

Fibre Stress-Strain Response of High-Temperature Chemi-Thermomechanical Pulp Treated with Switchable Ionic Liquids

Ran Duan,^{a,*} Bo S. Westerlind,^a Magnus Norgren,^{a,*} Ikenna Anugwom,^{b,c} Pasi Virtanen,^b and Jyri-Pekka Mikkola^{b,c}

The removal of lignin from a high-temperature chemi-thermomechanical pulp (HT-CTMP) using a switchable ionic liquid prepared from an organic superbase (1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU)), monoethanol amine (MEA), and SO₂ was investigated. The objective was to measure the fibre properties before and after removal of the lignin to analyse the contributions from lignin in the HT-CTMP fibre to the tensile properties. It was found that the fibre displacement at break - measured in zero span, which is related to fibre strain at break - was not influenced by the lignin removal in this ionic liquid system when tested dry. There was a small increase in displacement at break and a reduction in tensile strength at zero span when tested after rewetting. At short span, the displacement at break decreased slightly when lignin was removed, while tensile strength was almost unaffected when tested dry. Under rewetted conditions, the displacement at break increased and tensile strength decreased after lignin removal. Nevertheless, no dramatic differences in the pulp properties could be observed. Under the experimental conditions, treatment with the ionic liquid reduced the lignin content from 37.4 to 15.5 wt%.

Keywords: Ionic liquid; Delignification; Spruce; Cellulose; Zero span; Short span

Contact information: a: Fibre Science and Communication Network (FSCN), Mid Sweden University, SE-851 70 Sundsvall, Sweden; b: Technical Chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, Sweden; c: Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Finland;

* Corresponding authors: ran.duan@miun.se, magnus.norgren@miun.se

INTRODUCTION

The need to develop new, economically feasible techniques that can either replace or complement existing techniques or processes is of high importance. This would improve the properties of products and discover value-added products from woody biomass while aiming to break our dependency on fossil resources. Although several promising methods and solvents have already been introduced (Ramos 2003), new approaches are constantly being developed.

Ionic liquids (ILs) have been widely studied as efficient solvents for treatment, functionalization, or fractionation of lignocellulosic materials; their dissolution properties are unique and can, at best, offer an environmentally friendly option with an appropriate choice of cations and/or anions. ILs are salts composed primarily of organic cations and organic or inorganic anions and have melting points usually below 100 °C. Many ILs also exhibit high thermal and chemical stability and a wide range of fluid behaviour (Mäki-Arvela *et al.* 2010). Many ILs are able to dissolve lignocellulosic material or one or more

of its major components: cellulose, hemicelluloses, and lignin (Wasserscheid and Welton 2006; Sun *et al.* 2009; Tan *et al.* 2009). More recently, however, a new class of ILs called switchable ionic liquids (SILs) have been studied as fractionation solvents for lignocellulosic materials (Anugwom *et al.* 2012, 2014). A unique property of SILs is that they are solvents capable of ionic/non-ionic switching with the addition or removal of one compound, a so-called trigger (Heldebrant *et al.* 2005; Jessop *et al.* 2005; Anugwom *et al.* 2011). In addition, they can be prepared from inexpensive chemicals such as monoethanol amine (MEA), the amidine 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), and a typical trigger that can be obtained from industrial flue gases, such as CS₂, CO₂, and SO₂. The use of SILs as solvents for lignocellulosic material can facilitate selective extraction or selective enrichment of the material by the choice of the trigger (CS₂, H₂S, COS, NO_x, CO₂, SO₂, *etc.*) alkanol amine, or the organic superbases (amidine/guadinine) during the synthesis of the SIL (Fig. 1).

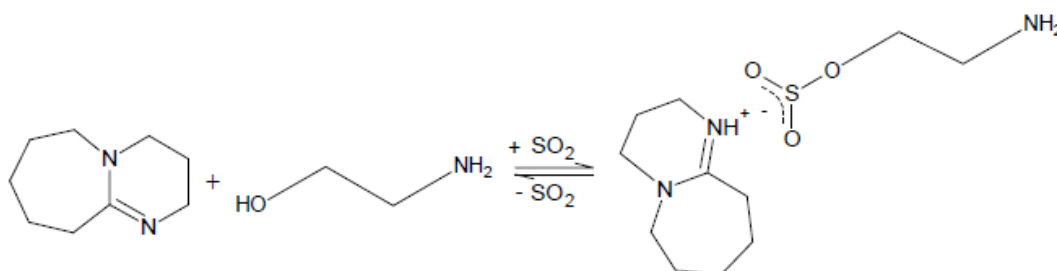


Fig. 1. Structure of the SIL: MEA-DBU-SO₂-SIL (adapted from Anugwom *et al.* 2012)

Methodology for Determining the Mechanical Properties of Paper

The typical limitations coupled to fractionation methods are associated with the cost of the whole process. It has been established that each of the three main components of woody biomass are themselves valuable resources, if selectively separated. As one of the most abundant natural polymers, lignin is expected to play a vital part in the near future as a raw material for production of bio-products as well as in bio-derived chemicals (Norgren and Edlund 2014). Nevertheless, large amounts of lignin are being produced as a by-product in the classical pulp and paper industry during delignification (Ramos 2003; Pu *et al.* 2007), thus producing degraded (and sulfonated) lignin. This lignin primarily finds use in low-added value applications and energy production. Extracting lignin in its native form has been rather challenging. This is attributed to its structure, which is irregular, with a highly condensed cross-linked polymer network that provides the lignocellulosic material with both mechanical strength and the rigidity to resist external forces (Ebringerova and Heinze 2000; Ebringerova 2005).

In pulp processing, the wood fibres are separated from each other (the wood chips) solely or by a combination of chemical and mechanical processes (Sjöström 1993). One of the differences between mechanical and chemical pulping is that mechanical pulping does not appreciably delignify fibres, while lignin is removed to a greater extent during chemical pulping and is almost completely removed after bleaching (Gellerstedt 1996).

Paper is a network of lignocellulosic fibres in which the in-plane tensile strength is determined by the tensile strength of individual fibres, the strength of the bonds between the fibres, the number of fibre-to-fibre contact points, the fibre length to diameter ratio, and the fibre orientation (Page 1969; Jayaraman and Kortschot 1998; Hägglund *et al.* 2004). Paper qualities made of chemical pulps are denser, stronger, stiffer, and more ductile than paper made from mechanical pulps derived the same wood source. This is due to the

differences in pulp properties resulting from different technologies used for liberating the fibres (Höglund and Wilhelmsson 1993; Seth 2004). The higher density results because lignin and hemicelluloses are removed from the fibre cell wall. Without lignin in the fibre wall, the fibre lumen will collapse more easily; the fibre will then be more flexible and conform easier to a fibre network, forming stronger fibre-to-fibre bonds (Seth 2004). Fibres from mechanical pulps generally have a lower zero span tensile strength than chemical pulp fibres (Seth *et al.* 1989). Furthermore, it has been shown that chemical cooking introduces changes in the structure of the fibre wall, which might influence the resulting mechanical response of the fibre (Hult *et al.* 2000). The strain at break for a paper made of bleached chemical pulp is also higher than that for unbleached pulp (Seth 2004). This might be due to the removal of lignin and internal delamination of the cellulose structure during bleaching, which lead to greater fibre conformability.

To measure the tensile strength of a single fibre, several methods have been developed (Duncker and Nordman 1965; Page *et al.* 1972; Groom *et al.* 2002). However, the short length of pulp fibres makes it difficult to measure the tensile strength of a single fibre, and the large variation among fibres from a given pulp requires many fibres to be tested to determine a representative average value. Fibre strength measured on a single fibre may also not be representative of the strength of a fibre in the paper because, in this case, the fibres are dried under the influence of stresses (Vainio and Paulapuro 2007). The zero span tensile test is considered to be an alternative for accessing fibre tensile strength because it is a fast method that provides an average value of all the fibres that bridge the gap between the two jaws in the tester. The zero span measurement method was introduced by Hoffman-Jacobsen in 1925 (Hoffman-Jacobsen 1925) and has been further improved over the past 50 years (Cowan and Cowdery 1974; Gurnagul and Page 1989; Batchelor *et al.* 2006). The boundary conditions in a zero span tensile test with a short clamped length give a non-homogenous stress field in the test zone, with stress concentrations at the edges of the specimen (Cook and Young 1985). Therefore, it is necessary to retain the weight and keep test conditions constant throughout the duration of a trial, allowing valid comparisons to be made between the samples (Batchelor *et al.* 2006). However, many authors support the idea that this test method can be used as an indicator of the fibre strength (Clark 1944; Van Den Akker *et al.* 1958; Varanasi *et al.* 2012).

The objective of this study was to preserve most of the original fibre properties using low-intensity, high-lignin content HT-CTMP as a starting material, and then to investigate how lignin removed by a switchable ionic liquid influences fibre strength. This was measured at zero and short span tensile strengths. Changes the hydrophobicity of the fibres were also investigated. Removing lignin with an ionic liquid might provide a gentle treatment for cellulose fibres, leaving the molecular weight and crystallinity of the cellulose intact while maintaining the length and orientation of the fibrils in the fibre wall.

EXPERIMENTAL

Norway spruce (*Picea abies*) high-temperature chemi-thermomechanical pulp (HT-CTMP) was obtained from SCA Östrand (Sundsvall, Sweden). The pulp was flash-dried in the mill and had a Canadian standard freeness (CSF) value of 742 mL and a brightness of 70 ISO. 1,8-Diazabicyclo-[5.4.0]-undec-7-ene (DBU, 99%) and monoethanol amine (MEA, 99%) were used as received from Sigma Aldrich (Finland). Sulphur dioxide (SO₂, 99.998%, H₂O < 3 ppm) was provided by AGA Oy (Linde Group, Finland).

The SIL was prepared from DBU, MEA, and SO₂ via a procedure described in detail previously (Anugwom *et al.* 2011). In short, an equivalent molar mixture of DBU and MEA was added to a three-necked flask, and the flask was placed in a cooling bath. Because of the addition of the acid gas, an exothermic reaction occurs. As SO₂ was bubbled through the mixture under rigorous stirring, the readily exothermic reaction was allowed to proceed freely upon sparging through the mixture, until the reaction to form the SIL was completed (Fig. 1). The molar ratio of the amidine (DBU) to the hydroxyl group-containing compound (MEA) was evaluated based on the number of hydroxyl groups in the alcohol/hydroxyl-containing compound.

SIL-Treated Pulp

The HT-CTMP was treated with the SIL (DBU/MEA/SO₂) and water mixture at 140 °C for 2 and 3 h and 160 °C for 2 h. The pulp: SIL: water wt-ratio was 1:5:3. The actual SIL treatment experiments were carried out in a stirred tank reactor (Parr) of 300 mL (nominal volume) equipped with an electric heater and an internal thermocouple. A continuous stirring of the reaction mixture was achieved using a custom-made impeller (SpinChem®, Sweden) driven by a variable speed motor (Parr 4843, Parr instrument company, USA). The SpinChem® device consisted of a hollow cylinder measuring 3.2 cm in diameter and 2.9 cm long; it was equipped with rounded orifices at the sides to permit SIL flux into and out of the embedded wood chips. After treatment, the reactor was cooled and the dissolved and non-dissolved materials recovered, washed, and analysed. The samples were described as non-treated HT-CTMP, 140 °C & 2 h SIL-treated HT-CTMP (HT-CTMP treated with SIL at 140 °C for 2 h), 140 °C & 3 h SIL-treated HT-CTMP (HT-CTMP treated with SIL at 140 °C for 3 h), and 160 °C & 2 h SIL-treated HT-CTMP (HT-CTMP treated with SIL at 160 °C for 2 h), respectively.

Handsheet Preparation

The pulp was disintegrated at 85 °C using a disintegrator code 003 (Lorentzen & Wettre AB, Sweden) operating for 30,000 revolutions. A Rapid Köthen Sheet Former (PTI, Vorchdorf, Austria) was used to prepare 65 g/m² handsheets from non-treated and SIL-treated pulp by following the ISO 5269-2 standard (2004). The paper sheets were conditioned at 23 °C and 50% relative humidity before testing.

Sheet Characterization

The dynamic contact angle (DCA) was measured with DAT1100 (Fibro system AB, Sweden) dynamic absorption tester at 23 °C and 50% RH. A 4 µL droplet of water was deposited on the paper specimen surface. A series of images were captured and analysed. The dynamic wetting response through the contact angle and droplet size was measured as a function of time. A minimum of eight readings were taken on every sample by following the procedure in TAPPI T 558 (2010).

The crystalline structures were analysed using a Bruker D2 Phaser X-Ray diffractometer (Bruker AXS, Germany). Ni-filtered Cu K α radiation ($\lambda = 0.1542$ nm) was generated using 30 kV voltage and 10 mA current. The intensity range was from 5° to 35° with a scan step of 0.3°. The crystalline index (Cr. I.) was defined according to Segal *et al.* (1959) using Eq. 1,

$$Cr. I. = (I_{002} - I_{am})/I_{002} \times 100 \quad (1)$$

Where I_{002} is the diffraction intensity from the (0 0 2) lattice plane ($2\theta = 21^\circ$ to 23°) and I_{am} is the diffraction intensity referring to the amorphous component of cellulosic fibres ($2\theta = 16^\circ$ to 18°).

Apparent crystallite size (ACS) was estimated using the Scherrer equation (Eq. 2),

$$ACS = (K \times \lambda) / \beta \cos \theta \quad (2)$$

where K is a constant with the value of 0.94, λ is the wavelength of the incident X-ray (1.542 Å), θ is the Bragg angle corresponding to the (0 0 2) plane, and β is the half-height width of the peak angle of the (0 0 2) reflection.

Lignin and Sugar Analysis

The carbohydrate content of the samples was analysed by GC after acid methanolysis followed by silylation, and acid hydrolysis followed by silylation, to determine the hemicellulose and cellulose contents, respectively (Sundberg *et al.* 1996; Willför *et al.* 2009). For GC analysis, approximately 2 μ L of the silylated sample was injected through a split injector (260 °C, split ratio 1:5) into a HP-1 capillary column coated with dimethyl polysiloxane (Hewlett Packard, USA). The column length, internal diameter, and film thickness were 30 m, 320 μ m, and 0.17 μ m, respectively. The following temperature program was applied: 4 °C/min from 100 to 175 °C, followed by 12 °C/min from 175 to 290 °C. The detector (FID) temperature was 290 °C. Hydrogen was used as a carrier gas. GC-MS was used only to identify different peaks prior to the GC analysis.

The lignin content was determined using a modified Klason lignin method in which boiling for 4 h to complete hydrolysis of the polysaccharides was replaced with an autoclave treatment at 125 °C and 0.14 mPa for 90 min (Iiyama and Wallis 1988; Schwanninger and Hinterstoisser 2002).

Surface lignin coverage was calculated from the data obtained from X-ray photoelectron spectroscopy (XPS) spectra. The XPS spectra were collected with a Kratos Axis Ultra DLD electron spectrometer (Kratos Analytical Limited, Japan), using a monochromated Al K source operated at 120 W. The analyser was operated at a pass energy of 160 eV for acquiring wide spectra and a pass energy of 20 eV for individual photoelectron lines. The surface potential was stabilised by the spectrometer charge neutralisation system. The binding energy (BE) scale was referenced to the C 1s line of aliphatic carbon, set at 285.0 eV. The built-in software was used for analysing the spectra.

Zero and Short Span Measurements

The isotropic paper sheets were cut into circles with diameters of 62 mm and tested using a Pulmac Z-Span 2000 zero and short span tensile tester (Pulmac Inc., Canada) both as dry and as rewetted in a controlled atmosphere. Three circular specimens were attached between two plastic foils with 24 rectangular cut-outs or windows, eight for each specimen. During the measurement, the test windows were positioned by a built-in XY-table under 22-mm-wide grips in an automatic sequence. The distance between the clamps was 400 μ m for the short span tensile test. A clamping pressure of 97.4 MPa (80 psi on an instrument gauge) and a tensile force were applied on the specimen at a loading rate of 25 ± 2 N/s by following the procedure in ISO 15361 (2000). The load in the zero span tensile tester is applied through a pneumatic cylinder, and the air pressure is measured and converted into load. A displacement transducer, Kaman KD2300 (Kaman Precision Products | Measuring, USA), was attached to the clamps; this measured the relative displacements of the clamps.

Air pressure and displacement as a function of time were recorded through a computer equipped with data acquisition software (Batchelor *et al.* 2003).

RESULTS

The Influence of Treatment Conditions on Hemicellulose and Lignin

It was important to analyse the total lignin content after treatment of the HT-CTMP pulp to be able to find out how the gentle removal of lignin influenced the fibre strength and displacement at break. The SIL treatment of the HT-CTMP pulp did indeed reduce the lignin content, as **Table** 1 shows. The lignin content for the untreated sample was 37.4 wt%, whereas the SIL treatment for 140 °C for 2 h reduced the lignin content to 22.0 wt%. Increasing the treatment temperature or extending the treatment time further reduced the lignin content. Meanwhile, the results from sugar analysis (Table 1 and Fig. 2) showed no obvious difference among samples treated at various conditions, which indicates that SIL is more selectively reacting with lignin.

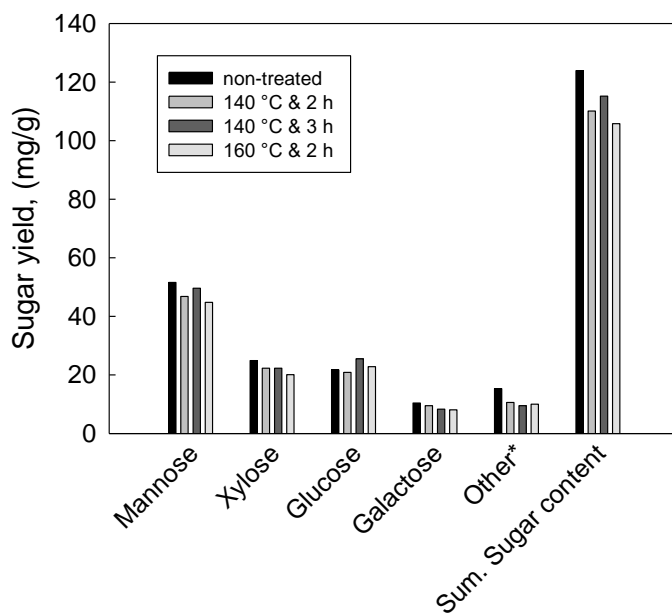


Fig. 2. Hemicelluloses contents (sugar yield) for a non-treated sample as well as 140 °C and 2 h, 140 °C and 3 h, and 160 °C and 2 h SIL-treated samples

Table 1. Sugar and Klason Lignin Content of the HT-CTMP Pulp Before and After SIL Treatment

Sample	Mannose (mg/g)	Xylose (mg/g)	Glucose (mg/g)	Galactose (mg/g)	Other* (mg/g)	Sum. Sugar content (mg/g)	Klason lignin (wt%)
non-treated	51.6	24.9	21.7	10.4	15.3	123.9	37.4
140 °C & 2 h	46.8	22.3	20.9	9.5	10.6	110.1	22.0
140 °C & 3 h	49.6	22.3	25.5	8.3	9.5	115.2	15.5
160 °C & 2 h	44.8	20.1	22.8	8.1	10.0	105.8	19.3

* Other includes Arabinose, Glucuronic acid, Galacturonic acid, and 4-O-MeGlcA

In addition to the total lignin content, the lignin content on the surface is also of importance, because this will be a part of the fibre-to-fibre bonding zone and influence the bonding strength. The results obtained from XPS analysis are shown in Table 2 and depicted in Fig. 3 and Fig. 4., respectively. In Table 2, O/C denotes the oxygen to carbon atomic ratio and C1-C4 list the relative amounts of carbon at different oxidation levels. As shown by the analysis (Fig. 3), the surfaces of all the samples consisted mostly of carbon and oxygen. The intensity of the C 1s peak indicates the amount of surface lignin coverage (Dorris and Gray 1978a,b, Wang *et al.* 2010).

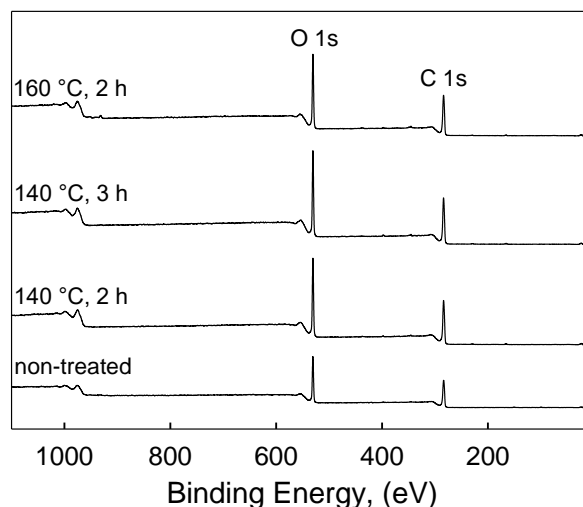


Fig. 3. Survey spectra and high-resolution O 1s spectra for a non-treated sample as well as 140 °C and 2 h, 140 °C and 3 h, and 160 °C and 2 h SIL-treated samples

Table 2. Atomic Composition and Carbon Deconvolution Measured by XPS for Pulp Samples

Sample	O 1s	C 1s	S 2p	O/C	C1 C-(C,H)	Lignin coverage (%)	Klason lignin (wt%)
Non-treated	28.1	70.5	-	0.396	29.0	80.0	37.4
140 °C & 2 h	31.0	68.5	0.5	0.452	25.3	71.3	22.0
140 °C & 3 h	31.6	68.4	trace	0.462	23.7	66.6	15.5
160 °C & 2 h	31.5	68.0	0.4	0.463	24.3	68.9	19.3

The deconvoluted high-resolution C 1s spectra are shown in Fig. 4. What is of interest here is the aliphatic carbon region (C1) centred at 285.0 eV, which relates to the lignin content on the surfaces (Johansson *et al.* 1999). The surface lignin can be estimated using Eq. 3.

$$\text{surface lignin} = 100\% \times (C1 - \alpha) / 49 \% \quad (3)$$

Here, C1 denotes the relative amount of the C–C component in the deconvoluted high-resolution C 1s spectrum of an extracted pulp sample, and α refers to the contribution to the C 1 peak representing the surface contamination. The value used in this article is 2.

As shown in Table 1, the surface lignin coverage decreased for the SIL-treated samples. Both prolonged treatment time and increased temperature resulted in decreasing amounts of surface lignin. Furthermore, it was estimated that the lignin surface coverage decreased from 80% to 67%, which was not as great as the change reported for the Klason lignin content. The differences between these two measurements might be attributed to the recondensation of lignin onto the fibres. In fact, one can find several studies where similar lignin recondensation has been shown to appear (Lee *et al.* 2002; Chen and Lu 2009; Candelier *et al.* 2013). As is widely accepted, lignin can undergo polymerisation and depolymerisation under acidic conditions, and the cleavage of lignin β -O-4 bonds results in the formation of reactive phenolic species, initiating the formation of precipitates that are difficult to process. Formation of reactive lignin structures is also followed by recondensation, decreasing lignin reactivity in subsequent treatments (Testova *et al.* 2009).

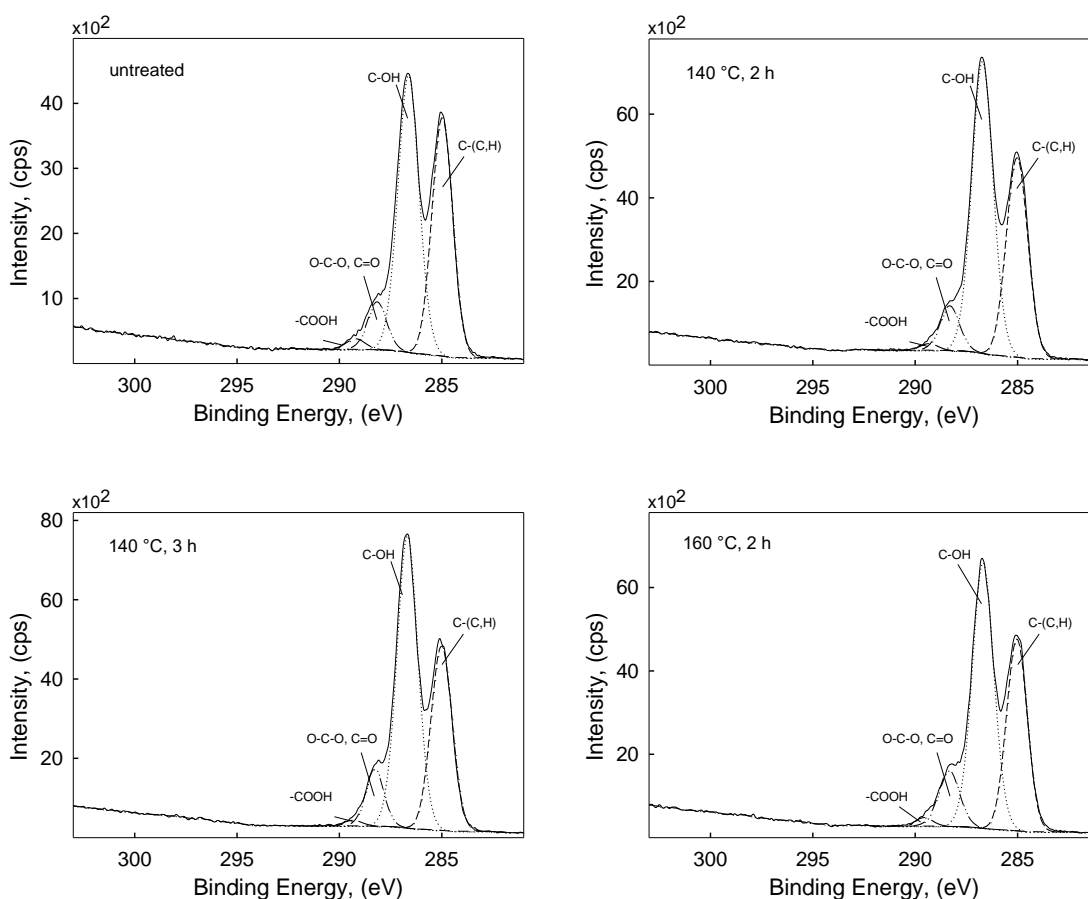


Fig. 4. High-resolution C 1s XPS spectra for a non-treated sample as well as 140 °C and 2 h, 140 °C and 3 h, and 160 °C and 2 h SIL-treated samples

Characterization of Handsheets

Table 1 shows that the total amount of lignin found on HT-CTMP fibres was reduced after the SIL treatment, as also reflected in the density of the handsheets; an increase in density from 385 kg/m³ for non-treated HT-CTMP to approximately 500 and 600 kg/m³ for the SIL-treated pulp is evident (Table 3). The lumen of the fibres collapsed more easily when the lignin was removed; this, in turn, leads to a lower thickness for the

handsheets prepared from treated pulp (approximately 130 μm for 2 h of treatment and 110 μm for 3 h of treatment, compared with 175 μm for non-treated pulp).

Table 3. Structural Properties and Contact Angles after 0.02 s of Absorption for a 4- μL Water Droplet

	Non-treated	140 °C & 2 h	140 °C & 3 h	160 °C & 2 h
Grammage (g/m^2)	68 \pm 4	66 \pm 1	66 \pm 1	67 \pm 1
Thickness (μm)	176 \pm 3	128 \pm 3	111 \pm 3	125 \pm 3
Density (kg/m^3)	385 \pm 7	513 \pm 7	591 \pm 8	536 \pm 8
Contact angle at 0.02 s (°)	97 \pm 5	102 \pm 4	99 \pm 2	99 \pm 4
Absorption time (s)	0.25 \pm 0.02	1.26 \pm 0.09	3.32 \pm 0.26	2.21 \pm 0.32

Dynamic Contact Angle Measurements

Table 3 shows the contact angle at 0.02 s and absorption time for the water droplet for the four tested samples. The handsheet made from 140 °C and 3 h SIL-treated HT-CTMP displayed the longest absorption time (3.32 s), followed by the handsheet made from 160 °C and 2 h SIL-treated HT-CTMP (2.21 s), then the handsheet from 140 °C & 2 h SIL-treated HT-CTMP (1.26 s). The non-treated HT-CTMP handsheet displayed the shortest time (0.25 s). The swelling also differed among these four samples, as depicted in Table 3. The swelling was homogenous in the non-treated and 3-h-treated samples; after that, the paper had absorbed the droplet. However, the handsheet made from 2 h SIL-treated HT-CTMP at 140 °C and 160 °C exhibited a bump on the spot where the droplet was applied and absorbed into the paper (Fig. 5).

. Even though the SIL treatment removed part of the lignin, it did not greatly affect the surface energy of the paper samples. This was due to the contact angle, which was similar and approximately 100° (hydrophobic by definition) for handsheets made from both non-treated and treated HT-CTMP.

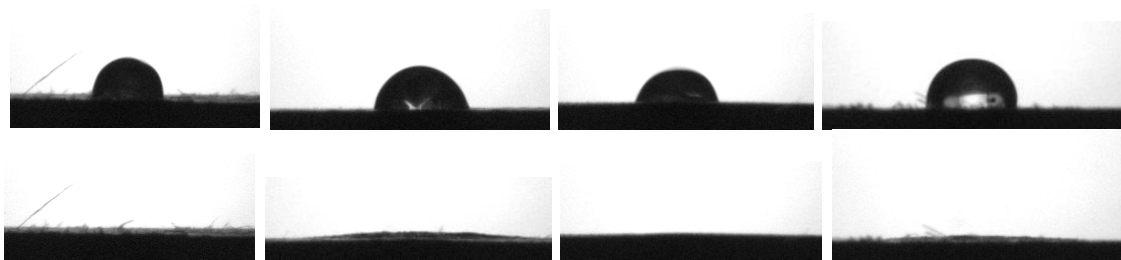


Fig. 5. Images from DCA test. Top: 0.02 s after applying the droplet. Bottom: after the drop has been fully absorbed. From left to right: handsheet made from non-treated HT-CTMP, 140 °C and 2 h SIL-treated HT-CTMP, 140 °C and 3 h SIL-treated HT-CTMP, and 160 °C and 2 h SIL-treated HT-CTMP

Effect of Treatment Conditions on Cellulose Crystallinity

X-ray powder diffraction spectra collected from various handsheets are shown in Fig. 6**Fig.**. The calculated crystallinity indices (Cr.I.) are listed in Table 4. For all the samples, the XRD patterns had a major peak centred at approximately 23° (0 0 2), which is typical for the cellulose I crystalline polymorph (O'Connor 1972). The Cr.I. values increased with increasing SIL treatment time and temperature from 70.6% to 71.6% and

74.9%, respectively. It is worth mentioning that, even if the method of Segal is frequently applied, the value of Cr.I. can still be overestimated (Park *et al.* 2010).

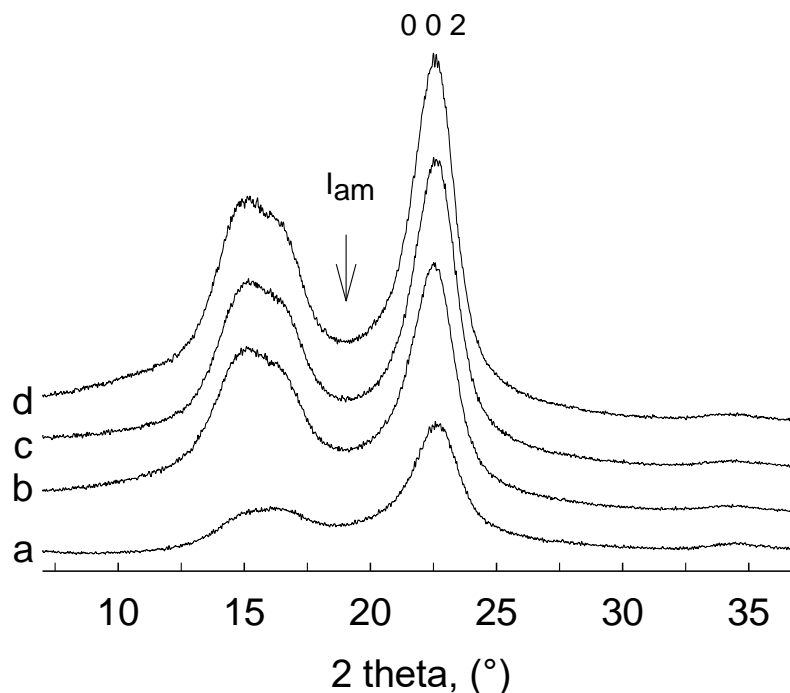


Fig. 6. XRD spectra for sheet made from (a) non-treated HT-CTMP; (b) 140 °C and 2 h; (c) 140 °C and 3 h; and (d) 160 °C and 2 h SIL-treated HT-CTMP

Table 4. Calculated Crystallinity Indexes for Handsheets

Sample	Crystallinity Index (%)	ACS (nm)
Non-treated	70.6	2.7
140°C & 2 h	71.5	3.2
140°C & 3 h	74.9	3.2
160°C & 2 h	74.9	3.1

Mechanical Properties of Handsheets

Removing lignin from the HT-CTMP pulp with the ionic liquid system influenced the mechanical response, as measured by a zero and short span tensile tester in both dry and rewetted conditions.

Table 5. Zero/Short Span Tensile Data for Dry and Rewetted Handsheets

	Dry				Rewetted			
	NT	140°C & 2 h	140°C & 3 h	160°C & 2 h	NT	140°C & 2 h	140 °C & 3 h	160 °C & 2 h
Zero span tensile test								
displacement at break (µm)	27±1	24±1	25±1	26±1	54±1	63±2	59±2	68±2
tensile strength index (kNm/kg)	89±2	90±2	102±2	93±2	70±2	66±2	67±2	62±2
tensile energy absorption (mN)	91±6	75±4	91±5	89±4	140±6	140±6	132±6	145±8
Short span tensile test								
displacement at break (µm)	41±1	37±1	36±1	37±1	68±1	81±2	77±2	80±2
tensile strength index (kNm/kg)	80±2	82±2	96±2	85±2	54±2	51±2	44±1	45±2
tensile energy absorption (mN)	128±7	112±5	133±4	122±5	132±6	132±6	110±5	120±5

Note: average values ± 95% confidence limits

The zero and short span stress-displacement curves of the handsheets are shown in Fig. 7 and Fig. 8, respectively. The data, mean values with confidence intervals, are listed in Table 5, while the sheet density data are listed in Table 3. In common for all samples is that the rewetted specific strengths were lower than the dry specific strength, while the displacement at breaks were higher.

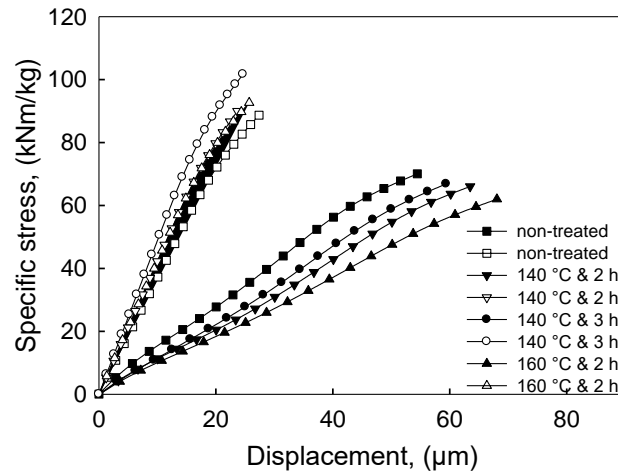


Fig. 7. Zero span tensile tests for handsheets. Treatment times and temperatures are denoted in the labels, triangles with the tip down (140 °C and 2 h), circles (140 °C and 3 h), and triangles with the tip up (160 °C and 2 h), in both dry (unfilled) and rewetted (filled) conditions

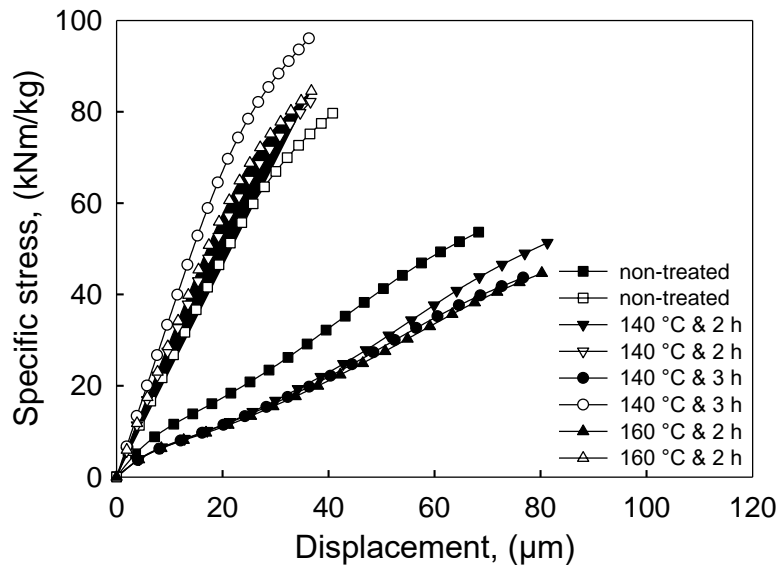


Fig. 8. Short span tensile tests for handsheets. Treatment times and temperatures are denoted in the labels, triangles with the tip down (140 °C and 2 h), circles (140 °C and 3 h), and triangles with the tip up (160 °C and 2 h) in both dry (unfilled) and rewetted (filled) conditions

Figure 7 shows the specific stress as a function of displacement in the zero span tensile test. The non-treated HT-CTMP handsheet demonstrated the lowest zero span specific stress at break (89 kNm/kg) and the highest displacement at break (27 μm) among the four samples when tested dry. The results were quite the opposite when testing the rewetted samples, whereupon the highest specific stress at break was 70 kNm/kg and the lowest displacement at break was 54 μm . The handsheet made from 140 °C and 3 h SIL-treated HT-CTMP demonstrated the highest specific stress at break in dry conditions, 102 kNm/kg, compared with approximately 90 kNm/kg for the other samples. Under rewetted conditions, the handsheet from 160 °C and 2 h SIL-treated HT-CTMP had the highest

displacement at break of 68 μm (compared with approximately 61 μm for the SIL-treated samples at 140 °C and 54 μm for the non-treated samples). Almost no difference could be observed in the specific stresses at break between non-treated and treated samples when they were tested rewetted.

The stress-strain curves at short span (Fig. 8) are similar to those at zero span. Again, the non-treated sample was the weakest, with the highest displacement at break when tested dry; the results were reversed when tested rewetted. The handsheet made from 140 °C and 3 h SIL-treated HT-CTMP displayed the highest stress at peak load, and there were no differences when tested rewetted. Normally, zero and short span tensile tests are made on refined pulps. This is because fibre-to-fibre bonding will be larger and the difference in tensile strength between zero and short span will be low. In the present case only unrefined pulps were tested, and hence the tensile strengths in dry conditions were approximately 10% lower for short span compared with zero span. In rewetted conditions, the differences were even larger because water loosens up fibre-to-fibre bonds and further enhances the differences in tensile strength between zero and short span.

DISCUSSION

Based on the XRD spectra, all samples had the (0 0 2) peak position and peak width that stayed almost constant and consistent with that of cellulose I. In this case, no evidence of cellulose transformation to form II was seen because of the absence of the most common observable change, moderately strong diffraction peaks for form II at 11.7° (1 1 0) and 20.1° (1 0 1) in the XRD spectra (Lenz 1994). It is difficult to explain the cause of such mild differences between samples, but one possible reason for the change of Cr.I. and crystal ACS is related to the drawback of 1D XRD itself; the result did not provide too much information about the degree or position of the crystal. In this experiment, for cellulosic materials, disorder in cellulose fibrils led to considerable uncertainties. The intensities and the determined peak widths could be positively influenced by assigning disordered cellulose as crystal, and negatively influenced by categorizing crystalline fragments as amorphous (Lindner *et al.* 2015).

The strength of the cellulose fibres, as measured by zero span tensile strength, might depend on fibre parameters such as the fibre damage, molecular weight of cellulose, crystallinity, lignin content, hemicellulose content, and internal fibrillation. Figure 9 shows that when lignin was removed by the SIL treatment, an obvious improvement in dry zero and short span tensile strength were observed with increasing treatment temperature and time. However, the responses in terms of the zero and short span tensile index were the opposite when tested rewetted compared with dry. As more lignin was removed by the SIL treatment, the rewetted zero and short span tensile indices decreased.

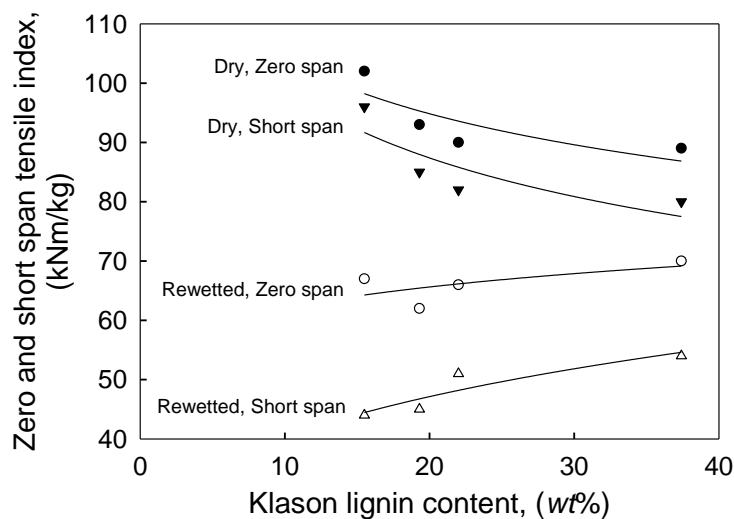


Fig. 9. Zero and short span tensile index as a function of total Klason lignin content

The lignin content was decreased from 37.4 wt% for non-treated sample to 15.5 wt% at 140 °C for 3 h (for about 22 units of percent) which corresponds to a theoretical increase of zero span tensile strength by 34% when comparing the handsheet made from non-treated HT-CTMP with the handsheet made from ionic liquid-treated HT-CTMP. It was assumed that the lignin does not contribute to load, and the strength was calculated according to the rule of mixture. If lignin does not take up any load, the tensile index for the cellulose component in the non-treated HT-CTMP handsheet with 37 wt% lignin content should be approximately 89 kNm/kg (Batchelor and Westerlind 2003). Consequently, a reduction of the lignin content to 15.5 wt% should give a zero span tensile index of 119 kNm/kg, while the measured value was 102 kNm/kg. The reason for this is unknown and it simply shows that lignin likely contributes to the load sharing in wood fibres. This also confirms that various treatments to remove lignin might affect not only lignin, but also induced structural changes in cellulose and hemicellulose. One possible explanation for the decrease in rewetted zero and short span strength with the removal of lignin is that lignin has a relatively higher load sharing than cellulose when tested rewetted compared with dry (Klüppel and Mai 2012; Zhang *et al.* 2013).

The water contact angles were similar for all samples and therefore the hydrophobic characteristics of the cellulose fibre surfaces. The XPS analysis showed a decrease in surface lignin content with increasing treatment time and temperature. Either the reduction of surface lignin was too low to have an effect on fibre surface energy, or the remaining compounds on the fibre surfaces after treatment had hydrophobic characteristics similar to the surface lignin. The time for water absorption of the test droplet increased with increasing treatment time and temperature. This was likely an effect of increased density; therefore, the decrease in pore volume was caused by delignification.

CONCLUSIONS

1. After the treatment with the tested switchable ionic liquid (SIL), the lignin in HT-CTMP fibres was selectively removed without changing the cellulose type. From the treatment conditions we studied, it shows either prolong the treatment time or increase the treatment temperature can achieve a lower lignin content.

2. The tensile strength of the fibres measured indirectly through zero and short span tensile strength revealed that the tested SIL had a small influence in terms of the stress-displacement response.
3. The removal of lignin leads to a decrease in the thickness of handsheets prepared from SIL-treated HT-CTMP, which naturally lead to a higher density when compared with handsheet made from non-treated HT-CTMP.
4. The contact angle towards water remained unchanged while adsorption time increased for the handsheet made from HT-CTMP treated with SIL under the more lignin removal condition, probably because of increased sheet density and hence lower pore volume.

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REFERENCES

- Anugwom, I., Mäki-Arvela, P., Virtanen, P., Damlin, P., Sjöholm, R., and Mikkola, J.-P. (2011). "Switchable ionic liquids (SILs) based on glycerol and acid gases," *RSC Advances* 1(3), 452-457. DOI: 10.1039/c1ra00154j
- Anugwom, I., Mäki-Arvela, P., Virtanene, P., Willför, S., Damlin, P., Hedenström, M., and Mikkola, J.-P. (2012). "Treating birch wood with a switchable 1,8-diazabicyclo-[5.4.0]-undec-7-ene-glycerol carbonate ionic liquid," *Holzforschung* 66(7), 809-815. DOI: 10.1515/hf-2011-0226
- Anugwom, I., Eta, V., Virtanen, P., Mäki-Arvela, P., Hedenström, M., Hummel, M., Sixta, H. and Mikkola, J.-P. (2014), "Switchable ionic liquids as delignification solvents for lignocellulosic materials," *ChemSusChem* 7(4), 1170-1176. DOI: 10.1002/cssc.201300773
- Batchelor, W. J., and Westerlind, B. S. (2003). "Measurement of short span stress-strain curves of paper," *Nordic Pulp and Paper Research Journal* 18(1), 44-50. DOI: 10.3183/NPPRJ-2003-18-01-p044-050
- Batchelor, W. J., Westerlind, B. S., Hägglund, R., and Gradin, P. (2003). "Effect of test conditions on measured loads and displacements in zero short span testing," *International Paper Physics Conference*, September 7-11, Victoria, BC, Canada, pp. 115-120.
- Batchelor, W. J., Westerlind, B. S., Hagglund, R., and Gradin, P. (2006). "Effect of test conditions on measured loads and displacements in zero-span testing," *TAPPI Journal* 5(10), 3-8.
- Candelier, K., Dumarçay, S., Pétrissans, A., Gérardin, P., and Pétrissans, M. (2013). "Comparison of mechanical properties of heat treated beech wood cured under nitrogen or vacuum," *Polymer Degradation and Stability* 98(9), 1762-1765. DOI: 10.1016/j.polymdegradstab.2013.05.026

- Chen, F., and Lu, Z. (2009). "Liquefaction of wheat straw and preparation of rigid polyurethane foam from the liquefaction products," *Journal of Applied Polymer Science* 111(1), 508-516. DOI: 10.1002/app.29107
- Clark, J. d. A. (1944). "The ultimate strength of pulp fibers and zero-span tensile test," *Paper Trade Journal* 118(1), 29.
- Cook, R. D., and Young, W. C. (1985). *Advanced Mechanics of Materials*, Macmillan, New York, NY.
- Cowan, W. F., and Cowdery, E. J. (1974). "Evaluation of paper strength component by short-span tensile analysis," *TAPPI Journal* 57(2), 90-93.
- Dorris, G. M., and Gray, D. G. (1978a). "The surface analysis of paper and wood fibers by Esca-electron spectroscopy for chemical analysis-I. Applications to cellulose and lignin," *Cellulose Chemistry and Technology* 12(6), 9-23.
- Dorris, G. M., and Gray, D. G. (1978b). "Surface analysis of paper and wood fibres by ESCA. II. Surface composition of mechanical pulps," *Cellulose Chemistry and Technology* 12(6), 721-734.
- Duncker, B., and Nordman, L. (1965). "Determination of the strength of single fibres," *Paper and Timber* 10, 539-552.
- Ebringerova, A. (2005). "Structural diversity and application potential of hemicelluloses," *Macromolecular Symposia* 232(1), 1-12. DOI: 10.1002/masy.200551401
- Ebringerova, A., and Heinze, T. (2000). "Xylan and xylan derivatives-Biopolymers with valuable properties, 1-Naturally occurring xylans structures, procedures and properties," *Macromolecular Rapid Communications* 21(9), 542-556. DOI: 10.1002/1521-3927(20000601)21:9<542::AID-MARC542>3.0.CO;2-7
- Gellerstedt, G. (1996). "Chemical structure of pulp components," in: *Pulping and Bleaching Principles and Practice*, C. Dence and D. Reeve (eds.), TAPPI Press, Atlanta, GA, 91-111.
- Groom, L. H., Mott, L., Shaler, S. (2002). "Mechanical properties of individual southern pine fibers. Part I. Determination and variability of stress-strain curves with respect to tree height and juvenility," *Society of Wood Science and Technology* 34(1), 14-27.
- Gurnagul, N., and Page, D. H. (1989). "The difference between dry and rewetted zero-span tensile strength of paper," *TAPPI Journal* 72(12), 164-167.
- Hägglund, R., Gradin, P. A., and Tarakameh, D. (2004). "Some aspects on the zero-span tensile test," *Experimental Mechanics* 44(4), 365-374. DOI: 10.1007/BF02428089
- Heldebrant, D. J., Jessop, P. G., Thomas, C. A., Eckert, C. A., and Liotta, C. L. (2005). "The reaction of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with carbon dioxide," *Journal of Organic Chemistry* 70(13), 5335-5338. DOI: 10.1021/jo0503759
- Höglund, H., and Wilhelmsson, K. (1993). "The product must determine the choice of wood type in mechanical pulping," *18th International Mechanical Pulping Conference*, June 15-17, Oslo, Norway.
- Hult, E.-L., Larsson, P., and Iversen, T. (2000). "A comparative CP/MAS 13C-NMR study of cellulose structure in spruce wood and kraft pulp," *Cellulose* 7(1), 35-55. DOI: 10.1023/A:1009236932134
- Hoffman-Jacobsen, P. M. (1925). "New method of determining the strength of chemical pulp," *Paper Trade Journal* 22(81), 216-217.
- Iiyama, K., and Wallis, A. F. A. (1988). "An improved acetyl bromide procedure for determining lignin in woods and wood pulps," *Journal of Wood Science and Technology* 22(3), 271-280. DOI: 10.1007/BF00386022

- ISO 5269-2 (2004) "Preparation of laboratory sheets for physical testing -- Part 2: Rapid-Köthen method," International Organization for Standardization, Geneva, Switzerland.
- ISO 15361 (2000) "Pulps -- Determination of zero-span tensile strength, wet or dry," International Organization for Standardization, Geneva, Switzerland.
- Jayaraman, K., and Kortschot, M. T. (1998). "Closed-form network models for the tensile strength of paper - A critical discussion," *Nordic Pulp and Paper Research Journal* 13(3), 233-242. DOI: 10.3183/NPPRJ-1998-13-03-p233-242
- Jessop, P. G., Heldebrant, D. J., Xiaowang, L., Eckert, C. A., and Liotta, C. L. (2005). "Green chemistry: Reversible nonpolar to polar solvent," *Nature* 436(7054), 1102-1102. DOI: 10.1038/4361102a
- Johansson, L.-S., Campbell, J. M., Koljonen, K., and Stenius, P. (1999). "Evaluation of surface lignin on cellulose fibers with XPS," *Applied Surface Science* 144, 92-95. DOI: 10.1016/S0169-4332(98)00920-9
- Klüppel, A., and Mai, C. (2012). "Effect of lignin and hemicelluloses on the tensile strength of micro-veneers determined at finite span and zero span," *Holzforschung* 66(4), 493-496. DOI: 10.1515/hf.2011.173
- Lee, S.-H., Teramoto, Y., and Shiraishi, N. (2002). "Biodegradable polyurethane foam from liquefied waste paper and its thermal stability, biodegradability, and genotoxicity," *Journal of Applied Polymer Science* 83(7), 1482-1489. DOI: 10.1002/app.10039
- Lenz, R. W. (1994). "Cellulose, structure, accessibility and reactivity," *Journal of Polymer Science Part A: Polymer Chemistry* 32(12), 2401-2401. DOI: 10.1002/pola.1994.080321221
- Lindner, B., Petridis, L., Langan, P., and Smith, J. C. (2015). "Determination of cellulose crystallinity from powder diffraction diagrams," *Biopolymers* 103(2), 67-73. DOI: 10.1002/bip.22555
- Mäki-Arvela, P., Anugwom, I., Virtanen, P., Sjöholm, R., and Mikkola, J.-P. (2010). "Dissolution of lignocellulosic materials and its constituents using ionic liquids – A review," *Industrial Crops and Products* 32(3), 175-201. DOI: 10.1016/j.indcrop.2010.04.005
- Norgren, M., and Edlund, H. (2014) "Lignin: Recent advances and emerging applications," *Current Opinion in Colloid and Interface Science* 19(5), 409-416. DOI: 10.1016/j.cocis.2014.08.004
- O'Connor, R. T. (1972). *Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose*, Marcel Dekker, New York, NY.
- Page, D. H. (1969). "A theory for the tensile strength of paper," *TAPPI Journal* 52(4), 674-681.
- Page, D. H., El-Hosseiny, F., Winkler, K., and Bain, R. (1972). "The mechanical properties of single wood-pulp fibres Part I: A new approach," *Pulp and Paper-Canada* 73(8), 72-77.
- Park, S., Baker, J. O., Himmel, M. E., Parilla, P. A., and Johnson, D. K. (2010). "Cellulose crystallinity index: Measurement techniques and their impact on interpreting cellulase performance," *Biotechnology for Biofuels* 3, 10. DOI: 10.1186/1754-6834-3-10
- Pu, Y., Jiang, N., and Ragauskas, A. (2007). "Ionic liquid as a green solvent for lignin," *Journal of Wood Chemistry and Technology* 27(1), 23-33. DOI: 10.1080/02773810701282330

- Ramos, L. P. (2003). "The chemistry involved in the steam treatment of lignocellulosic materials," *Quimica Nova* 26(6), 863-871. DOI: 10.1590/S0100-40422003000600015
- Schwanninger, M., and Hinterstoisser, B. (2002). "Klason lignin: Modifications to improve the precision of the standardized determination," *Holzforschung* 56(2), 161-166. DOI: 10.1515/HF.2002.027
- Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Textile Research Journal* 29(10), 786-794. DOI: 10.1177/004051755902901003
- Seth, R. (2004). "Understanding sheet extensibility," *Annual Meeting-Pulp And Paper Technical Association of Canada*, 90(A), 51-60.
- Seth, R., Jantunen, J., and Moss, C. (1989). "The effect of grammage on sheet properties," *Appita* 42(1), 42-48.
- Sjöström, E. (1993). *Wood Chemistry: Fundamentals And Applications*, Academic Press, New York, NY.
- Sun, N., Rahman, M., Qin, Y., Maxim, M. L., Rodriguez, H., and Rogers, R. D. (2009). "Complete dissolution and partial delignification of wood in ionic liquid 1-ethyl-3-methylimidazolium acetate," *Green Chemistry* 11(5), 646-655. DOI: 10.1039/b822702k
- Sundberg, A., Sundberg, K., Lillandt, C., and Holmbom, B. (1996). "Determination of hemicelluloses and pectins in wood and pulp fibers by acid methanolysis and gas chromatography," *Nordic Pulp and Paper Research Journal* 11(4), 216-219. DOI: 10.3183/NPPRJ-1996-11-04-p216-219
- Tan, S. S. Y., MacFarlane, D. R., Upfar, J., Edye, L. A., Doherty, W. O. S., Patti, A. F., Pringle, J. M., and Scott, J. L. (2009). "Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid," *Green Chemistry* 11(3), 339-345. DOI: 10.1039/b815310h
- TAPPI T 558 (2010). "Surface wettability and absorbency of sheeted materials using an automated contact angle tester," TAPPI, Norcross, USA.
- Testova, L., Vilonen, K., Pynnönen, H., Tenkanen, M., and Sixta, H. (2009). "Isolation of hemicelluloses from birch wood: Distribution of wood components and preliminary trials in dehydration of hemicelluloses," *Lenzinger Berichte* 87, 58-65
- Vainio, A., and Paulapuro, H. (2007). "Interfiber bonding and fiber segment activation in paper," *BioResources* 2(3), 442-458. DOI: 10.15376/biores.2.3.442-458
- Van Den Akker, J. A., Lathrop, A. L., Voelker, M. H., and Dearth, L. R. (1958). "Importance of fiber strength to sheet strength," *TAPPI Journal* 41(8), 416-425.
- Varanasi, S., Chiam, H. H., and Batchelor, W. (2012). "Application and interpretation of zero and short-span testing on nanofibre sheet materials," *Nordic Pulp and Paper Research Journal* 27(2), 343-351. DOI: 10.3183/NPPRJ-2012-27-02-p343-351
- Wang, B., He, B., and Li, J., (2010) "Study on lignin coverage of masson pine fiber." *BioResources* 5(3), 1799-1810. DOI: 10.15376/biores.5.3.1799-1810
- Wasserscheid, P., and Welton, T. (2006). *Ionic Liquids In Synthesis*, Wiley-VCH, Weinheim, Germany.
- Willför, S., Pranovich, A., Tamminen, T., Puls, J., Laine, C., Suurnäkki, A., Saake, B., Uotila, K., Simolin, H., Hemming, J., *et al.* (2009). "Carbohydrate analysis of plant materials with uronic acid-containing polysaccharides – A comparison between different hydrolysis and subsequent chromatographic analytical techniques," *Industrial Crops and Products* 29(2), 571-580. DOI: 10.1016/j.indcrop.2008.11.003

Zhang, S.-Y., Fei, B.-H., Yu, Y., Cheng, H.-T., and Wang, C.-G. (2013). "Effect of the amount of lignin on tensile properties of single wood fibers," *Forest Science and Practice* 15(1), 56-60.

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