TECHNISCHE UNIVERSITÄT WIEN
Vienna | Austria

Institute of Applied Synthetic Chemistry

cubicure

Lignin als Baustein für 3D-gefertigte Produkte

PdZ-Projekt “3DFabBio - Maßgeschneiderte 3D gefertigte Produkte aus bio-basierten erneuerbaren Rohstoffen“

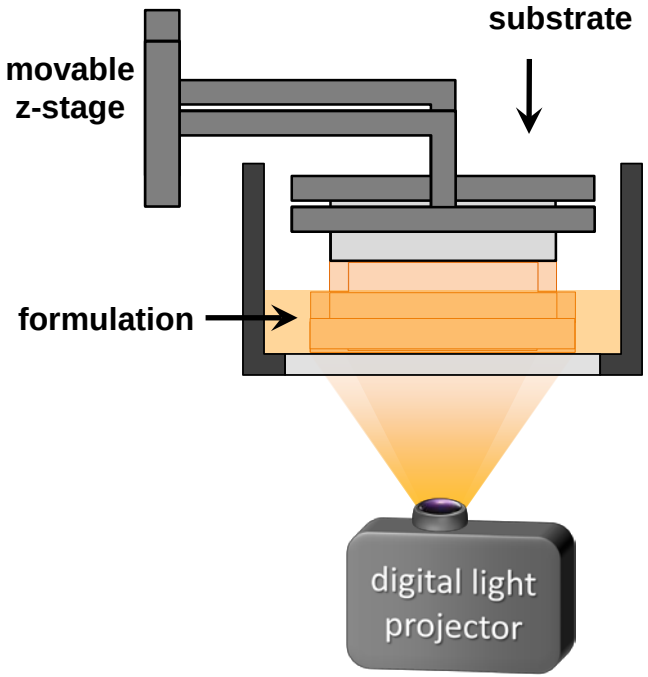
FFG

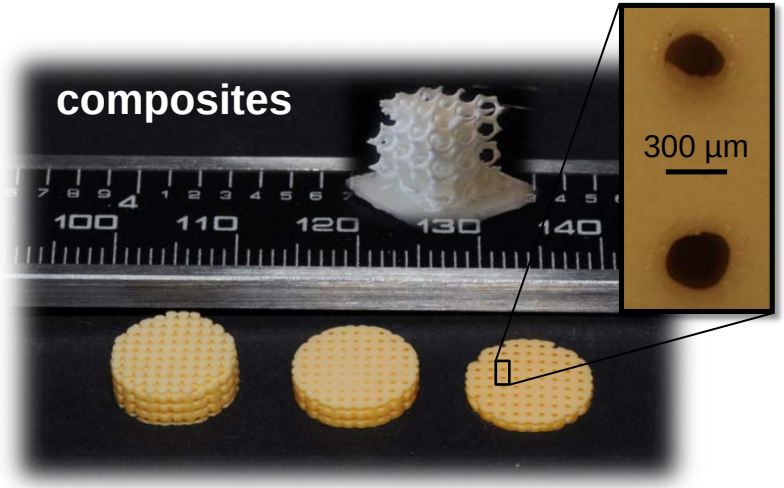
Bundesministerium für Verkehr, Innovation und Technologie

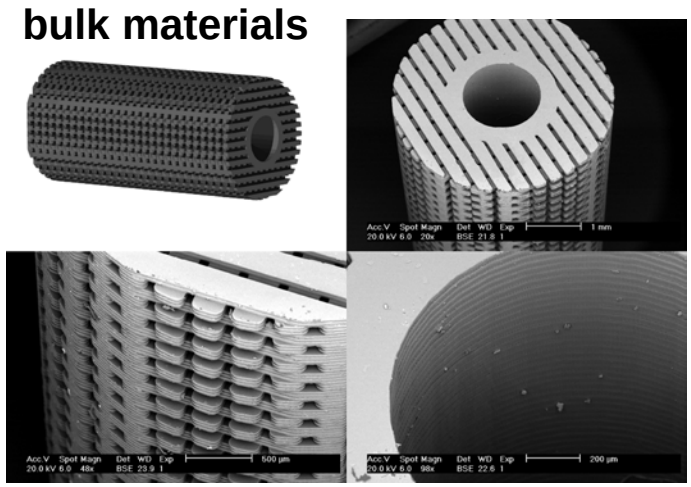
STEFAN BAUDIS (TU WIEN)

ROBERT GMEINER (CUBICURE GMBH)

3D Printing: Stereolithography





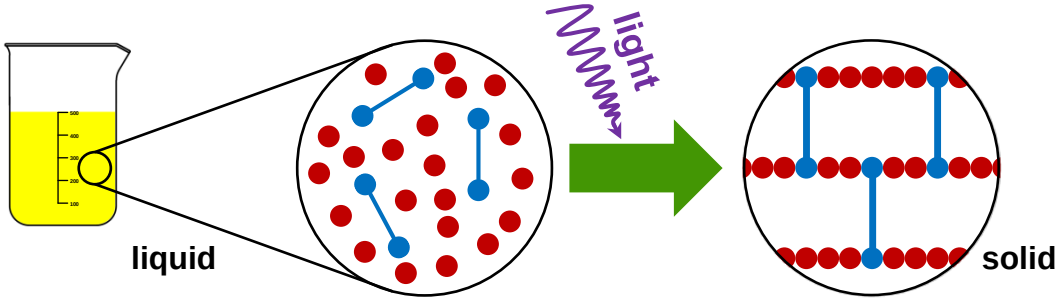


J. Stampfl, S. Baudis, C. Heller, R. Liska, A. Neumeister, R. Kling, A. Ostendorf, M. Spitzbart, *J. Micromech. Microeng.* 18(12) (**2008**) 125014.

S. Baudis, C. Heller, R. Liska, J. Stampfl, H. Bergmeister, G.Weigel, *J. Polym. Sci. A* 47 (**2009**) 2664-2676.

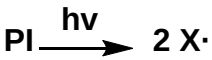
S. Baudis, F. Nehl, S.C. Ligon, A. Nigisch, H. Bergmeister, D. Bernhard, J. Stampfl, R. Liska, *Biomed. Mater.* 6(5) (**2011**) 055003.

Photopolymerization

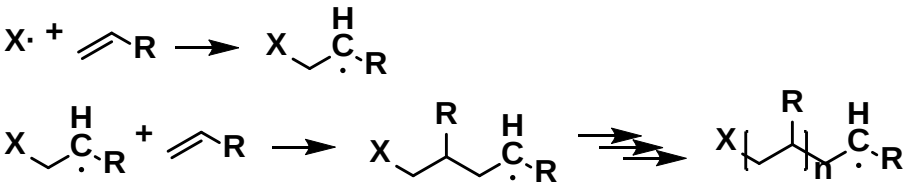


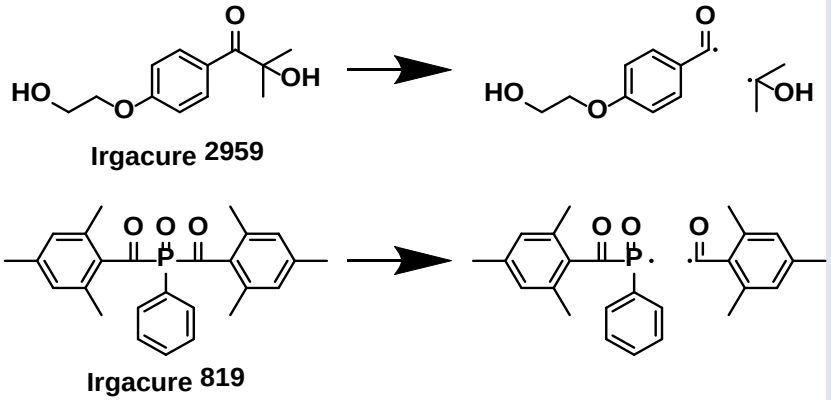
key component: ***Photoinitiator***

Initiation

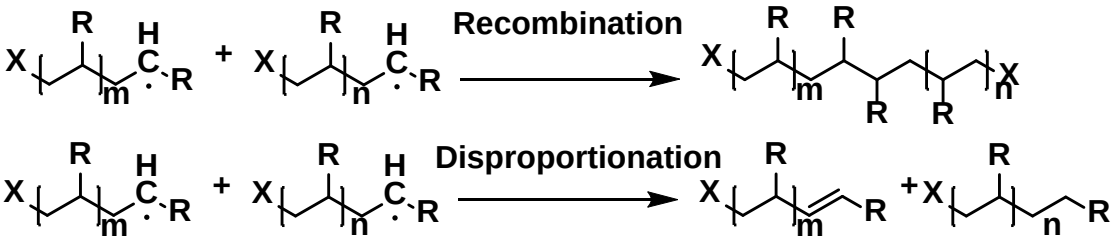


Propagation





Termination

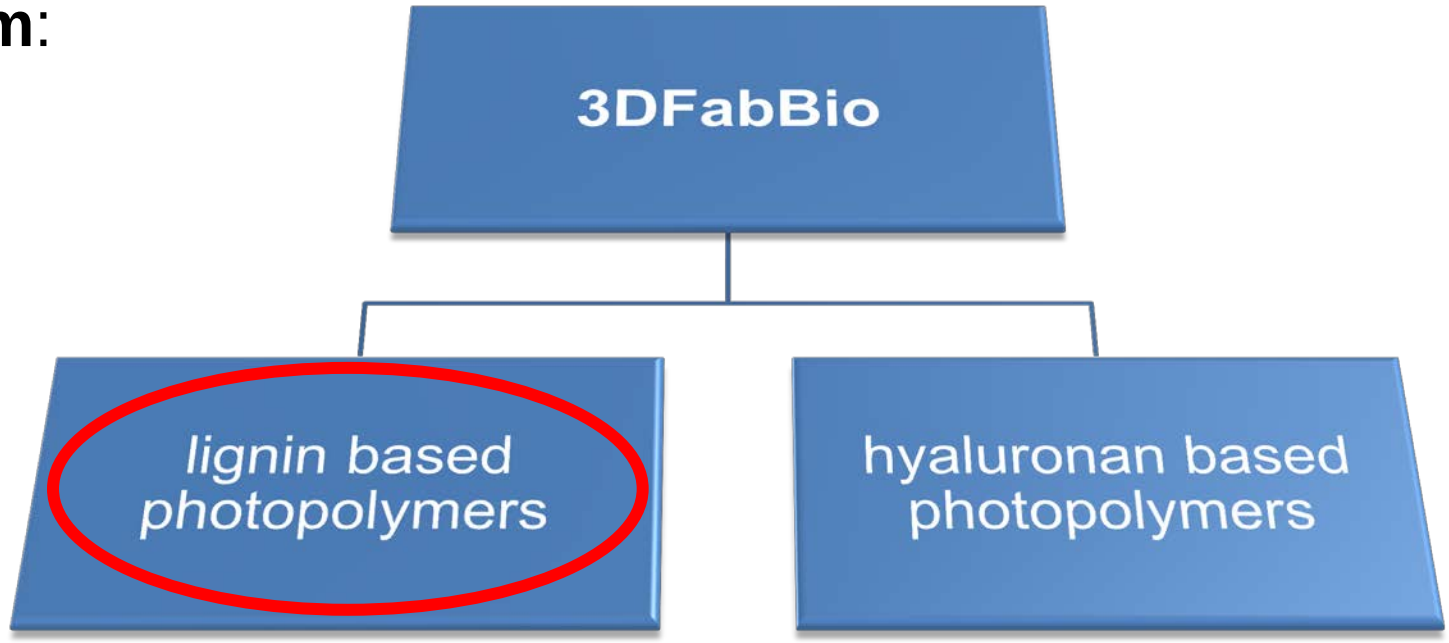


3DFabBio Project: Motivation and Aim

Motivation:

- Low/no sustainability of the process and underlying chemistry
- Hazardous (meth)acrylate chemistry
- Migratability, esp. photoinitiator

Aim:

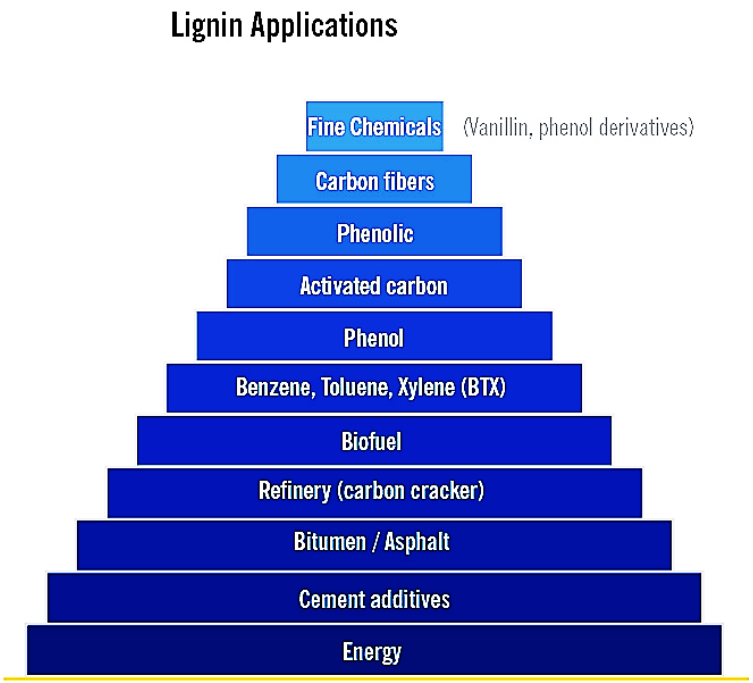


Introduction: Lignin

- latin word *lignum* = wood
- is available in wood and is present in annual plants e.g. wheat straw
- second most abundant renewable carbon source after cellulose; plants contain between 27 and 33 % lignin
- binder of cells, fibrils and vessels
- represents 30 % of all non-fossil organic carbon

Structure of lignocellulose: Edward M. Rubin, Genomics of cellulosic biofuels, *Nature* 454, 841-845 (**2008**)

Why to use Lignin for Photopolymerization?!



- ✓ demand for renewable materials
- ✓ the second most abundant natural raw material
- ✓ a natural product
- ✓ biodegradability
- ✓ availability
- ✓ new application field
- ✓ for 3D printing as active and reactive compound

Lignin: Technology, Applications, and Markets, http://www.risiinfo.com/product/lignin-technology-applications-and-markets/, access: 26.05.2017.

Modification of Lignin

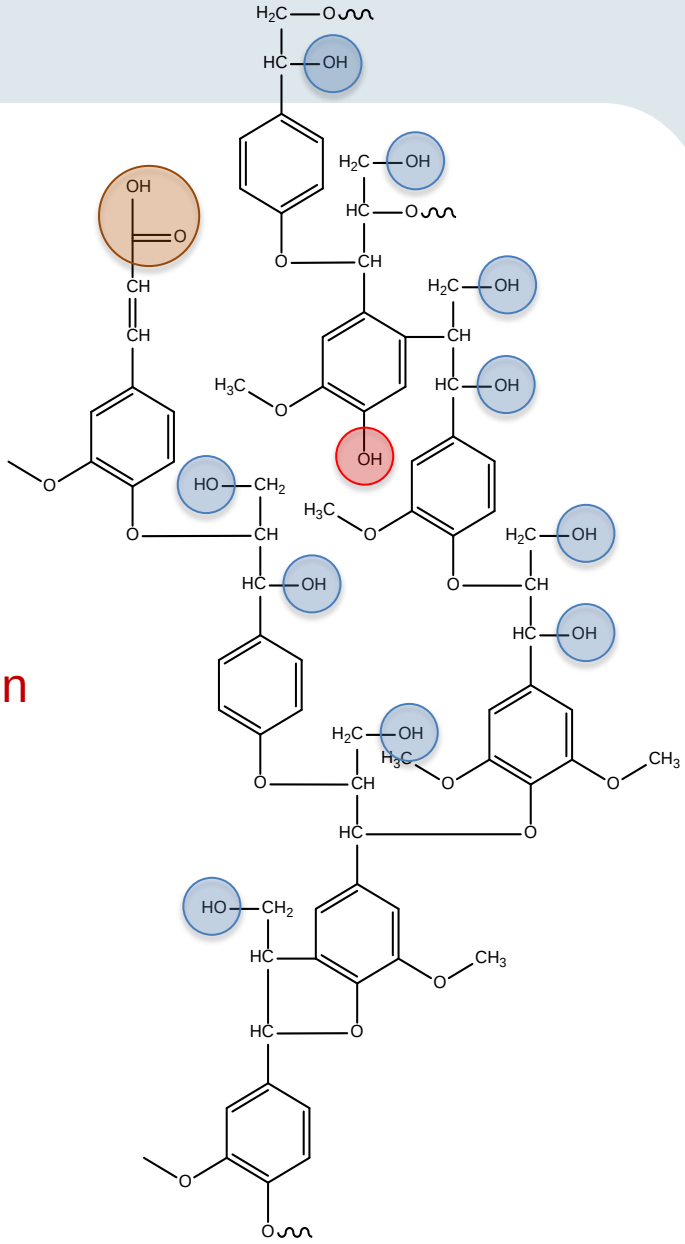
Unmodified lignin

- non-uniform structure
- different functional groups
- different chemical reactivities
- poor accessibility of reactive sites
- poor solubility

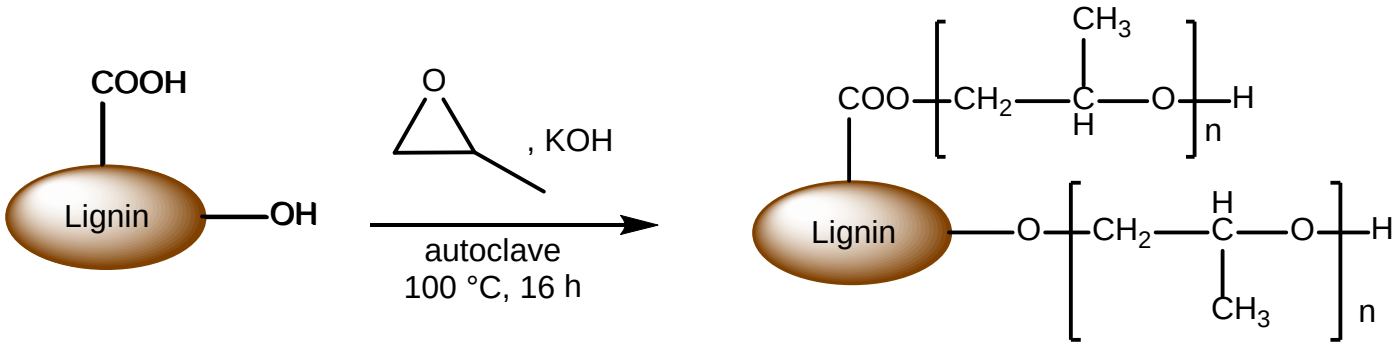
oxyalkylation

Modified lignin

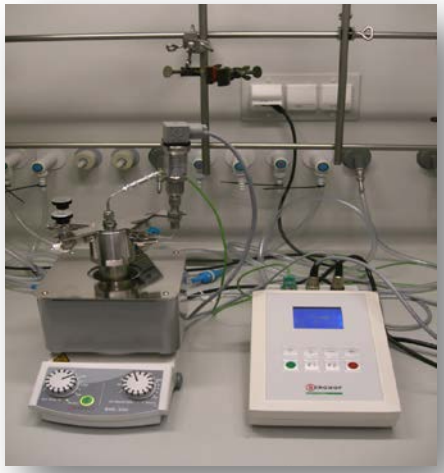
- improved uniformity
- improved solubility
- increased reactivity
- desreased viscosity
- liquefaction of biopolymer



Oxyalkylation of Lignin



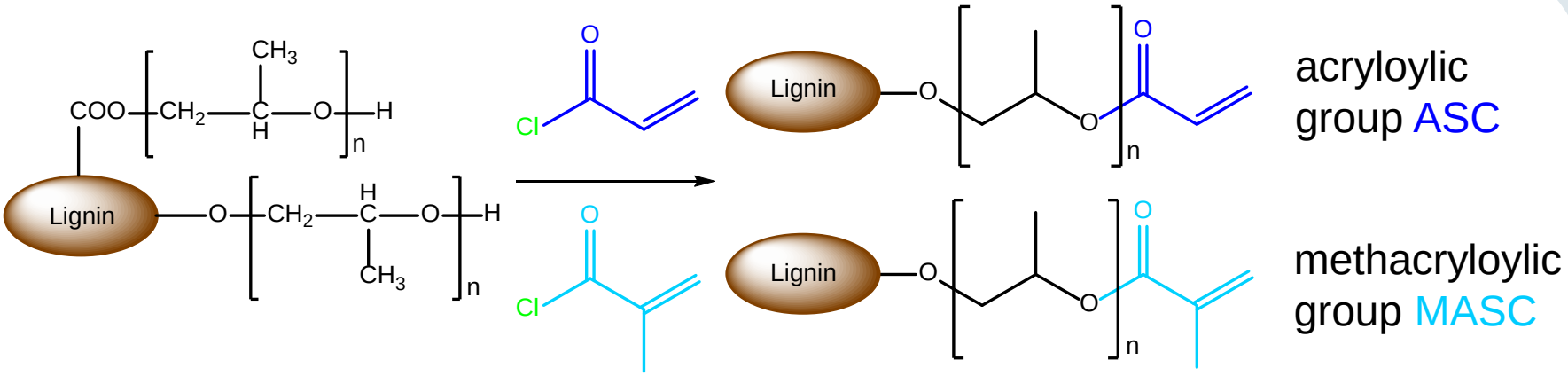
naturally brown powdery lignin = unmodified



Berghof autoclave

oxyalkylated liquefied lignin = modified

Modification with (meth)acrylate groups



photopolymerizable (meth)acrylate groups converted with lignopolyol

	total OH [mmol/g]	COOH [mmol/g]	viscosity [Pas]
PB1000	4.5	1.0	solid
OL	3.4	0.1	23.9*
ASC	0.1	0.0	2.62
MASC	0.1	0.1	0.983

decreasing viscosity

* measured at 75 °C, all other at 25 °C
OL = oxyalkylated lignin

Curing of meth(acrylate) lignopolyols

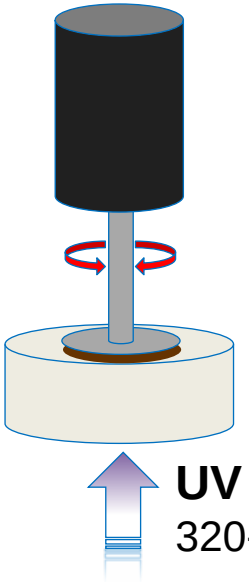
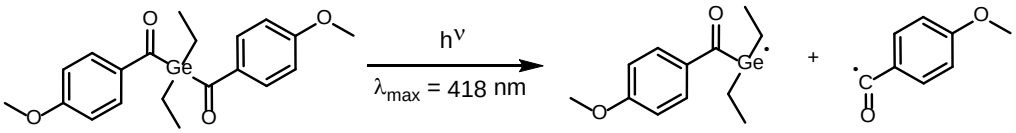


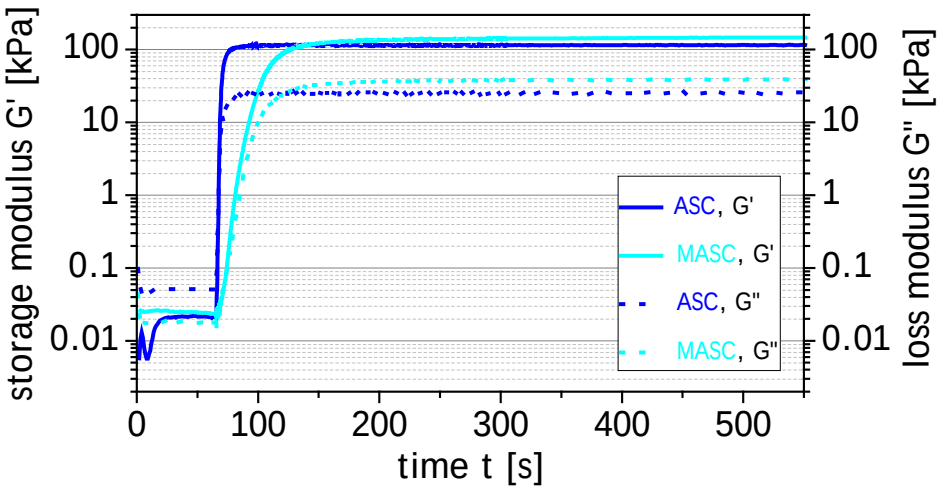
Photo-rheology
measuring system
PP25

(meth)acrylated
lignopolyol on a
quartz plate

UV light
320-500 nm



diacylgermanium-based photoinitiator Ivocerin®



(meth)acrylate
ligninopolyol resin

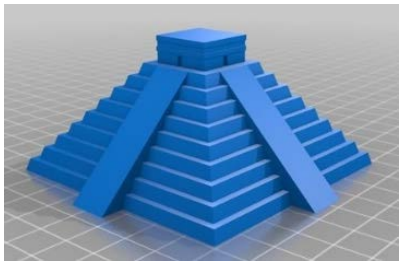
UV light

gap: 30 µm

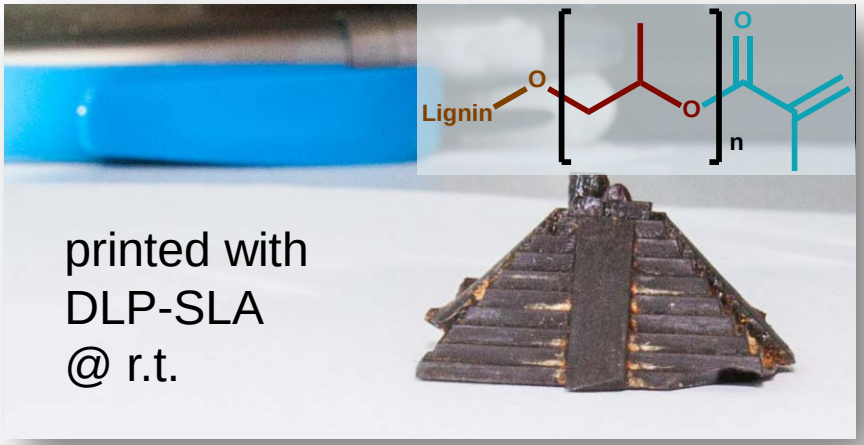
cured (meth)acrylate
lignopolyol film

Proof of Concept: 3D Printing

adjustments for the 3D print of the pyramid:
- 27 x 26 mm side length
- 474 layers á 30 µm,
- max. intensity of 84 mW/cm²
- wavelength 460 nm



a CAD profile of the pyramid



lithography-based additive manufacturing of methacrylate-modified lignopolyol

3D printed pyramid

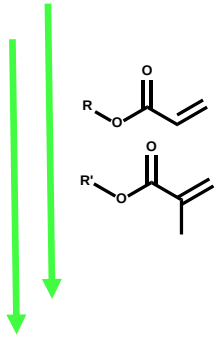
Conclusion

- oxyalkylation converts lignin in polyols with lower viscosities
  solubility is improved and
  OH functional groups are homogenized

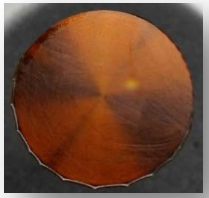

extraction

liquefaction


- uniformity of functional groups in lignopolyol enable further modification with reactive compounds such as (meth)acrylate groups



- complex structures of (meth)acrylated lignopolyols are accessible by lithography-based additive manufacturing techniques


several layers
photopolymerized

one layer
photopolymerized


Outlook

- Up-scaling and material transfer to partner
  - Optimization of formulation
  - Improvement of mechanical properties
- Investigation of alternative reactive groups
  - Vinyl ester
  - Fatty acids
- Improvement of photoinitiator
  - Low migratability

Thank you for your attention!!!

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