Eco-friendly and innovative catalytic surface modifications of cellulosic materials and nanocellulose

This project describes a metal-free method for versatile surface engineering of the cellulosic nanomaterials via organocatalysis and click chemistry. This study not only addresses challengs for the future utilization of nanocellulose but also enables new applications for nanocellulosic materials in different areas.

Background and motivation

Cellulose is the most abundant and most versatile biopolymer on the earth. [1] This renewable, nontoxic, and hydrophilic polysaccharide has excellent material properties, which have made it very useful to society. There is significant research activity on future applications of this cellulose-derived nanomaterial by scientists in both industry and academia.

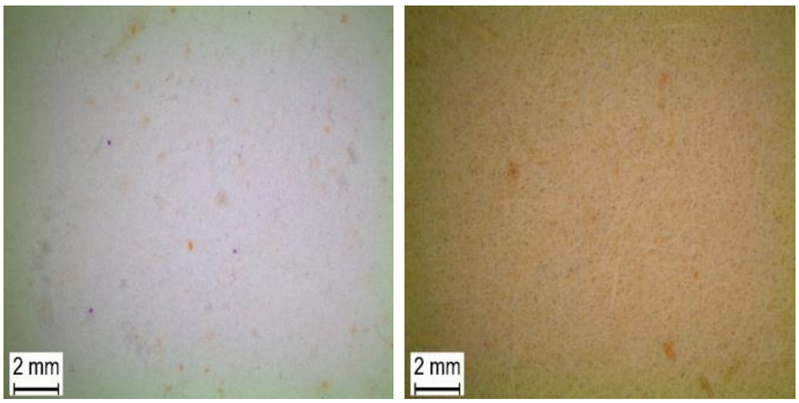
In 2005, Hafrén and Córdova reported the direct functionalization and hydrophobization of heterogeneous lignocelluloses using organocatalysis. [2] My research focuses on the direct catalytic functionalization of nanocellulose under eco-friendly conditions. We have started the sialylation of the NFC foam, then we performed click reactions on the thiol and olefin-functionalized NFC under UV light allowed further surface engineering.[3] Silylation of nanocellulose help us to have hydrophobic material which facilitates new applications of nanocellulose in different areas.

Quinidine and quinine exhibit important biological activities and they are also used as fluorescent markers, organocatalysts, and organic chiral ligands. These pharmaceutical compounds were attached to the NFC surface using click reaction via this method.

a b c

Figure 1. Modification of nanocellulose a: Hydrophobic NCC film after modification b: Comparing hydrophobicity of modified and unmodified NFC (left : unmodified, the others are modified) c: UV active NFC with quinidine and quinine(left : NFC, middle : Quinidine- TPSi-NFC, right: Quinine- TPSi-NFC)

We have started to improve the strength property of chemimechanical pulp (CTMP) and bleeched sulphite pulp (BSP) using cationic starch (CS) and carboxymethyl cellulose (CMC). Several experiments were performed in presence and absence of organocatalyst. The results revealed high strength property (up to 100% of Z-strenght in CTMP pulp) in presence of organocatalyst. In order to elucidate how the specific strength additives are distributed on the sheets, we decided to put on fluorescent molecules on the CS and CMC in a similar fashion as we and others have done on nanocrystalline cellulose. [4] Thus, tartaric acid-catalyzed silylation of aminopropyl silane (AMPSi) was performed on the CS and CMC and followed with attachment of 5-(and-6)-carboxy fluorescein succinimidyl ester (FAM-SE) on CS and 5-(and-6)-carboxy tetramethylrhodamin succinimidyl ester (TAMRA-SE) on CMC. These marked additives were used to form paper sheet to explain the distribution of additives on the sheets. Further fluorescence microscopy studies as well investigation of other strength additives, lignocelluloses and nanocelluloses are ongoing in our laboratories.



a b

Figure 2. Marked paper sheet a: BSP-(FAM-CS-TAMRA-CMC-CA) sheet b: CTMP-(FAM-CS-TAMRA-CMC-CA) sheet.
CA: Organocatalyst

Refrences

[1] A. Payen, *C. R. Hebd. Seances Acad. Sci.* **1838**, *7*, 1052.
[2] J. Hafren, A. Córdova, *Macromol. Rapid Commun.* **2005**, *26*, 82.
[3] S. Afewerki, R. Alimohammadzadeh, S. H. Osong, C.-W. Tai, P. Engstrand, A. Córdova, *GlobalChallenges* **2017**, *1*, 1700045
[3] L. J. Nielsen, S. Eyley, W. Thielemans, J. W. Aylott, *Chem. Commun*. **2010**, *46*, 8929