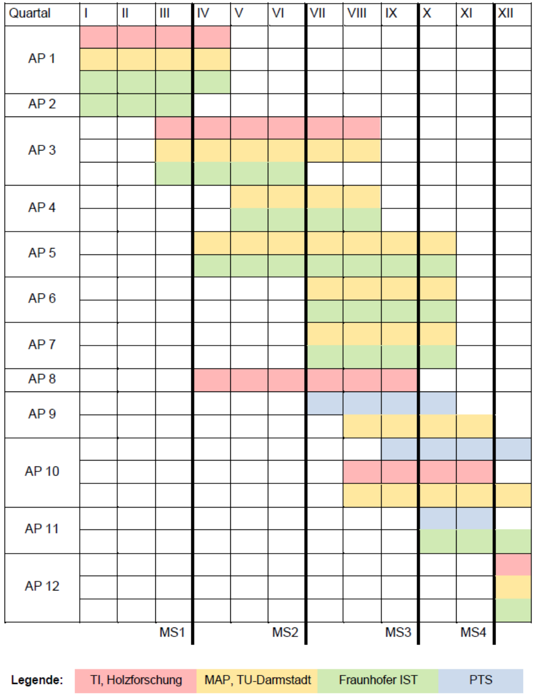

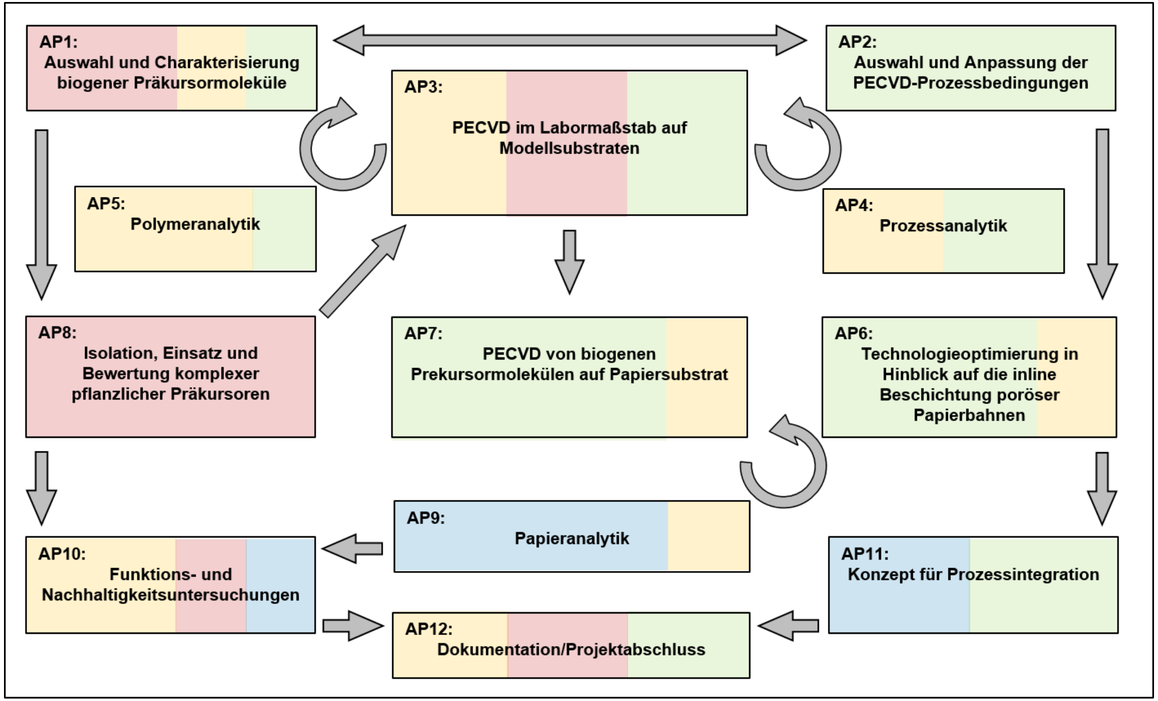

Industriepartner / Projektbegleiter

- Arwed Löseke Papierverarbeitung und Druckerei GmbH
- Papair GmbH
- proFagus GmbH
- Schoeller Technocell GmbH & Co. KG
- SIK Holzgestaltung GmbH
- Tantec A/S
- Thimm Packaging Systems GmbH & Co. KG
- Papiertechnische Stiftung (PTS)