Dry-Jet Wet Spinning of Technical and Textile Filament Fibers from a Solution of Wood Pulp and Waste Cotton in an Ionic Liquid

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Abstract

This dissertation presents the further development of IONCELL technology for the production of modified and composite man-made cellulose fibers using waste and virgin lignocellulosic materials. IONCELL technology consists of a dry-jet wet spinning process using an ionic liquid as a polymer solvent.

Different structural features of the IONCELL fibers spun from cellulose- [DBNH]OAc solution were studied against their mechanical properties with wide- and small-angle scattering techniques. It was observed that the change in crystallite size or orientation does not correlate with any mechanical properties. However, by increasing the draw ratio, the sample crystallinity, amorphous and void orientation, specific surface, and sorption/desorption properties of the fibers change significantly.

The effect of the addition of lignin and/or xylan to the spinning dope on the fibers' mechanical properties and surface chemistry was also studied. The results showed the surface properties can be fine-tuned by changing the composition of the fibers. In addition, the fibers produced from cellulose with xylan and/or lignin as an additive showed declined tensile strength. The fibers deformability increased since these additives contributed to the amorphous parts of the fibers. Moreover, the swelling test indicated the three-component fibers had the least change in their cross-sectional area.

Chemical modification in the solution of cellulose and its spinning to acetylated cellulose filaments was investigated. This study proved the degree of substitution can be adjusted precisely to achieve the desired properties. For instance, cellulose with the degree of substitution values of 0.05–0.75 was successfully spun, and fibers reached particularly high tensile strength values (525–750 MPa conditioned and 315–615 MPa wet) and elastic moduli values between 10 and 26 GPa.

The IONCELL process was utilized for the chemical upcycling of cotton wastes. Implementing this process, complete and residue-free dissolution of waste cotton and the conversion of this material into virgin cellulose fibers with high tensile strength (850 MPa) were achieved. We addressed the problem that waste cotton is an inhomogeneous feedstock with a broad variation in molecular properties. In order to reduce and adapt the required degree of polymerization of the cotton waste, either an aqueous acid or an enzymatic treatment was conducted. Alternatively, the cotton waste was mixed with pre-hydrolysis kraft pulp with a low degree of polymerization to obtain the macromolecular properties necessary for spinning. In addition, we described the physicochemical properties of the respective solutions as a key to ensure successful spinning of high-performance fibers. The resulted IONCELL fibers showed significantly better mechanical properties than the

Keywords cellulose, regenerated cellulose fibers, cellulose acetate, ionic liquid, dry-jet wet spinning, cotton recycling
Preface

This thesis was completed in the Department of Bioproducts and Biosystems (formerly the Forest Product Technology Department), Aalto University, School of Chemical Engineering, from December 2013 to March 2018. It was made possible by funding from Business Finland (formerly TEKES) through the project Design Driven Value Chains in the World of Cellulose, the Horizon 2020 EU project Trash-2-Cash, COST Action STSM FP1205, and the School of Chemical Engineering. I would like to thank the Walter Ahlström Foundation and the Paper Engineers’ Association of Finland (puunjalostus-insinoorit) for the additional financial support that allowed me to attend conferences and workshops.

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I am thankful to all my own and in-law family members. I would like to say a big thank you to Robab and Hooshang, who are always thinking and caring about me and offering their unconditional love. Shima and Danial always encouraged and motivated me by suggesting exciting plans for after my defense. Special thanks to my patient, caring, best friend for life, Mahmoud. We went through this whole journey together, and he helped me survive all the stressful moments, celebrated the happy moments with me, and reminded me that life is beautiful and that I should just take it easy! Doosetoon daram!

Karlstad, August 2019
Shirin Asaadi
## Contents

Preface .......................................................................................................................... 1  
List of Abbreviations and Symbols ................................................................................ 5  
List of Publications ........................................................................................................ 7  
Author’s Contribution ..................................................................................................... 8  
Introduction .................................................................................................................... 10  
Research questions ....................................................................................................... 12  

1. Background .............................................................................................................. 13  
   1.1 Structure and properties of cellulose ................................................................. 13  
   1.2 Structure and chemistry of lignin and hemicelluloses ........................................ 16  
   1.3 Direct cellulose solvents (with special emphasis on ionic liquid) ................. 19  
   1.4 Fundamentals and practice of lignocellulosic dissolution ......................... 22  
   1.5 Acetylation of cellulose solutions ..................................................................... 22  
   1.6 Rheological characterization of cellulose solutions ....................................... 24  
      1.6.1 Rheology in fiber spinning of cellulose solutions ................................... 25  
   1.7 Dry-jet wet spinning of cellulose-ionic liquid solutions .............................. 26  
   1.8 Flow processes in spinning .............................................................................. 28  

2. Experiment ............................................................................................................... 34  
   2.1 Materials ........................................................................................................... 34  
      2.1.1 Cellulose, hemicellulose and lignin sources ............................................ 34  
      2.1.2 Solvent ([DBNH][OAC] ionic liquid) ......................................................... 35  
   2.2 Grinding and viscosity measurements .............................................................. 35  
   2.3 Viscosity adjustment ....................................................................................... 35  
   2.4 Molar mass distribution .................................................................................... 36  
   2.5 Dope preparation ............................................................................................. 36  
   2.6 Rheology measurement .................................................................................... 37  
   2.7 Fiber spinning ................................................................................................... 37  
   2.8 Fiber characterization ....................................................................................... 38  
      2.8.1 Chemical composition of fibers ................................................................. 38  
      2.8.2 Physical and mechanical properties analysis of the fibers .................... 38  
      2.8.3 Structural characterization of the fibers ................................................. 39  
      2.8.4 Water interaction characterizations of fibers ........................................ 41  

3. Results and discussion ............................................................................................ 43  
   3.1 Spinnability studies ............................................................................................ 43  
      3.1.1 Effect of cellulose molar mass distribution on fiber spinning .... 43
3.1.2 Effect of homogeneous acetylation of cellulose in solution on spinnability ................................................................. 47
3.1.3 Effect of lignin and xylan on fiber spinning .................. 50
3.2 Structure property relationship ........................................... 52
  3.2.1 Pure cellulose ................................................................. 52
  3.2.2 Polymer blends vs. fiber structure and mechanical properties 58
3.3 Application for waste upcycling ....................................... 65
4. Concluding remarks ............................................................ 68
5. Future work and outlook ..................................................... 70
References ............................................................................. 73
**List of Abbreviations and Symbols**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>[DBNH]OAc</td>
<td>1,5-diazabicyclo[4.3.0]non-5-enium acetate</td>
</tr>
<tr>
<td>ACF</td>
<td>acetylated cellulose fiber</td>
</tr>
<tr>
<td>B-PHK</td>
<td>birch pre-hydrolysis kraft</td>
</tr>
<tr>
<td>COP</td>
<td>cross-over point</td>
</tr>
<tr>
<td>CoW</td>
<td>waste cotton</td>
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<tr>
<td>DMA</td>
<td>dynamic mechanical analysis</td>
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<tr>
<td>DP</td>
<td>degree of polymerization</td>
</tr>
<tr>
<td>DS</td>
<td>degree of substitution</td>
</tr>
<tr>
<td>DR</td>
<td>draw ratio</td>
</tr>
<tr>
<td>DVS</td>
<td>dynamic vapour sorption</td>
</tr>
<tr>
<td>E-PHK</td>
<td>eucalyptus pre-hydrolysis kraft</td>
</tr>
<tr>
<td>eq</td>
<td>equivalent</td>
</tr>
<tr>
<td>G'</td>
<td>storage modulus</td>
</tr>
<tr>
<td>G''</td>
<td>loss modulus</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>HH</td>
<td>Hailwood Horrobin</td>
</tr>
<tr>
<td>HH – MLs</td>
<td>Hailwood-Horrobin water monolayer sorption</td>
</tr>
<tr>
<td>HH – MLd</td>
<td>Hailwood-Horrobin water monolayer desorption</td>
</tr>
<tr>
<td>IL</td>
<td>ionic liquid</td>
</tr>
<tr>
<td>IpAc</td>
<td>isopropenyl acetate</td>
</tr>
<tr>
<td>MMCF</td>
<td>man-made cellulosic fiber</td>
</tr>
<tr>
<td>MMD</td>
<td>molar mass distribution</td>
</tr>
<tr>
<td>M_a</td>
<td>number average molecular mass</td>
</tr>
</tbody>
</table>
\( M_w \) weight average molecular mass

NACF non-acetylated cellulose fiber

NMR nuclear magnetic resonance

PDI polydispersity index

RH relative humidity

RSS relative specific surface

SAXS small-angle X-ray scattering

vdW van der Waals

WAXS wide-angle X-ray scattering

\( \Delta G_h \) free energy of hydrate

\( \Delta G_d \) free energy of dissolved

\( \Delta n \) birefringence

\( \eta_0 \) zero-shear viscosity
List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their Roman numerals.


IV. **Asaadi, Shirin;** Kakko, Tia; King, Alistair W.T.; Kilpeläinen, Ilkka; Hummel, Michael; and Sixta, Herbert. 2018. High-Performance Acetylated Ioncell-F Fibers with Low Degree of Substitution. ACS publications. ACS Sustainable Chemistry & Engineering, volume 6, issue 7, page 9418–9426. ISSN 2168-0485. DOI: 10.1021/acssuschemeng.8b01768.
Author’s Contribution

Publication I: Renewable high-performance fibers from the chemical recycling of cotton waste utilizing an ionic liquid

SA was responsible for the experimental design, performed the experimental work, carried out the experimental work, analyzed the results and wrote the manuscript as principal author under the supervision of HS. The manuscript was proofread and edited by MH and HS. SH contributed to the revision of the manuscript, TH supplied the waste cotton (bed sheets) as the raw material, YM and AM contributed to the spinning process.

Publication II: Structural analysis of Ioncell-F fibres from birch wood

SA was responsible for the experimental design and the fiber spinning, analyzed the corresponding results and wrote the manuscript as principal author under the supervision of HS. The manuscript was proofread and edited by MH and HS. MG and UO provided the X-ray scattering equipment, designed and performed the Wide- and small angle X-ray scattering (WAXS/SAXS) experiments. PA contributed to the evaluation of the SAXS data and interpretation of the WAXS results.

Publication III: Conversion of wood-biopolymers into macrofibers with tunable surface energy via dry-jet wet-spinning

SA was responsible for experimental design of dope preparations and dry-jet wet spinning of the fiber samples. SA analyzed the mechanical properties of the fibers and performed the carbohydrate analysis of the fibers. TN, GK and JK were responsible for experimental design of the fiber surface analysis, and analyzed the surface properties of the fibers. TN wrote the manuscript as principal author. The manuscript was proofread and edited by SA, HS and JK.

Publication IV: High-Performance Acetylated Ioncell-F Fibers with Low Degree of Substitution.

SA was responsible for the experimental design, performed the experimental work of spinning, analyzed the mechanical properties of the fibers, interpreted the WAXS results, carried out and interpreted the dynamic vapour sorption (DVS) test results and wrote the manuscript as principal author under the supervision of HS. The manuscript was proofread and edited by TK, MH and HS. TK, AK, and IK were responsible for the experimental design of the cellulose
acetylation. TK was responsible for nuclear magnetic resonance (NMR) analysis of fibers, and prepared the acetylated dopes at Aalto University together with SA.
Introduction

The cultivation of cotton, currently produced on 2.5% of the total arable land, has a long history and due to its indispensable use for textile application, cotton will certainly remain one of the most important crops in the world. However, prevailing problems associated with cotton cultivation are high water consumption and extensive use of pesticides and insecticides. In the light of a rapidly increasing demand for textile fibers, overcoming these problems will become increasingly important. Despite recent achievements in agricultural technologies and genetic engineering to produce cotton seeds with higher drought tolerance and integrated pest management, there is an imperative need to develop novel and environmentally friendly technologies for the production of regenerated cellulose textile fibers. The application spectrum of the so-called man-made cellulosic fibers (MMCFs) has become very broad, ranging from regular textile fibers to smart textile and technical fibers, such as reinforcement in composite materials or precursor for bio-based carbon fibers.

Finnish forest industry offers an excellent source of cellulose for this purpose. Forest industry based products are a significant part of Finnish export accounting for ca. 13 % of the export value. This industry is seeking for new business opportunities due to the declining market of paper and newsprint. The current annual growth of Finnish wood biomass is ~104 million m³. However, the current annual use accounts for only 61 million m³ of wood. Therefore, there is a great potential of increasing the usage of Finnish forest resources. Additionally, there is an opportunity to replace the water intensive and food production competing cotton cultivation with local wood based alternatives, which is beneficial both for Finnish economy and for Europe's dependency on cotton imports. However, cellulose is a non-meltable biopolymer and it is non-soluble in conventional solvents. The present industrial processes, i.e. the viscose and the Lyocell processes, are toxic and energy-intensive while the solvent systems suffer from low stabilities.

Recent studies on the application of ionic liquids (ILs) in cellulose chemistry have attracted a lot of commercial interest, including the production of regenerated and modified cellulose fibers. Processing dissolved cellulose in ionic liquids provides various benefits. Firstly, ionic liquids have low vapor pressure, which prevents the emission of volatile organic compounds (VOCs), a major
source of environmental pollution. Secondly, dry-jet wet spun regenerated fibers demonstrate high tensile strength in comparison to commercial Viscose fibers and non-commercial wet spinning processes such as the Carbamate or the Biocelsol processes (Ciechańska 2005; Voges, Brück, Fink, & Gensrich, 2000).

The IONCELL process is a dry-jet wet fiber spinning process, using the ionic liquid 1,5-diazabicyclo[4.3.0]non-5-ениum acetate [DBNH]OAc as a cellulose solvent. The process allows for the production of cellulosic staple fibers surpassing the properties of commercial Lyocell fibers.

The overall objective of this thesis was to contribute to the development of the IONCELL spinning process for the production of high strength fibers regenerated from a cellulose solution in an ionic liquid. IONCELL- fibers were produced from different cellulosic sources and the spinnability has been tested by studying different parameters such as cellulose sources, polymer concentration, and spinning solution modification. In addition, the spinnability of spinning dopes from waste cellulosic material has been investigated. Finally, comprehensive structural analyses of the IONCELL fibers were performed to gain insight into the supramolecular structure of these fibers for the further development of the process.
Research questions

The thesis work started in 2013 based on the first achievements in dry-jet wet spinning of the cellulose-ionic liquid solutions at Aalto University. The aim was to develop this spinning process to produce high-strength man-made cellulosic fibers and modified cellulosic fibres that are competitive or even better than commercial man-made cellulosic fiber (MMCF) available in the market. In addition, there is an interest in biomaterial science to utilize lignin and hemicelluloses as an additives to cellulose for production of all-wood-biopolymers. Within this scope, the spinnability of different dopes and properties of the produced fibers have been investigated. In particular, the following research questions have been addressed.

- How does the structure of the IONCELL fibers change by the increase of the total orientation? How does this affect the fiber properties?
- How can cellulose direct esterification in the spinning solution affect the fiber properties? Are the resulting dopes spinnable?
- How can the addition of xylan and/or lignin to cellulose-ionic liquid solution affect the properties of the spun fibers? Are the dopes spinnable?
- Can waste material, such as waste cotton, be utilized in the IONCELL process to produce high tenacity cellulose fibers? Which parameters are crucial and should be adjusted to make the dope spinnable?
1. Background

1.1 Structure and properties of cellulose

The elemental cellulose composition was first determined by Anselm Payen in 1838 with 44–45% carbon, 6–6.5% hydrogen and the rest oxygen, with an empirical formula of \((\text{C}_6\text{H}_{10}\text{O}_5)_n\). The prolonged hydrolysis of the cellulose yields cellobiose \((\text{C}_{12}\text{H}_{22}\text{O}_{11})\) and finally glucose \((\text{C}_6\text{H}_{12}\text{O}_6)\).

In 1920, Haworth recognized the nature of the bonds between the glucose units and their atoms in the unit. He proposed the chain-like macromolecule (Figure 1) structure for the cellulose unit, which has now been accepted generally (Krässig, 1993).

![Constitutional formula of the cellulose molecule (Krässig, 1993)](image)

The repeating unit of cellulose is often referred to as cellobiose instead of glucose, which corresponds to the nomenclature conventions of IUPAC and IUMMB. Convincing arguments have recently been put forward which define glucose residues as the repeating unit of cellulose in accordance with the nomenclature of IUPAC and IUBMB (French et al., 2017).

The glucose units are linked by \(\beta\)-1, 4-glucosidic bonds formed between the carbon atoms C(1) and C(4) of adjacent glucose units. The \(n\) in the empirical formula designates the number of anhydroglucose units linked together in the long cellulose chain and is known as the degree of polymerization (DP). Native cellulose has a DP higher than 10,000. However, the cellulose substrates used in processes, depending on the severity of the isolation process (Krässig, 1993), have lower DPs in the range of 800 to 3000. Viscosimetry and gel permeation chromatography (GPC) are two common methods to determine cellulose DP.
Viscosimetry provides the viscosity average DP (DP_V) while GPC gives the number average (DP_N) and weight average DP (DP_W) of the cellulose polymer (Axelsson et al., 2011).

The hydroxyl groups in the cellulose chain are known to be responsible both for chemical reactivity and for the formation of secondary valence hydrogen bonds within one molecule (intramolecular) or with neighboring molecules (intermolecular). Therefore, cellulose chains have a high tendency to make parallel arrangements of crystallites and crystallite strands to form the supramolecular structure of cellulose fiber (Krässig, 1993).

The polymorph of cellulose is well documented. Six polymorphs of cellulose exist: I, II, III, IIII, IV, and IVI. These polymorphs are distinguished by nuclear magnetic resonance (NMR), infrared and diffraction techniques. The polymorphs can be interconverted as shown in Figure 2 (O’sullivan, 1997). Cellulose I is the native form of cellulose that can be found in nature. Wood pulp is the main source of cellulose I and is mainly used for paper and cardboard production, it is also used for synthesizing of cellulose esters and ethers (Klemm et al., 2005). Cellulose II is the second most studied form, which can be obtained from cellulose I by alkali treatment, mercerization or recrystallization from a solution known as regeneration which can be used for production of films and fibres. Cellulose III is obtained from cellulose I by treatment in liquid ammonia or various amines followed by the removal of the reagents. According to some studies, cellulose IV cannot be produced directly from cellulose I. It can be prepared by treatment in glycerol at 260 °C after transformation of cellulose I into cellulose II or III (Wada, Heux, & Sugiyama, 2004). However, some studies show that cellulose IV is cellulose I with a lateral disorder (Wada et al., 2004).

The difference between cellulose I and III originates from hydrogen bonds. In cellulose I, the hydrogen bonds exist solely between cellulose molecules within the sheets, and the bonds between the sheets are van der Waals (vdW) forces. In contrast, in cellulose III, the hydrogen bonds also exist between the sheets (Wada, Nishiyama, & Langan, 2006). Cellulose allomorphs show different stiffness properties. Cellulose I has the highest elastic modulus (138 GPa) and cellulose IIII has the lowest elastic modulus (58 GPa) (Nishino et al., 2003).
Due to its complex structure, cellulose I has been investigated with many different methods, such as Fourier transform infrared spectroscopy (FTIR), Cross Polarisation/Magic Angle Spinning (CP/MAS) nuclear magnetic resonance (NMR), scanning electron microscopy (SEM), electron diffraction, Raman spectroscopy atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning tunnelling microscopy (STM), small and wide-angle X-ray scattering and computer-based stereochemical modelling (O’sullivan, 1997). Atalla and Vanderhart (Atalla and Vanderhart 1984) found out that cellulose I exist in two distinct crystalline forms namely $I_{\alpha}$ and $I_{\beta}$. Higher plants are richer in cellulose $I_{\beta}$ while algae cellulose and less developed plants are richer in cellulose $I_{\alpha}$. In cellulose $I_{\alpha}$, the structure is a one-chain triclinic unit cell with identical glycosyl linkages and hydroxymethyl groups. The adjacent sugar ring alternates in conformation and the chain repeating univalent is glucose. The chains in sheets are packed in a “parallel-up” fashion (Langan, Nishiyama, & Chanzy, 2003). Cellulose $I_{\beta}$ has a monoclinic unit cell and is a more stable form than $I_{\alpha}$. In cellulose $I_{\alpha}$, the structure consists of two parallel chains with slightly different conformations forming sheets packed in a “parallel-up” fashion similar to $I_{\alpha}$. The hydroxymethyl groups have trans-gauche conformation (Nishiyama et al., 2002).

Specific hydrogen bonds are formed between adjacent residues of the same chain (intra-chain) and between adjacent residues of different chains in the same sheet (inter-chain). Many C-H-O bonds and van der Waals (vdW) forces connect residues between the sheets (inter-sheet). All these interaction networks give rise to the rigidity and strength of cellulosic materials (Gross and Chu, 2010).

The molecular dynamics simulation of the interaction networks of cellulose $I_{\alpha}$ and $I_{\beta}$ has shown that intersheet interactions that involve C-H-O pseudo hydrogen bonds and vdW interactions are the strongest and most robust components in the network interactions. Although the interaction energy of individual C-H-O hydrogen bond is lower than that of an O-H-O hydrogen bond, the addition
of vdw interactions makes intersheet interactions stronger than interchain interactions (Gross and Chu, 2010).

The hydrogen bonds presented in cellulose II have been studied with the neutron fiber diffraction technique (Langan, Nishiyama, and Chanzy 1999). The proposed structures are shown in Figure 3, where only the atoms involved in the hydrogen bonding have been labeled and the hydrogen bonds are shown by dotted lines. In this study, the z coordinate of the O5, if it larger than C6, is referred to as the “origin” chain and otherwise as the “center” chain. Intermolecular hydrogen bonds are located between O2-D ... O6 in sheets containing only original molecules whereas in sheets with only center chain molecules, O6-D ... O2 bonds exist. In the sheet containing both center and origin molecules, hydrogen bonds occur between O6-D ... O6 and O2-D ... O2, while the former involve O5 and O3 as acceptors. Intramolecular hydrogen bonds exist between O3-D ... O5 in each molecule with a minor component involving O6 as the acceptor.

Figure 3. Hydrogen bonds in cellulose II (Langan et al., 1999)

1.2 Structure and chemistry of lignin and hemicelluloses
The terrestrial plants’ cell wall polysaccharides have been grouped into cellulose, hemicellulose, and pectin. Hemicelluloses are heteropolysaccharides and differ from cellulose. They consist of several sugar moieties, are branched and have low molecular masses with a degree of polymerization (DP) of 50 to 200. They are characterized by a (1→4)-linked backbone of glucose, mannose or xylose with an equatorial configuration at C1 and C4 (Sixta 2006; Scheller and
Ulvskov 2010). Figure 4 shows the repeating disaccharides of hemicelluloses. The main role of the hemicelluloses is to strengthen the cell wall by interacting with cellulose and lignin.

Hemicellulose residues are present in the native wood-based cellulose fibers and affect the association between cellulose units (Hult et al., 2001). They can have a significant effect on processability and yield (Chaker et al., 2013). Hemicelluloses include xyloglucans, xylans, mannans and glucomannans, and β-(1→3,1→4)-glucans.

Xylans are heteropolysaccharides with a backbone of β-(1→4)-linked xylose residues. They are the most common hemicelluloses and second-most abundant biopolymer after cellulose (Ebringerová and Heinze, 2000).

Xylan can be isolated from the side-stream of the pulp and textile industry or directly from plant sources and products (Lisboa et al., 2005; Mais and Sixta, 2009). After extraction from a pulp side-stream, the xylan is enriched in the retentate by membrane filtration before precipitation by addition of a non-solvent. However, the extraction from plant sources can be performed by various methods, such as alkaline extraction, extraction with dimethyl sulfoxide, steam, microwave or hot water treatment (Alekhina et al., 2014). When xylan is extracted from bleached hardwood kraft pulp, it has high purity and high molar
mass with minimum degradation. Therefore, there is no need for further purification, since it is free from lignin and any contaminants (Carpita, 1983; Fuhrmann and Krogerus, 2009).

Generally, the presence of hemicellulose in the spinning process is unfavorable. For example, in the viscose process, xylan is largely extracted in the alkaline steeping step, which leads to an accumulation in the steeping lye that is circulated. The presence of xylan in the alkali cellulose causes a higher consumption of carbon disulfide during the xanthation step. The viscose fibers, which contain degraded xylan short-chain polymers, have shown low tensile strength, and their brightness is affected unfavorably (Schild and Liftinger, 2014). The deliberate addition of isolated hemicelluloses to cellulose can, however, lead to a desired modification of the properties of the spun-fiber properties (Nypelö et al., 2018; Schild and Liftinger, 2014).

The third major cell wall polymer is lignin. It is an abundant and important biopolymer in vascular plants. It gives mechanical strength and allows efficient liquid transport in vascular plants. Lignin is also a large potential source of carbon for chemical and energy purposes (Sixta 2006).

Lignin is a complex phenolic polymer formed by radical coupling. The three primary precursors (Figure 5) are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which are also called monolignols (Duval and Lawoko, 2014; Suhas et al., 2007). The proportion of the monolignols defines the structure of the lignin in the plant species and can be very diverse (Duval and Lawoko, 2014).

Figure 5. The three main lignin precursors (monolignols): (a) p-coumaryl alcohol, (b) coniferyl alcohol, (c) sinapyl alcohol (Suhas et al., 2007)

Radical coupling between monolignols leads to many different inter-unit linkages such as the β-O-4 linkage, where the β-carbon of one unit and the phenolic hydroxyl of the other unit are involved. This linkage accounts for almost 50% of all linkages in softwood and more than 60% in hardwood lignin.

In addition, there are other ether bonds (α-O-4, 4-O-5) along with carbon-carbon bonds, (β-β, β-5, β-1) and some more complex structures, all involving dibenzodioxocin, which is a main linkage in softwood lignin (Duval and Lawoko, 2014).

Lignins contain several functional chemical groups, such as hydroxyl phenolic, primary and secondary hydroxyl groups in larger amounts, carbonyl and carboxyl in rather small amounts. To utilize lignin as a chemical substrate, its functionalities should be known precisely, as they are responsible for the reactivity
of lignin. The phosphorous-NMR method developed by Argyropoulos and his co-workers is a convenient method to quantify the carboxyl and hydroxyl groups of lignin. It can also differentiate between aliphatic and phenolic groups in a short-term analysis (Duval and Lawoko, 2014).

The extraction process of lignin from wood can be divided into two categories: analytical scale and industrial scale. Lignins extracted from analytical scale processes are milled wood lignin (MWL), mild acidolysis lignin (MAL), cellulolytic enzyme lignin (CEL), and enzymatic mild acidolysis lignin (EMAL). Lignins from industrial processes are referred to as kraft lignin (KL), Lignosulfonates (LS), soda lignin (SL), and organosolv lignin (OSL) (Duval and Lawoko, 2014).

In the organosolv process, lignocelluloses are treated with organic solvents or acids under mild conditions to obtain lignin with \( M_n \) of 1000 to 3000 Da (Singh and Dhepe, 2016). Organosolv lignins have high phenolic functionality because of the cleavage of the aryl ether linkages, and their structure is more similar to native lignin when compared to lignin from other industrial processes (Duval and Lawoko, 2014). They are sulfur free and are a good source for polymer applications.

There are many application opportunities for lignin in different fields. Lignin is used as an absorbing material and a precursor to produce lightweight carbon material, and unmodified lignin is blended with other bio or synthesized polymers to produce material with specific properties (Duval and Lawoko, 2014).

1.3 Direct cellulose solvents (with special emphasis on ionic liquid)

Cellulose dissolution is an important topic nowadays for the production of cellulose-based materials. There is high demand for new techniques suitable for shaping, homogenous modification and defined degradation of cellulose solutions (Liebert, 2010). Even though cellulose is made up of repeating anhydroglucose units, each with 3 hydroxyl groups with notable hydrophilic character, it is insoluble in water (Medronho et al., 2015). The hydroxyl groups form a network of inter- and intra-molecular hydrogen bonds that make the cellulose insoluble in common solvents (Klemm et al., 2005). Therefore, cellulose is insoluble in nonpolar and polar solvents due to its strong inter- and intra-molecular hydrogen bonds.

According to Lindman et al, the hydrophobic interactions between the cellulose sheets in the crystal play the most important role in the cellulose solubility. Insolubility in water is mainly caused by the amphiphilic character of cellulose which is revealed through its dissolution in both strong alkali and acidic aqueous solutions, with the hydrophobic inter-sheet interactions playing a predominant role. This is known as Lindman hypothesis (Lindman et al., 2010; Medronho and Lindman, 2015).

The anisotropy in cellulose structures clearly shows that there are areas of different polarity within the cellulose molecule and that it has both hydrophobic and hydrophilic features (Diddens et al., 2008; Yamane et al., 2006). Figure 6 shows the proposed hydrophilic and hydrophobic parts of the cellulose molecule.
The amphiphilic character of the cellulose has been confirmed by different studies and the hypothesis is comprehensively discussed in scientific media (Burchard et al., 2012; Hauru et al., 2012; Licl et al., 2013; Östlund et al., 2013). The amphiphilic characteristic of cellulose is confirmed by computer models (Nishiyama et al., 2012). In earlier studies of French et al., the idea that van der Waals forces were more important than hydrogen bonds was defended (French, Miller, and Aabloo 1993; French et al. 1995).

The first experiment of cellulose dissolution was conducted in 1850 and consisted of treating cellulose with sulfuric and nitric acid to produce cellulose nitrate, which is soluble in an ethanol-ether mixture. Since then, many different cellulose solvent systems have been developed, such as N-methylmorpholine oxide (NMMO); N,N-dimethylacetamide/lithium chloride (DMAc/LiCl); 1,3-dimethyl-2-imidazolidinone/lithium chloride (DMI)/LiCl; N,N-dimethylformamide/nitrous tetroxide (DMF/N2O4); dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF); some molten salt hydrates, such as LiClO4·3H2O, LiSCN·2H2O; and some aqueous solutions of metal complexes (Kauffman, 2009a; Wang et al., 2012). Some of the traditional cellulose solvents are shown in Figure 7.

Cellulose can be dissolved directly in NMMO monohydrate without derivatization; therefore NMMO monohydrate can be designated as a non-derivatizing
cellulose solvent. The resulting solution is referred to as a dope. In the DMAC/LiCl solvent system, the Li⁺ ions interact with the oxygen atoms of the carbonyl groups of the DMAC and Cl ions as nucleophilic bases, breaking up the inter- and intra-molecular hydrogen bonds in cellulose (Striegel, 2009). Likewise, N₂O₄ in the DMF/N₂O₄ system is responsible for the dissolution of cellulose (Portnoy and Anderson, 2009).

Cellulose solvents have been divided into derivatizing and non-derivatizing, and aqueous and non-aqueous solvents (Philipp et al., 1986). Alternatively, solvents can be grouped into certain modes of interaction with cellulose based on the morphological changes of the polymer determined by microscopy (Cuissinat and Navard, 2006).

The only industrial direct solvent for cellulose is NMMO and the procedure is known as the Lyocell process (Greek word lyein which means dissolve). However, due to the fibrillation of the produced fiber upon mechanical treatment under wet conditions and the still relatively high production costs, it has not yet replaced the viscose process. Additionally, NMMO is thermally unstable and requires a major investment in safety technology. Due to its oxidant nature, side reactions may be initiated, leading to solvent and cellulose degradation (Rosenau et al., 2001; Wang et al., 2012).

Ionic liquids are in the group of unicomponent solvents in the non-derivatizing category. In 1934, Charles Graenacher demonstrated that low-melting-point organic salts could be applied as non-aqueous and non-derivatizing cellulose solvents (Liebert, 2010). The initial interest in utilizing ionic liquids as solvents in reactions or separation processes was due to the set of readily available physical properties, such as non-volatility, non-flammability, thermal stability, and wide liquid range. However, these properties are very much dependent on the structure of the ionic liquid and cannot be generalized (MacFarlane and Seddon, 2007).

A wide range of ionic liquids is known today, and organic salts with low melting point are increasingly synthesized. However, according to the literature, ionic liquids (ILs) with ammonium and imidazolium cations are able to properly dissolve cellulose. Only organic salts with asymmetric cations produce melts that can properly interact with the cellulose backbone (Liebert, 2010).

After the dissolution of cellulose in IL, cellulose can be regenerated by precipitation into anti-solvents such as water, alcohols, acetone, or compressed carbon dioxide (Liebert 2010; Sun, Chi, and Mu 2014; Swatloski et al. 2002).

In 2002, Swatolski et al. published initial results on direct dissolution and regeneration of cellulose performed without activation or pretreatment of cellulose. Combining a 1-butyl-3-methylimidazolium cation with different anions, they found that chloride, as a small hydrogen bond acceptor, was the most effective anion to dissolve cellulose (Swatloski et al., 2002). However, these ionic liquids have high melting points and the corrosive character of their halides toward metal equipment has led to execution of other anions such as acetate and dialkylphosphate. In addition, imidazolinum based ionic liquids degrade cellulose especially at high temperatures. A non-imidazolinium ionic liquid has been introduced for fiber spinning by Hummel et. al (Hummel et al., 2015).
1.4 Fundamentals and practice of lignocellulosic dissolution

The physicochemical interactions between cellulose and ionic liquid (IL) are not yet fully understood. Therefore, the mechanism of cellulose dissolution remains elusive. ILs are known as non-derivatizing solvents that do not make any covalent bonds.

The data obtained from different studies show that both anion and cation of the ionic liquid affect the dissolution of cellulose, with the role of the anion being better understood than that of the cation. The higher the hydrogen bond basicity and dipolarity, the greater the ability of the salts of that anion to dissolve cellulose (Wang et al., 2012). However, it should be pointed out that not all the available data support this idea and more parameters, such as the presence of impurities in ILs, the dissolution techniques, the polymer concentration, the degree of polymerization (DP) of the solute etc., affect solubility (Erdmenger and Schiller, 2015).

Multiple studies show that the dissolution mechanism is mainly based on the interaction of the hydroxyl group of cellulose and the anions of ILs (Wang et al., 2012). On the other hand, the results from many other experiments and simulations have shown that the cation also has a role in the dissolution of cellulose in ILs. Moreover, there are many interpretations of its mechanism and more investigation is still needed on this subject (Rabideau et al., 2014; Wang et al., 2012).

As the available data show, the viscosity of the IL is not a key factor in cellulose dissolution; the net basicity and polarity of the anion are better indicators (Hauru et al., 2012). Microwave heating and sonication are more effective than thermal heating in the dissolution process of lignocellulosic materials (Wang et al., 2012).

1.5 Acetylation of cellulose solutions

Cellulose acetate is one of the most important commercial cellulose derivatives with a wide range of applications (Varshney and Naithani, 2011). It was developed by Schutzenberger in 1865 as the first organic ester of cellulose (Curtis and Crowley, 2009). However, it was the discovery of cellulose diacetate (CDA) by Miles and Eichengruen in 1904–1905 that allowed for a commercial breakthrough, as CDA was soluble in acetone and other readily available and comparatively cheap solvents like methyl acetate and ethyl acetate. The industrial success of this new artificial fiber was due to the Dreyfus brothers. Based on the Miles acetone process, they began producing photographic films in 1910. A few years later, they started the production of acetate lacquers and a so-called “Cel-lonit” film (Bonten, 2008; Kauffman, 2009b; Rustemeyer, 2004; Schaller et al., 2013).

Today, CDA with a typical degree of substitution (DS) of 2–2.7 is the most widely used form of cellulose acetate, which is mainly dry-spun into fibers for the production of cigarette filters. Further applications are in the fields of coatings, films, membranes, and textile fibers (Glasser, 2004; ISOGAI, 2013). On
the other hand, cellulose triacetate (CTA, DS>2.8), with its special optical properties, is used mainly as a film base for photographs and for supporting films for liquid crystal displays (Atalla and Isogai 2010).

In commercial acetate fibers, 74% to 92% of the hydroxyl groups are acetylated, which leads to lower crystallinity compared to unmodified regenerated cellulose fibers. Consequently, they are weaker, more extensible, less dense, and absorb less water than regenerated cellulose fibers (Hillier, 2003; Mistra, 2005).

Industrial acylation methods are heterogeneous processes. Cellulose is converted to cellulose acetate through a mixture of acetic acid, acetic anhydride, and sulfuric acid as a catalyst. The process consists of four steps including preparation of triacetate, partial hydrolysis, re-dissolving in acetone, and fiber spinning. Therefore, it is more expensive than other man-made cellulosic fiber (MMCFs), and it requires massive amounts of toxic chemicals (Schaller et al., 2013).

Extensive knowledge on the homogeneous derivatization of cellulose is available (Edgar et al., 2001; Heinze, T., And Liebert, 2001; Thümmler et al., 2010). The homogenous esterification of cellulose has distinct advantages over the heterogeneous esterification. In addition, the reaction conditions are milder and the distribution of acetate groups along the chain and within the anhydroglucose unit are more even (Heinze et al., 2006; Kakko et al., 2017). For homogenous esterification, many different cellulose solvents have been studied and developed. However, due to their high toxicity (e.g., N,N-dimethylformamide DMF/N$_2$O$_4$ (Liebert, 2010)) and high reactivity, which lead to side reactions or the formation of gels or de-swollen particles precipitated from the reaction medium, only a few of them (such as N-ethylpyridinium chloride, 1-allyl-3-methyl-imidazolium chloride, N-methylmorpholine-N-oxide, DMAc/LiCl and DMSO/TBAF) have the potential to be utilized for a controllable and homogenous esterification of polysaccharides (Heinze et al., 2006).

Solvents that are liquid at room temperature with low viscosities are of growing interest for cellulose modification reactions (Liebert, 2010). There are various studies on cellulose derivatization in ionic liquids (ILs), including those of (Abbott et al., 2005; Heinze and Barthel, 2006; Wu et al., 2014). Barthel and Heinze studied acetylation in [bmim]Cl ionic liquid without a catalyst under mild conditions and in a short reaction time using acetyl chloride as the acetylation reagent (Heinze and Barthel, 2006). Furthermore, Abbott et al. investigated the efficient O-acetylation of cellulose by using zinc-based ionic liquids (Abbott et al., 2005). Additionally, Wu et al. reported acetylation of cellulose in [amin]Cl liquid with a wide range of degree of substitution utilizing acetic anhydride as an acetylation reagent (Wu et al., 2014). The distribution pattern of acetyl groups and the degree of substitution of the backbone define the final properties of the cellulose acetate products (Iijima et al., 2005; Kamide and Saito, 1984; Miyamoto et al., 2003).

As shown in many studies, ILs have great potential for processing cellulose into value-added shaped products such as fibers and films (Swatloski et al. 2002; Feng and Chen 2008; Hummel et al. 2015; Sixta et al. 2015). ILs can be utilized to obtain homogenous biodegradable modified fibers in a one-step reaction with
common reagents avoiding complex multi-step derivatization procedures (Ass et al., 2004; Chen et al., 2017; Kakko et al., 2017; Schenzel et al., 2013).

Figure 8 shows the mechanism of the cellulose acetylation in [DBNH][OAc] (Kakko et al., 2017). When isopropenyl acetate (IpeAc) is used as the acetylation reagent, the only by-product is acetone, which can be easily removed by vacuum. There is no need to add any base or do any other activation on [DBNH][OAc] to reach a high reactivity. The IL acts as a catalyst to the acetylation reaction. The progress of the acetylation can be followed by infrared spectroscopy. A signal of ester carbonyl appears at \( \approx 1740 \text{ cm}^{-1} \) and the signal of hydroxyl decreases at \( \approx 3400 \text{ cm}^{-1} \). The signal of C-O-C around 1100 cm\(^{-1}\) remains unchanged during acetylation (Figure 9). Therefore, carbonyl signal changes are used as a reference to follow the acetylation and it correlates well with degree of substitution (DS) values (Kakko et al., 2017).

![Figure 8. Acetylation of cellulose in DBNHOAc by IpeAc (Kakko et al., 2017)](image.png)

![Figure 9. IR spectra to track the acetylation progress (Kakko et al., 2017)](image.png)

### 1.6 Rheological characterization of cellulose solutions

The basic principle of rheology is the correlation of the deformation of a fluid with the occurring stresses during flowing processes. Polymer solutions show complex flow properties, unlike water or oil, which have constant viscosity independent from the nature and velocity of the applied deformation. In a polymer solution, the viscosity is dependent on the deformation. Rheology uses three different measurement principles for the characterization of polymer solutions including steady shear, small amplitude oscillatory shear, and elongation deformation (Chemie, 2005).

The great majority of (polymer) solutions shows a rheology with characteristics of a liquid as well as a solid. Being both elastic and viscous, they are referred to
as “viscoelastic”. By determining both elastic and viscous properties of the fluids, we can get an insight into their molecular structure and modify this structure to meet special application requirements (Han et al., 2007). The elasticity results in the Weissenberg effect and the die swell effect, which give direct insight into the rheological behavior.

1.6.1 Rheology in fiber spinning of cellulose solutions

Understanding the concentration-dependent shear and extensional rheology of cellulose-ionic liquid (IL) is an important step toward utilizing ILs as a processing media in fiber spinning and to understand dynamic and thermodynamic properties of cellulose chains in ILs. Cellulose and cellulose derivatives are characterized by a high intrinsic viscosity, large radius of gyration, and large characteristic ratio, \( C_\infty \). They also have a small second virial coefficient, show viscous shear thinning in semidilute and concentrated solutions, and have a large persistence length, \( l_p \). These characteristics result in semi-flexible conformations of cellulose chains in solutions (Haward et al., 2012).

Small amplitude oscillatory shear testing can be utilized to determine the viscoelastic properties of spinning solutions. In this test, the response of a fluid is determined using a sinusoidal small amplitude deformation. In this method, the amplitude is kept very small over the whole measurement range, so that the viscoelastic regime is retained and the shear-sensitive structures are not destructed (Han et al., 2007).

The frequency sweep, which describes the time-dependent behavior of a sample in the non-destructive deformation range, can provide complex viscosity \( \eta^* \), storage modulus \( G' \), and loss modulus \( G'' \) of cellulose solutions. Storage modulus is the proportion of the total rigidity (the complex modulus) of a material that is attributable to elastic deformation while the loss modulus is the proportion of the total rigidity of a material that is attributable to viscous flow. The complex viscosity is the complex modulus divided by angular frequency. To determine the zero shear viscosity, which is the viscosity at the limit of low shear rate, the complex viscosity curves can be fitted with the Carreau or Cross viscosity models. The Cross viscosity model was recommended for cellulose-IL solutions (Sammons et al., 2008).

The Cox-Merz rule should be valid to calculate the zero shear viscosity from complex viscosity. According to the empirical Cox-Merz rule, for the linear viscoelastic materials with identical frequency and shear rate, the complex viscosity \( \eta^* \) is identical to steady shear viscosity \( \eta \). Molten polymers and entangled solutions are examples of a perfect match between \( \eta^* \) and \( \eta \). The validity of this rule is disputed for cellulose solutions. While some have found the rule to be invalid (Wang et al., 2008), others have confirmed the Cox-Merz rule for cellulose solutions (Haward et al., 2012).

Storage and loss moduli are frequency-dependent and reflect the elastic and viscous behavior of the cellulose-IL solution. For highly concentrated cellulose-IL solutions (>10%), at high angular frequency, the storage and loss moduli intersect at the so-called cross-over point (COP) at which the sample behavior changes from predominantly viscous to elastic. The COP also represents a mean-relaxation time, which depends on the molecular weight of the cellulose.
Through the increase of the temperature or decrease of the cellulose concentration or cellulose degree of polymerization (DP), the COP shifts to lower angular frequencies (Schauberger and Moslinger, 1999).

The rheological properties of the cellulose-IL solutions, prepared for spinning, can provide good information to define the stable spinning window (Sixta et al. 2015). The viscoelastic properties of the spinning dopes should be in a defined range to guarantee good spinnability (Michud, Hummel, and Sixta 2015; Ziabicki and Takserman-Krozer 1964a, 1964b). For IONCELL fibers from eucalyptus pre-hydrolysis kraft (E-PHK) pulp, the spinning solutions showed good spinnability when the cross-over point of the dynamic moduli was approximately 4000-5000 Pa at an angular frequency of around 1 s⁻¹, and the “zero shear” viscosity was ca. 30000 Pa.s. In a study by Michud et al., a good spinnability was observed when the zero shear viscosity is between 27000 and 40000 Pa.s., the COP of storage modulus ($G'$) and loss modulus ($G''$) is between 0.8 and 1.5 s⁻¹, and the dynamic moduli at COP is between 3000 and 6000 Pa (Michud, Hummel, and Sixta 2015).

1.7 Dry-jet wet spinning of cellulose-ionic liquid solutions

The study of natural fibers is one of the most interesting fields of modern scientific research. Scientists are trying to provide a satisfying explanation for the unusual and invaluable properties of these fibers by studying the chemistry and physics of the fibers. All fibers seem to have one common feature: the molecules are always long and thread-like. Thousands of atoms are strung together one after another. For instance, in cellulose, several hundred glucose units have formed a long thin chain. One of the most prominent properties of the fibers is their strength. Relative to its cross-sectional area, the strength of silk fiber, for example, is extraordinarily high, and it can support a weight of several grams. In addition, it is flexible and resilient (Cook, 2012).

The first step in fiber spinning is to prepare the fiber-forming material into a liquid or semi-liquid state. This can be done by dissolving the material in a solvent or by heating it until it melts. This helps the long molecules to get free from closed entanglements and move independently. The fiber-forming material is then extruded from the spinneret, and then the fine jets are hardened to form filaments; this process is referred to as spinning.

There are three types of spinning including wet, dry and melt spinning. In wet spinning, the spinning solution is extruded into an aqueous coagulation bath in which the filaments are hardened as a result of a combined or successive coagulation and regeneration. This type of spinning is used in viscose production. During dry spinning, as used in CDA production, the solvent is evaporated by a stream of hot air once the spinning solution is extruded from the spinneret. In melt spinning, the fiber-forming material is heated until it melts, and the jet hardens as it is extruded out of the spinneret. Nylon production is an example of this process (Cook, 2012).

In the dry-jet wet spinning process, the polymer solution is extruded out of the spinneret through fine holes. Then, the emerging fluid jet is stretched into a filament of the desired diameter in an air gap. Afterward, the filaments are im-
mersed in a coagulation bath of a non-solvent. In the coagulation bath, precipitation occurs under tension and the polymeric filament is taken up on the godet. Water can be used as the nonsolvent in the coagulation bath (Haward et al., 2012).

Structure formation of the filaments during the spinning process of cellulose-IL solutions is an important step to control the properties of the final product. The structure formation of Lyocell fibers has been studied by Fink et al. (Fink et al., 2001). The structure is formed by the deformation of the spinning dope in the spinneret and air gap during the coagulation of cellulose and during the washing and drying of the fibers. The structure formation is determined by orientation, crystallization, and coagulation processes (Dube and Blackwell, 1983).

The typical fiber parameters that are affected in the spinning process are shown in Figure 10. Solidification of the filaments happens by cooling (quenching) or in the coagulation bath. Solidification is associated with an increase in zero shear viscosity. In a viscose mass, the relaxation is slower. Accordingly, the elongation forces and the increase in viscosity correspond with the increase of orientation along the fiber axis (Stibal et al., 2004).

![Figure 10. Fiber parameters change in spinning process](image)

This orientation is maintained in the as-spun fibers and can be measured by birefringence. The crystallization of the fibers is complicated to predict, since it depends on many different factors, such as the interaction of the polymer properties, spinning conditions, and orientation.

In the spinning process, a filament is under different force components. This issue was first studied by Ziabicki (Ziabicki, 2005). At any given distance from the spinneret, this force is given by

$$F_{\text{rheo}}(x) = F_{\text{ext}} + F_{\text{grav}}(x) - F_{\text{inert}}(x) - F_{\text{fric}}(x) - F_{\text{surf}}(x)$$

where $F_{\text{rheo}}$ is the rheological force or tensile force; $F_{\text{ext}}$ denotes the external take-up force, which is constant along the entire threadline; and $F_{\text{grav}}$ is the force of gravity (weight of filament suspended from point $x$). If the fiber is spun vertically upward, $F_{\text{grav}}$ is negative, while it is zero if the fiber is spun horizontally. Moreover, $F_{\text{inert}}$ is the force of inertia (due to acceleration to reach the velocity $V_L$ at the end of the spinning path), $F_{\text{fric}}$ is the frictional force between the surface of the filament and the spinning medium, and $F_{\text{surf}}$ is the force due to the surface
tension (which tends to minimize surface area of the filament by shrinkage). Figure 11 shows the balance of forces in filament spinning.

At the solidification point \((x = x_s)\) and thereafter, \(F_{\text{inert}}\) is zero. Additionally, the surface and interfacial tension are often negligible. At the end of the spinning path \((x = x_L)\), \(F_{\text{grav}}\) (in downward spinning) and \(F_{\text{fric}}\) are zero. At this point, the tensile force applied to the filament, \(F_{\text{rheo}}\), is therefore equal to the external take-up force. Complicated mathematical procedures are required to calculate the force component of Equation 1 (Stibal et al., 2004).

Instabilities in the fiber spinning process can influence the quality of the fiber. These instabilities can be determined by the pulling rate, surface tension, inertia, and material characteristics. Amongst instabilities, “draw resonance” can occur when the pulling rate exceeds a certain threshold.

![Figure 11. Balance of forces in filament spinning (Stibal et al., 2004)](image)

The spinning process can be divided into two categories: internal and external processes. The internal process occurs before the spinning mass extrudes out of the spinneret holes, while the external process commences from the time the spinning mass leaves the spinneret hole. Therefore, the drawing and solidification of the filament are also part of the external process (Stibal et al., 2004).

The flow processes are controlled by the shear flow properties (shear viscosity \(\eta\), and shear rate \(\dot{\gamma}\)) of the spinning solution under the extrusion conditions (Stibal et al., 2004). Further flow processes are characterized by extensional or elongational viscosity \(\eta_D\), and elongational rate \(\dot{\varepsilon}\).

### 1.8 Flow processes in spinning

The schematic of flow processes in fiber spinning is depicted in Figure 12. Simple shear and tubular flow are shown in Figure 12A, where the layers are assumed infinitely long in the flow direction. The simple shear flow occurs when tangential force is applied to a given plane. Then, an equal and opposite force acts on the opposing interface. Thin laminar layers are displaced in parallel and show a velocity profile. The energy brought into play is converted to frictional heat. In tubular flow, the force is applied to the circular face, and the opposing force from the friction is created against the tube wall. In the steady-state, the
fluid leaving the element under investigation is persistently replaced. In laminar, linear shear flow, the shear rates read
\[ \dot{\gamma} = \frac{dv(x)}{dx} \] (2)
for a planar surface, and
\[ \dot{\gamma} = \frac{dv(r)}{dr} \] (3)
for a tube. The shear stress is given by
\[ \tau = \frac{F}{A} \] (4)
while the shear viscosity (also called Newtonian viscosity or dynamic viscosity) is given by
\[ \eta = \frac{\tau}{\dot{\gamma}}. \] (5)

Here, \( x, v, r, F, \) and \( A \) are the coordinate axis, velocity, tube radius, applied force, and area, respectively.

**Figure 12.** Schematic of flow processes in fiber spinning. A) Laminar shear flow shown as simple shear between horizontal layers and as tubular flow with telescopic shearing; B) Monoaxial, steady-state elongational flow \( F = \) force; \( A = \) area; \( x = \) coordinate axis; \( r = \) radius; \( v = \) velocity. (Stibal et al., 2004)

Hence, to reach a given average flow rate, a force proportional to the shear viscosity of the material must be applied.

The spinning solutions are non-Newtonian fluids and show complex behavior under shear rate testing. These solutions are pseudoplastic (\( \eta \) decreases as the shear rate increases) or viscoelastic (viscosity is time dependent) and display elastic deformation.

The most entropically favorable conformation of the polymer solution is the ball with randomly-coiled chains. Once there is a lack of external elongational force, the macromolecular polymer chains will adopt this conformation (Gordon, 2007). However, such conformation mainly depends on the thermodynamic and structural properties of the solvent (Taylor, 2004). As reported for cellulose in NMMO solution, instead of ball with randomly-coiled chains, the
conformation occurs as a fringe micelle model (Arndt et al., 2000). Elongational flow occurs when a force acts perpendicular to an area with a finite cross section (Figure 12B), and a simultaneous lateral contraction of fluid is accompanied by elongation to keep the fluid volume constant. Thus, during steady elongational flow, a very small volume of fluid with an initial cross section \( A_0 \) accelerates in the direction of flow under elongating force (Stibal et al., 2004).

In the steady-state, the outflow is continuously replaced by inflow through the area \( A_0 \). The following terms can be defined and are equivalent to those mentioned for shear flow.

\[
\dot{\varepsilon} = \frac{\text{dv}(x)}{\text{dx}} 
\]

\[
\sigma = \frac{F}{A(x)} 
\]

\[
\eta_D = \frac{\sigma}{\dot{\varepsilon}} 
\]

\( \dot{\varepsilon} \) is Elongation rate, \( \sigma \) is the tensile stress (also called elongational or normal stress), and \( \eta \) elongational viscosity (also called extensional or Trouton viscosity). Incompressible Newtonian fluids and non-Newtonian fluids only at low shear rates, show the following relation

\[
\eta_D = 3\eta. 
\]

With the increase of the shear rate and elongation rate, the shear viscosity decreases. However, the shear force increasingly orients the randomly coiled ball-shaped molecules (e.g. molten branched polyethylene) to the elongated threads. Therefore, the flow resistance drops. The elongational viscosity first increases and then decreases (Stibal et al., 2004).

Die swell is a common phenomenon in the processing of non-Newtonian fluids. In the spinning process, it happens when the spinning solution is extruded out of spinneret, and the diameter of the solution is larger than the diameter of the spinneret hole. This is also known as the Barus effect or onion formation, which originates from the elastic behavior of the polymers and their solution. There are two reasons for die swell. The first reason is that the spinning solution is exposed to elongational and shear deformation when entering the spinneret capillaries. Flowing through the capillary, the resultant elastic stress partially relaxes, but the residual elasticity increases with the decrease of the residence time (due to a lower ratio of a capillary’s length to its diameter). When the solution comes out of the spinneret, the residual elasticity recovers, and die swell happens. The second reason is that even when the solution emerges from a long tube and there is no capillary, shear flow produces entropy-elastic molecular orientation (Stibal et al., 2004).

In fiber spinning, the degree of stretching applied to the fluid filament within the air-gap of distance \( d \) between die and roller is quantified as a draw ratio (DR).

\[
DR = \frac{V_f}{V_0} 
\]
$V_t$ is the take-up velocity (cm.s$^{-1}$) and $V_0$ is the extrusion velocity, which is calculated from the ratio of the volume throughput (cm$^3$.s$^{-1}$) to the free cross-sectional of the spinneret holes (cm$^2$). The draw ratio varies with the spinning process; it can range from several hundred in melt spinning to less than one in solution spinning, which means the extrusion velocity exceeds the take-up velocity (Stibal et al., 2004).

Based on the preorientation of a filament and the desired mechanical properties, the filament can be drawn to various extents. With the increase of the draw ratio, the tenacity-at-break value increases and the elongation-at-break value decreases. If the macromolecules are straightened and aligned along the fiber axis during the spinning process, the maximum strength can be achieved (Stibal et al., 2004).

When the cellulose component of the cellulose-IL solution is precipitated in the anti-solvent, cellulose adopts a modified crystal structure. The structure can be studied with the X-ray diffraction technique, which shows a notably different pattern from native cellulose (Krässig, 1993). Small and wide-angle scattering can provide more insight into the structural features of regenerated cellulose fibers (Zugenmaier, 2009).

X-rays interact with matter in three different ways: (1) High-energy X-rays expel electrons from electron shells close to atom nuclei, which results in material-specific radiation used in X-ray spectroscopy; (2) the interaction of the X-rays and the substrate occurs in form of impacts, resulting in a deflected radiation of changed wavelength known as incoherent diffraction; or (3) the interaction causes the electrons in the radiated material to vibrate so they become the source of radiation with identical wavelengths to the incoming X-rays, known as coherent diffraction, which mainly occurs in crystalline materials (Krässig, 1993).

When using the X-ray diffraction technique for fiber analysis, the bundles should be well aligned. It is widely accepted that the orientation of the crystalline domains can be evaluated from X-ray diffraction measurements. If the crystallite orientation is random around a given axis, the wide-angle diffraction pattern is in continuous circle form. If the fibrillary crystallite strands are oriented along the fiber axis, the reflections appear as arcs. By increasing the orientation, the arcs become narrow (Krässig, 1993). Figure 13 shows the wide-angle scattering of the low- and high-stretched IONCELL fibers. The intensity distribution along the arcs shows the orientation in the fiber specimen.

Wide-angle X-ray scattering can be utilized to evaluate the degree of crystallinity and orientation of the fibers (Ahvenainen et al., 2016; Krässig, 1993; Park et al., 2010; Segal et al., 1959). The width at half-maximum intensity of the meridional and equatorial reflections can be used to determine the crystallite length and width, respectively (Krässig, 1993). The total intensity of the X-ray scattering gives information on the fraction, overall volume, and dimensions of voids (Krässig, 1993).
Small-angle X-ray scattering (SAXS) analysis can reveal the inner structure of cellulose. In the classical two-phase model, the polymer consists of a series of periodical crystalline and amorphous domains. The structure of flexible and crystallizable polymers like aliphatic polyamides and polyesters matches this model. However, this model is used due to its simplicity and the ease of interpreting and correlating the mechanical properties of these polymers (Sharma et al., 1997). In semi-crystalline fibers, two meridional spots can be seen in their SAXS pattern. They originate from the differences in the electron density of amorphous and crystalline domains. This periodic fluctuation along the fiber axis is known as the long period. Polymers with rigid chains, such as aramids, do not show this SAXS pattern, which is an indication of a single-phase paracrystalline structure (Northolt, 1985).

The high-tenacity technical cellulose fibers, namely Cordenka EHM and Fortisan, do not show the two SAXS meridional spots unless they are heated to 200°C in water. This can be explained by a model in which crystalline domains have been separated from less ordered domains. In Northolt’s opinion, the high- and low-oriented cellulose fibers have single-phase structures (Northolt, 1985).

According to a study by Schurz on the structure of the regenerated cellulose fibers, namely Modal and Lyocell, four different domains including A, B, C, and D exist in cellulose elementary fibrils (Figure 14). The crystallites (A) are connected with amorphous regions (B) in an alternating manner. Additionally, adjacent amorphous zones (C) or adjacent crystalline zones (D) may connect laterally. Therefore, the lateral strength between the fibrils can be the result of the formation of the aggregates known as crystallite clusters. The lateral cohesion is lower for Lyocell fibers in comparison to viscose fibers, which leads to a higher tendency of fibrillation.
In Lyocell fibers, the long and highly oriented crystallites within the elementary fibrils and highly oriented amorphous region are responsible for the superior mechanical properties. The high tensile strength and modulus under wet conditions were attributed to the high total orientation of the fibrils, including the less-ordered domains, which prevents the distortion of the fibrils by the penetration of water (Lenz, Schurz, and Wrentschur 1993; Lenz, Schurz, and Wrentschur 1994; Schurz and Lenz 1994).
2. Experiment

2.1 Materials

2.1.1 Cellulose, hemicellulose and lignin sources
Different cellulose sources have been employed in this PhD thesis. Their specification can be found in table 1. Waste cotton, from hospital bed sheets, with different intrinsic viscosities, \( \eta \), were employed for the experiments in paper I. Spruce sulfate pulp was used in paper I. Birch pre-hydrolyzed kraft (B-PHK) from Stora Enso was used in paper I, II and III. Eucalyptus pre-hydrolyzed kraft pulp (E-PHK) from Bahia was employed in paper IV.

<table>
<thead>
<tr>
<th>pulp</th>
<th>publication</th>
<th>producer</th>
<th>( \eta ) cellulose</th>
<th>xylan</th>
<th>mannan</th>
<th>Mn</th>
<th>Mw</th>
<th>PDI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-PHK</td>
<td>IV</td>
<td>Bahia</td>
<td>468</td>
<td>94.0</td>
<td>2.5</td>
<td>0.0</td>
<td>79.8</td>
<td>268.7</td>
</tr>
<tr>
<td>B-PHK</td>
<td>I, II, III</td>
<td>Stora Enso (Enocell)</td>
<td>476</td>
<td>94.3</td>
<td>5.3</td>
<td>0.0</td>
<td>68.2</td>
<td>274.3</td>
</tr>
<tr>
<td>Spruce-Sulfite</td>
<td>I</td>
<td>Domsjö</td>
<td>540</td>
<td>1.4</td>
<td>0.0</td>
<td>54</td>
<td>406.6</td>
<td>7.5</td>
</tr>
<tr>
<td>Waste Cotton</td>
<td>I</td>
<td>Hospital bed sheets</td>
<td>750</td>
<td>99</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>83.8</td>
<td>203.2</td>
</tr>
<tr>
<td>Waste Cotton</td>
<td>I</td>
<td>Hospital bed sheets</td>
<td>587</td>
<td>99</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>119.8</td>
<td>307.1</td>
</tr>
<tr>
<td>Waste Cotton</td>
<td>I</td>
<td>Hospital bed sheets</td>
<td>452</td>
<td>99</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>151.6</td>
<td>348.4</td>
</tr>
</tbody>
</table>

*Poly dispersity index*

Hemicellulose source
The xylan used in paper III, was the same as reported in Alekhina et al (Alekhina et al., 2014), isolated by cold caustic extraction from a birch Kraft pulp. It contained 1 mol% glucose, 96.7 mol% xylose, 0.5 mol% mannose, 0.3 mol% arabinose and 1.5 mol% 4-O-Methyl glucuronic acid. The weight average molecular
mass of the xylan was 30600 g.mol⁻¹ as determined by gel permeation chromatography (GPC) measurement.

Lignin source
The lignin was a beechwood organosolv lignin used also by Ma et al. (Ma et al., 2015) and consists of 90.2 wt% lignin, 9.6 wt% hemicelluloses and 0.2 wt% cellulose. The lignin originates from the Fraunhofer Institute CBP, Germany.

Isopropenyl acetate
Isopropenyl acetate (IpeAc) from Sigma Aldrich has been utilized for esterification of the cellulose in paper IV.

2.1.2 Solvent ([DBNH][OAC] ionic liquid)
Ionic liquid, 1, 5-diazabicyclo 4.3.0 non-5-ene acetate ([DBNH][OAc]) was synthesized at Helsinki University (paper IV) and Aalto University (paper I, II & III) by slowly adding equimolar amounts of acetic acid (glacial, 100%, Merck, Germany) to 1,5-diazabicyclo 4.3.0 non-5-ene (DBN, 99%, Fluorochem, UK) in a 2000 cc reactor at 70 °C with a constant mixing rotation speed (Parviainen et al., 2015).

2.2 Grinding and viscosity measurements
The pulp and bed sheets were cut into a powder using a Wiley mill with a 1 mm sieve, then oven-dried to constant weight at 105 °C. The intrinsic viscosity of the ground waste cottons was determined in cupriethylenediamine (C.E.D.) by capillary viscometer following the standard method (SCAN-CM 15:99).

2.3 Viscosity adjustment
The intrinsic viscosity of the cellulose substrate and the polymer concentration are decisive for the rheology of the spinning solution and thus for the spinnability of the fibers. An intrinsic viscosity of the polymer of 450 ± 50 mL/g proved to be the ideal compromise for excellent spinnability and the highest possible polymer concentration (≥13 wt%). Acid and enzyme hydrolysis were performed to decrease the degree of polymerization and adjust the intrinsic viscosity of the waste cottons in the paper I to the range of 390-450 ml.g⁻¹, suitable for spinning. For the acid treatment, sulfuric acid with a concentration of 0.3 mol.L⁻¹ was used. The liquor-to-pulp ratio was 100:3 and the temperature set to 90 °C, while the incubation time has been varied to reach different viscosities. The results can be seen in table 2. The enzymatic treatment of the milled waste cotton was carried out in a temperature controlled sigma mixer (Farinograph, Brabender, Duisburg, Germany) using a cotton batch size of 50 g (dry weight) at VTT Finland. The cotton sample was first placed into a plastic bag and the enzyme solution (Ecopulp R, AB Enzymes Oy, Finland) diluted with 0.1M sodium acetate buffer pH 5 was sprayed into the powdered cotton giving a nominal enzyme dosage of 10 mg protein per 1 g of cotton. After thorough mixing, the cotton sample was loaded into the mixer and treatment was performed under mixing (40 rpm) at 50 °C for 4 hours. Thereafter the cotton slurry was transferred into a glass bottle, which was placed into a boiling water bath (100 °C) for 15
min to inactivate the enzyme. Finally, the waste cotton pulp was filtered in a Büchner funnel, washed thoroughly with distilled water and stored at +4 °C until used. The softwood sulfite dissolving pulp (intrinsic viscosity 540 ml/g) was degraded (intrinsic viscosity 268 ml/g) at a temperature of 165 °C for 90 minutes using a sodium hydroxide concentration of 0.9 mol/L \(^{-1}\) and the liquor-to-pulp ratio of 20:1.

**Table 2.** Acid hydrolysis time and resulting intrinsic viscosity of cotton waste (CoW) 750 ml/g

<table>
<thead>
<tr>
<th>Acid hydrolysis Time (min)</th>
<th>Final Intrinsic viscosity (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>315</td>
</tr>
<tr>
<td>30</td>
<td>365</td>
</tr>
<tr>
<td>10</td>
<td>438</td>
</tr>
</tbody>
</table>

**2.4 Molar mass distribution**

Molar mass distribution of pulps and fibers is determined by gel permeation chromatography (GPC). Prior to the analyses, the samples are activated by a water–acetone–N,N-dimethylacetamide (DMAc) sequence. The activated samples were dissolved in 90 g/L lithium chloride (LiCl) containing DMAc at room temperature and under gentle stirring. The samples were then diluted to 9 g/L in LiCl/DMAc, filtered with 0.2 \( \mu \)m syringe filters, and analyzed in a Dionex Ultimate 3000 system with a guard column, four analytical columns (PLgel Mixed-A, 7.5 x 30 mm), RI-detection (Shodex RI-101) dual-angle light scattering and viscometer. The flow rate of 0.75 mL/min was used. Narrow pullulan standards (343 Da–2500 kDa) were used to calibrate the system. The molar masses \((\text{MM})\) of the pullulan standards are modified to correspond to those of cellulose and acetylated cellulose \((\text{MM}_{\text{cellulose}} = q * \text{MM}_{\text{pullulan}})\), as proposed by (Berggren et al., 2003). The coefficients \(q = 12.19\) and \(p = 0.78\) were found by a least-squares method using the data published in their report.

**2.5 Dope preparation**

In all the studies for dope preparations, the ground pulp samples have been oven-dried at 105 °C to constant weight and then dissolved in the ionic liquid (IL) in the vertical kneader. The dissolution conditions varied in different studies. As reported in paper I, the dope preparation was performed at 100 mbar, 80 °C, stirring speed of 10 rpm and a duration of 90 minutes. For the spinning results presented in paper II, the ground pulp was solubilized at a pressure of 10 mbar, a rotational speed of the kneader of 30 rpm, at 80 °C, and for the duration of 90 minutes. In the paper III, the rotation of the kneader for dope preparation was 30 rpm, the temperature was between 80 to 85 °C, and dissolutions were performed for 90 to 120 minutes depending on the solutes.

In paper IV, the dope preparation and acetylation has been done in one-step by Tia Kakko at Aalto University. The temperature was set to 90 °C and mixing rate was between 25 rpm. The pulp was dissolved for 0.5-1.0 h until the reaction mixture was clear. During the dissolution, a vacuum was applied to the system.
for keeping moisture out of the reaction vessel. When the dissolution was complete, the temperature was lowered to the reaction temperature (70 °C) and isopropenyl acetate (IpeAc) was added dropwise with a syringe and needle through a septum. The reaction vessel was connected to a reflux condenser and CaCl2–tube. Reaction time was 1 hour. After the reaction, the vacuum was applied again in order to remove unreacted reactant and the forming side product (acetone). The reactions have been made with different equivalents (eq) of reactant per an anhydroglucose unit of cellulose. The used equivalents were 0.75, 0.5, 0.25 and 0.05 respectively.

The solutions (spinning dopes) were kept under vacuum for an additional hour to remove air bubbles. Subsequently, it was press-filtered through a layered filter mesh (GKD Ymax2, 5 μm nominal, Gebr. Kufferath AG, Germany) under 2 MPa.

Spinning dopes were prepared from waste cottons with different viscosities, with different concentrations, and by blending the waste cotton and softwood sulfite pulp. The cellulose concentrations were 7, 10, 13 and 15 wt%. In paper II and IV, the dopes’ concentrations were 13wt% cellulose-ionic liquid. In paper III, Cellulose and cellulose/xylan (75:25) dopes prepared in 13 wt% concentration and cellulose/lignin (75:25) and cellulose/xylan/lignin (50:25:25) in 15 wt%.

2.6 Rheology measurement

The rheological characteristics of the cellulose-IL solutions under shear stresses were measured. The viscoelastic behavior was studied by means of an Anton Paar MCR 300 rheometer with parallel plate geometry (25 mm plate diameter, 1 mm gap size). The dynamic frequency sweep was performed with a strain of 0.5% within the angular velocity range of 0.1-100 s⁻¹ at various temperatures from 60 to 85 °C. Complex viscosity, storage, and loss moduli were recorded. Assuming that the Cox-Merz rule was valid (Cox and Merz, 1958; Lu et al., 2012), the zero shear viscosity was determined by fitting the complex viscosity data with the three-parameter Cross viscosity model (Sammons et al., 2008).

2.7 Fiber spinning

Filament spinning was performed with a laboratory spinning system (Fourné Polymertechnik, Germany) with a 36 multifilament spinneret [papers I, II and IV] and a 200 holes spinneret [paper III], with a capillary diameter of 100 μm, and a capillary length of 20 μm. The spinning temperature has been selected from rheology measurements to satisfy the requested viscoelastic properties. The dope was spun via an air gap into a cold water bath (10-15°C), where the formed filament was led over a PTFE guide roller (at 20 cm depth) and via another guide onto a motor-driven godet couple. The rate of extrusion (Ve) was kept constant while the take-up velocity (Vtu) of the godet couple was varied according to the targeted draw ratios (DRs) (Vtu/Ve).

The filaments were collected on the godet, carefully removed with a razor blade, washed with hot water (70 °C), air-dried and stored under controlled conditions (23 °C, 50% RH paper I, IV, 20 °C, 65% RH, paper II and III) for tensile strength measurements.
2.8 Fiber characterization

2.8.1 Chemical composition of fibers

2.8.1.1 Carbohydrate analysis

The chemical composition (carbohydrate, Klason lignin and acid-soluble lignin) of the fibers in the paper III, were analyzed according to NREL/TP-510-42618. The amount of carbohydrates was detected by high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) by using a Dionex ICS-300 system. The cellulose and hemicellulose content was calculated according to the amount of monosaccharides following the Janson formula (Jonson, 1970). The acid-soluble lignin (ASL) was determined by using a Shimadzu UV 2550 spectrophotometer at a wavelength of 205 nm using an absorption coefficient of 110 Lg⁻¹cm⁻¹.

2.8.2 Physical and mechanical properties analysis of the fibers

2.8.2.1 Tensile strength measurement

Filament testing was done with 10 samples of each spinning trial at 23 ºC, 50% RH paper I & IV, 20 ºC, 65% RH, paper II & III. Linear density (titer) was determined with a vibroscope (Vibroskop 400, Lenzing Instruments GmbH & Co KG, Austria) with at least 50 mg.dtex⁻¹ pretension. Tensile strength and elongation were determined using a Vibrodyn 400 (Lenzing Instruments GmbH & Co KG, Austria) in both dry and wet conditions. Ten fibers from each sample were tested. The gauge length was 20 mm and the speed was 20 mm.min⁻¹ according to DIN 53816.

2.8.2.2 Elastic moduli

Elastic moduli were determined from the slope of the stress-strain curve of the fiber in the elastic part according to the ASTM D2256 standard. The stress-strain curve data was obtained from the vibroscopic measurements and the calculation using a MATLAB script (MathWorks, Inc.).

2.8.2.3 Birefringence

Birefringence is an optical property of fibers, which was determined from three selected filaments with a Zeiss Axio Scope A1 microscope equipped with a Leica B 5λ-Berek tilting compensator. Titer was measured three times with the vibroscope, permitting 1.5 % variation to exclude artifacts, and the diameter was calculated assuming a density of 1.5 g.ml⁻¹ (Männer et al., 2011). During the measurement, the filaments are extended between two pieces of double-sided tape on a microscope slide. The optical retardation \( \Gamma \) is determined in triplicate from a selected spot. Birefringence \( \Delta n \) is defined as the retardation divided by the diameter \( d_s \). Total orientation \( f_i \) of fibers was determined by \( \Delta n \) divided by the maximum birefringence of cellulose 0.062 which is assumed to be equivalent to 100 % orientation (Adusumalli et al., 2009; Schurz and Lenz, 1994).

\[
\Delta n = \frac{\Gamma}{d_s}
\]  
(9)
2.8.2.4 Dynamic mechanical analysis (DMA)
Fibers in the paper II were characterized by DMA temperature scans using a TA Instruments Q800 Analyzer. Film tensile mode was used during the analysis using an amplitude of 20 μm and a frequency of 1 Hz. The average length of the fibers was approximately 10 mm. The samples were first equilibrated at 30 °C for 5 minutes, after which the storage modulus ($E'$), loss modulus ($E''$), loss tangent (tan δ) and dynamic moduli were measured at 30 to 280 °C at a heating rate 3 °C/min.

2.8.3 Structural characterization of the fibers

2.8.3.1 Solid state nuclear magnetic resonance (NMR)
Approximately 200 mg of fibers have been cut to small pieces and tightly packed into a 4 mm zirconium rotor (paper I). Solid-state 13C CP-MAS nuclear magnetic resonance (NMR) analyses were conducted on a Bruker AVANCE™ NMR system with UltraShield Plus 400 MHz magnet operating at 100.6 MHz. The spectrometer was equipped with a 4 mm Bruker MAS probe and samples were spun at 8000 Hz MAS speed. Measurements were performed at room temperature with the following acquisition parameters: cross-polarization (CP) contact time 2 ms, repetition interval 3 s, acquisition time 41 ms, SPINAL-64 1H decoupling, at least 2048 accumulations per T1 increment or CP-MAS spectrum. The delay between pulses was 5 s. Chemical shifts were referenced externally against glycine (13C-shift = 176.03 ppm for the carbonyl signal). The acquired free inductions decay (FIDs) were Fourier transformed without apodization. The cellulose II CP/MAS NMR spectra characterization has been studied by Isogai et al (Isogai et al., 2005) and the chemical shifts have been assigned as at the following: 105.8-106.3 C1 region, 88.7-88.8 C4 and 63.5-64.1 C6 region. The crystallinity index was calculated through deconvolution of the C4 peak using Lorentzian and Gaussian functions as suggested by Zuckerstätter et al. by means of Mathematica (Wolfram Research) (Park et al., 2010; Zuckerstätter et al., 2013; Zuckerstätter and Schild, 2009).

2.8.3.2 X-ray scattering analysis
Wide- and small-angle X-ray scattering experiments were carried out by means of a laboratory-scale X-ray instrument (SAXS LAB Ganesha) with $\lambda = 0.154$ nm for dry and swollen fibers in Kemicentrum, Lund University, Sweden for paper II. A bundle of cellulose fibers was mounted vertically on the sample holder with the fiber direction perpendicular to the X-ray beam for dry fibers. Typical acquisition times for a WAXS experiment were 300 s and for the SAXS 2700 s, respectively. The WAXS analysis for paper IV performed at Fraunhofer Institute in Germany.

2.8.3.2.1 Wide-angle X-ray scattering (WAXS) analysis

2.8.3.2.1.1 Crystallinity
According to (Ahvenainen et al., 2016) the best methods for evaluating crystallinity when having different crystallite sizes are area-based methods.
Herein, an amorphous subtraction method was used and the crystallinity was calculated by

\[ C = 1 - \frac{\int_{2\theta_1}^{2\theta_2} I_{\text{am}} d(2\theta)}{\int_{2\theta_1}^{2\theta_2} I_{\text{sample}} d(2\theta)} \] (10)

where \( I_{\text{am}} \) is the intensity of the fitted amorphous model and \( I_{\text{sample}} \) is the total scattering intensity of the sample, including both amorphous and crystalline contributions. A region between \( 2\theta_1 = 4.9 \) and \( 2\theta_2 = 35.9 \) degrees was used to determine the sample crystallinity. Lyocell fibers were tested as a reference.

2.8.3.2.1.2 Crystallite size

The average crystallite size \( L_{hkl} \) perpendicular to the reflection planes \((h k l)\) was determined according to the Scherrer Equation:

\[ L_{(hkl)} = \frac{0.9 \lambda}{\beta \cos \theta} \] (11)

where \( \lambda \) is the wavelength of the X-ray, \( \beta \) is the FWHM (full width at half maximum) of the reflection plane \((h k l)\), and \( \theta \) is half of the diffraction angle \((2\theta)\). The FWHM of reflections 110, 110, 020 were estimated by fitting cellulose II (Langan et al. 2005) reflection peaks to the integrated WAXS intensities over the range of 0 to 15 degrees near the equatorial plane. The instrumental broadening was estimated to be 0.01 Å\(^{-1}\) on the \( q \)-scale.

2.8.3.2.1.3 Orientation factor

The crystalline orientation factor along the fiber axis was calculated from the WAXS pattern by Hermans’ orientation parameter \( f_c \) as

\[ f_c = \frac{3 \langle \cos^2 \varphi \rangle - 1}{2} \] (12)

with

\[ \langle \cos^2 \varphi \rangle = \frac{\int_0^{\pi/3} I(\varphi) \cos^2 \varphi \sin \varphi d\varphi}{\int_0^{\pi/3} I(\varphi) \sin \varphi d\varphi} \] (13)

where \( \varphi \) is the azimuthal angle and the intensity \( I(\varphi) \) is integrated over the 110/020 reflections (for 1.3 Å\(^{-1}\) < \( q < 1.6 \) Å\(^{-1}\)) (Samuels, 2003). The integration region was chosen to be from 0 to 60 degrees (azimuthal angles) to cover the entire peak width while avoiding neighboring reflection peaks.

2.8.3.2.2 Small-angle X-ray scattering (SAXS) analysis

Porod length, correlation length, the radius of gyration, length of coherence, specific surface and orientational broadening can be derived from the SAXS data of a two-phase heterogeneous structure, without any presumption on the type of the structure (Vickers et al., 2001). Since the SAXS data obtained here did not extend to the Guinier region, the \( Q \) invariant or the radius of gyration could not be determined. Specific surface and the orientation of the voids could be determined.
2.8.3.2.2.1 Specific surface

Information on the nanoscale structures can be obtained from a power law fit to the SAXS intensities in the Porod region according to

\[ I(q) = A q^{-n} + C \]  \hspace{1cm} (14)

The specific surface of phase 1, \( S_1 \), is given by

\[ S_1 = \frac{KA}{2\pi(\Delta \rho)^2 \rho_1 d_1} \]  \hspace{1cm} (15)

where \( \rho_1 \) is the density of phase 1, \( K \) is a coefficient that scales the intensities onto absolute values, \( A \) is the Porod coefficient, \( \Delta \rho \) is the scattering length contrast between the phases, and \( d_1 \) is the optical thickness of phase 1 given by

\[ d_1 = -\ln T / \mu_1 \]  \hspace{1cm} (16)

where \( T \) is the sample transmission and \( \mu_1 \) is the linear absorption coefficient of phase 1. Phase 1 was assumed to be cellulose (C\(_6\)H\(_{10}\)O\(_5\)) and \( \mu_1 \) was estimated based on assuming a cellulose density of 1.5 g/cm\(^3\) and calculating the mass attenuation coefficient based on the data available at the NIST XCOM: Photon Cross Sections Database (Berger and Olsen 2010). The specific surfaces were calculated relative to the specific surface of the sample with DR 1. The calculations were done by Patrik Ahvenainen (Svedström, 2012).

2.8.4 Water interaction characterizations of fibers

2.8.4.1 Dynamic vapor sorption (DVS)

DVS intrinsic apparatus (Surface Measurement system, London, UK) with a measuring accuracy of 0.1 \( \mu \)g was used for water vapour sorption analysis of fibers (paper II and IV). Approximately 10 mg of a pre-dried fiber bundle was added in the sample pan and preconditioned to relative humidity (RH) of 0% at 25 \(^\circ\)C until the equilibrium was reached using nitrogen (flow rate 100 cm\(^3\) s\(^{-1}\)). The adsorption cycle was performed in 10% RH steps to a maximum of 90% RH. The desorption circulation employed a reverse sequence in the same manner. In both cases, the RH was kept constant until a defined equilibrium condition was reached, i.e. dm/dt was less than 0.001% per minute over a 10 minutes period. The hysteresis of the sorption and desorption isotherms reads

\[ \text{Hysteresis} = \frac{M_{\text{desorption}} - M_{\text{ sorption}}}{M_{\text{ sorption}}} \]  \hspace{1cm} (17)

2.4.8.1.1 Derivation of absorption isotherm

The sorption isotherms were fitted by the model developed by Hailwood and Horrobin (HH model) (Hailwood and Horrobin, 1946). The HH model considers a monolayer (ML) coverage of the cellulose surface by water molecules and follows the presentation of Skaar (Skaar, 1988).

The sorption isotherm \( m(h) \) is described by three coefficients \( m_0, K_h, \) and \( K_d \) according to the following equations.

\[ \frac{h}{m} = A + Bh - Ch^2 \]  \hspace{1cm} (18)

\[ A = 1 / \left[ m_0 K_h (K_h + 1) \right] \]  \hspace{1cm} (19)

\[ B = (K_h - 1) / \left[ m_0 (K_h + 1) \right] \]  \hspace{1cm} (20)
where \( h \) is the relative humidity \((0 \leq h \leq 1)\) and \( m \) is the adsorbed amount of water per unit of dry mass. \( A, B, \) and \( C \) are constants derived from a second-order polynomial fit. \( m_0 \) is the water mass per unit dry mass of cellulose that saturates sorption sites at the solid cellulose surface to form a ML coverage. \( K_h \) is the equilibrium constant of the ML hydration and \( K_d \) is the equilibrium constant of the water dissolution in the solid cellulose. The coefficients \( m_0, K_h, \) and \( K_d \) are calculated from \( A, B, \) and \( C \) based on the system of equations 20-23.

Standard free energy changes \( \Delta G_h \) and \( \Delta G_d \) (with the unit \( J/g \)) are calculated from \( K_h \) and \( K_d \), respectively, using

\[
\Delta G_{h,d} = -(RT / MM_{H_2O}) \ln(K_{h,d})
\]

\[
\Delta G_{total} = \Delta G_h + \Delta G_d
\]

where \( R \) is the gas constant \((8.314 \text{ JK}^{-1} \text{ mol}^{-1})\), \( T \) is the absolute temperature, and \( MM \) is the water molar mass \((18 \text{ g mol}^{-1})\). \( \Delta G_h \) represents the free energy change of the hydrophilic cellulose surfaces, while \( \Delta G_d \) represents the resistance of the fiber matrix to a volumetric expansion as required by the dissolution of water. \( \Delta G_{total} \) is the change in free energy when one mole of liquid water interacts with the dry polymer to form one mole of monohydrate (Hailwood and Horrobin, 1946).

### 2.8.4.2 Swelling test

Fibers in paper II were soaked in deionized water overnight. The diameter of fibers before and after swelling was measured to follow the change in fibers diameter using a Zeiss Axioplan Universal Microscope.
3. Results and discussion

The IONCELL process is a novel and promising Lyocell fiber process that has recently been developed. The ionic liquid 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH]OAc) utilized in this process has been identified as an excellent cellulose solvent for dry-jet wet fiber spinning. The exceptionally high-strength properties of the fibers spun from a cellulose solution in [DBNH]OAc and the low sensitivity of the process towards the use of different cellulosic raw materials have attracted our interest to scientifically investigate three aspects of the IONCELL process that are crucial for further commercial development. First, the spinning behavior of mixtures of cellulose, lignin and xylan as well as homogeneously functionalized cellulose acetates were studied and optimized. Secondly, the structure-property relationship of the staple fibers was investigated, which contributes to a better understanding of the properties of IONCELL fibers. Thirdly and lastly, the process parameters for recycling cotton waste into high-quality new cellulose fibers were successfully demonstrated.

3.1 Spinnability studies

3.1.1 Effect of cellulose molar mass distribution on fiber spinning

The spinnability of spinning dope depends on many different physical and chemical factors, such as the rate of crystallization, diffusion, gelation, cross-linking, supramolecular structure, temperature, and phase behavior (Haward et al. 2012; Gupta and Kothari 1997; Michud, Hummel, and Sixta 2015). According to Ziabicki, “a fluid is spinnable under given deformation condition if steady-state, continuous elongation of the fluid jet proceeds without a break of any kind” (Ziabicki, 1976). Ziabicki proposed two different physical mechanisms that can quantitatively explain the breakage of the fluid thread based on determination of the maximum thread length. The first mechanism, leading to breakage in viscoelastic materials, is the cohesive, brittle fracture. It occurs when the tensile stress of viscoelastic material in the jet passes some critical limits. The second mechanism associated with the surface tension is called “capillary-waves”. This phenomenon occurs on the free surface of the liquid jet, leading the jet to break into drops (Ziabicki, 1976). In addition, a complex set of rheological parameters can also be used to explain the breakage in the spinning solution. However, mentioned rheological properties are commonly used more in a qualitative rather than quantitative manner to explain spinnability theories. These theories are valid for steady-state or isothermal conditions, which is not the case in the real spinning process. Main factors controlling the spinnability are viscosity and
surface tension for capillary mechanism, deformation rate, and viscoelastic characteristics for cohesive fracture. Only cellulose solutions with specific viscoelastic properties can withstand the elongational stress of the draw without filament ruptures in the air gap (Ziabicki and Takserman-Krozer, 1964b, 1964a). Therefore, it is essential to connect the macromolecular properties of cellulose to the rheological properties of the resulting spin solution to develop and understand the spinnability of fiber.

The spinning behavior of dopes with a cellulose concentration of 7–15 wt% and the use of spinnerets with the specifications described in the experimental part were categorized as follows on the basis of many measurement series: DR<2 not spinnable, DRs 2–8 poor, DRs 8–14 good, and DR>14 excellent spinnability. The molar mass distribution of the carbohydrate solute has a fundamental effect on the viscoelasticity of the spinning solution (Michud, Hummel, and Sixta 2015). In paper I, the effect of molar mass distribution (MMD) on spinnability of the IONCELL fibers from waste cotton is studied (Asaadi et al. 2016).

![Figure 15. Dynamic moduli of cross-over point (COP) as function of the angular frequency of COP (red line: spinnable dopes; black line: non-spinnable dopes) for different combination of the cotton wastes (CoW) and cotton waste and softwood sulfite pulp (CoW/SW) at 60–85 °C. (The numbers in the sample names are showing the intrinsic viscosity in ml/g). (paper I)](image_url)

The viscoelastic properties of the solutions were determined by measuring complex viscosity and dynamic moduli in the range of 0.01 s⁻¹–100 s⁻¹ at 60–85°C. If we assume that the Cox–Merz rule is valid for these solutions, the Cross model can be applied to calculate the zero shear viscosity (Lu et al., 2012). The cellulose concentration has a noticeable effect on the dynamic modulus at the cross-over point (COP). The spinnable and non-spinnable dopes are shown in red and black in Figure 15, respectively. As shown in Figure 15, the dynamic moduli are increasing along with an increase in concentration, which is due to the enhanced entanglement of the cellulose chains (Härdelin et al., 2013). An increase in cellulose concentration or degree of polymerization (DP) enhances the extent of entanglements of the cellulose network with restricted motions.
The solution behaves like an elastic body and the COP is shifted to lower frequencies. The limiting viscosity of the dissolving pulp used in the Lyocell process should be between 400 and 500 mL g\(^{-1}\) so that at an economically acceptable temperature (<85 °C), the angular frequency and the dynamic modulus of the COP of the resulting cellulose solution are in the spinnable range. As illustrated in Figure 15, the dopes prepared from the cellulose with higher or lower viscosities were not spinnable under the chosen spinning arrangement, even when blending with a pulp with a wider molar mass distribution (McKinley and Sridhar, 2002). An increase in temperature results in a decrease of the viscosity and a shift in the angular frequency of the COP to higher values. However, the number of chain entanglements is independent of the temperature, which can be observed by the insignificant changes of the dynamic modulus at the COP with the increase in temperature (Michud, Hummel, and Sixta 2015; Lu et al. 2012; Härdelin et al. 2013; Chen et al. 2009).

![Graph showing zero shear viscosity as a function of the angular frequency of COP for different CoW and CoW/SW mixtures at 60–80 °C.](image)

**Figure 16.** Zero shear viscosity as a function of the angular frequency of COP of different CoW and CoW/SW mixtures at 60–80 °C. (The numbers in the sample names are showing the intrinsic viscosity in ml/g). (paper I)

The zero shear viscosity is sensitive to the polymer concentration and the molecular weight of the cellulose solutes. The influence of the temperature on the zero shear viscosity and angular frequency of COP is shown in Figure 16. Higher temperatures facilitate the flow of the cellulose chains in the solution and thus weaken their entangled structure. Consequently, a decrease of the zero shear viscosity and a shift of the COP to higher angular frequencies is showing the prevalence of viscous behavior over elastic behavior at higher temperatures (Michud, Hummel, and Sixta 2015; Lu et al. 2012; Härdelin et al. 2013; Chen et al. 2009).

As depicted in Figures 15 and 16, the values of complex moduli, the angular frequency of the COP, and zero shear viscosity of the non-spinnable dopes
showed a distinct deviation from the spinnable dopes. A high cross-over modulus at a given angular frequency is an indication of the narrow molar weight distribution. The poor or non-spinnable dopes were prepared from the cellulose samples with narrow molar mass distributions with either a high or rather low proportion of long chains.

The molar mass distribution, the polydispersity and the degree of polymerization (DP) of the pulp play a significant role in the processability of the polymers. Waste cotton, partly blended with pulp, showed good spinnability with a polydispersity index (PDI) between 2.2 and 5.9; a short-chain fraction measured as DP<100, from 1.2 to 7.3 wt%; and a long-chain fraction, measured as DP>2000, from 16 to 22.5 wt%. This is in accordance with the study by Michud et al. (Michud et al., 2015b), which found that for eucalyptus pulp, a combination of a high fraction of high-molecular-weight cellulose chain with a low proportion of low-molecular-weight (4.1 % DP<100) and an intermediate PDI is favorable for spinning.

![Figure 17. Molar mass distribution of cotton wastes, pulps and spun fibers. Dashed line: pulps. Solid lines: fibers. (The numbers in the sample names are showing the intrinsic viscosity in ml/g). (paper I)](image)

Table 3 summarizes the gel permeation chromatography (GPC) data of all the pulps and spun fibers. The PDI of the pulps was 2.2–5.9, and 2.3–2.8 for spun fibers. The proportion of long cellulose chains in fiber samples for DP>2000 was between 19 and 17%, and for short chains (DP<100), between 1.3 and 3.3%. The table also shows that with very a narrow MMD, as in the case of CoW 438, spinnability suffers despite the relatively high proportion of long fibers. As can also be seen from Figure 17 and Table 3, cellulose dissolution and the spinning process slightly shift the molar mass to lower values due to degradation processes (Michud et al. 2015).
Table 3. Molar mass distribution data of spun fibers from cotton waste blends, cotton waste (CoW)/softwood pulp (SW), and PHK-pulp and the maximum draw ratio obtained in the spinning

<table>
<thead>
<tr>
<th>Fiber and pulp</th>
<th>Mn</th>
<th>Mw</th>
<th>PD</th>
<th>DP&lt;100</th>
<th>DP&gt;2000</th>
<th>Max draw ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg.mol⁻¹</td>
<td>kg.mol⁻¹</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>CoW 438* pulp</td>
<td>95.2</td>
<td>205.7</td>
<td>2.2</td>
<td>1.2</td>
<td>17.0</td>
<td>-</td>
</tr>
<tr>
<td>CoW 438 fiber</td>
<td>90.8</td>
<td>211.1</td>
<td>2.3</td>
<td>1.6</td>
<td>19.0</td>
<td>8.8</td>
</tr>
<tr>
<td>(CoW/SW) 468 pulp</td>
<td>46.9</td>
<td>257.7</td>
<td>5.9</td>
<td>7.3</td>
<td>22.6</td>
<td>-</td>
</tr>
<tr>
<td>(CoW/SW) 468 fiber</td>
<td>67.8</td>
<td>190.6</td>
<td>2.8</td>
<td>3.4</td>
<td>15.9</td>
<td>15.9</td>
</tr>
<tr>
<td>(CoW/SW) 393 pulp</td>
<td>62.9</td>
<td>190.4</td>
<td>3.0</td>
<td>3.9</td>
<td>16.1</td>
<td>-</td>
</tr>
<tr>
<td>(CoW/SW) 393 fiber</td>
<td>63.8</td>
<td>181.5</td>
<td>2.8</td>
<td>3.8</td>
<td>15.4</td>
<td>14.1</td>
</tr>
<tr>
<td>CoW 452 pulp</td>
<td>83.8</td>
<td>203.2</td>
<td>2.4</td>
<td>2.0</td>
<td>17.4</td>
<td>-</td>
</tr>
<tr>
<td>CoW 452 fiber</td>
<td>96.4</td>
<td>206.4</td>
<td>2.1</td>
<td>1.3</td>
<td>17.6</td>
<td>14.1</td>
</tr>
<tr>
<td>PHK 476 pulp</td>
<td>65.9</td>
<td>269.3</td>
<td>4.1</td>
<td>4.7</td>
<td>24.2</td>
<td>-</td>
</tr>
<tr>
<td>PHK 476 fiber</td>
<td>68.8</td>
<td>218.7</td>
<td>3.2</td>
<td>4.3</td>
<td>20.5</td>
<td>17.6</td>
</tr>
</tbody>
</table>

*numbers in the sample name show the intrinsic viscosity in ml/g

3.1.2 Effect of homogeneous acetylation of cellulose in solution on spinnability

The spinnability of the dope after in-situ acetylation in solution was also investigated, described and discussed in detail in Paper IV for different degrees of substitution (DS). Dopes with four degrees of cellulose substitution were produced, all of which exhibited good spinnability. The investigation of the viscoelastic behavior of the cellulose solution along with the molar mass distribution provides valuable information for the depolymerization behavior of cellulose in these solutions (Collier et al., 2009; Dupont and Mortha, 2004).

Rheological properties of the spinning dopes are presented in table 4 and figure 18. By increasing the DS of acetylation from 0.05 to 0.75, the complex viscosity and dynamic moduli decrease, while the angular frequency at cross-over point (COP) increases, indicating a shift toward a more viscous behavior of the solutions. Since the rheological properties typically react very sensitively to molecular weight changes, especially in the high-molecular components (Michels and Kosan, 2003), these changes need to be investigated by GPC.
Figure 18. Rheological properties of spinning dopes of acetylated cellulose fibers (ACF) with the highest and lowest degrees of substitution (DS) compared to non-acetylated (NACF) dope at 65°C (the number in sample name shows the degree of substitution). (paper IV)

Figure 19 shows the molar mass distribution (MMD) of the non-acetylated fiber (NACF) and acetylated fiber (ACF). A comparison of the MMD of the NACF pulp with the corresponding fiber reveals a slight degradation. With acetylated fibers, however, the DP degradation is even lower and therefore hardly significant. Thus, it can be concluded that the changes in the rheological properties are not caused by degradation, but may result from the reduction of hydrogen bonds between the cellulose chains due to the partial substitution of the hydroxyl groups with acetyl groups, whereby the cellulose chains become less rigid in solution and thus reduce viscosity (Kosan et al., 2010; Michels and Kosan, 2003). The increase of flexibility of the cellulose structure result in changes in the hydrodynamic volumes of the solutes.
Figure 19. Molar mass distribution of the substrate pulp, NACF, and ACF with different degrees of substitution. (paper IV)

Table 4. Molar mass distribution (MMD) data of the original cellulose pulp, acetylated and reference spun fibers and the rheological data of their corresponding spinning dopes. (paper IV)

<table>
<thead>
<tr>
<th>Sample /unit</th>
<th>wt%</th>
<th>eq</th>
<th>kDa</th>
<th>Pa.s</th>
<th>s⁻¹</th>
<th>Pa</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHK pulp</td>
<td>-</td>
<td>-</td>
<td>3.4</td>
<td>268.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NACF*</td>
<td>13</td>
<td>0</td>
<td>2.8</td>
<td>203.0</td>
<td>0</td>
<td>26102</td>
<td>0.66</td>
</tr>
<tr>
<td>ACF* 0.05</td>
<td>13</td>
<td>0.05</td>
<td>3.6</td>
<td>239.9</td>
<td>0.05</td>
<td>18148</td>
<td>0.83</td>
</tr>
<tr>
<td>ACF 0.25</td>
<td>13</td>
<td>0.25</td>
<td>3.3</td>
<td>238.1</td>
<td>0.21</td>
<td>17827</td>
<td>0.85</td>
</tr>
<tr>
<td>ACF 0.5</td>
<td>13</td>
<td>0.50</td>
<td>3.1</td>
<td>238.7</td>
<td>0.44</td>
<td>10613</td>
<td>0.98</td>
</tr>
<tr>
<td>ACF 0.75</td>
<td>13</td>
<td>0.75</td>
<td>2.9</td>
<td>256.5</td>
<td>0.62</td>
<td>7000</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Table 4 contains the rheological data of the dopes. The acetylated spinning dopes showed zero shear viscosities outside the optimum range found in our previous studies with pure cellulose solutions (Asaadi et al., 2016). The cellulose acetate solution with a DS of 0.75 had a very low dynamic modulus at the COP, which indicates a broadening of the molecular mass distribution and reduced stiffness/hardness or resistance to deformation. The simultaneous shift of the angular frequency to higher values at the COP confirms this behavior by showing that the elastic properties of the solution only dominate at higher frequencies. However, all dopes were spinnable and could be drawn up to a DR of 8.8, which is considered as good spinnability.

With the increase of the DS, the maximum achievable DR decreases. This behavior is due to a reduction in the viscoelastic properties, indicated by the decrease in the angular frequency of the COP and dynamic moduli.

3.1.3 Effect of lignin and xylan on fiber spinning
There is an interest in biomaterial science to prepare all-wood-biopolymer fibres and develop fibre spinning based on ionic liquids, to reduce the raw materials costs and tune certain properties of the fibres such as water interactions. Therefore in Paper III, we have analyzed the effect of the addition of lignin and xylan to IONCELL fibers on the surface energy of the fibers and we have analyzed the fibres mechanical properties (Nypelö et al., 2018). To produce the fibers, spinnable dopes are first produced from blends of cellulose, xylan, and lignin. A matrix of zero-shear viscosity, angular frequency of cross-over point (COP), and dynamic modulus of COP of the cellulose-ionic liquid solution has been identified for successful spinning (Michud 2016). This matrix is not entirely valid when studying spinning solution from a cellulose blend with low molecular weights such as lignin and xylan. However, the principle relationships are still visible.
Depending on the composition, polymer solutions were prepared with different concentrations, as shown in Table 5. For cellulose/xylan, the standard consistency of 13% has been chosen according to previous studies (Sixta et al. 2015; Michud et al. 2016), but for the addition of lignin, a higher concentration had to be adjusted, namely 15%, to compensate for the very low molecular weight of lignin (Ma et al., 2015). The addition of xylan and lignin has reduced the maximum draw ratio. However, the dopes made from cellulose blends are still spinnable and can be stretched up to DR 7.

As expected, despite higher consistency (15%), the modulus at COP and the zero shear viscosity decreased compared to the pure cellulose dope due to the very low molecular weight of the organosolv lignin (Frank et al., 2014; Ma et al., 2015). A lower spinning temperature than that used with a pure cellulose solution had to be set to compensate for the effect of the lower modulus at COP. The melting temperature range of the spinning dope should also be considered in the spinning process.

Due to the low molar mass of xylan, its addition to the cellulose dope had a decreasing influence on the modulus at COP and the zero shear viscosity. However, it was compensated by lowering the spinning temperature. By adding xylan and lignin to cellulose-ionic liquid solution, the spinning dopes were made spinnable, but the maximum DRs were reduced to half the maximum DR of the pure cellulose dope.

Therefore, the existence of a high fraction of high-molecular-weight cellulose in the blends contributes to enhanced spinnability of the solution and collection of the samples at higher draw ratios. There are more cohesive fiber networks in

<table>
<thead>
<tr>
<th>sample/unit</th>
<th>dope consistency</th>
<th>cellulose</th>
<th>xylan</th>
<th>lignin</th>
<th>η₀</th>
<th>ω</th>
<th>modulus at COP</th>
<th>spinning temperature</th>
<th>max. draw ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>cellulose</td>
<td>13</td>
<td>94.2</td>
<td>5.5</td>
<td>0</td>
<td>40060</td>
<td>0.54</td>
<td>3819</td>
<td>75</td>
<td>15.7</td>
</tr>
<tr>
<td>cellulose/xylan</td>
<td>13</td>
<td>75.25</td>
<td>78.2</td>
<td>19.6</td>
<td>20284</td>
<td>0.60</td>
<td>2019</td>
<td>65</td>
<td>7</td>
</tr>
<tr>
<td>cellulose/lignin</td>
<td>15</td>
<td>75.25</td>
<td>71.3</td>
<td>4.34</td>
<td>39878</td>
<td>0.29</td>
<td>2454</td>
<td>60</td>
<td>7</td>
</tr>
<tr>
<td>cellulose/xylan/lignin</td>
<td>15</td>
<td>50:25:25</td>
<td>52.8</td>
<td>23.7</td>
<td>53837</td>
<td>2.21</td>
<td>1250</td>
<td>95</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 5. Cellulose, xylan and lignin contents composition and the rheological data of the spinning dopes at spinning temperature.
the air gap, which result in more homogenous and uniform structures and fewer breaks.

3.2 Structure property relationship
This section includes the structure-property relationship study of the IONCELL. Fiber orientation, crystallinity, tensile strength properties, and water interaction are studied and discussed.

3.2.1 Pure cellulose
Paper II reports the comprehensive structural study of the IONCELL fibers from PHK-pulp from birch. The effects of increasing DR on crystallinity, orientation, and crystal dimensions of the IONCELL fibers are studied for further understanding of the structural development of fibers and optimization of the spinning process.

3.2.1.1 Orientation
The cellulose molecules are aligned by stretching the dissolved cellulose molecules along the fiber axis in the air gap. When the cellulose solution passes through the spinneret channel, the cellulose molecules are slightly pre-oriented due to the shear forces acting on them. The further extension of the molecules along the molecular axis in the air gap becomes increasingly difficult due to the interaction between neighboring cellulose molecules. At very high DRs, chain slippage and even the breakage of intermolecular hydrogen bonds lead to relaxation of the cellulose molecules and a decrease of the total orientation.

Total orientation consists of crystalline and amorphous orientations and can be determined from birefringence measurements by polarized microscopy. The crystalline orientation can be evaluated from WAXS data (from 110 and 020 reflections) using the Herman’s orientation factor $f_c$, and it plays an important role in the deformation behavior of the regenerated cellulose fibers (Lenz et al. 1990).

The total orientation increases with the increase of DR, while the crystalline orientation shows only a slight increase. As illustrated in Figure 20, the crystalline orientation is already high at low DRs and increases only slightly with the increase in DR. Therefore, it is concluded that the reason for the increase of the total orientation is the increase in amorphous orientation.
Figure 20. (a) Crystalline orientation, void orientation, and total orientation parameters from WAXS/SAXS and birefringence measurement of IONCELL fibers as a function of DR in conditioned state. (paper II)

The void orientation can be evaluated from SAXS data if we assume that the contrast of SAXS arises from the difference in electron density of the air (voids) and the matrix (cellulose). Figure 21 shows the 2D-SAXS pattern of the fibers with different DRs. According to Vickers et al. (Vickers et al., 2001), the equatorial scattering originates from structures that are oriented along the fiber axis, which is more enhanced at DR 15 in comparison with DR 0.5.

The void orientation also increases with the increase in DR. Therefore, the crystalline orientation varies slightly, while the void and amorphous orientation vary considerably. Both components of the orientation influence the tensile strength, as with viscose and NMMO-based Lyocell fibers.

At DR>2, the difference between amorphous and crystalline orientation becomes rather small, which means the one-phase model is more favorable at higher orientations (Northolt, 1985). However, the difference between crystalline and total orientation can justify the existence of the two-phase model (Northolt, 1985).
Figure 21. Two-dimensional small-angle X-ray scattering (SAXS) patterns of the IONCELL fiber bundles with different draw ratios in the conditioned state. The DR is marked on top of each figure. The x-axis shows the absolute value of the horizontal component of the scattering vector q (in units of Å⁻¹) for scale (q = 0 is marked with a red cross). The colormap shows the intensity in logarithmic scale. DR 0.5 show pronounced meridional broadening while the fibres with the highest DR of 15 reveal an elongated sharp streak along the equator due to the high void orientation (paper II).

Figure 22. Relative Specific Surface (RSS) as a function of the DR (DR, RSS=1 for DR=1) for IONCELL fibers spun in a conditioned state, evaluated from SAXS data. (The solid line serves as a guide for the eye.) (paper II)

The relative specific surface (RSS) can be calculated using Equation 16. The RSS is increasing non-linearly with the increase of the DR (Figure 22).

The RSS is low when the voids are close to a spherical shape, so the relative specific surface is low. When the filaments are drawn in the spinning process, the voids start to deviate from the spherical shape by elongation, which results
in an increase of the RSS. High inner RSS is an indication of the high anisotropy in fibers (Schurz et al., 1995).

3.2.1.2 Crystallinity

Several models have been proposed to describe the cellulose supramolecular structure, such as crystalline micelles, defective crystals, amorphous stacks, folded fibrils, fringed fibrils, crystalline fibrils with the amorphous surface, and amorphous–crystalline fibrils with straightened chains. All have specific features, advantages, and drawbacks (Ioelovich, 2016).

The crystallinity index is used to describe the relative amount of crystalline or highly ordered material in cellulose. The crystallinity values are very dependent on the evaluation methods. Therefore, they are only comparable when using the same evaluation methods. In this study, we have used the area-based method. An amorphous subtraction method (lignin as an amorphous model) has been used (Ahvenainen et al., 2016).

Figure 23. Effect of DR on the crystallinity of the IONCELL fibers spun from 13% PHK-kraft pulp–[DBNH](OAc) solution. (The solid line shall merely serve as a guide for the eye.) (paperII)

Figure 23 depicts the strain-induced crystallization of the IONCELL fibers. The significant change in crystallinity happens at low DR between DR 0.5 and 2, and beyond that, there is not any notable change in the crystallinity. This is consistent with results reported earlier (Sixta et al. 2015).

It has been found that the size of crystallites of the IONCELL fibers is independent of the DR (Asaadi, Hummel, et al. 2018). Based on the 110 reflection (Asaadi, Hummel, et al. 2018), the average crystallite width was determined to be around 3 nm in the cross-section. The reflections that can be used for evaluating the crystallite sizes have a lot of overlap, making it impossible to accurately evaluate the sizes. However, the size that has been calculated from 110 reflection data was similar to the Enka Viscose fibers but smaller than Fortisan filaments (Northolt et al., 2001).
3.2.1.3 Tensile strength and modulus

Figure 24 shows the tensile strength (conditioned test), linear density, and orientation of the fibers as a function of the DR. The orientation of the fibers is increasing except when the DR is very high (between DR 14 and 15), at which point molecular chain slippage occurs and the orientation decreases (Mortimer et al., 1996; Mortimer and Peguy, 1996; Mortimer and Péguy, 1996).

Overall, increasing the DR results in the cellulose chains becoming aligned parallel to the fiber axis and the fibers becoming stronger and more oriented. It should be noted that the significant increases in tensile strength and orientation occur before reaching a DR of 5, and the increases are relatively small thereafter. Mortimer and Peguy have reported the same behavior for NMMO-based Lyocell fibers (Mortimer and Peguy, 1996). The same trend can be observed for the wet tensile strength test (supporting information paper II (Asaadi, Hummel, et al. 2018)) at a slightly lower level.

The hydrogen bond network in amorphous regions is disrupted when fibers absorb water; therefore, the wet-to-dry tensile strength ratio can be used to estimate the proportion of accessible hydrogen bonds in the amorphous region. This value is calculated for typical IONCELL fibers (DR>3.5) and ranges from 0.86 to 1.0, which is similar to the value of Lyocell fibers (0.8—0.9) but higher than the value of viscose fibers (0.5) (Lewin and Pearce 1998; Sixta et al. 2015).

3.2.1.4 Water vapor sorption/desorption

The fiber-water interaction is an important product property of the fiber and, at the same time, provides information on morphology and ultrastructure of the fibers. The Hailwood-Horrobin model (HH-model) can be used to study the water sorption in fibers and calculate the specific surface area and change of free energy of dissolved and hydrated water (Hailwood and Horrobin, 1946).
calculations are based on the assumption that when water interacts with regenerated cellulose fibers, an ideal solid solution forms.

Table 6 contains the data of the hydration layer (the monolayer (ML) of water) in sorption and desorption cycles for IONCELL with different DRs. The ML gives an estimate of the amount of water in direct contact with the solid matrix and thus the specific surface area (Hailwood and Horrobin, 1946).

**Table 6.** Results from the Hailwood-Horrobin water monolayer (HH-ML) model for sorption (HH-MLs) and desorption (HH-MLd) of typical IONCELL (from PHK-birch pulp with different DRs) and changes in the free energy of hydrated ($\Delta G_h$) and dissolved ($\Delta G_d$) water in sorption and desorption cycles (paper II).

<table>
<thead>
<tr>
<th>DR unit</th>
<th>DR</th>
<th>ML water (g/g)</th>
<th>Hysteresis (%)</th>
<th>Surface area (m$^2$/g)</th>
<th>Surface area (m$^2$/g)</th>
<th>$\Delta G_h$ (J/g)</th>
<th>$\Delta G_d$ (J/g)</th>
<th>$\Delta G_h$ (J/g)</th>
<th>$\Delta G_d$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ION-CELL 0.5</td>
<td>0.0647</td>
<td>0.08</td>
<td>97</td>
<td>39</td>
<td>194</td>
<td>269</td>
<td>-199</td>
<td>29</td>
<td>-243</td>
</tr>
<tr>
<td>ION-CELL 3</td>
<td>0.0631</td>
<td>0.07</td>
<td>84</td>
<td>24</td>
<td>189</td>
<td>235</td>
<td>-181</td>
<td>34</td>
<td>-270</td>
</tr>
<tr>
<td>ION-CELL 7</td>
<td>0.0635</td>
<td>0.07</td>
<td>60</td>
<td>20</td>
<td>190</td>
<td>228</td>
<td>-186</td>
<td>35</td>
<td>-273</td>
</tr>
<tr>
<td>ION-CELL 15</td>
<td>0.0578</td>
<td>0.07</td>
<td>43</td>
<td>29</td>
<td>173</td>
<td>223</td>
<td>-275</td>
<td>24</td>
<td>-299</td>
</tr>
</tbody>
</table>

When studying the effect of the draw ratio on sorption–desorption behavior of the fibers, we found that with the increase of the draw, the specific surface area decreases due to the strain-induced crystallization and orientation. This can be seen in the decrease of Hailwood-Horrobin water monolayer sorption (HH-MLs) and Hailwood-Horrobin water monolayer desorption (HH-MLd). In addition, the free energy of dissolved ($\Delta G_d$) decreases, while free energy of hydrate ($\Delta G_h$) increases with increasing DR. This indicates that there is an impaired accessibility of the water molecules at a high DR. These results are in agreement with the data from viscose fibers, which show that the increase of the DR leads to decrease of accessibility measured by isotopic exchange of cellulose OH groups with D$_2$O (Klemm et al., 2004).
Figure 25. Dynamic vapor sorption test, hysteresis of the sorption and desorption isotherms as a function of relative humidity, and effect of DR on IONCELL fibers. (paper II)

Figure 25 shows the hysteresis as a function of the relative humidity for IONCELL fibers with different DRs. The highest hysteresis has been observed for the lowest DR, showing that the structure is more unstable than structures at higher DRs. With the increase of the relative humidity, the slope of the curves decrease, showing that the changes are more pronounced in the dry state than the wet state. The surface, pores, and the less-oriented amorphous parts are the main sites for water sorption (Cordin et al., 2017; Schurz et al., 1995). The existence of energetically active molecular conformation due to the high number of the unsaturated active groups of cellulosic materials can be the reason for high uptake of moisture at low relative humidity (Salmén, polymers, & 2018).

3.2.2 Polymer blends vs. fiber structure and mechanical properties

3.2.2.1 Blends of cotton linters and wood dissolving pulps
Paper I investigates some structural properties of IONCELL fibers from pure waste cotton and their blends with wood dissolving pulps.

3.2.2.1.1 Orientation
The orientation and draw ratio of all fibers, from blends and pure cellulose, show a similar relationship. Orientation increases rapidly at low DRs and moderately at DR 5-8, and then levels-off and sometimes even declines at a higher DR due to an enhanced slippage of the cellulose chains (Figure 26). The higher orientation of CoW 452 and (CoW/SW) 468 can be due to the higher portion of long chains which surpass the larger number of crystallites. This leads to a more uniform and oriented fiber network resulting in increased fiber strength (Asaadi et al., 2016).
Figure 26. Total orientation of waste cotton spun fibers as a function of draw ratio. (paper I)

The solid-state NMR results (paper I) showed that increasing the orientation of the fibers (and the increase of DR) also increases their crystallinity. The observed increase in crystallinity can be attributed to the crystallite core, while the contribution of the fibril surface remains unaffected (Asaadi et al., 2016). The crystallinity of the fiber samples is between 53% and 57%, which is higher than that of NMMO-based Lyocell fibers, as reported by Röder et al. (Röder et al., 2006). According to several studies, one reason for the high crystallinity of these samples may be the high crystallinity of native cotton, since dissolved cellulose remains in the form of aggregates, which consist of several hundred cellulose chains (Kuzmina et al., 2010; Morgenstern and Ro, 1999).

3.2.2.2 Blends of cellulose, xylan and lignin
Paper III reports on spinning dopes prepared from cellulose blends with xylan and/or lignin.

3.2.2.2.1 Orientation
All dopes were spinnable up to a DR of at least 7. This stretching range (0.5 to 7) was used as a comparative value for the development of the total orientation, measured by birefringence. The orientation of the fibers from blends of lignin and xylan initially increased to a DR of 3.5, after which the rate of increase in orientation decreased significantly.
Figure 27. Orientation vs. draw ratio of spun fibers from cellulose (Enocell birch prehydrolysis kraft pulp), beechwood organosolv lignin, and xylan, extracted from birch Kraft pulp blends. (paper III)

Figure 27 shows the orientation as a function of DR for different blends (including cellulose, lignin, and xylan). The cellulose contents of the samples are 94%, 78%, 71% and 53% for cellulose, cellulose/xylan, cellulose/lignin, and cellulose/xylan/lignin, respectively. With the decrease in cellulose content, the orientation decreases. The mixture with xylan only shows an almost comparable increase in orientation compared to pure cellulose, which indicates the close interaction between the two polymers. In contrast, the presence of lignin does not contribute equally to the orientation of cellulose. Therefore, the lignin molecules do not behave as strength elements but as fillers preventing the cellulose molecules to orient according to the applied draw ratio.

Since the orientation of cellulose along the fiber axis is the most important parameter for fiber strength, the incorporation of a non-oriented copolymer leads to a decrease in the resulting strength of the fibers (Krässig, 1993). The strength-reducing effect of the lowered cellulose content has also been reported by Sun et al. (Sun et al. 2011). The highest orientation has been observed at the lowest draw ratio for cellulose/xylan fibers. The presence of hemicelluloses, i.e., xylan, contribute to the orientation and thus tensile strength, but to a lesser extent than cellulose. However, it should be noted that there are inaccuracies in the draw adjustment at low DRs; this requires further attention.

3.2.2.2 Tensile strength and stress-strain behavior
Figure 28 shows the stress-strain of fibers of different blends. With the addition of lignin and xylan to the cellulose-IL spinning dope, the tensile strength of the spun fibers decrease when compared at the same draw ratio (DR 7) of different blends.
As stated earlier, the decrease of orientation in the composite fibers also results in the reduction of the tensile strength. The fibers with lignin and/or xylan show improved elongation, so the deformability of the fibers have been increased by the addition of lignin and xylan. The presence of the lignin reduces the elasticity of the dope which decreases the ability to straighten the cellulose molecules upon drawing the filament. According to Ma et al. (Ma et al., 2015), the addition of lignin impedes the formation of the homogenously ordered structure, which causes the decrease of tensile strength and increase of elongation. The specific energy required for the deformation can be quantified by total energy density (modulus of toughness). It is the area of the stress-strain curve that indicates how much energy can be absorbed for plastic deformation without rupture. The toughness has been calculated for the fibers in Figure 28, with levels between 24 J/g and 32 J/g, with the highest level representing cellulose fibers and the lowest representing the three-component fiber (lignin/xylan/cellulose). Toughness levels of the viscose and NNMO-based Lyocell fibers are reported to be 21.8 J/g and 23 J/g (Adusumalli et al., 2009). When comparing cellulose with the composite fibers, it can be concluded that the addition of xylan and/or lignin reduces the ductility of the fibers, causing them to absorb less energy before rupturing. However, they are still more ductile than commercial Lyocell and viscose fibers. The strength of the fiber is governed by the cellulose purity, its molar mass distribution, and its orientation (Krässig, 1993).

3.2.2.3 Homogeneously acetylated Cellulose
In paper IV, the effect of a low degree of acetylation on the mechanical properties of the fibers is studied.
3.2.2.3.1 Orientation and mechanical properties

The acetylation of the IONCELL fibers leads to a structural change that can affect the physical properties of the fibers.

![Graph showing the change in orientation, tensile strength, and Young's modulus of non-acetylated fiber (NACF) and different acetylated fibers (ACF1-4) at DR 8.84 vs. DS.](image)

**Figure 29.** Tensile strength, total orientation, and Young's moduli of non-acetylated fiber (NACF) and different acetylated fibers (ACF1-4) at DR 8.84 vs. DS. (paper IV)

Figure 29 shows the change in orientation, tensile strength, and Young’s modulus of the non-acetylated fiber (NACF) and acetylated fibers (ACF), each at a DR of 8.84. The three parameters in Figure 29 run almost parallel as a function of the degree of substitution (DS). Only with a low DS there are minor deviations. While the tensile strength increases at a DS of 0.05, the modulus of elasticity decreases and the orientation increases to a DS of 0.25 before decreasing again and being proportional to the tensile strength.

As mentioned above, the highest tensile strength was measured for fibers with a DS of 0.05, but only in the conditioned state. In the wet state, non-derivatized cellulose had the highest tensile strength (paper IV, supporting information (Asaadi, Kakko, et al. 2018)). This is also true when comparing all the fibers regardless of the DR. The overall trend of tensile strength vs. DS is that with an increase in DS, the tensile strength decreases. The tensile strength is related to the degree of the total orientation, crystallinity, and the length of the cellulose chain (Krässig, 1993). Accordingly, the decrease in tensile strength can be explained by the decrease of the orientation of cellulose chains, especially in the amorphous region. With an increasing amount of acetate groups attached to the cellulose chains, the molecular and supramolecular structures of the fibers are changing. The lateral chain-to-chain interaction is distorted within the plane and between the sheets (Schaller et al., 2013). This applies, in particular, to the higher degrees of substitution. However, for lower DS values, mainly DSs of 0.05 and 0.25, the acetyl groups increase the total orientation, which translates into a more oriented fiber network. At these low DS values, the cellulose chains...
can be stretched more freely in the amorphous region, since the lower number of hydrogen bonds does not restrict them as much. However, for higher DS values, such as 0.5 and 0.75, the increasing steric hindrance through the attached acetyl groups impairs the alignment of the molecules along the molecular axis. According to the results in paper II, the amorphous orientation is very sensitive to the draw ratio, especially at lower draw ratios, while the crystalline orientation varies only a little with an increase of the draw ratio (Asaadi et al. 2017; Sixta et al. 2015).

3.2.2.3.2 Crystallinity and crystal dimensions
The results from mechanical properties of the acetylated fibers are in line with the crystallinity studies. The data from WAXS measurement has shown that the crystallinity and crystallite sizes decrease with the increase in draw ratio (DR), which is similar to the results of IONCELL fibers without modification. The detailed data and results are presented in the supporting information of paper IV (Asaadi, Kakko, et al. 2018).

![Crystallite width change from different planes for NACF and ACF (0.25-0.75)](image)

**Figure 30.** Crystallite width change from different planes for NACF and ACF (0.25-0.75)

The crystallite size of the 1-10 and 020 lattice planes decreases for the fibers with a higher degree of acetylation (0.5 and 0.75), while the size of the 110 lattice plane remains on the same level, independent from the degree of substitution (DS) (Figure 30). This decrease in 1-10 crystallite size was also observed for cellulose I during acetylation (Chanzy, 1984; Kim et al., 2002) and was explained by the decrease in the direction perpendicular to the wider surface, meaning that acetylation begins from the surface while the core initially remains unreacted (Kim et al., 2002). At a high DS, there is a slight decrease of the ordered structure toward ductility observed in SEM images (supporting information, paper IV).

The wet-to-dry ratio has also been calculated for these samples. The non-acetylated fibers showed the highest value (0.91) and it decreases with the increase
of the DS (0.82-0.61), indicating that the hydrogen bond network is disrupted in the amorphous region in a wet state (Lewin and Pearce, 1998).

3.2.2.3 Water vapor sorption/desorption

Water sorption behavior depends on factors such as chemical composition, orientation, and morphology (Bingham, 1964; Okubayashi et al., 2004). In cellulose derivatives, the moisture regain depends on the nature of substitution, the distribution of the functional groups along the cellulose chain, and the degree of crystallization (Zugenmaier, 2004).

Table 7 contains the water monolayer (ML) and free energy values calculated from the Hailwood-Horrobin (HH) model. The dynamic vapour sorption (DVS) tests reveal that the amount of adsorbed and desorbed water monolayer rises to a degree of substitution (DS) of 0.5 and decreases at a DS of 0.75.

The increase in adsorbed water up to a DS of 0.5 is due to an increase in the accessible surface area, which correlates with the decrease in crystallinity. Only at a higher DS does the increasing hydrophobic input of the acetyl groups affect the water adsorption behavior of cellulose. When comparing the change in free energy, the non-acetylated fiber (NACF) shows the highest change caused by the deteriorated accessibility of water molecules.

Figure 31 shows the hysteresis as a function of the relative humidity for ION-CELL fibers with different DS levels. The highest hysteresis has been recorded for DS 0.5. Moreover, as explained previously in the interaction of water with typical IONCELL fibers, the high slope of the curves shows when the fibers are dry. More structural change occurs when the fibers absorb water. In modified fibers, the pores and the less-oriented amorphous parts are the main sites for water sorption (Cordin et al., 2017; Schurz et al., 1995). At a lower DS, the moisture regain increases due to the higher surface area and more accessible hydroxyl groups. In contrast, with the decrease of the surface area and hydroxyl groups at a higher DS, fibers develop hydrophobicity.

![Figure 31](image-url)

**Figure 31.** Dynamic vapor sorption test, hysteresis of the sorption and desorption isotherms as a function of relative humidity, effect of degree of acetylation for non-acetylated and acetylated IONCELL fibers. (paper IV)
Table 7. Results from the Hailwood-Horobbin water monolayer (HH-ML) model for sorption (HH-MLs) and desorption (HH-MLd) of typical IONCELL (from PHK-birch pulp) and acetylated fibers (from PHK-eucalyptus pulp) with different draw ratios (DRs), and changes in the free energy of hydrated ($\Delta G_h$) and dissolved ($\Delta G_d$) water in sorption and desorption cycles. (paper IV)

<table>
<thead>
<tr>
<th>DR unit</th>
<th>ML water (g/g)</th>
<th>Hysteresis (g/g)</th>
<th>Surface area ($m^2/g$)</th>
<th>Surface area ($m^2/g$)</th>
<th>$\Delta G_h$ (J/g)</th>
<th>$\Delta G_d$ (J/g)</th>
<th>$\Delta G_h$ (J/g)</th>
<th>$\Delta G_d$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NACF</td>
<td>5.3</td>
<td>0.0618</td>
<td>0.0783</td>
<td>37</td>
<td>186</td>
<td>235</td>
<td>-203</td>
<td>33</td>
</tr>
<tr>
<td>ACF 0.05</td>
<td>5.3</td>
<td>0.0651</td>
<td>0.0864</td>
<td>33</td>
<td>195</td>
<td>259</td>
<td>-164</td>
<td>34</td>
</tr>
<tr>
<td>ACF 0.25</td>
<td>5.3</td>
<td>0.0728</td>
<td>0.0906</td>
<td>25</td>
<td>218</td>
<td>272</td>
<td>-134</td>
<td>37</td>
</tr>
<tr>
<td>ACF 0.5</td>
<td>5.3</td>
<td>0.0804</td>
<td>0.0943</td>
<td>17</td>
<td>241</td>
<td>283</td>
<td>-112</td>
<td>39</td>
</tr>
<tr>
<td>ACF 0.75</td>
<td>5.3</td>
<td>0.0674</td>
<td>0.0923</td>
<td>27</td>
<td>202</td>
<td>277</td>
<td>-177</td>
<td>32</td>
</tr>
</tbody>
</table>

3.3 Application for waste upcycling

The textile industry is one of the most polluting industries in the world (Roy Choudhury, 2014). There are many aspects of this industry that have negative impacts on the environment, such as massive consumption of water and chemicals, pollution of the ecosystem with chemicals in production steps, and, finally, the generation of post-consumer waste (Boström and Micheletti, 2016; Roy Choudhury, 2014). The textile industry shows high energy consumption with low energy efficiency (Blackburn Richard, 2009). Therefore, water, chemicals, and energy (e.g., electricity) are in high demand in the textile industry. The main source of water consumption is in cotton production, which requires 8.5 tons of water per kilogram of cotton (Pfister et al., 2009). One solution to reduce the production of the virgin textile fibers and lower the environmental impact is to reuse and recycle the textiles (Sandin and Peters, 2018). Textile recycling can be divided into three categories including mechanical, chemical and thermal.

In Paper I, a novel chemical recycling method that allows for the production of higher-quality than conventional mechanically recycled fibers is presented. This paper introduces a novel chemical recycling process that enables cotton textile waste to be recycled into fibers of better quality than virgin cotton fibers (upcycling).

Since the waste cotton samples are very heterogeneous with a broad range of molar mass distribution (MMD) and degree of polymerization (DP), it is necessary to adjust the DP to ensure good and uniform spinnability. The DP of the cellulose can be set by acid or enzymatic hydrolysis or by blending samples with a wood pulp comprising a lower DP than the target DP. The next step is to dissolve the solute in the 1,5-diazabicyclo[4.3.0]non-5-enium acetate
(DBNH)(OAc) ionic liquid and prepare a spinning dope for the production of the filaments.

Interestingly, fibers with a tensile strength of up to 870 MPa (58 cN/tex) were spun, exceeding the tensile strength of native cotton and commercial man-made cellulosic fibers. Figure 32 shows the tensile strength versus the Young’s modulus of the fibers spun from waste cotton in comparison to commercially regenerated cellulose fibers and virgin cotton (Gassan and Bledzki, 1999). Table 8 reports the mechanical properties of the fibers.

![Figure 32. Tensile strength and Young’s moduli of fibers from cotton waste and its blends with softwood pulp and reference fibers (grey). (paper I)](image)

It can be seen that all the fibers spun from waste cotton show significantly higher elastic moduli than commercial Lyocell and viscose fibers. The fibers spun from untreated waste cotton (CoW 452) revealed the highest (conditioned) tensile strength (876 MPa) and Young’s modulus (29 GPa) among the fibers investigated. A small share of a low molecular weight of cellulose in CoW 452 and applicable draw ratio (DR) over 8 can explain the high tensile strength and Young’s modulus of the fibers spun from CoW 452. The higher strengths compared to fibers made from wood pulps result from a higher proportion of long chains forming a more uniform and stronger oriented fiber network and from the complete absence of low molecular weight hemicelluloses.
### Table 8. Mechanical properties of spun fibers from cotton waste (CoW) and cotton waste blended with softwood pulp (SW). (paper I)

<table>
<thead>
<tr>
<th>Spun fibers</th>
<th>Max draw ratio</th>
<th>Titer</th>
<th>Tenacity conditioned (cNtex⁻¹ MPa)</th>
<th>Tenacity wet (cNtex⁻¹ MPa)</th>
<th>Elongation conditioned (%)</th>
<th>Elongation wet (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoW 438*</td>
<td>8.84</td>
<td>2.5±0.23</td>
<td>45.7±3.3 (685±50)</td>
<td>41.1±3.7 (616±56)</td>
<td>9.5±1.12</td>
<td>10.0±0.63</td>
</tr>
<tr>
<td>(CoW/SW) 468</td>
<td>15.9</td>
<td>1.3±0.1</td>
<td>52.0±3.3 (780±50)</td>
<td>43.2±4.0 (648±60)</td>
<td>8.7±0.71</td>
<td>9.8±0.75</td>
</tr>
<tr>
<td>(CoW/SW) 393</td>
<td>14.1</td>
<td>1.4±0.15</td>
<td>50.7±2.6 (760.65±40)</td>
<td>47.8±3.7 (717±56)</td>
<td>9.0±0.61</td>
<td>10.7±0.95</td>
</tr>
<tr>
<td>CoW 452</td>
<td>14.1</td>
<td>1.4±0.17</td>
<td>58.4±3.1 (876±47)</td>
<td>52.4±3.0 (785±45)</td>
<td>7.9±1.30</td>
<td>10.2±0.82</td>
</tr>
</tbody>
</table>

*the numbers in sample name is showing the intrinsic viscosity values in ml/g
4. Concluding remarks

This work identified the effect of direct cellulose modification in the spinning dope and blending of cellulose with various lignocellulosic material in the spinning dope, on spinnability and spun fiber structural properties. We have addressed the structure–property development of the spun fibers for further development of the IONCELL technology. In addition, the IONCELL process is utilized to upcycle the waste cotton garments and produce high-quality filament fibers. The study provides a comprehensive assessment of the relationship between raw lignocellulosic material properties and the viscoelasticity of the resulting spinning dope, their spinnability, and structural and mechanical properties of the spun fibers. After all, the successfully spun fibers present tensile strength levels that are equal to or higher than those of commercial viscose and Lyocell fibers.

The structure–property relationship of the IONCELL fibers from birch prehydrolyzed kraft pulp was studied with X-ray scattering techniques to further develop the spinning process. It was found that at a given polymer concentration, which was 13% in this study, the mechanical properties of the IONCELL fibers can be controlled by the draw ratio (DR). Moreover, increasing the total orientation induced by increase of DR results in the decrease of the IONCELL fibers’ accessible surface area. The orientation of the cellulose molecules along the chain axis is the reason for high tensile strength and high modulus. Additionally, the increase of the void orientation correlates well with the increase of strength properties of the fibers. In terms of the crystallites, however, their width and crystallinity are independent of the DR. The increased fibrillation tendency of these fibers should be similar to the highly oriented Lyocell fibers, since the lateral strength is reduced due to the formation of the elongated voids.

Acetylated IONCELL fibers with an intentionally low degree of substitution (DS<1) were spun successfully from a dope that was prepared in a one-step process without catalysts. The acetylation and spinning processes did not degrade the cellulose. The increase of DS resulted in the reduction of the solutions’ stiffness and allowed the fibers to be drawn up to high DRs, which meant they showed good spinnability. The mechanical properties of the fibers, such as conditioned tensile strength and elastic modulus, can be improved through acetylation with low degrees of substitution (DS<0.5) due to a slightly enhanced total orientation of the cellulose chains. However, at higher DS levels, the amorphous orientation decreases, which results in the decrease of the tensile strength. Moreover, fibers are more hydrophilic at lower DS values (up to DS 0.5) and
more hydrophobic with increased DS levels. Lastly, the degree of substitution is controllable and can be adjusted according to the desired fiber properties.

Furthermore, our attempt to produce composite fibers with tunable surface energy by adding xylan and/or lignin to the cellulose spinning dope was successful. The addition of the low-molecular weight additive to the cellulose solution which results in reduced dope viscosity, can be compensated by increasing the concentration of the solutes to ensure good spinnability. The ratio of these additives to the cellulose content was chosen in a way that ensured the fiber properties would be comparable to each other. All the mixtures showed good spinnability properties, and the fibers could be drawn up to DR 7. Lignin and xylan mainly contributed to the amorphous part of the fiber structure, increasing the deformability of the fibers and decreasing their tensile strength, while the long-chain cellulose delivered the strength to the fibers. Lignin and xylan can decorate the fibers’ surfaces with charged groups that can be tailored to tune the surface energy. As a result, the three-component fiber showed reduced surface energy, increased strain, and decreased swelling in water.

The upcycling (recycling) of waste textiles is a hot topic because of the negative environmental impact of textile production and consumption. Accordingly, the IONCELL process was utilized to upcycle waste cotton and produce high-quality fibers. The spun fibers are characterized by very high tensile strengths of 680–880 MPa and elastic moduli of 20–29 GPa. The most important finding of this study is that the viscoelastic properties of the spinning dope play an important role in increasing the orientation of the cellulose chains along the fiber axis, especially in the amorphous domains. Together with the chemical purity of the solute and the molar mass distribution, this increase leads to the production of high-strength fibers, even from waste materials. The results from this study show that the fibers’ mechanical properties are even superior to the mechanical properties of commercial Lyocell, viscose, and virgin cotton fibers.
In the textile industry, there is a strong necessity for innovative, green and sustainable technologies in fiber and fabric production that address resource efficiency to optimize energy use and material flow to reduce the strain on the environment (Shui and Plastina, 2013; Swatloski et al., 2002). The application of cellulose as an eco-friendly raw material in textile manufacturing is a step toward sustainability in this industry.

The overall objective of this thesis was to tailor the developed dry jet-wet spinning process (IONCELL process) for the production of high-strength fibers regenerated from a cellulose solution in [DBNH]OAc ionic liquid. This has been achieved with the comprehensive structural analyses of the fibers and spinnability studies, which were necessary steps to further develop the process.

The structural study of the fibers by X-ray scattering revealed some structural characteristics of the IONCELL fibers that should be investigated further in future work. Firstly, electron microscopic characterization of the inner-voids’ structures is required to fully interpret the SAXS data. Secondly, ultra-small-angle neutron scattering experiments can be utilized for clarification of the sizes of the voids, allowing the Guinier region to be explored reliably (Jericha et al., 2004).

Moreover, the modification of the IONCELL fibers with different reactants can be further investigated. Homogeneous acetylation up to higher DS values is another interesting topic to be investigated, as there will certainly be a need for more economical acetate fibers in the future. In addition, it would be interesting to study chemical modification of the fibers with tunable properties using a green and sustainable IONCELL technology.

Furthermore, all-wood-biopolymer fibers are of current interest in biomaterial science since wood biopolymers are abundant, renewable and biodegradable. The IONCELL technology can be utilized to develop these kinds of fibers as well. The composition, structure and surface chemistry of the fibers can be investigated to determine whether they can be the future composite materials.

Lastly, the IONCELL process has already been used to recycle waste cotton. In the closed loop of fibers, where there is potentially no concept of waste, the solvent recovery and the purification of the solvent is an issue which is particularly important in the closed loop operation is an important issue and is under investigation. In addition, the removal of the impurities accumulated in the spin bath should be considered in the process. In the future, by carrying out these investigations to develop a non-cellulosic compounds recycling
process and targeted removal of Elastanes for discarded clothes, we can build a new platform of fiber recycling, which will provide a stronger base for circular fashion.
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Dry-Jet Wet Spinning of Technical and Textile Filament Fibers from a Solution of Wood Pulp and Waste Cotton in an Ionic Liquid

Shirin Asaadi