Final report to the project
“Biobased aerogels and foams with an ultrahigh charge density”
ÅForsk nr 23-349

Summary

The ability to tailor the charge on cellulose-rich fibers is central in converting this highly relevant bioresource to more high-end applications. However, the more we charge the fibers, the harder it becomes to retain the nanostructural integrity, leading to dissolution at high degrees of substitution. This work addresses this challenge by developing a new synthetic concept for creating cellulose-rich fibers with high and tailorable charged content (1.4 – 6.7 mmol/g). The concept is based on radical transfer grafting to-and-from polymerization of acrylic acid from thiolated fibers in water. Emphasis is on analyzing every step of the reaction in detail, as well as on how the surrounding system influences radical transfer. Overall, this work provides a highly versatile and direct method that merges free radical polymerization with biopolymer science. We also demonstrate how the highly charged fibers can be applied for water remediation. Unprecedented high absorption values for biobased fibers, comparable and even better than the state-of-the-art MOF (Metal Organic Framework) materials, were found. Beyond the direct sustainability benefits, we believe that the outlined synthetic strategy will become standard practice in creating new biobased materials with tailored functions

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Synthesis of Thiolated Fibers

In this project we used a previously developed modification technique for never dried high cellulose content wood fibers using Maleic anhydride (MA) in Acetic acid (AcOH). The reaction with MA, besides a carboxylic acid, also simultaneously introduce an electron poor alkene to the fibers (Figure 1A). The total charge of the fibers was increased from 0.065 to 0.751 mmol/g after the MA modification, meaning that the degree of modification (DS) was 0.131 (Figure 1D). The FTIR spectra of both the pristine cellulose fibers and the MA-Fibers in the deprotonated form are shown in Figure 1C. Deprotonation can directly assess covalent attachment, as shown by the appearance of two bands at 1579 cm^{-1} and 1718 cm^{-1} in the MA-Fibers, attributed to the stretching vibration of carboxylates (Na^+ counter ions) and ester groups introduced by grafting of MA onto the cellulose fibers. In addition, the band at 1637 cm^{-1} is assigned to the stretching of electron-poor alkene. Diffusion-edited liquid state ^1H NMR also corroborates the success of the reaction with a clear presence of alkene protons at 6.19 and 5.50 ppm (Figure 1B). During the chemical modification of fibers with MA in AcOH, we also observed the formation of acetate groups, visible by ^1H NMR at 2.05 ppm(Figure 1B). Hence, there is a competing reaction between MA-cellulose and nucleophilic displacement with AcOH.

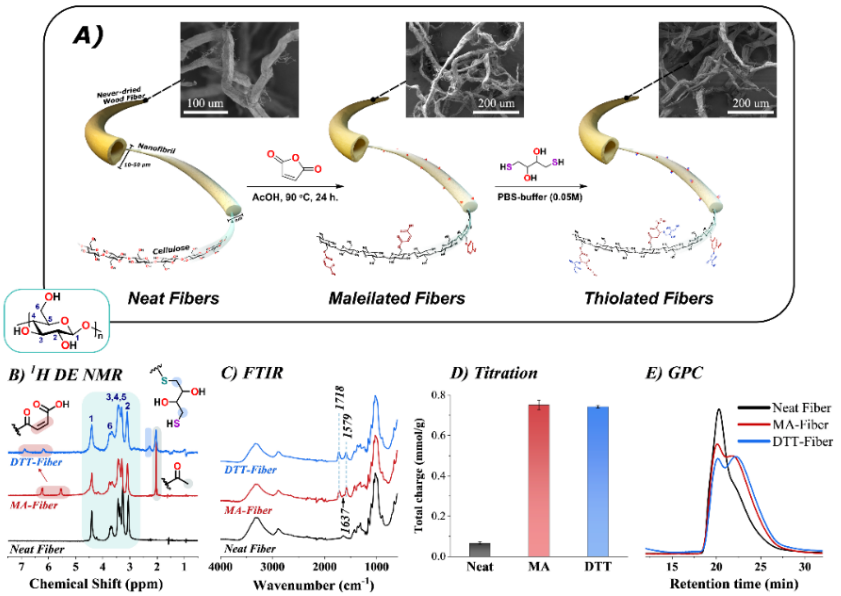

Figure 1. A) Synthetic overview towards thiolated wood fibers, B) diffusion edited ^{1}H NMR, C) FTIR, D) charge density obtained from conductometric titration, E) Size Exclusion Chromatography (SEC) performed in DMAc/LiCl (0.5 wt%) of the hydrolyzed fibers after chemical modification.

Apart from the maleilation, the treatment of the fibers under acidic conditions also resulted in a decrease of the molecular mass as is obvious in figure 1E which shows GPC measurements of the cellulose in reference fibers , the maleilated fibers and the maleilated fibers after thiolation. Despite a considerable decrease in molecular mass of the cellulose no release of low molecular mass fractions of cellulose could be detected and the fibres showed no major changes in electron microscopy images. This allows for the use of fibres for subsequent preparations of materials from the modified fibers.

Since the reactivity of the substituted alkene group is low, due to the presence of the carboxylic acid group, it was necessary to further modify the fibers. Here, we selected thiol-ene Michael addition with DL-dithiothreitol (DTT) in basic conditions as the synthetic strategy towards thiolated fibers. DTT is a difunctional thiol known to undergo Michael addition under basic conditions in water. Basic conditions ensure the deprotonation of the acids, further swelling the wood fiber to facilitate the accessibility of the reaction. Following DTT modification, the signal at 1637 cm^{-1} relating to electron-poor alkenes reduced after the reaction (Figure 1C). Diffusion-edited NMR also revealed a new peak at 2.26 ppm that can be assigned to the aliphatic protons of DTT (Figure 1B). The amount of DTT grafted onto MA-fibers was quantified by sulfur content and found to be 0.389 mmol/g while charge density was measured in average at 0.743 mmol/g (Figure 1D). This indicates a conversion for the DTT addition of 52%, and a DS of 0.139, which is in agreement with the DS measured for the MA-Fiber. The remaining alkene peaks observed by diffusion-edited ^{1}H NMR for the DTT-Fiber align with the previous characterizations.

Thiolated fibers as chain transfer agents during free radical polymerization

In order to radically increase the charge of the fibers they were further subjected to AA's radical transfer graft polymerization onto the DTT-fibers through a classical radical polymerization of AA using ammonium persulfate (APS) as initiator and N,N,N',N'-tetramethylethylenediamine (TEMED) as catalyst in water (Figure 2A). Mechanistically, polymerization is initiated in the aqueous system and transferred to the fiber structure by a radical transfer. Hence, the formed thiyl radical can either initiate polymerization, or combine with a growing polymer chain in the system, leading to a mixed grafting to-and-from polymerization approach. Critical here is to have chemical accessibility of the

polymer chains in the aqueous system to the fibril/fibril aggregate surfaces inside the fiber. Hence, the first step was to assess the effect of pH on the graft efficiency of the fibers, with four different pH values of 2.5, 3.5, 4.5, and 5.5 at a set AA/MA molar ratio of 50. The viscosity increased in all systems, indicating the formation of high molar mass polymers. However, the viscosity increase was higher at pH 5.5 compared to 2.5. It is important to note that higher pH leads to a higher degree of ionization of poly(acrylic acid) (PAA), leading to higher viscosity; in addition to that, lower pH values impede the catalytic effect of TEMED, thereby reducing the reaction rate. After polymerization the fibers were rinsed with a 1 M $NaHCO_3$ solution to assess the relative extent of polymer grafted onto the DTT-Fibers by FTIR. As shown in Figure 2B, the intensity at 1567 cm^{-1}, which relates to the sodium carboxylate, is significantly enhanced for AA-Fibers synthesized at lower pH values (pH 2.5 and 3.5), demonstrating a higher degree of AA initiation from the fibers. Given the slower polymerization rate and lower viscosity at lower pH, it is likely that PAA polymers within the system will react with the thiol groups and either initiate the polymerization or combine. The total charge of the AA-fibers prepared at pH 2.5 and 3.5, was measured with conductometric titration as 4.1 mmol/g and 3.8 mmol/g, respectively. Consequently, pH 2.5 was identified as the suitable pH for the polymerization of AA monomers from the fibers under the selected conditions.

With the optimized pH conditions, we further assessed the impact of changing the relative molar content of AA to DTT-Fibers on the graft outcome ranging from 10 to 120 at a pH = 2.5. The total charge of the resulting AA-Fibers altered from 1.36 ± 0.04 mmol/g for AA_{10X}-Fibers to an impressive amount of 6.71 ± 0.26 mmol/g for the AA_{120X}-Fibers (Figure 2C) which is the highest achieved so far for wood-based fibres with an intact structure, at least to to the knowledge of the authors. This level of charge for the cellulose fibers is significantly higher than what can be achieved by conventional treatment methods such as carboxymethylation, TEMPO-oxidation, sulfoethylation and sulfonation since the cellulose will simply be dissolved at these charges using these types of treatments. In addition, higher charge values of up to 3.5 mmol/g have been reported through the combination of periodate oxidative cleavage and TEMPO and $NaClO_2$ oxidation. However, since these oxidation methods also involve ring-opening of the anhydroglucose unit, the decreased crystallinity indeed promote cellulose dissolution, or fiber defibrillation. In the present work, AA oligomers/low-molecular-weight polymers are grafted onto the fibers with average degrees of polymerization up to 10.8 for AA_{120X}-Fibers based on charge measurements (Figure 2C), further supported by NMR of the hydrolyzed PAA_{80X} grafts, which gave an estimated DP of ~10. As a result, high charge densities can be achieved even at relatively low grafting densities, allowing the fibers to retain their structural integrity and crystalline structure. This is shown by SEM (Figure 2A), where the fibers appear slightly swollen and straightened but remain intact.

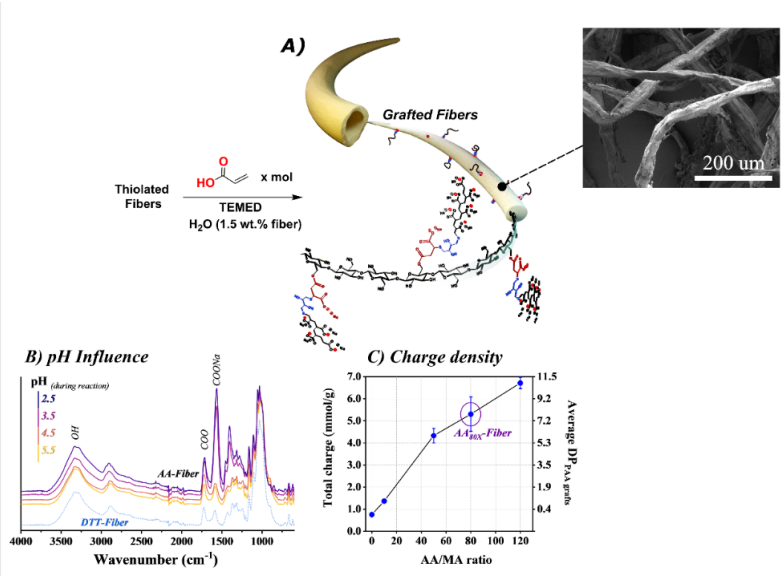

Figure 2. A) Synthetic overview for radical transfer graft polymerization onto the thiolated fiber and SEM imaging of the AA-Fiber B) FTIR on graft outcome as a function of pH, C) Charge density measured by conductometric titration and the associated average degree of polymerization of the PAA graft depending on the initial AA/MA ratio.

Highly Charged Wood fibers for Water Remediation

To explore the use of the highly charged wood fibers in water remediation, we investigated the adsorption potential of MB as a model dye, as well as Pb (II), Cu (II), and Zn (II) as model metal compounds. Figure 3A schematically shows how the experiments were performed and 3B shows that the pH, as expected, significantly influences the adsorption capacity of the AA_{80X}-Fibers for MB. The ionization degree of PAA is highly dependent on pH, while MB predominantly exists within the studied pH range in cationic form. According to the literature, the apparent pKa value of PAA in the absence of added salt ranges from approximately 5.5 to 6.5. Therefore, at pH 8.5, where earlier experiences have shown that around 85% of AA units are negatively charged, the highest adsorption capacity for MB is obtained (1036 mg/g) due to the charge-driven interactions between the negatively charged AA units and positively charged MB due the entropy gain resulting from the release of counterions. In contrast, at pH 2.5, where most PAA units are not ionized, the adsorption is minimal. However, even at pH 2.5, a substantial adsorption capacity of 320 mg/g is observed. This indeed indicates that the counterion release is not the exclusive mechanism behind the adsorption, but also, that the entropy gain due to the release of water molecules, sometimes popularly classified as hydrophobic interactions, significantly contribute to the adsorption mechanism even under acidic conditions. Figure 3C illustrates the adsorption potential of AA_{80X}-Fibers for Cu (II), Zn (II), and Pb (II). Impressive adsorption capacities of 173 mg/g, 138 mg/g, and 581 mg/g were achieved for Cu (II), Zn (II), and Pb (II), respectively. It should be stressed though that the molar content of the absorption between the different ions is similar. Previous work has suggested that improved Pb(II) absorption relates to the electronegativity and lower hydration energy compared to Zn (II) and Cu(II). Pb(II) ions can more readily undergo dehydration and be adsorbed onto the fibers. However, in this case, charge seems to be the determining factor. During adsorption, the release of dissociated water molecules into the system as well as the release of counterions from the total charges of the cellulose fibers, results in an entropy gain, facilitating spontaneous adsorption. It is worth mentioning that the adsorption experiments for metal ions were performed at pH 4.8 to prevent the formation of metal hydroxides

and consecutive precipitation of the metal ions. However, at this pH, the carboxyl groups of AA oligomers are not fully ionized, and the full adsorption capacity of the fibers is hence not utilized.

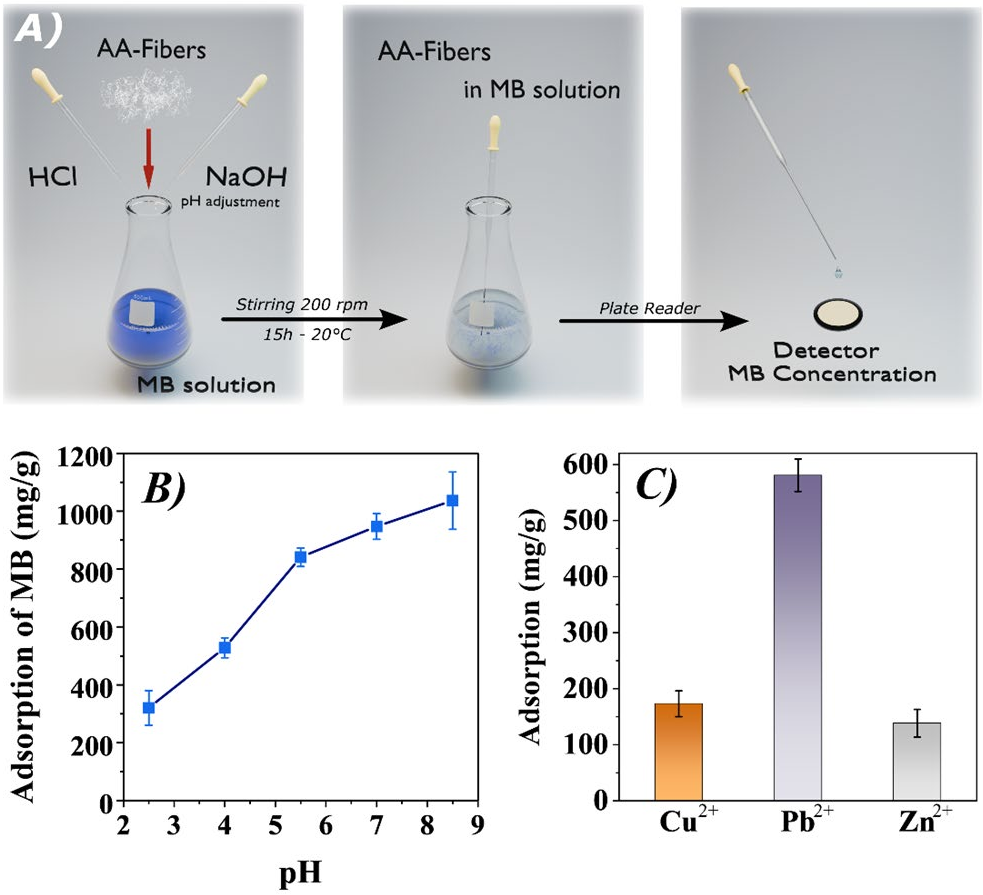

Figure 3. A) Schematic representation of the adsorption procedure of MB by the AA-Fibers, and the quantification of the remaining MB solution. Adsorption of B) MB at different pHs and C) Cu (II), Pb (II), and Zn (II) at pH 4.8 on AA_{80X}-Fibers.

It can hence be concluded that the AA-80X-Fibers exhibit significantly higher capacity than most chemically modified cellulose-based fibers previously reported in the literature, as well as the majority of carbon-based materials, including functionalized carbon nanotubes, activated carbons, and graphene oxide composites. The adsorption capacity of AA-80X-Fibers also exceeds or matches that of several high-performing metal–organic frameworks (MOFs). Among MOFs, zirconium–sulfonic-based frameworks demonstrate particularly high capacities for MB, though their synthesis typically involves complex procedures and hazardous reagents, which may limit large-scale application. In contrast, the AA-80X-Fibers provide a bio-based, water-compatible, and potentially scalable alternative that delivers competitive performance under similarly rigorous or milder conditions.

Conclusion

Cellulose-rich fibers were modified by grafting AA oligomers onto the fibers via a radical transfer mechanism. The modification process comprised three steps: i) maleilation of fibers to introduce alkene functionalities, ii) thiolation via Michael addition iii) graft polymerization of AA via radical transfer grafting polymerization. The optimum pH for radical transfer was determined to be 2.5, and by adjusting the AA concentration, the resulting fibers could be tailored to a total charge ranging from

1.4 to 6.7 mmol/g, marking one of the highest, if not the highest, reported charge values for cellulose fibers to date. The chemical structure of the resulting fibers was characterized in detail by FTIR, NMR, GPC, XPS, Raman spectroscopy and conductometric titration, and their microstructure was analyzed by SEM and XRD, demonstrating that the grafting of AA oligomers did not cause defibrillation or dissolution of the fibers. The fibers appeared more swollen and straightened compared to unmodified fiber. The highly charged fibers were explored for water remediation and had an exceptionally high adsorption capacity of 1036 mg/g for MB and 581 mg/g for Pb(II). The adsorption capacity of the fibers was highly pH dependent, and a pH above the apparent pKa value of PAA favored reaching the full adsorption potential of the fibers.

The synthetic strategy outlined bridges effectively radical polymerization chemistry with biopolymer science, in essence combining the most industrially used polymerization method with a highly relevant biobased building block in a future material economy. The sustainability benefits of this work go well beyond the apparent study, with numerous possible applications in soft functional material science.