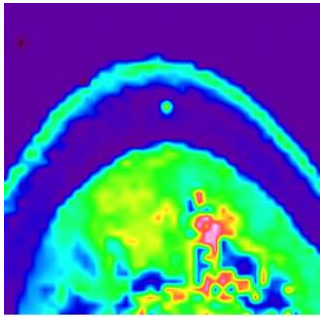
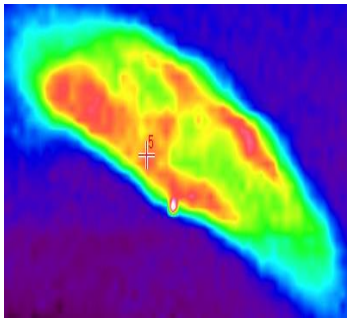
Raman Spectroscopy and Imaging in Organization, Processing and Functionalization of Polysaccharide Materials





Pieter Samyn,[1] Pieter Billen,[2] Dries Vandamme,[1] Peter Adriaensens,[1] Yael Politi,[3] Anayancy Osorio[4]

[1] Hasselt University, Applied and Analytical Chemistry, Institute for Materials Research (IMO-IMOMEC), Belgium

[2] University of Antwerp, Intelligence in Processes, Advanced Catalysts & Solvents, Belgium

[3] Technische Universität Dresden and Biomaterial Department, Max-Planck Institute of Colloids and Interfaces, Germany

[4] University Freiburg, Institut für Mikrosystemtechnik – IMTEK, Bioinspired Materials for Biomedical Engineering, Germany

UHASSELT
KNOWLEDGE IN ACTION

Pieter.Samyn@uhasselt.be

IMO-IMOMEC
UHASSELT imec

Motivation

Raman spectroscopy and micro-Raman imaging as a tool for biomass and polysaccharide evaluation

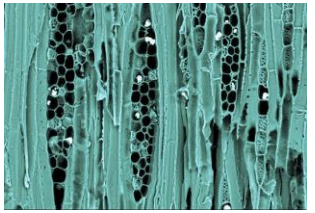
I M A G I N G

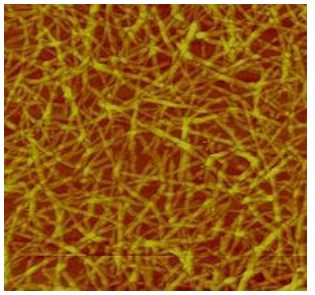
1. Hierarchical organization of biomass

Understanding structural organization of components in biomass allows for design of dedicated extraction routes and bio-mimicking of organization in biocomposite materials: chitin and cellulose

2. Biomass processing and optimization

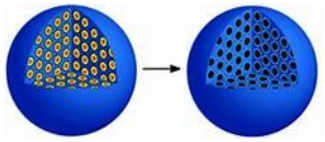
Optimization of processing conditions and efficiency, maximizing properties and structure of the obtained components (e.g. crystallinity, homogeneity): fibrillated cellulose





3. Biomaterial functionalization and applications

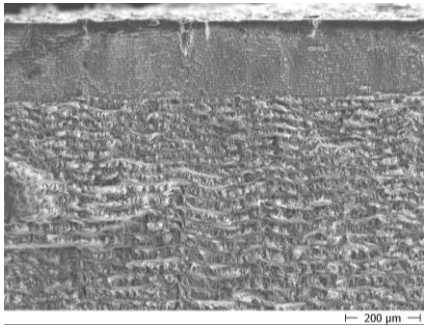
Designing surface structures with active functionality such as functionalized nanofibers and coatings, thermal release in nanoparticles, melt-processing of nanocomposites: cellulose fiber composites

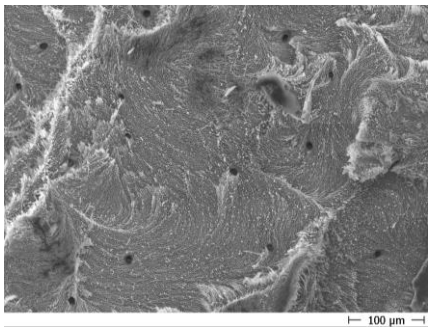


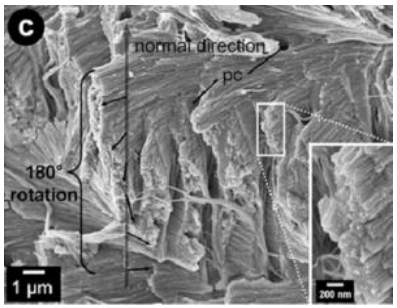
1. Hierarchical organization of biomass

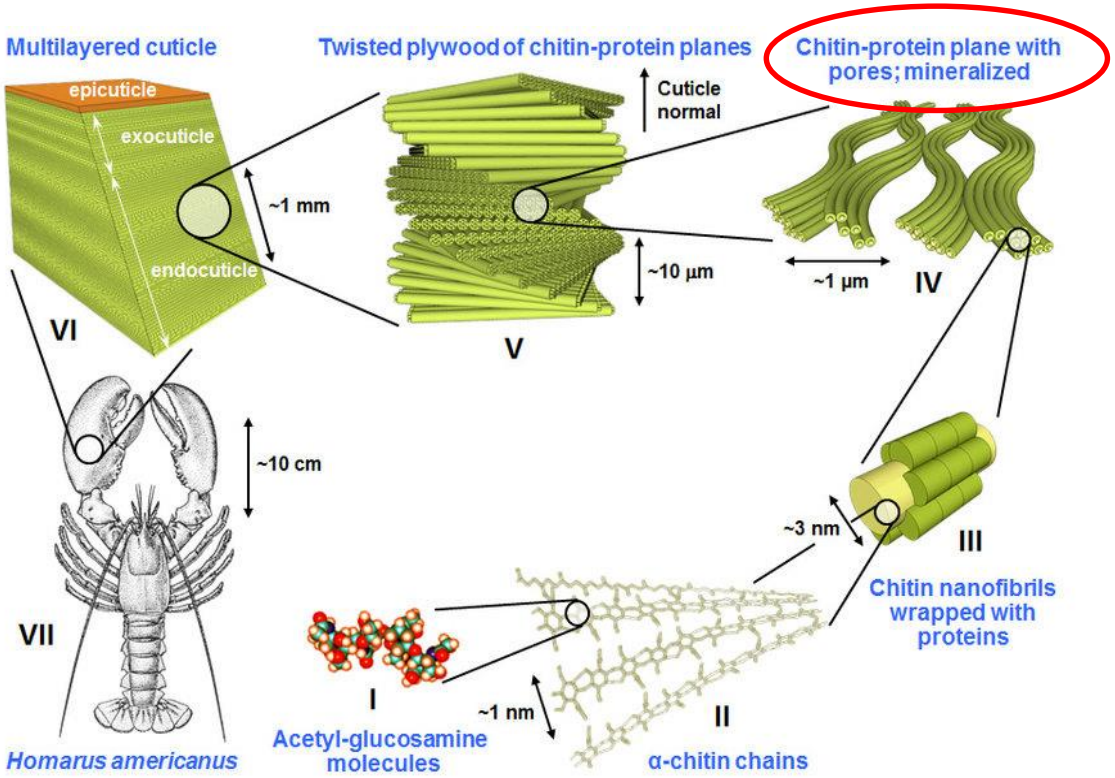
The crustacean ***cuticle*** is a biological material that covers the animal and forms a continuous exoskeleton. The cuticle consists of a inorganic/organic chitin-protein based nanocomposite with hierarchi-cally order over several levels. The different levels have differences in structure together with a heterogeneous mineralization pattern. The cuticle contains minerals like magnesium-/calcite, amorphous calcium carbonate and amorphous calcium phosphate. The composition of the different layers can be studied by several analytical techniques, e.g. chemical mapping by Raman spectroscopy. It is a versatile material adapted to different functions, constituting a source of bio-inspiration for the development of advanced bio-based materials.

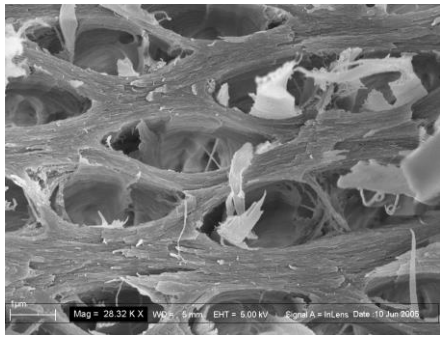
The Lobster Cuticle Ultrastructure

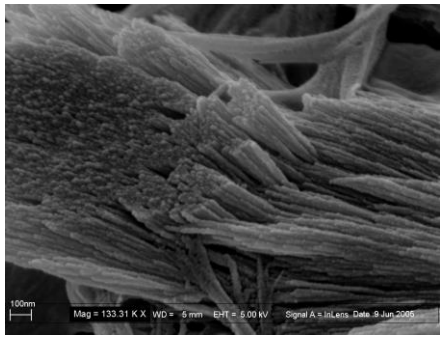










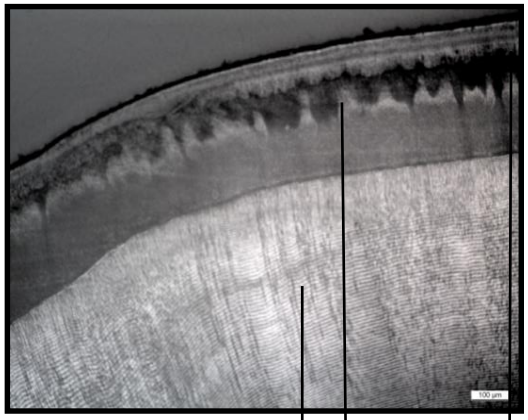


S. Nikolov, M. Petrov, L. Lymperakis, M. Friak, C. Sachs, H. Fabritius, D. Raabe, J. Neugebauer, Adv. Mater. 22 (2010) 519-526

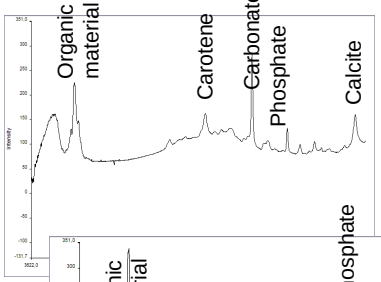
D. Raabe, P. Romano, C. Sachs, H. Fabritius, A. Al-Sawalmih, S. Yi, G. Servos, H. Hartwig, Mater. Sci. Eng. A 421 (2006) 143–153

A. Al-Sawalmih, C. Li, S. Siegel, H. Fabritius, S. Yi, D. Raabe, P. Fratzl, O. Paris, Adv. Funct. Mater. 18 (2008) 3307-3314

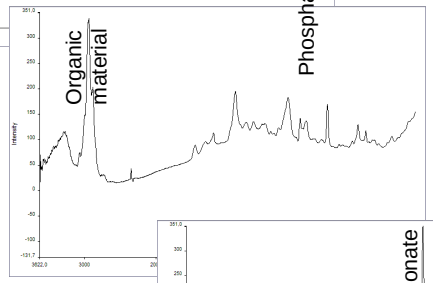
Organization of Cuticle Layers



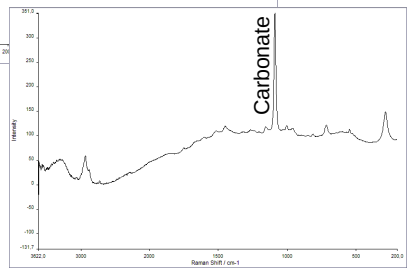
Endo

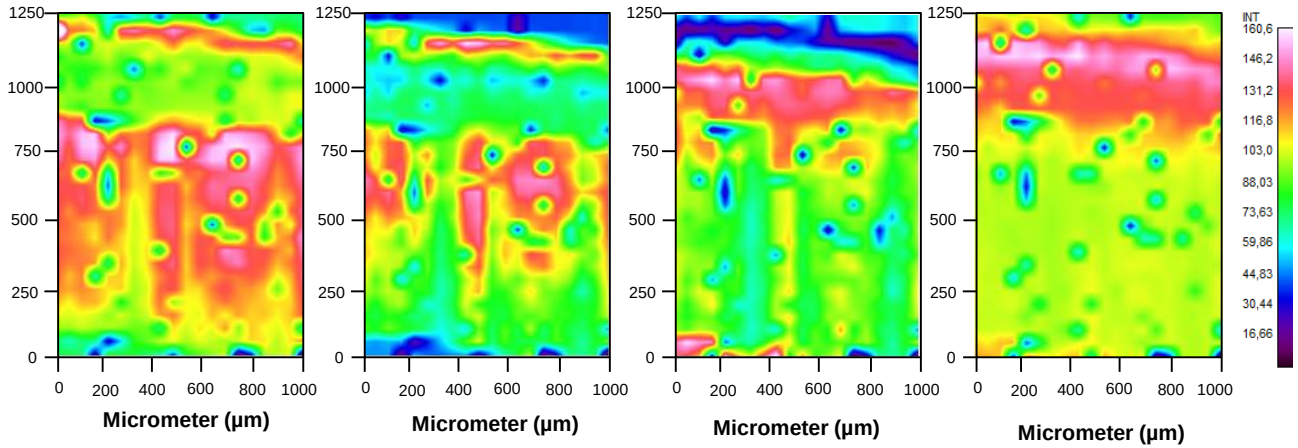


Exo

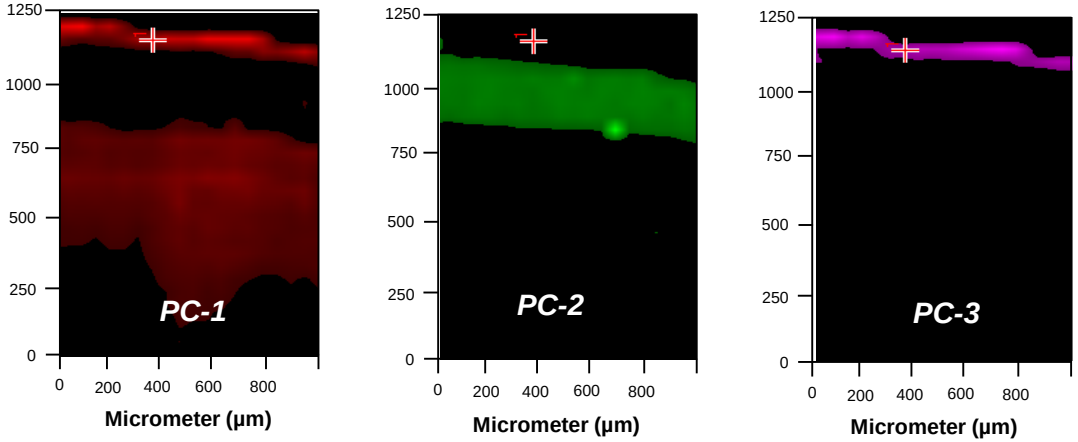


Epi





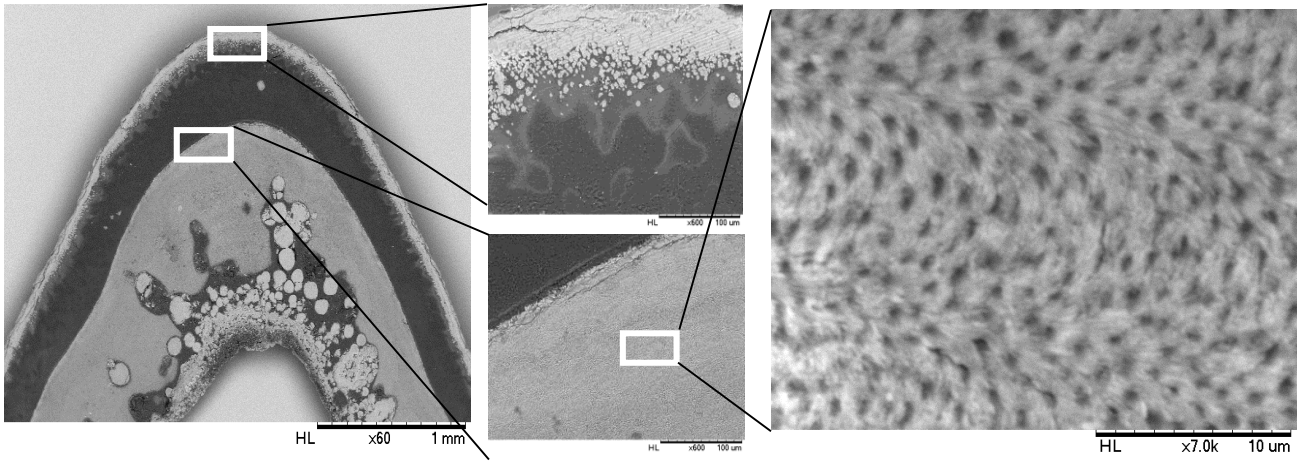
282 cm^{-1} (Calcite) ***1085 cm^{-1} (Carbonate)*** ***3279 cm^{-1} (Organic)*** ***960 cm^{-1} (Phosphate)***



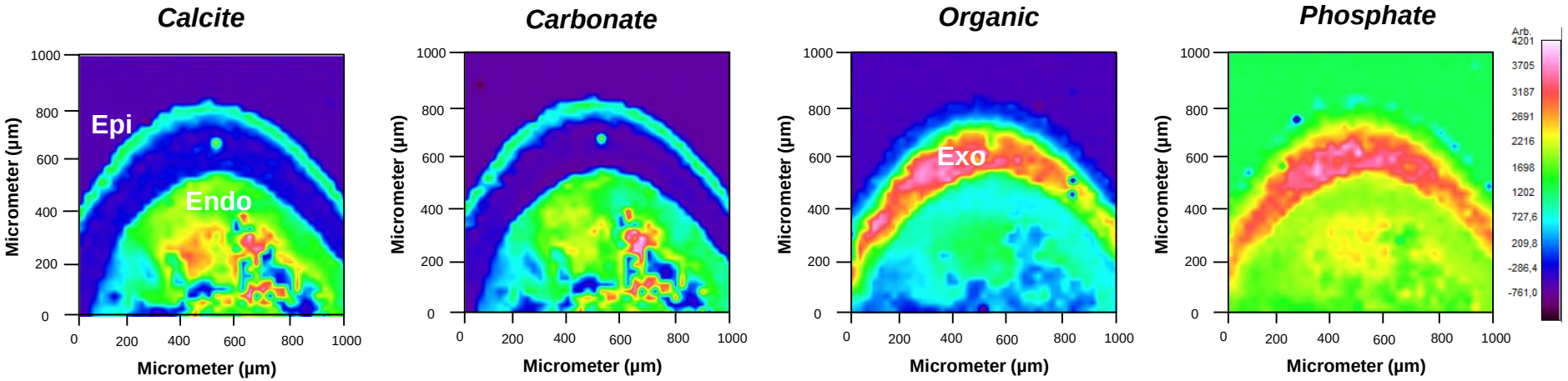
The different cuticle layers have a characteristic composition with different main components. The Raman maps with the distribution of the different components were obtained by integration of specific areas in the spectra. The transitions and different compositions of the several layers can clearly be visualized. The structure of the cuticle can be resolved by principal component analysis (PC) of Raman maps.

Bio-mineralization of the Spiny Region

Organic phase = formation of crystalline chitin core fibers surrounded by sheet of ordered proteins
Minerals = crystalline (calcite), amorphous calcium carbonate (ACC), amorphous calcium phosphate (ACP)



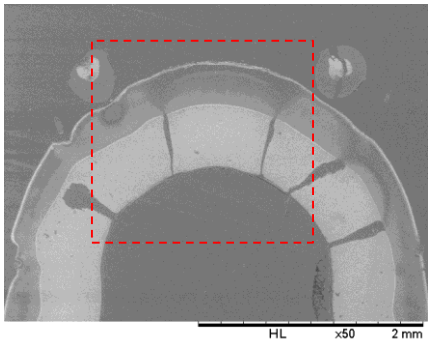
The minerals are not distributed homogeneously and mineralization proceeded to different amounts through the structure

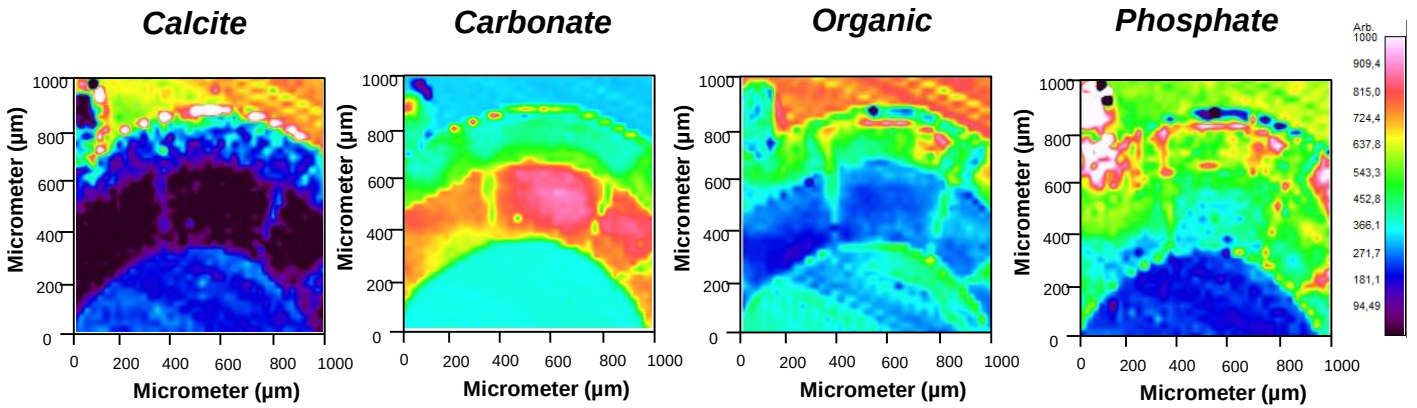


The epicuticle is strongly mineralized and mechanically protects the underlaying structure. The exocuticle contains organic material together with amorphous calcium phosphate and provides flexibility to the structure. The endocuticle progressiveyl undergoes mineralization with highest carbonate content, but both calcite and phosphate

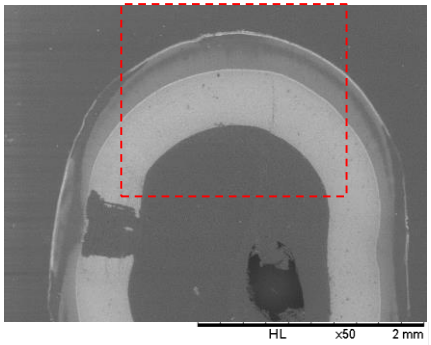
Bio-mineralization of the Antenna Region

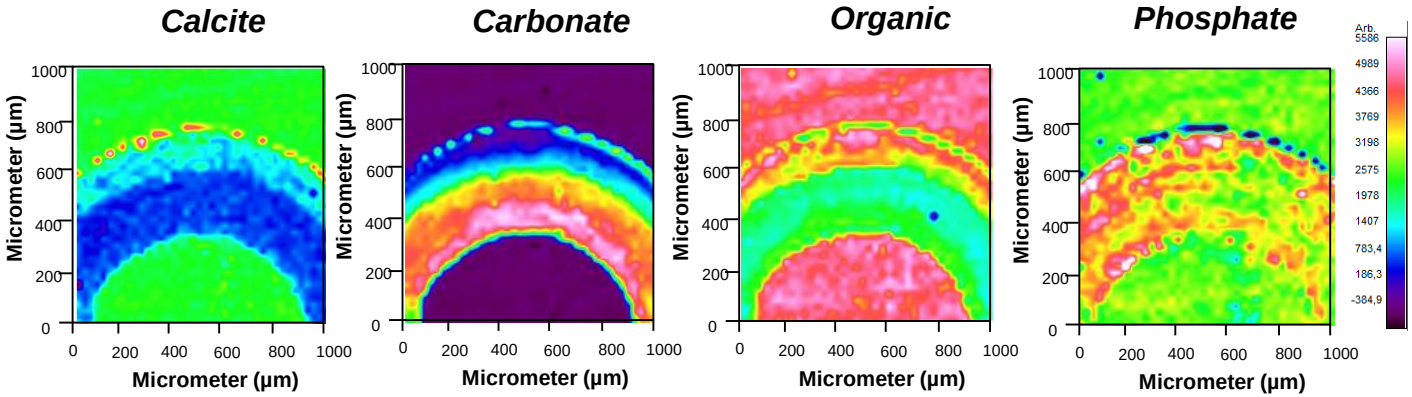
Antenna region with spine





Antenna region without spine

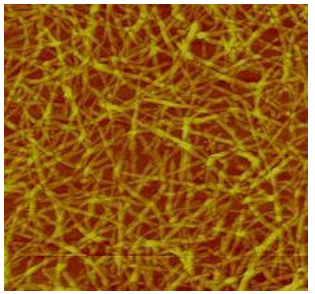




In the cuticle of Antenna regions, calcite was not observed in the Endocuticle but still a high percentage of carbonate was observed, wich is assumed it is constituting amorphous calcium carbonate (no crystalline mineral: Calcite). For Antenna region with spine, very low proportion of phosphate was observed, practically a very thin layer at the upper part of the Exocuticle and at the surrounding of the spine was observed. In antenna regions without spine, phosphate could be identified in the whole endocuticle region. The degree of mineralization is clearly different in the observed antenna regions.

2. Biomass processing and optimization

Driven by continuous efforts to develop more sustainable products and processes, the processing of cellulose in alternative solvents rather than in common organic chemicals recently came in the spotlight, in particular using ionic liquids (IL). The IL and (NA)DES provide favourable environments for creating both cellulose nanocrystals and fibrillated cellulose, but the swelling properties of the cellulose fibers should be narrowly controlled in combination with a strict understanding of the changes in cellulose structure. In parallel with the use of advanced analytical tools, the effects of ionic liquid types with different alkyl chain length and composition on cellulose crystallinity were quantified, indicating an increase in crystallinity with swelling time and higher crystallinity after fibrillation in contrast with processing in pure water that provides lower crystallinity.



Swelling Cellulose Pulp Fibers in IL

Experimental conditions

- Softwood cellulose pulp fibers
- Selection of IL (imidazolium chloride) with variable alkyl chain

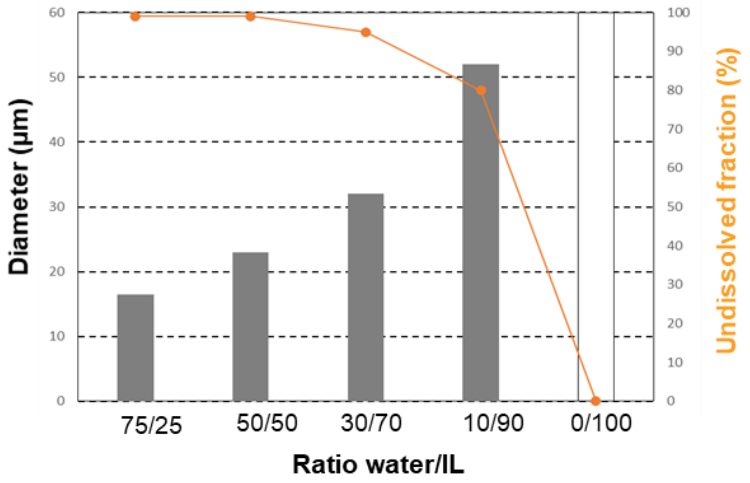
  [Bmim]Cl

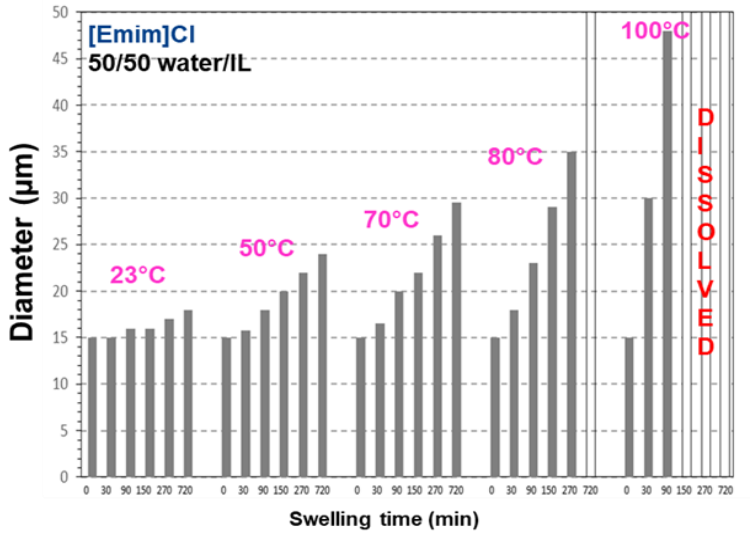
  [Emim]Cl

  [Amim]Cl

- Concentration IL:water = 50:50
- Temperature 23 to 100°C
- Time 30 min to 12 h

Selection of appropriate swelling conditions (practical kinetics)

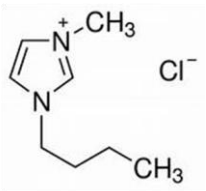


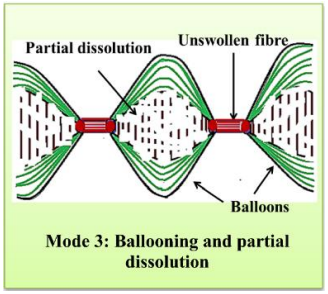


Swelling Cellulose Pulp Fibers in IL

Butyl

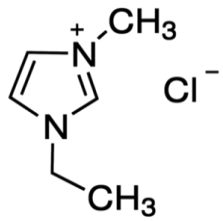
NANO WHISKERS

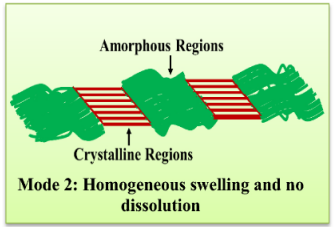




Ethyl

FIBRILLATED CELLULOSE

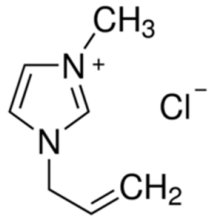




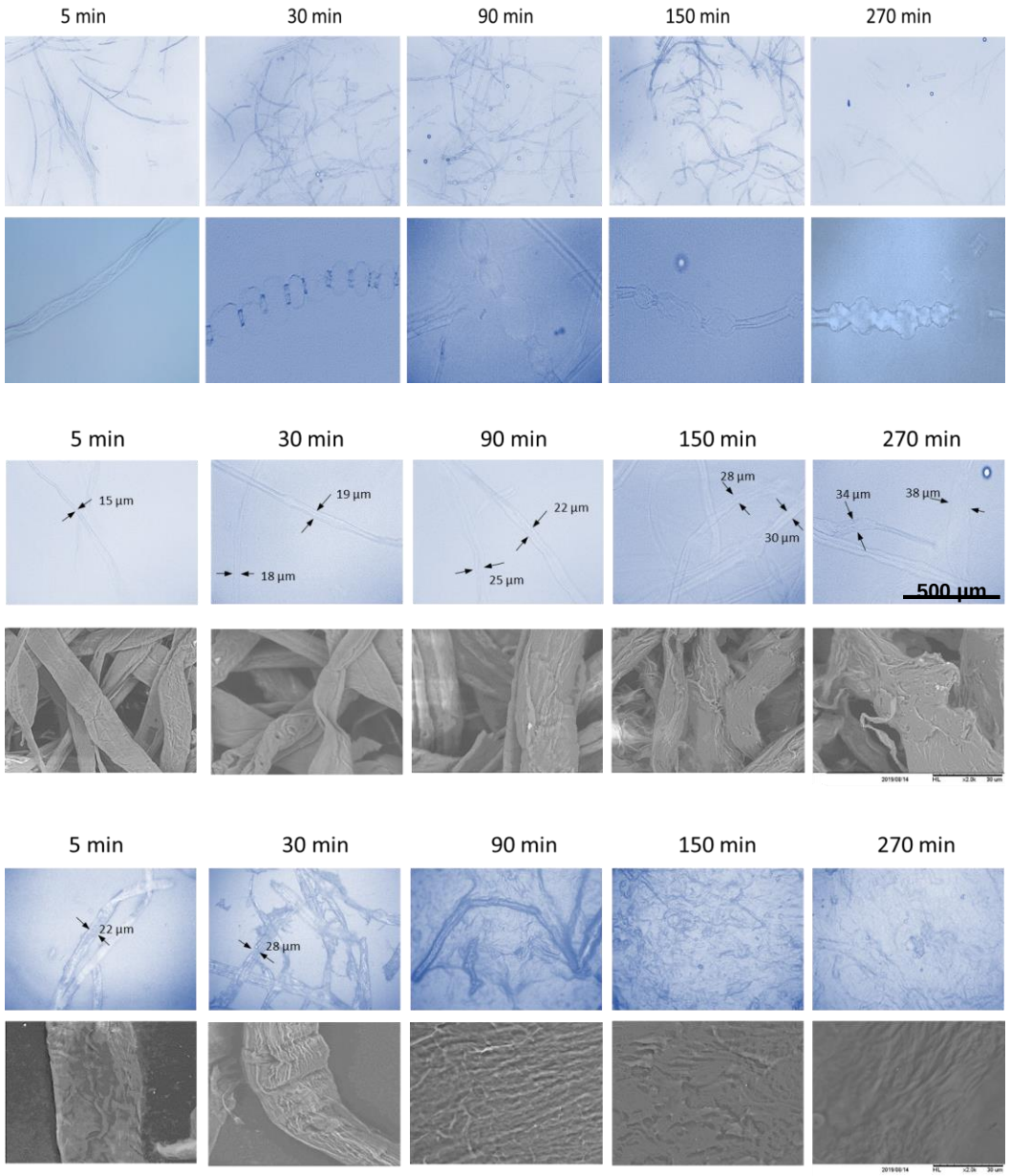
The [Emim]Cl causes **homogeneous fiber swelling** favourable for further fibrillation. The selection of temperature, time, concentration, leads to controlled swelling with **favourable kinetics to liberate elementary fibrils without dissolution**.

Allyl

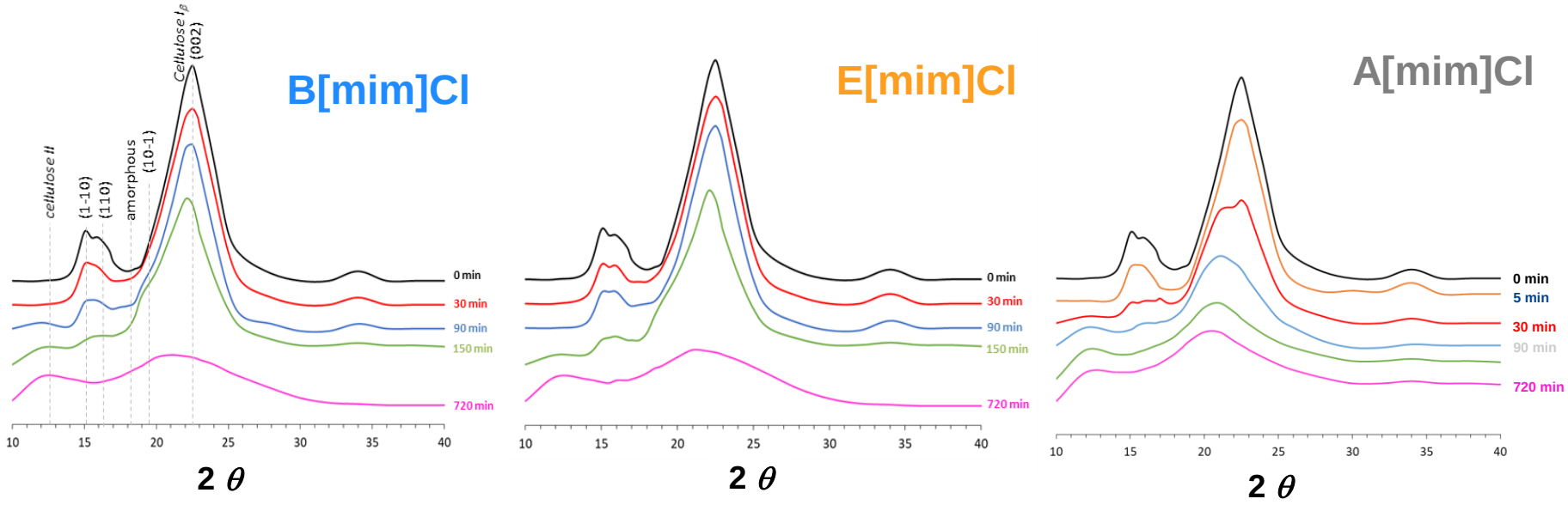
REGENERATED CELLULOSE



Dissolved

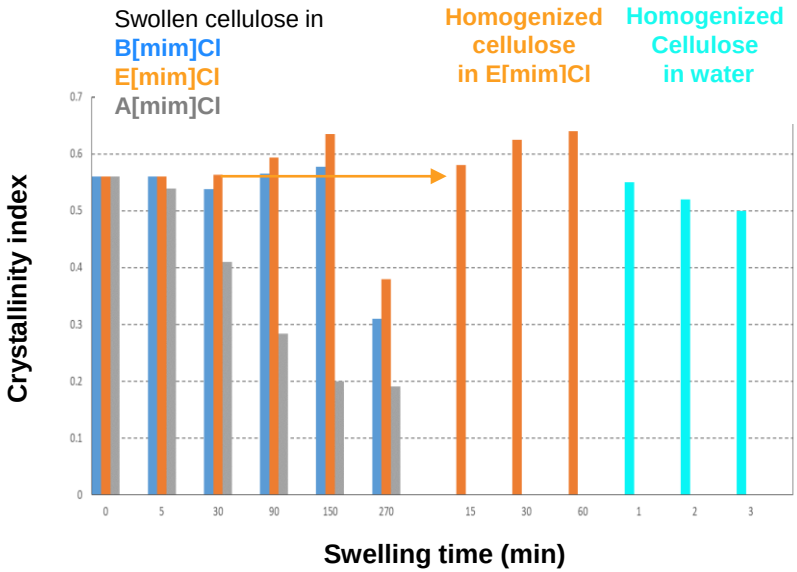


Crystallinity : Traditional XRD Analysis

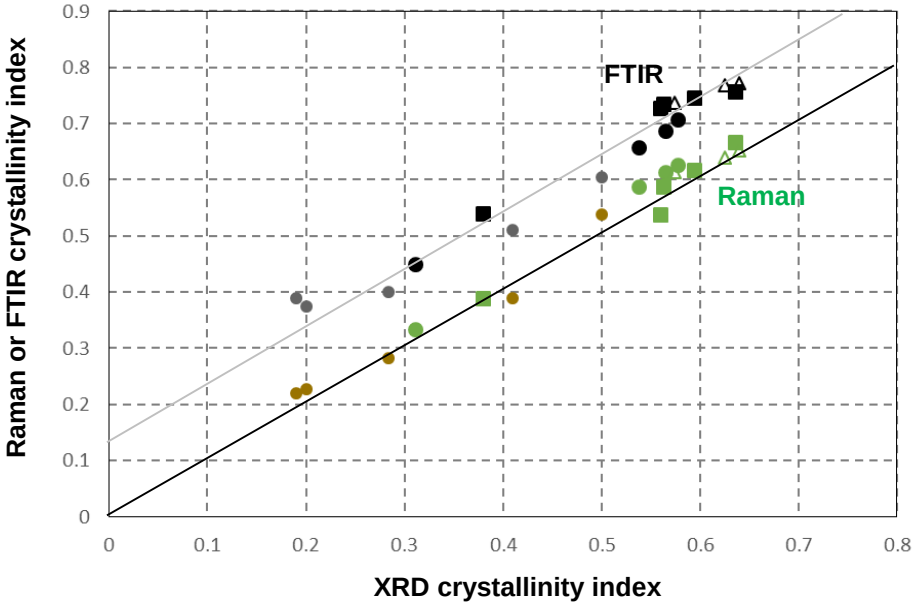


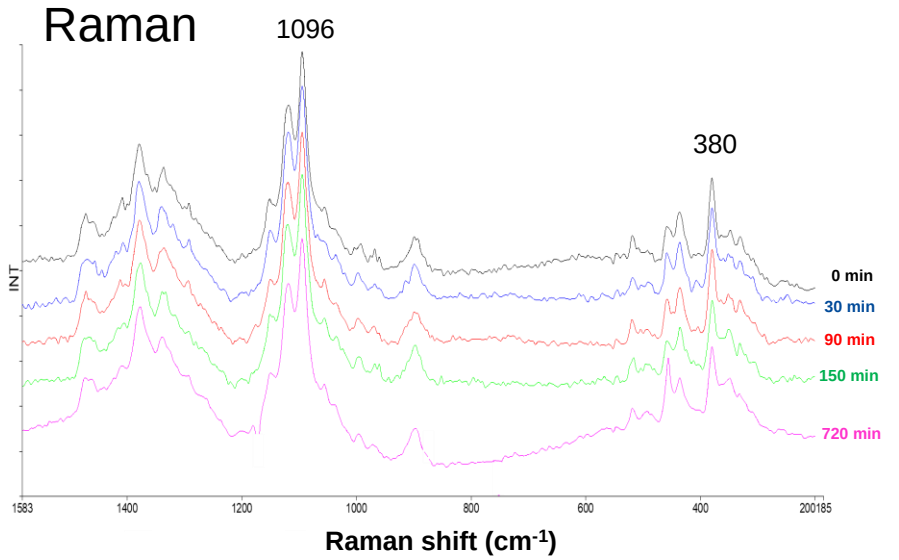
$$XRD = \text{ratio } (I_{200} - I_{AM}) / I_{200}$$

The **crystallinity after homogenization in E[mim]Cl is higher** and progressively increases with time in contrast to homogenization in pure water (reference), where higher forces likely fully disrupt the crystalline structure.



Relation XRD versus Raman/FTIR Crystallinity

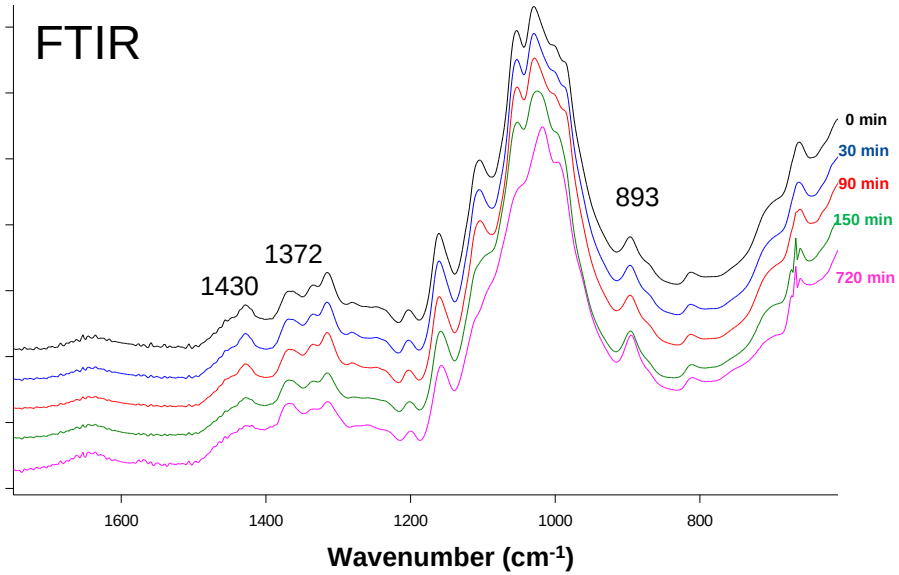




Raman = ratio I_{380} / I_{1096}

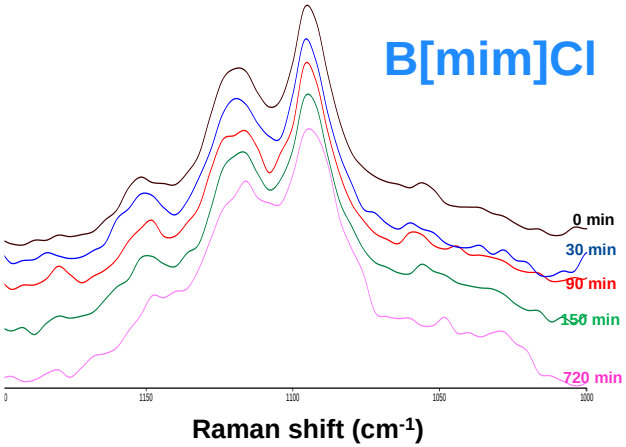
FTIR = ratio (A1 + A2) / 2 $\quad A1 = I_{1372} / I_{2900}$

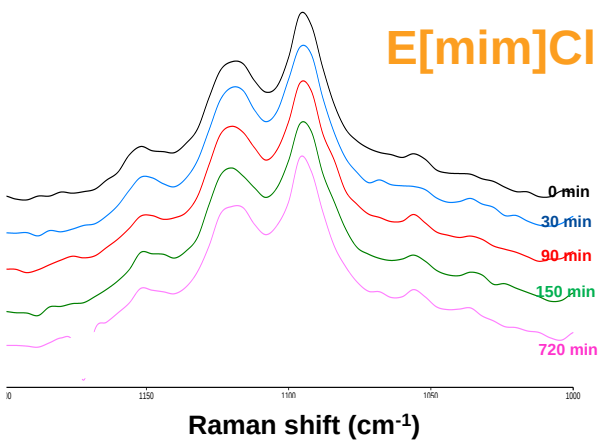
$A2 = I_{1430} / I_{893}$

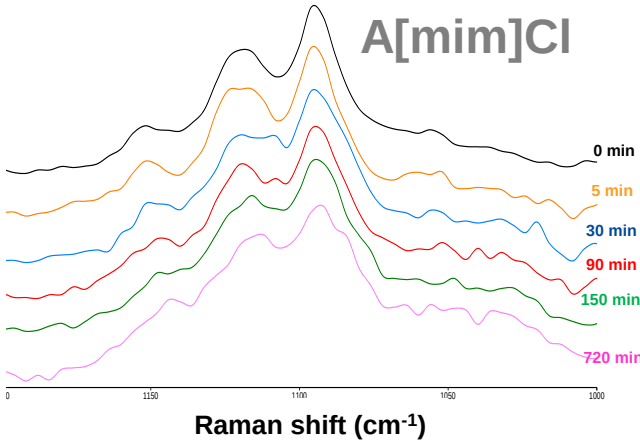


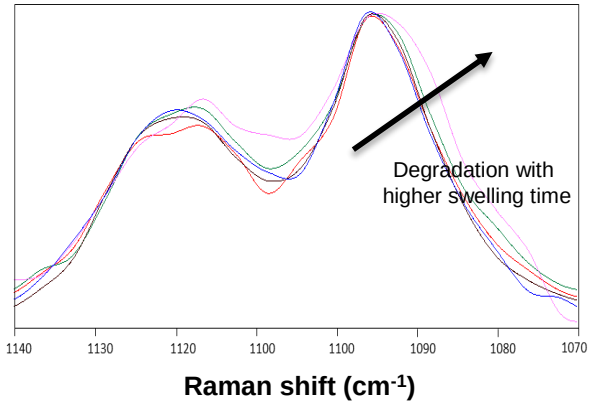
Crystallinity index from XRD is overestimated by FTIR spectroscopy due to influences of multiple oriented structures monitored by FTIR, while there is very good agreement with calculations from Raman spectroscopy.

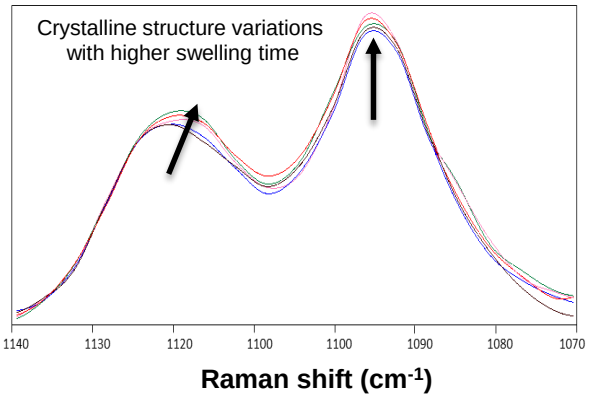
Detailed Raman 1095 cm^{-1} Region

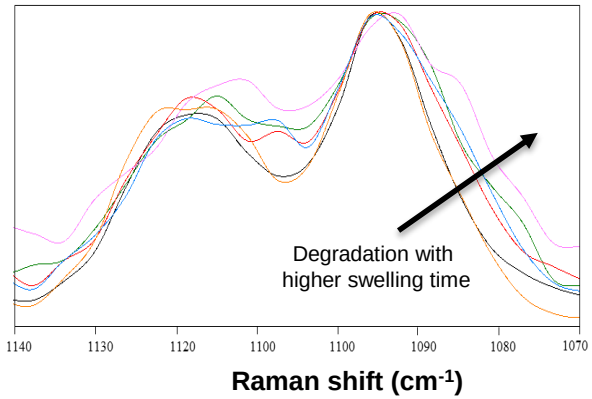








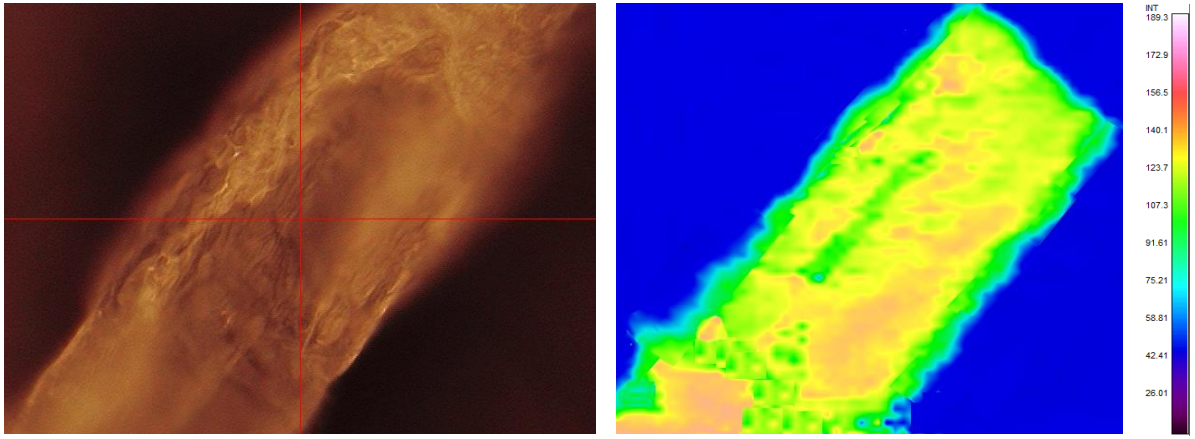




The variations in 1095 cm^{-1} band with time clearly indicate **internal stress distribution within the fiber** that is medium high during swelling and becomes extremely high during homogenization. The crystallinity during processing in E[mim]Cl remains superior and gradually increases with time, while there is destruction of the crystalline domains in B[mim]Cl.

Monitoring Swelling in Single Fibers

Reference cellulose fiber (non-treated)



Single wavenumber 1095 cm^{-1} mapping

Even distribution of stresses over the surface of native fibers with relatively surfaces. Sometimes the exposure of some more fibrils are seen as a slight increase in intensity over the fiber surface.

Following tests = on-line monitoring swelling of single fibers over time in

[Emim]Cl

[Bmim]Cl

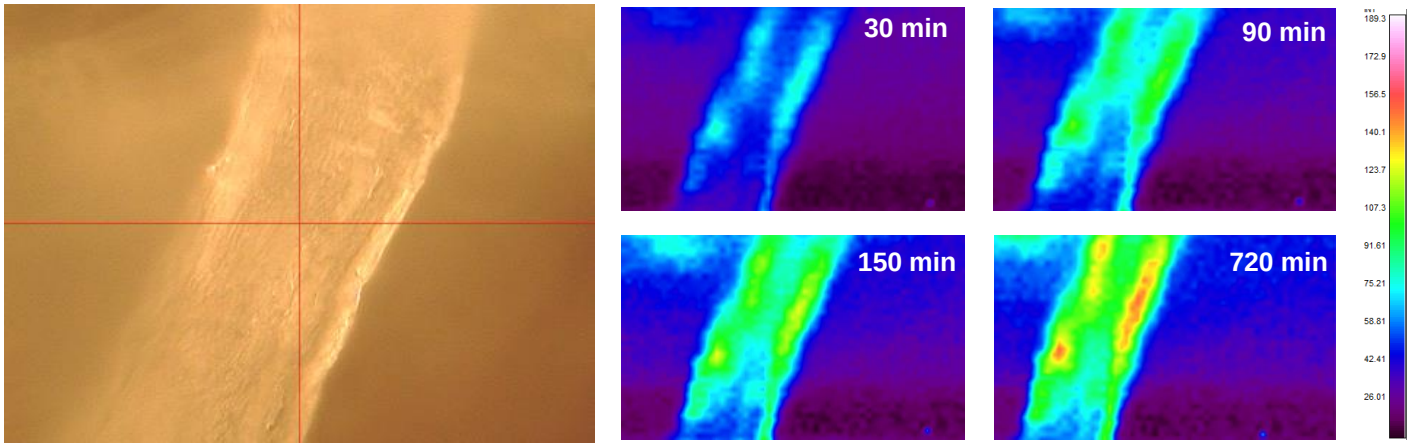
[Amim]Cl

Variations in "***mild***" conditions and "***heavy***" conditions artificially tuned by changing the concentration water:IL from 50:50 and 30:70,

in order to speed up the swelling process for monitoring.

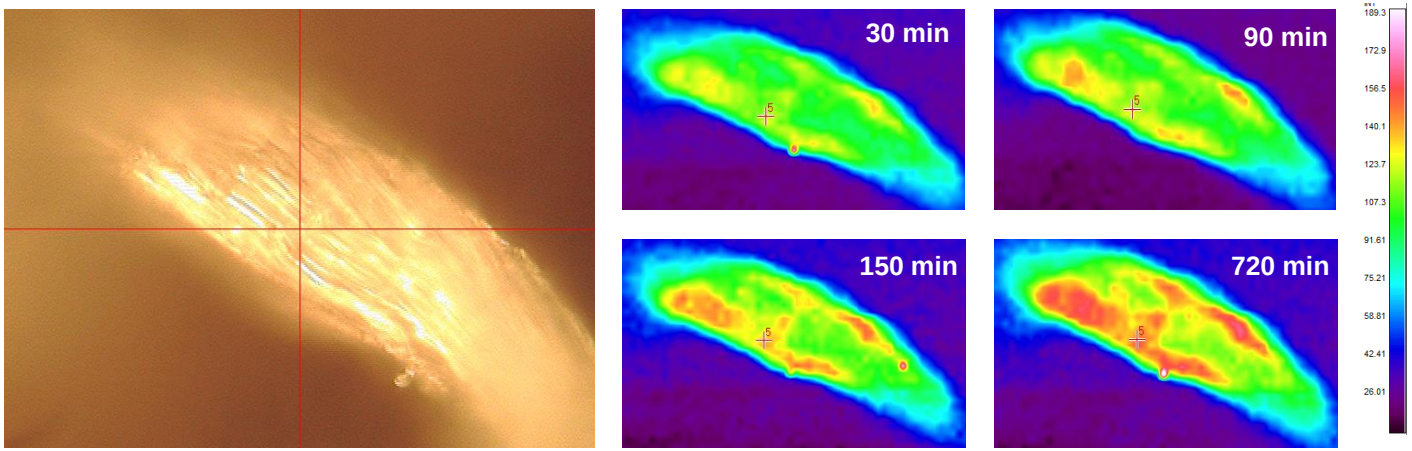
Monitoring Swelling in Single Fibers

Cellulose fiber swollen in [Emim]Cl : “mild conditions”



Very weak stresses mainly located near the fiber borders.

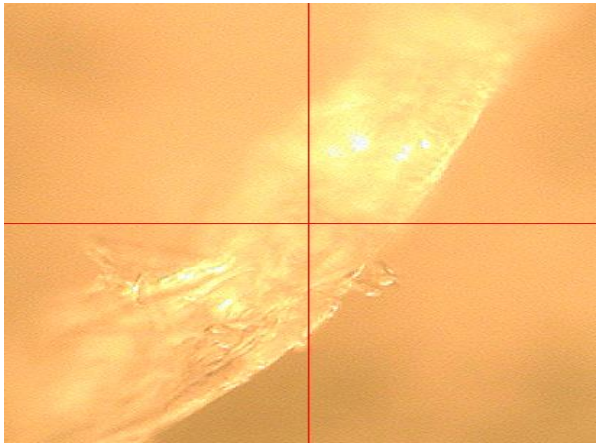
Cellulose fiber swollen in [Emim]Cl : “heavy conditions”

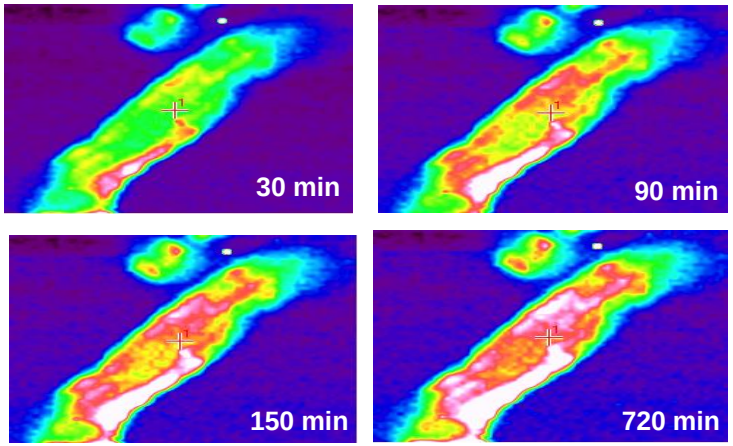


Progressive visualization of single microfibrils on the fiber surface. There is a gradual and mild, smooth increase in stresses progressing from the broders to the inside of the fiber with time (mainly near fiber borders), towards medium stresses at the end of swelling period.

Monitoring Swelling in Single Fibers

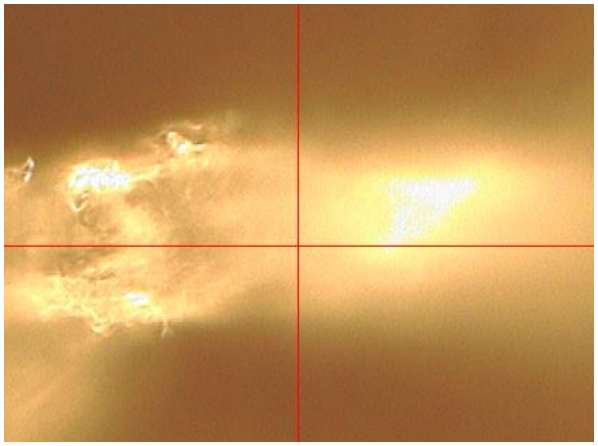
Cellulose fiber swollen in [Bmim]Cl: “mild conditions”

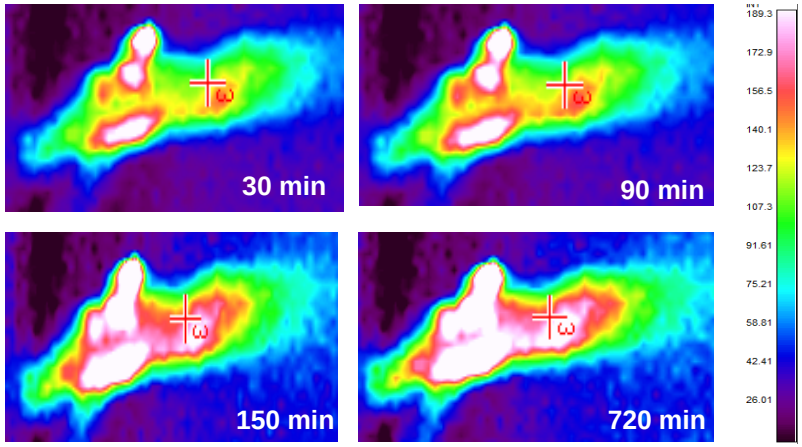




Much faster progression of the swelling stresses, leading to finally much higher stress concentrations in the centre of the fiber.

Cellulose fiber swollen in [Bmim]Cl: “heavy conditions”

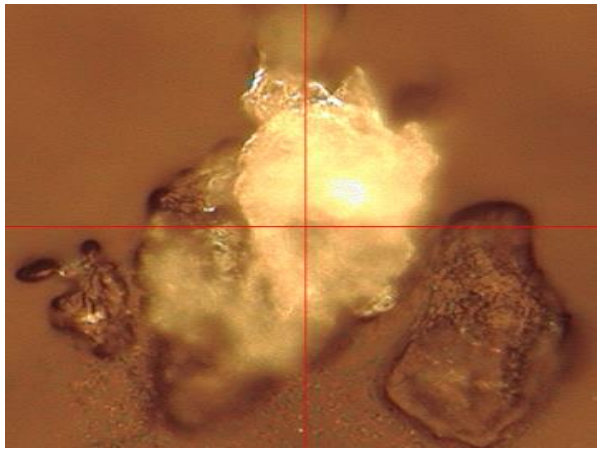


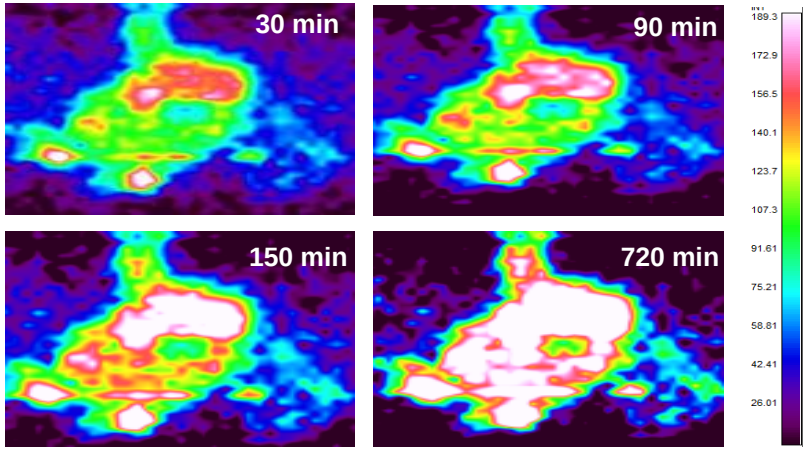


Local disruption of the fiber surface due to “ballooning” effact causes extremely high stresses in the fibers and transformation in crystalline structure

Monitoring Swelling in Single Fibers

Cellulose fiber swollen in [Amim]Cl : “mild conditions”

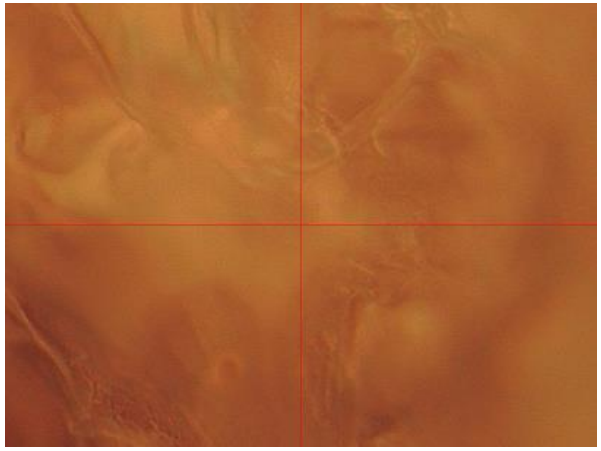


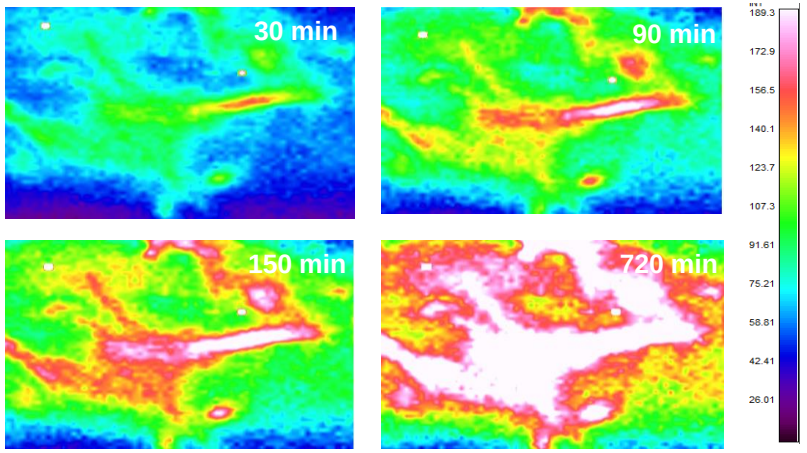


Fiber fragmentation and particle formation

Fast fragmentation of the cellulose fibers and complete disruption of the fiber structure with high local stresses in the centre of the fiber fragments.

Cellulose fiber swollen in [Amim]Cl : “heavy conditions”



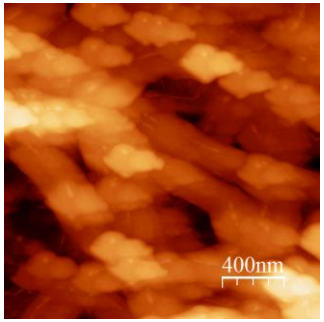


Full film formation

Progressive dissolution of fiber fragments leads to the formation of films with high structural variations and internal stresses.

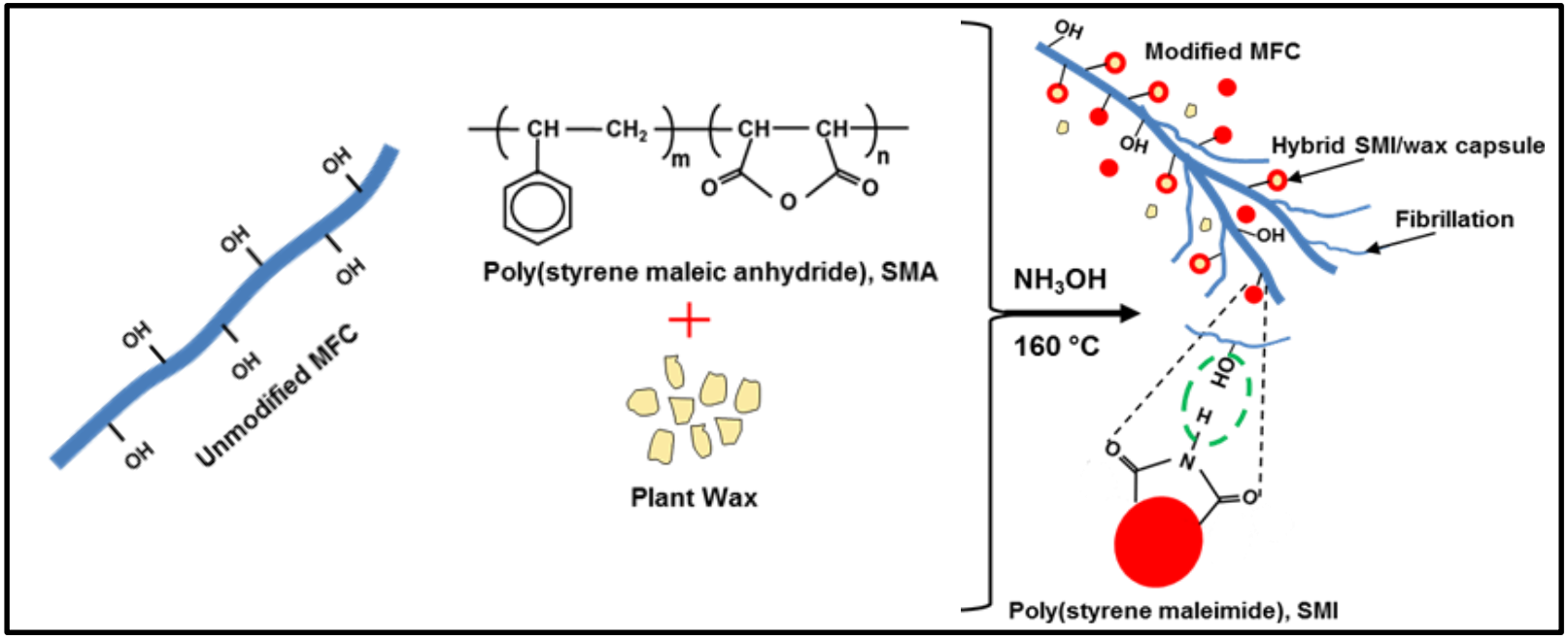
3. Biomaterial functionalization and applications

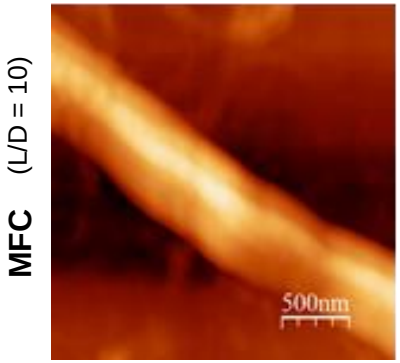
The hydrophobic properties of cellulose can be altered by surface modification, which has been done by the deposition of functional nanoparticles with encapsulated vegetable oils. The progressive thermal release of oil during heating allows to tune the hydrophobicity of the cellulose surface and cellulose films towards required value of contact angle, as a result of combined surface topography and chemistry. The mechanism can be used for creation of hydrophobic paper coatings or enhancing the incorporation of nanocellulose in polymer composites. Thanks to use of Raman spectroscopy, the variations in hydrophobic moieties at the fiber surface can be monitored in parallel with the changes in crystalline structure of the polymer matrix phase.

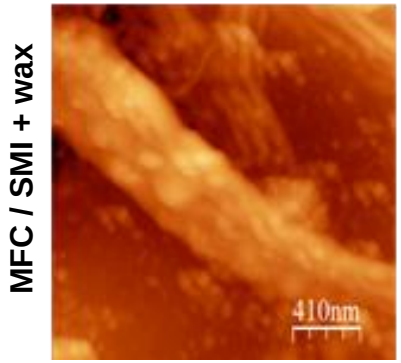


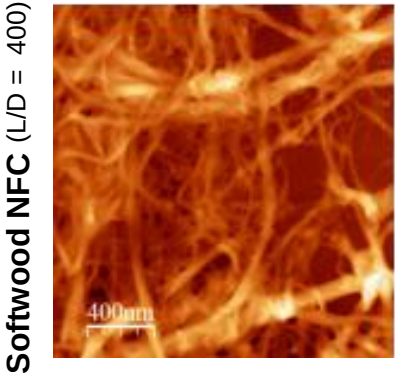
Microfibrillated Cellulose Surface Modification

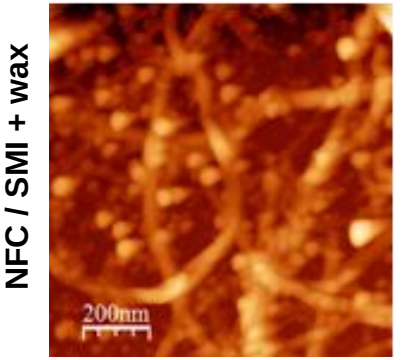
Hydrophobic surface modification of cellulose nanofibers by nanoparticle deposits, resulting in stable aqueous pulp suspension.







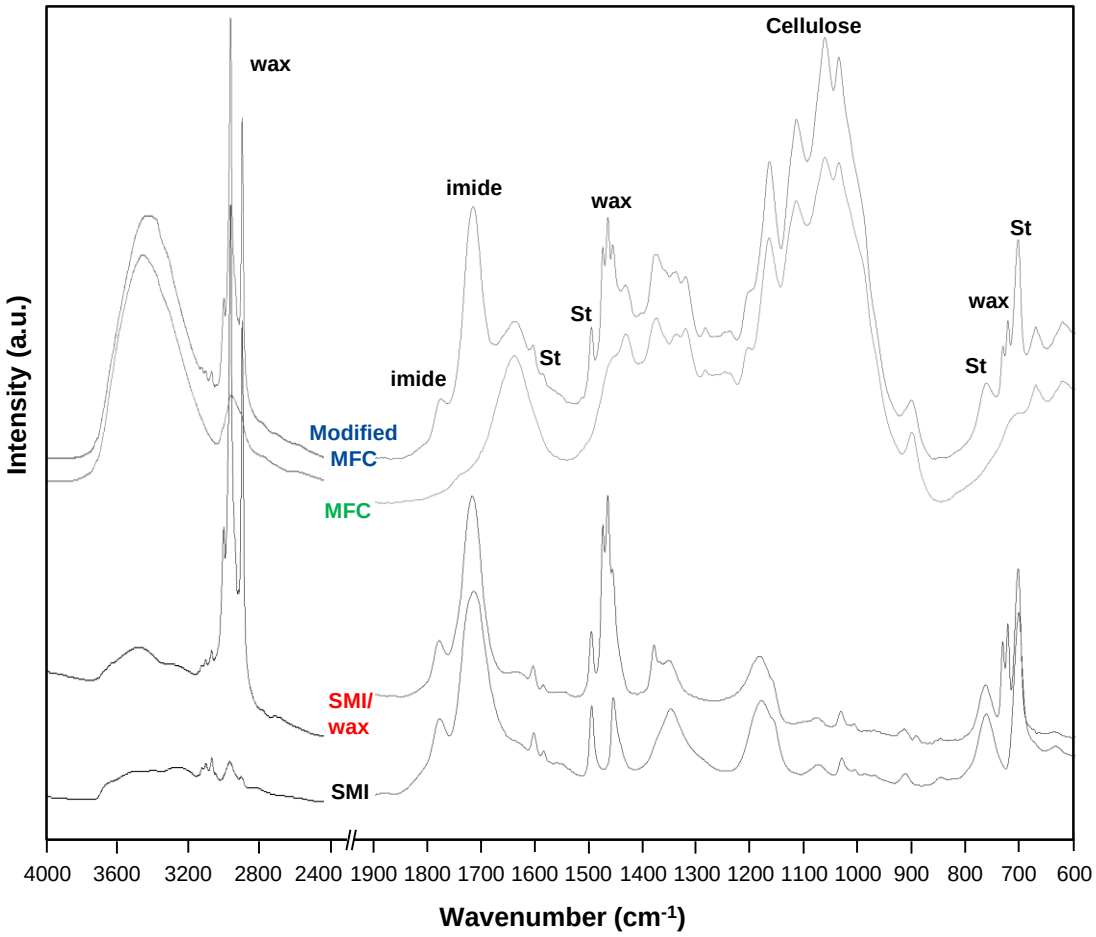




V.K. Rastogi, D. Stanssens, P. Samyn, Mater Lett 120 (2014), 196-199.

Chemistry of Modified Fibers, e.g. MFC

Raman spectroscopy of MFC, mMFC, SMI+wax

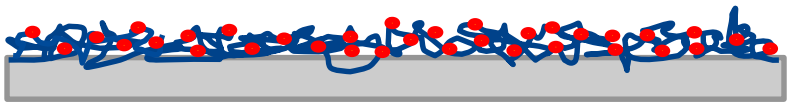


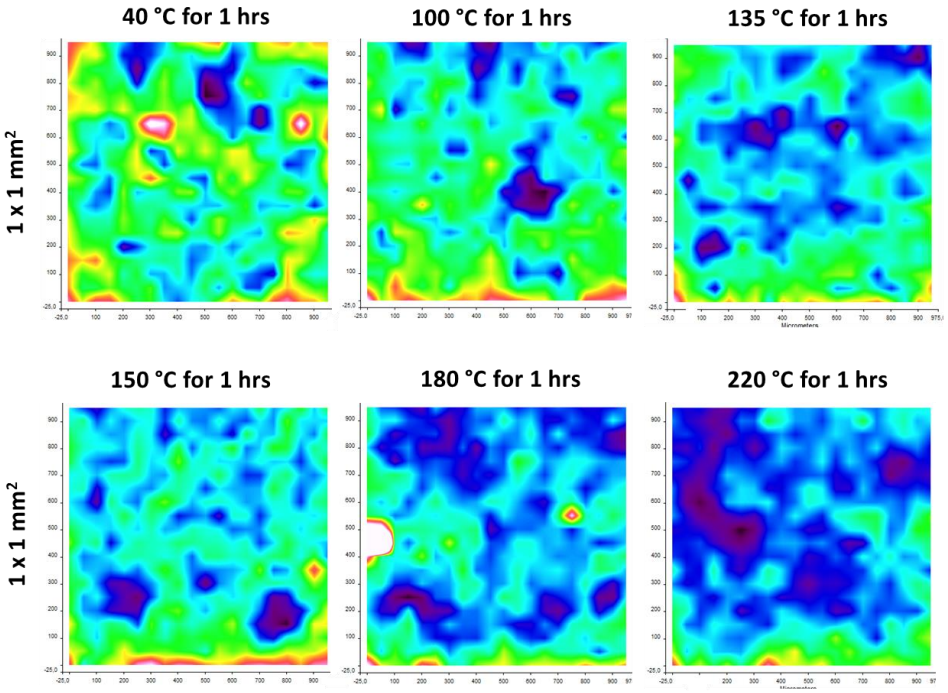
- No chemical degradation of the cellulose main chain (e.g. chain scission) after reaction with ammonia.
- Degree of **imidization** is quantatively lower for modified MFC and SMI/wax than for pure SMI.
- Formation of a small plateau near the 3421 cm^{-1} band (OH-stretching) in modified MFC, with Δ = 368 cm^{-1} (unmodified) or Δ = 406 cm^{-1} (modified): physical interactions among cellulose and SMI through the formation of **hydrogen bonding**.
- Flatting and broadening of 1430, 1372 and 1336 cm^{-1} bands in modified MFC, indicating some variations in the well-ordered cellulose web through hydro-gen bonding.

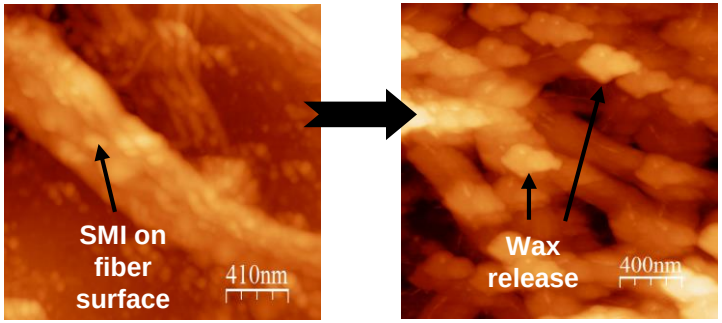
Raman allows for perfect quantification of the degree of imidization

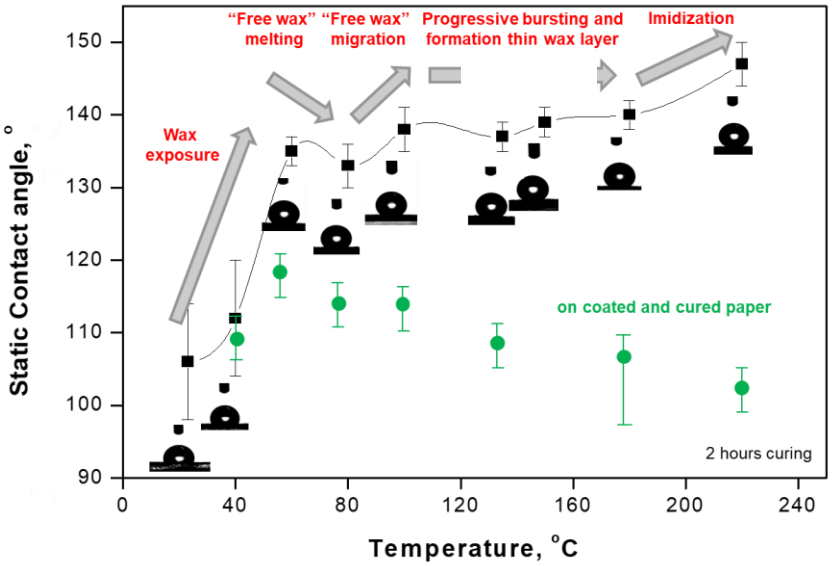
Monitoring Thermal Release of Wax from Nanoparticles

Thermal release above the glass transition temperature allows for deposition of a very thin wax layer on fiber surfaces providing highest CA.







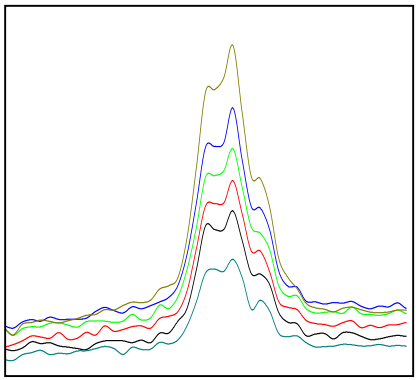


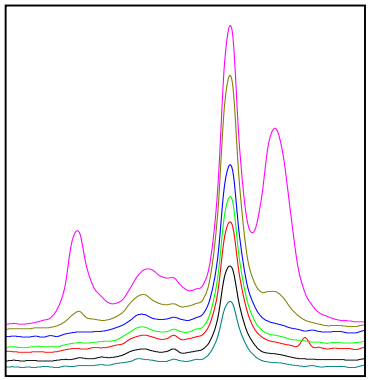
V.K. Rastogi, D. Stanssens, P. Samyn, Materials 7 (2014), 7196-7216.

Monitoring Nanocellulose in Polymer Composites

Introduction of MFC additives induces differences in PLA crystalline structures

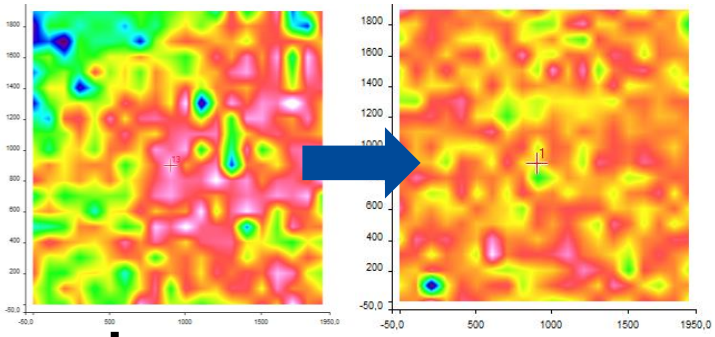
C=O (1720 to 1810 cm^{-1}) is sensitive to conformation and degree of crystallinity





PLA

PLA/MFC



Lateral mapping of crystalline band shows better homogeneity in presence of MFC due to nucleating effect

Alteration of traditional helix crystalline structure

C=O

Deformation C=O

Increasing content MFC

cellulose

Intensity (a.u.)

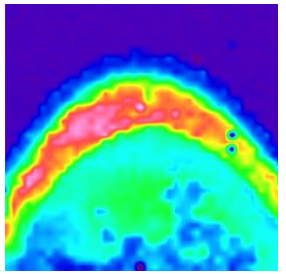
1895,9 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200,0

Raman shift (cm^{-1})

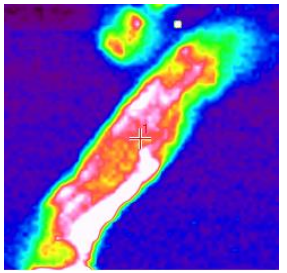
Conclusion

The strength of Raman spectroscopy in several fields of bio-based materials engineering has been proven to provide consistent information and additional insight in materials and processes:

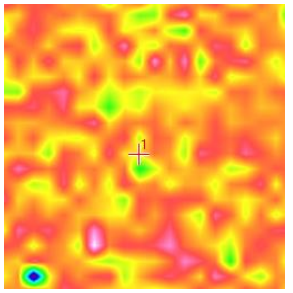
- The organization of chitin/protein organic matrix in crustaceans and degree of mineralization depends on the location : the organic phase is intermixed with amorphous calcium phosphate, while crystalline calcite might be present in outer shell and/or internal structure.



- The severity of fiber swelling in IL depends on the alkyl chain length and progressive ingress of the swelling can be monitored as internal stresses and/or variations in crystalline structure.



- Surface modification by nanoparticle deposits show hydrogen bonding interactions with the cellulose, with tunable thermal release of encapsulated ingredients (oil) from the surface. The variations and spatial homogeneity in composite crystallinity can be monitored.



By comparing with other techniques, the Raman spectroscopy mostly allows to extract direct quantitative information through baseline correction, normalization and band intensity ratio.