CEBIPRO - New Analysis Technologies for Circular Economy Biorefinery Processes

Duration: 01.01.2023 to 30.04.2025

Budget: 1,345,714 €

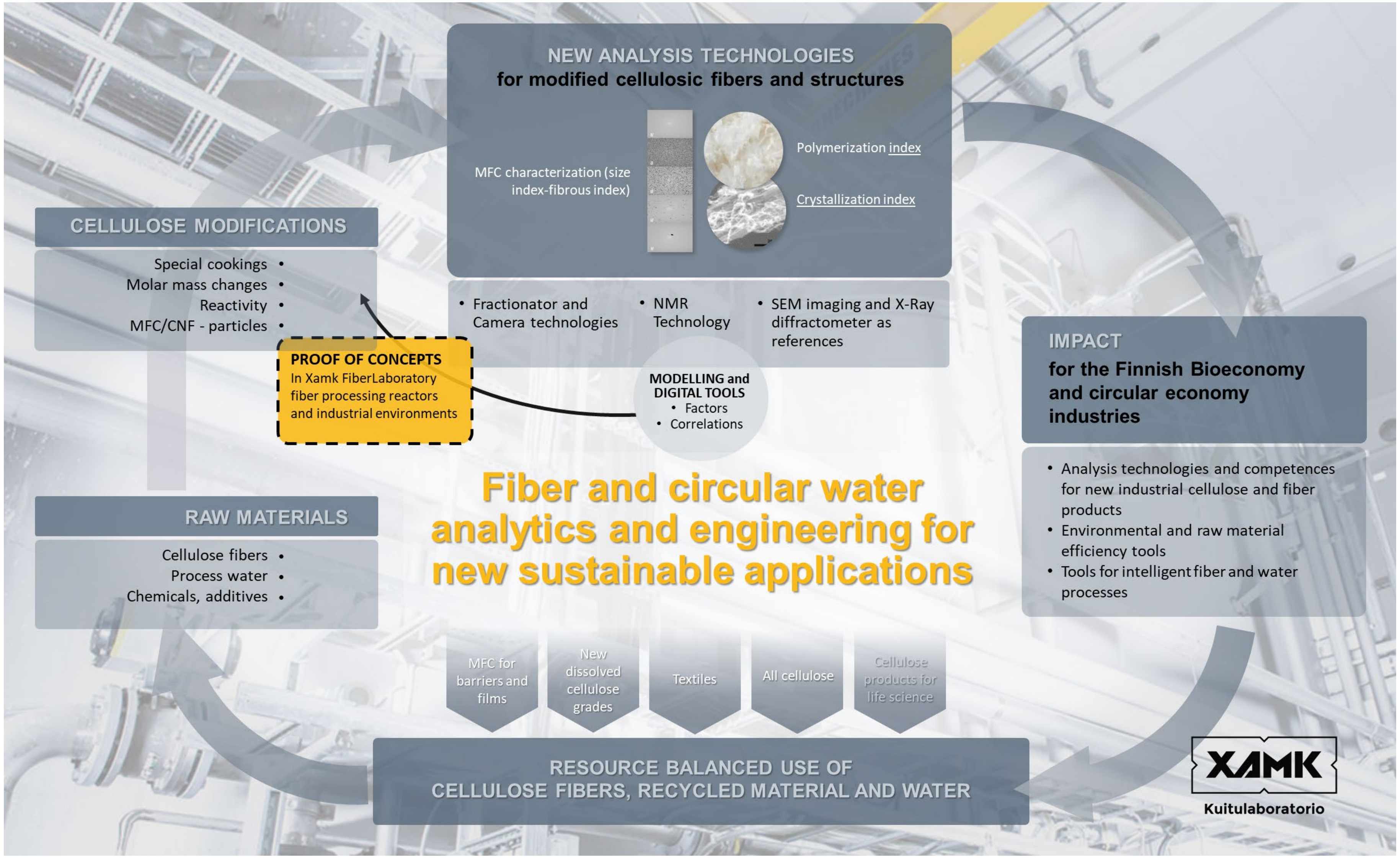
Coordinator: XAMK

Partners: Valmet Automation, Stora Enso Oyj, AquaFlow Oy, UPM-Kymmene Oyj, Wetend Technologies Oy, Fiber-X Finland Oy

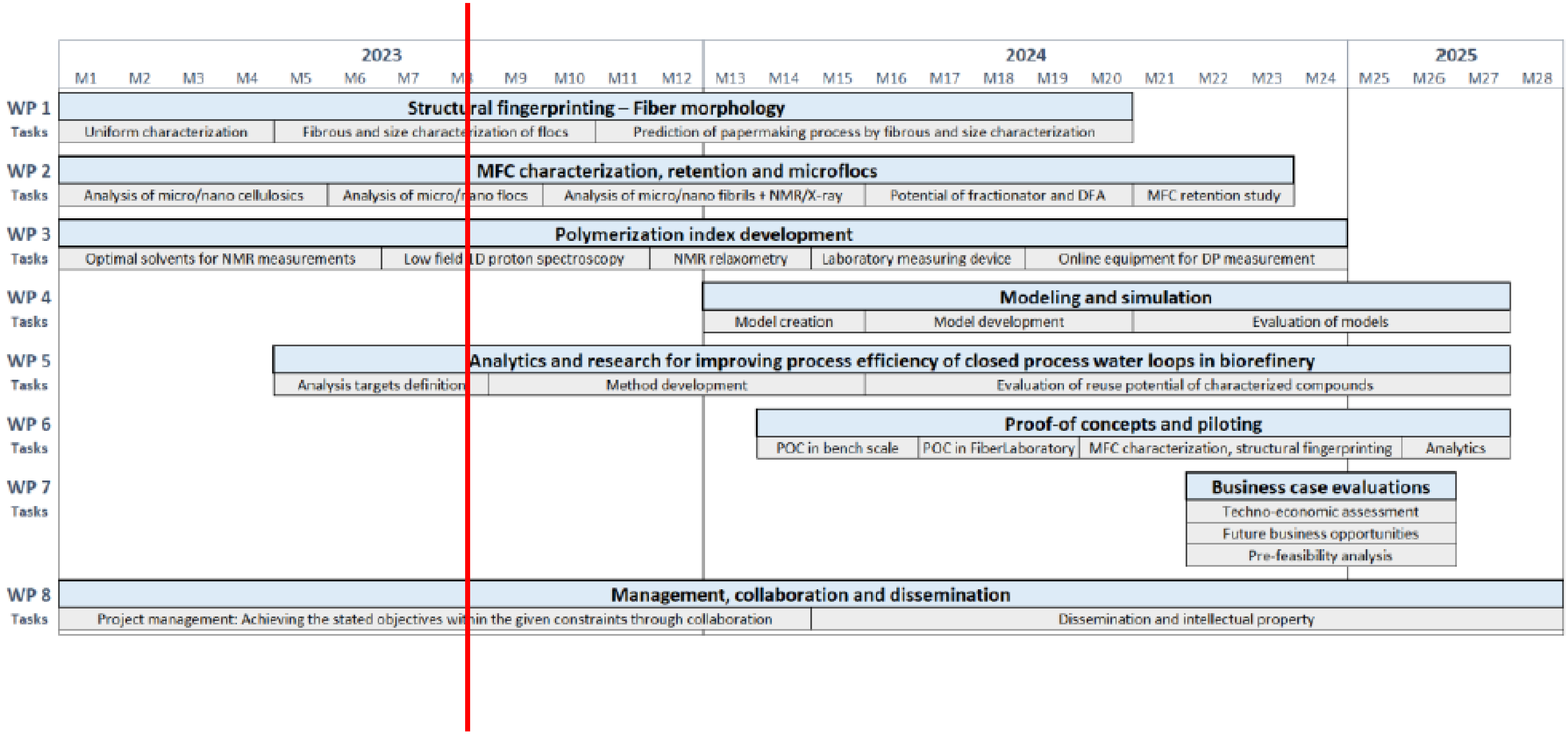
BUSINESS FINLAND

Euroopan unionin rahoittama – NextGenerationEU

CEBIPRO – PROJECT OBJECTS



Project schedule



Xamk resources (full and part time)

- Yrjö Hiltunen, projektipäällikkö
- Ekaterina Nikolskaya, projektitutkija
- Ella Tirronen, projektitutkija
- Juhani Turunen, TKI-asiantuntija
- Maria Luukkanen, projektitutkija
- Prof. Levente Csóka, kv-asiantuntija
- Worakan Csóka, kv-asiantuntija
- Sanni Härkönen, kesätyöntekijä
- Elmeri Pöllänen, kesätyöntekijä
- Jere Järvenpää, kesätyöntekijä

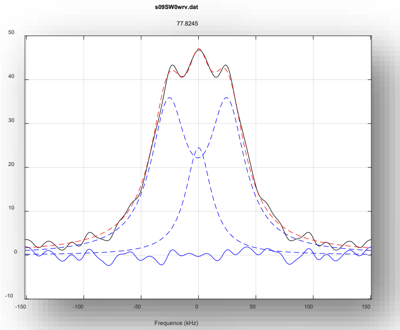
WP3. Crystallinity index by Low Field NMR

- The method in CEBIPRO project based on low-field 1H NMR
- The method is simple =>

  (1) sample overnight in oven

  (2) measurement for 5-15 min

  (3) analysis result immediately

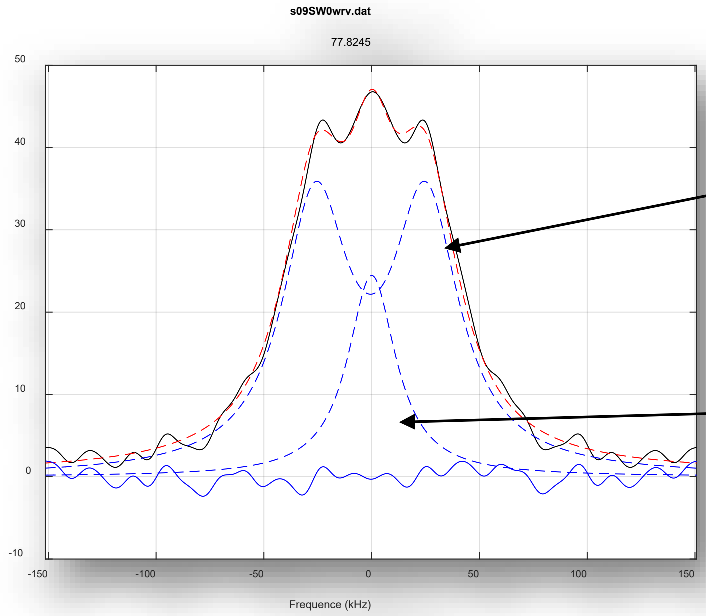


Sample → **Water removal** → **FID measurement** → **FFT** → **Frequence domain fitting** → **Areas of lines S_s, S_m** → **CI = $S_s/(S_s+S_m)$**

Reference methods
- X-ray Diffraction (XRD)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Solid-State Nuclear Magnetic Resonance (NMR)

Polymerization and crystallinity indexes are important in order to improve the properties, production efficiency, durability and competitiveness of cellulose-based

Analysis of ^{1}H NMR spectrum of dry pulp



- Fitting using Lorentzian line shapes
- A doublet from a crystalline part of the pulp (due to dipolar coupling between two protons)
- A singlet from an amorphous part of the pulp

Crystallinity CI = doublet area/total spectrum area * 100%

Repeatability test:
- the same sample overnight in an oven
- measurements in the morning (15 measurements)

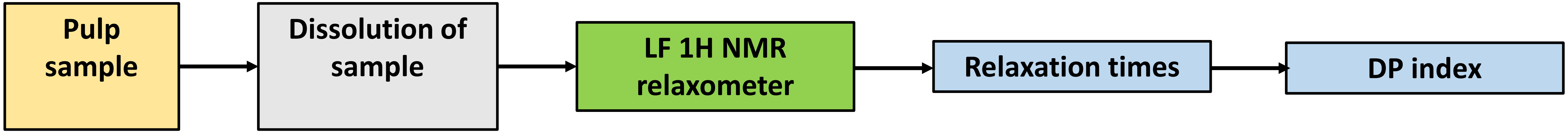
	Mean	Stdev
SW	88.4	2.8
HW	90.2	1.9

Sructural ordering of material

WP3: Polymerization degree DP by NMR

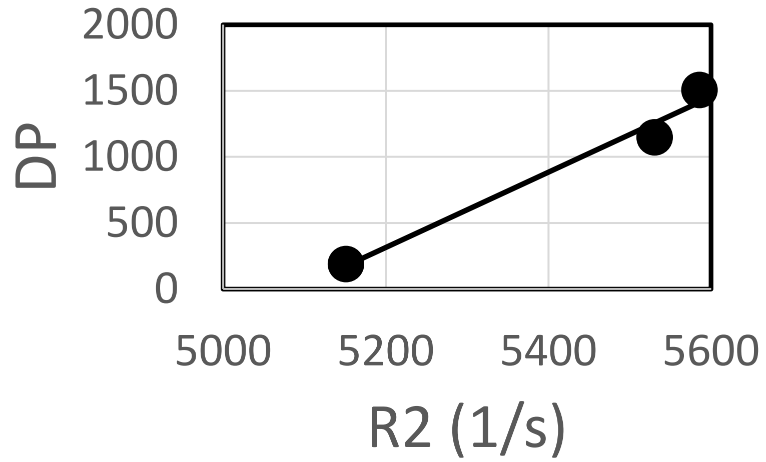
DP = molecular weight of cellulose / molecular weight of one anhydroglucose unit

- There is a dependency between viscosity and DP index, which can be used to calculate DP values for pulp samples
- The dependence between relaxation times and viscosity is also generally known => relaxation times can be used to determine DP values



Reference methods

- Viscometry
- High field NMR



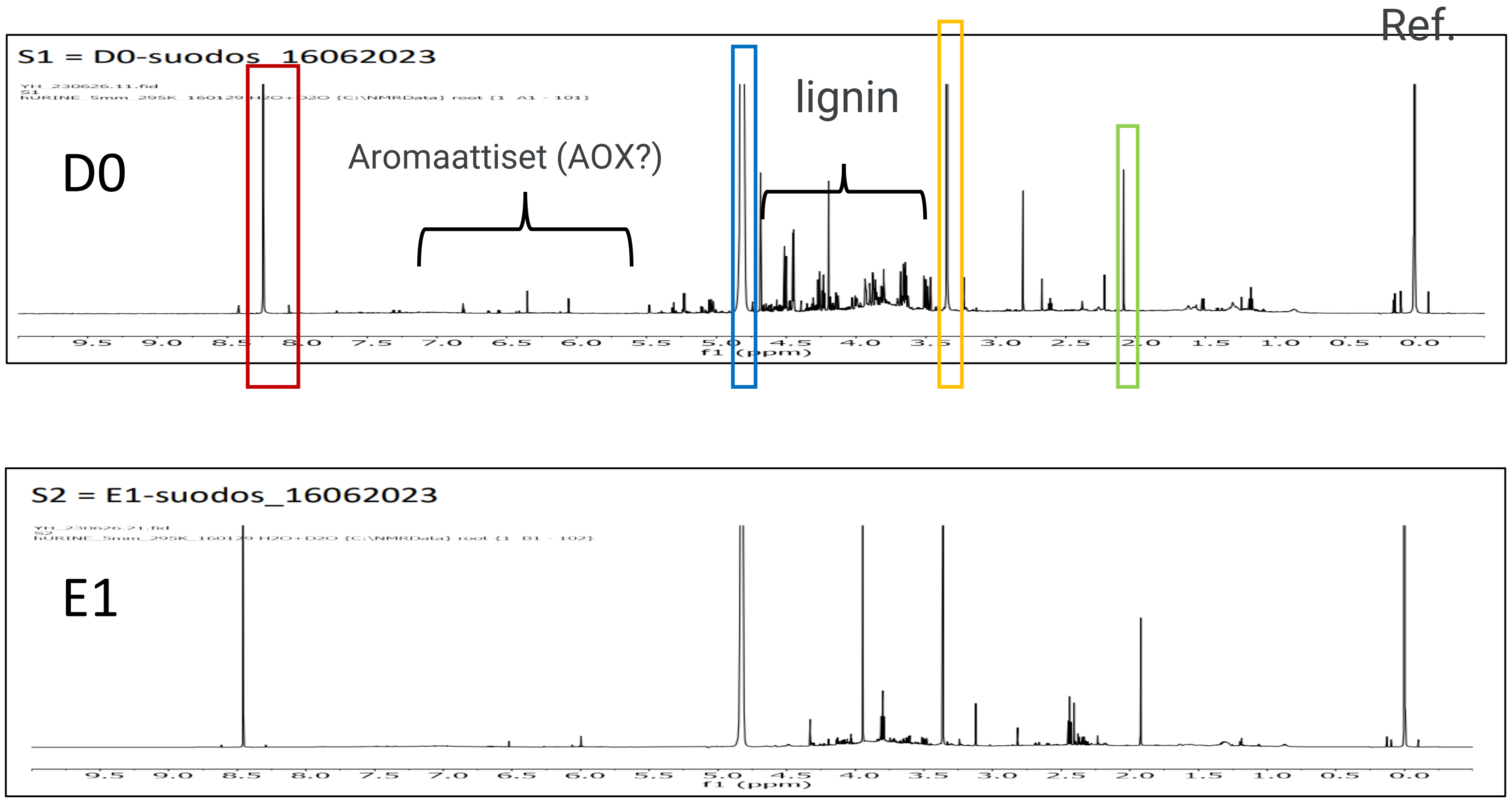
WP5: Closed Process Water Loop Analytics

A goal: the applicability of the NMR method to the analysis of process waters

=> Quantification of organic compounds (including AOX compounds)

Examples of identification:

- Formic acid and methanol from the production of chlorine dioxide
- Acetic acid
- Water



Conclusion

WP3:

- The development of the CI measurement method is well advanced, and it can be applied to the research of new pulp grades and processes
- Research on DP index measurement methods has been started and new results are expected later this year => The goal: Determination of DP values without dissolving pulp samples

- WP5:
  - The NMR method seems to be suitable for the analysis of process and wastewater
  - Questions in the future:
    - the water recycling potential of a pulp mill
    - the possibilities of improving the biodegradability of the wastewater
    - the possibilities of reducing water pollution

Comparing optical and imaging measurement with fractional DFA method

FiberTech 2023

Ella Tirronen, ella.tirronen@xamk.fi

Need for the MFC -analytics development

Characterization of MFC particle size can be divided into:

1. High-precision morphology characterization
2. Rapid characterization of properties that are indirectly linked to the morphology

Fiber analyzer based on fractionation and camera detection

= Size and shape data for every particle

Fractionation and Dynamic Fractional Analysis

- The DFA algorithm can be exploited with tube flow fractionation
  - **Fibrous index** distribution derived from the DFA algorithm describes the quality of the sample and enables monitoring of fiber refining
  - **Size index** distribution becomes important with nanomaterials in a suspension

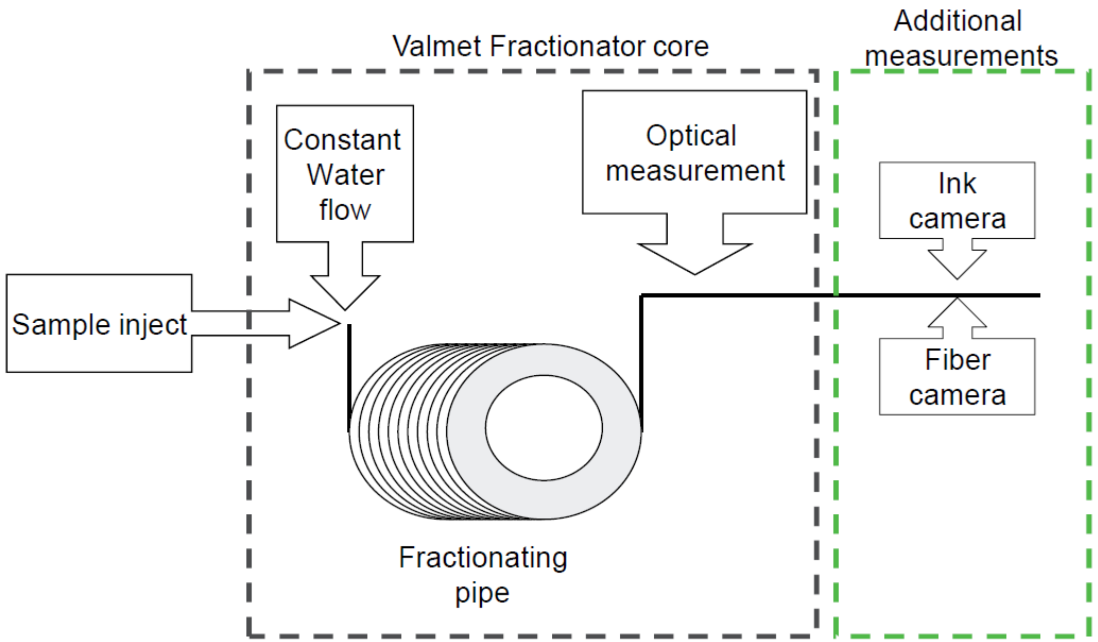
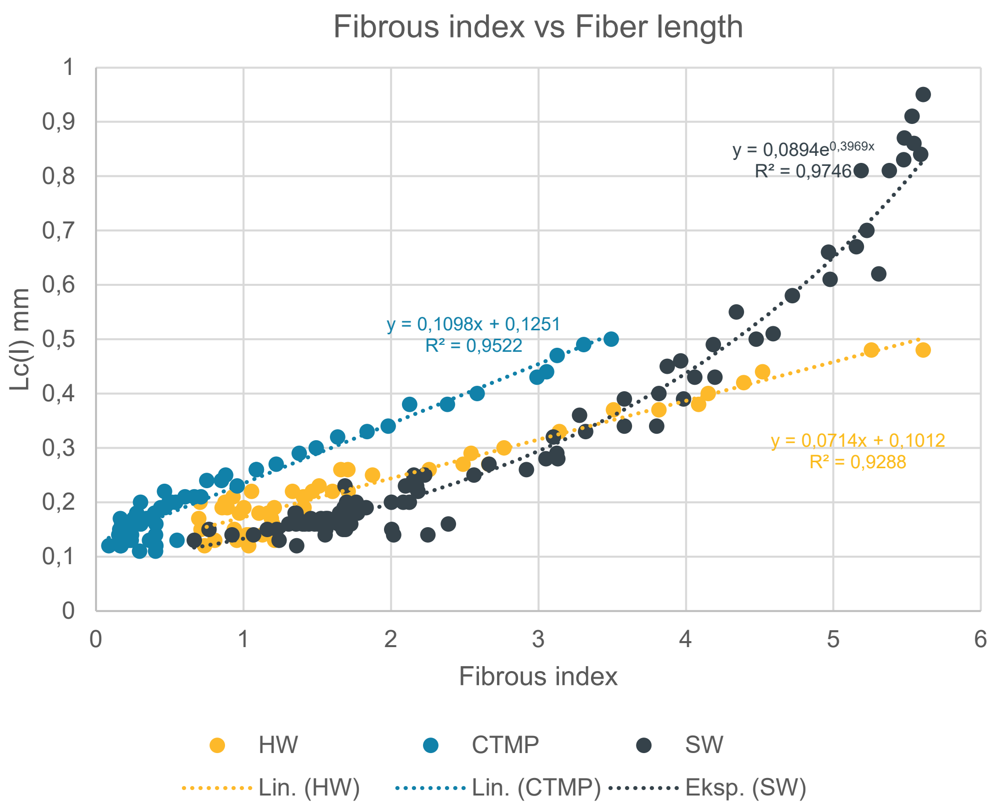


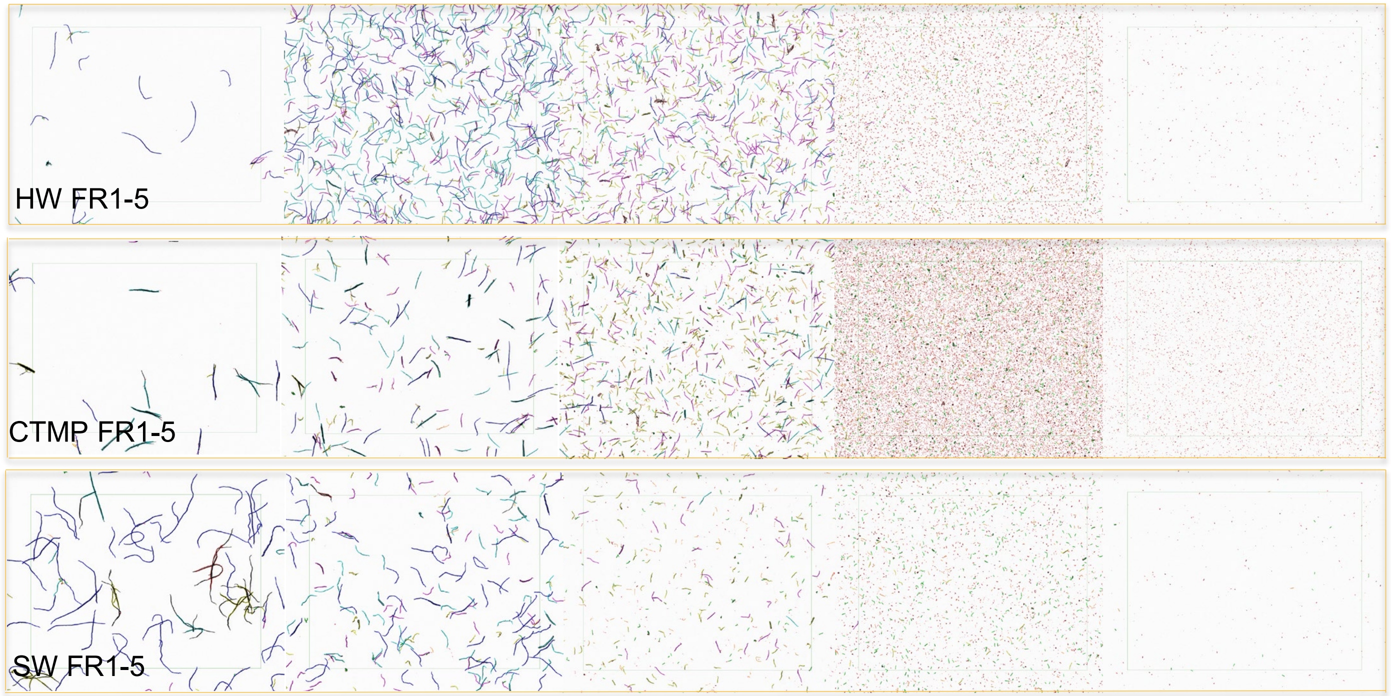
Fig 1. Schematic presentation of Valmet Fractionator (Valmet)

Reference: Törmänen, Matti. 2021. Improved analysis of tube flow fractionation data for measurements in the pulp and paper industry.

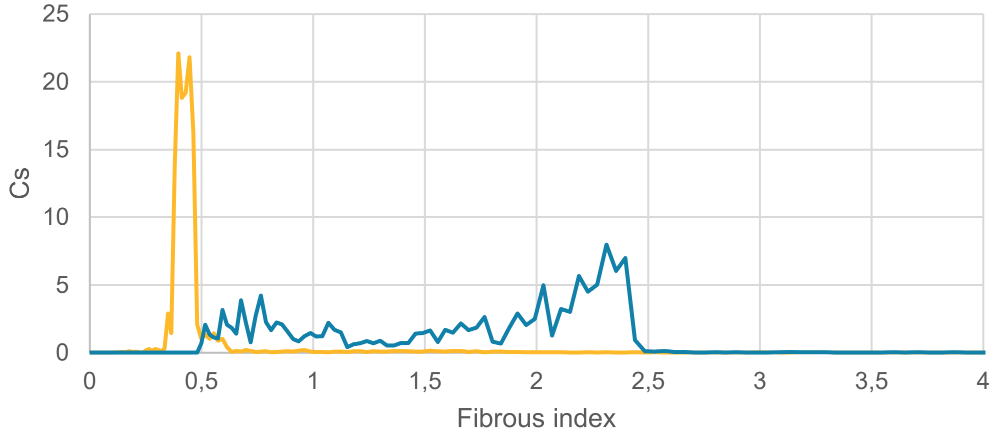
XAMK

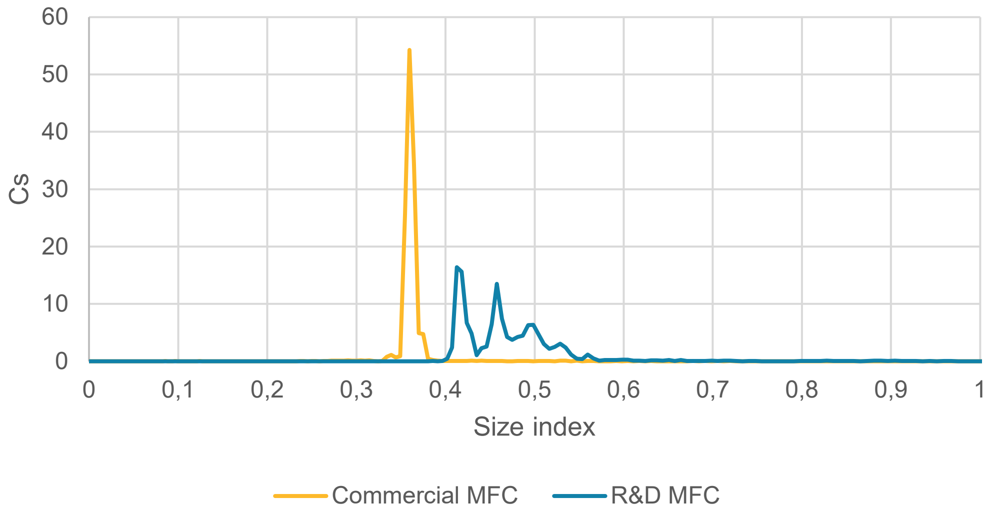
Correlation of fibrous index and fiber length in different pulp fractions

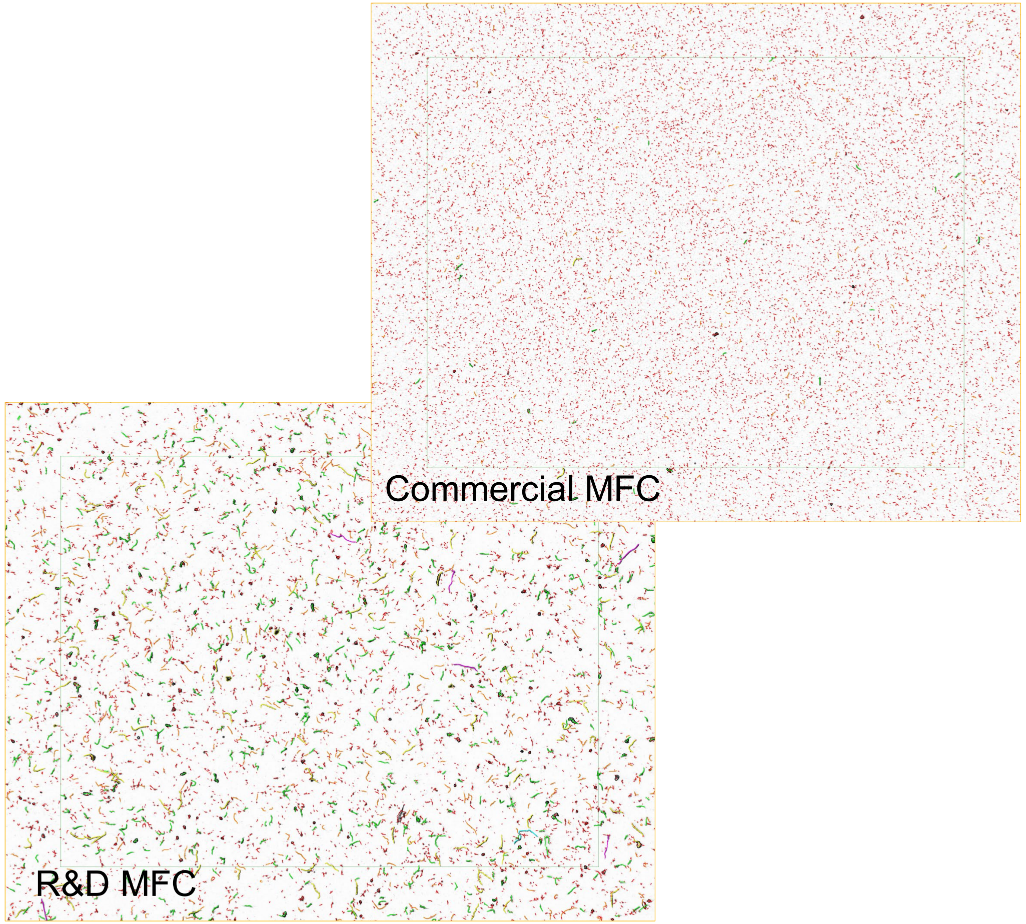




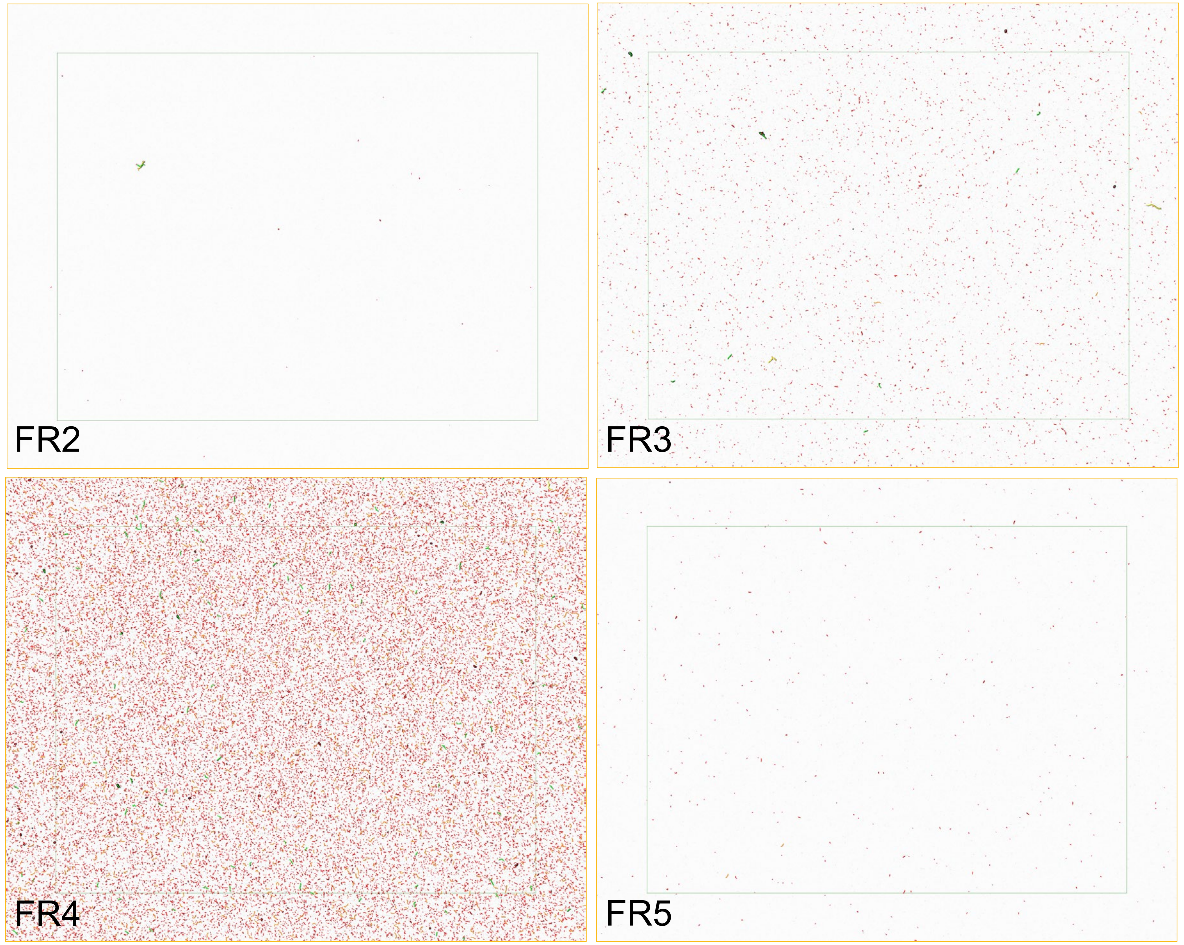
Difference in MFC qualities

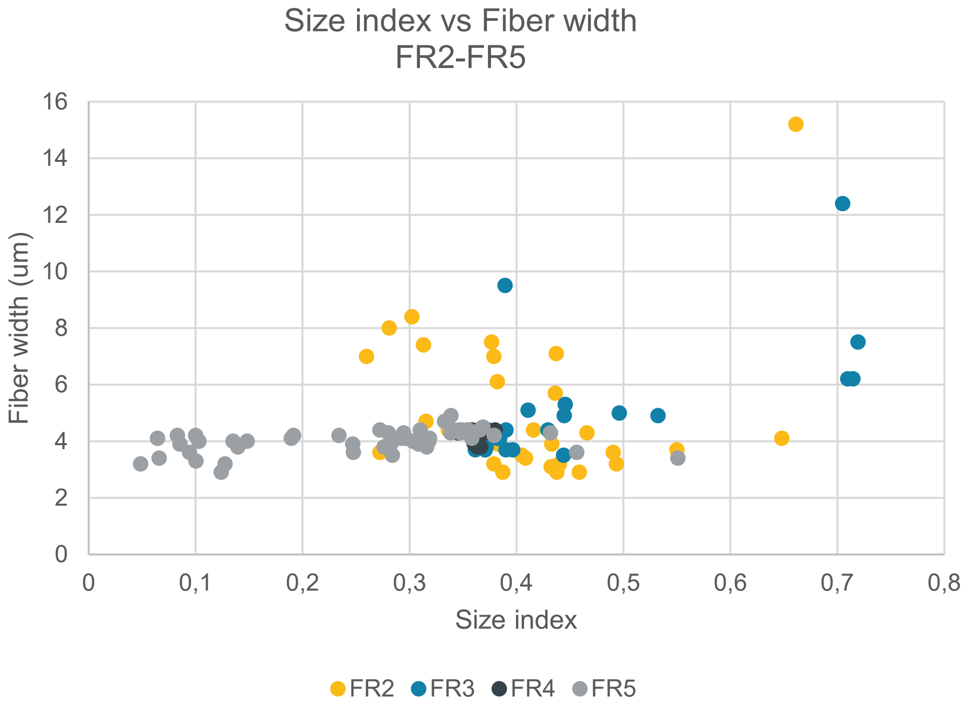






Size index in relation to fiber width in MFC fractions





Conclusion

- In the future micro- and nanomaterials production will increase and there will be a greater need for more selective measurements to identify these complex materials
- Using fractional measurement is possible to optimize processing efficiency and product qualities

The fractional DFA method and imaging measurement could provide a useful tool especially for nanoscale materials, otherwise difficult or unpractical to characterize when moving to an industrial scale

Thank you!

Dr. Worakan Csóka
Visiting researcher

I am a chemist researcher at Celltech-paper Ltd, Hungary. I received my PhD in 2019 in material science and technology aiming to use bacterial cellulose and silk fibroin in thin film applications. I was involved in CEBIPRO project to fabricate thin films from Valmet fractioned suspensions using evaporation casting fiber clustering method in order to widening the knowledge of MFC unique fingerprint.

Objectives

- A zero-waste perspective has been applied to collect the fibrous content from Valmet fractionator. (Temperature-induced MFC fibre clustering and evaporation casting drying technique)

- Level-off degree of polymerization (Dried or dissolved state can be effective for an online DP/NMR measurement?)

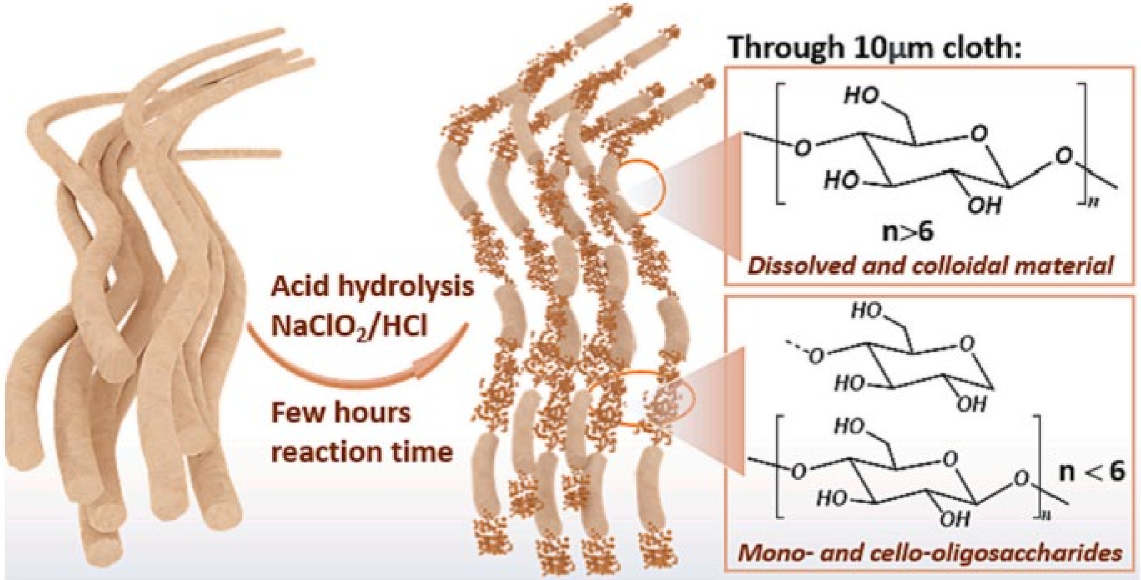
Temperature-induced MFC fibre cluster

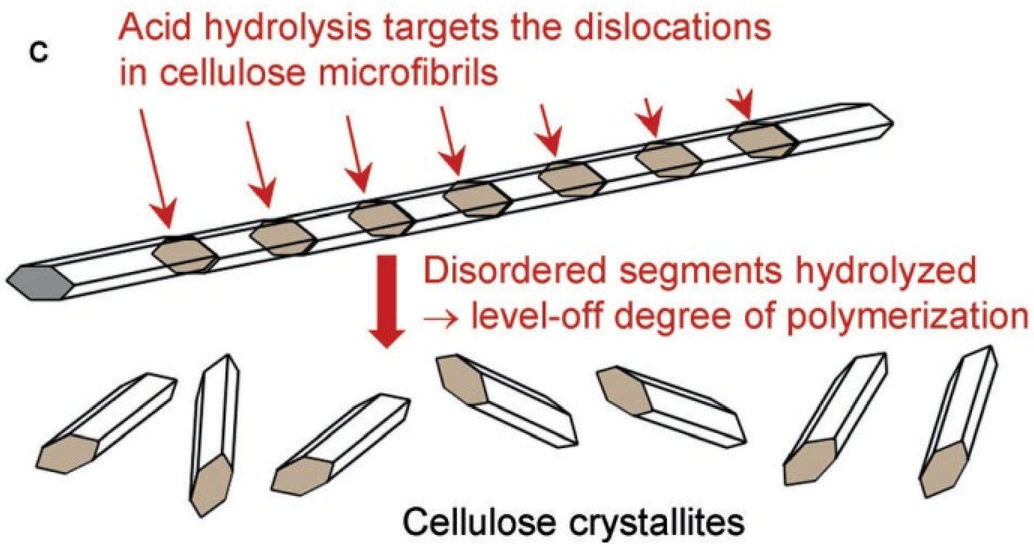
- The aligned water molecule sorption on the cellulose surfaces
- Some researchers confirmed that cellulose nanomaterials are severely agglomerated during oven drying process due to strong intermolecular hydrogen bond and water evaporation. [1,2]
- In order to collect all fractions separately, temperature-induced fibre clustering method was applied.

1. https://www.sciencedirect.com/science/article/pii/S1359836820333473
2. https://www.sciencedirect.com/science/article/pii/S0926669016300723?via%3Dihub

Level-off degree of polymerization

- “Simplified structure of a cellulose microfibril with crystalline segments irregularly interrupted by disordered segments. Disordered segments can be selectively targeted with controlled acid hydrolysis, leading to the isolation of cellulose nanocrystals.” Eero Kontturi





https://onlinelibrary.wiley.com/doi/10.1002/anie.201606626

Samples Preparation

HW and SW MFCs suspensions (different refining times)

Acid hydrolysis untreated HW dried sheets @2,38 kPa HCl vapor

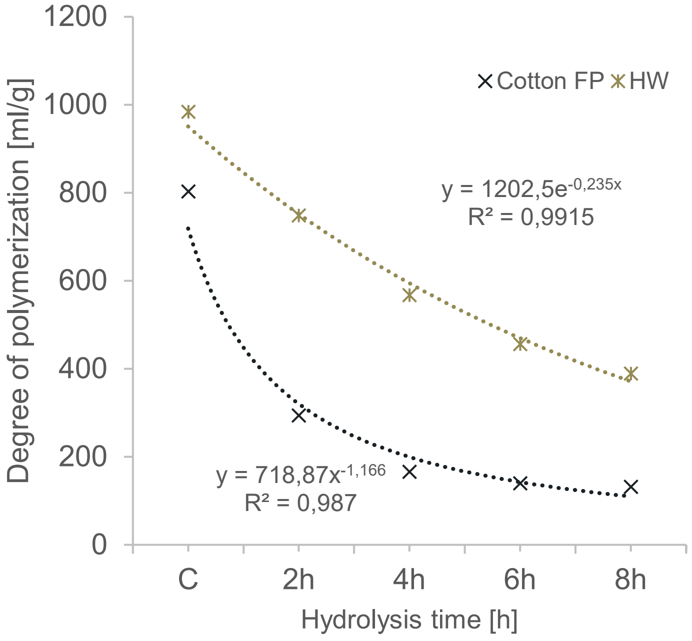
DP , NMR, RDB-PAS measurements of CNC samples

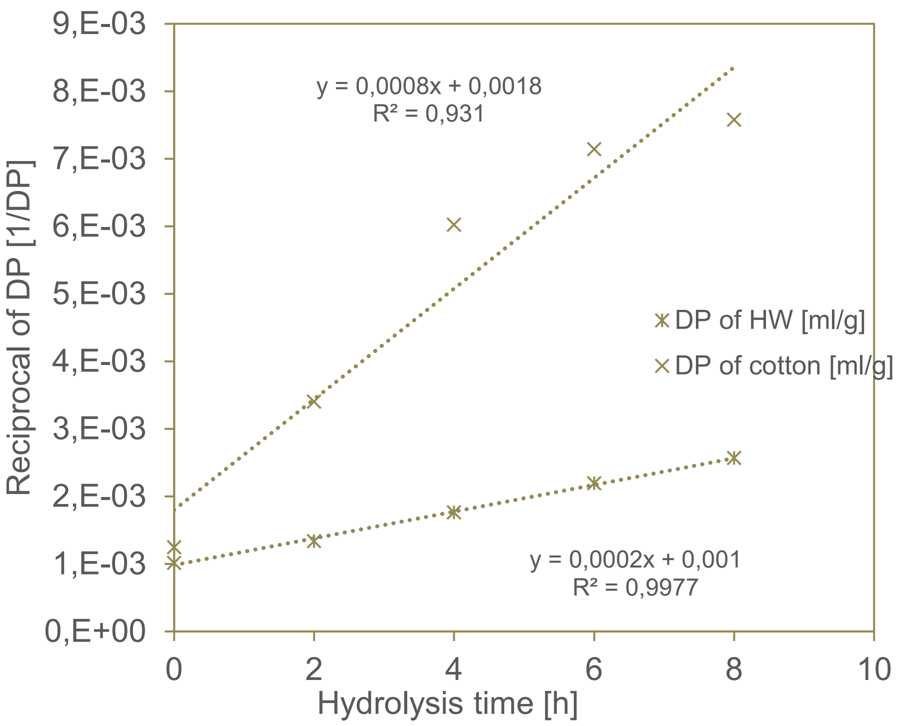
HW and SW MFCs dried cluster samples @60℃

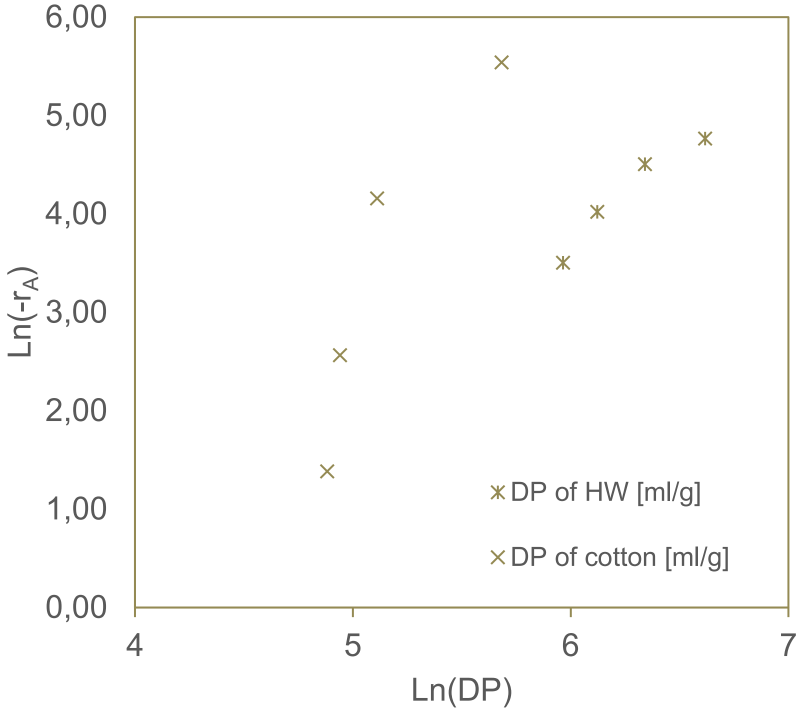
NMR measurement

RDB-PAS measurement

Traditional DP measurement (For Dried state NMR)

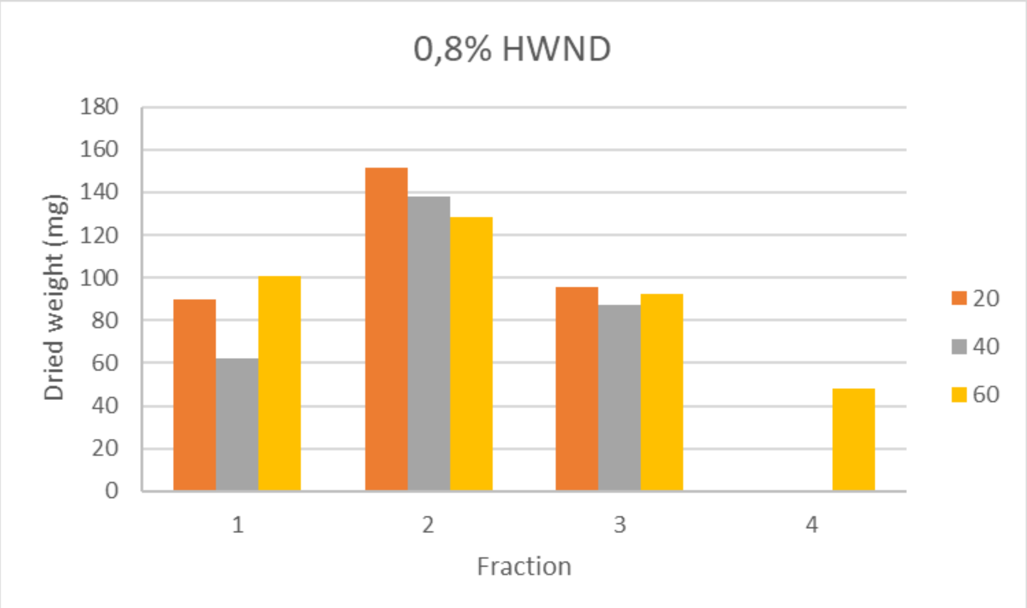


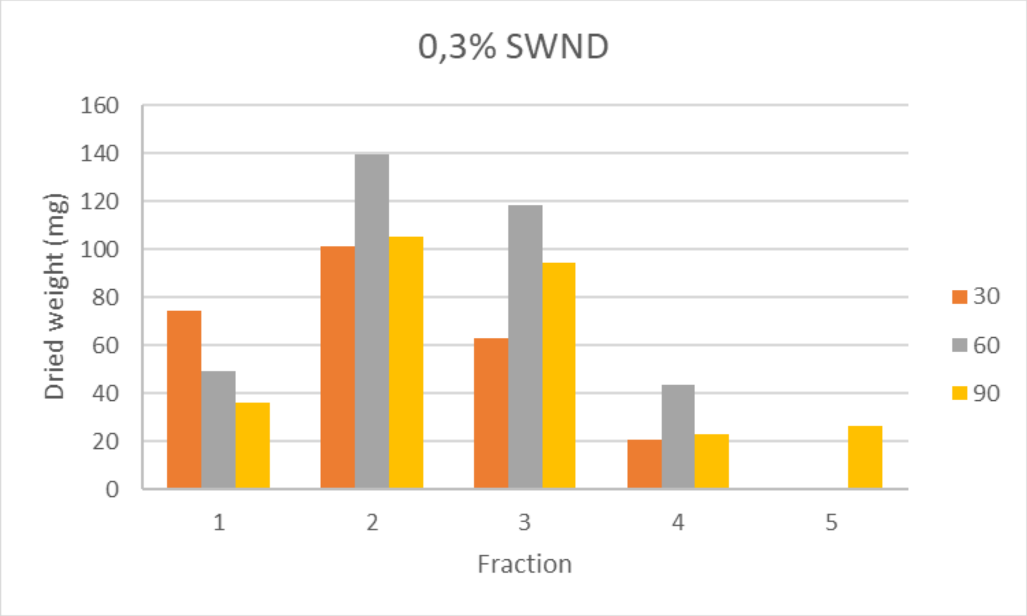


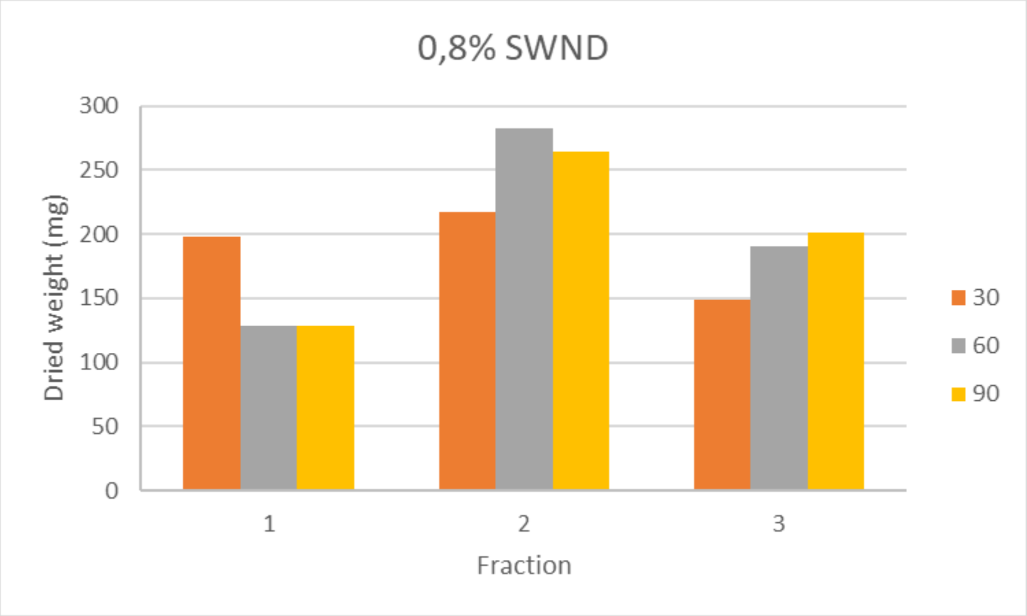


Dried weight of samples

- HW showed no significant trend between refining time in each fraction due to the heterogeneous fibrous components.
- SW showed significant 40-200% trend between refining time in each fraction due to the homogenous fibrous component.







Conclusion

- A zero-waste perspective has been successfully applied to collect the fibrous content from the fractionator.
- Temperature-induced MFC fibre clustering seems an effective way to collect the fractions for further analysis.
- Evaporation casting resulted thin films to be able to investigate the fractions separately and provide MFC fingerprint data.
- Further investigation of DP measurements are necessary to be done!

Thank you for your kind attention!

CEBIPRO - fingerprint

Prof. Dr. Levente Csóka

visiting professor ELTE → XAMK^{2023}

International cooperations

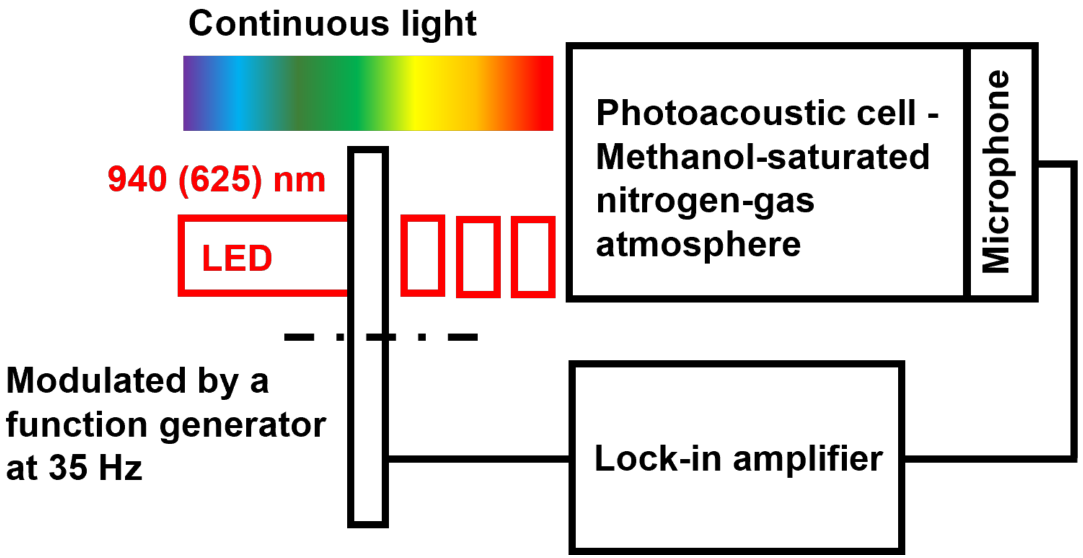
- Levente Csóka: I am a pulp and paper scientist, full professor since 2016, and working at ELTE University in Hungary. I gained international experience in Japan, Canada, USA and Finland. I am an author of more than 70 scientific articles, most of them in high impact journals.

- International research cooperation with **Prof. Dr. Bunsho Ohtani**, through Hokkaido University. Prof. Ohtani is a renowned scientist about his semiconducting research and achievements having more than 300 scientific articles. He is retired and now operating his Nonprofitable Organization touche NPO in Sapporo, Japan.

Methodology

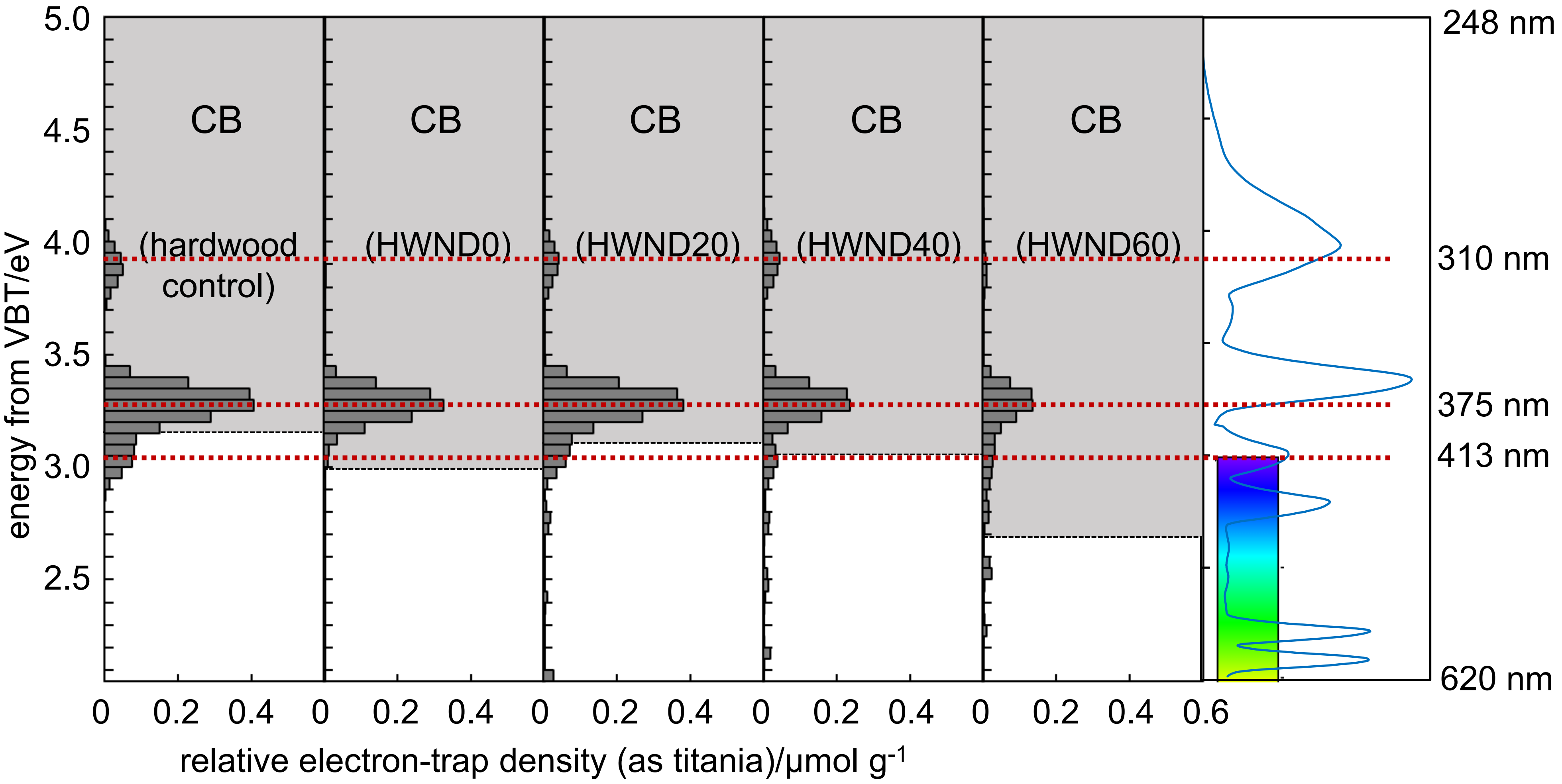
- Wood fibre grinding is an essential mechanical process that contributes to the efficient utilization of wood resources, creates MFC and a wide range of fibre-based products.

- Photoacoustic spectroscopy (PAS) is a powerful technique used to study the interaction of light with matter. It provides valuable insights into the optical and acoustic properties of materials, offering a non-destructive and sensitive approach. When a sample absorbs modulated light, it undergoes localized heating, resulting in the generation of a pressure wave due to thermal expansion. This radiation-less spectroscopic state is an irreversible transformation of light into heat, which is measured by an acoustic microphone. The pressure wave, detected by a sensitive microphone, is proportional to the absorbed light energy and can be analyzed to extract information about the sample.



L. Csóka et al.: Reversed double-beam photoacoustic spectroscopic analysis of photoinduced change in absorption of cellulose fibres
https://www.nature.com/articles/s41598-022-18749-w

Results



5.0
4.5
4.0
3.5
3.0
2.5
energy from VBT/eV
CB
CB
CB
CB
CB
(hardwood control)
(HWND0)
(HWND20)
(HWND40)
(HWND60)
0
0.2
0.4
0.6
relative electron-trap density (as titania)/μmol g-1
248 nm
310 nm
375 nm
413 nm
620 nm

Conclusion

- It has been shown that PA spectroscopy is a powerful tool for the study of the density of ETs in cellulose fibres.
- An important advantage of this method over regular absorption measurements is that it can be used to determine the ETs that are formed on the surface of cellulose fibres after mechanical exposure
- The RDB-PAS spectroscopy showed that the energy differences between the ETs are bigger after 20 min and smaller after longer mechanical treatment.
- The results reveal that cellulose possess a unique response to photo induced changes and can inspire a new approach of smart material design and promotes further applications.