



A method for chemical and physical modification of oriented pulp fibre sheets

Diana Carolina Reyes Forsberg · Per-Oskar Westin · Lengwan Li · Anna Svedberg · Hans Grundberg · Lars A. Berglund

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Abstract Wood pulp fibres are promising reinforcements for biocomposites due to their renewable resource origin and mechanical properties. An oriented and dense fibre reinforcement structure is beneficial for biocomposite properties. We present a method of modifying fibres (e.g. to increase strain to failure) in pre-formed oriented high-density paper structures intended for biocomposites or as hot-pressed fibre materials. Mildly delignified, well-preserved holocellulose fibres from softwood are used. Cold alkali treatment (hemicellulose removal) and mercerisation (conversion to cellulose II) were

carried out successfully on oriented fibre sheets. Controlled anisotropy and sheet density are achieved from untreated and straight fibres in the sheet formation step. High mechanical properties and increased ductility of mercerised sheets were observed, which may be valuable for hot-pressed fibre materials ($E \approx 7.1$ GPa, strength of 108 MPa and strain to failure of 5.3%) and biocomposites. In contrast, modified wood pulp fibres were difficult to orient, resulting in higher sheet porosity and weak interfibre bonding.

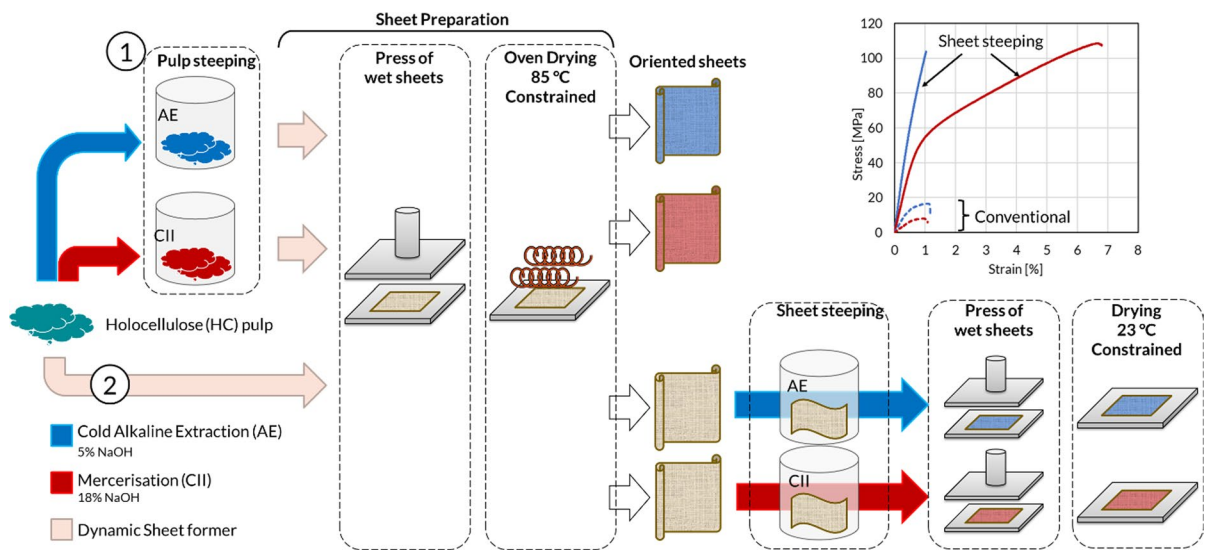
Diana Carolina Reyes Forsberg and Per-Oskar Westin have contributed equally to this work.

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D. C. R. Forsberg · P.-O. Westin · A. Svedberg · H. Grundberg
MoRe Research AB (RISE), Box 70, 89122 Örnsköldsvik, Sweden

L. Li · L. A. Berglund (✉)
Department of Fibre and Polymer Technology, Wallenberg Wood Science Center, KTH Royal Institute of Technology, 10044 Stockholm, Sweden
e-mail: blund@kth.se

Graphical abstract



Keywords Biocomposites · Cold alkaline extraction · Mercerisation · Cellulose II · Hot-pressed fibres

Introduction

Biocomposites and fibre materials based on plant fibres are an alternative to non-biodegradable plastics and glass fibre composites due to their renewable resource origin and good mechanical properties (Faruk et al. 2012; George et al. 2001; Niskanen 2012). To take advantage of these properties, plant fibres have been modified to improve cell wall accessibility and fibre/polymer interface adhesion (Li et al. 2007; Saheb and Jog 1999). Modifying natural fibres by simple NaOH-treatment changes the fibre/matrix interface and can induce structural changes for increased fibre ductility (Faruk et al. 2012; Goda et al. 2006; Gomes et al. 2004; Nakagaito and Yano 2008). The effect of alkali treatment varies depending on the fibres and process conditions (Hashim et al. 2012). Another fibre modification method is cell wall bulk-ing by acetylation. Increased degree of acetylation decreases the moisture adsorption of fibres (Bledzki et al. 2008; Bledzki and Gassan 1999; Rowell 2004) and improves the wet strength of composites (Joffre et al. 2017).

In addition to chemical modification, the effects of densification and fibre orientation have been explored. Reduced porosity (higher fibre volume fraction) improves network strength in fibre sheets and facilitates high fibre volume fraction in the final biocomposite (Bajpai 2018; Niskanen 2012). Moreover, aligning fibres in a preferential direction during sheet formation improves mechanical performance along the direction of fibre alignment compared to randomly oriented fibres (Dufresne 2008; Niskanen 2012). Most often, cellulose fibres are first modified by wet chemistry and then used in composites melt-processing (e.g. Bledzki and Gassan 1999). It often means that the amount of liquids and chemicals used are high and that multiple processing steps are needed, where detrimental mechanical fibre damage is often induced. Therefore, there is a need for further biocomposite investigations on chemical modification methods for cellulose fibres combined with well-organised fibre reinforcements. Furthermore, most of the available cellulose reinforcement studies focus on plant fibres such as jute, hemp, and ramie (e.g. Gomes et al. 2004; Goda et al. 2006; Hashim et al. 2012; Faruk and Sain 2015) and few on wood-based reinforcements (e.g. Nakagaito and Yano 2008; Yang et al. 2019). Here, we suggest a method for chemical and physical modification of dense wood fibre

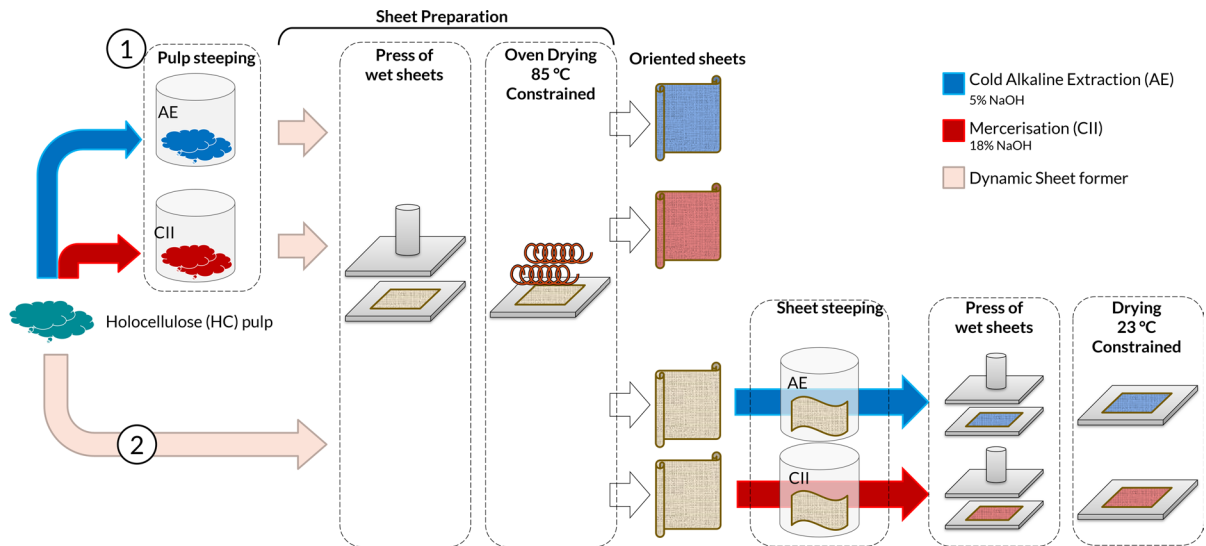


Fig. 1 Schematic representation of the two evaluated protocols to produce oriented fibre sheets of chemically modified fibres. Protocol (1) modification of holocellulose pulp followed

by sheet formation, here referred to as pulp steeping. Protocol (2) sheet formation from holocellulose pulp followed by modification, referred to as sheet steeping

network reinforcements (dense paper), and transformation to cellulose II via mercerisation as an example of chemical modification, where NaOH can be recycled. The proposed method is simpler than more aggressive and time-consuming methods dominating the practice, although continued efforts on reduced consumption of chemicals are desirable.

We propose a protocol for chemical and physical fibre modification in sheet form using an oriented fibre network, thus achieving higher mechanical performance of composites and fibre materials in the predominant fibre direction. The protocol allows better control of fibre organisation and sheet density. Alkali treatment is used as an example for chemical modification. First, well-preserved holocellulose fibres (high hemicellulose content, almost no lignin) were obtained via a single step peracetic acid (PAA) delignification of wood (Westin et al. 2021). Secondly, the holocellulose fibres were used as starting material for cold alkali extraction and mercerisation processes, using two different protocols as shown in Fig. 1. One protocol (1) consisted of cold alkali extraction or mercerisation of wet holocellulose pulp, here referred to as *pulp steeping*, followed by washing. A dynamic sheet former was then used in a second stage to produce fibre sheets with a high degree of preferred orientation. In the alternative

protocol (2), holocellulose fibres were first assembled in a dynamic sheet former, dried, and the sheets were then used as starting material for cold alkali extraction or mercerisation, a process referred to as *sheet steeping*. Additionally, some samples from the sheet steeping protocol were subjected to hot pressing to test possible sheet property improvements by densification. Finally, sheets from the two protocols were compared for mechanical properties of the fibre “mat”, intended for hot-pressed fibre materials or as reinforcement in polymer matrix composites.

Experimental

Materials

Wood chips

Spruce wood chips with a dry content between 40 and 60% were provided by Högland Såg & Hyvleri AB sawmill, Örnsköldsvik. Bark and knots were excluded manually prior to delignification process. Chips were predominantly from the sapwood region of the logs, where microfibril angle is expected to be higher than average in the log.

Chemicals

The reactants, glacial acetic acid (100%, Merck KGaA), hydrogen peroxide (30%, Merck KGaA), and NaOH ($\geq 98\%$, VWR) were used without any further purification. Ultrapure Milli-Q H₂O was used for preparation of the NaOH solutions. NaOH solutions were kept in vessels protected from atmospheric CO₂. Deionised H₂O was used for washing the alkali-treated samples.

Methods

Holocellulose pulp preparation

A single step peracetic acid (PAA) delignification process was used to extract holocellulose fibres with minimal lignin content while preserving cellulose and hemicellulose contents and causing minimal mechanical degradation of the wood fibre (Westin et al. 2021). PAA containing liquor was prepared by mixing 30% hydrogen peroxide and 100% acetic acid at a molar ratio of 1:1.9 and kept at room temperature for 24 h to allow equilibration. Wood chips were placed in an autoclave reactor, after which the PAA-containing liquor was added. Impregnation of the wood chips was assured by applying 5 bars of pressurised air to the autoclave. The reaction was then carried out in a heated rotating setup at 70 °C for 25 h. At the end of the reaction, the liquor was removed, and the obtained holocellulose pulp washed using deionised water. PAA delignification yields a holocellulose pulp composed of ~23% preserved hemicelluloses and residual lignin content of 1–2% (Westin et al. 2021).

Preparation of paper sheets

Sheets with preferred fibre orientation were prepared from a pulp suspension at 1 g/L consistency using a dynamic sheet former (Formette, Fibertech AB, Sweden) and a drum rotation speed of 1300 m/min. Wet sheets were pressed with blotters for 5 min at a pressure of 0.3 MPa to remove excess water, after which they were dried under mechanical constraint at 85 °C temperature for 7 min, see Fig. 1. The dried sheets with a thickness of 0.1–0.2 mm, were conditioned for at least 24 h at 23 °C and 50% RH prior to further processing, testing and measurements. The fibre orientation achieved by using the dynamic sheet former

is intended to improve mechanical performance along the direction of the fibre alignment (machine direction, MD) compared to that of a sheet of randomly oriented fibres.

Alkali treatment of holocellulose in pulp and sheet form

For cold alkali extraction, 5% NaOH at 5 °C was used. Mercerisation was carried out using 18% NaOH at room temperature. The used experimental conditions were selected since low NaOH concentration (i.e., 5% NaOH) allows for the removal of hemicellulose (Sixta 2006) without causing a transformation into cellulose II (Porro et al. 2007). While the use of 18% NaOH is expected to yield cellulose II almost instantaneously (Albán Reyes et al. 2016; Langan et al. 2001; Nishiyama et al. 2000). The samples were then gently introduced into the container containing lye to minimise the risk of damaging the sample. This step was crucial for the pre-formed sheet samples.

For pulp steeping, wet holocellulose pulp was used as a starting material at 5% (w/w) holocellulose content. Note that no agitation was used to avoid damage of the well-preserved holocellulose fibres. The first filtrate was taken for Chemical Oxygen Demand (COD) analyses, and the reaction was quickly stopped by washing the alkali samples with deionised H₂O in a Büchner funnel. The samples were then suspended

Table 1 Overview of used experimental conditions for cold alkali extraction and mercerisation

Samples	T (°C)	[NaOH] (%)	t (min)	
Pulp	HC			
	AE-1	5	5	10
	AE-2	5	5	200
	AE-3	5	5	1200
	CII-1	23	18	10
	CII-2	23	18	1200
Oriented sheets	HC-O	–	–	–
	AE-1-PS	5	5	10
	AE-1-SS	5	5	10
	CII-1-PS	23	18	10
	CII-1-SS	23	18	10
	CII-2-PS	23	18	1200
CII-2-SS	23	18	1200	

Sample from sheet steeping and pulp steeping are labelled as SS and PS, respectively

in deionised H₂O for 2 h, and their pH was measured to ensure neutrality before sheet preparation.

Cold alkali extraction via pulp steeping was carried out using a pre-cooled 5% (w/w) NaOH solution, and the cold temperature (5 °C) was maintained during the reaction. Reaction time was set to 10-, 200- and 1200-min. Samples were then subjected to alkali wash to remove as much of the hemicellulose as possible. Mercerisation via pulp steeping was carried out using 18% (w/w) NaOH solution at room temperature with reaction times of 10 min and 1200 min. Then, the samples were subjected to alkali wash prior to sheet preparation as described in previous section.

Sheet steeping of dry oriented holocellulose paper sheets (~5% moisture content, MC) was carried out using a 0.4% (w/v) consistency to ensure that the whole sheet surface was covered with the NaOH solution. Otherwise, the experimental conditions used for cold alkali extraction and mercerisation were the same as those described for pulp steeping. Sheet samples were subjected to alkali washing followed by excess washing with deionised water to ensure neutrality prior to further processing. Then, wet sheets were pressed with blotters for 5 min at a pressure of 0.4 MPa to remove excess water. Drying was then performed under constraint at controlled conditions (23 °C and 50% RH) for at least 24 h, according to ISO 5269–1:2005 prior to mechanical evaluation. An overview of the used experimental conditions and setup are shown in Table 1 and illustrated in Fig S1 (Supplementary materials), respectively.

Densification

Selected samples from sheet steeping were densified by hot pressing to explore the possibility to further enhance the mechanical performance. Samples were compressed in a continuous press manufactured by IPCO AB, described in detail by Joelsson (Joelsson et al. 2021). The press is designed with an infrared-heated steel belt carrying the sample into a roll nip pressure point, applying a line pressure across the sample as it passes through. Samples were pressed at a temperature of 105 °C with a line pressure of 27.5 kN/m, approximated to 5.5 MPa, with a speed of 0.5 m/min.

Analysis

Intrinsic viscosity

The intrinsic viscosity of the pulp samples was determined according to the standard method ISO 5351:2010. Pulp samples were weighted, dispersed in water, and dissolved in 1 M cupri-ethylenediamine (CED) solution. The dissolved pulp in CED was then analysed by timing flow through a capillary tube viscometer (Viscomat II) using a shear rate of $200 \pm 10 \text{ s}^{-1}$.

Chemical oxygen demand

The COD was measured using a Lange LCK 114 COD cuvette tube test (150–1000 mg/L O₂). The first filtrate sample from the Büchner filtration was diluted with Milli-Q H₂O to a dilution factor of 20. After this, 2 ml of sample was pipetted into the test tube. The sample was then heated in a thermostat at 148 °C for 2 h and was then allowed to cool before it was measured in the HACH LANGE DR 2800 spectrophotometer.

Molecular weight distribution

The molecular weight of holocellulose pulp and selected alkali-treated pulp samples was determined by size exclusion chromatography (SEC), using an Agilent PL-GPC 220 with a refractive index (RI) detector. Three 20 µm Mixed-A columns (Polymer lab) were used, one guard column and two 30 cm columns in series. The eluent DMAc containing 0.5% LiCl was used at a flow-rate of 1 ml/min and at 70 °C. For calibration, Pullulan polysaccharide standards (Polymer lab) were used with a molecular weight of 708 000, 344 000, 200 000, 107 000, 47 100, 21 100, 9 600 and 6 100 Da. Samples were subjected to solvent exchange with methanol and DMAc, then dissolved in 8% (w/v) LiCl in DMAc and left for at least 2 days at room temperature with constant stirring. Samples were diluted to a concentration of 1.6% (w/v) and filtered before analysis.

Carbohydrate composition

Carbohydrate analysis was carried out according to SCAN-CM 71:09, briefly described as follows.

Samples were subject to two-stage hydrolysis by treatment 72% (w/w) and 2.5% (w/w) sulfuric acid solution at 30 °C and at 120 °C, respectively. The level of saccharides in the samples were determined using Ion Chromatography (Thermo Fischer Scientific).

Fourier transform infrared spectroscopy

All spectral data were collected by a PerkinElmer Fourier Transform Infrared (FT-IR) spectrometer (Frontier), equipped with a PerkinElmer Spotlight 200 FT-IR Microscope and with an integrated Micro-ATR including a 100 μm Germanium ATR crystal. Spectra collection was obtained using 128 scans, in a spectral region of 4000–580 cm^{-1} , at a 4 cm^{-1} spectral resolution. All spectral data were normalised ($A = 1$).

Wide-Angle X-ray diffraction

Wide-Angle X-ray Diffraction (WAXD) measurement was carried on an Anton Paar's SAXSpoint 2.0 system (Anton Paar, Graz, Austria) equipped with a Microfocus X-ray source (Cu $K\alpha$ radiation, wavelength 1.5418 Å) and an Eiger R 1 M detector with

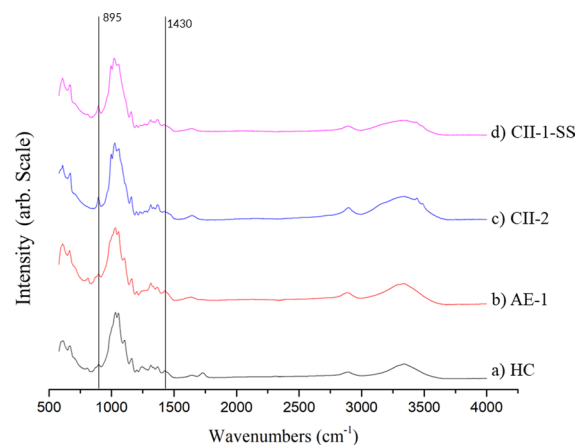


Fig. 2 FT-IR spectra of alkali treated holocellulose after washing with deionised H₂O and dried. **a** Holocellulose pulp (HC), **b** AE-1 (pulp, 5%NaOH, 5 °C), **c** CII-2 (pulp, 18%NaOH, 1200 min), and **d** CII-1-SS (oriented sheets, 18%NaOH, 10 min). The peaks marked at 895 cm^{-1} and 1430 cm^{-1} are attributed to cellulose II and cellulose I, respectively

75 \times 75 μm pixel size. All samples were measured with a beam size of 500 μm at room temperature. The sample to detector distance was 77 mm. The samples were exposed for 10 min. The data reduction was performed by using SAXS analysis software. The crystallinity was calculated based on the amorphous and crystalline area determined from WAXD peaks.

Scanning electron microscope

SEM imaging was performed to determine the pulp samples morphologies using a JEOL microscope, model JSM – 6610LV, equipped with an X-ray detector from Oxford instruments. Prior to SEM observations, the pulp samples were air-dried on a specimen holder and coated with a thin layer of carbon. The oriented sheet fibres morphologies were investigated using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan). Prior to imaging,

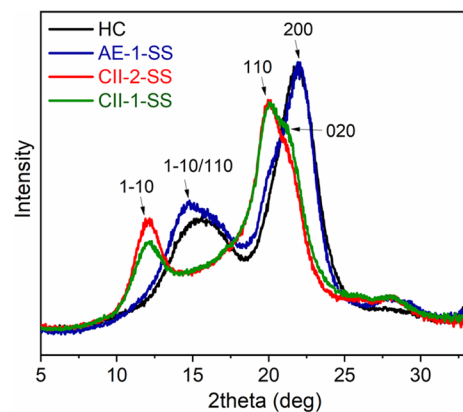


Fig. 3 WAXD curves for untreated holocellulose sheet (HC), alkali extracted (AE) (5%NaOH) and mercerised (18%NaOH) oriented sheet steeping samples (CII-1-SS (10 min) and CII-2-SS (1200 min))

Table 2 Crystallinity of untreated holocellulose sheet (HC), alkali extracted (AE) and mercerised sheet steeping samples determined from WAXS curves

Samples	Crystallinity (%)
Holocellulose HC	43.2
AE-1-SS	38.3
CII-1-SS	33.7
CII-2-SS	35.5

the samples were sputter-coated with Pt/Pd (Cressington 208H, UK).

Paper mechanical testing

Prior to mechanical evaluation, paper sheets were conditioned for a period of at least 24 h at 23 °C and 50% RH. Strips of paper sheets were cut to 10- or 15-mm width and ~65 mm length and tested for tensile properties using a gauge length of 50 mm in a Lorentsson & Wettre paper testing setup at a speed of 100 mm/min.

Results and discussion

Characterisation of wood pulp fibre sheets

FT-IR and WAXS were used to characterise cellulose structure after alkali treatment according to Table 1. The FT-IR technique can characterise the

two polymorphs of cellulose; cellulose I and cellulose II. For example, Dinand et al. 2002; Hurtubise and Krassig 1960; Nelson and O'Connor 1964; Oh et al. 2005 showed that the bands at 1430 cm^{-1} and 895 cm^{-1} could be used to study cellulose crystal structure since cellulose I and cellulose II spectra differ in these two bands. In cellulosic pulp fibres with a significant amount of cellulose I, the characteristic band is at 1430 cm^{-1} . For samples with more cellulose II, the absorption band at 895 cm^{-1} should be more pronounced. In cold alkali treated samples, the band assigned to cellulose I (1430 cm^{-1}) is present in the AE-1 sample (pulp, 5%NaOH, 10 min, 5 °C) (Fig. 2), and the cellulose I form is maintained. For samples CII-2 (pulp, 18%NaOH, 1200 min) and CII-1-SS (oriented sheets, 18%NaOH, 10 min), the band 895 cm^{-1} shows increased intensity. Furthermore, in the spectra range of 3000–3500 cm^{-1} , cellulose II samples (i.e. CII-2 and CII-1-SS) show significant differences in the bands at 3446 cm^{-1} and 3488 cm^{-1} . These bands are assigned to –OH stretching

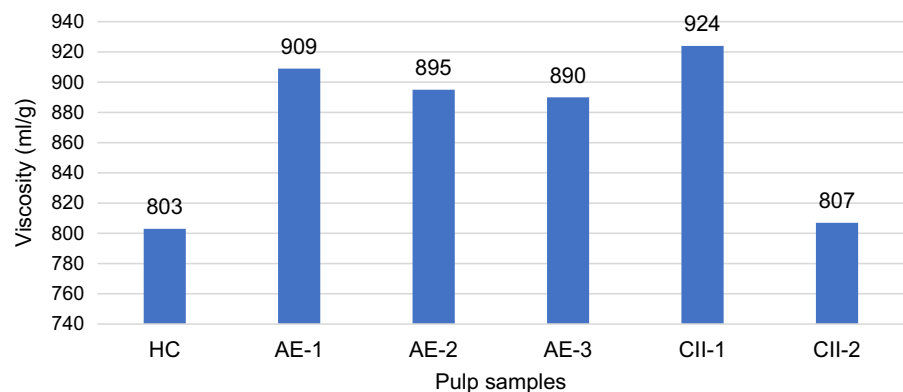
Table 3 Carbohydrate composition of holocellulose pulp and selected alkali treated pulp

Samples	t (min)	Glucose (g kg^{-1})	Hemi- cellulose ^a (g kg^{-1})	Arabinose (g kg^{-1})	Galactose (g kg^{-1})	Xylose (g kg^{-1})	Mannose (g kg^{-1})
HC	0	705	210,5	1	3,1	54,8	114
AE-1	10	842	93,0	0	0,6	6,9	64,3
AE-3	1200	829	99,6	0	1	5,8	69,8
CII-1	10	871	93,463	0,4	1,3	10,5	61,1
CII-2	1200	948	30,5	0	0	4,8	19,3

Note that NaOH concentration is much lower for AE samples (5%, 5 °C) compared with CII samples (18%, 23 °C)

^aTotal amount of hemicelluloses is expressed as the sum of xylose, arabinose, galactose, and mannose, assuming an addition of glucose at glucose: mannose ratio of 1:3

Fig. 4 Intrinsic viscosity for holocellulose (labelled as HC) and alkali treated samples (labelled as AE, and CII, see Table 1)



intermolecular hydrogen bonds in cellulose II and not observed in cellulose I (Carrillo et al. 2004; Široký et al. 2010); see Fig. 2. These changes confirm that at higher NaOH concentration, 18% (w/w), cellulose I was transformed to cellulose II.

WAXS data are presented in Fig. 3 and Table 2, and it is confirmed that the treatment in 18% NaOH results in conversion from cellulose I to cellulose II. In Fig. 3, the intensities of the lattice plane peaks are apparent by colour coding for the four different materials: the unmodified holocellulose reference (HC), alkali extracted at 5% NaOH (AE-1-SS) and at 18% (CII-1-SS and CII-2-SS), see conditions in Table 1. Intensities of peaks from different planes are quantified in Fig. 3, and estimated crystallinities are in * MERGEFORMAT Table 2. It is interesting that the holocellulose reference and the cold alkali sample AE-1-SS show almost identical (200) plane peaks, indicating that the cellulose microfibril structure is undamaged by the 10-min treatment, although hemicellulose content is reduced (Table 3). In contrast, the CII-1-SS and CII-2-SS samples show not only cellulose II structure ((1–10), (110) and (020) peaks in Fig. 3) but also that the fraction of disordered regions is increased.

The intrinsic viscosity of the pulp steeping samples (alkali treatment of pulp fibres rather than sheets) was measured to determine conditions in cold alkali extraction and mercerisation in which hemicelluloses could be removed without significant cellulose degradation (see Fig. 4). Dissolved pulp viscosity is known to increase when low molar mass molecules (mainly hemicelluloses) are removed through alkali treatment (Sixta 2006). For cold alkali extracted pulp, viscosity reaches its highest value after 10 min treatment (see AE-1 sample). After that, the viscosity decreased. Fast removal of primarily hemicelluloses during the first 10 min of cold alkali extraction was supported by SEC data, in accordance with increased viscosity AE-1 (see MWD curve in Fig S1). Results from MWD need to be interpreted with care since full dissolution was not confirmed. Samples treated with higher NaOH concentration show similar behaviour; viscosity increases after 10 min treatment but decreases after prolonged treatment (Fig. 4). Wood cellulose shows almost instantaneous swelling at low temperature, facilitating the extraction of low molar mass fractions (mainly hemicelluloses) (Sixta 2006). The drop in viscosity with longer treatment (samples

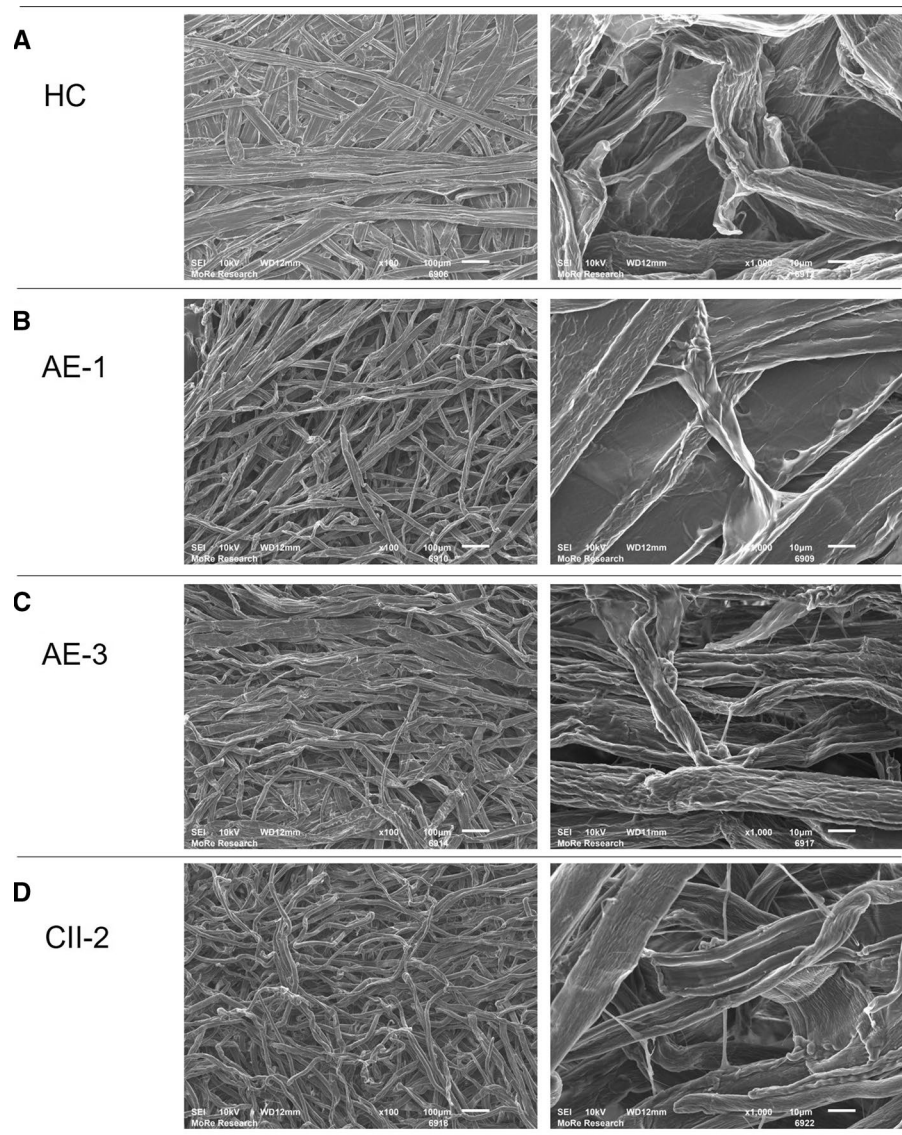
AE-2, AE-3, and CII-2) is due to reduced cellulose molar mass during prolonged alkali treatment (Golova and Nosova 1973; Knill and Kennedy 2002; Saukkonen et al. 2012; Albán Reyes et al. 2016).

Next, the carbohydrate composition of the holocellulose pulp, cold alkali extracted pulp and mercerised pulp was measured, see Table 3. The cold alkali treatment effectively removed hemicelluloses, especially xylose. The increased viscosity must then be due to the removal of hemicelluloses. In the first 10 min of the extraction, the hemicellulose content decreased by 56%. However, prolonged extraction time (1200 min, sample AE-3) does not necessarily mean a decrease in hemicellulose fraction. On the contrary, data show a slight increase in hemicellulose fraction (w/w), possibly by reduced glucose content from cellulose degradation. Reduced viscosity (see Fig. 4) and increased COD, i.e., dissolved organic material in the filtrate, with prolonged time (see supplementary material Fig S2), are in support of reduced cellulose molar mass and weight fraction due to degradation.

When holocellulose pulp is mercerized, the hemicellulose content is reduced from 210.5 g/kg to only 30.5 g/kg, see sample CII-2, Table 3. The two materials treated for 10 min (AE-1 and CII-1) show very similar levels of hemicelluloses despite NaOH concentration differences. Note that although the same alkali treatment conditions were used for wet pulp and dry oriented fibre sheets, wet pulp shows slightly higher reduction in hemicellulose content than dry sheets, see supplementary material Fig. S3. This is in accordance with results by Spinu et al. 2011.

The SEM micrographs show significant fibre shape effects from alkali treatments (Fig. 5). The untreated holocellulose fibres spontaneously collapse during drying and appear flat, ribbonlike and straight, while the alkali-treated fibres show a more porous network in the dried state with smaller, irregular diameters and shapes. Alkali treated fibres are also more swirled in an irregular manner, rather than straight, see Fig. 5. When comparing cold alkali extracted pulp (B and C) with mercerised pulp (D), the mercerised fibres appear to have a more tubular shape and be more curved and wavy. It is worth noting that (C) samples treated for an extended time (20 h) show rougher fibre surface morphologies, perhaps related to microfibrils. A short treatment time (10 min) of holocellulose wood fibres seems to make fibres wavier, less flat, and, as established, with lower hemicellulose content.

Fig. 5 SEM images of pulp fibres; **A** holocellulose (HC), **B** 10 min cold alkali treatment (AE-1), **C** 20 h cold alkali treatment (AE-3), and **D** mercerised 20 h (CII-2). All samples were washed with deionised H₂O and air-dried



Pulp or sheet steeping in alkali?

The two methods, pulp steeping and sheet steeping, were compared to consider these routes for subsequent preparation of hot-pressed fibres or biocomposites. Fibre orientation was achieved by a dynamic sheet former. Cold alkali treated and mercerised holocellulose with 10 min treatment times were used as examples of chemical modifications for pulp and sheet steeping methods.

For pulp fibre steeping, the pulp was easy to handle during alkali treatment. The fibres became highly swollen once in contact with the lye. However, in the

following oriented sheet preparation step, the handling of wet fibre sheets was challenging. This was especially problematic for the mercerised fibre sheets, which tended to disintegrate during removal from the wire mesh (see Fig S4).

Sheet steeping, in contrast, meant that it was straightforward to prepare high quality, oriented sheets from holocellulose fibres. The steeping stage of dry holocellulose sheets was slightly more elaborate than for pulp and required care to prevent damage of submerged holocellulose sheets in the swollen state. Cold alkali extracted paper sheets easily fell apart if mishandled. The mercerised sheets were less

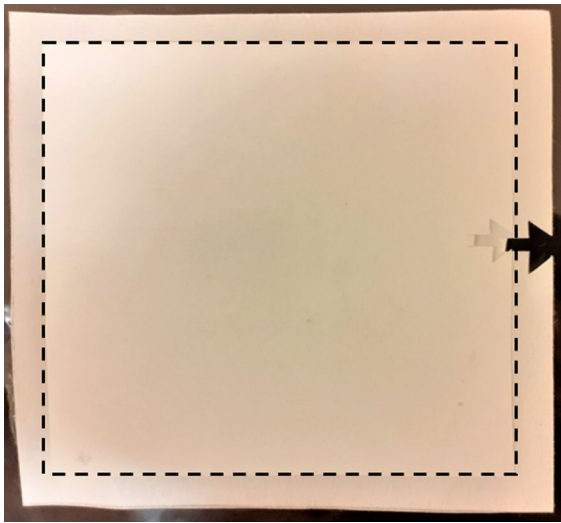


Fig. 6 Shrinkage of holocellulose sheet during submersion in lye for mercerisation. The dashed square represents the new dimensions of the mercerised sheet after shrinkage

sensitive but showed notable shrinkage once get in contact with the lye (see Fig. 6). The level of shrinkage is in the order of 13–14%. Similar shrinkage was also reported when sheets from bleached kraft pulp and microfibrillated cellulose were treated with 20% NaOH (Nakagaito and Yano 2008). A possible explanation for the observed shrinkage is the longitudinal contraction of microfibrils proposed by Nakano (Nakano et al. 2000; Ishikura and Nakano 2007), and here we observed that fibres themselves also changed shape, possibly due to microfibril shrinkage. No shrinkage was observed for cold alkali treated sheets.

SEM micrographs of the oriented fibre sheets were obtained to investigate the morphological effects on the sheet network from the two protocols (pulp steeping and sheet steeping). The untreated holocellulose fibres are straight, flat and aligned from the dynamic sheet forming step (Fig. 7A). Sheets made from pulp steeping protocol in Fig. 7C, E (first alkali treatment, then sheet preparation) have less oriented fibres, also curved. This must be due to changes in fibre shape during alkali treatment (see Fibre properties section, Fig. 5). The straight holocellulose fibres are much easier to orient in the dynamic sheet former than the alkali treated fibres, which are curved and wavy. Materials made via sheet steeping protocol appear to preserve the orientation of the holocellulose sheet, with more straight fibres. It is evident that the degree

of fibre orientation is higher in sheet steeping than pulp steeping protocols (see B and C for cold alkali extraction, and D and E for mercerisation in Fig. 7). Furthermore, it is noted that despite the observed shrinkage of mercerised sheets, the fibres appear to broadly maintain their preferred orientation.

Materials were then subjected to physical and mechanical testing. Results are shown in Fig. 8 and summarised in Table 4. Sheets made from untreated holocellulose fibres show excellent properties. The density is 706 kg/m^3 , anisotropy of longitudinal/transverse strength ~ 5 , tensile strength 172 MPa, and Young's modulus 16.8 GPa. The reason is better utilization of axial fibre properties in sheets with preferred fibre orientation in one direction. Since the level of anisotropy in properties should correlate with the degree of fibre orientation in the sheet, a higher anisotropy value is desirable. Pulp steeping samples (AE-1-PS and CII-1-PS) have an anisotropy of strength of < 2 , while sheet steeping samples (AE-1-SS, CII-1-SS) maintain the anisotropy of the untreated sheet at ~ 5 . These results are supported by SEM micrographs in Fig. 7 in that there is less orientation in the fibre network of pulp steeping samples. This reduces tensile properties in the machine direction.

We observe that the choice of alkali treatment protocol affects mechanical performance. Pulp steeping results in lower density and inferior mechanical performance, more noticeable in mercerised samples (Table 4; Fig. 8). Samples prepared by sheet steeping show higher density and better mechanical performance. The difference in mechanical performance is dramatic; samples prepared by sheet steeping are 8–10 times stronger than those prepared from the pulp. Modulus is also superior for sheet steeped samples, but here the effect is less pronounced. Lower stiffness in mercerised samples is expected since cellulose II is less stiff than cellulose I (Nishino et al. 1995), although interfibre bonding and fibre orientation also are of obvious importance. The superior mechanical strength and modulus of materials from the sheet steeping protocol is due to higher density (higher volume fraction fibres), a higher degree of orientation and possibly better interfibre adhesion.

Figure 9 shows stress–strain behaviour for representative materials. A significant increase in strain to failure (ϵ) is observed for the mercerised materials prepared by sheet steeping, and the behaviour is

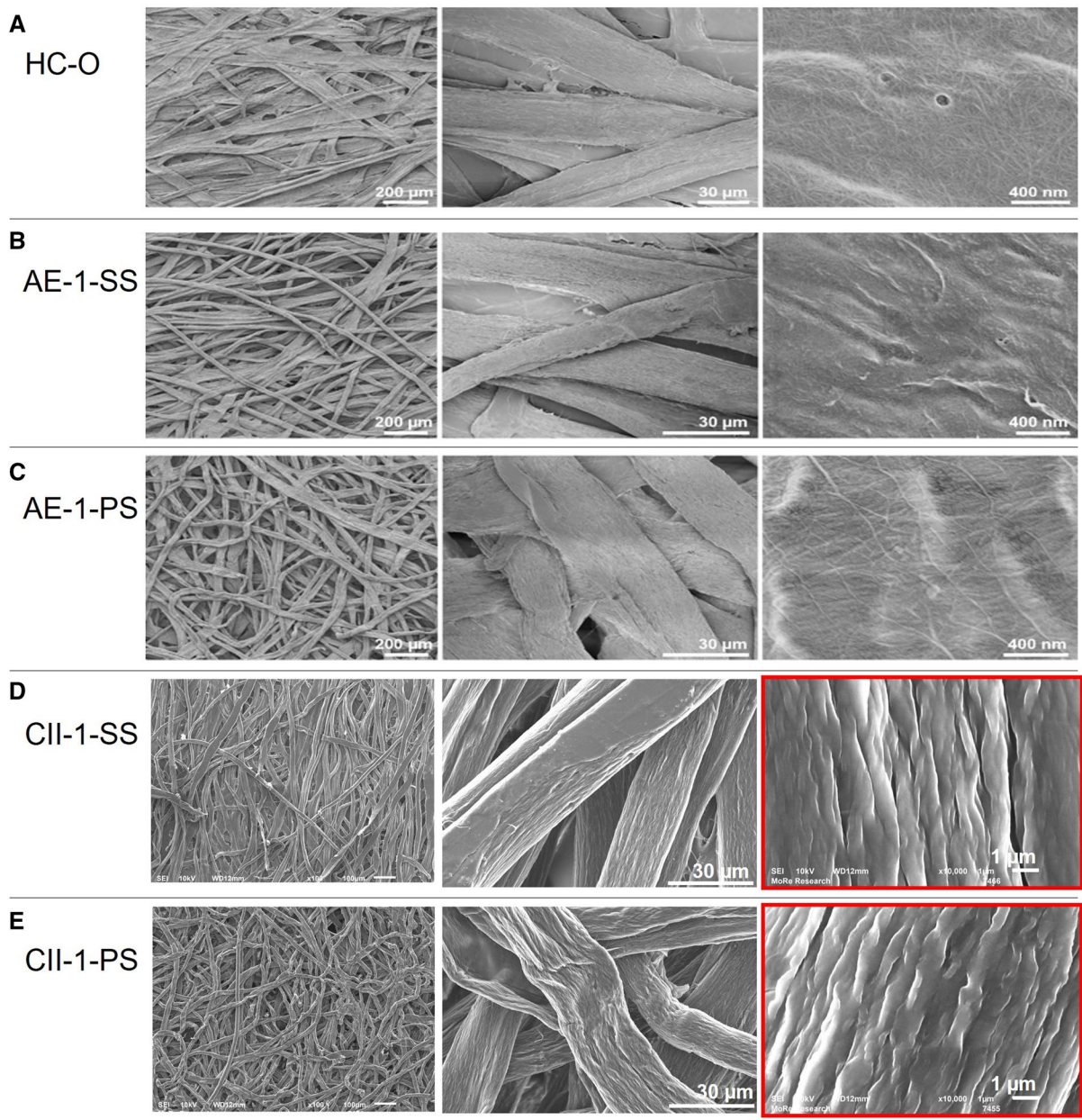


Fig. 7 SEM micrographs of the dried oriented fibre sheets from **A** holocellulose (HC-O), **B** 5% alkali-extracted holocellulose sheet (AE-1-SS), **C** 5% alkali-extracted holocellulose pulp (AE-1-PS), **D** cellulose II transformed sheet (CII-1-SS, 18% NaOH, 10 min), and **E** cellulose II transformed pulp (CII-

1-PS, 18%NaOH, 10 min). Note that image orientation is not aligned with fibre orientation and that the scale bar in the third image for **D** and **E** is different from **A–C**. Images 7a–c courtesy of C. Montanari

more non-linear with lower yield stress and more ductile behaviour. Nakagaito et al. previously showed an increased ductility in microfibrillated cellulose (MFC) sheets mercerised by sheet steeping. This effect was also observed in composites reinforced

with mercerised MFC or wood pulp sheets (Nakagaito and Yano 2008). Although the experimental conditions were different Gomes et al. reported a doubling in strain to failure from 4% to ~9% for individual curaua fibres treated for 2 h with 15% NaOH

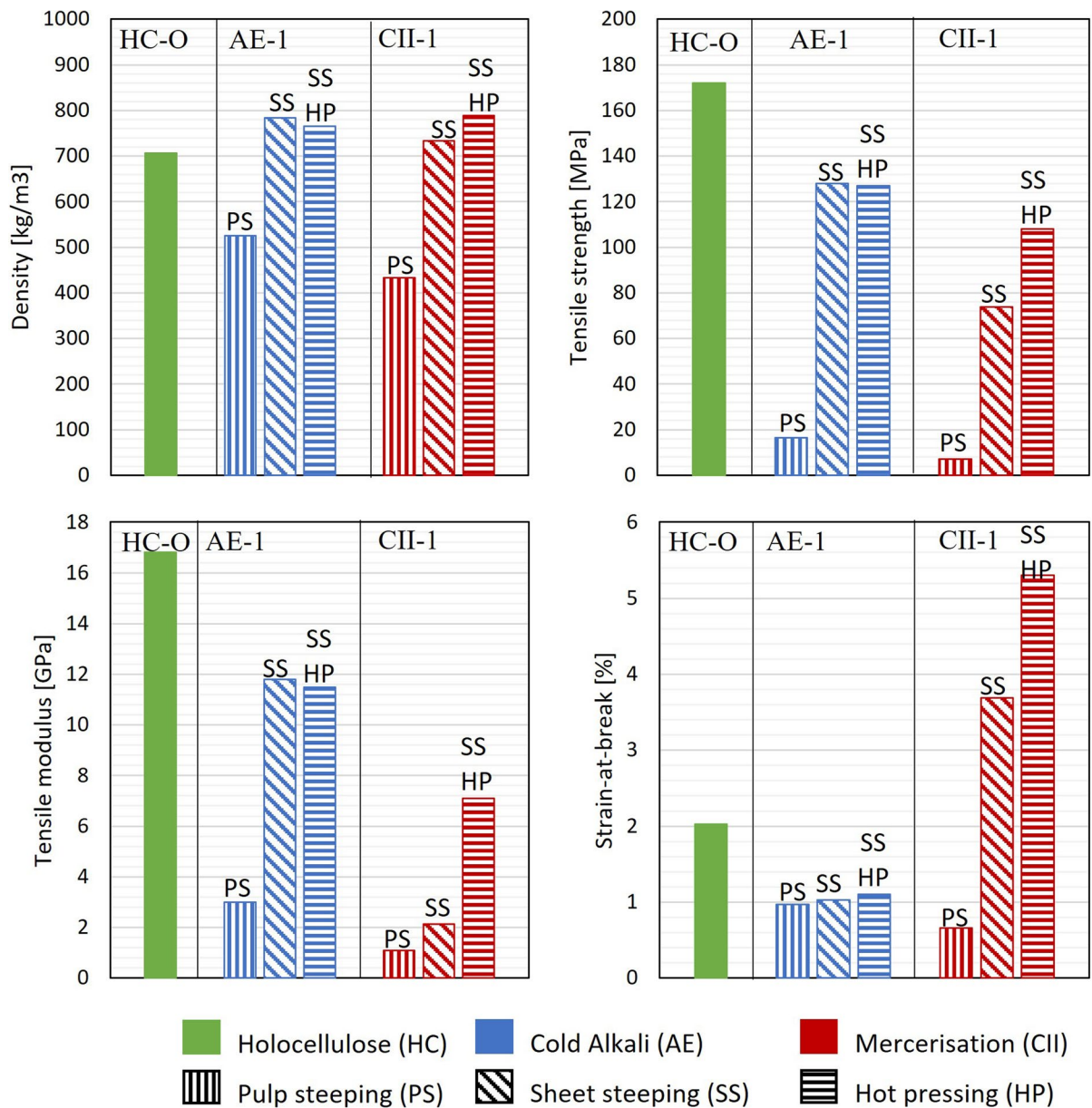


Fig. 8 Comparison of mechanical performance of oriented fibre sheets from holocellulose reference (green), cold alkali treated (blue) and mercerised (red). Pulp steeping (vertical

lines), sheet steeping (slanted lines), and effect of hot pressing on samples from sheet steeping (horizontal lines). Time of alkali treatment = 10 min

solution (Gomes et al. 2004). The increase in ductility is helpful in that the original brittleness problem of the oriented fibre material is solved. It is worth noting that in paper-making, the shrinkage of fibre networks during the drying process is associated with an increased strain-at-break (see, e.g. Nagel 2001; Strand et al. 2018). In the present study, the shrinkage was observed immediately once the sheet got into

contact with the lye, and not during the drying process. Nevertheless, it would be of interest to analyse the possible association between shrinkage and gain in strain-at-break and how this is translated into composites applications in future studies. It is noted that for sheets prepared from mercerised pulp, increase in ductility was not observed (see Table 4). Possibly, the poorly bonded fibre network (low density and low

Table 4 Physical and mechanical properties of prepared pulp fiber sheets

	Grammage	d	ρ	V_f^b	σ^c	E	ϵ	Strength
Sample ^a	[g/m ²]	[μ m]	[kg/m ³]	[%]	[MPa]	[GPa]	[%]	Anisotropy
HC-O	103 (1)	145 (4)	706 (14)	46	172	16.8	2.03	5.4
AE-1-PS	102	194	525	34	16.5	3.0	0.97	1.8
AE-1-SS	103 (1)	132 (2)	784 (21)	51	128	11.8	1.03	4.8
AE-1-SS/HP	80 (2)	105 (3)	765 (14)	49	127 (10)	11.5 (1.1)	1.1 (0.1)	N/A
CII-1-PS	77.8	180	433	28	7.25	1.1	0.66	1.4
CII-1-SS	120 (2.6)	164 (3.1)	733 (25)	47	73.8	2.14	3.69	5
CII-1-SS/HP	115 (3.8)	146 (2.3)	789 (29)	51	108 (7.2)	7.1 (0.3)	5.3 (0.4)	N/A

Data for oriented sheets are measured along the axis of preferred orientation. Standard deviations are available in parentheses. Note that d —thickness, ρ —density, V_f —fibre volume fraction, σ —tensile strength, E —Youngs modulus and ϵ —strain to failure

^aPS indicates sample was prepared from pulp steeping, SS indicates sample was prepared using sheet steeping, HP indicates sample was densified by hot pressing

^bFibre volume fraction as calculated based on $V_f = \rho/1550\text{kg}/\text{m}^3$

^cFor reference, typical paper structures from spruce have a strength value of 50 MPa (Pettersson et al. 2021)

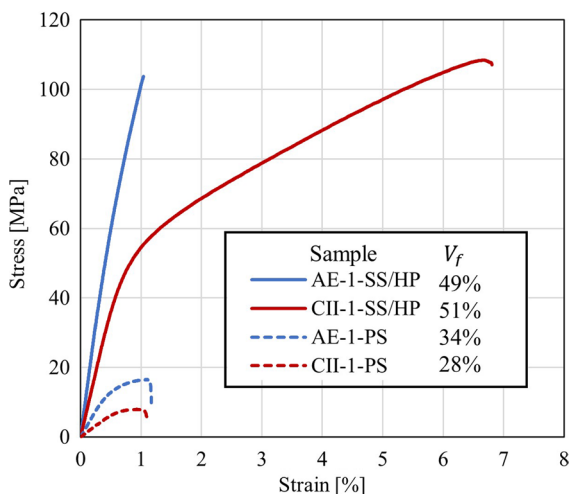


Fig. 9 Stress–strain curves for representative samples of cold alkali extracted fibres (AE-1, 5% NaOH) and mercerised fibres (CII-1, 18%NaOH) prepared by sheet steeping with hot pressing (SS/HP) and pulp steeping (PS). Time of alkali treatment = 10 min. Note differences in fibre volume fraction

strength) resulted in poor interfibre stress transfer; thus, any gain in ductility of the fibres is not reflected in the sheet behaviour.

We next used sheet steeping samples to explore the possibility of further improving mechanical performance by using a continuous hot press (105 °C, ~5.5 MPa) available as an industrial process. In our test with cold alkali treated sheets,

no significant effect was observed. The mercerised sheets, however, showed substantial increase in strength (108 vs 74 MPa), modulus (dramatic increase: 7.1 GPa vs 2.1 GPa) and strain to failure (5.3% vs 3.7%) accompanied by an increase in density and fibre volume fraction, see CII-1-SS/HP in Table 4. The increase in modulus is remarkable, becoming more than 3 times higher than non-densified sheets, although the density is only mildly increased. The most likely explanation is improved interfibre bonding from hot-pressing.

Sheet steeping potential

Collectively our results show that the sheet steeping protocol allows physical and chemical modification of fibres without sacrificing good network properties such as density and fibre orientation for the studied chemical modification (alkali treatment). The main challenge of the developed protocol is handling of the modified sheets, especially alkali extracted samples. Nevertheless, sheet steeping protocol allows for increased fibre orientation and density (fibre volume fraction) in the sheet compared with pulp steeping. Higher fibre orientation and density are important for mechanical performance. The high degree of fibre orientation is due to well-preserved, straight holocellulose fibres that facilitate subsequent fibre alignment. For the pulp steeping protocol in contrast, alignment

of the chemically treated pulps is challenging due to changes in fibre shape, as treated fibres were observed to be more wavy and curved than untreated holocellulose fibres. For sheet steeping, transformation to cellulose II and extraction of hemicelluloses, at comparable levels to pulp steeping, was achieved while maintaining the network structure. The mercerised sheet steeping material showed increased strain to failure in tensile testing. Rapid hot-pressing of mercerised sheets using a scalable belt-press resulted in much improved Young's modulus, strength and strain to failure; this is an inspiration for further studies of thermoformed "molded fibre" type of materials.

Conclusions

The use of wood fibre reinforcement for biocomposites or for hot-pressed fiber materials, based on holocellulose fibres and mild chemical treatments is rather unexplored, despite advantages, e.g. compared with melt-compounded wood fibre biocomposites. Fibres will have improved intrinsic strength since mechanical, thermal and chemical fibre degradation is relatively low. In addition, fibres can be of very high aspect ratios, straight and have controlled orientation. The present fibre volume fraction of the reinforcement was around 50%, which facilitates the manufacturing of high fibre volume fraction biocomposites.

This approach to fibre modification of preformed, oriented wood fibre sheets (high fibre volume fraction paper structures) is promising. Both cold alkali treatment (hemicellulose removal) and mercerisation (conversion from cellulose I to cellulose II) were carried out successfully; the potential of modified sheets as biocomposites reinforcement is encouraging. The wood fibre sheets showed high mechanical integrity, and the increased ductility of mercerised sheets is relevant to load-bearing applications of pulp fibre materials. The increased ductility is not only from the cellulose II structure but also from changes in fibre shape, from straight to more curved and wavy fibre segments.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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