

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Spinning of lignin-cellulose carbon-fiber precursors

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CHALMERS UNIVERSITY OF TECHNOLOGY

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Cover picture: Lignin-cellulose filaments entering the coagulation bath.
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ABSTRACT

Filaments of both cellulose and lignin, the two main constituents of wood, can be used as precursors for carbon fibers. Carbon fibers have high specific strength and are often used in composites for light-weight constructions. Either cellulose or lignin can be spun into precursor filaments individually, or together, as in the work presented in this thesis. By combining cellulose and lignin, it is possible to gain advantages from both materials. Cellulose is a stiff and linear polymer that contributes to the strength of a precursor fiber, while lignin, with its high carbon content, enhances the final yield after conversion into carbon fiber.

The specific characteristics of solution spinning of lignin and cellulose together are investigated in this thesis. To assess the full potential of the system, the lignin-cellulose filaments that were produced were also converted into carbon fibers. It was shown that minor parts of the lignin leach out during coagulation in the spinning process. Leaching of lignin may complicate solvent recovery and decrease yield and was, therefore, considered as one of the main challenges during solution spinning of lignin-cellulose solutions. This issue was addressed, and the leaching of lignin was studied in different coagulation baths. Promising findings include that an addition of lignin resulted in an increase in yield after conversion to carbon fibers. Additionally, solutions that contained lignin were spun with a higher draw ratio than pure cellulose solutions. The mass transport during coagulation was also studied, and it was found that the addition of lignin does not hinder the coagulation of filaments.

Keywords: lignin, cellulose, ionic liquid, dry-jet wet-spinning, carbon fibers

List of Publications

This thesis is based on the following papers:

- Paper I. **Improved yield of carbon fibers from cellulose and kraft lignin**
Andreas Bengtsson, Jenny Bengtsson, Carina Olsson, Maria Sedin,
Kerstin Jedvert, Hans Theliander and Elisabeth Sjöholm
Holzforschung, **2018**, 72, 1007-1016.
- Paper II. **Mass transport and yield during spinning of lignin-cellulose carbon fiber precursors**
Jenny Bengtsson, Kerstin Jedvert, Artur Hedlund, Tobias Köhnke
and Hans Theliander.
Holzforschung, **2019**, ahead of print.
- Paper III. **Identifying breach mechanism during air-gap spinning of lignin-cellulose ionic-liquid solutions**
Jenny Bengtsson, Kerstin Jedvert, Tobias Köhnke
and Hans Theliander.
Submitted manuscript.

Contribution report

The author's contribution to the papers presented in this thesis:

- Paper I. Partly responsible for the planning of experimental design. Conducted all experimental work regarding production and characterization of lignin-cellulose precursor filaments. Contributed to evaluating results and preparing the manuscript.
- Paper II. Main author. Responsible for experimental outline, experimental work, evaluation of results, and manuscript preparation.
- Paper III. Main author. Responsible for experimental outline, method development, experimental work, interpretation of results, and manuscript preparation.

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List of Abbreviations

COP	Cross-over point
DMSO	Dimethyl sulfoxide
EMIMAc	1-Ethyl-3-methylimidazolium acetate
GPC	Gel permeation chromatography
MW	Molecular weight
MWD	Molecular weight distribution
NMMO	N-methyl morpholine oxide
PAN	Polyacrylonitrile
RH	Relative humidity
RL5	Retentate lignin 5 kDa MW cut-off
RL15	Retentate lignin 15 kDa MW cut-off
SEM	Scanning Electron Microscopy
SKL	Softwood Kraft lignin
UV	Ultraviolet

I Introduction

Carbon fibers have unique physical properties, such as high specific strength and modulus, creep resistance, and chemical inertness. This combination makes them ideal materials in many construction applications.¹ Carbon fiber production has increased by more than 10% annually for over a decade, and the demand is predicted to continue to grow in coming years.² Carbon-fiber-reinforced composites can replace traditional construction materials, such as steel, and, thereby reduce the weight and environmental impact, for example, of electric windmills,³ concrete,⁴ and vehicles.^{5,6}

According to definition, carbon fibers have a carbon content of >92%.⁷ Commercial carbon fibers are less than 10 μm in diameter and are produced as continuous filaments.⁸ Carbon fibers are traditionally produced in three main steps: spinning of a precursor filament, stabilization, and finally carbonization. Stabilization is performed in air at around 200-300 °C to prevent the fusion of the precursor in the following step. In the carbonization step, the stabilized precursor is heated in an inert atmosphere up to 1000 °C, or even higher. During this last step, the precursor is dehydrogenated, deoxygenated, and cross-linked until basically only carbon remains in the molecular structure.

The first time carbon fibers were mentioned in a patent was in 1879 by Thomas Edison, for use in his electric lamp.⁹ Edison used cotton yarns as the precursor, however, the carbon-fiber filament was soon replaced with tungsten. It was not until the 1960's that interest in carbon fibers really started to grow. The primary reason was to supply new materials for space applications. Still, the main precursor material was cellulose, in the form of viscose filaments. Japanese researchers were the first to carbonize polyacrylonitrile (PAN), which soon became the preferred precursor to produce strong carbon fibers with a high yield.⁷ To this day, carbon fibers are mainly produced from PAN, which is dissolved in a polar, often organic, solvent and wet-spun into precursor filaments.¹⁰ PAN-based carbon fibers have excellent mechanical properties, but there is a major drawback; they are very expensive and are, therefore, limited to applications where cost is not a major factor.¹ Additionally, cost was the main

concern regarding the future of PAN-based carbon fibers when Edie¹¹ summarized the field in 1990. It could also be argued that another noteworthy disadvantage of PAN is that it is fossil based.

Apart from cellulose and PAN, several other materials have been tested as carbon fiber precursors.⁷ Some other types of carbon fibers have even been commercialized, before PAN outgrew practically all of these. Melt-spun precursors from lignin were produced for a few years under the brand Kayacarbon in the 1960's. Lignin was identified as an attractive carbon fiber precursor because of its aromatic structure, which results in a high carbon content.¹² In the early 1990's, lignin-based carbon fibers appeared on the agenda once again.¹³ At that time, it was the fact that lignin was an inexpensive and underutilized bioresource that attracted attention.¹⁴ However, melt-spun lignin filaments do not yet have acceptable mechanical properties for industrial applications.¹⁵ Consequently, lignin alone might not be sufficient as a precursor for carbon fibers.

The concept of lignin-based carbon fibers has recently attracted new interest through the idea of combining the advantages of lignin with the advantages of cellulose: yield and strength.¹⁶⁻¹⁹ The high molecular weight cellulose contributes to the strength of fibers, while lignin, with the higher carbon content of the two, increases yield when converted into carbon fibers. Lignin and cellulose from wood are available in large amounts in existing production, for instance, the pulping industry. Precursor filaments of lignin and cellulose can be created by wet-spinning of mixed solutions in which lignin and cellulose are first dissolved in a common solvent and then precipitated in a coagulation bath.¹⁶ The goal is to create an inexpensive carbon fiber with a low environmental impact that can be used in a broader range of applications than the expensive PAN.

1.1 OBJECTIVES

The main objective of this work was to investigate the air-gap spinning process of lignin-cellulose filaments and to gain knowledge on how to efficiently utilize the advantages of both cellulose and lignin in a bio-based carbon-fiber precursor.

To evaluate the system, it was necessary to combine studies on the choice of raw material, the dissolution of lignin and cellulose with extrusion, and shaping into filaments. Detailed investigations of the different characteristics of lignin and cellulose and how each of these affect the spinning process and the properties of the final carbon fiber were included. It was also relevant to investigate how to avoid significant yield loss of lignin during coagulation. New methods to characterize the “spinnability” of solutions, and the break mechanisms during air-gap spinning, were developed with the aim of achieving better mechanical properties.

2 Wood components

Cellulose and lignin are the two most abundant bioresources on the planet. They are mainly found in the cell walls of wood and other plants, for example, softwood typically consists of around 40% cellulose and 26% lignin. The cell walls in wood are constructed of two main parts: the primary wall and secondary walls; and the cells are bound together with middle lamella, see an illustrated example in Figure 1. Cellulose microfibrils act as a reinforcement embedded in a lignin matrix in both the primary and the thicker secondary walls.²⁰ Although the middle lamella and primary wall are more lignin rich, the major part of the total amount of lignin in wood is located in the secondary walls.^{21,22} The biological function of lignin in cell walls is more complex than that of cellulose. Lignin contributes to strength, but perhaps mainly the toughness of wood, by acting as a glue that holds the cells and cellulose microfibrils together in the cell wall. The hydrophobicity of lignin may also be equally important for water transport in a tree.²³

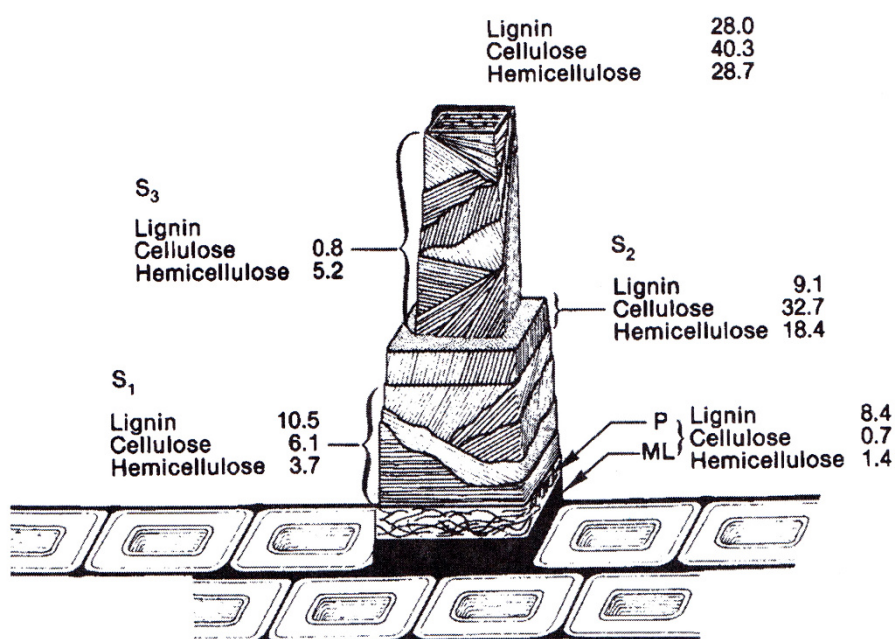


Figure 1. Chemical composition (%) of the cell wall of scots pine. ML: Middle lamella, P: Primary cell wall, S: Secondary walls. Reprinted with permission.²¹

A chemical fractionation process is necessary to separate cellulose and lignin in wood. About one hundred million tons of softwood are harvested annually and fractionated predominantly with the sulfate process, or as it is usually called: the Kraft process.²⁴ In this pulping method, wood chips are cooked at approximately 150 °C in aqueous sodium hydroxide and sodium sulfide in the digester. The cellulose-rich pulp is, thereafter, bleached and washed. Practically all the lignin can be removed from the fibers in the final bleaching, which results in a white fiber. The major part of the lignin is made soluble in the cooking liquor in the digester and is most commonly spent as fuel by incineration, which in a modern mill results in a surplus of energy. This approach results in low raw material utilization in the overall process (40-55%) since only carbohydrates, cellulose, and hemicelluloses are recovered for further valorization. However, the advantage of the Kraft process is that the pulp, especially if made from softwood, is very strong.²⁵ Applications of Kraft pulp include cardboard and other types of strong paper products as well as tissue and printing paper. To produce more refined cellulose products, such as regenerated cellulose fibers, the pulp must be very pure with regard to cellulose. The preferred pulp type for such applications is a dissolving pulp, with a cellulose content above 90%. Dissolving pulps account for only a few percentages of the total market of Kraft pulps, although increasing annually.²⁶ The chemical structure of lignin and cellulose is presented in more detail below.

2.1 LIGNIN

There is currently only consensus about the fact that native lignin is an amorphous polyphenolic; the true composition and structure are not fully understood. Lignin is synthesized originally from D-glucose, the end-product of the photosynthesis. The first sequence of lignin synthesis is known as the shikimate pathway, which ends in the key intermediate of phenylalanine. The following sequence is referred to as the cinnamate pathway and ends in three conventional, and predominant, monomers of lignin: p-coumaryl, coniferyl, and sinapyl alcohols,²² shown in Figure 1. There are most likely several other types of lignin monomers as well. The other types of monomers are mainly differentiated from conventional monomers by various acetyl groups linked to the γ -hydroxyl.²⁸ The ratio of lignin monomers in different types of wood has been investigated and the lignin in softwood consists mainly of coniferyl alcohol (>95%) while hardwood includes a mixture of mainly coniferyl and sinapyl alcohols.¹²

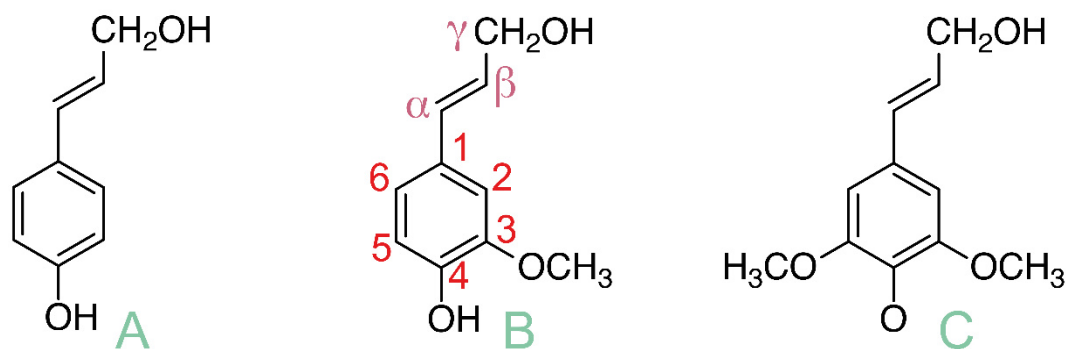


Figure 2. Predominant monomers of lignin.¹² From the left: A. p-coumaryl alcohol, B. coniferyl alcohol, C. sinapyl alcohol.

Many investigations have characterized the different types of linkages in lignin structure. The most prominent linkage in lignin structure is the ether bond β -O-4.¹² However, several other ether and ester linkages are present.²⁸ There are indications that two main different types of native lignin occur in a wood cell, one more linear and the other a more branched lignin. Lignin may also be covalently bonded in the cell wall, mainly to hemicelluloses, and these structures are referred to as lignin-carbohydrate complexes, which is a research field of its own.²⁹

It is important to distinguish between different types of isolated lignin. There are two main types of available lignin, isolated from the major chemical pulping methods: Kraft and sulfite.²⁷ The lignin from the sulfite process has sulfonate groups incorporated and is, thereby, water soluble, and these groups are usually referred to as lignosulfonates. Kraft is the dominant pulping method, and only the lignin isolated using this process will be discussed hereinafter.

Kraft lignin

Lignin is degraded in the Kraft process, and the fragments are solubilized at the high level of pH used in the digester. Phenolic lignins are the most reactive; at alkaline conditions and high temperatures they are cleaved off into the quinonemethide intermediate. In the presence of a strong nucleophile, which in the Kraft process is hydrosulfide ions (HS^-), the β -O-4 bond is cleaved, creating a new phenolic lignin, and so on.²⁵ Many other lignin reactions occur simultaneously. For example, chromophores, which are highly conjugated compounds, are created, giving the pulp and the cooking liquor their dark brown color. As mentioned in the beginning of this chapter, lignin is nowadays predominately recovered as an energy source during the Kraft process.

Incineration is done as part of the chemical recovery in a Kraft mill. From the digester, the black liquor is led to the evaporation plant where water is removed. The now viscous black liquor is incinerated in the recovery boiler, and the remains, a salt smelt, are recovered to produce new cooking chemicals. In modern mills, the recovery boiler often limits the capacity of the mill.³⁰ This issue, the limited capacity of the pulp mill, can be improved by extracting a fraction of the lignin from the process for further utilization, e.g. through the LignoBoost process.³¹ Further valorization of lignin can also increase the revenue of the mill.

In the LignoBoost process, lignin is precipitated from the black liquor by decreasing the level of pH using carbon dioxide.³² The precipitate is, thereafter, washed in aqueous sulfuric acid at approximately a level of pH of 3-4.³³ Due to the harsh conditions in the digester, the structure of native lignin is highly modified, and many of the phenylpropane side chains are either modified or removed. Crestini et al.³⁴ have tried to evaluate this degradation and proposed the partition of Kraft lignin into an acetone-soluble and insoluble part. The acetone insoluble part is more linear whereas acetone-soluble lignin has fewer similarities with native lignin since the phenylpropane side chains have been eliminated, and it has a more branched structure. Phenolic groups are the foremost functional groups in Kraft lignin. Carboxyl groups are also present, and these are enriched in the low molecular weight fraction. Kraft lignin also contains a few percentages of sulfur.

The lignin market

Lignin constitutes the largest bio-based reservoir of aromatic compounds and, consequently, has received a lot of attention with the aim of developing new products and fuels. The sulfite process (representing only a few percentages of the total pulp market) renders water-soluble lignosulfonates.²⁴ This kind of lignin is excellent for use as a dispersing agent or emulsifier. Lignosulfonates can also be converted into vanillin, which is commercially done by Borregaard, Sarpsborg, Norway.³⁵ Lignin may be mixed into epoxy resins and polyurethane foams and, thereby, reduce the need for non-renewable raw materials.³⁶ It is also possible to use lignin as feedstock for other chemical compounds. After lignin has been depolymerized, it can be converted either chemically or biologically into fine chemicals. The largest challenge with this route is to combine the polydispersity of lignin with the high purity of the formed

compounds.³⁷ Kraft lignin is used in the present work, and the high carbon content of lignin is utilized to render high yield when a precursor filament is converted into a carbon fiber.

2.2 CELLULOSE

Cellulose belongs to the polysaccharides and is built of D-glucopyranose units, which are linked via $\beta(1\rightarrow4)$ glycosidic bonds.³⁸ As early as at six repeating units, the properties of the chain start to differentiate from sugar as the chain is no longer water soluble. Cellulose chains are very rigid and are organized in a recalcitrance structure with high crystallinity.

The three hydroxyl groups on each glucopyranose unit, together with the ring oxygen, can form both inter- and intramolecular hydrogen bonds, see example in Figure 3. The hydrogen bonds arrange the cellulose chains into sheets. The sides of a cellulose sheet can be differentiated in two ways. First, the ends of the cellulose chains are chemically different. The ends are often called reducing and non-reducing ends, where the former is in equilibrium with an aldehyde.³⁹ Second, the chains are polar since the hydroxyl groups are all equatorial. The results of this arrangement are that the sides of the sheets are more polar, and the sheet surfaces, with no hydroxyl groups, are more hydrophobic.⁴⁰

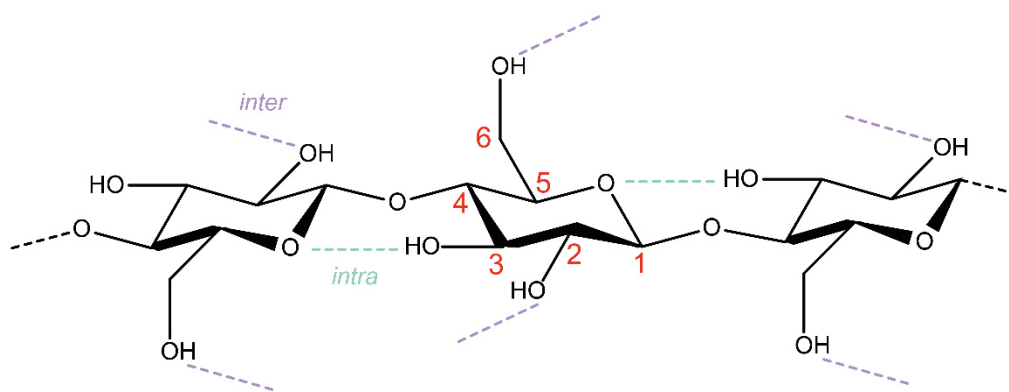


Figure 3. The molecular structure of cellulose, including intra- and intermolecular hydrogen bonds. The hydrogen bond pattern of cellulose II, reproduced from Klemm et al.³⁹

Depending on the rotational conformation of the C6-hydroxyl group, the cellulose chains can form intermolecular hydrogen bonds in various manners, giving rise to several different crystalline arrangements of cellulose.⁴⁰ Native cellulose exists in the form of Cellulose I, which in turn is composed of two crystal phases, $I\alpha$ and $I\beta$, and they vary in proportion depending on cellulose source. These phases are both composed of cellulose sheets with parallel chains

but differ in how the sheets are stacked on top of each other, with different offset to the previous plane.⁴¹ If cellulose is dissolved and then coagulated or regenerated, it will crystallize into Cellulose II, where the cellulose chains are arranged antiparallel to each other. Other types of crystalline structures exist, however, none of them are of the same technical importance as I and II.⁴² However, cellulose is not purely crystalline. Cellulose is arranged in semi-crystalline microfibrils, with alternating crystalline and amorphous, i.e. less ordered, parts. One cellulose chain can run from one microfibril to another, and the morphology is then called the “fringed fibril model.”³⁹ The microfibrils are further aggregated into macrofibrils, and those are arranged in the layers of the cell walls of plants, see Figure 1.

Cellulose is rarely delivered in high purity from nature. It occurs in high concentrations in, for example, cotton, flax, and hemp. However, the cellulose concentration in wood is only about 40%. To further valorize cellulose from wood, it must be separated from lignin and hemicelluloses. During the isolation of cellulose in the harsh conditions of the Kraft process, known reactions take place, such as peeling and alkali hydrolysis, which lead to the degradation of the cellulose chains.²⁵ In a recent study, Atalla et al. have proposed that the semi-crystalline structure of cellulose in pulp is actually a consequence of the pulping process.⁴³ Drying of pulp will also affect the cellulose and its properties. Drying can cause the cellulose to coalesce, which decreases the accessibility of the cellulose. The resulting agglomeration of microfibrils is referred to as “hornification.” The initial degradation of cellulose fibers, such as in the primary step of acid hydrolysis, may also result in a structure that is less accessible since this step removes the less ordered parts of the cellulose and the surfaces of crystallites first.⁴⁴

Owing to its rigid structure, created by the many hydrogen bonds, and its crystallinity and high molecular weight, cellulose has excellent mechanical properties.³⁹ In this work, cellulose is used to reinforce lignin filaments.

3 Shaping of polymers into filaments

Cellulose cannot melt; thus, it must be dissolved in order to be reshaped into continuous filaments. There are fewer solvents to choose from for cellulose than for lignin, which means that cellulose limits the potential solvents for the co-spinning of lignin-cellulose precursor fibers. In the present thesis, “lignin” refers to softwood Kraft lignin.

3.1 SOLVENTS FOR CELLULOSE AND LIGNIN

There are several factors that complicate cellulose dissolution: the high degree of polymerization, the vast number of hydrogen bonds between chains, and the hydrophobic interactions that stabilize the stacking of sheets.⁴⁵ A solvent must first of all break both hydrogen bonds and hydrophobic interactions in order to dissolve cellulose. Second, long polymer chains, especially rigid ones such as cellulose, do not undergo a large entropic gain when dissolved. This fact limits, as for most polymers, the number of solvents to choose from.⁴⁶

More variety in solvents is available for lignin than for cellulose. This is due to the lower molecular weight (MW) of lignin than of cellulose and that lignin is amorphous. For example, lignin is soluble in aqueous solutions at a level of $\text{pH} > 10-11$ through ionization of the phenolic hydroxyl.¹² Minor parts of lignin are even water soluble at neutral pH .⁴⁷ Solvents that dissolve cellulose can usually dissolve even higher concentrations of lignin.

Commercially available man-made cellulose filaments are mainly manufactured using the viscose or Lyocell process. Viscose is produced by the derivatization of cellulose with carbon disulfide (CS_2) and is, thereafter, dissolved in sodium hydroxide (NaOH). However, CS_2 is a known cancerogenic substance, i.e. emissions must be controlled carefully during production.⁴⁸ The other main type of commercially available man-made cellulose filament is Lyocell. In the Lyocell process, cellulose is directly dissolved in N-methyl morpholine oxide (NMMO).⁴⁹ The main issue with the Lyocell process is that NMMO is thermally unstable and stabilizers must be added already during the dissolution of cellulose to prevent runaway reactions and cellulose degradation.⁵⁰

Ionic liquids have been identified as promising and safe solvents for cellulose. Ionic liquids are organic salts with a melting point below 100 °C; many of them are interesting because of their ability to dissolve cellulose at low temperatures, and they are temperature stable.⁵¹ An even larger share of the ionic liquids also efficiently dissolve lignin.^{52,53} For cellulose, the main dissolving effect of ionic liquids is proposed to come from the anion, which creates new hydrogen bonds with cellulose, thereby, separating the cellulose chains.⁵⁴ But, breaking the hydrogen bonds may not be sufficient to completely dissolve cellulose and choice of cation will also influence cellulose solubility. However, the role of the cation is not fully understood. Different ionic liquids render solutions with very different rheology and, consequently, the choice of solvent will affect the potential to form cellulose fibers.⁵⁵ The dissolution of lignin in ionic liquids is, as for cellulose, highly dependent on the choice of anion.^{53,56} Results from modelling of lignin dissolution have also indicated that lignin moieties exhibit π -stacking with imidazolium cations.^{57,58} In the present investigation, cellulose and lignin are dissolved in the ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIMAc). EMIMAc is a liquid at room temperature, and the solvent has been used extensively in cellulose fiber spinning studies.⁵⁵ It can dissolve high amounts of both lignin and cellulose at low temperatures. EMIMAc is more stable than NMMO, but to avoid both solvent and cellulose degradation, solutions with EMIMAc should be handled below 120 °C.^{59,60}

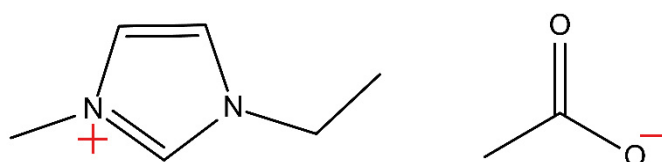


Figure 4. 1-Ethyl-3-methylimidazolium acetate (EMIMAc).

3.2 RHEOLOGY OF SOLUTION

Rheological measurements can provide the stress response of a fluid when it is subjected to mechanical deformation, i.e. strain. For a solid, elastic material, the stress response for small values of strain is independent of rate of strain, often called shear rate, but dependent on the magnitude of strain. In contrast, the stress response of a viscous fluid, again valid for small strain amplitudes, is strongly dependent on shear rate while stress is independent of the magnitude of strain. Materials that show both elastic and viscous behavior are called viscoelastic. Viscoelasticity also means that the fluid can, under shear or

elongation, store some energy. After the stress is released, the fluid relaxes back to its original shape. A purely viscous solution will dissipate all energy under shear and will not relax after stress is recovered.⁶¹ Polymer melts and homogenous polymer solutions, including solutions of lignin and cellulose, are viscoelastic.

As mentioned, at small strains, the viscosity of a fluid only depends on shear rate, not on the magnitude of strain. This dependence is referred to as the linear viscoelastic region. However, if the strain increases, the viscosity will also depend on strain. Within the linear region, the complex viscosity measured with an oscillating deformation is analogue to the shear viscosity measured for rotational deformation; this is known as the Cox-Merx rule.⁶² The zero-shear viscosity can be calculated if the viscosity is extrapolated to the “zero shear rate”, η_0 . The magnitude of the zero-shear viscosity is dependent on the polymer concentration in a solution and the average molecular weight and type of solvent. Zero-shear viscosity can be calculated by fitting the complex viscosity to the Cross Model.⁶¹ If the viscosity at infinite shear rates, η_∞ , is set to zero, the Cross Model becomes Eq. 1. ⁶¹

$$\eta = \frac{\eta_0}{1 + (K\dot{\gamma})^{1-n}} \quad (1)$$

In Eq. 1, η is the complex viscosity, η_0 is the zero-shear viscosity, K is a time constant, $\dot{\gamma}$ is the shear rate, and n is a power-law exponent.

When shear is applied to a polymer solution, some of the chains will orientate in the shear direction, which lowers viscosity. But at low shear rates, other polymer chains might have time to relax and entangle, which leads to a constant viscosity for low shear rates often referred to as a Newtonian plateau. At a critical shear rate the polymer chains no longer have time to relax, resulting in a net orientation of the chains and a lower viscosity. Solutions with higher polymer concentrations and/or higher average molecular weight shows onset of shear thinning at lower shear rates.⁶³

The modulus is also an important property for a viscoelastic solution; it is comparable to the shear modulus of an elastic material. The modulus is only dependent on shear rate within the linear range. Linearity means that if the strain varies sinusoidally, the stress response (τ) will oscillate with the same

frequency as the strain (γ). For an elastic material, the stress response is in phase with the oscillating strain; as an ideal elastic material responds instantly to deformation. However, in viscoelastic materials where some energy is dissipated, the stress will be out-of-phase with the strain with a certain phase angle δ . The stress can, thereby, be divided into two components: one that is in phase with the strain (τ') and one that is out-of-phase by 90° (τ''), as illustrated in Figure 5.⁶⁴ Two moduli can be calculated from these two components (τ' and τ''), a storage and a loss modulus. The point at which the two moduli are of equal magnitude is called the cross-over point (COP). The amplitude of the moduli and the COP depends on the polymer concentration in solution and molecular weight distribution (MWD).⁶³

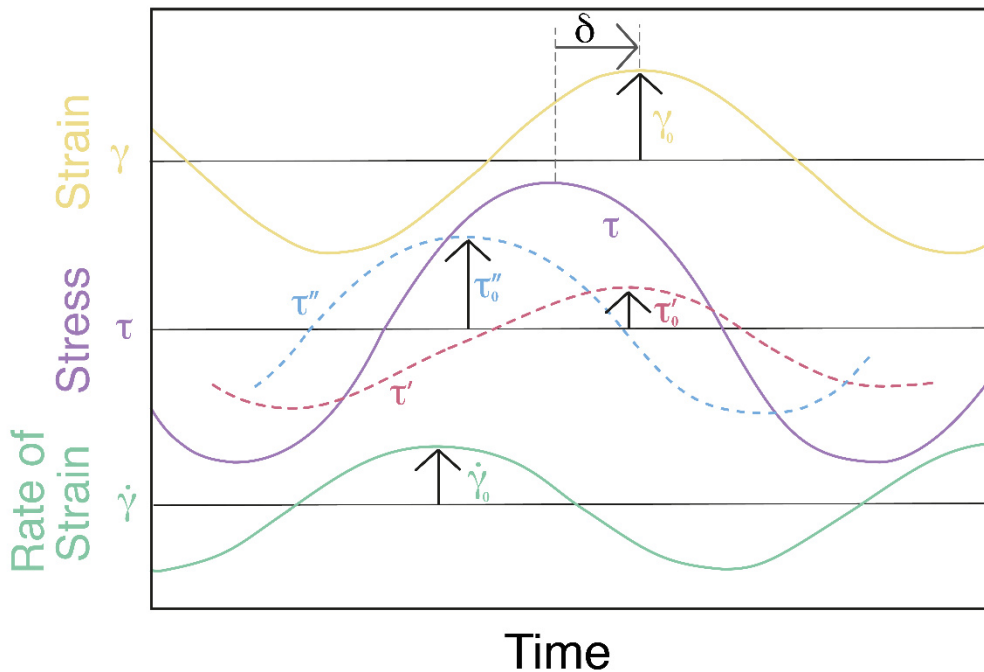


Figure 5. The stress response of a viscoelastic material. Reproduced from Macosko.⁶⁴ γ is the applied strain, τ is the stress response where τ' and τ'' are the in- and out-of-phase components, respectively. δ is the phase angle, and $\dot{\gamma}$ is the rate of strain, i.e. the shear rate.

3.3 SPINNING

All spinning processes have in common that filaments are formed by a fluid being forced through a nozzle, in many cases a die with multiple capillaries, and thereafter, the extruded filaments are solidified. There are traditionally three main spinning processes: melt, wet, and dry spinning. In both wet- and dry-spinning the fluid is a polymer solution.⁶⁵ Additionally, there is a newer type of spinning: dry-jet wet spinning, also known as air-gap spinning, which is the

method used in the present work. This method also belongs to solution spinning, and is a modification of wet spinning; the extruded polymer solution is first let through air before entering a coagulation bath, see Figure 6.⁶⁶ One of the advantages of dry-jet wet spinning over wet spinning is that the air gap allows for stretching of the solution and, consequently, orientation of the polymers before coagulation.⁶⁷

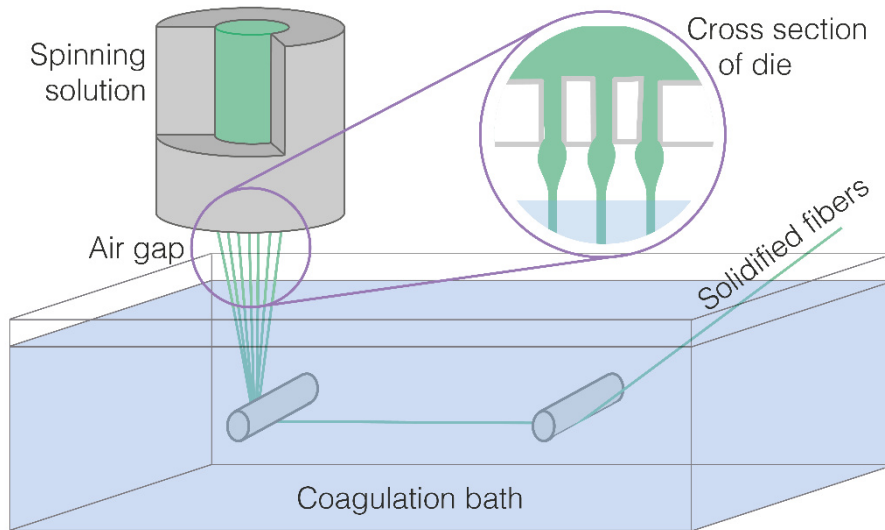


Figure 6. Overview of the dry-jet wet-spinning process, including a cross section of the die showing die swell of the extruded filaments.

The parameters in spinning that highly affect the filament properties are, e.g. draw ratio and choice of coagulation liquid. Draw ratio is defined as the ratio between take-up velocity (v_t), and extrusion velocity (v_e). The tenacity of cellulose filaments improves with draw ratio up to approximately a draw ratio equal to 5-6 after which the tenacity reaches a plateau value.⁶⁷ However, the draw ratio at which a tenacity plateau is reached for lignin-cellulose filaments has not yet been determined.

When the solution exits the die, the stored elastic energy from shearing into the capillaries causes the solution to swell, as illustrated in Figure 6.⁶⁸ This elastic recovery is called die swell. As a consequence of die swell, the velocity of the filament is slower than the set extrusion velocity.⁶⁹ The true draw ratio might, therefore, be higher than the measured draw ratio during spinning due to the lower velocity of the filament at the die.

When the extruded filament enters the coagulation bath, the coagulation liquid, i.e. a nonsolvent, first causes the filament to swell. The entered nonsolvent then

solvates the cellulose solvent, which in turn starts to diffuse out of the filament.⁷⁰ Coagulation proceeds at different speeds depending on the nonsolvent used. A higher affinity between nonsolvent and solvent contributes to faster coagulation. The choice of nonsolvent also affects the morphology of the filaments, both porosity and crystallinity.⁷¹

The extrusion of solutions and shaping of polymers into continuous filaments has been performed for over a hundred years, especially with cellulose.⁴⁸ Commercial cellulose fibers include, among others, viscose and Lyocell. Viscose fibers are wet spun. The derivatized cellulose is dissolved in NaOH and extruded into an acidic coagulation bath where cellulose is regenerated.⁴⁸ The viscose process offers high flexibility, and fibers with very different properties can be produced, from textile-grade fibers to high-strength tire cords. Lyocell fibers, on the other hand, are air-gap spun. As a result of air-gap spinning, due to the ability of the solution to stretch before coagulation and, thereby, align the polymers, Lyocell fibers have greater mechanical strength than viscose.⁶⁵

A crucial part of the industrialization of a spinning process is recycling the solvent. In the NMMO process, 99% of the solvent is recycled.⁷² There is currently no efficient way of recycling EMIMAc or other ionic liquids; however, there is ongoing research.⁷³ There are, as of yet, no problem-free solvents for cellulose, as discussed in “Solvents for cellulose and lignin”; both of the industrially used processes have their share of issues. Therefore, despite the current lack of recycling, ionic liquids are regarded as suitable for dissolving and spinning cellulose and/or lignin, such as in the present study.

3.4 INSTABILITIES DURING SPINNING

Breakage of the filaments may occur during spinning due to imperfections of the fluid or disturbances in the spinning set up, or breakage can be caused by the limitation of the inherent properties of the fluid. The latter is known as critical breach, and a few types of critical instabilities during melt spinning are described in the scientific literature. In contrast, the mechanisms leading to spinning failure during wet spinning and air-gap spinning are not as extensively studied. However, some analogies to air-gap spinning can be drawn from melt spinning since a concentrated polymer solution can, in many cases, be compared to a polymer melt.⁷⁴ Two of the described critical instabilities in melt spinning originate from the theory for the disintegration of a fluid thread,

cohesive and capillary breaches, and these are illustrated in Figure 7.^{75,76} The application of an external force is required to extend and shape a viscoelastic fluid into a filament, as is done during spinning. This force is balanced by viscous and elastic forces which develop in the deforming fluid.⁷⁷ When an elastic force divided by the cross-sectional area equals the breaking stress, the filament will break. This breach is known as cohesive breach. A colder polymer melt with higher viscosity needs a stronger pulling force to be elongated, and will, therefore, break at lower draw ratios.^{78,79}

Other types of instabilities have also been identified during melt spinning, melt fracture, and draw resonance. A problem with melt fracture occurs at high extrusion velocities, however, this type of instability is not relevant for air-gap spinning. Draw resonance is a periodic fluctuation in diameter that grows substantially above a critical draw ratio.^{80,81} If the amplitude of the fluctuation becomes large enough, it can split the filament into droplets, a capillary breach. On the other hand, breach may also occur at the narrow cross sections, the formed nodes of the filament, and break when they cannot bear the force.⁷⁴

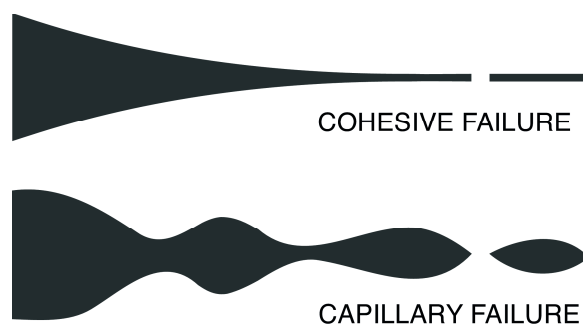


Figure 7. Breaking mechanisms of liquid threads.

The surface tension of a polymer solution is often neglected and not considered when spinning is discussed. The surface tension of a cellulose-EMIMAc solution decreases with polymer concentration but increases with temperature.⁸² Simulations of draw resonance indicate that surface tension destabilizes spinning and might play a part in inducing draw resonance in the system.⁸³

3.5 PREVIOUS WORK ON LIGNIN-CELLULOSE FILAMENTS

The first documented work on lignin and cellulose spun together into continuous filaments is a patent by Otani et al.⁸⁴ from 1964. In this patent, cellulose, in the form of a viscose solution, is mixed together with lignin,

dissolved in alkali, and wet-spun. It was noted that a higher molecular weight polymer, such as cellulose, increased the strength compared to pure lignin fibers. Lignin has, thereafter, been blended with several other polymers, mostly synthetic, in the endeavor to produce strong and inexpensive carbon fibers.^{85,86} Lignin has also been blended with cellulose and cellulose derivatives with the aim of recreating wood. The ambition was that the addition of lignin would strengthen the cellulose fibers, however, this was only achieved when cellulose was spun from a few solvents and with a very low lignin concentration.⁸⁷

It took nearly a decade into the new millennium until lignin and cellulose once again were identified as a promising combination for making carbon fibers. This was mainly due to the newly adapted techniques for separating lignin from the black liquor in the Kraft process, which resulted in available lignin without a specific application. Around the same time, stricter regulations on fuel economy for cars were coming into force, creating encouragement from the automotive industry to find inexpensive light-weight materials. Additionally, dry-jet wet spinning was by this time an industrial method for making cellulose fibers,⁶⁵ and the same technique was applied to make lignin-cellulose filaments.^{88,89,90} After these initial contributions, further investigations into the variation in both lignin and cellulose sources, as well as solvents, have been published, supporting this robust concept of making bio-based carbon fibers.^{16,17,19} However, there are challenges to this system that need further investigation, such as leaching lignin in the coagulation bath.⁹¹ To render high-strength carbon fibers, the precursor filaments should be highly oriented and, consequently, the spinning process should be examined and further adjusted in order to obtain better mechanical properties.

4 Materials and Methods

This section briefly describes the materials and methods used in the appended papers. Detailed information on the used equipment, chemicals, and precise experimental protocols are available in the appended papers.

4.1 RAW MATERIALS

Softwood Kraft lignin (SKL) was used for fiber spinning in all papers as well as in the mass transport and solubility experiments in Paper II. This lignin was obtained from LignoBoost Demo (Bäckhammar, Sweden) and was produced with the LignoBoost process. Two retentate lignins were additionally used in Paper I, where different membranes were used to remove a part of the lower MW molecules. The different lignins were produced using either a 5 kDa (RL5) or 15 kDa (RL15) MW cut-off. Retentate lignins were produced with the ultrafiltration of the initial lignin; more information on retentate production can be found in Paper I.

Two different pulps were used for fiber spinning in Paper I, a softwood Kraft dissolving grade pulp and a fully bleached paper grade softwood Kraft pulp, which were purchased from Georgia Pacific (Atlanta, GA, USA) and provided by SCA Forest Products (Sundsvall, Sweden), respectively. The former was also used in the coagulation study in Paper II and for fiber spinning in Paper III. Information on purity and the degree of polymerization is presented in Table 1. The solvent for the dissolution of lignin and cellulose was consistently EMIMAc (95%), which was purchased from Sigma-Aldrich (Steinheim, Germany) and was used as received.

Table 1. Viscosity and results from carbohydrate analysis of the pulps used.

Pulp type	Intrinsic viscosity / ml·g ⁻¹	Carbohydrate composition / ml·g ⁻¹			
		Glucose	Xylose	Mannose	Galactose
Dissolving pulp	465	860	27	19	0.5
Paper grade pulp	630	730	64	52	2

Characterization of lignin and cellulose

Intrinsic viscosity, which gives an indication of the average MW, was determined for the pulp according to ISO 5351:2010, i.e. “determination of limiting viscosity number in cupri-ethylenediamine solution”. The MW distribution of lignin was analyzed with gel permeation chromatography (GPC). Lignin and lignin-cellulose filaments were mixed with the mobile phase (10 mM LiBr in DMSO). Regarding the filaments, the cellulose did not dissolve and formed a milky-white gel at the bottom of the vials. Consequently, all of the lignin was considered to be dissolved, and the supernatant was used for analysis.

The purity of the raw materials and spun filaments was analyzed with respect to carbohydrate and Klason lignin content after hydrolysis in 72% sulfuric acid. The solid residue after complete hydrolysis is defined as Klason lignin. The monomeric sugars in solution were analyzed with high performance liquid chromatography.⁹² Lignin in solution, referred to as acid soluble lignin, was measured in a UV spectrometer at 205 nm, and, thereafter, quantified with the Lambert-Beer law using an absorptivity constant of $110 \text{ l g}^{-1} \text{ cm}^{-1}$.⁹³

4.2 SOLUTIONS OF LIGNIN AND CELLULOSE

To ensure good impregnation of the solvent during dissolution, the pulp was ground and the lignin sieved before mixing with the solvent, EMIMAc. Lignin powder was mixed in after the cellulose, which was easiest performed stepwise, i.e. little by little with mixing in between, since the lignin otherwise tended to form tough clumps. The solution mixture was added to a closed reactor, heated to 70 °C, and stirred at 30 rpm using an anchor impeller. In our set-up, any faster stirring caused the solution to rise against the impeller, a classic example of the Weissenberg effect.⁶¹ Prior to fiber spinning, it is important to remove air from the solution since air bubbles may cause filament breakage. The solution was transferred to the container used during spinning, and deaeration was performed at 60 °C below 10 kPa pressure for at least 5 h.

Characterization of solutions

The quality of dissolution was observed using an optical microscope from Nikon Eclipse Ci-POL (Nikon Instruments, Tokyo, Japan). When a solution is placed between two orthogonal polarizers, any non-dissolved fibers will be clearly visible, as they are birefringent. The viscoelastic properties of solutions were analyzed with oscillating rheometry using a CS Rheometer (Bohlin

Instruments, Cirencester, UK). The temperature was controlled to obtain the viscosity, storage, and loss modulus at selected temperatures.

4.3 FILAMENT SPINNING

The solution was spun in a bench-scale spinning instrument, which consisted of a piston spin pump, a spin bath, and take-up rolls, see illustration of the setup in Figure 6. Extrusion was performed with a multi-filament die, see details of the different die geometries in the appended papers, and it generally progressed with less smudging of the die outlet if the solution was colder. However, a solution that is too cold cannot be fully drawn. During spinning start-up, the air gap was several centimeters in order for the solution to exit without wetting the die. When extrusion was stable, the air gap was reduced to about 10 mm. It was found that a higher draw ratio could be attained if the coagulation bath was cold, preferably around 5 °C. This observation is also in line with previous findings for similar solvent systems.⁹⁴ The lignin-cellulose filaments appeared much stickier than the pure cellulose fibers, and the take-up rolls had to be covered with Teflon to be able to collect the filaments. The filaments were, thereafter, washed in deionized water for 24 h and subsequently dried at 80 °C for 45 min. By treating the filaments with fabric softener (Neutral, Unilever) before drying, they became easier to separate from tow into single filaments, and the softener also seemed to prevent the filaments from breaking up during drying.

Evaluation of breach mechanism

The air gap was photographed and recorded during spinning to be able to analyze the mechanisms causing filament breach. By using a Makro lens on a digital camera, the magnification and resolution were high enough to calculate the die swell of the extruded filaments. Die swell was calculated by dividing the maximum thickness of the extruded filament with the capillary diameter. The air gap was also recorded with a high-speed video camera (500 frames per second) equipped with an “End trigger”⁹⁵ function enabling the capture of filament breach. The slow-motion videos enabled the identification of the location of the breach and any diameter fluctuation (draw resonance) preceding the breach. In total, 10-12 videos were collected for each temperature and were evaluated anonymously by three persons separately. The films were then rated with a score of 1 for a clear draw resonance and a score of 0.5 if a tendency for draw resonance was present.

4.4 MASS TRANSPORT DURING COAGULATION

Mass transport during the coagulation of a lignin-cellulose filament includes the diffusion of EMIMAc out of the filament, the inward diffusion of water, and the leaching of lignin. Membrane coagulation was applied as a model system for filament coagulation and is illustrated in Figure 8. The method is described in detail in a publication by Hedlund et al.⁷⁰ In short, a well-defined tube-shaped membrane was coagulated in a stirred coagulation bath with known mass. The residence time in the coagulation bath was varied from 3 s up to 72 h to cover the whole course of coagulation. After removal from the coagulation bath, the membranes were put in new vials filled with deionized water, denoted washing baths, and were left for at least 3 days to reach apparent equilibrium.

Three different conditions in the coagulation bath were investigated: acidity and solvent content (15% EMIMAc), and a combination of the two. Pure MilliQ-water was used as the reference. A coagulation bath containing EMIMAc was included since this situation would occur in industry, which utilizes counter-current washing of fibers. To limit the energy demand during solvent recovery, the solvent content should be as high as possible,⁹⁶ and 15% EMIMAc was chosen accordingly. The acidic coagulation baths contained either acetic acid or sulfuric acid.

Leached lignin was quantified through UV absorbance at 280 nm converted to g L^{-1} with the Lambert-Beer law using the extinction coefficient of $24.6 \text{ L g}^{-1} \text{ cm}^{-1}$.⁹⁷ The possible absorption of carbohydrate conversion products at 280 nm, such as furfural, could be ignored since such products were not expected in any quantities in the coagulation baths.

Apparent diffusion coefficients were calculated using the same methodology as applied by Hedlund et al.⁷⁰ For short times the time range used was $15 < t_i < 240$ s, the EMIMAc concentration adjacent to the steel rod can be considered constant and the coagulation can be described by the equation of Fickian diffusion into an infinite slab in a single dimension, see Eq. 2.

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (2)$$

In Eq. 2, c is the concentration, x is the distance from the solution-coagulation bath interface in meters, and D is the diffusion coefficient in m^2s^{-1} . By using the

boundary conditions clarified by Hedlund et al.⁷⁰ the final diffusion coefficients were calculated as the average of the used time range, according to Eq. 3.

$$D_i = \frac{\pi}{t_i} \left(\frac{M_i(t)}{M_{i_tot}} \frac{d}{2} \right)^2 \quad (3)$$

In Eq. 3, D is the diffusion coefficient in m^2s^{-1} , t is the time in seconds, and d is the thickness of the membrane in meters corrected for the curvature of the membrane. $M(t)$ is the mass of EMIMAc transported out from the membrane after time t , normalized against M_{tot} , which was the mass of EMIMAc transported out after 60000 s.⁹⁸ The efflux of EMIMAc was found from the amount of EMIMAc that remained in the membrane after a certain time, given by the concentration of EMIMAc in the washing bath, which was measured with conductivity.

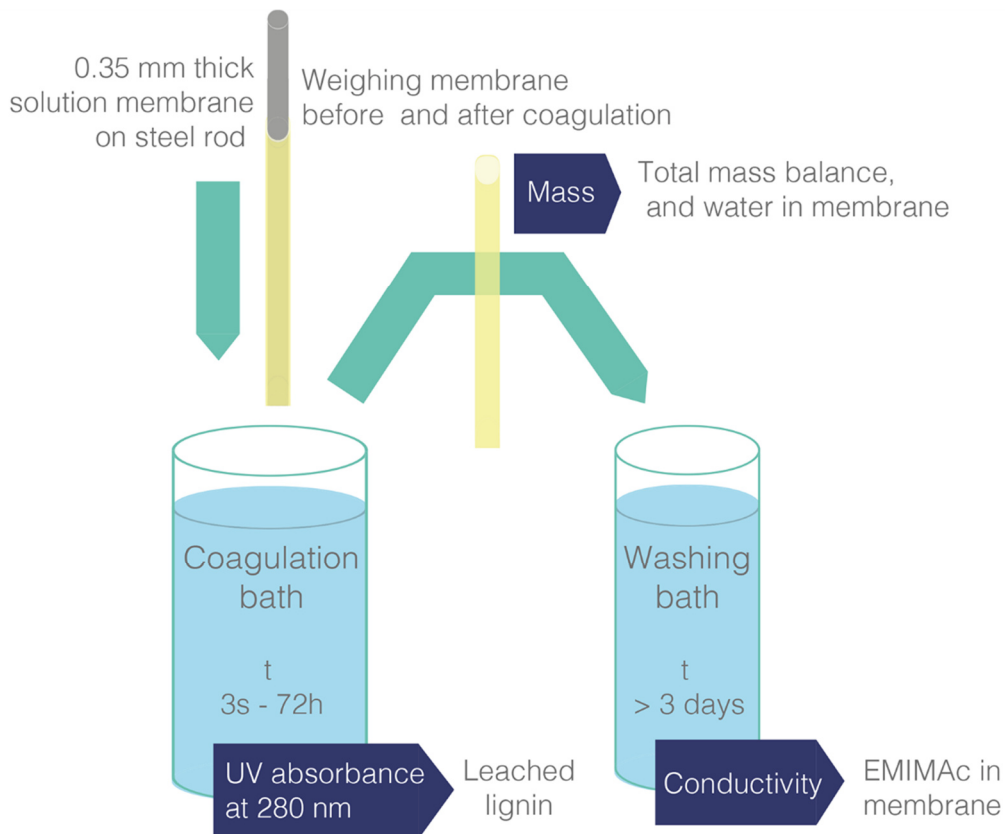


Figure 8. Illustration of the membrane coagulation method, including the analytical tools used.

4.5 CHARACTERIZATION OF FIBERS

Linear density, often called titer, of filaments was measured with a Vibroskop (Lenzing Instruments). It determines the linear density (in dtex, i.e. g/10000 m) by inducing a vibration and, thereafter, changing the length of the free filament until resonance is obtained. When titer is known, the tenacity and elastic modulus (both in cN/tex) can be measured with a Vibrodyn (Lenzing Instruments), which performs a tensile stretch of the filament until breakage. The results from tensile tests of polymeric fibers are highly affected by humidity. Therefore, all measurements were done in a controlled climate of 21.5 °C and 65% RH. By measuring the density of the filaments with a pycnometer and assuming a circular cross section, the mechanical properties could be converted into SI units.

Fibers are birefringent, meaning they have a different refractive index along, n_y , and orthogonal, n_x , to the fiber axis ($\Delta n = n_y - n_x \neq 0$), which originates from the orientation of the polymers along the fiber axis. It is possible to measure how birefringent a filament is by quantifying Δn , and, thereby, obtaining an idea of the average orientation of the crystalline and amorphous phases. In the present study, birefringence was measured with a polarized light microscope equipped with a 3λ Berek compensator. The thickness of the fiber was calculated from the measured titer. Birefringence was calculated as the ratio between the retardation of the polarized light for maximum darkness divided by fiber thickness.

Scanning Electron Microscopy (SEM) was used to observe the surfaces and cross sections of filaments. To receive high resolution images, a high vacuum is needed. However, since lignin-cellulose filaments are poor electrical conductors, there is often a problem with charging and image distortion. This problem can partly be avoided by coating the sample with 1-1.5 nm of platinum and lowering of the accelerating voltage applied to the electron beam. For cross sections, sample preparation in the present study also included cold mounting in epoxy (using vacuum impregnation) and cutting with Broad Ion Beam milling. Polishing was performed with a Gatan Ilion+ Precision Ion Polishing System with an ion gun energy of 5 keV and cooled with liquid nitrogen to avoid heat damage. Images were captured with a SEM from JEOL, model JSM-7800F. Secondary electrons and backscattered electrons images of fiber cross sections and top views of the lignin fiber surfaces were acquired typically using an accelerating voltage of 5 kV and a working distance of 10 mm.

5 Results and Discussion

5.1 THE IMPACT OF LIGNIN ON CELLULOSE SOLUTIONS

The solubility of lignin in EMIMAc is greater than the solubility of cellulose.⁵² This is partly due to the difference in molecular weight; the MW of SKL is approximately 7900^{16} g·mol⁻¹, and cellulose dissolving pulps range between 100 000 and 200 000³⁹ g·mol⁻¹. Another noteworthy difference between cellulose and lignin is that lignin consists of branched molecules while cellulose is a linear polymer. Mainly as a consequence of the higher MW, cellulose has the largest impact on the viscosity of the solution. In the present study, the impression was, that the addition of lignin improved the ability of the solution to form strings, especially noticeable when the solution was transferred from the dissolution reactor to the spinning container. The solutions that contained lignin could also withstand a higher draw ratio, which was found during spinning in Paper I. The addition of lignin also rendered dark solutions that limited the evaluation of the degree of dissolution, since dark solutions absorb a lot of light. However, the darkness of the solutions that contained lignin simplified the analysis of the spinning process, by an enhanced contrast, especially in comparison to pure cellulose solutions, which are virtually transparent.

Rheology

The zero-shear viscosity of solutions with a different solid content and lignin:dissolving pulp ratio are plotted against temperature in Figure 9. This graph shows that the addition of 30% lignin to a cellulose solution has virtually no additional impact on the zero-shear viscosity at any temperature. The same trend was observed by Olsson et al.¹⁶ and may be explained by the relatively low MW of lignin compared to cellulose. A further increase in the addition of lignin, 50 and 70%, resulted in an increase in viscosity, probably due to the high solid content of the solution.

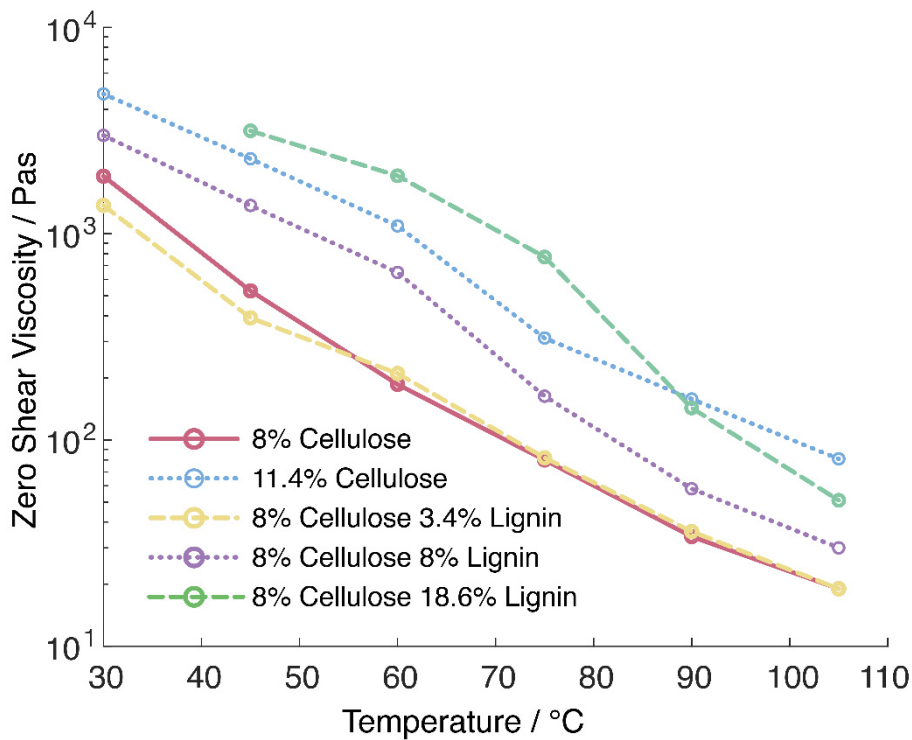


Figure 9. Zero Shear viscosity of pure cellulose solutions, dissolving pulp, and solutions that contain lignin (SKL).

5.2 FILAMENT SPINNING AND BREACH MECHANISMS

A high draw ratio during spinning is often needed to achieve acceptable mechanical properties. The draw ratio together with the extrusion rate through a specific die also sets the diameter of the filaments.⁶⁶

The value of the critical draw ratio, i.e. the draw ratio that causes filament breakage, can be considered as a way of quantifying spinnability.⁹⁹

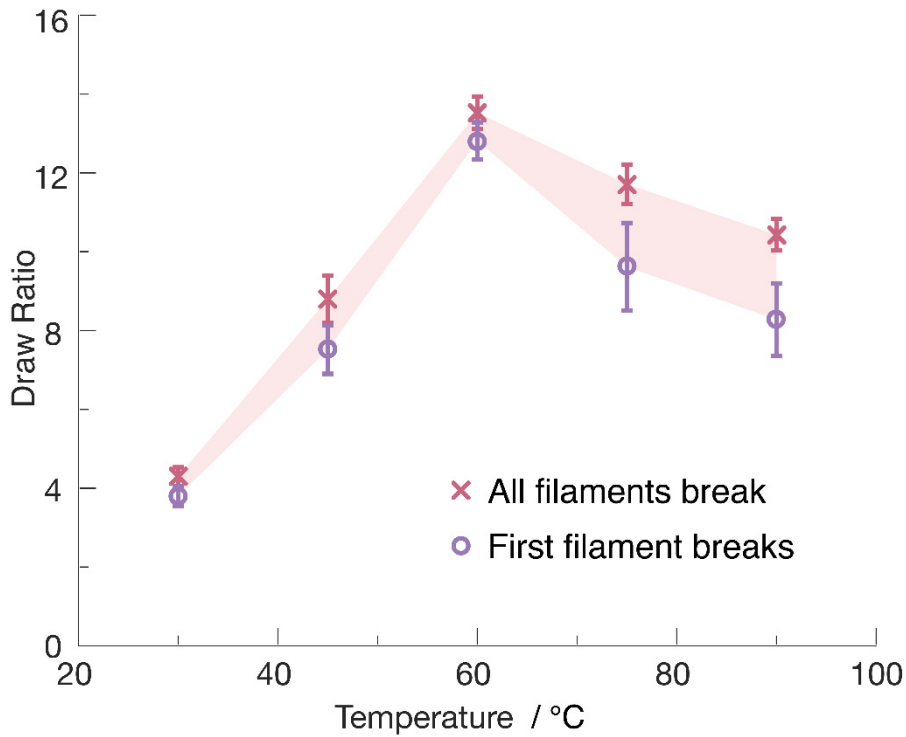


Figure 10 shows the critical draw ratio for a temperature range of 30 to 90 °C for a 16 wt% solution with a lignin:cellulose ratio of 1:1. A maximum in critical draw ratio was clearly found around 60 °C. Spinning was performed with a die consisting of 4 capillaries, and it was noted when both the first and when the last filament broke. The breakage of the first filament may have been a consequence of imperfections in the solution, such as air bubbles or other inhomogeneities. However, the breakage in the last filament was most likely a critical breach. Since a maximum in critical draw ratio was found with respect to temperature, the assumption was made that filament breakage is caused by at least two mechanisms, one at low temperatures and one at higher temperatures.

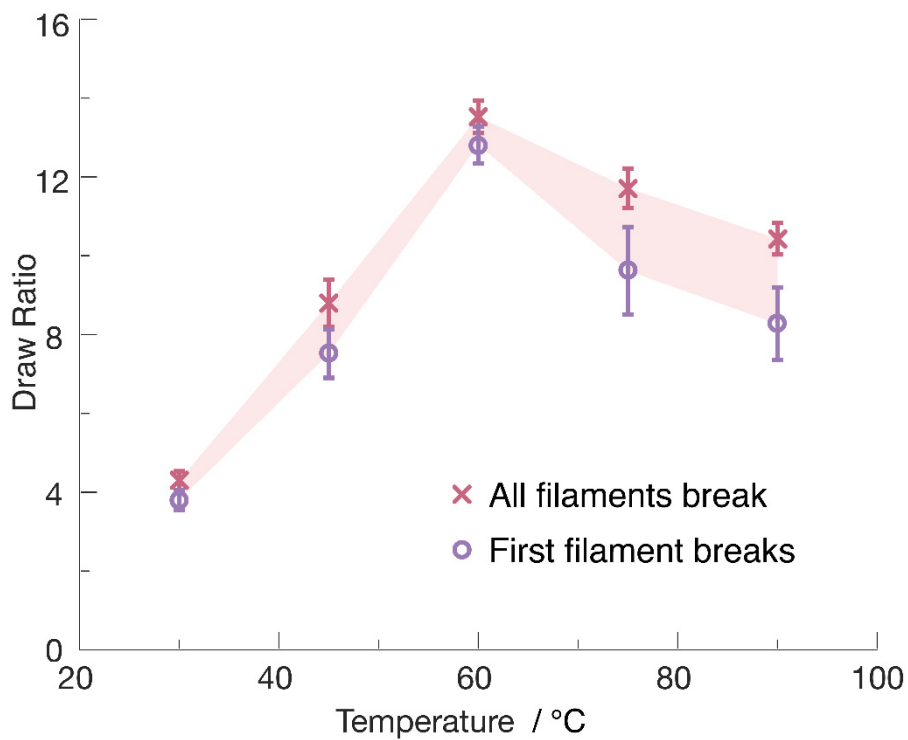


Figure 10. Critical draw ratio (v_e/v_t) at different temperatures for a 16 wt% lignin-cellulose solution, 50:50. $n = 5$.

Analyzing the breach mechanism

Die swell does not cause breach per se, but it might decrease the measured critical draw ratio, since this phenomenon will reduce the velocity of the extruded filament. A true draw ratio would, therefore, consider this new reduced velocity as the extrusion velocity. A colder and thus more elastic solution can be expected to experience a more pronounced die swell⁶⁸ and, subsequently, the true draw ratio might be higher. Consequently, if considering the true draw ratio, the decrease in the critical draw ratio when lowering the

temperature would be somewhat less severe than what is shown in

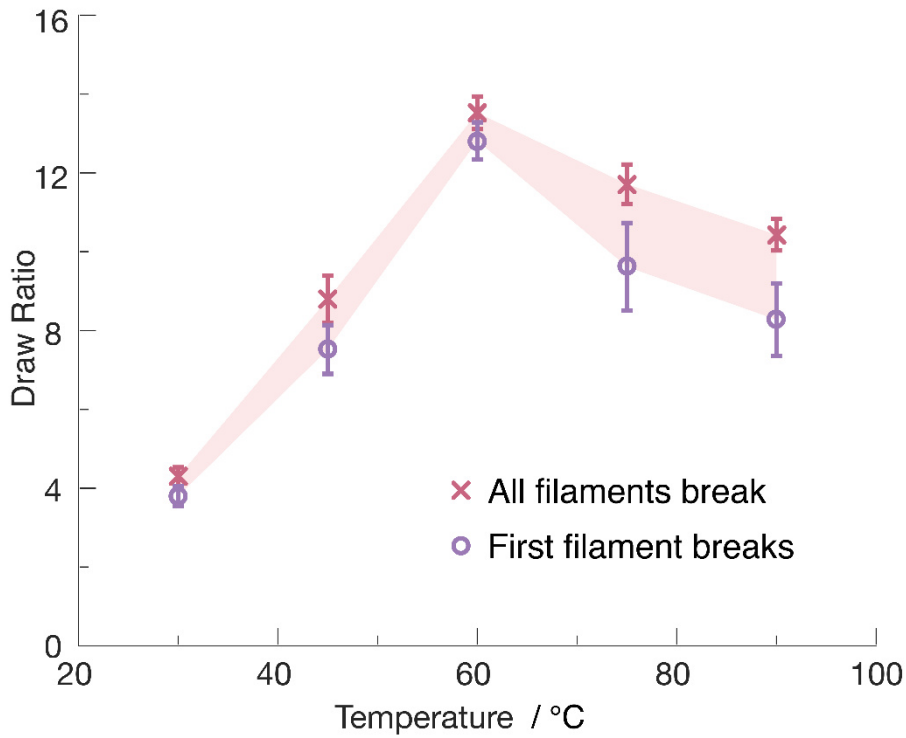


Figure 10. However, this assumption was not the case. No difference was found for die swell 30, 45, or 60 °C calculated from photographs, as presented in Table 2. An example of die swell is shown in Figure 11 with both a photo of the capillary exit and a photo taken during the extrusion of a filament. Consequently, die swell is likely not the cause of the lower critical draw ratio at lower temperatures.

Table 2. Calculated die swell for each temperature of solution.

Temperature / °C	Die swell
30	1.9 ± 0.10
45	2.0 ± 0.07
60	1.8 ± 0.03

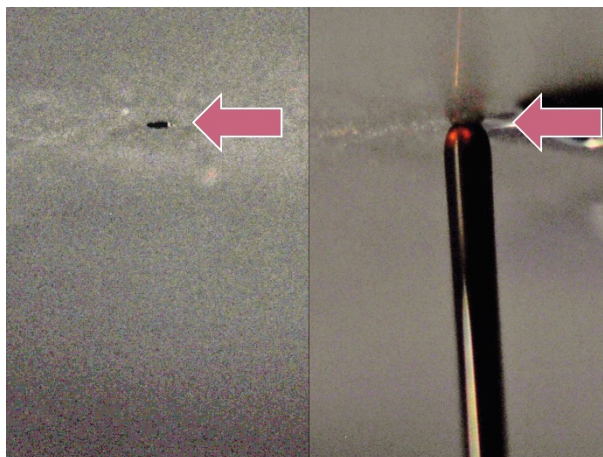


Figure 11. Example of die swell. The image to the left shows one capillary in the die before extrusion of solution. The image to the right shows the capillary and an extruded filament. The pink arrow indicates the same point in both images.

After die swell was excluded, other mechanisms that could cause a breach at lower temperatures were considered. When temperature increases, the force to extend the filament decreases due to lower viscosity, and the breaking stress is reached at a higher draw ratio.⁷⁸ Therefore, the dominant breach mechanism up to 60 °C was proposed to be a cohesive breach.

At higher temperatures, the decrease in the critical draw ratio was not as easily described. To investigate the breach mechanism at higher temperatures, the actual breakage was recorded with a high-speed video camera. When analyzing the video recordings of the critical draw ratio that included a breakage, the existence of a periodic fluctuation of the filament diameter was noticed, i.e. draw resonance. Images captured from one video recording are shown as an example in Figure 12. To determine if there was any correlation between draw resonance and temperature, the videos were anonymized and evaluated by three persons individually. As can be seen in Figure 13, a correlation with temperature was found, and the occurrence of draw resonance at breakage increased dramatically above 60 °C. Therefore, the breach at higher temperatures is suggested to be caused by draw resonance.⁷⁴

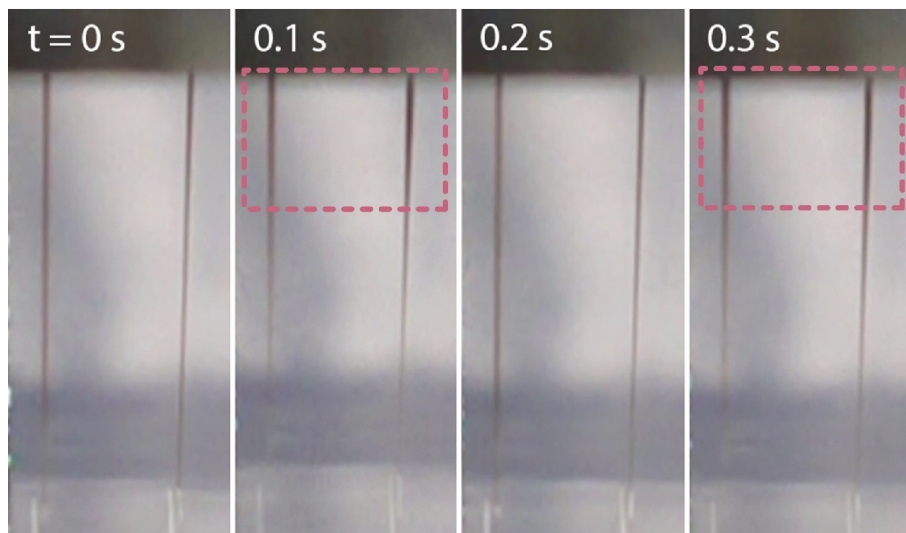


Figure 12. Still photos captured from a video recording of the extrusion of solution at 75 °C. Draw resonance is shown for both filaments, indicated with dashed rectangles, as both filaments were slightly thicker at 0.1 and 0.3 s than at 0 and 0.2 s.

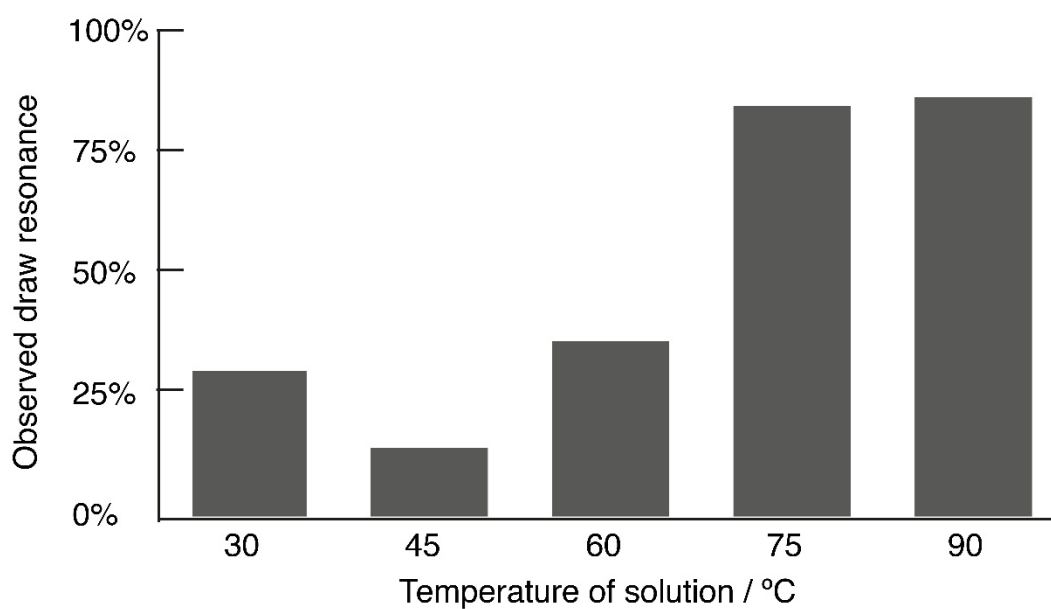


Figure 13. Statistics of draw resonance observed in video recordings for each temperature. The average score from the evaluation is presented.

5.3 COAGULATION OF LIGNIN-CELLULOSE SOLUTIONS

One of the major issues when spinning solutions that contain both lignin and cellulose is that a minor part of lignin is water soluble. This results in lignin leaching out into the coagulation bath. Lignin dissolved in the coagulation bath might aggravate solvent recovery, reduce lignin yield and, consequently, the final carbon yield of the carbon fibers. To investigate if it is possible to limit or even inhibit leaching of lignin, it is important to analyze the coagulation process and identify the type and quantity of the leached lignin. This was investigated by performing model experiments using different coagulations baths, as described in Table 3.

Table 3. Compilation of coagulation baths used, the soluble fraction of dry SKL powder and SKL dissolved in EMIMAc.

Conditions in coagulation bath	Soluble fraction of SKL (dry powder)	Soluble fraction of SKL (12 wt% SKL in EMIMAc)
MilliQ water, pH 7	1.6% ± 0.4%	5.9% ± 0.5%
0.6% Acetic acid, pH 4	2.1%	6.2%
12% Acetic acid, pH 2.4	4.2%	10.0%
15% EMIMAc, pH 7	5.4 %	13.0%
15% EMIMAc, 12% Acetic acid, pH 4	13.3%	26.3%
Sulfuric acid, pH 2.4	1.1%	5.6%
Sulfuric acid, pH 1.3	0.9%	4.4%

The coagulation baths containing EMIMAc were included since this situation would occur industrially in a counter-current washing step of fibers, and the solvent content should be as high as possible to limit the energy demand during solvent recovery.⁹⁶

Total mass transport during coagulation

Figure 14 presents the total mass transport during coagulation. As seen in the figure, during coagulation, the mass of the membrane first increased. This is due to an influx of water into the solution. First, thereafter, EMIMAc really started to diffuse out of the solution and the total mass decreased. This observation is consistent with the results from Hedlund et al.⁷⁰ who investigated neat cellulose-EMIMAc solutions. Hedlund et al. have proposed that the inflow of water causes cellulose to precipitate into an aggregated fibril network and enables the desorption of EMIMAc from cellulose. The lignin that leaches out can almost be neglected when considering the total mass of solution.

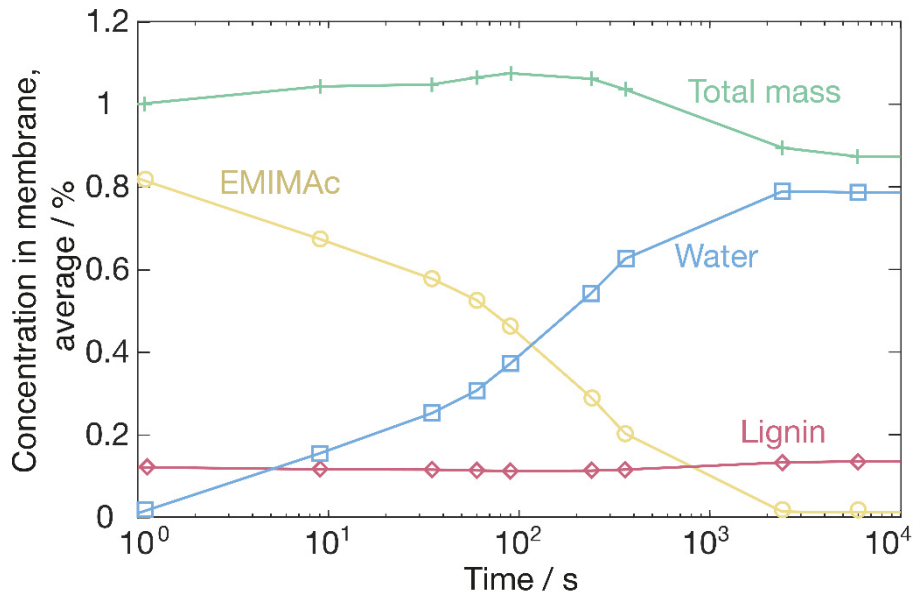


Figure 14. The mass flows during coagulation. Note that the time on the x-axis is presented in logarithmic scale.

The diffusivity of EMIMAc was found not to be dependent on the solid content of the solution, when comparing 18 and 27 wt%, as shown in

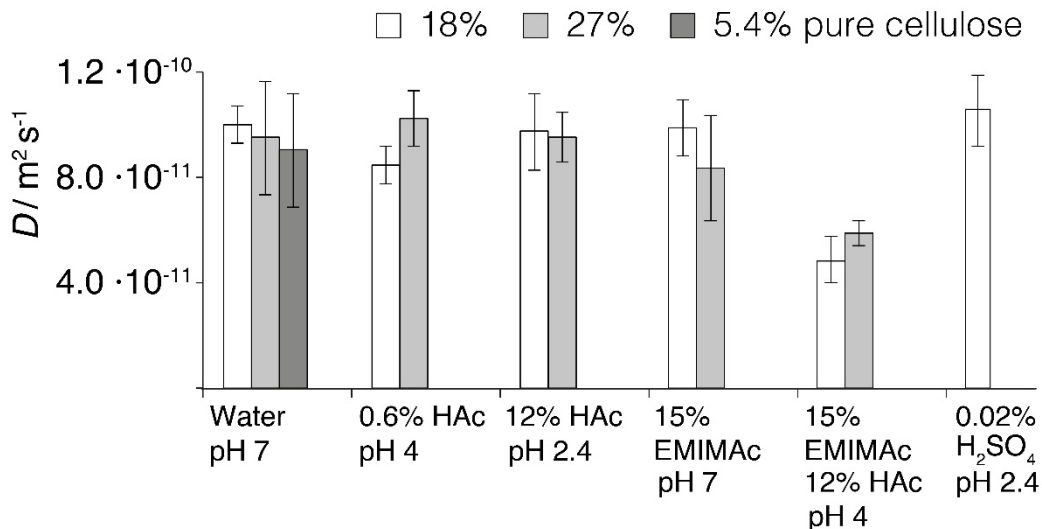


Figure 15. Hedlund et al.⁷⁰ have further suggested that during coagulation, the diffusion of EMIMAc and water take place in the open pores formed by the precipitated cellulose fibrillar network. Subsequently, EMIMAc diffusion is independent of cellulose concentration in the initial solution, as was found in the studied range.

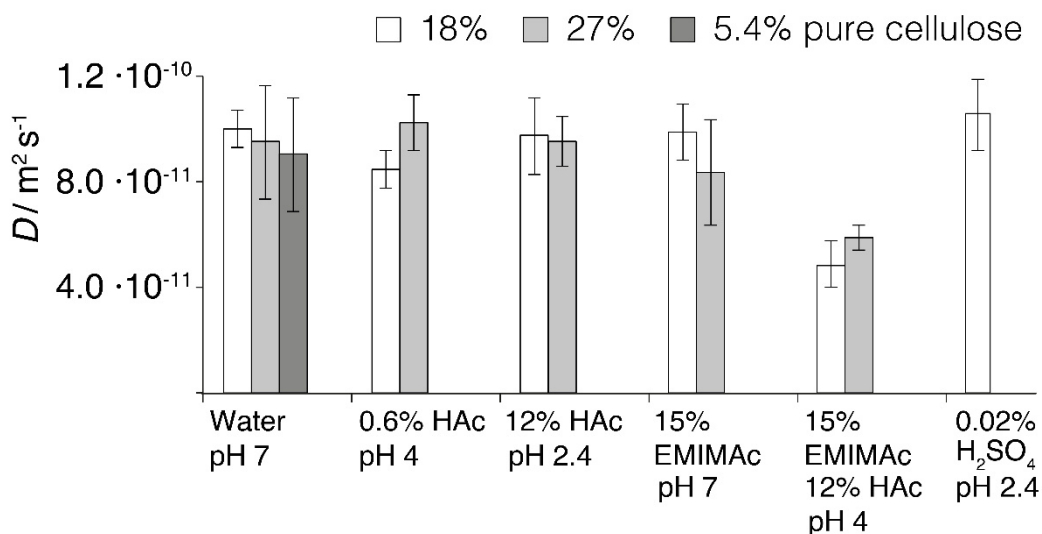


Figure 15. Diffusion coefficients for EMIMAc during coagulation in different coagulation baths for the two solutions with different solid contents.

However, when the coagulation bath contained both EMIMAc and acetic acid, the diffusivity of EMIMAc was found to be significantly lower than in the other coagulation baths. A plausible explanation found in this case was that the diffusion of EMIMAc was hindered by the high concentration of soluble lignin, as seen in Table 3. In other coagulation baths, in which the solubility of lignin was lower, essentially all of the lignin had precipitated from the coagulation liquid and adsorbed onto the cellulose network and, consequently, did not interfere much with EMIMAc diffusion. When the combination of EMIMAc and acetic acid was used, a high concentration of lignin was solubilized in the liquid phase inside the pores of the coagulated cellulose network. Consequently, it was suggested that the dissolved lignin interacted with the EMIMAc and retarded mass transport.

Molecular weight of leached lignin

When analyzing the MWD of lignin in spun filaments and comparing it with the initial lignin, it was possible to conclude that low molecular weight lignin leaches out into the coagulation bath, according to Figure 16. Another phenomenon visible in Figure 16 is that, when a filtered lignin (RL5 and RL15), was used, the MWD of lignin in filaments was more similar to the added lignin than the unfiltered lignin (SKL).

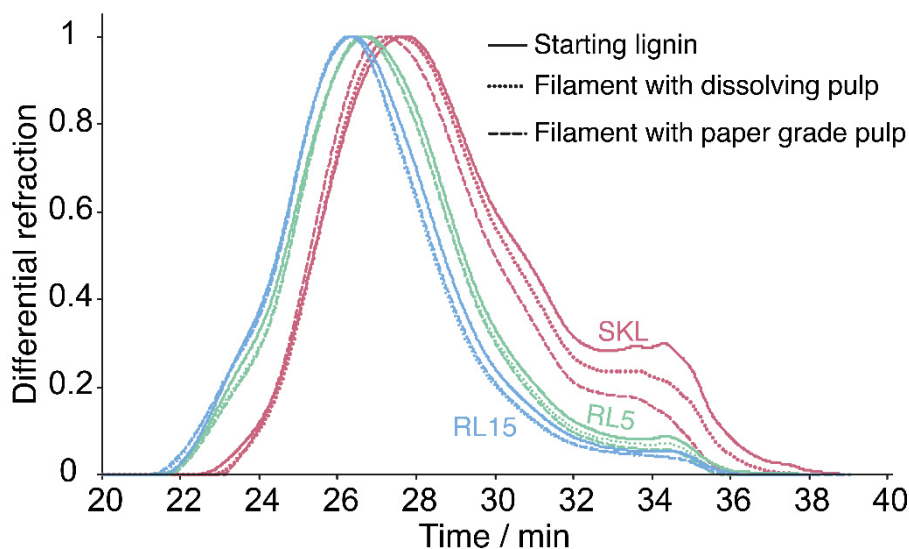


Figure 16. MWD of softwood kraft lignin (SKL) and retentate lignins (RL5 and RL15), and of filaments spun with the same lignin both in combination with dissolving and paper-grade pulp. Small molecules take a longer time to elute than larger molecules.

Lignin yield during coagulation

Figure 17 presents absolute amounts of lignin leached from membranes and coagulated for certain times. A correlation between lignin solubility, Table 3, and leached lignin was found. As shown in the table, leaching of lignin was clearly more pronounced when EMIMAC was present in the coagulation bath than if pure MilliQ water was used. The amount of lignin leached from the membrane increased even further, as did lignin solubility, when the bath contained both EMIMAC and acetic acid.

Another systematic difference between the two solid contents of solution is clear in Figure 17. The same absolute amount of lignin leached from the solution regardless of its solid content, 18 or 27 wt%. For a solution with a 27% solid content, relatively less lignin was leached in the same coagulation liquid. A plausible explanation is that the lignin solubility limit is reached in the liquid phase inside the pores formed during the coagulation of cellulose, which causes excess lignin to precipitate. Consequently, a higher solid content of solution would lead to the encapsulation of a larger fraction of the lignin and, consequently, a higher lignin yield.

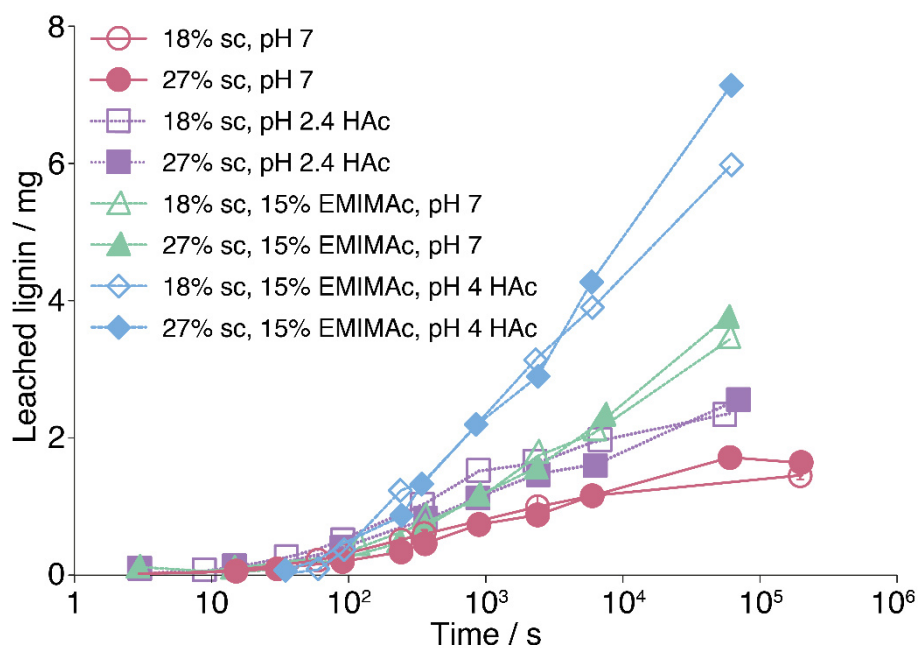


Figure 17. Absolute amounts of lignin leached into the coagulation bath after different amounts of time. Standard deviations of measurements with 18% solid content in MilliQ water, $n = 3$. SC = solid content.

Based on the MWD results, it was concluded that predominately low MW lignin leaches out during coagulation. Previous literature has reported an enrichment of carboxylic groups in low MW lignin^{100,101} which have a pK_a of around 4.4.¹⁰² The carboxylic groups are, therefore, neutralized in a level of pH 4 or lower. Subsequently, in an attempt to reduce leaching of lignin, the level of pH was lowered in the coagulation bath to reduce the solubility of the low MW lignin. When the lignin content of washing baths was analyzed, a clear pH trend was found where the residence times were long enough to reach equilibrium, as shown in Figure 18. When the coagulated membrane was transferred from the coagulation bath to the washing bath, it carried some liquid and, in most cases, rendered a washing bath with a level of pH similar to the coagulation bath. A clear trend towards less lignin leached was found when the pH dropped to a level of 4 or below in the washing baths. Consequently, these results indicate the influence of the protonation of carboxylic groups on lignin yield.

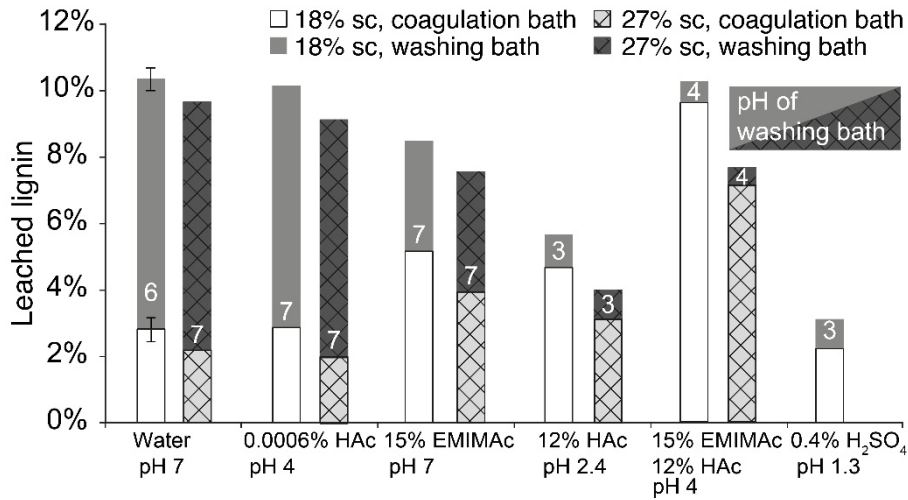


Figure 18. Lignin leached after 6000 s in the coagulation bath (light shaded bars) and in the washing baths (dark shaded bars). White digits inside the washing bath bars indicate the level of pH.

However, during the initial stage of coagulation, a low pH level had no benefit for lignin yield, as shown in Figure 19. Rather it seemed, at times below 6000 s, the value of pH had no effect on leached lignin. This observation is visible in the black curves in Figure 19 where pH was reduced with sulfuric acid. On the other hand, a fair assumption based on Figure 19 is that equilibrium had not been reached, apart perhaps from membranes coagulated in pH 1.3 (sulfuric acid).

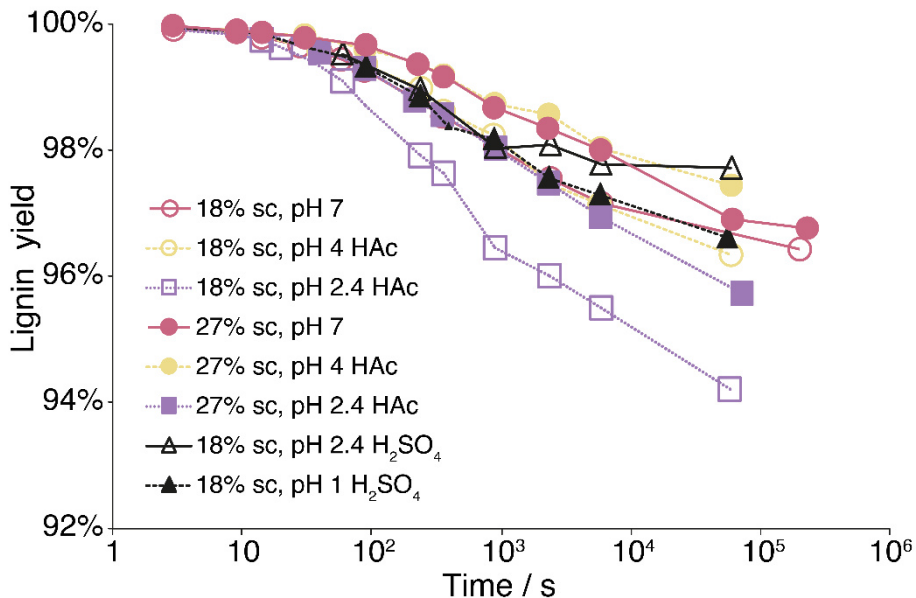


Figure 19. Leaching of lignin as a function of time in coagulation baths with different levels of pH. SC = solid content.

In a comparison of the coagulation of a membrane and mixing of dry SKL in the same coagulation bath, it was found that a larger share of the lignin leached during coagulation than the soluble part of SKL. This relation is visible in a comparison of the percentage of leached lignin during membrane coagulation, Figure 18, with the values in Table 3 for each coagulation bath. However, less lignin leached during the coagulation of a membrane than if an EMIMAc solution containing lignin only was coagulated. These results indicate that the cellulose network, one way or another, encloses lignin. Based on the membrane coagulation results, a coagulated structure was proposed and is illustrated in Figure 20. The figure shows a porous network where lignin is dissolved inside the pores of the cellulose. Leaching of lignin is, thereby, limited by the solubility of lignin within these pores.

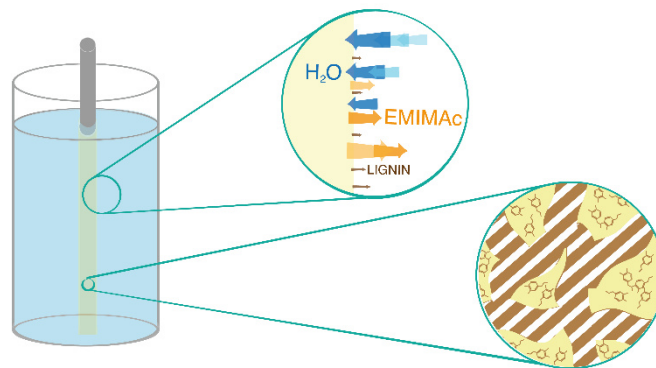


Figure 20. Illustration of the coagulation of a lignin-cellulose membrane. The different mass flows are in the upper circle, and a proposed structure and plausible mechanism of leaching of lignin are in the lower circle.

5.4 PROPERTIES OF FILAMENTS AND CARBON FIBERS THEREOF

SEM imaging

After observation using SEM, it was clear that dry-jet wet spinning of lignin-cellulose EMIMAc solutions renders filaments with smooth surfaces, as shown in Figure 21. The filaments also have an even diameter distribution, see Figure 22. Both of these attributes are suitable for carbon fiber precursors.⁷ The fibers were also flexible and easy to handle, even with a lignin ratio as high as 70%. An example of flexibility is illustrated by the small knot in Figure 23.

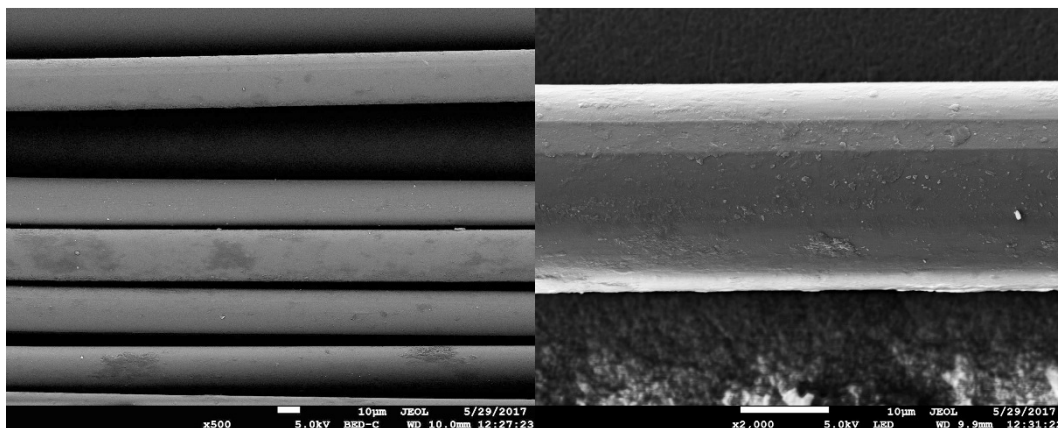


Figure 21. SEM-image of the surface of precursor filaments with SKL:dissolving pulp, 70:30.

Mechanical properties

The results in Table 4 show that the lignin-cellulose filaments had a consistent diameter, in line with impressions from SEM observations, see Figure 22. Expectedly, the tenacity and the modulus of lignin-cellulose filaments decreased compared to pure cellulose filaments. The impaired mechanical properties are likely due to the lower MW of lignin in comparison with cellulose and a result of the changed structure within the filament with the addition of lignin. This observation is in line with literature data on similar cellulose-lignin filaments.¹⁷ Furthermore, no significant differences in the mechanical properties of the precursor filaments were found for the different types of lignin, filtered (RL5 and RL15), non-filtered (SKL), or cellulose (paper grade or dissolving pulp).

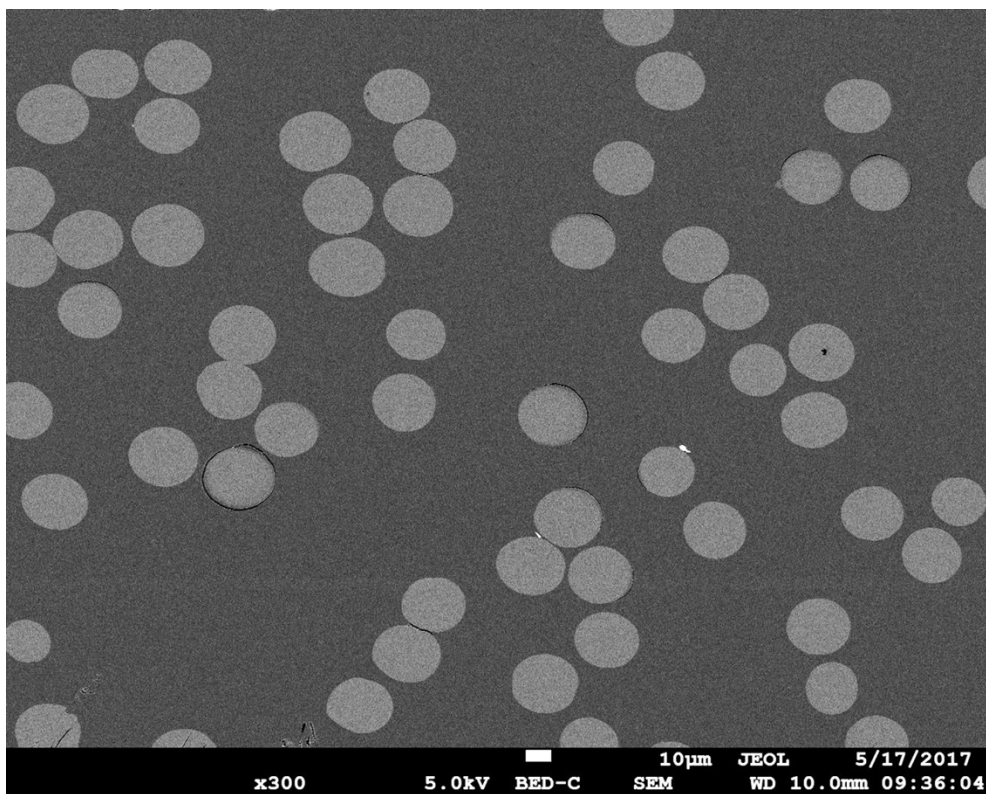


Figure 22. SEM-image of cross sections of SKL:dissolving pulp filaments, 70:30.

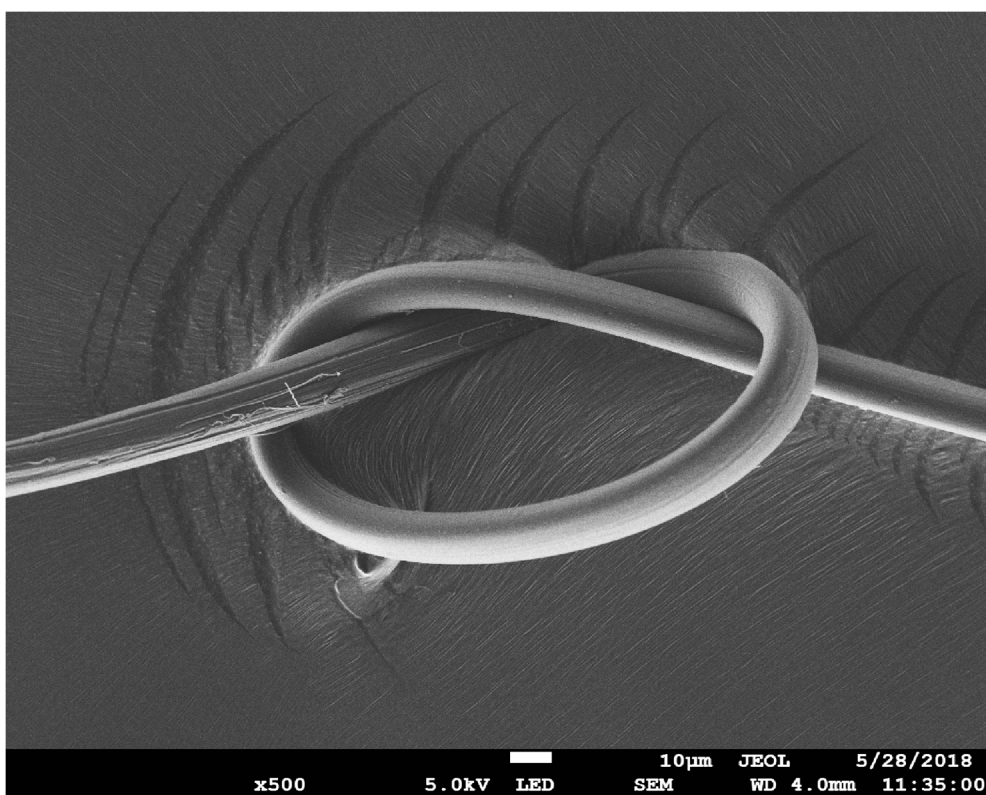


Figure 23. SEM-image of flexible precursor filament with SKL:paper grade pulp, 70:30.

Table 4. Precursor filaments spun with different types of lignin and pulp: one type of carbon fiber is also included.

Filament type	Diameter / μm	\pm	Tenacity / MPa	\pm	Tensile Modulus / GPa	\pm
Dissolving pulp	21.3	1.0	382	31	15.2	0.8
Paper grade pulp	26.9	2.1	452	28	14.6	1.4
SKL:Dissolving pulp	24.8	1.2	198	14	8.2	0.5
SKL: Paper grade pulp	22.1	1.5	183	61	8.9	0.5
Carbon fiber from SKL:Paper grade pulp	14.0	1.6	680	170	66	10
RL15: Dissolving pulp	24.0	1.3	189	33	7.7	0.8
RL15: Paper grade pulp	23.8	1.4	182	31	8.3	0.4
RL5: Dissolving pulp	24.4	0.9	191	22	7.5	0.4
RL5: Paper grade pulp	25.1	0.9	154	35	7.9	0.4

Draw ratio is one of the spinning parameters that has the most pronounced effect on the strength and, particularly, the stiffness of cellulose fibers.⁶⁷ To evaluate if draw ratio can be used to also enhance the mechanical properties of lignin-cellulose fibers, the draw ratio was varied over a broad interval for a 50% lignin, 50% dissolving pulp filament. The results are presented in Figure 24 and show that the mechanical properties of lignin-cellulose filaments can be improved with an increase in draw ratio.

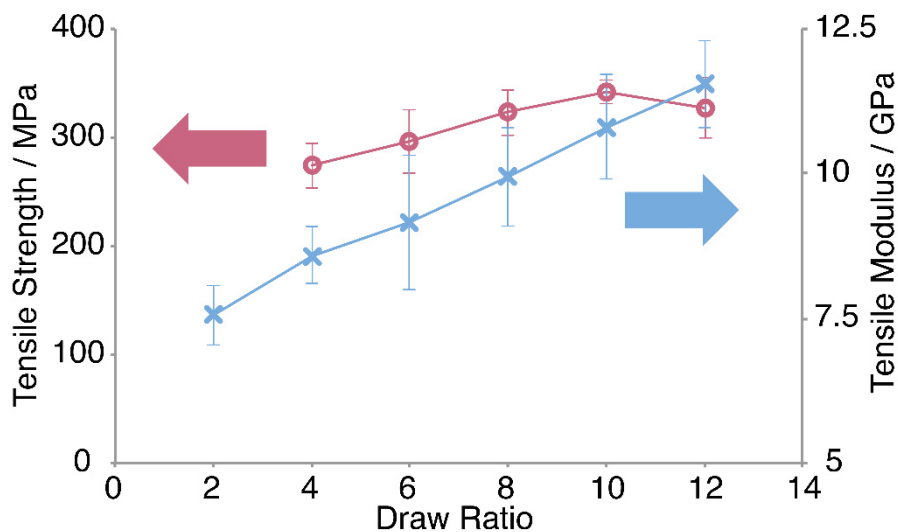


Figure 24. Tensile strength and modulus versus draw ratio for lignin-cellulose filaments consisting of 50% SKL and 50% dissolving pulp, spun from a 16 wt% solution.

Mechanical properties of converted filaments (carbon fibers)

Lignin-cellulose filaments were also spun with smaller capillaries of the die, 80 μm compared to 120 μm , and the draw ratio was increased to 7; the results are presented in Table 5. This change in process parameters rendered thinner precursor filaments with a diameter of about half, but with the same range in strength and modulus, of the lignin-cellulose filaments in Table 4. In contrast, the carbon fibers made from the thin filaments were stronger than the carbon fibers made from the lignin-cellulose filaments in Table 4. It is known that the strength of carbon fibers is highly dependent on diameter,⁷ which was also found in this case.

Table 5. Mechanical properties of precursor filaments, SKL:Paper grade pulp (70:30) and carbon fibers made thereof.¹¹²

Sample	Diameter / μm	\pm	Tenacity / MPa	\pm	Tensile Modulus / GPa	\pm
Precursor	13.9	0.8	200.2	35.9	7.3	0.6
Carbon fiber ¹¹²	7.6	0.7	1070	200	76	8.9

Commercial carbon fibers are available with a wide range of mechanical properties as the strength and stiffness of the final carbon fiber depends on production parameters, for example, the amount of stretching and temperature during coagulation. The choice of precursor will also highly influence mechanical properties. An overview of the mechanical properties of carbon fibers divided into type of precursor is available in Figure 25; the graph includes both commercial fibers, published research results, and the results from the present thesis. With PAN and pitch, it is possible to produce fibers with excellent mechanical properties, which are not included in the graph. This type of high performance carbon fiber can have a tensile strength up to 5-7 GPa and a modulus of from 200 to even 500 GPa.¹⁰³ No bio-based precursor has yet reached up to such values, but bio-based carbon fibers can be compared to the general-purpose-grade carbon fibers¹⁰⁴ shown in Figure 25. The research results of Jin et al.¹⁰⁵ and Spörl et al.,¹⁰⁶ in particular, show that lignin- and cellulose-based carbon fibers have great potential.

Bio-based carbon fibers may be used instead of glass fibers, especially if they are less expensive than the current commercial carbon fibers. Glass fibers have quite a high tensile strength, but a low modulus compared to commercial

carbon fibers, as seen in Figure 25. However, glass fibers have a density of approximately 2.5-2.6 g/cm³ and are, thereby, heavier than carbon fibers, which have a density of about 1.75-2 g/cm³.¹⁰⁷ Consequently, the specific tensile strength of carbon fibers is generally in the same range of or higher than the specific strength of glass fibers. As for stiffness, the specific modulus of carbon fibers is substantially higher than the specific modulus of glass fibers.

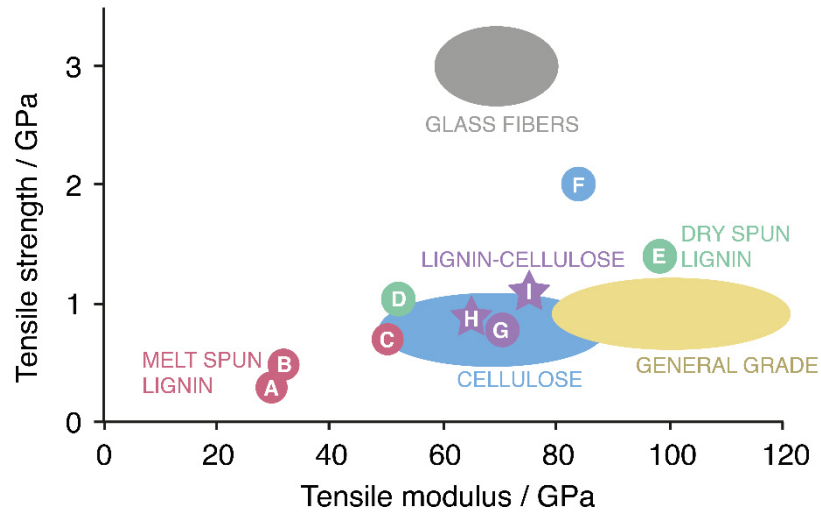


Figure 25. Compilation of carbon fibers divided into type of precursor; glass fibers are included for comparison. Mechanical properties of commercial fibers are represented by ellipsoids and research results with circles: **A.** Nordström et al.¹⁰⁸ **B.** Salmén et al.¹⁰⁹ **C.** Kleinhans et al.¹¹⁰ **D.** Zhang et al.¹¹¹ **E.** Jin et al.¹⁰⁵ **F.** Spörl et al.¹⁰⁶ **G.** Olsson et al.¹⁶ **H.** Results obtained in this thesis. **I.** Bengtsson et al.¹¹²

6 Conclusions

Studies on dissolution, spinning, and characterization were combined in the present work to assess and deepen the understanding of dry-jet wet spinning of lignin-cellulose filaments. The aim was to evaluate the suitability of these filaments as carbon fiber precursors.

Considering the simultaneous dissolution of lignin and cellulose in EMIMAc, lignin did not affect the viscosity of solution as dramatically as cellulose, since lignin has a lower molecular weight than cellulose. In this particular solvent system, solutions that contained lignin could also be spun at higher draw ratios than pure cellulose solutions.

During air-gap spinning, two main types of breach mechanisms were found to limit draw ratio, and the dominant type of mechanism changed with temperature. At lower temperatures, after excluding die swell, the critical draw ratio was suggested to be limited by the breaking stress of the filament. As the temperature of the spinning solution increased, draw resonance became visible in the video recordings of the breakage. Thus, draw resonance was proposed to be the dominant mechanism at higher temperatures. Consequently, an optimal spinning temperature exists for each solvent composition and for specific spinning parameters, such as choice of die and extrusion velocity.

Lignin leaches out into the coagulation bath during the coagulation of a lignin-cellulose solution. The amount of leached lignin was found to depend on lignin solubility in the coagulation bath and lignin concentration in the spinning solution. Leaching of lignin was suggested to be limited by the solubility of lignin within the pores formed by the coagulated cellulose.

The mechanical properties of the precursor fibers were not significantly affected by the choice of pulp or lignin, fractionated or not. However, it was possible to increase the strength and modulus of the precursor fibers by applying a higher draw ratio.

These findings suggest that a dissolving pulp, or even a paper-grade pulp, and unfractionated lignin are suitable to use as the raw material for bio-based carbon fibers. To increase the strength of the final carbon fiber, the draw ratio during spinning should be maximized to achieve as fine and stiff fibers as possible.

7 Future work

The challenges during the spinning of lignin-cellulose fibers need to be addressed before the process is upscaled. These issues include choice of solvent, yield during coagulation, and the strength of the precursor fiber.

Ionic liquids are safe and powerful solvents for cellulose and lignin. However, no efficient recycling method exists for this type of solvents. Recycling of the solvent would be necessary to achieve an economically viable process. As alternative routes, or before methods of recycling are implemented, other solvents for lignin and cellulose should also be investigated.

The leaching of lignin during coagulation was found to be highly dependent on lignin solubility in the same coagulation bath. To improve the lignin yield during coagulation further, the lignin solubility of the coagulation bath might be reduced by chemical modification or the fractionation of the lignin, or by the use of other coagulation baths.

The strength of the lignin-cellulose-based carbon fibers is currently not high enough to replace commercial carbon fibers. All carbon fibers produced in the present investigation were produced without dynamic stretching during stabilization and carbonization. Applying dynamic stretch may substantially enhance the mechanical properties of carbon fibers. The structure of lignin and cellulose within the precursor filaments should be investigated to understand the link between process parameters and the strength of both precursor filaments and carbon fibers.

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