“Optimized procedure for the synthesis of dialcohol cellulose pulp and its thermomechanical properties”

Progress in Paper Physics, Lodz

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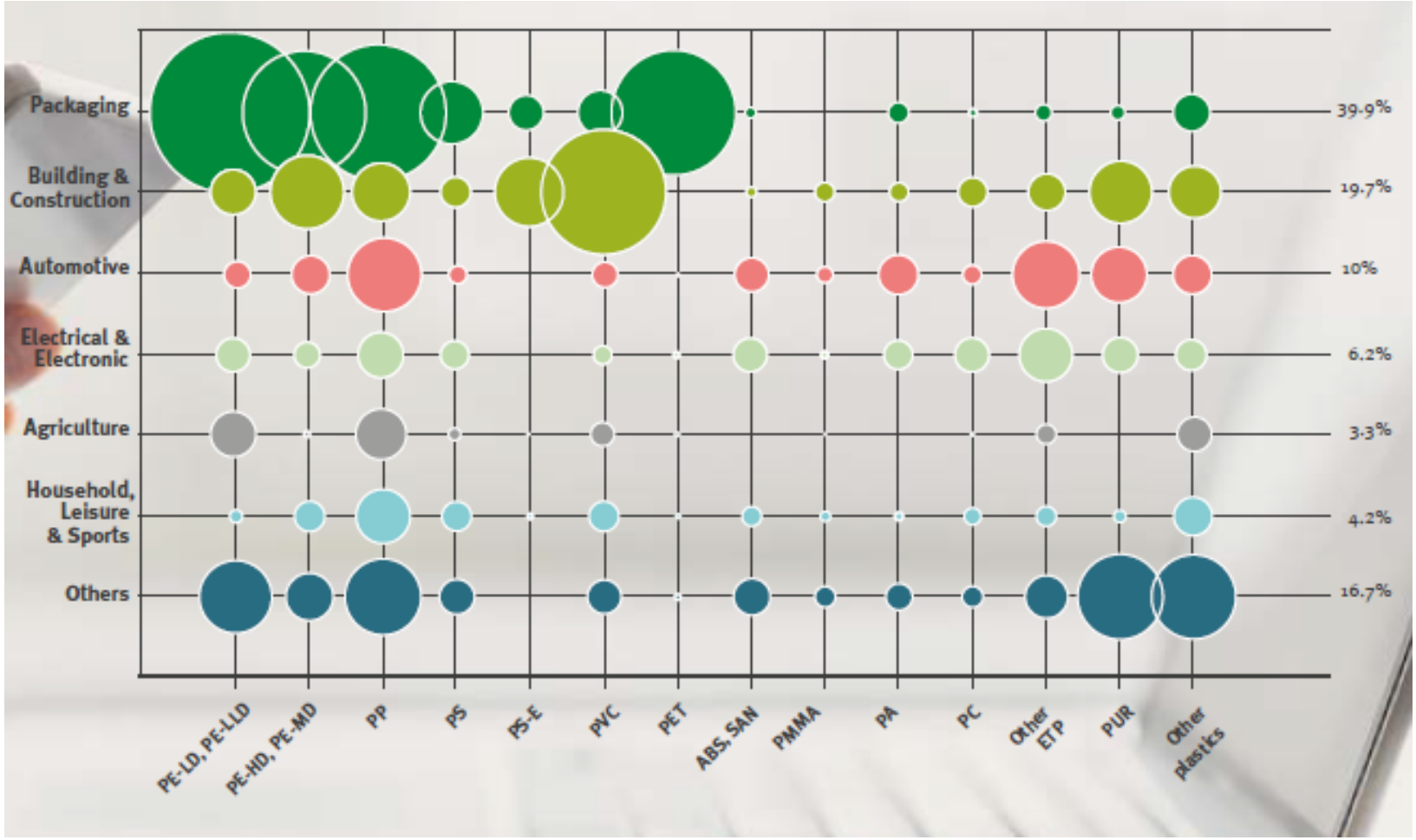
Outline

1. Introduction and motivation
2. Determination of optimized preparation method
3. Thermal and thermomechanical properties
4. Thermoforming
5. Summary and outlook

European Plastics Demand

60 mio tonnes



Reference: Plastics Europe, Plastic – the Facts 2017

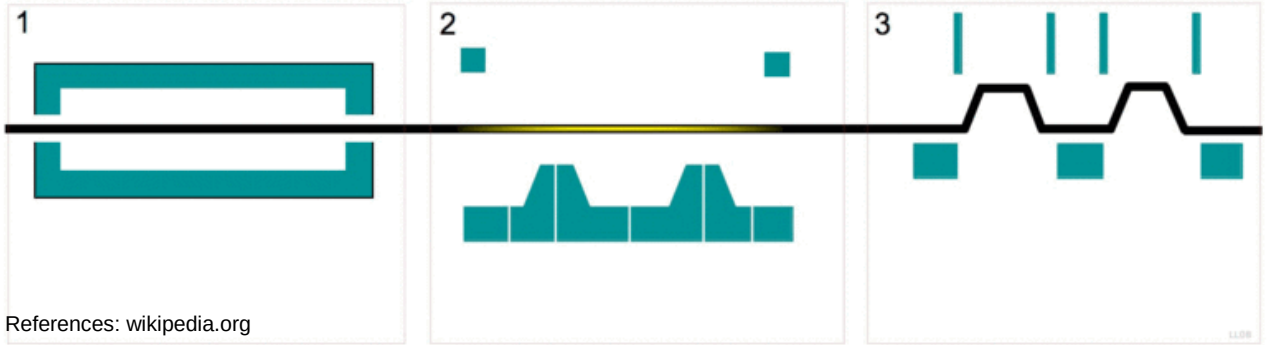
PTS FIBRE based solutions

Motivation:
Making cellulose (paper) thermoplastic

References: vdp-online.de; plastikbecher.de; elcoindustries.com; aeroupholstery.com; wipak.com.

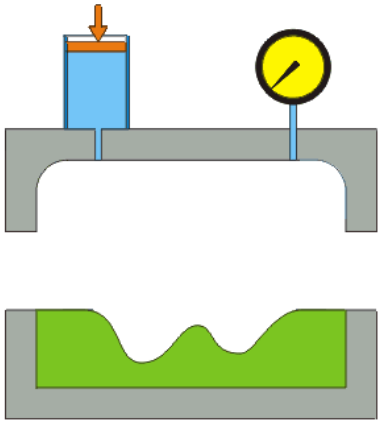
Fixed Blank Process

Thermoforming



References: wikipedia.org

Hydroforming

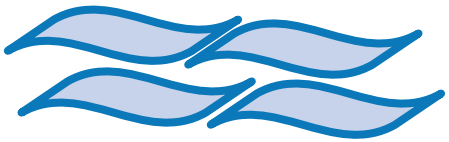


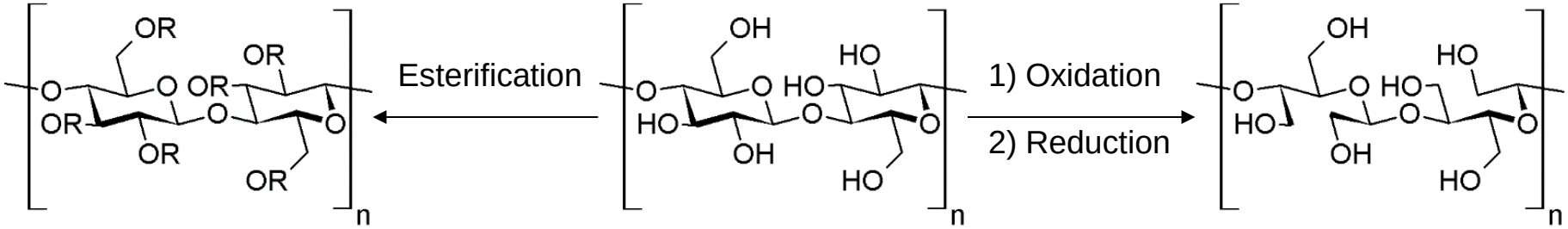
	Soften	Elongate	Solidificate
Thermoplastics	✓	✓	✓
Paper	●	✗	●

PTS FIBRE based solutions

Principles of chemical modification of cellulose fibers

Surface modification ← → **Fiber modification**



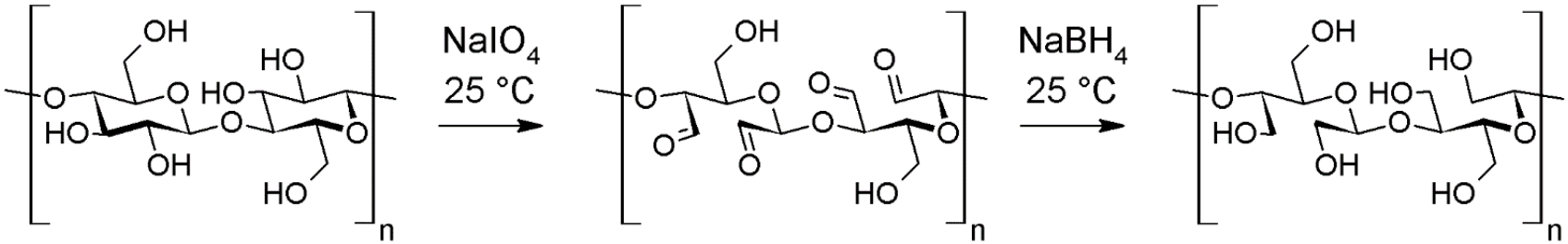


Celluloseester | Cellulose | Dialcoholcellulose

Celluloseester	Cellulose	Cellulose	Dialcoholcellulose
+	-	+	-
One-pot-reaction	Anhydrophilic reagents, solvent exchange process before reaction, Labsheets with low strength, **no thermoplasticity**	Aqueous medium, good fibre swelling, good accessibility for reagents, homogeneous reaction, **thermoplasticity observed**	2-step-reaction process Excess of chemicals required

References: P. Larsson, L. Wagberg, *Green Chem.* **2016**, *18*, 3324–3333., M. Zahel, S. Möckel, T. Arndt, *Advances in Pulp and Paper Research, Oxford 2017*, **2017**.

Demand of optimization of dialcohol cellulose preparation



Cellulose | Dialdehyde cellulose (DAC) | Dialcohol cellulose (DOH)

Oxidation:

- Excess of 4.1 equivalents (per AGU) of $NaIO_4$ is applied in literature

Reduction:

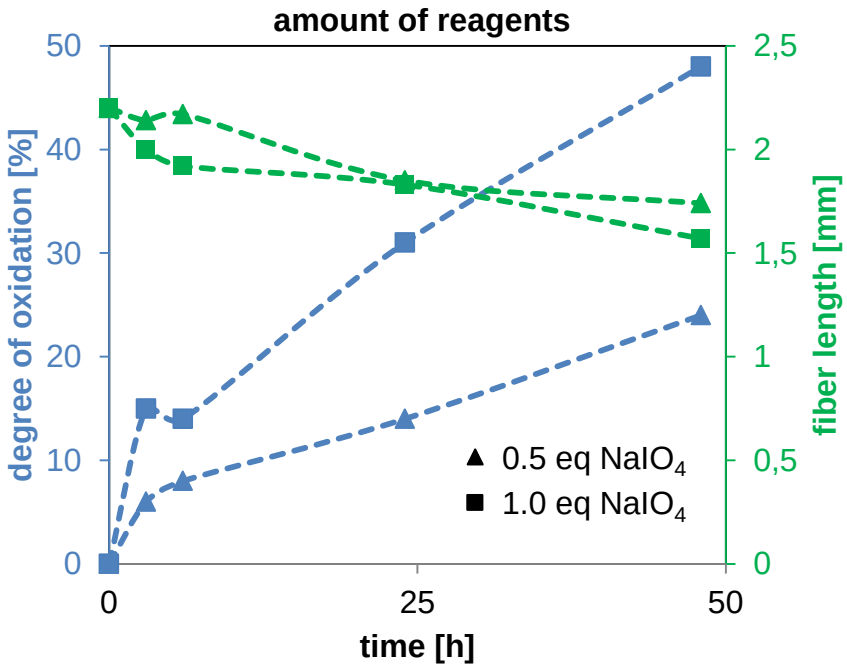
- Excess of 2.1 equivalents (per AGU) of $NaBH_4$ is applied in literature
- Phosphate buffering system is applied in literature which theoretically increases amount of necessary $NaBH_4$

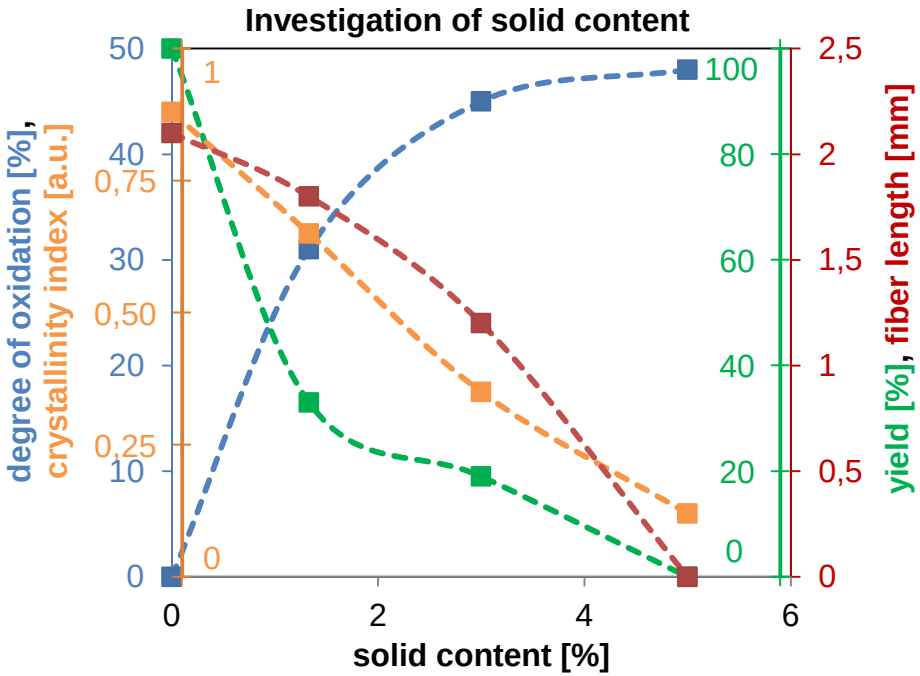
AGU = anhydroglucose unit

References: P. Larsson, L. Wagberg, *Green Chem.* **2016**, *18*, 3324–3333.

Optimization of oxidation reaction

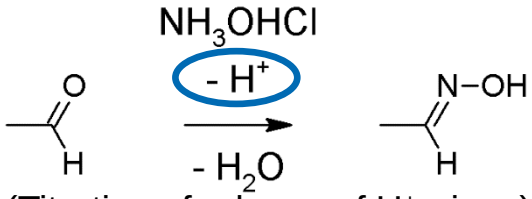
- Optimizations were done using Spruce/pine sulfate pulp





1 eq of $NaIO_4$ leads to oxidation of approx. 50 %

Determination of degree of oxidation (DO):



(Titration of release of H^+ - ions)

Optimization of reduction reaction

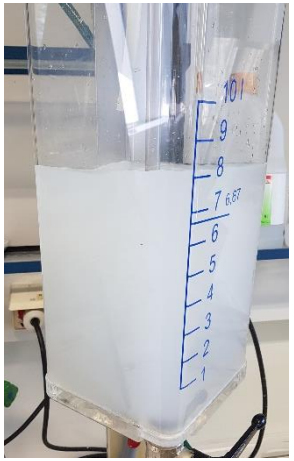
- For this investigation a oxidized Spruce/pine sulfate pulp (DO = 37 %) was used

Entry	Eq. $NaBH_4$ (AGU)	Eq. $NaBH_4$ (CHO)	c NaH_2PO_4 [mol/l]	Residual CHO [%]	Overall yield [%]	Fibre length Lc(l) [mm]
1	2.10	22.7	0.38	3	66	1.6
2	**1.00**	**10.8**	**0.00**	**< 1**	**64**	**1.6**
3	0.37	4.0	0.00	6	66	1.7
4	0.19	2.0	0.00	9	62	1.6
5	0.19	2.0	0.38	26	86	0.4

- Best reduction of CHO obtained for 1 eq of $NaBH_4$ (per AGU)
- Buffering system (see entry 4 and 5) is disadvantageous for reduction and seems to consume sodium borohydride

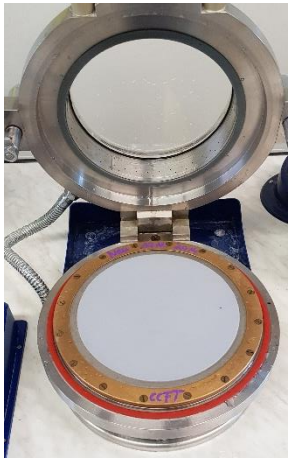
AGU = anhydroglucose unit, CHO = aldehyde group, overall yield = yield after both reaction steps based on cellulose used

Preparation of lab sheets



1

2



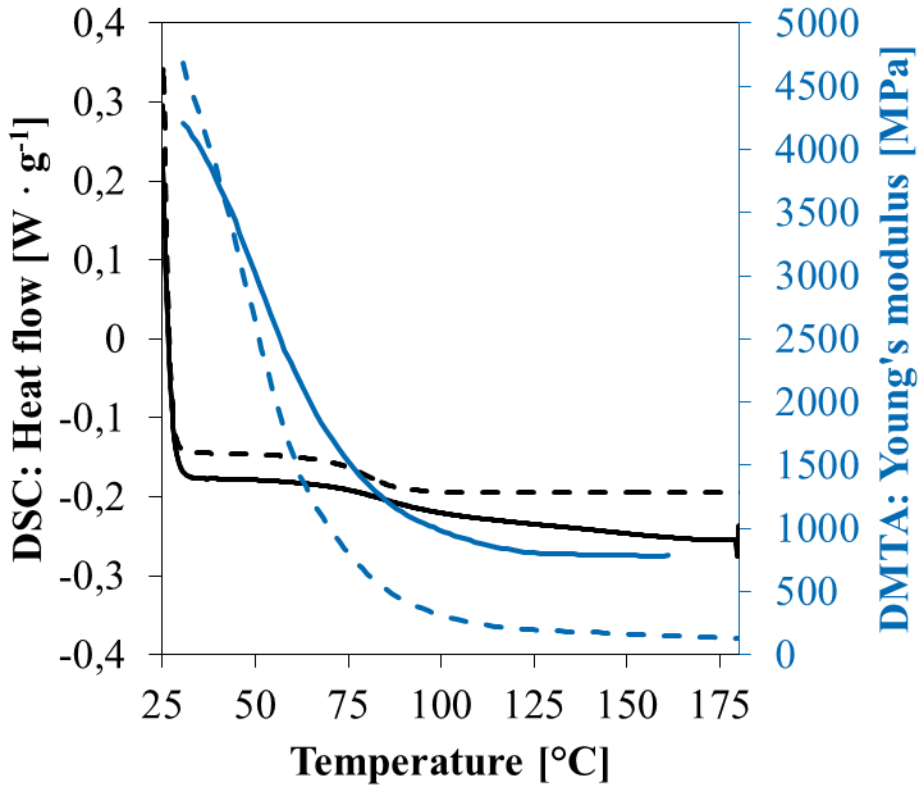
3

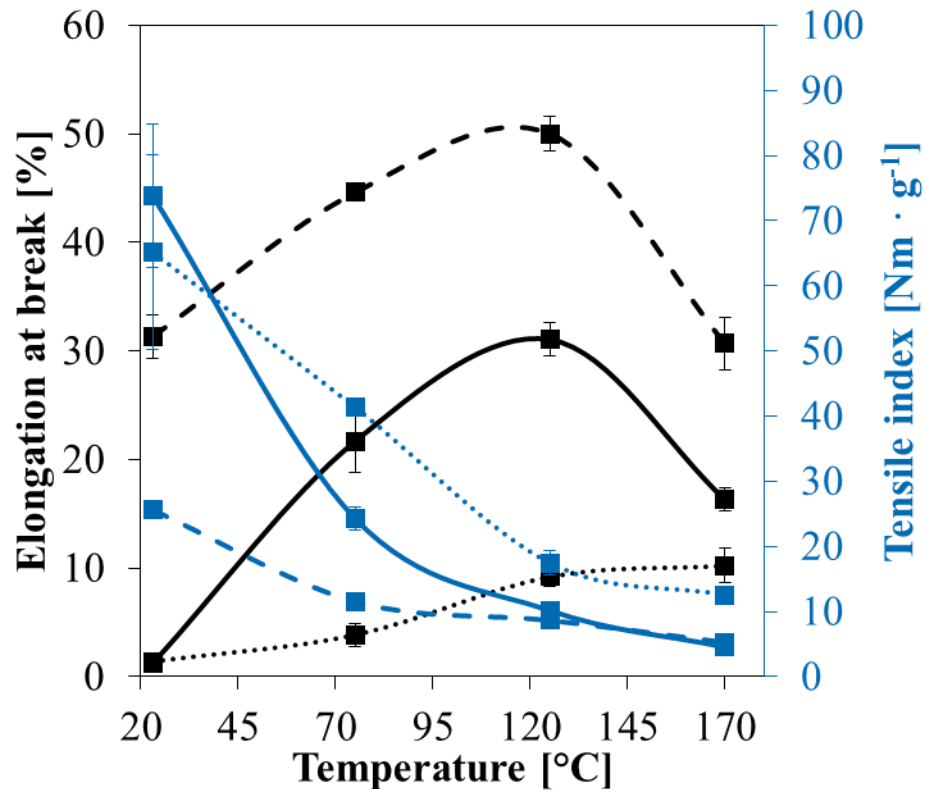
4

5

1 Suspending of fibers
2 homogenization in lab sheet former bin
3 formation of fiber web
4 couching on siliconized paper
5 drying 10 min at 94 °C and additional 15 min at 94 °C under vacuum

Thermomechanical properties of optimized materials





- DSC 1 eq $NaIO_4$; 0.5 eq $NaBH_4$
- DMTA 1 eq $NaIO_4$; 0.5 eq $NaBH_4$
- DSC 4.1 eq $NaIO_4$; 2.1 eq $NaBH_4$
- DMTA 4.1 eq $NaIO_4$; 2.1 eq $NaBH_4$
- elongation 2 eq $NaIO_4$; 2.1 eq $NaBH_4$
- elongation 1 eq $NaIO_4$; 0.5 eq $NaBH_4$
- Tensile index 1 eq $NaIO_4$; 1 eq $NaBH_4$
- elongation 1 eq $NaIO_4$; 1 eq $NaBH_4$
- Tensile index 2 eq $NaIO_4$; 2.1 eq $NaBH_4$
- Tensile index 1 eq $NaIO_4$; 0.5 eq $NaBH_4$

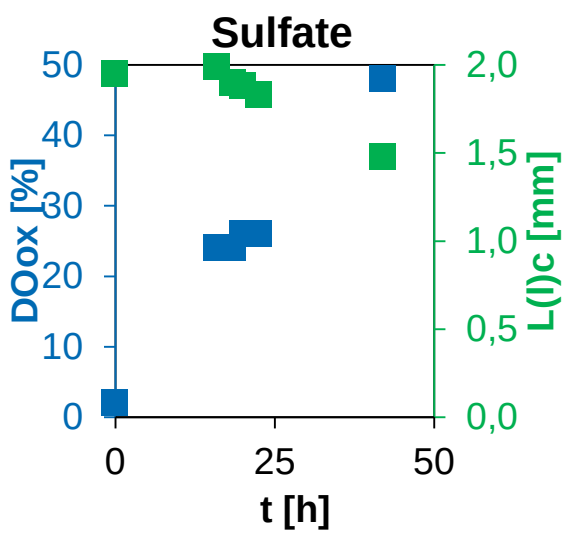
Choice of cellulose pulp materials

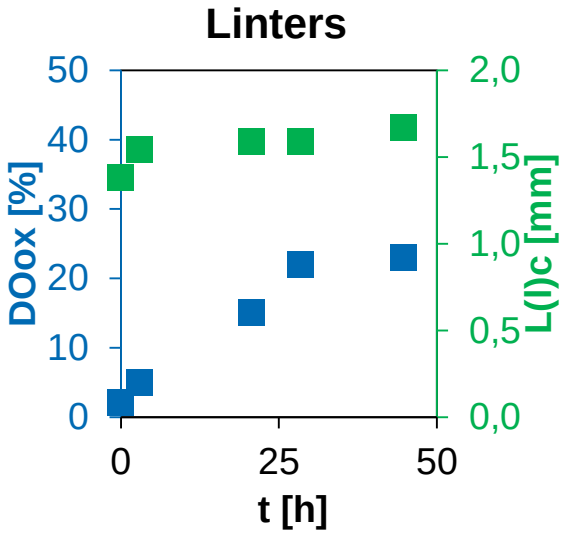
Spruce/pine sulfate

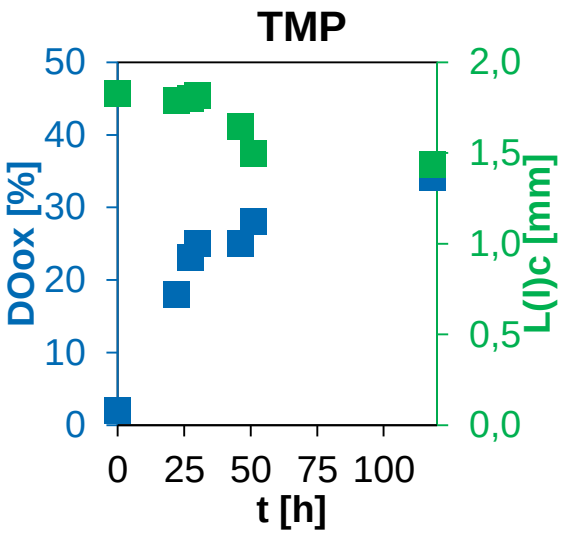
Cotton Linters

Pine TMP

Monitoring of oxidation reaction of different cellulose pulps



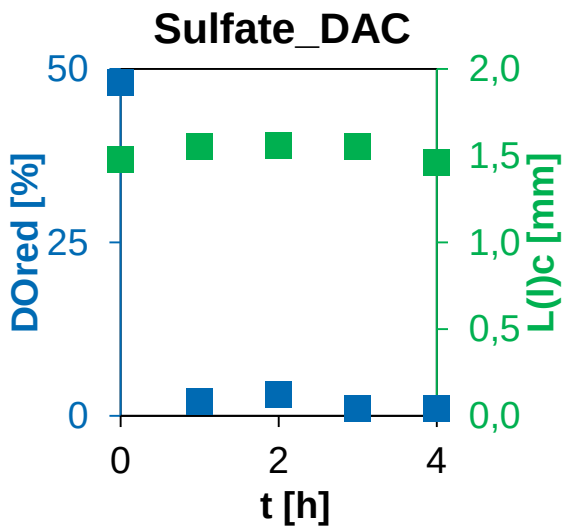


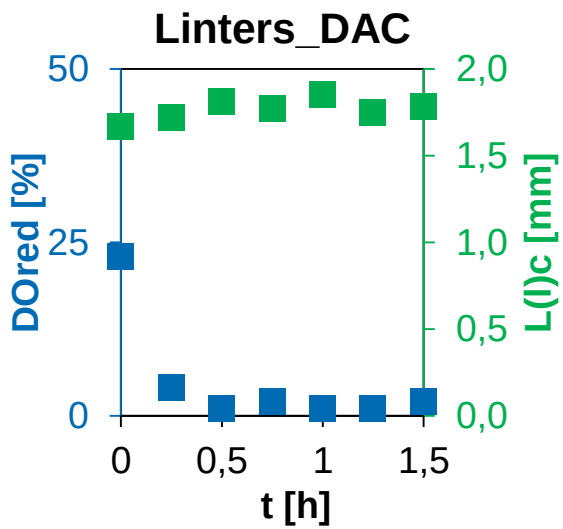


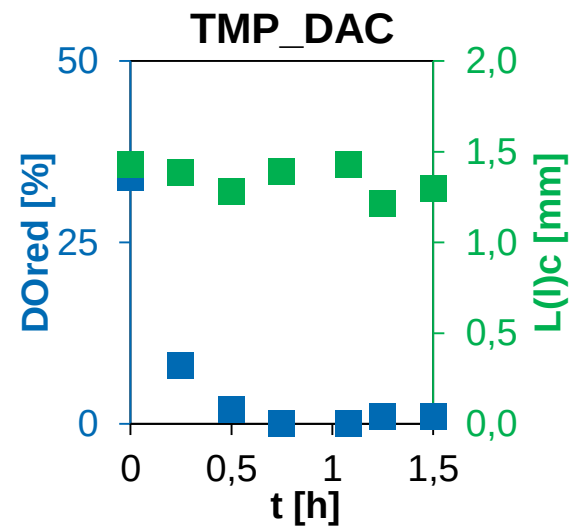
- DO of 40-50 % was targeted during reaction
- Sulfate: DO of 47 % was reached after 2 days
- Linters: DO of 23 % was reached after 2 days; stationary phase of reaction reached
- TMP: DO of 34 % was reached after 120 h; stationary phase of reaction begins

DO = degree of oxidation, oxidized Anhydroglucose units

Monitoring of reduction reaction of different dialdehyde cellulose (DAC) pulps



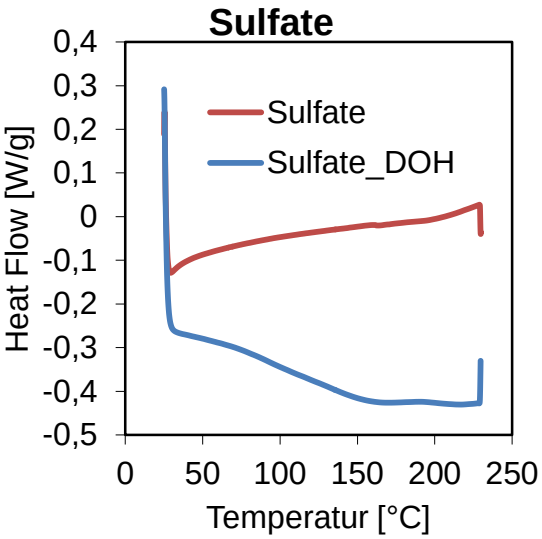


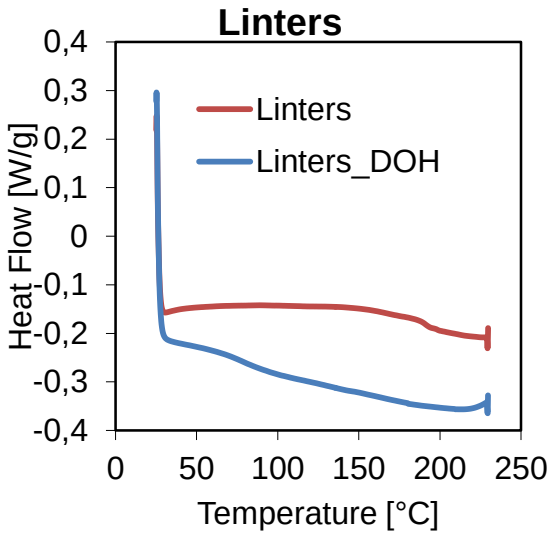


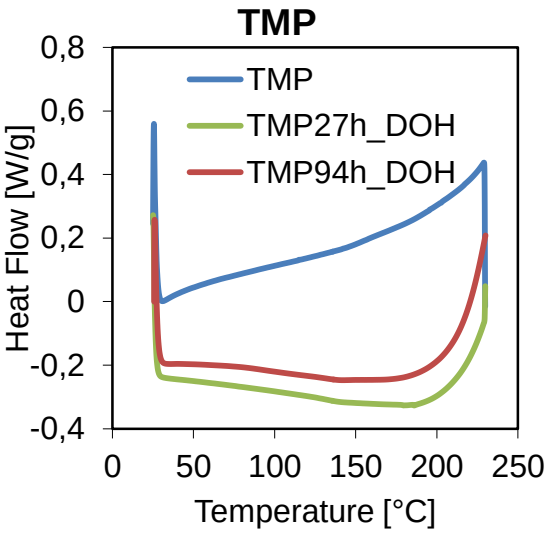
- Low DO after reduction essential to obtain thermoplastic material
- Complete reduction of all DAC pulp materials reached after 1 h of reduction with sodium borohydride

DO = degree of oxidation, oxidized Anhydroglucose units; DAC = Dialdehyde cellulose

Thermal properties: Differential scanning calorimetry



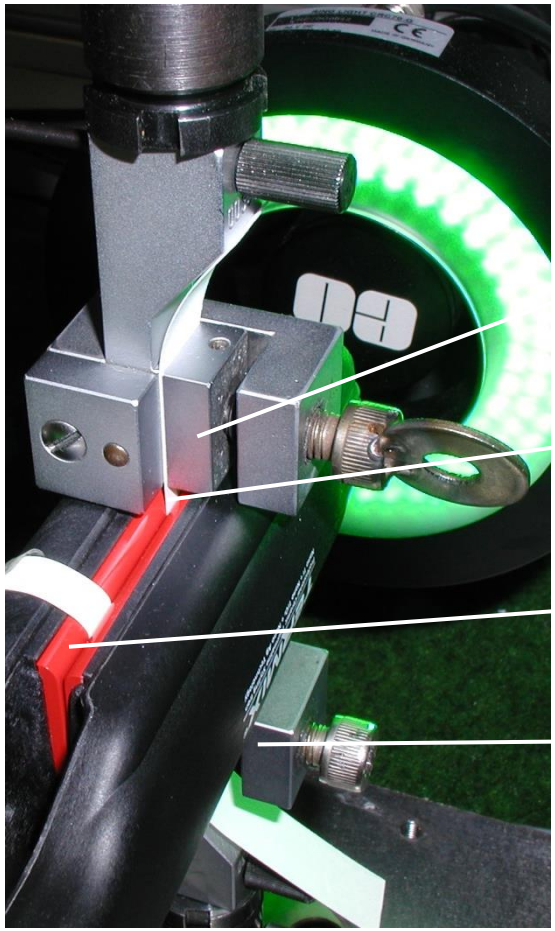


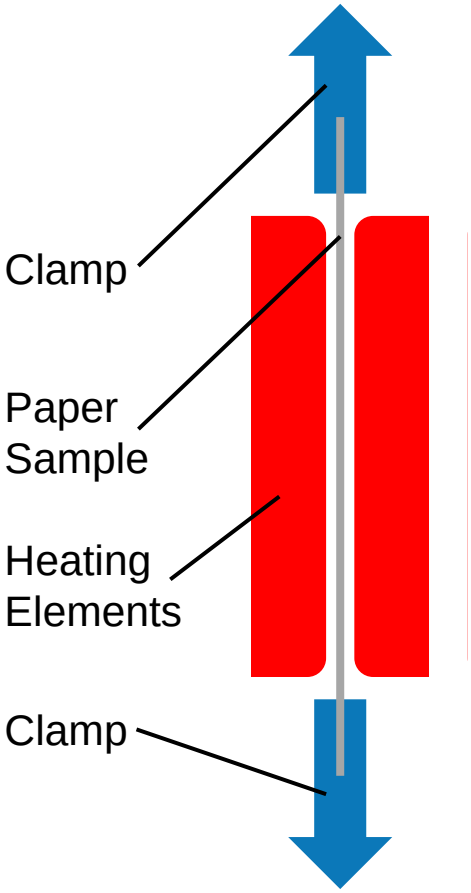


- Glass transition point for DOH of sulfate and linters at approx. 60-80 °C
- Glass transition of DOH of TMP shifted to higher temperature (approx. 100-120 °C)
- Decomposition of lignin in DOH of TMP starts at 200 °C

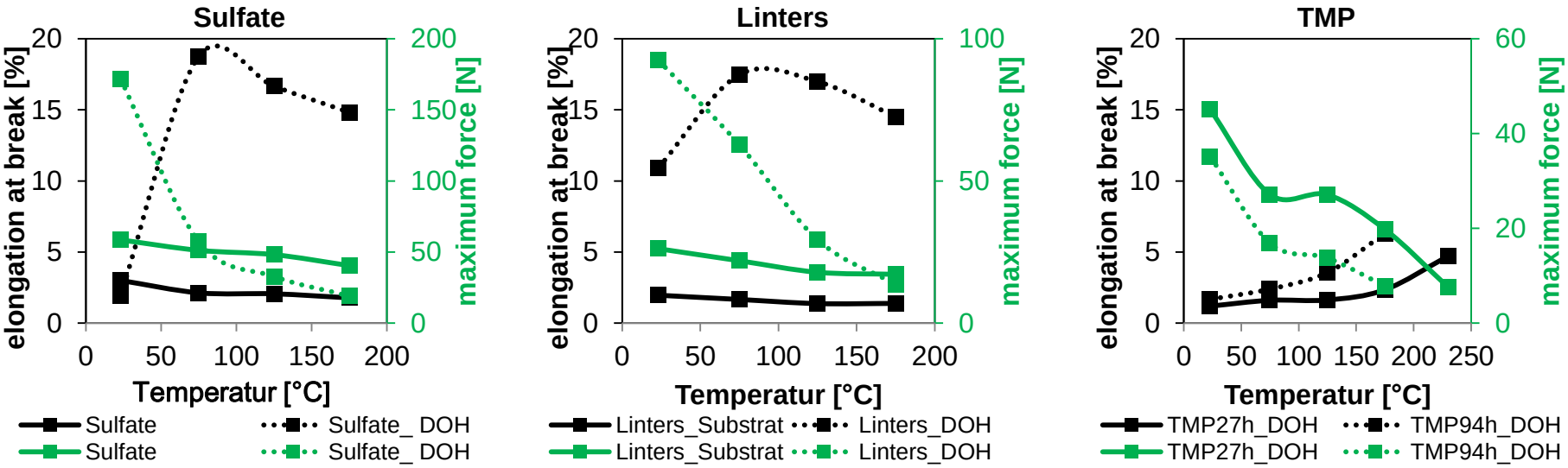
DOH = Dialcohol cellulose

Thermomecahnical properties: Temperature assisted tensile testing





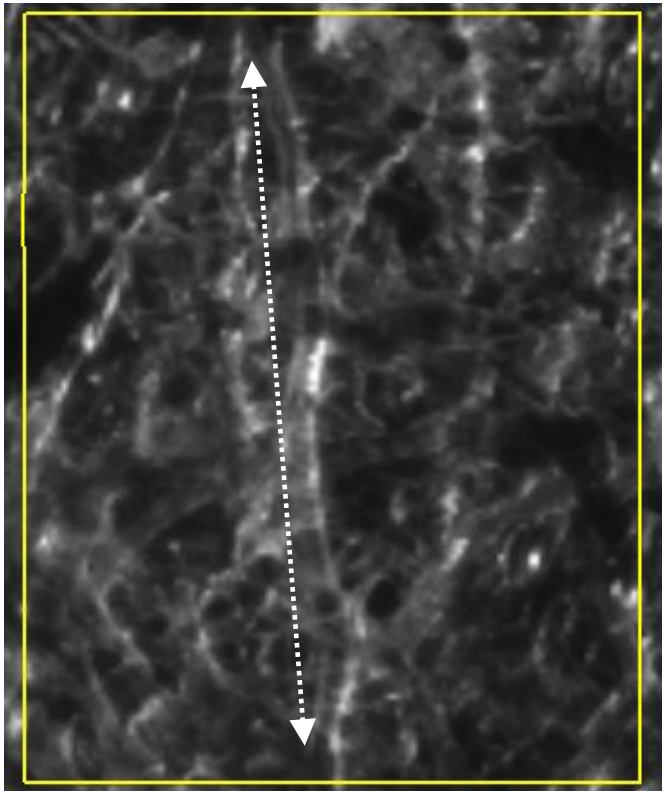
Thermomecahnical properties: Temperature assisted tensile testing



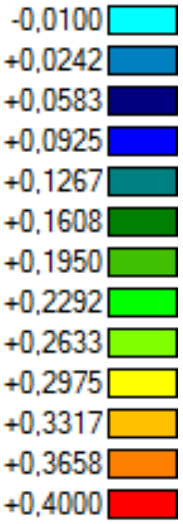
- All DOH-sheets show temperature induced softening (decrease in elongation at break and decrease in maximal force)
- Highest elongation of approx. 20 % obtained for Sulfate_DOH at 75-125 °C
- Continuous increase in elongation at break determined for TMP materials before their thermal decomposition at circa 200-230 °C

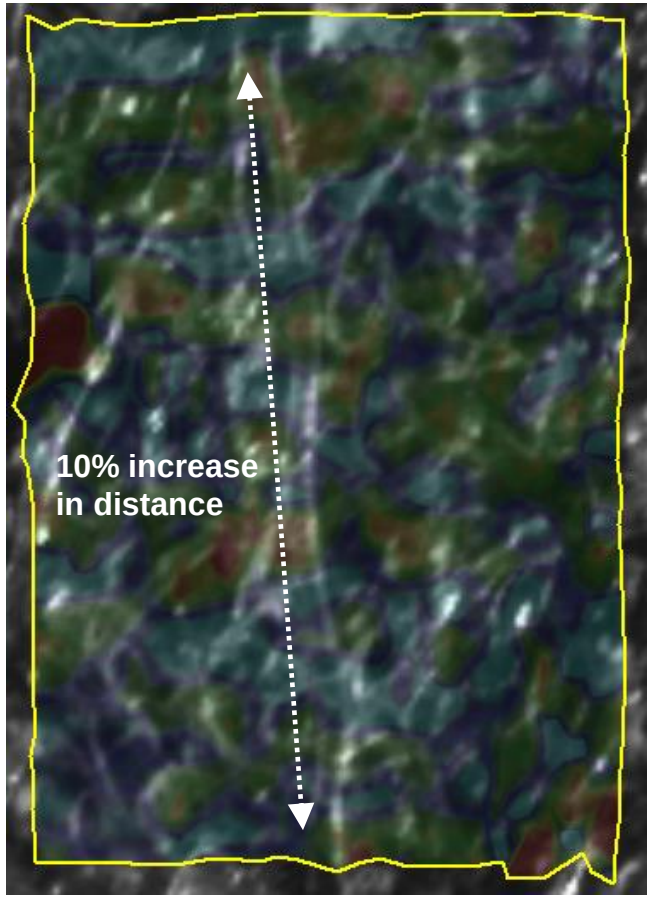
DOH = Dialcohol cellulose

Optical Strain Field Measurement of Dialcoholcellulose Paper



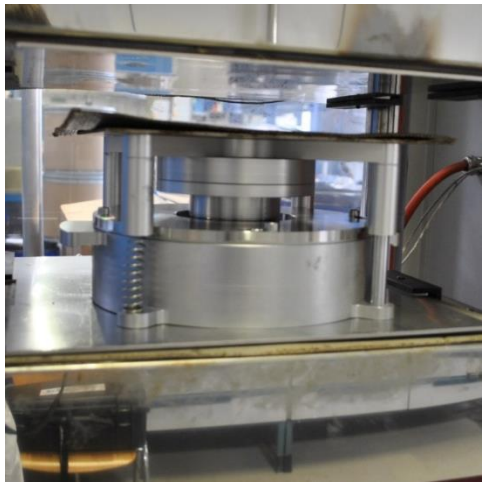
10% Global Strain

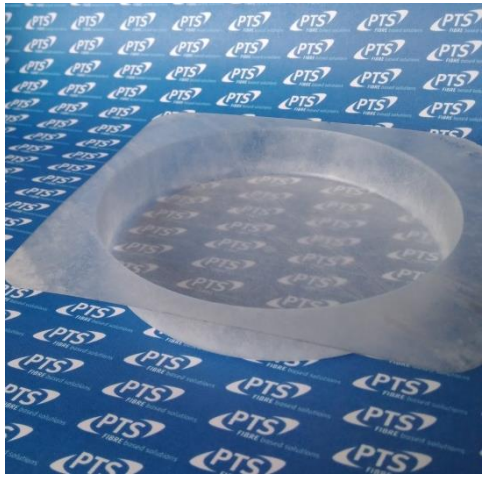




40 g/m² Sheet of Dialcoholcellulose Pulp (DO=41%) before and after Straining to 10 % at 100 ℃

Thermoforming





Summary and outlook

Summary:

- Dialcohol cellulose pulp can be prepared in kg scale
- Optimized oxidation procedure requires 1.0 eq of $NaIO_4$ instead of 4.1 eq per AGU
- Optimized reduction procedure requires 1.0 eq of $NaBH_4$ instead of 2.1 eq per AGU and is done without buffering system and in 1 hour
- Obtained dialcohol cellulose pulp/ lab sheets show temperature induced softening and elongation

Outlook:

- Investigation of application of fillers into paper materials
- Investigation of application of external plastification of materials
- Scale up of reaction and application of continous papermaking

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