Processing of (nano)cellulose in alternative solvents: opportunities and challenges

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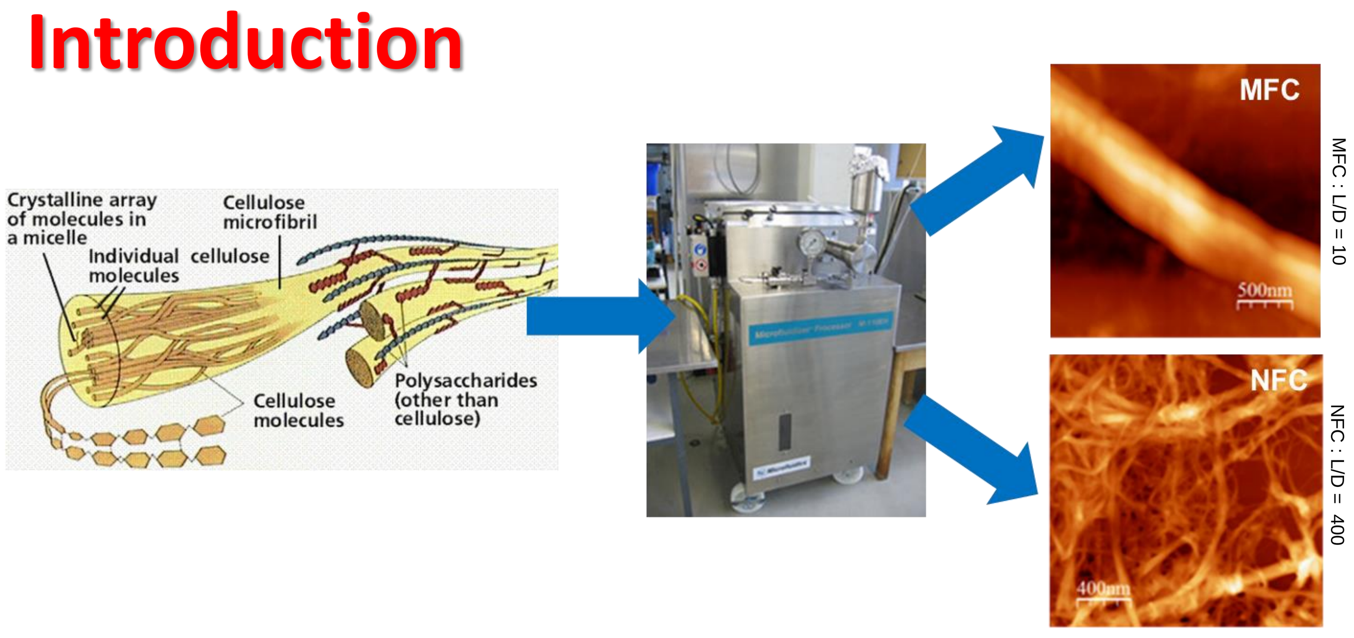
Introduction

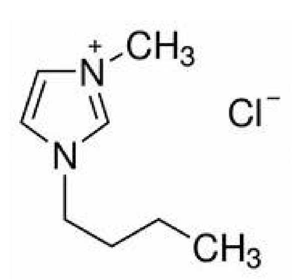


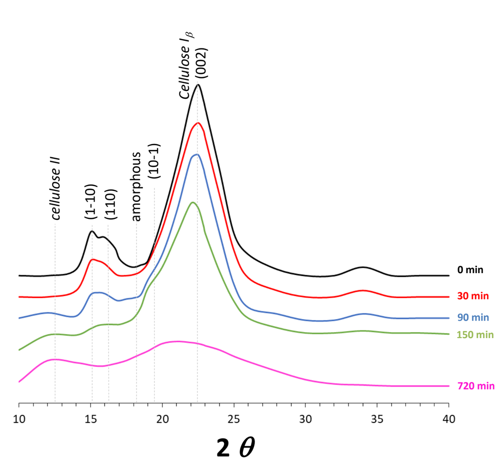
Driven by continuous efforts to develop sustainable products and processes, the processing of cellulose in alternative solvents rather than in common organic chemicals becomes urgent, in particular using **ionic liquids** (IL) and **natural deep-eutectic solvents** (NADES). The solvents are readily available at moderate cost, have low toxicity and allow for mild processing conditions with intrinsic recycling potential. Whereas alternative solvents are frequently applied for extraction of specific components from biomass or for complete dissolution of cellulose and regeneration, they may be interestingly used as a **medium to create functional nanocellulose**. Therefore, **swelling properties of cellulose fibers should be narrowly controlled in combination with understanding of the changes in cellulose structure**. In this study, the effects of ILs with different alkyl chain length 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**. The functionalization of cellulose surfaces with specific hydrophobic properties can be achieved by selecting appropriate solvents. Novel trends include in-situ fibrillation of pre-treated lignocellulose fibers and embedment in polymer nanocomposites during continuous extrusion. Besides the abundance in presented opportunities, the strict control of processing parameters and rheological properties remain of utmost importance.

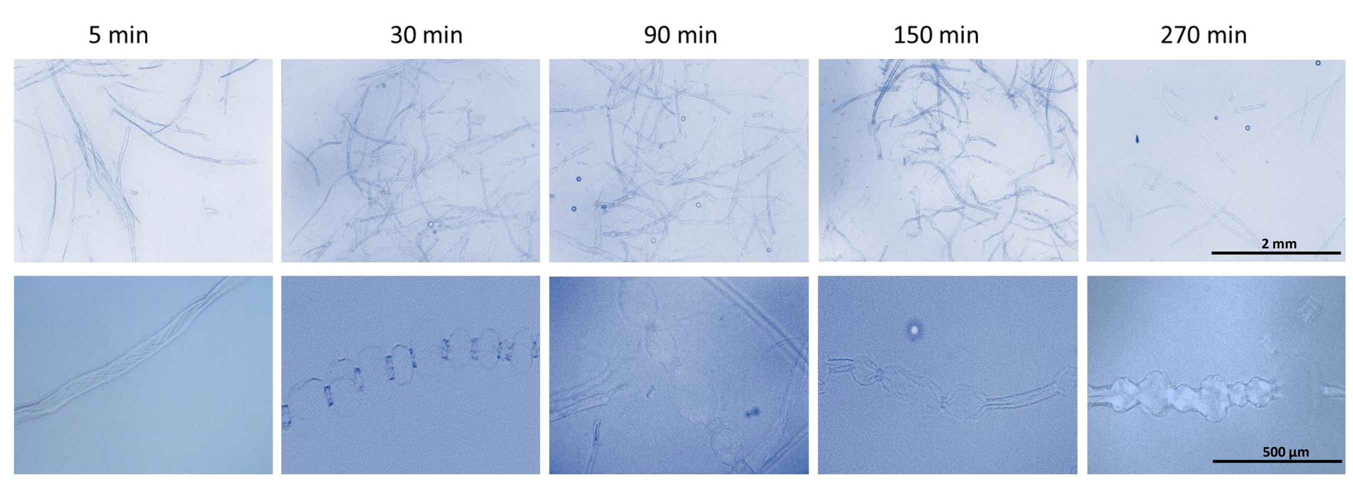
Ionic liquids

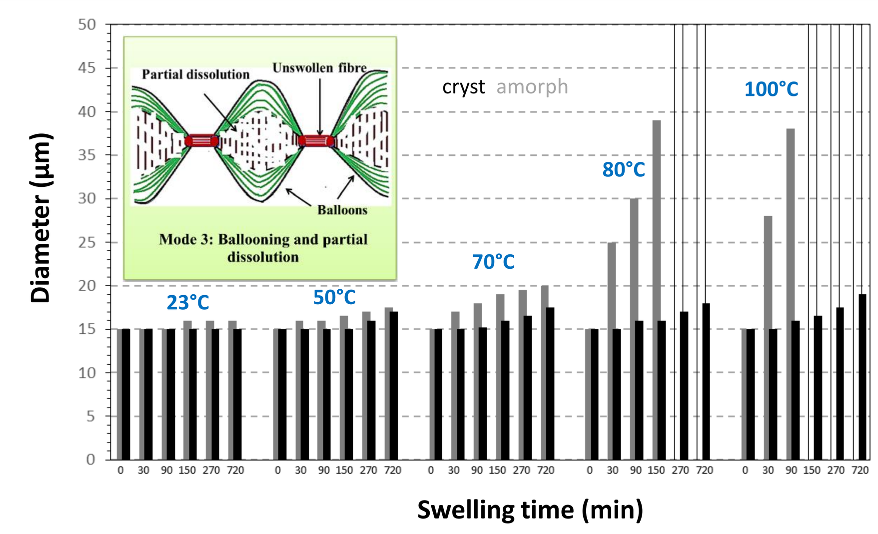
NANO WHISKERS

Butyl



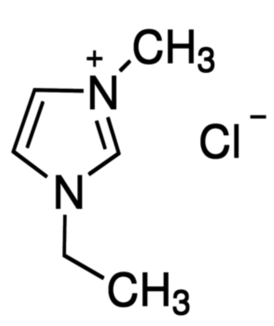


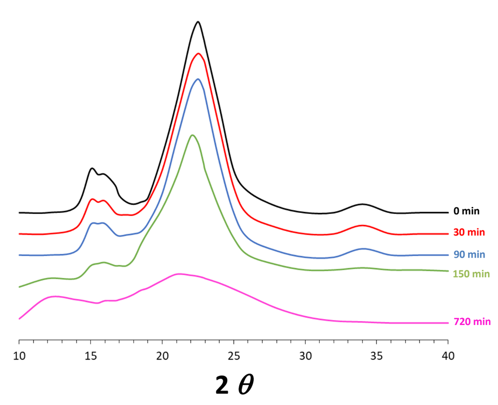




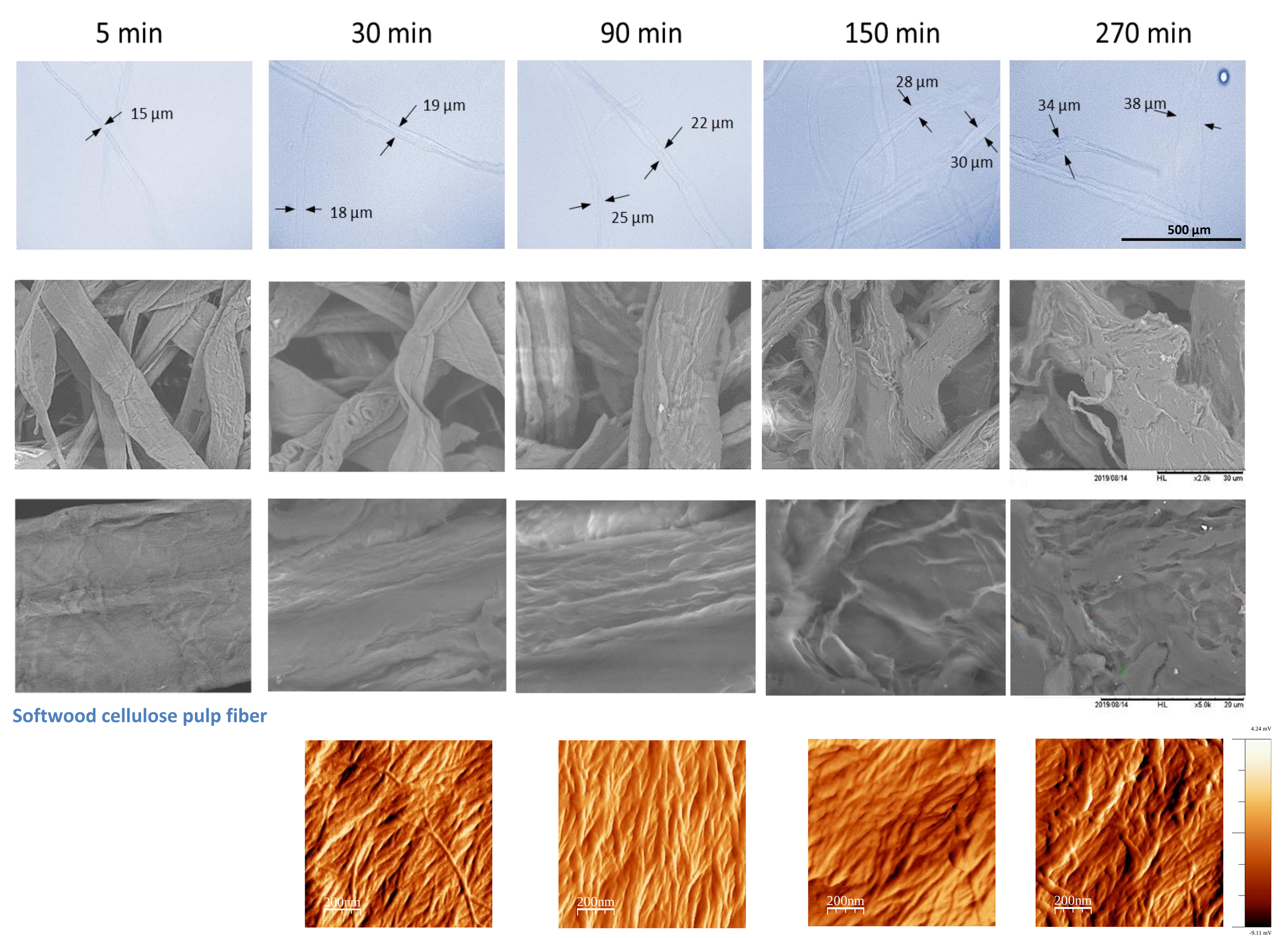
FIBRILLATED CELLULOSE

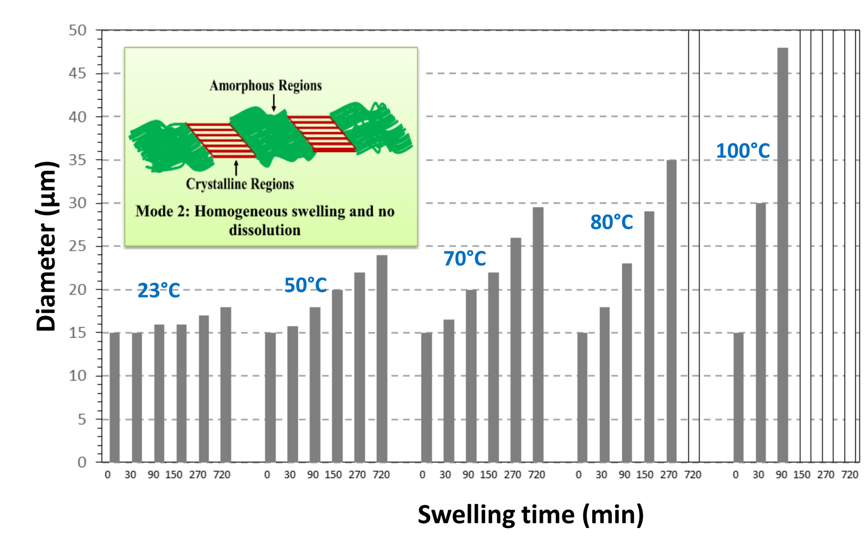
Ethyl

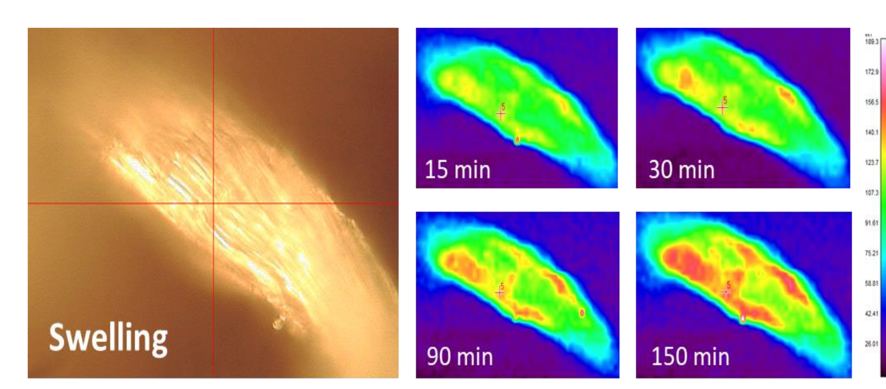




The [Emim]Cl causes **homogeneous fiber swelling** that is favourable for further fibrillation. The selection of optimum parameters (temperature, time, substrate concentration, water, stirring) leads to controlled swelling with **favourable kinetics to liberate individual elementary fibrils without complete dissolution**. There is no significant effect on fiber length while fibrils were unfolding. Local **structural variations** and **internal stress concentrations** are monitored by micro-Raman chemical mapping on single fibers.

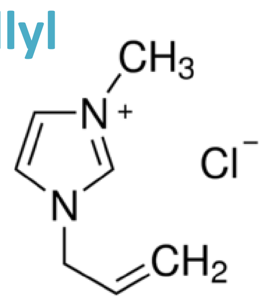


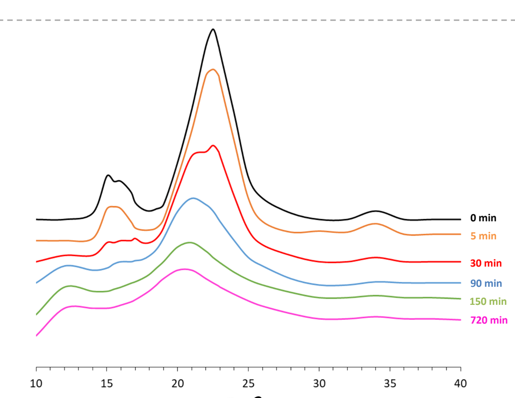


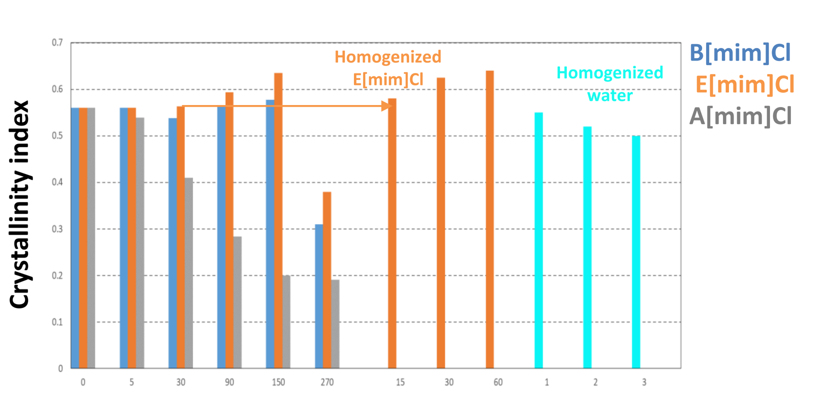


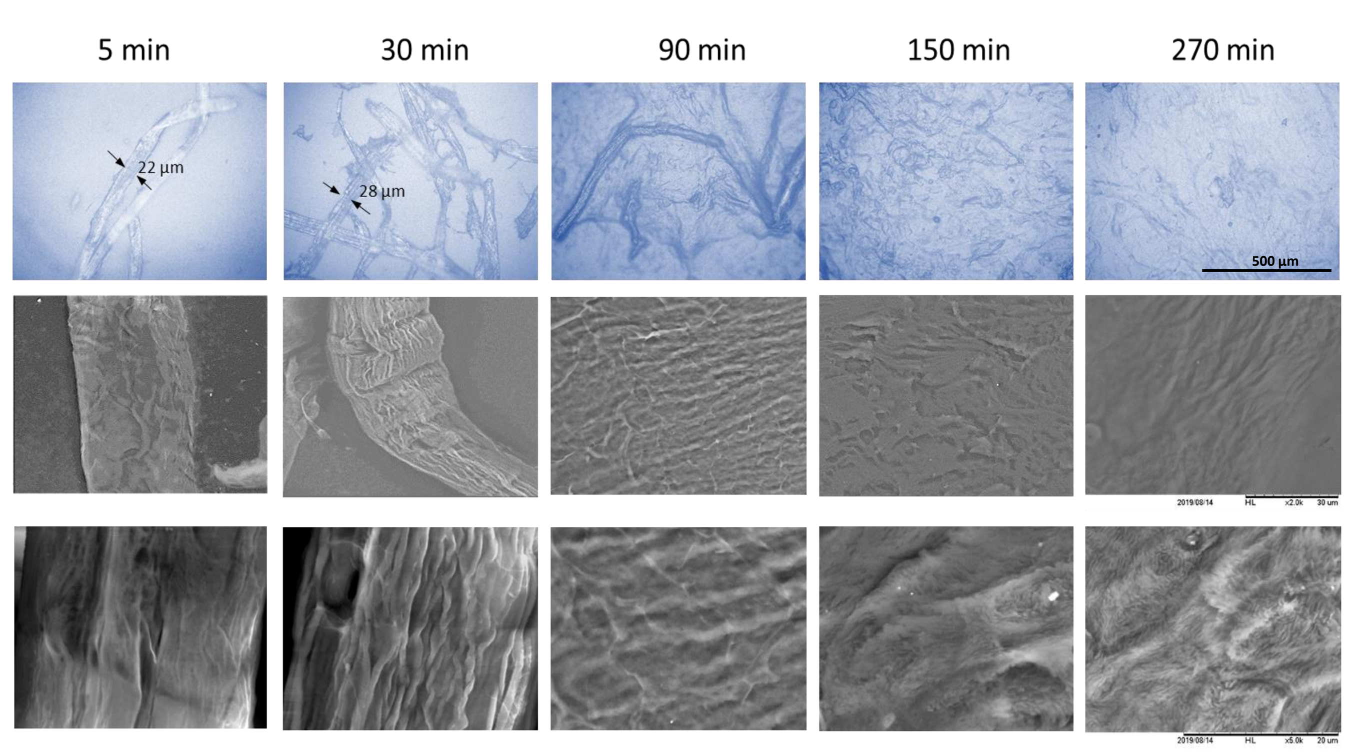
REGENERATED CELLULOSE

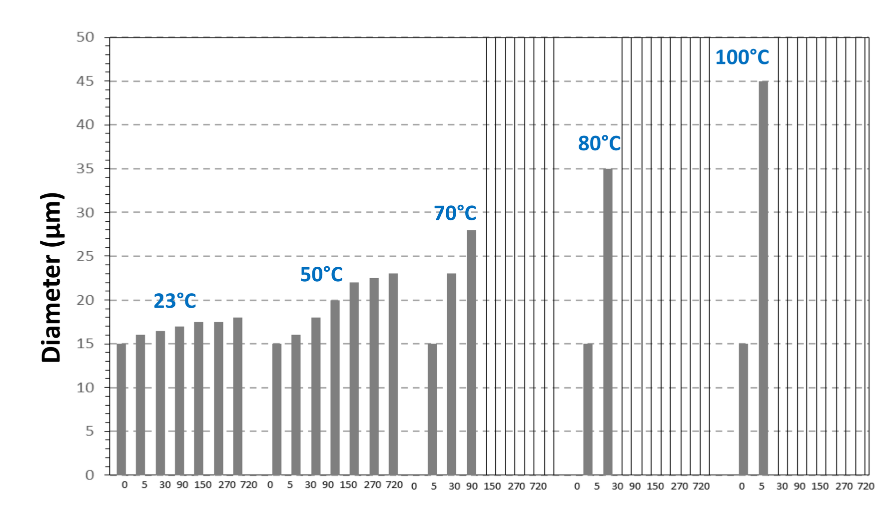
Allyl





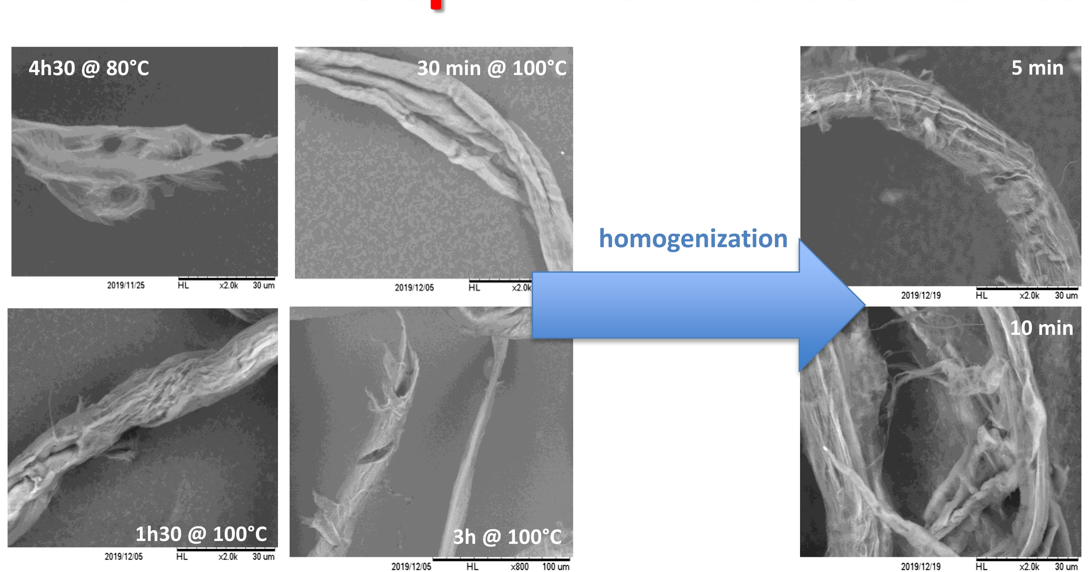






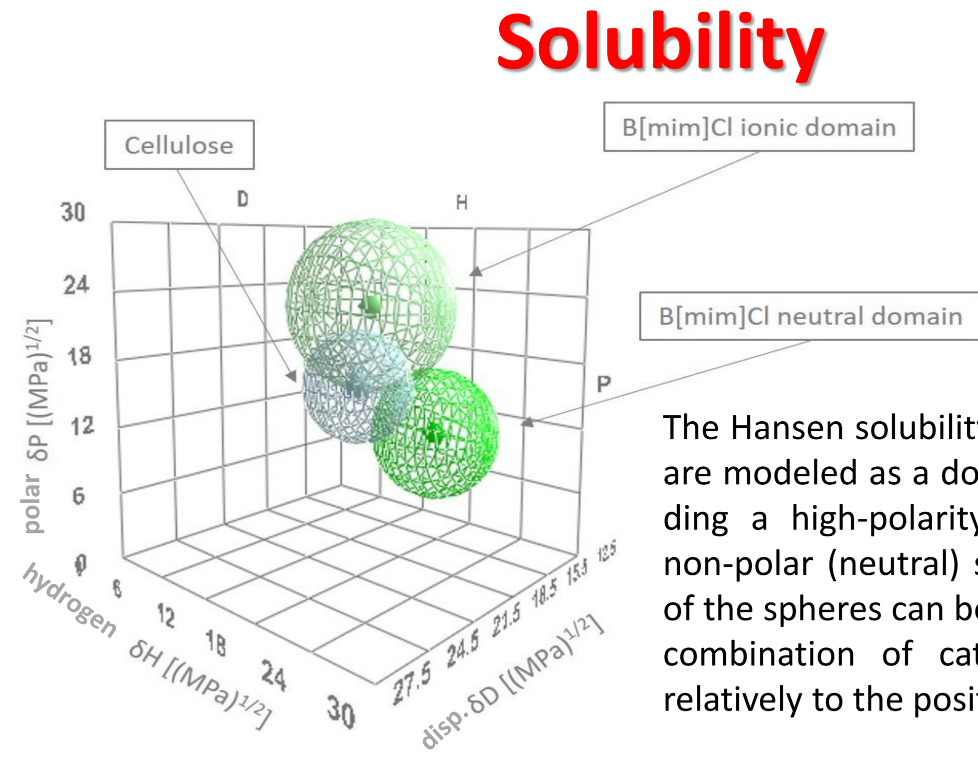
A cellulose film is obtained after **full dissolution** and regeneration from the IL in water. The addition of electric withdrawing groups (e.g., allyl) to the side chain of the imidazolium cation increases the overall interaction energy between the solvent and cellulose, hence the solubility.

Natural Deep Eutectic Solvents



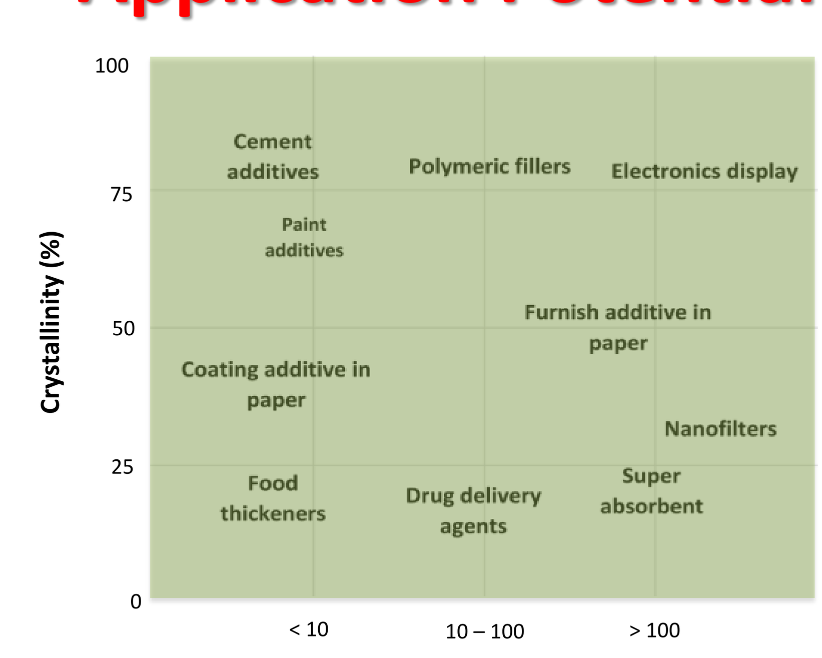
Favourable swelling and **easy fibrillation** in choline chloride / urea (100°C)

Solubility



The Hansen solubility parameters for IL are modeled as a double-sphere, including a high-polarity (ionic) side and non-polar (neutral) side. The positions of the spheres can be influenced by the combination of cations and anions, relatively to the position of cellulose.

Application Potential



Conclusion

Opportunities

- Good control over swelling properties depending on solvent type and parameters
- Towards one-pot processing route for functionalization
- Easy fibrillation of pretreated cellulose fibers
- Reduction in processing times
- High solid contents

Challenges

- Solvent recyclability route
- Definition of an “ideal designer solvent”
- Instrinsic viscosity of the system & rheology control
- Generalized prediction model for dissolution versus swelling
- Extensive analytical approach needed for understanding interactions

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