TECHNISCHE UNIVERSITÄT WIEN

Influence of swelling spruce fibers with different organic and inorganic solvents

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DI Cornelia Hofbauer

In cooperation with…

Cornelia Hofbauer[1*], Sebastian Serna-Loaiza[1], Luis Zelaya[2], Thomas Harter[1,3], Ulrich Hirn[3], Luisa Scolari[1], Josef Füssl[2], Markus Lukacevic[2], Michael Harasek[1]

[1] Christian Doppler Laboratory for Next-Generation Wood-Based Biocomposite, Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Vienna, Austria

[2] Christian Doppler Laboratory for Next-Generation Wood-Based Biocomposite, Institute for Mechanics of Materials and Structures, TU Wien, Vienna, Austria

[3] Institute of Bioproducts and Paper Technology, TU Graz, Graz, Austria

CD Laboratory for Next-generation wood-based biocomposite

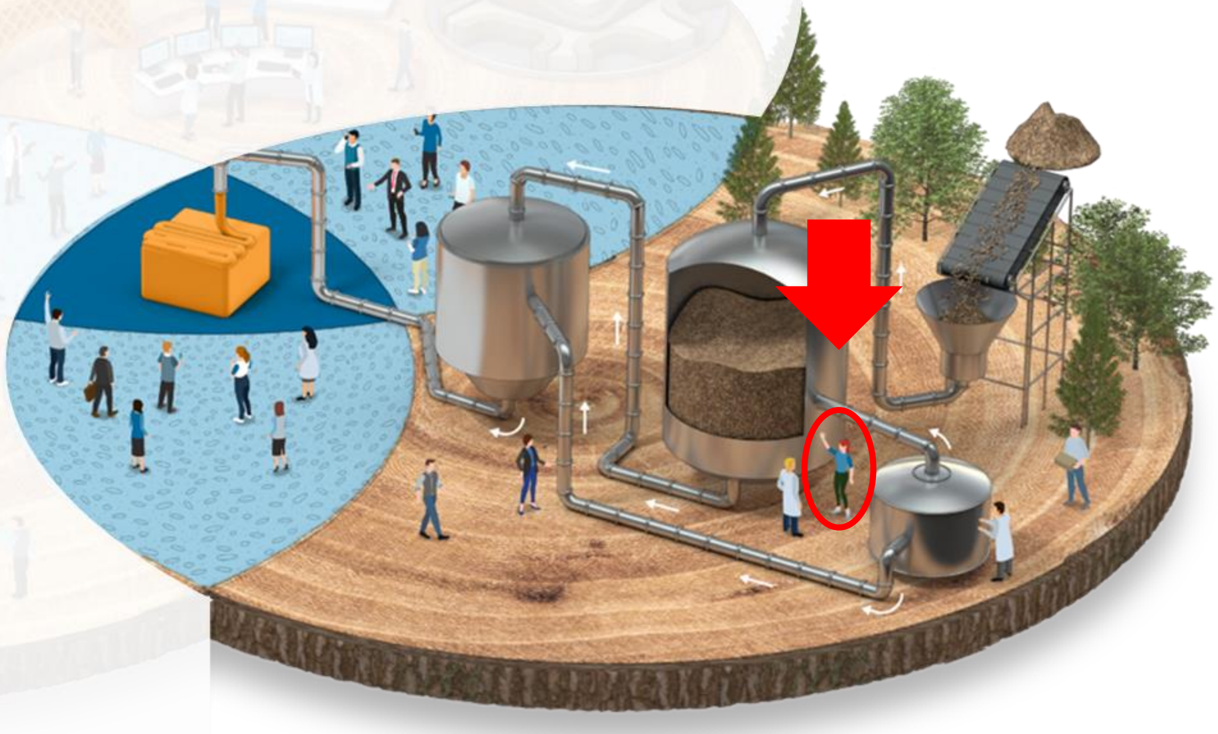
Analysis

Modelling

Fractionation

Fractionation

- Sawmill by-products are used as raw material
- Material is pre-treated chemi-mechanically and thermally
- Components are fractionated to be transformed into a new form
- During forming fibers are re-arranged and re-compacted



What is the purpose…

- Long-term CO_2 storage
- Composites without nondegradable synthetic adhesives
- Biodegradable and environmentally friendly building material
- Improve the value chain of sawmill by-products (wood chips, sawdust, etc.)

Background and aim of the study…

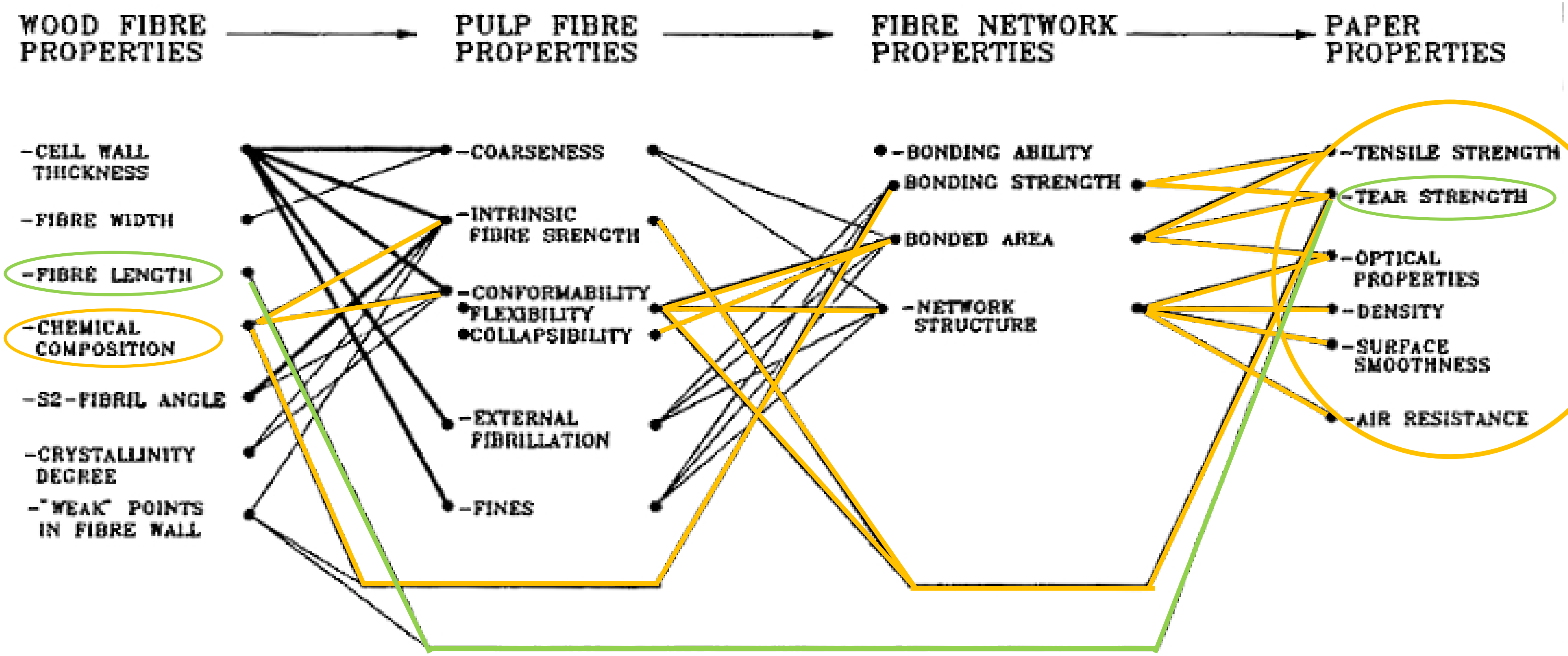
Enhancing the characteristics of **reinforcement material for biocomposites**

- Working with by-products of the wood industry
- Pulping with “green” solvents
- Swelling pulping material to enhance fiber properties
  - Well established method in the paper industry
  - Makes the fibers more accessible and increases the uptake capacity of solvents
  - Important for solvents which can act as an additive carrier for matrix material

Finding sufficient swelling agents to prepare the fibers for impregnation with additives and/or matrix material, to create an **intermediate product for biocomposites.**

Why pulping?

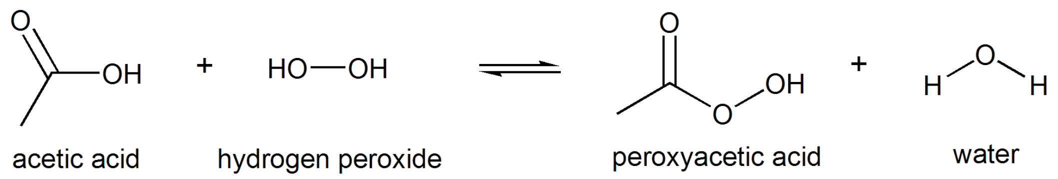
[1]



[1] PAAVILAINEN, Leena. Influence of fibre morphology and processing on the softwood sulphate pulp fibre and paper properties. 1993.

Why peracetic acid-pulping (PAA)?

- Fibrillation process without severe mechanical treatment
- Initial fiber length almost completely preserved
- Pulping at 80-100°C – moderate temperatures
- Selective extraction of lignin
- Preserving hemicellulose to enhance the binding ability[2-4] – **holocellulose pulp**



Why swelling?

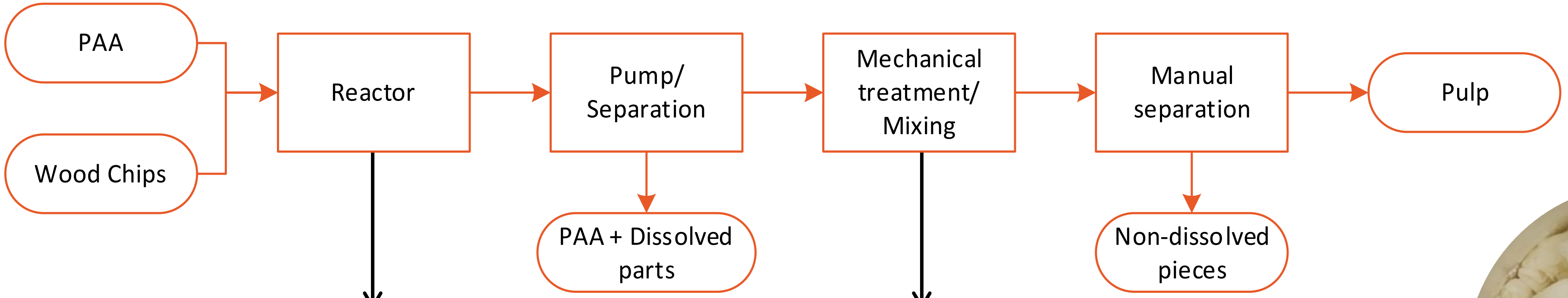
- Increases surface area for hydrogen bonding, enhances fiber bonding in variable products
- Improves fiber flexibility and elasticity
- Enhances the accessibility and uptake of solvents (with additives or matrix material)
- Improves tensile strength and tear resistance

Feedstock

- Spruce wood chips (softwood)
- Different particle sizes (1mm < x < 5cm)
- Air dried and stored at controlled temperature and humidity

PAA – process

Peracetic Acid[5]



Specific parameters for the reactor

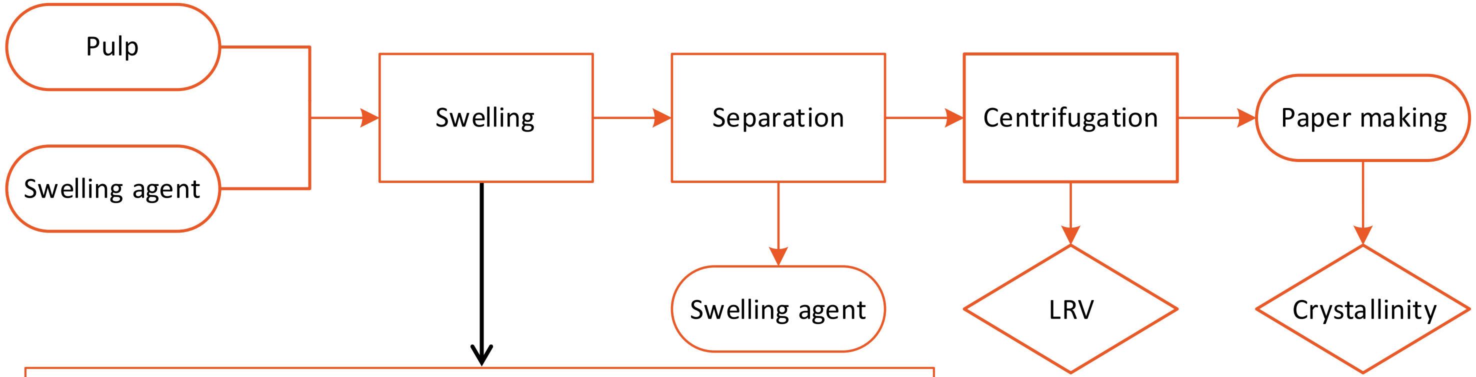
- Temperature: 90 °C
- Time: 120 min
- Solid Load: 3 wt%
- Mixing: 60 min axial 700 rpm

Specific parameters for the mechanical treatment

- Room temperature
- Solid Load: 1.5 wt%
- Mixing 1: 20 min axial 1700 rpm
- Mixing 2: 5 min with electric whisk

Holocellulose pulp

Swelling
Different solvents



Specific parameters for swelling

- Temperature: 25 °C
- Time: 4 h
- Solid Load: 5 wt%
- Swelling agents:
  - 49.9 wt% aqueous ethanol (50% ethanol)
  - 69.9 wt% aqueous ethanol (70% ethanol)
  - 99.8 wt% aqueous ethanol (100% ethanol)
  - 2 wt% aqueous NaOH
  - 4 wt% aqueous NaOH

Methods for analysis

- Liquid retention value (LRV) [6]
  - Capacity of the fiber for liquid uptake
- Microscopy
  - Optical analysis of the fibers
- Crystallinity Index
  - Determination of crystalline and amorphous content
  - Wide Angle X-ray Diffraction (WAXD)

Results

Liquid retention value
Different solvents

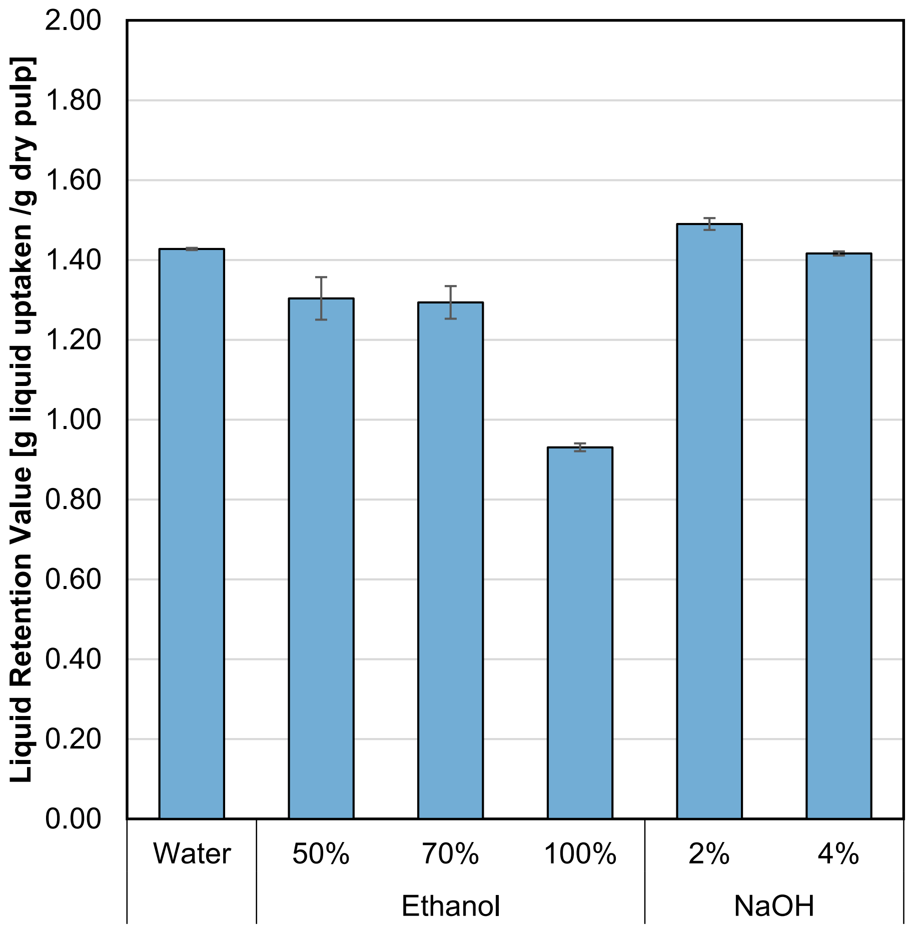
- Liquid retention value (LRV)
  - Reflects on the liquid holding capacity

$$LRV(g/g) = \frac{m_{wet} - m_{dry}}{m_{dry}}$$

m_{wet} represented the mass of the pulp before drying (after centrifugation)
m_{dry} the dry weight of the pulp

- The best results were achieved with NaOH 2%
- At ethanol 100% is the lowest uptake

With increasing ethanol content, the LRV is decreasing



Swelling - Water

- Uniformly swollen along the length
- Width between 50-60µm
- Flexible and soft structure

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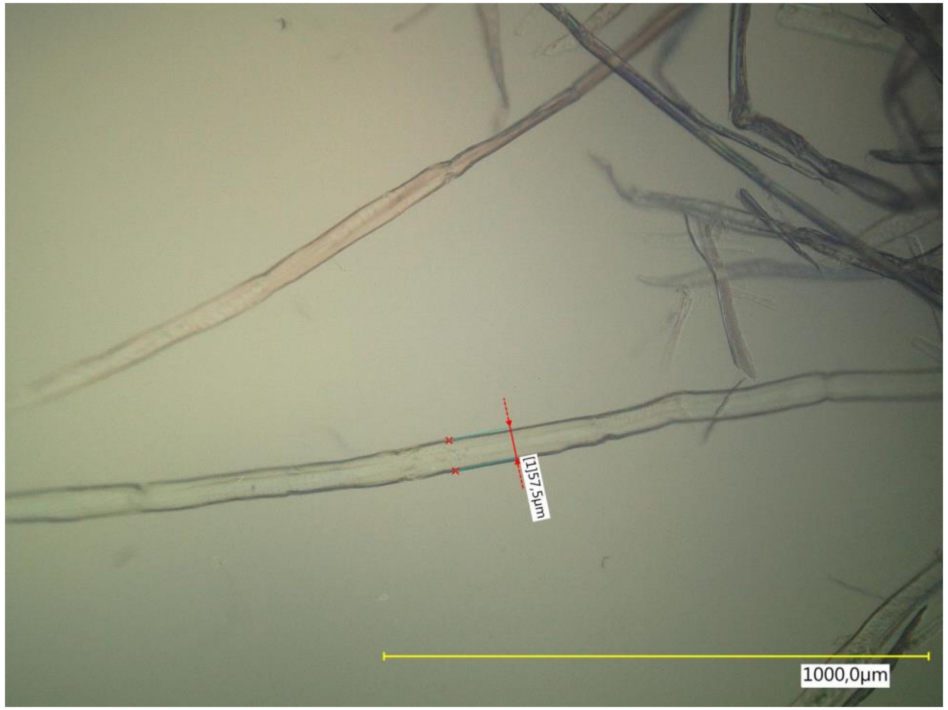

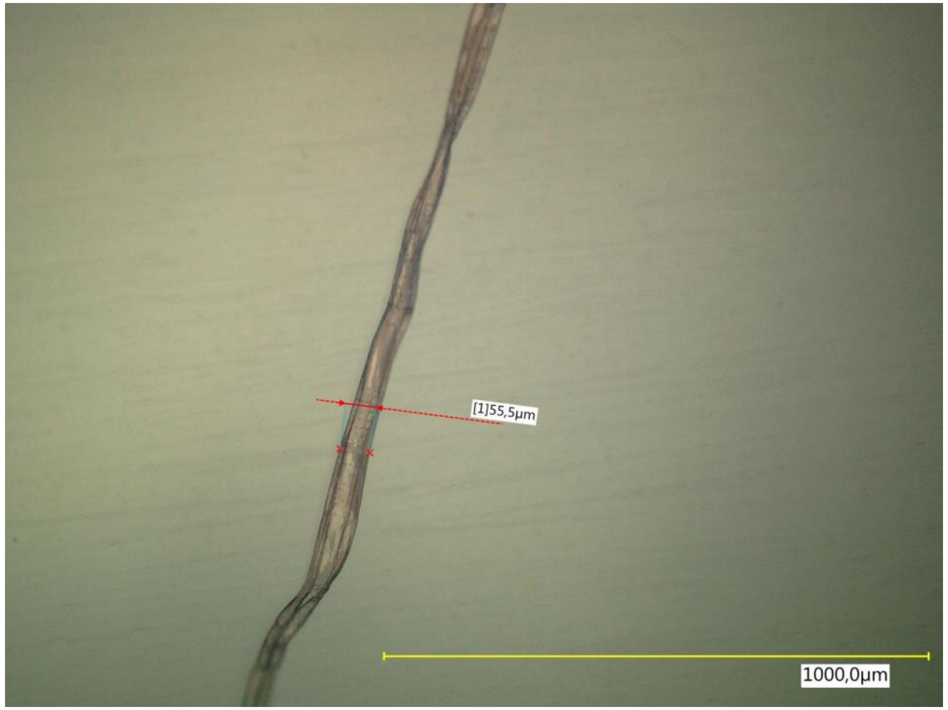

Swelling – Ethanol (EtOH) 50% to 100%

- Uniformly swollen with increasing water content
- Width 30-50µm, more even distributed with increasing water content
- Dried out to soft structure (100% → 50% EtOH)

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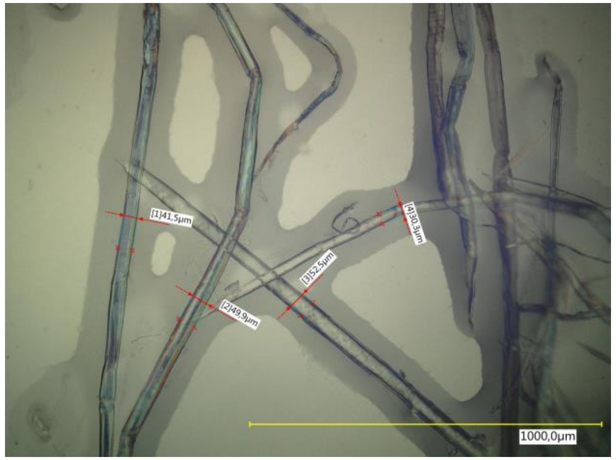
Swelling
Ethanol 50%



Swelling
Ethanol 70%

Swelling
Ethanol 100%

Increasing water content

Soft Dry

Swelling – Sodium hydroxide (NaOH) 2wt% and 4wt%

- Uniformly swollen along the length
- Width between 40-65µm
- Flexible and soft structure

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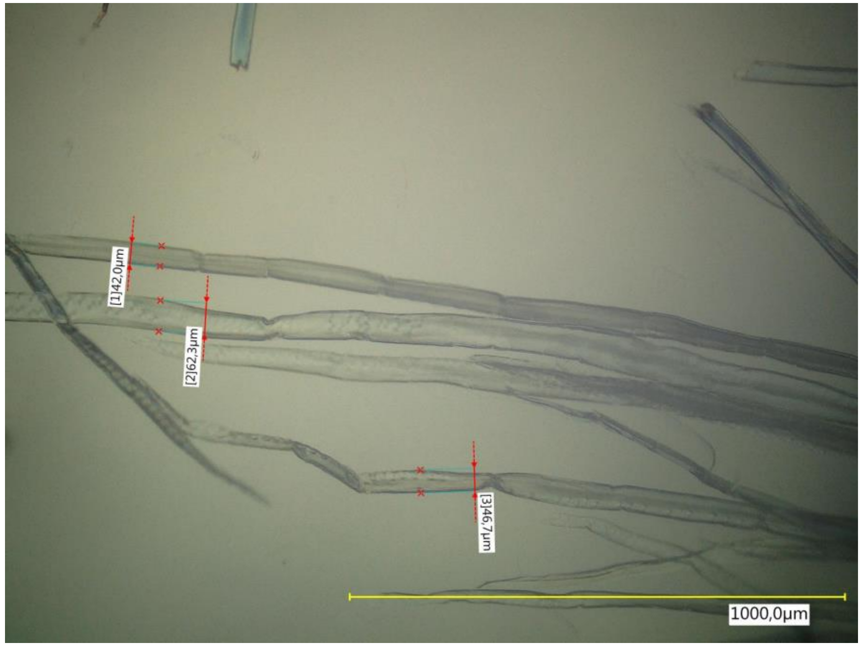
Swelling
NaOH 2wt%

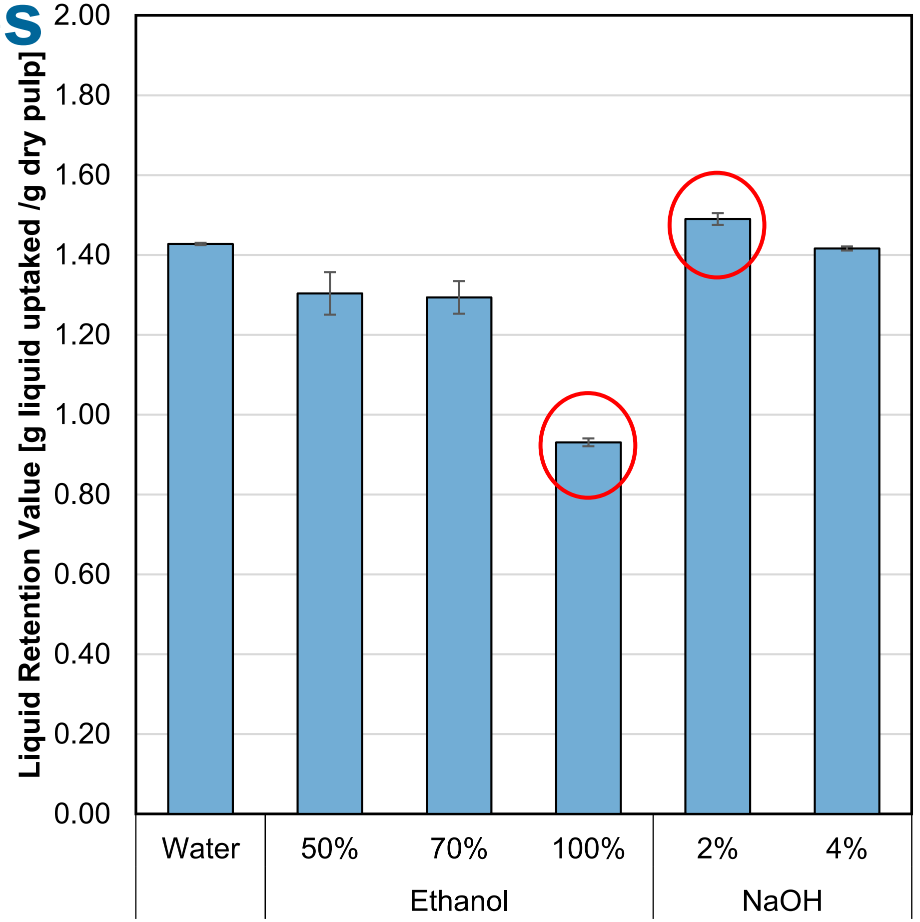


Swelling
NaOH 4wt%

Optical comparison of the LRV values

EtOH 100% and NaOH 2wt%

- Difference is noticeable on the surface and the morphology
- EtOH 100%
  - Dired out and brittle structure
- NaOH 2wt%
  - Swollen and soft structure



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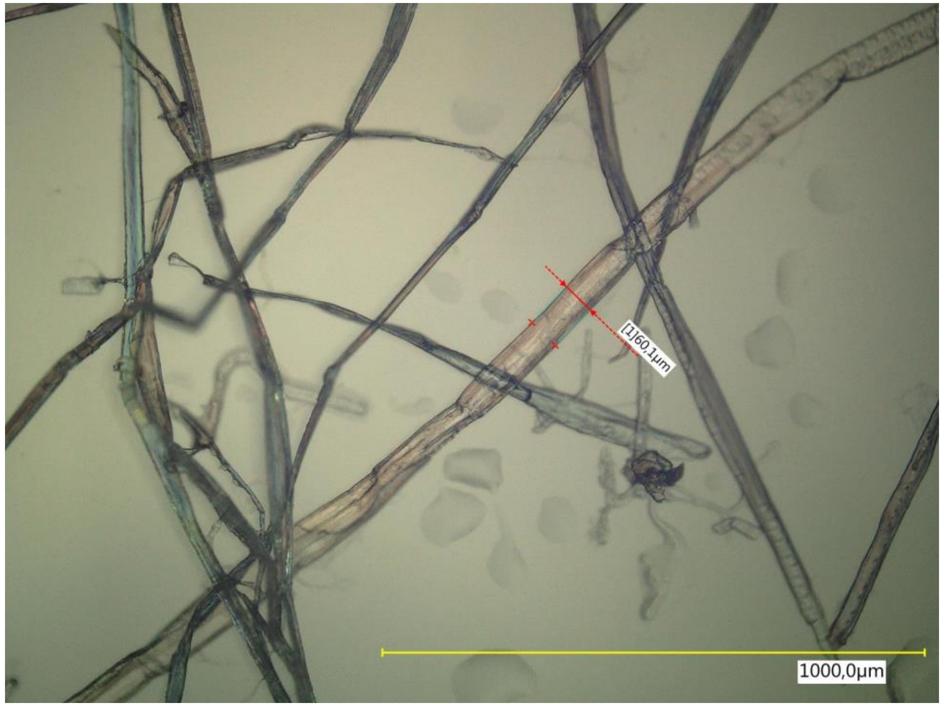
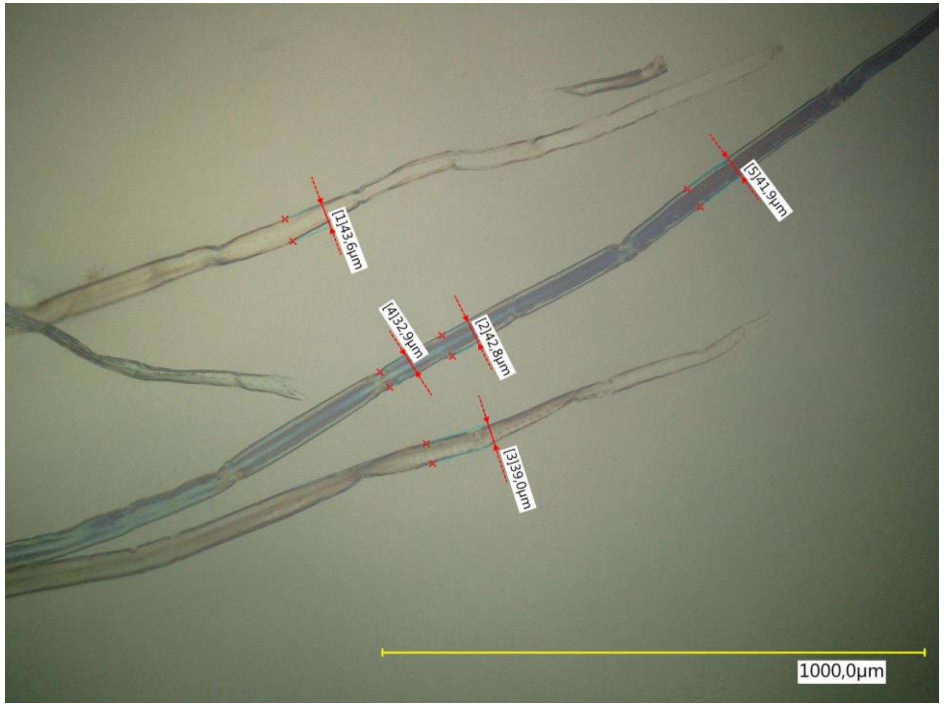
Swelling
Ethanol 100%



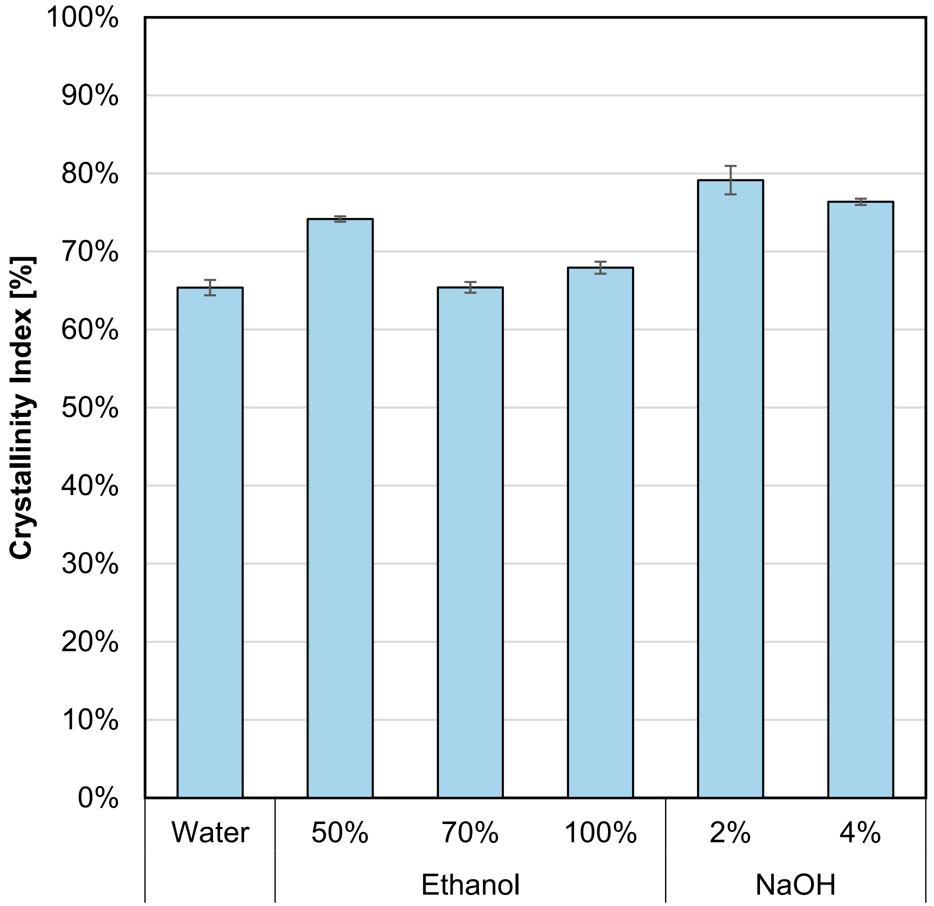
Swelling
NaOH 2wt%



Crystallinity Index
Wide Angle X-ray Diffraction (WAXD)

- Investigation of crystalline and amorphous part
  - Reflects on flexibility (amorphous part) and strength (crystalline part)
- Crystallinity Index slightly increases with treatment
- Dissolution of amorphous components like hemicelluloses by NaOH and EtOH.

The reduction in amorphous content leads to a relative increase in the crystalline background.



What we learned…

- NaOH 2wt% resulted in the highest uptake capacity in the fibers
- Pure ethanol caused the fibers to have the lowest uptake capacity
- Compared to water and NaOH solution, ethanol and ethanol solutions swell the fibers unevenly along their length
- The slight increase in Crystallinity Index suggests that NaOH and EtOH treatments dissolve amorphous components, such as hemicelluloses, resulting in a higher relative crystalline content

Outlook

- Screening for matrix material (additives) and other swelling agents
- Testing the swelling agents with the matrix material on holocellulose fibers
- Impregnation with additives or matrix material after swelling
- Study of methods for the analysis of impregnated fibers for biocomposites

Thank you!

And a big thank you to my colleagues and mentors :)

cornelia.hofbauer@tuwien.ac.at

References

[1] PAAVILAINEN, Leena. Influence of fibre morphology and processing on the softwood sulphate pulp fibre and paper properties. 1993.

[2] J. Pere, et al, „Influence of the hemicellulose content on the fiber properties, strength, and formability of handsheets“, BioResources, 2018, doi: 10.15376/biores.14.1.251-263.

[3] Q. Wang, et al, „The effect of hemicellulose content on mechanical strength, thermal stability, and water resistance of cellulose-rich fiber material from poplar“, BioResources, 2019, doi: 10.15376/biores.14.3.5288-5300.

[4] Z. Han, et al „Effect of Hemicellulose on the Wet Tensile Strength of Kozo Paper“, Molecules, 2023, doi: 10.3390/molecules28196996.

[5] Adapted from: WESTIN, Per-Oskar, et al. Single step PAA delignification of wood chips for high-performance holocellulose fibers. Cellulose, 2021, 28. Jg., Nr. 3, S. 1873-1880.

[6] ISO 23714:2014 - "Pulp — Determination of water retention value (WRV)