

Rapid preparation of all-cellulose composites by solvent welding based the use of aqueous solvent

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Abstract In the present study, the dissolution of softwood fibers and fabrication of all-cellulose composites was investigated using aqueous tetraethylammonium hydroxide solution (TEAOH, 35 wt%) at room temperature. The bulk of the cellulose fibers were instantly dissolved when mixed with the solvent, and suspensions up to 3wt% were fabricated with ease. During the dissolution, a few remaining larger fiber flocks were fully dissolved within 3 h of mixing at room temperature. TEAOH was further studied in the production of all-cellulose composites by solvent welding (partial dissolution) of cellulose fiber sheets. Tensile strength of the original cellulose sheet increased from 3.3 to 55.0 MPa only after 30 s of room-temperature solvent welding, and an increase of over 23-fold (up to 76.7 MPa) was obtained by high-pressure-aided hot-pressing of the partially dissolved sheets before drying. The demonstrated fabrication of all-cellulose composites yielded many benefits in comparison to the current dissolution systems,

such as short treatment time, ambient operation conditions, and readily applicable processing solutions, which makes it a potential methodology applicable even at an industrial scale.

Introduction

Cellulose is the most abundant organic polymer on earth, and its broad availability makes it a promising raw material for novel applications.[1] Chemical modification or solvent-based shaping (including dissolution) of cellulose can broaden its properties, as required by various applications.[2,3] However, owing to its hydrogen bonding interaction and high crystallinity, cellulose has poor solubility in most common solvents.[4] Therefore, novel dissolution methods of cellulose have high importance in the field of sustainable chemistry and materials fabrication.

Cellulose can be dissolved using chemical derivatization (e.g., esterification[5] or carbamation[6,7]). However, these systems change the chemical and physical properties of cellulose. Cellulose can also be dissolved in various non-derivatizing solvent systems, including N-methylmorpholine-N-oxide (NMMO)[8], dimethylacetamide/LiCl[9], and molten salt hydrates[10]. However, these systems exhibit certain disadvantages, such as solvent instability, degradation of cellulose, and high toxicity. Ionic liquids are currently one of the most utilized solvents for cellulose dissolution.[11,12] Some novel ionic liquids and organic solvent mixtures (termed as organic electrolyte solutions) have been shown to rapidly dissolve cellulose.[13] With respect to sustainability, aqueous alkaline (sodium or lithium) hydroxides together with urea or thiourea are some of the most promising cellulose solvents.[14–16] Minor disadvantages of these systems include the requisite for dissolution at a chilled temperature of $-12\text{ }^{\circ}\text{C}$ [17] and limited capacity to dissolve high-molecular-weight cellulose.[18] Recently, tetra-alkylammonium hydroxides were shown to efficiently dissolve cellulose even at room temperature (however, the dissolution of high-molecular-weight cellulose generally requires elevated temperatures).[19–21]

Despite the apparent toxicity of alkylammonium cations, the recyclability makes tetra-alkylammonium hydroxides a suitable solvent for isolation of cellulose originating from different sources.[20,22]

All-cellulose composites (ACCs) are a relatively new class of cellulosic material, in which dissolved cellulose is utilized as a matrix to bond together natural cellulose fibers.[2] ACCs can be produced by mixing together dissolved cellulose and cellulose fibers (supposing that fibers do not dissolve during the processing) followed by casting and regeneration. Another way is solvent-based modification of cellulose sheets by partial dissolution and regeneration (referred as surface selective dissolution[23], partial fibre dissolution[24], or solvent welding[25]). Several different solvent systems have been studied for solvent welding of cellulose fibers, including dimethyl acetamide/LiCl[24], NMMO[26], ionic liquids[27], or NaOH-urea[28,29]. With these systems, ACCs were successfully produced with good properties, but they all pose some shortcomings, including long dissolution times and requirement of either high (e.g., 80 °C) or low temperatures (<0 °C). Use of high or low temperature can be environmentally desirable due to the high energy consumption, in addition to increase of the product cost. Especially from an industrial point of view, the dilatory dissolution of cellulose can be challenging to implement if a continuous process operation is desired.

In this study, the dissolution of high-molecular-weight cellulose fibers from dissolving pulp was studied using aqueous tetraethylammonium hydroxide (TEAOH, 35 wt% in water). The effect of dissolution and regeneration on the degree of polymerization (DP) and crystallinity of cellulose were studied using limiting viscosity and wide-angle X-ray diffraction (WAXD), respectively. ACCs were produced based on the rapid dissolution efficiency of TEAOH by solvent welding cellulose sheets. The effect of the dissolution time and hot-pressing on the

surface morphology and mechanical properties of ACCs were investigated by scanning electron microscopy (SEM) and tensile testing, respectively.

Material and Methods

Materials

Cellulose dissolving pulp (softwood) was obtained as dry sheets, whose properties are presented elsewhere.[30] TEAOH (35% in water) was obtained from Sigma Aldrich (Germany). Ethanol and HCl (0.1M) were acquired from VWR (Finland).

Dissolution of cellulose

Dissolving pulp sheets were disintegrated in water using standard procedure [31] followed by filtration, washing with technical ethanol for 30 min, and filtration again before drying in an oven (60 °C). Fibers were then dissolved in 35 wt% TEAOH in water by mixing the fibers directly in the solvent using magnetic stirrer or by adding the solvent to the fibers (0.5–3 wt% cellulose solutions) while simultaneously mixing at room temperature. After solvent addition, the suspensions were mixed for 3 h until all the fibers were dissolved, and the solubility was verified using an optical microscope. Cellulose was regenerated by pouring the solution into ethanol while mixing. Regenerated cellulose was filtered and washed using ethanol until the washing liquid was neutral (checked using pH paper).

Fabrication of all-cellulose composites

Laboratory hand sheets (80 g/m²) were prepared from the dissolving pulp, according to a standard procedure to produce sheet with thickness around 180 µm.[32] Around 5 cm x 7 cm pieces were cut from the laboratory sheets and immersed in excess of TEAOH for 30, 60, 120, or 180 s for solvent welding of the fibers. No mixing of the solvent applied. The sheets were then

carefully lifted from the solvent and placed in 0.1 M HCl solution for 120 s. After acid coagulation, ACCs were first washed in a beaker containing deionized water (500 ml) for 30 min and then rinsed under running deionized water until the surfaces were neutral (checked using pH paper). Two different drying procedures were applied in the finalization of ACCs fabrication. The ACCs were placed between a filter paper and hand sheet on both sides and dried either in a drying grill (temperature of plates was around 125 °C) for 5 min or under high-pressure and heat (high-pressure aided hot-pressing, hp) using the Fontune Press (the Netherlands). In the latter, two consecutive steps were applied: 1) the sample was dried using a force of 45 kN together with the filter papers. 2) The dried ACC without filter papers was placed between the hot metal plates and pressed with a force of 300 kN to remove possible residual moisture. The temperature in both steps was 150 °C.

Attenuated total reflection infrared spectroscopy

The chemical characterization of raw, regenerated, and ACCs was performed using an ATR-IR. The spectra were collected from dried samples using a Bruker Tensor II FT-IR Spectrometer with a Hyperion 3000 FT-IR Microscope (USA). Spectra were obtained in the 600–4000 cm^{-1} range, and 40 scans were taken at a resolution of 4 cm^{-1} for each sample.

Degree of polymerization

The average degree of polymerization (DP) of the dissolving cellulose pulp and regenerated cellulose were evaluated using the limiting viscosity number, as measured in the CED solution according to the ISO 5351 standard. The samples were freeze-dried prior to the measurement. The limiting viscosity numbers were converted to DP using Eq. (1),

$$DP = \left(\frac{(1.65[\eta] - 116H)}{C} \right)^{1.111}$$

where $[\eta]$ is the limiting viscosity number, C is the mass fraction of the cellulose, and H is the mass fraction of the hemicelluloses. This calculation corrects for the contribution of the hemicelluloses to the limiting viscosity number and DP of the cellulose, assuming that the average DP of the hemicelluloses is 140.

Mechanical properties

The tensile tests were performed using a universal material testing machine (Instron 5544, USA) equipped with a 100 N load cell. The laboratory sheet from the dissolving pulp and ACCs were cut into thin strips with a specimen width of 5 mm, and their thicknesses were measured using a precision thickness gauge (Hanatek FT3, UK). For the tensile testing, a 40-mm gauge length was set under a strain rate of 4 mm/min and six specimens were measured. The tests were conducted in 50% RH at a temperature of 23 °C and under a pre-load of 0.05–0.1 N. Prior to testing, the specimens were conditioned for at least one day in the same environment. The elastic modulus was calculated from the initial linear portion of the stress–strain curve, and the ultimate tensile strength was defined as the stress at the specimen breakage. At least five specimens from each samples were measured and specimens flailed at the clamps were excluded.

X-ray diffraction

The crystalline structures of the dissolving pulp, regenerated cellulose, and ACCs were investigated using WAXD. Measurements were conducted on a Rigaku SmartLab 9kW rotating anode diffractometer (Japan) using a Co $K\alpha$ radiation (40 kV, 135 mA) ($\lambda = 1.79030$ nm). Samples from the dissolving pulp and regenerated cellulose were prepared by pressing tablets of

freeze-dried celluloses to a thickness of 1 mm. ACCs were measured similarly. Scans were taken over a 2θ (Bragg angle) range from 5° – 50° at a scanning speed of $10^\circ/\text{min}$, using a step width of 0.5° . The degree of crystallinity was determined by the method of Nam et al.[33] with the modifications suggested by Piltonen et al.[29] Since it is known from the literature that regenerated cellulose tends to have a preferred orientation, the March–Dollase parameter for the (110)-plane in cellulose II was adjusted in the simulated patterns for each sample to find the best matching fit.[34] The March–Dollase parameter was then converted to the degree of preferred orientation of cellulose II using Eq. 2,[35]

$$\eta_{PO} = 100\% \cdot \sqrt{\frac{(1-r)^2}{1-r^2}}$$

where η_{PO} is the degree of the preferred orientation, and r is the March–Dollase parameter.

Scanning Electron Microscopy

SEM (Zeiss Zigma HD VP, Germany) images of ACCs and untreated reference dissolving pulp sheet were obtained using Zeiss Zigma HD VP (Germany), with an accelerating voltage of 5 kV during imaging. Prior to the measurement, the samples were placed on carbon tape and sputter coated with Pt for 30 second using one coating cycle.

Results and Discussion

Dissolution of cellulose in tetraethylammonium hydroxide solution

Prior the ACC production, the efficiency of TEAOH on the cellulose dissolution at room temperature was investigated. Most of the cellulose fibers dissolved completely in TEAOH (35

wt% in water) immediately after coming into contact with the solvent. However, some of the fiber bundles or “chunks” were difficult to dissolve, and complete dissolution was achieved after 3 h of mixing at room temperature (Figure 1b). The completely dissolution (1–3%) was dependent on the mixing speed and cellulose concentration (Figure 1c and Figure S1). The formation of less soluble chunks in the solvent were noted to occur when bigger shreds of fibers were added into the solvent. The gelation of the outer layer of the less soluble shreds hindered the diffusion of the solvent. Similar behavior is encountered when methyl cellulose is dissolved in cold water.[36] One way to improve fiber dissolution and minimize the formation of gel-coated chunks was to rapidly add the solvent on the top of the fiber network for improved penetration while simultaneously mixing. The 3 % solution was easily obtained at room temperature, however, due to the high viscosity, no attempt to produce higher concentration solution was performed as the aim of the current study was to investigate the preparation of ACCs at room temperature. Higher solution concentrations could be achieved combining more intensified mixing or by applying higher temperature.

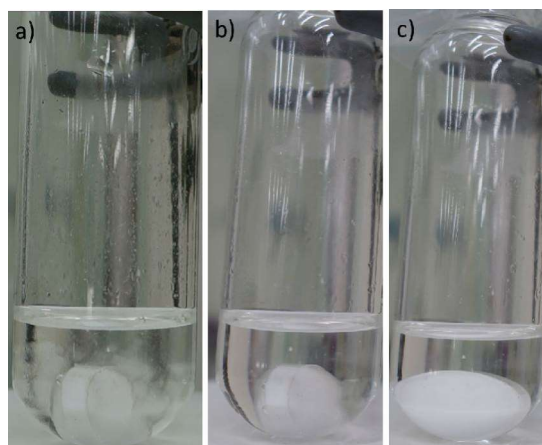


Figure 1. a) 1% cellulose solution in TEAOH (35 wt% in water) a) after addition of solvent, and b) after one hour, and c) after three hours under mixing.

After dissolution, cellulose could be regenerated by the addition of ethanol as an anti-solvent (or by using acid such as dilute HCl solution, which was used when in the production of ACCs). DP of the cellulose remained intact after regeneration. Mild dissolution conditions (3 h at room temperature) might help prevent the unwanted hydrolysis of cellulose as the initial DP of dissolving pulp remained at 1862 after regeneration. The yield of the regenerated cellulose was over 90%, and it is most likely that the yield loss is owing to the sample handling and the possible removal of residual hemicelluloses (< 6%) in the pulp. In addition, based on the elemental analysis, all the TEAOH was removed after washing.

Previous studies have indicated poor solubility of cellulose in aqueous TEAOH (Avicel PH-101 cellulose powder).[19] In the current study 35 wt% TEAOH solution obtained from Sigma Aldrich exhibited good dissolution capacity towards cellulose. However, in our studies we observed with similar solution obtained from different supplier (TCI Chemicals) poor dissolution capacity. According to the supplier, some TEAOH solutions might contain bromide-ion as impurity (TEAOH is obtained from corresponding bromide salt), which might alter the properties of solvent. Previously it has been observed that impurities, such as alkaline metal ions can hinder the dissolution of cellulose in tetrabutylammonium hydroxide.[37] Therefore, further studies are needed to investigate the exact effect of the impurities on the dissolution of cellulose in TEAOH.

Fabrication and characterization all-cellulose composites

The laboratory sheets were prepared from the dissolving pulp, and ACCs were fabricated by room-temperature welding of fibers using TEAOH. Visual shrinking of the cellulose sheet was observed immediately after submersion into TEAOH. Partially transparent ACC hydrogel was obtained after coagulation in an acid bath (0.1 M HCl) and washing with deionized water. HCl

was used to ensure rapid coagulation of cellulose, however, further studies should be conducted to verify the effect of coagulation bath on the properties of ACCs. All of the samples could be easily handled and washed under running water after coagulation. After drying, the ACCs After drying, the ACCs appeared relatively transparent when placed on top of the background (Figure 2a), resembling those previously obtained by dimethyl acetamide/LiCl[23,38], which, however, required several hours for partial dissolution of cellulose. However, The haziness was apparent when stripes from the ACCs were held one centimeter above the background image (Figure 2b).

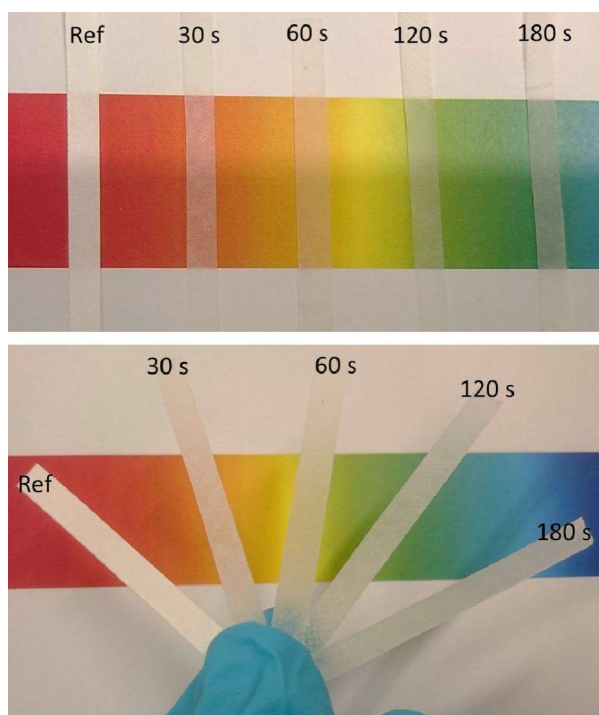


Figure 2. Visual appearance of reference cellulose sheet and ACCs after various treatment times directly on the top of (upper photo) and around one centimeter above (lower photo) the background demonstrating the semi-transparency of ACCs.

The ATR-IR spectrum of the original dissolving pulp (Ref), completely dissolved and regenerated dissolving pulp (Reg), and ACC after 30 s treatment (30s) are presented in Figure 4

(similar spectra were acquired for the other ACCs and spectra are presented in Figure S2 in Supporting information). Several alterations in the spectrum of the ACC compared to that of the dissolving pulp indicates the partial transformation of cellulose I crystalline structure to either cellulose II crystalline structure or amorphous cellulose.[34] The peak in the –OH region (around 3300 cm^{-1}) was broadened, and new shoulders appeared around 3480 and 3440 cm^{-1} (Figure 3a). The flattening and the change in the peak maximum from 1427 to 1421 cm^{-1} was related to symmetric CH_2 bending or scissoring motions in cellulose I, further indicating the transformation of cellulose I to cellulose II crystalline structure or to amorphous cellulose during the ACC preparation (Figure 3b). The clear separation of the 1313 and 1336 cm^{-1} peaks, related to the CH_2 wagging motion and to the –OH in-plane bending of the crystalline forms of cellulose I and cellulose II, respectively, indicates that cellulose was not entirely transformed to amorphous or poorly crystalline cellulose. In contrast, the regenerated cellulose exhibited a broader peak at 3300 cm^{-1} compared to the original fibers and ACC. In addition, a broad peak can only be observed at around 1420 cm^{-1} , and the absence of a clear peak at 1313 cm^{-1} indicates that the dissolution and regeneration of the dissolving pulp converts cellulose I to cellulose II and to amorphous or poorly crystalline cellulose. Differences in the ATR-IR spectra of ACCs and regenerated cellulose is most likely due to the use of different coagulation bath, which can cause differences in the crystallinity and surface properties of cellulose. [39,40]

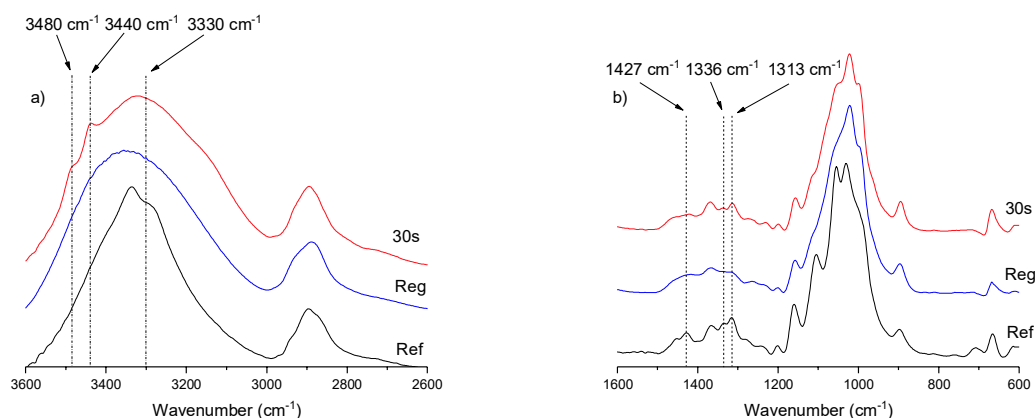


Figure 3. ATR-IR spectra of original cellulose pulp (Ref), completely dissolved and regenerated cellulose (Reg), and ACC obtained after 30 s treatment time (30s).

For further investigating the crystallinity changes during the cellulose dissolution and ACC production, XRD patterns were recorded and then fitted (XRD diffraction patterns and fitting are presented in Figure S3 in Supporting information). The amount of amorphous cellulose remains nearly at the same level in the original pulp and ACCs, but the crystalline parts changed from 67% to around 25% and from 20% to 60% for cellulose I and cellulose II, respectively (Table 1). The ACCs showed a high preferred orientation of ca. 30% in cellulose II along the (110)-plane. These results support the findings of the ATR-IR spectroscopy for the ACCs. It has been reported that despite being natural cellulose, dissolving pulp can contain both cellulose I and cellulose II crystalline structure[41,42], which was also observed here. Presence of small amount of cellulose I in regenerated pulp might be due to the presence of minimal amount non-dissolved highly crystalline cellulose, which could not be observed with microscope (possible nanosized materials). The dissolution time did not have a visible influence on the crystallinity of the ACCs. Previous studies with NaOH-urea showed lower conversion rate of cellulose I to cellulose II with similar treatment times (after treatment, cellulose II content were around 30%)[29]. On the other

hand, similar cellulose II content (around 60%) than in current study were observed using long treatment time (20 minutes) with NaOH-urea.[34] Higher degree of amorphous or non-crystalline cellulose in regenerated cellulose compared to ACCs is mostly likely due to the use of ethanol as coagulation bath for fully dissolved cellulose, whereas aqueous HCl solution was used during the production of ACCs.[40]

Table 1. Relative amounts of cellulose I, cellulose II, and amorphous cellulose of original dissolving pulp (Ref), regenerated cellulose (Reg), and ACCs with different treatment times (η is the degree of the preferred orientation and r is the March–Dollase parameter).

Sample	r	η_{PO} (%)	Amorphous (%)	Cellulose I (%)	Cellulose II (%)
Ref	1	0	13.2 ± 0.5	67.1 ± 0.7	19.6 ± 0.8
Reg	1	0	24.2 ± 0.8	18.0 ± 1.5	57.7 ± 1.2
30 s	0.6	28.6	10.8 ± 0.3	33.0 ± 0.5	56.2 ± 0.5
60 s	0.5	37.8	8.7 ± 0.3	29.8 ± 0.4	61.5 ± 0.5
120 s	0.6	28.6	11.1 ± 0.4	19.6 ± 0.6	69.3 ± 0.6
240 s	0.6	28.6	8.1 ± 0.5	29.3 ± 0.8	62.6 ± 0.7

SEM images showed partial dissolution of fibers on the surface of the ACCs (Figure 4). Some small fragments of cellulose fibers were observed, but most of the ACCs exhibited an even and slightly rough surface pattern. Interestingly, it was noted that a longer dissolution time led to a slightly more uneven surface structure. This might indicate that a longer dissolution time leads to release of the cellulose into solvent, causing erosion of the surface. Some of the dissolved cellulose might also be lost during the coagulation and washing of the sample.

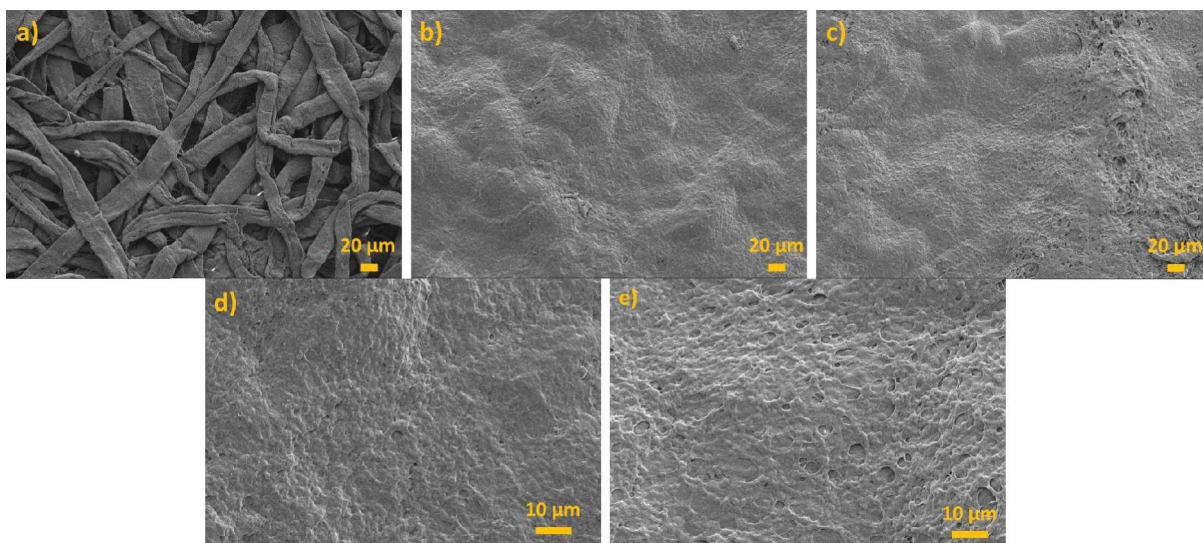


Figure 4. SEM surface images of a) reference cellulose sheet, ACCs after b) 30, c) 60, d) 120, and e) 180 s dissolution times.

Cross-sectional images of the ruptured reference cellulose sheet showed completely fibrous structure, with random pulling of fibers after breakage in tensile testing (Figure 5), whereas clear cutting of the ACC was obtained after tensile testing. The images in higher magnification showed that, in addition to the dissolved fibers on the surface, most of the inner fibers were also welded together and only small fiber fragments or fibers parts with sub-micron diameters were present. This further confirms the efficient solvent welding ability of TEAOH.

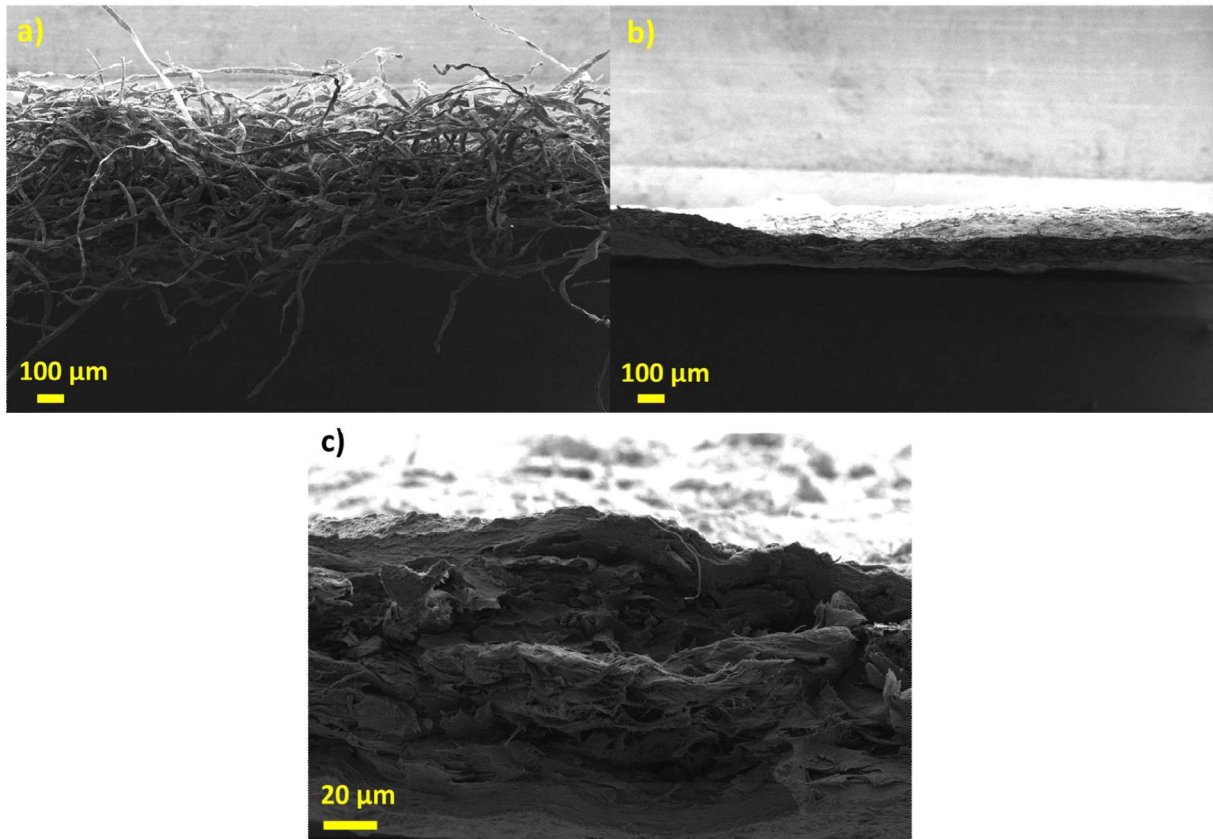


Figure 5. SEM images of cross-section of tensile test samples after rupture: a) reference cellulose sheet and b) and c) ACC after 30 s treatment time at different magnification.

The tensile strength of the dissolving pulp sheet increased from 3.3 to 57.8 MPa only after 30 s treatment time (Table 2, average stress-to-strain curves are presented in Figure 6). In addition, the elastic modulus increased around tenfold, from 0.5 GPa to 5.1 GPa, whereas the elongation at break remained at the same level. This demonstrates the efficient and rapid solvent welding properties of TEAOH to produce strong and stiff ACCs. There were no significant differences between the tensile strengths of ACCs when the treatment time was increased from 30 to 180 s.

The tensile properties of the ACCs obtained in the current study are generally lower compared to several reported in literature.[2] However, very high tensile strength (several hundred MPa) are obtained in the longitudinal direction of the samples where fibers were pre-aligned before

ACC production.[23] In addition, tensile strength over 100 MPa could be obtained even from random-orientated fibers using DMAc/LiCl at 20 °C,[43] which is higher than in current study were the preparation of cellulose sheets also results in the random alignment of fibers. However, the relative improvement of tensile strength of the cellulose sheet during the ACC production using TEAOH was very high. For example, the use of ionic liquids to produce ACC from filter paper increased the tensile strength to around seven times the initial value after 160 min of treatment time at 80 °C.[44] Using 12 hours dissolution time in aqueous polyethylene glycol-NaOH at -12 °C, tensile strength of filter paper improved around three times from the initial value [45], whereas around four times increase in the tensile strength has been observed using DMAc/LiCl with six hours at 30 °C.[38] In current study, over 17 times higher tensile strength was obtained only after 30 s treatment time using TEAOH at room temperature. Previously, similar results were reported using NaOH-urea solution to produce ACCs (increase in tensile strength from 3.4 to 48.8 MPa after 30 s treatment times).[29]

Table 2. Effect of the treatment time (s, seconds) and hot-pressing (hp) on the properties of ACCs (error represents standard deviation).

Sample	Elastic modulus (GPa)	Elongation at break (%)	Stress at break (MPa)	Thickness (μm)
Reference	0.5 ± 0.01	1.8 ± 0.2	3.3 ± 0.2	179 ± 1
30 s	5.1 ± 0.6	1.7 ± 0.2	55.0 ± 2.7	122 ± 1
60 s	4.4 ± 0.7	2.1 ± 0.3	51.7 ± 4.9	134 ± 1
120 s	4.7 ± 0.9	1.8 ± 0.5	53.5 ± 5.9	132 ± 1
180 s	4.6 ± 1.1	1.6 ± 0.3	48.6 ± 6.7	142 ± 2
30 s, hp	7.2 ± 0.4	2.0 ± 0.2	75.0 ± 4.5	99 ± 0
60 s, hp	6.7 ± 0.7	2.2 ± 0.1	75.9 ± 8.9	111 ± 1
120 s, hp	6.8 ± 0.6	2.3 ± 0.0	72.5 ± 4.7	91 ± 0
180 s, hp	6.8 ± 0.6	2.2 ± 0.1	76.7 ± 7.8	109 ± 0

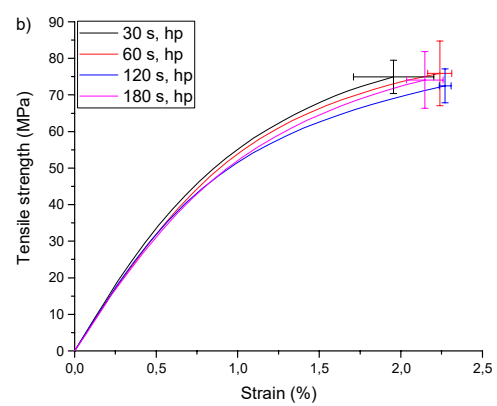
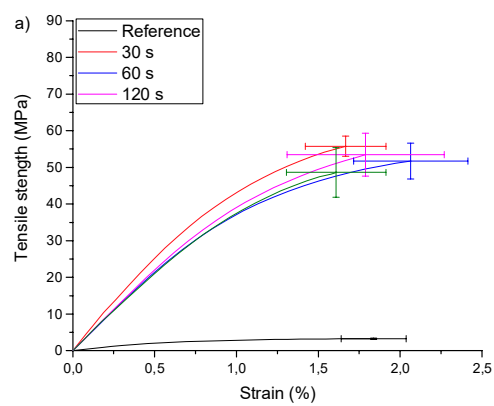


Figure 6. Average stress–strain curves of cellulose sheet (reference) and ACCs after a) different treatment times (s, second) and b) high-pressure aided hot-pressing (hp) (error bars represents standard deviation).

The tensile properties of AACs were further improved by high-pressure aided hot-pressing of the washed samples. For instance, the tensile strength of the ACC after 30 s treatment time increased to 75 MPa (36% higher compared to samples prepared by hand sheet grill drying) when high-pressure-aided hot-pressing was utilized (Table 2). It has been previously shown that use of high pressure can increase the mechanical properties of the ACCs.[46] The increase in the tensile properties was most likely due to the formation of a more compacted structure, which was observed as a decrease in the thicknesses of the samples (from 122 to 99 μm when 30 s dissolution time was applied).

Conclusions

Dissolving softwood pulp could readily be dissolved in an aqueous TEAOH solution at room temperature within three hours. Up to 3 wt% dissolved cellulose solution could be attained using simple magnetic stirring, whereas a higher concentration might require more intense mixing. No hydrolysis of cellulose occurred as the DP of cellulose was observed to remain intact after dissolution and regeneration. TEAOH could be used to produce ACCs at room temperature by solvent welding of the cellulose fiber sheets. Over 17 times higher tensile strength was obtained only after 30 s dissolution time, demonstrating the efficient solvent capacity of TEAOH. The high-pressure aided hot-pressing of ACCs prior to drying could be used to further increase the tensile properties up to 22-fold (compared to original cellulose sheets) with 30 s treatment time. This study demonstrated a sustainable procedure for both cellulose dissolution and rapid

production of strong ACCs using methodologies that could be feasible even at the industrial scale.

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