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Properties affecting the rheology of alkaline cellulose solutions

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Tiivistelmä

Selluloosa on maailman yleisimmin esiintyvä biopolymeeri ja sen rakennetta voidaan hyödyntää useissa eri käyttökohteissa, kuten paperi- ja kartonkiteollisuudessa, tekstiiliteollisuudessa sekä sen derivaattoina, kuten selluloosa asetaattina, -eettereinä tai -estereinä, esimerkiksi lääketeollisuudessa ja pakkausmateriaaliteollisuudessa. Selluloosan hyödyntäminen korkean vaatimustason kohteissa kuitenkin vaatii kuidun liuottamisen, jotta rakennetta voidaan uudelleen regeneroida. Selluloosan liuotus on haasteellista, koska sen rakenne koostuu vuorottelevista kiteytyneistä ja kiteytymättömistä vyöhykkeistä, rakenteessa on vahvoja vetysidoksia polymeeriarkkien sisällä ja lisäksi, polymeeri sisältää sekä hydrofiilisiä että -fobisia päitä. Tästä syystä selluloosa vaatii joko rakenteen muokkaamista derivoinnin avulla tai muuten kuitujen avaamista ja reaktiivisuuden lisäämistä esimerkiksi entsymaattisesti.

Työn tarkoituksena oli verrata eri aktivointimenetelmiä ja raaka-aineita, ja kuinka nämä vaikuttavat liuoksen reologiaan ja stabiiliuteen, joka on merkittävä tekijä liuosta prosessoitaessa esimerkiksi kuiduiksi tai filmeiksi.

Kirjallisuusosuus käsittelee selluloosan rakennetta, eri aktivointimekanismeja ja liuotusta, sekä siihen vaikuttavia tekijöitä. Lisäksi teoriassa on lyhyesti käyty läpi regeneroitavuuteen ja reologiaan vaikuttavia tekijöitä. Kokeellinen osuus työssä sisälsi eri tavoilla esikäsiteltyjen selluloosamassojen liuotukset, jonka jälkeen tutkittiin näiden käsittelyjen vaikutusta liukoisuuteen ja liuoksen stabiiliuteen.

Referenssimateriaalina toiminut viskoosi oli selkeästi parhaiten liuennut liuos ja käyttäytyi odotetusti, geeliytyen noin viiden päivän kuluttua. Tärkeimpiä tuloksia työssä oli entsymaattisen esikäsittelyn positiivinen vaikutus liuoksen pysyvyyteen, liuoksen pysyessä stabiilina viskoosia pidemmän ajan. Lisäksi voitiin todeta, ettei yhteneväisiä olosuhteita voi käyttää eri raaka-aineille vaan prosessi tulee optimoida jokaisen selluloosamassalle kullekin erikseen.

Avainsanat selluloosa, aktivointi, liuotus, natriumhydroksidi, liukoisuus, stabiliteetti, viskositeetti, reologia

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Abstract of master's thesis

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Abstract

Cellulose is the most abundant biopolymer on earth and it is a versatile building block for multiple purposes, for example in paper, board and textile industries, and as its derivative form, such as cellulose acetate, ethers or esters, it can be exploited for example in pharmaceuticals and packaging. However, utilization of cellulose in high performance purposes requires its dissolution, in order to enable the regeneration of the structure. Cellulose dissolution is challenging due to the semi-crystalline structure, tight hydrogen bonds within the polymer sheets and the structure with both hydrophilic and hydrophobic heads. For this reason, cellulose structure first needs to be altered through derivatization or otherwise increasing its accessibility, for example by means of enzyme treatment prior to dissolution.

The aim of the study was to compare different activation mechanisms and raw materials, and examine how these factors affect the solution rheology and stability. The latter is a significant factor affecting processability of the solution in regeneration of the solution into a form of fibres or films.

Literature part covers chapters of cellulose structure, different activation mechanisms and dissolution, as well as factors affecting it. Additionally, theory shortly discusses of the features affecting regeneration and rheology of solution. Experimental part consists of dissolving cellulose pulps with different pretreatments, after which, solutions are examined in means of solubility and stability.

As a reference material, viscose performed as expected, exhibiting the highest level of dissolution, and gelled after around five days. Most importantly, enzyme-treated cellulose exhibited positive effect on solution stability, remaining processable longer that viscose. It was also concluded that consisted process conditions cannot be applied for different raw materials without optimizing the process for each raw material individually.

Keywords cellulose, activation, dissolution, sodium hydroxide, solubility, stability, viscosity, rheology

Preface

This thesis was carried out in VTT Technical Research Centre of Finland Ltd and it was funded by the Governmental Grant for Cellgrowth project. During the process, my interest towards bio-based high performance products increased potentially and I am excited about what the future has in hold, in relation to this topic.

I am highly grateful that I had an opportunity to do my thesis in such an educated environment amongst all the professionals in VTT. Their help and shared knowledge has been irreplaceable for this thesis process. I have gained valuable information in a field of research and development and I want to use this moment for expressing my deep gratitude for Professor Ali Harlin, who kept encouraging me during the process, was patient and always found the time to help despite his full calendar. In addition, Professor Herbert Sixta deserves a special honouring for supervising the project and especially, guiding towards this topic and encouraging to reach out to Ali Harlin for a thesis topic. I would also want to express my great appreciation for Marianna Vehviläinen and Marjo Määttänen for all their guidance and comments, and creating a positive atmosphere throughout the project, the thesis would not have be the same without their substantial contribution.

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Symbols and units

G	Gibbs energy [J]
G'	storage modulus [Pa or mPa]
G''	loss modulus [Pa or mPa]
H	enthalpy
K	constant in Mark-Houwink's equation, dependent on the solvent, polymer and temperature
N	number of pixels
S	entropy
T	temperature [K, °C]
$T\%$	light transmittance percentage
c	concentration [wt%]
α	constant in Mark-Houwink's equation, dependent on the solvent, polymer and temperature
γ	strain
η	viscosity [mPa·s]
$[\eta]$	intrinsic viscosity [mL g^{-1}]
Δ	change
$\Sigma_i \Sigma_j M$	sum of the matrix of pixels

Terminology

Alkaline solution	a solution with a pH higher than 7
Allomorph	crystalline mode of cellulose (I_α, I_β, II or III)
Amorphous	non-ordered region of cellulose
Amphiphilic	a molecule having both hydrophilic and hydrophobic heads
Anhydroglucose	the most simple repeating unit of cellulose chain
Biocelsol	technology that applies enzymatic treatment for increasing cellulose solubility into aqueous alkali
Covalent bond	a chemical bond that involves the sharing of electron pairs between atoms
Crystalline	ordered region of cellulose
De-crystallization	a breakdown of a solid, crystalline structure
Degree of polymerization	for cellulose, a number of anhydroglucose units
Degree of substitution	average number of substituent groups attached per base unit (e.g. carbamate groups in anhydroglucose unit)
Cellulose derivatization	increasing solubility of cellulose by adding functional groups to the structure (e.g. xanthation or carbamation)
Elasticity	ability of a matter to resume its normal shape after being stress
Enthalpy	total heat energy of a system
Entropy	quantity of system's unavailable thermal energy for conversion into mechanical work
Gelation	a solution phenomenon in which polymers start to aggregate into a form of network that is trapped within a liquid (usually as a function of temperature or time), and most often phenomenon is irreversible
HefCel	technology to prepare microcrystalline cellulose with high dry matter content
Hydrophilic	attracted to water molecules
Hydrophobic	repellent to water molecules
Hydroxyl group	a functional group with oxygen bonded to hydrogen
Intercellular	occurring between cells
Intracellular	occurring within a cell or cells
Intrinsic viscosity	measure of a solute's influence to the viscosity of a solution
Light transmittance	an effectiveness in transmitting radiant energy

Mercerisation	cellulose activation method through swelling with sodium hydroxide
Morphology	arrangement of microfibrils and interstitial spaces in relation to the cell wall
Open time	time gap for modifying properties of a solution in a process (related to solution stability)
Polar solvent	solvent with large dipole moments, contain bonds between atoms with very different electronegativities
Reactivity	accessibility of chemicals to the cellulose structure
Recalcitrant	an tenaciously uncooperative attitude towards solubility
Regeneration	reshaping crystallinity mode of cellulose structure from native I (parallel) to II (antiparallel)
Rheology	deformation and flow of matter
Supramolecular	crystal and molecular structure and hydrogen bonding -system of cellulose
Thermoplastic	material that becomes mouldable at elevated temperature and solidifies upon cooling
Thixotropic	time-dependent shear thinning property in which solution becomes fluid when agitated but exhibits solid-like behaviour in rest
Twin-screw extruder	device used for extensive mixing, compounding, or reacting polymeric materials
Viscose	a man-made cellulose based fibre
Viscosity	a measure of a resistance to deformation when force is applied (e.g. syrup has a relatively high viscosity)

Abbreviations

AGU	anhydroglucose unit
AlkOx	Alkali-oxygen treatment
ASTM	American Society for Testing and Materials
CCA	cellulose carbamate
CH_4N_2O	urea
CS_2	carbon disulphide
DP	degree of polymerization
DP_v	viscometric average degree of polymerization
DS	degree of substitution [mol substituent per mol AGU]
H-bond	hydrogen bond
H_2O_2	hydrogen peroxide
H_2SO_4	sulphuric acid
ISO	International Organization for Standardization
NaOH	sodium hydroxide
NH_4Cl	ammonium chloride
OH-bond	hydroxide bond
STD.DEV.	standard deviation
TCF	totally chlorine-free
ZnO	zinc oxide

1 Introduction

The objective of the study is to compare alkaline cellulose dissolution mechanisms and their effects on the solution rheology over time.

Soft cotton fibre around the cotton seed was discovered thousands of years ago and is the most used fibre material in modern textile industry. It is one of the cellulosic plant based materials that can be spun into a yarn without using any chemical regeneration, which makes it a desirable fibre material. (Olsson & Westman 2013; Woodings 2001.) However, cotton cultivation requires substantial amounts of irrigation and pesticides to grow profitably (Bevilacqua et al. 2014; Olsson & Westman 2013). Whilst cotton has a high water-demand, it is also extremely sensitive to both excess rains and humidity. Therefore, most of the cotton cultivation is performed in arid lands, where excess moisture is not an issue and irrigation can be provided in a controlled manner. (Clay 2004) Using the limited clean water resources of dry areas for textile yarn cultivation, instead of food cultivation, can be seen as a socially questionable practice, which also leads to further drying of the land. Additionally, high amounts of pesticides used in the cultivation can further leach to groundwater and fresh waters from the field or through wastewaters, posing a potential risk to the environment and human health (Clay 2004). Renouncing pesticides is not that straightforward either, as cultivation of organic cotton has even higher water consumption during growth seasons (Clay 2004).

Polyester, acrylic, polyethylene and other materials derived from fossil-based petroleum (Woodings 2001; Morgan 2006), have been promising fibre and film material options, because of their good thermoplastic properties and durability as well as good moisture and oxygen permeability (Lange & Wyser 2003). Nevertheless, the problem of these materials is their fossil-based origin, which raises serious environmental concerns. Also, the issue with release of micro-plastic particles during the use and washing of clothes (Hernandez et al. 2017) and from degradation of disposable plastic films (Klein et al. 2018) has been discussed lately.

In addition to cotton processing and petroleum-based polymers, a typical plant-based fibre and film processing technique has been viscose production, which mostly utilizes wood cellulose. Viscose process is these days questioned, due to the use of carbon disulphide in the process. Carbon disulphide is a hazardous chemical from both occupational and environmental aspects. (Liebert 2010; Abadin & Liccione 1996.) Hazards in the use of carbon disulphide could be mitigated with emission control, but most of the viscose plants are located in China (Chen et al. 2016), where the environmental regulation and resources are still limited.

Alternative cellulose dissolution processes, without the use of hazardous chemicals, have been developed to compete with viscose process. For example, the conversion of cellulose into alkali soluble cellulose derivative, cellulose carbamate (CCA), is one route for producing regenerated cellulose fibres like viscose, but without the use of hazardous chemicals. The structure of cellulose is altered into a form that is soluble in a mild alkali solution with the assistance of urea, which is considered as a non-toxic and inexpensive additive. (Woodings 2001; Liebert 2010.) Another highly promising process is Biocelsol technology, which utilizes enzymes and mechanical treatment for increasing active surface area, thus, making it soluble in mild alkali solution (Vehviläinen 2015).

The European Commission set a directive ((EU) 2018/851) obligating its Member States to organize a selective collection of textile waste by the year 2025 (Ministry of the Environment 2017). Due to this, recycling of textile materials for varying purposes has also been a research field of increasing interest. The versatility of different materials and their origins, ranging from natural fibres to petroleum-based and to regenerated fibres, was previously an issue in the textile recycling (Sandin & Peters 2018). At present, recirculation of raw materials has been made possible, for example, by a selective dissolution, in which the desired particles are dissolved into the solution whereas the rest can be filtered for disposal or other purposes (Sandin & Peters 2018). There is a high and constantly growing amount of recyclable textile material formed annually, but the recycling rate, collection and handling processes are not keeping up the pace. Simultaneous development of all value chain processes is required to make the ends meet. Nevertheless, even if recycling of textile materials was optimized to its full potential, it still might not eliminate the need of virgin raw materials for textile production. (Dahlbo et al. 2017.) Furthermore, recycling of fibres often leads to downcycling, which means, for example, converting textiles into downgraded products such as industrial rags, low-grade blankets or insulation materials (Schmidt et al. 2016). Therefore, virgin material is still needed to fill the gap in textile demand.

As the level of knowledge on hazardous substances and environmental consciousness has increased, there is a need to develop fibre and film processes, which are economically profitable, non-polluting, and easily processable. At this moment, viscose is the dominant cellulose fibre produced with wet-spinning process. The success is based on reasonably high solubility of applied cellulose xanthate and modifiers improving fibre's mechanical properties. This work compares alternative alkaline processes and different cellulose raw materials in respect of their ability to produce high quality solution to be applied in wet-spinning process. This is described in terms of rheological properties and related open time of the dope.

In order to optimize cellulose regeneration processes, more information on stability, as in means of rheology, is needed. This factor is an important knowhow that affects the processability of cellulose both in continuous and batch-based processes. Stability and processability of the dissolved dope determine, for example, how long time there is to remove or alter disturbance factors of the process in an industrial scale. Therefore, this study focuses on the ratio of viscosity and elasticity, and how that ratio changes as a function of time.

I Literature part

2 Cellulose - the most abundant biopolymer on earth

Cellulose is a biobased polymer, appearing in all plants, both in herbaceous and woody, as well as in small tunicates living in aquatic environment, and extracellularly in some bacteria (Sixta 2006, 23-24). Highest quantities of cellulose are found in secondary walls of higher woody plants, where it is tightly bonded with lignin, hemicelluloses and pectins (Sjöström 1993, 12). Various cellulose resources grow annually to the extent of 1500 milliard tons, which makes it, without a doubt, the most abundant biopolymer on earth. Cellulose is a raw material for various products in board, paper and textile industries. Its derivative forms, include cellulose acetate, ethers and esters, which are used, for example in fields of pharmaceuticals, construction, paints and packaging. Cellulose is a versatile building block, which makes it a desirable material for both bulky and high performance purposes. (Olsson & Westman 2013, 143.)

Cellulose has some special characteristics, including that it is amphiphilic (i.e. having both hydrophobic and hydrophilic heads), it has a chiral structure and broad chemical modifying capacity. Furthermore, it is capable of transforming between different crystalline morphologies, which exhibit varying properties (Ciolacu & Popa 2010, 5-28; Olsson & Westman 2013, 152). Properties of cellulose depend on the molecular weight distribution, length of the polymer chain, purity, as well as its supramolecular and morphological structure. Supramolecular structure is used as a term in the discussion of crystal and molecular structure and hydrogen bonding -system of cellulose, while morphology refers to the arrangement of microfibrils and interstitial spaces in relation to the cell wall. (Wertz et al. 2010, 87.)

2.1 Molecular structure

Cellulose is a polysaccharide, consisting of carbon, oxygen and hydrogen atoms, and its most simple repeating unit is anhydroglucose (AGU), which is more commonly known as D-glucose. The molecular structure of cellulose is presented in Figure 1. The AGU units are linked to each other with β-1,4-glucosidic bonds that rotate 180 degrees in respect to each other and this forms cellulose chains. (Sixta 2006, 24.) Lengthwise, 36 of these cellulose chains form bundles, which are held together by hydrogen (H) bonds, and these are called the elementary fibrils (Sjöström 1993, 12.) These fibrils have alternating regions of ordered (crystalline) and disordered (amorphous) structures (Ciolacu & Popa 2010.)

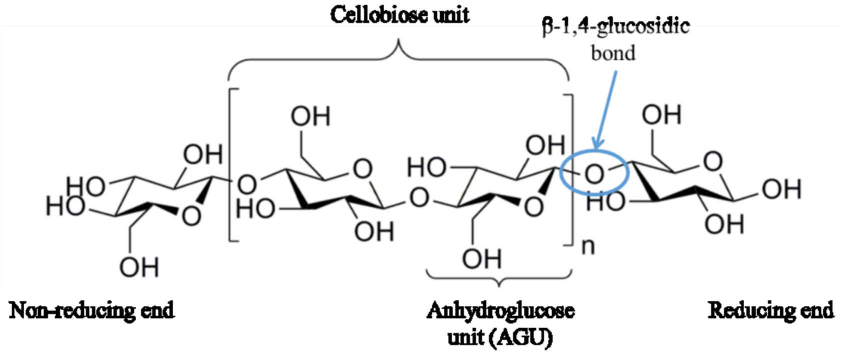

Figure 1. Molecular structure of celluloses repeating units with its reducing and non-reducing ends, based on Olsson & Westman 2013, 149.

Repeating AGU units of cellulose have three hydroxyl (OH) groups attached in them: secondary ones on C2 and C3 and the primary group on C6. These may be considered as the active sites of the molecule, since they are able to undergo all reactions typical for primary and secondary alcohols, provided that energy needed for the reaction is present. Furthermore, the longer the polymer chain is, the more recalcitrant it is for reaction. (Sixta 2006, 24.)

The rotational alternation of AGU unit arrangements, C6 set to up or down, impacts on the hydrogen (H) bonds, which further determine the crystallinity of the cellulose metastructure (Nishiyama et al. 2002). The strong intramolecular H-bonds provide cellulose with its natural stiffness and, thus arrange the linear polymers into tight sheet structures. The aforementioned sheets connect to each other by hydrophobic interactions (van der Waals bonds) into different allomorphs of cellulose polymer: native I_α or I_β, regenerated II, or III_I or III_{II}. (Olsson & Westman 2013, 149-150.) The structure model of cellulose polymer, as we know it now, in which molecules are attached to each other by covalent bonds, was discovered by Hermann Staudinger in 1920s and he received a Nobel prize for this work in 1953 (Olsson & Westman 2013, 145).

As said, allomorphs I_α and I_β are native and cellulose chains in these run parallel, and these two allomorphs always coexist in the fibre. Allomorph II instead runs antiparallel and is irreversibly a result of regeneration or alkaline treatment and thus, the most stable. This polymorph is the most desired in textile industry due to its silky texture. Forms III_I and III_{II}

can be received either from I_α/I_β or II and are resultants of liquid ammonia or diamine treatments. (Langan et al. 2001)

In one end of the cellulose polymer, the anomeric carbon is involved in a glucosidic bond. This end is more commonly known as a non-reducing end of a sugar polymer. In the other end, the anomeric carbon is free to convert into an aldehyde, and these two states are in equilibrium. This end is the reducing end of the sugar. (Olsson & Westman 2013, 149-150.) The reducing and non-reducing ends of cellulose chains results as a chemical polarity, which makes it especially difficult to dissolve. (Ciolacu & Popa 2010, 2-3)

2.2 Degree of polymerization

The lengths of cellulose polymer chains vary depending on the source and the treatment it has gone through. Molecular weight distribution and branching of cellulose is noticed to have a major influence on properties of the polymer, such as solubility. (Olsson & Westman 2013, 145-146.) For this reason, degree of polymerization is an important factor when planning, for example, dissolution experiments. Number of repeating AGU units in a consistent cellulose polymer chain, determines the degree of polymerization (DP) (Olsson & Westman 2013, 150).

Elmer O. Kraemer (1938) studied the intrinsic viscosity of celluloses, originating from different sources, and cellulose derivatives in relation to their molecular weights. He discovered that there lies a simple relation between the two when suitable solvents are used. He also observed that there is high variation in molecular weights of different cellulosic materials and that the heterogeneity is not discontinuous character as was believed by some researchers. Kraemer (1938) found that DP of purified cotton linters (the pure cellulose around the cotton seed) varies usually from 1000 to 3000, whereas the native wood cellulose molecule is at least 10 000 glucose units (Sjöström 1993, 12). Kraemer (1938) also noticed that chemical modification of wood, for example by pulping, lowers the degree to 600-1000 and DP of commercial regenerated celluloses, such as viscose fibres, is usually as low as 200-600.

Mark-Houwink equation (1) can be used to determine the DP as it gives a relation between intrinsic viscosity value and DP (IUPAC 1997). The viscometric average degree of polymerization (DP_v) can be calculated according to following:

$$[\eta] = K \cdot DP^{\alpha} \quad (1)$$

where		
	$[\eta]$	intrinsic viscosity [mL g^{-1}]
	K	1.33, constant (depends on the solvent, polymer and temperature)
	DP	molecular weight
	α	0.905, constant (depends on the solvent, polymer and temperature)

3 Cellulose pulping

Cellulose pulping is separation of lignocellulosic material into two or three separate streams of cellulose, lignin and hemicellulose. Pulping is carried out to result fibrous cellulose mass, called pulp. Lignocellulosic material can be processed into pulp by chemical or mechanical treatment, or by a combination of the two. Mechanical pulping can be for example temperature or pressure accelerated. Traditional chemical pulping is degradation of lignin into cooking liquor with assistance of elevated temperature which simultaneously causes some cellulose and hemicellulose degradation as well. Bleaching is usually carried out to remove any residual lignin. (Sixta 2006, 109-110.)

3.1 Dissolving pulp

The production of dissolving pulp differs from regular pulping by an additional pre-treatment step, such as acidic pre-hydrolysis or cold caustic extraction. The aim in pretreatment is to separate hemicellulose from fibres in the early stage, thus reducing the amount of hemicellulose as low as possible in resulting pulp. Dissolving grade pulp has a high alpha-cellulose content, high accessibility, relatively narrow molecular weight distribution, low degree of microfibril aggregation and high porosity. These qualities makes it one desirable option of wood-based cellulose grades for transforming the cellulose for multiple products, such as viscose and cellulose esters and ethers. (Sixta 2006, 1022; Chen et al. 2016.)

3.2 Alkali-oxygen treatment (AlkOx)

A two-stage alkali-oxygen assisted liquid hot water pretreatment, AlkOx in short, is a biomass fractionation technology that is used to convert cellulosic raw materials, such as birch chips, into separate streams of cellulose, lignin and hemicellulose by a selective removal and oxidative modification. The two-stage process is initiated with hot-water extraction, which is followed by grinding and alkaline cooking in presence of sodium carbonate. After pulping, mass is screened in order to remove unfractionated particles and bleached to remove any residual lignin. Bleaching consists of cold alkaline extraction, ozone bleaching, hydrogen peroxide bleaching, and lastly, acid washing. (VTT 2014; Siika-aho et al. 2015; Servaes et al. 2017.) Unlike common pulping processes, such as kraft pulping, AlkOx is not initiated with existence of sulphuric compounds. Instead, AlkOx operates by solubilising majority of lignin in water-soluble fraction, while the insoluble fraction is left with majority of water-insolubles, such as cellulose and hemicellulose. Additionally, AlkOx method is suitable to be applied for various cellulose sources, such as birch and spruce (Kallioinen et al. 2013).

3.3 Organosolv cooking

Organosolv cooking is another efficient way to fractionate cellulose, lignin and hemicellulose into each separate stream, and it is more environmentally benign option for traditional pulping methods. Organosolv cooking applies mixing lignocellulosic biomass, water and several different organic solvents, such as formic acid, and cooking the mixture. As a consequence, lignin and hemicelluloses are deconstructed and dissolved in cooking liquor. Separation of lignin can be carried out by precipitating it with water. Method usually results three high purity streams of cellulose pulp, lignin as a solid precipitate and hemicellulose rich liquid. (Sundquist & Poppius-Levlin 1989; Nitsos et al. 2017)

4 Modification of cellulose structure

Cellulose has some desirable characteristics, such as the durable and relatively strong structure, but this has a negative effect on plasticity. The issue with cellulose modification is that it does not melt but decomposes at elevated temperatures. Therefore, in order to modify the shape of cellulose, it should first be transformed from solid state to liquid, by either dissolution or other chemical modification. Different methods are provided, but they all have a shared interest to add functionality to the reactive OH-sites and preferably, with a controlled degree of substitution. (Olsson & Westman 2013, 144.)

4.1 Activation of cellulose

Cellulose does not dissolve in water and is extremely recalcitrant to dissolve in any traditional polar solvents, due to the semi-crystalline structure, tight H-bonds within the polymer sheets and the structure with both hydrophilic and hydrophobic heads. In order to make the dissolution possible for further processing, cellulose structure needs to be altered through derivatization or activation. (Lindman et al. 2010; Ciolacu & Popa 2010; Wei et al. 2008.)

Cellulose fibres have regions alternating in ordered crystalline and disordered amorphous domains. This type of two-phased alternating structure dominates the physical and chemical properties of cellulose molecules and especially the accessibility and reactivity are affected by this. Most solvents enter only the amorphous regions and set on the surface of crystalline regions, thus leaving the crystalline domains undisrupted. Therefore, accessibility of cellulose must be increased by either swelling or de-crystallization of the fibre by mechanical, chemical or enzymatic modification. (Ciolacu & Popa 2010; Fink et al. 1995.)

Swelling or de-crystallization enlarges the pores, which disrupts the tight interfibrillar H-bonds within the cellulosic material by breaking them and thus, appears as an increase in reactivity of the surface. The higher reactivity further facilitates, as the number of solvent accessible OH-sites increases. The more accessible OH-sites there are in the cellulose polymer chain, the more soluble it is towards the solvent in question. (Ciolacu & Popa 2010; Fink et al. 1995.) Nevertheless, solvent does not enter these free OH-sites if it is not chemically compatible with cellulose or cellulose derivative polymer, meaning that there has to be a good coordination between cellulose polymer and solvent polymer (Olsson & Westman 2013, 148).

Mercerisation of cellulose with NaOH is one way to swell the fibre and it is used to activate the OH-groups of cellulose for further modification or dissolution. The method was discovered by John Mercer and patented in 1850. The principal in mercerisation is to expose fibres to strong alkali conditions, which makes the alkali of the solution act on the cell wall morphology, loosening the strong hydrogen bonds between cellulose chains, and change crystalline structure of cellulose from native I to allomorph II. The alkali solution penetrates first to amorphous regions of the fibre and forces the fibre to swell. After amorphous regions are disrupted, they tend to be mobile and disperse. After interfering with amorphous regions, crystalline regions of cellulose structure are disrupted. (Zhang et al. 2012; Friebel et al. 2019.)

4.1.1 Xanthation

Mercerisation is an essential step of viscose process as an activation method prior to xanthation. Mercerisation decreases the crystallinity making cellulose more accessible for latter derivatization. (Friebel et al. 2019.)

Prior to dissolution, cellulose is converted to cellulose xanthate by substituting H-atom in one or more reactive OH-group, principally in C2 and C3 as these are thermokinetically more favourable, with xanthate group (Figure 2). Derivatization is proceeded by using carbon disulphide (CS_2) in aqueous NaOH. (Liebert 2010)

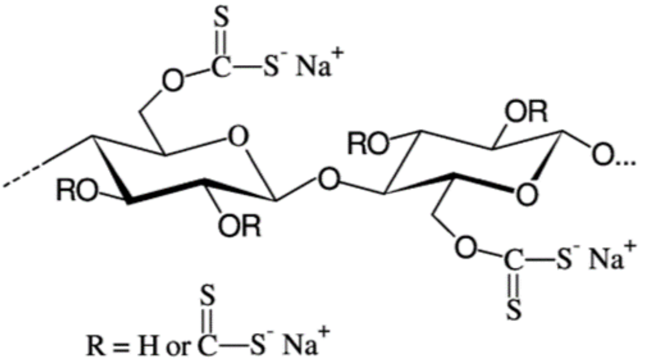

Figure 2. Cellulose xanthate, the derivative formed during the viscose process, from Liebert (2010).

Latter step is to dissolve the cellulose derivative, cellulose xanthate, in aqueous NaOH producing a viscous liquid, called viscose (Woodings 2001, 47-48). Viscose dope is used to prepare films and fibre filaments by precipitating it in sulphuric acid bath, which alters the structure back to pure, regenerated cellulose fibres with crystalline form of cellulose II (Liebert 2010).

Major disadvantage of viscose process is the use of CS_2, which is a hazardous neurotoxin causing danger of explosion and high security risks (Abadin & Liccione 1996), in the activation of the cellulose. Also, by-products are formed during the process, which require that air and water streams must be sufficiently purified to meet today’s regulations. (Liebert 2010; Olsson & Westman 2013, 144-145.)

4.1.2 Carbamation

Cellulose carbamation is a commercial alternative for xanthation in viscose production and it does not require using any hazardous chemicals, such as CS_2.

Cellulose carbamation process relies on utilization of urea as an additive to prepare cellulose carbamate derivative, which is soluble in aqueous alkali (Liebert 2010). Cellulose carbamate (CCA) was a result of a long development project, aiming to find a solution for the problem of hazardous chemicals used in traditional viscose process. CCA is a multifunctional cellulose derivate, which can be processed into a form of textile fibres, films, membranes as well as foams, by avoiding the utilization of harmful chemicals, such as carbon disulphide. (Woodings 2001; Liebert 2010.) Some of the advantages in CCA are that it is economically viable for the use of urea in derivative step and the processing of CCA can be also applied to an already existing viscose production equipment (Olsson & Westman 2013, 144-145). Besides the absence of hazardous chemicals in the production, CCA has a major benefit also in the storability in its derivative stage. CCA is dry, rather stable material and can be stored for a relatively long time, unlike cellulose xanthate, and this is a feature that makes it superior when compared to cellulose xanthate. Thus, CCA can be transferred to another deposit prior its dissolution step, and for this reason, the operation is not needed to be continuous. (Woodings 2001; Liebert 2010.)

Production of dissolved cellulose through CCA derivative relies on adding carbamate groups into celluloses reactive OH-sites by treating cellulose with urea (CH_4N_2O). This step is called carbamation and it is applied to increase celluloses solubility prior to the dissolution in alkali solution. Conversion of molecular structure of cellulose to cellulose carbamate (CCA) is presented in Figure 3. (Woodings 2001, 19; Olsson & Westman 2013, 144-145.)

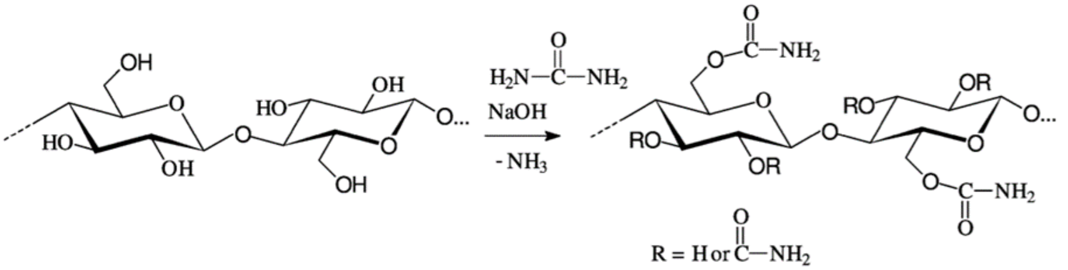

Figure 3. Treating cellulose structure with urea (CH4N2O) in aqueous NaOH results cellulose carbamate (CCA), in which one or more H-atom is replaced with a carbamate group (CH2NO2), from Liebert (2010).

Dissolved cellulose carbamate can be spun into fibres either with assistance of sulphuric acid, aqueous sodium carbonate, or alcoholic solution, and it results pure cellulosic fibres similar to viscose (Liebert 2010; Olsson & Westman 2013, 144-145). Modification and further regeneration of cellulose through CCA derivative is noted to have lower environmental impact as well as lower energy consumption, than through cellulose xanthate in viscose process (Paunonen et al. 2019).

4.1.3 Biocelsol technology

Biocelsol technology is another non-hazardous cellulose activation alternative but it is not yet commercial. Biocelsol technology is a process in which cellulosic raw material (e.g. dissolving grade pulp) is modified by cellulase enzymes and there after dissolved in water-based solvent. The solution can be regenerated into fibres by wet-spinning technique. (Vehviläinen 2015.)

In Biocelsol process, moist dissolving pulp is treated with enzymes and grinded mechanically in a twin-screw extruder (Grönqvist et al. 2015). The mechanical grinding improves the accessibility for enzymes by increasing the porosity of cellulose fibres. The treatment results in a controlled decrease in cellulose DP and increased porosity, which benefit the following dissolution (Grönqvist et al. 2014; Grönqvist et al. 2015).

4.1.4 HefCel technology

HefCel treatment is a cost-efficient technology to produce cellulose nanofibrils at high consistency (30-40%) and resulting fibrillated material that is not gel-like. The technology is based on enzymatic treatment of cellulose with an optimized composition of different cellulases enzymes and with the tailored enzyme mixture, extensive hydrolysis is not needed to break down the cellulose into nanofibrils. This is the main benefit of HefCel treatment, thus resulting nanoparticle sized cellulosic material with high dry matter content. (Kangas & Pere 2016) The main difference between two enzymatic treatments of Biocelsol and HefCel is that in Biocelsol the enzyme used increases the cellulose activity by opening the pores of the fibre, thus enhancing the solubility, whereas in HefCel treatment the enzymes target to break down the ordered crystalline and non-ordered amorphous regions into microcrystalline cellulose. Small size of the particles provides a wider area for the solvent polymers to react with the molecule of cellulose, greater surface area means increase in reactivity.

4.2 Dissolution and solubility

Dissolution of cellulose is a prerequisite for cellulose regeneration. In dissolution, the solvent disrupts the intra- and intermolecular connections of AGU. This phenomenon results as a deconstruction of amorphous and crystalline region network. Dissolution forces the individual cellulose chains to separate, which has a gel-like medium. (Ghasemi et al. 2018.) With the current level of understanding, it is not fully understood why certain solvents are able to dissolve cellulose and others not (Olsson & Westman 2013, 144), but some reports suggest that the hierarchical fibre morphology is one key factor determining the solubility of cellulose in a certain solvent (Le Moigne & Navard 2010).

Cellulose dissolution mechanism is initiated as the solvent polymer penetrates outer layer of the cellulose polymer, which causes cellulose fibre to swell. Fibre swelling can be observed, for example by a ballooning phenomenon in microscopic images. (Medronho et al. 2015.) Swelling increases the reactive surface area of the fibre, allowing solvent to penetrate the amorphous regions of the fibre. As amorphous regions are disrupted, they tend to be mobile and disperse. After interfering with amorphous regions, crystalline regions of cellulose structure are disrupted. (Zhang et al. 2012; Friebel et al. 2019.) Structure disruption disintegrates the fibre into individual cellulose chains, which can be distinguished as a gel-like medium (i.e. dissolved cellulose). (Medronho et al. 2015; Ghasemi et al. 2018.) Solubility of cellulose is affected by length of cellulose polymer chain, molecular weight distribution (interchain forces), crystallinity and number of polar groups of cellulose (Olsson & Westman 2013, 147).

Gibbs equation of free energy, with entropy (the quantity of system's unavailable thermal energy for conversion into mechanical work) and enthalpy (total heat energy of a system) terms, is often used when discussing of the dissolution of cellulose (Gibbs 1873, 400):

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

where	ΔG	Gibbs energy
	ΔH	change in enthalpy
	T	temperature
	ΔS	change in entropy

Gibbs free energy (G) must be negative for dissolution to occur. If enthalpy (H) is positive, polymer and solution are at their lower energy state, whereas with negative enthalpy, polymer solution is at its lower energy state. (Gibbs 1873, 400.)

Dissolution requires a good coordination of polymers between cellulose and solvent. This means that polymers of the solvent will interact with polymers of cellulose only if the interaction between these items is more favourable than the interaction between cellulose molecules, and this further results as swelling and later as detanglement of cellulose polymer. However, solubility can be enhanced to some extent by heat control or agitation. Agitation shortens the diffusion path for all molecules in polymer chain entering the bulk solution, thus, all molecules have an access to the solution, not only the ones on the surface of polymer. (Olsson & Westman 2013, 148.)

4.2.1 Derivatizing and non-derivatizing solvents

With the current level of understanding, it is not fully known why some solvents are able to dissolve cellulose, whereas some typical ones are not. Nevertheless, some ideas on how to group dissolving solvents have arisen. (Liebert 2010)

In 1846, Christian Friedrich Schoenbein first introduced the formation of cellulose nitrate and that was noticed to be an organo-soluble cellulose derivate. This finding lead to further studies of chemical modification prior to cellulose dissolution, and is nowadays more commonly known as derivatization of cellulose before dissolution. In 1857, Eduard Schweizer discovered that cuprammonium hydroxide solution can dissolve cellulose. This can be categorized as an aqueous system dissolution. In 1934, Charles Graenacher revealed that cellulose is also possible to be dissolved additionally with low melting salts, later on known as ionic liquids. (Liebert 2010.)

Derivatization of cellulose means simply chemical modification of cellulose before its dissolution (Olsson & Westman 2013, 153). Ionic liquids, also known as direct solvents, are non-derivatizing and this means that the dissolving polymer does not form covalent bonds with the cellulose polymer but instead, acts by physical means. In non-derivatizing solvents, the chemical composition of cellulose is not altered but the inter- and intramolecular H-bonds are deconstructed. In a favourable situation, this deconstruction results as H-bond formation between celluloses OH-groups and components of the solvent system. If dissolution occurs, solvent is able to disturb the self-assembling H-bonding of the AGU unit of cellulose. (Sen et al. 2013.)

4.3 Dissolution in alkaline solutions

Yamashiki et al. (1988) discovered that native cellulose I can be dissolved in mild (app. 7.5 wt%) aqueous NaOH if the intramolecular H-bonds are broken down prior to dissolution attempt. The amount of cellulose theoretically possible to dissolve in aqueous NaOH depends on molecular weight of cellulose, mode of crystallinity and especially cellulose concentration added into the solution. (Kamide et al. 1984.) Mercerisation is often used as an activation step in dissolution of cellulose into aqueous alkali to activate the OH-groups of cellulose for further modification or dissolution (Friebel et al. 2019.)

Various additives to enhance the reactivity of cellulose have been studied for decades. The research of using aqueous NaOH based solvents in dissolution is desired because these processes can be applied on already existing viscose production lines. (Vehviläinen 2015, 27.) Spinning trials of NaOH based solutions, without any additives, have been studied but none reported with sufficient fibre qualities (Yamashiki et al. 1990; Vehviläinen et al. 1996; Yamane et al. 1996). Urea as an additive has been studied for example by Cai et al. (2004), Cai et al. (2007), Chen et al. (2007) and Qi et al. (2008). Thiourea has been of high interest for research groups of Ruan et al. (2004) and Chen et al. (2006), as well as the combination of urea and thiourea by Zhang et al. (2009). Vehviläinen et al. (1996) researched the effect of zinc oxide in dissolution and Zhang et al. (2010) the effect of polyethylene glycol (PEG). These studied additives have all noticed to increase the solubility of cellulose and fibres obtained had improved properties when compared to dissolution in bare NaOH/water solution.

5 Regeneration of cellulose

Dissolution of cellulose and further the regeneration of the dissolved solution are both research fields of growing interests. Purpose of the regeneration of cellulose polymer is to stabilize cellulose solution in a desired physical form and yet redeem its original chemical composition (Olsson & Westman 2013, 167). Regeneration of cellulose is a prerequisite to produce films, membranes and fibres (Olsson & Westman 2013, 155). Cellulose has a uniquely strong structure that is beneficial to use as a building block for multiple purposes (Servaes 2017).

Regeneration of cellulose starts with additional pretreatment and derivatization steps and is followed by dissolution. Once cellulose is dissolved into a liquid state, it can be stretched to a desired shape and size, usually films or filaments. (Olsson & Westman 2013, 155.) For producing fibres of dissolved cellulose solutions, there are two typical procedures for the spinning of solution into long strands: wet and dry-jet wet spinning. Wet-spinning is applied when the solvent in the solution cannot be evaporated and requires it to be removed by chemical means. Some solutions do not properly coagulate when spinning is guided directly to coagulation bath, in that case, dry-jet wet spinning is applied, in which filaments are first provided with an air gap before entering the coagulation bath. (Lundahl et al. 2017.)

Requirements for spinnability are discussed in multiple papers (Vehviläinen et al. 2008; Vehviläinen 15, 27-29; Lundahl et al. 2017), but one of the highly known factors is the viscosity of the solution. Prior to the spinning, solution must be filtrated and deaerated in order to remove impurities and air bubbles, and these steps are highly hindered with excessive viscosity. Filtration is important because undissolved fragments and gel particles distract the spinning by clogging the spinneret orifices. Deaeration also is a prerequisite because if air gaps enter the spinneret orifices, it breaks the continuous filament and this causes coagulation of the dope prematurely and this further clogs the orifices as well. (Vehviläinen 2015, 28.)

DP of cellulose is crucial in spinning activity in order to estimate a proper cellulose concentration in dope, which further affects the solution viscosity and other properties (Vehviläinen 2015, 42). DP is also proved to affect the tenacity of prepared regenerated fibres and already a small addition of cellulose with high DP increases the viscosity substantially and hinders the solubility in a water-based solvent (Vehviläinen 2015, 27). DP of the cellulose is an important indicator to produce dope with sufficiently high cellulose content and low viscosity for processability and for achieving desired mechanical properties. Additionally to viscosity of the solution and DP of cellulose, also molecular weight distribution affects the solution properties and spinning behaviour as well as the obtained fibre properties. (Vehviläinen 2015, 28.)

6 Rheology

Rheology is a science that studies, whether a material deforms or flows when an external force is applied on it as a function of time. The deformation or flow of a material is determined by its internal properties, such as viscosity and elasticity. Less fluidic material with higher viscosity has a higher resistance to pouring, whereas highly liquid material with low viscosity acquires only a light force for it to flow. Whether the system, on which the force is applied, deforms, it has elastic behaviour properties. Whereas, when the system flows by an external force, it has viscous behaviour properties. (Van Vliet & Lyklema 2005)

6.1 Stability of alkaline cellulose solutions

Stability of cellulose solution is an important factor, because it determines the time to alter the processing conditions or to remove disturbing factors, such as solid content or bubbles, from the solution. It is preferable that solution is stable for some period of time so that all the essential actions can be carried out.

Gelation of a solution is a phenomenon in which polymers start to aggregate into a form of network that is trapped within a liquid, usually either as a function of temperature or time, and most often this phenomenon is irreversible. (Cai & Zhang 2006) Gelation is a phenomenon induced by factors, such as polymer concentration, molecular weight of the polymer, temperature or storage time, and it can be reversible or in some cases, irreversible (Luo & Zhang 2013). Gelation is observed by the changes in solution rheology and the ratio of viscosity and elasticity, and in its critical point, solutions viscosity is high and it starts to exhibit elastic behaviour (Gooch 2011, 339). Gels are divided in physical or chemical gels by the interactions of the polymer and formation method: physical gels have stable intermolecular regions formed through physical interactions, for example H-bonds, and chemical gels are covalently-linked polymer chains. (Williams & Phillips 2009, 16; Cai & Zhang 2006.)

Cellulose dissolved in NaOH-based solutions have a tendency to gel due to passing of time or when it is induced to too high or low temperature, different from its optimum (Vehviläinen 2015, 19). Nevertheless, stability of alkaline cellulose solutions can be enhanced with a use of additives (Kihlman et al. 2013) and also by optimum dissolution conditions.

II Experimental part

7 Structure and objectives of the experimental work

The scope of the experimental part of this thesis was outlined to study, whether defined pre-treatment and activation methods (derivatization/control of DP) of different raw materials affect the solubility and rheology of alkaline solutions prepared from the modified cellulosic raw materials. The time dependency of solution rheology based on cellulose type and activation method was examined by the viscosity change over time. The undissolved material content in each process and raw material combination was determined by means of microscopy and sample filtering. The study aimed to examine following research questions:

PART I

- *How does the defined activation (derivatization/control of DP) and dissolution conditions affect the solution viscosity and rheology over time?*

- *How does the defined activation (derivatization/control of DP) and dissolution conditions affect the amount of undissolved material?*

PART II

- *What is the time dependency of solution rheology based on cellulose source?*

- *How does the defined cellulose material source affect the amount of undissolved material?*

The focus in the rheology measurements was on dope’s viscoelastic behaviour and especially, determination of the moment of time when the solution starts to exhibit more elastic properties typical for gel-like structures and loose its viscous properties. This moment, the gelling point, is important because after that, the solution’s stability changes and it is less processable, for example, for filtering. The general rheological behaviours of the samples prepared in defined activation and dissolution procedures were studied by measuring viscosities as a function of strain with gradually increasing frequency at certain moments of time. When evaluating the processability of a solution, it is not sufficient to determine only the viscosity, because elastic deformation behaviour effects may occur and it highly influences the processability. Due to this, rheology measurements (ratio of G’ and G’’) were conducted along with ball-drop viscosity measurements.

The study was divided into two test parts: first one reviewing the effect of the activation procedure on the solution quality and stability, and the second studying the variance in solubilities of defined raw materials, as well as their effects on solution quality and stability. In the first part, different cellulose activation methods (xanthation, enzyme-aided extrusion, carbamation, peroxide-aided extrusion and HefCel treatment) were evaluated with a pre-defined reference material (commercial dissolving grade softwood total chlorine-free (TCF) sulphite pulp). Different activation steps were evaluated in respect to their ability to activate cellulose structure and capability to increase solubility as well as the changes in solution rheology over time.

The second part followed with uniform dissolutions of cotton, AlkOx cooked birch pulp, and organosolv cooked birch pulp. Cotton and AlkOx went through an enzyme-aided extrusion activation prior to dissolution, in which the aim was to adjust the conditions for each material to yield cellulose with an equal, comparable intrinsic viscosity value for a consistent comparison. Aim was to alter raw material and keep the preparation procedure conditioned. Dissolution of organosolv cooked birch pulp was completed without any activation, despite the former plan. The enzyme-aided extrusion of organosolv cooked birch was not done because the intrinsic viscosity was too low for that. The research plan was adjusted to examine the effect of low DP on dissolution hindrance for this material in question. Treatment route of examined samples is presented in Figure 4.

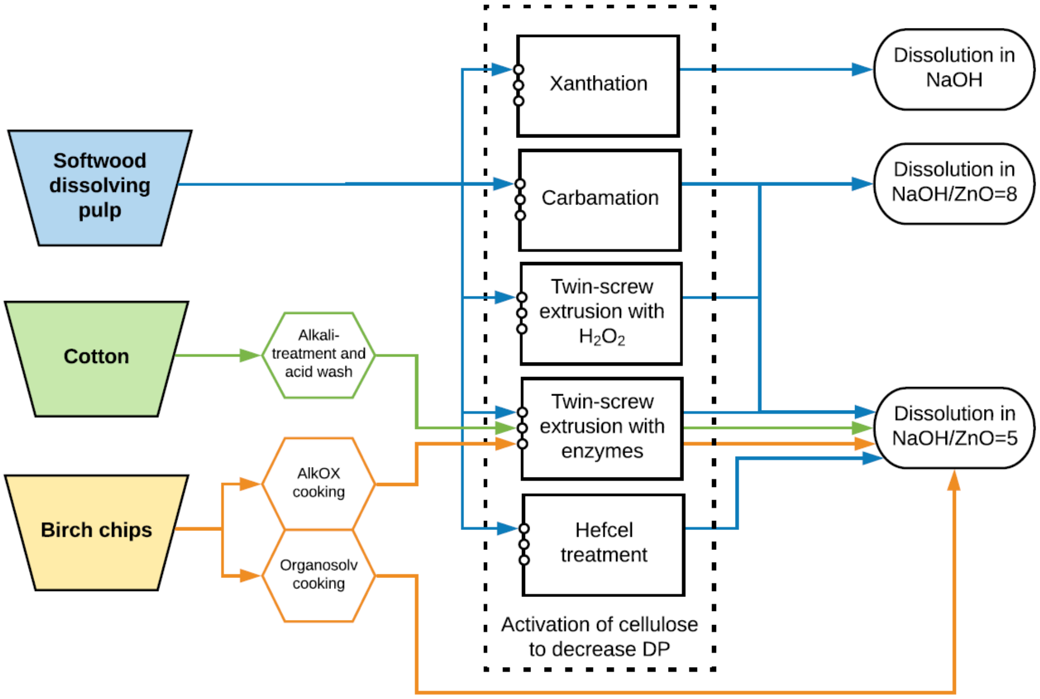

Figure 4. Process scheme of the examined cellulose solution samples.

8 Materials and methods

In the following sections, the examined raw materials, dissolution procedure, as well as characterization methods for determining the solution qualities and stabilities are presented.

8.1 Raw materials

The raw materials and their characteristics are presented in Table 1. The intrinsic viscosities of the starting materials varied from 430 to 540 mL g^{-1}. Test materials went through different additional chemi-mechanical treatments (such as alkali-acid treatment of cotton or varying cooking conditions), which are not discussed separately as they were considered as a part of properties of each specific material.

Table 1. Raw materials examined in this study, their initial intrinsic viscosity values as well as activation conditions and latter intrinsic viscosity values. Dissolution conditions can be seen in the last column.

Pulp	**SCAN-visco* before activation**	**Activation**	**SCAN-visco* after activation**	**Dissolution conditions**
Commercial **dissolving grade softwood sulphite pulp** (TCF). Delivered by Domsjö Fabriker AB	~ 540 mL g^{-1}	Xanthation (32 wt% CS_2 / abs. dry cellulose)	230 mL g^{-1}	Performed by Scitech-Service Oy (18°C/120min; 5.6wt% NaOH)
	~ 430 mL g^{-1}	Enzyme-extrusion (0.4 mg FiberCare R (protein 14.6 mg/mL) / g abs. dry cellulose)	250 mL g^{-1}	-5°C/15min; Two batches: 8wt% NaOH, 1.6wt% ZnO and 8.5wt%NaOH, 1.1wt% ZnO
		Carbamation (0.36% H_2O_2 / g abs. dry cellulose; 17.7% urea / total mass)	210 mL g^{-1}	
		Peroxide-extrusion (3 wt% H_2O_2 (conc. 127.49 g/L) / g abs. dry cellulose)	240 mL g^{-1}	
		Hefcel treatment (enzymatic)	240 mL g^{-1}	-5°C/15min; 8wt% NaOH, 1.6wt% ZnO
Short fibered, excess **cotton**. Alkali-treated and acid-washed to remove heavy metals and impurities	~ 430 mL g^{-1}	Enzyme-extrusion (0.6 mg FiberCare R (protein 14.6 mg/mL) / g abs. dry cellulose)	260 mL g^{-1}	-5°C/15min; 8wt% NaOH, 1.6wt% ZnO
AlkOx cooked birch dissolving pulp (bleached)	~ 410 mL g^{-1}	Enzyme-extrusion (0.5 mg FiberCare R (protein 14.6 mg/mL) / g abs. dry cellulose)	300 mL g^{-1}	-5°C/15min; 8wt% NaOH, 1.6wt% ZnO
Organosolv cooked birch dissolving pulp (bleached)	~ 190 mL g^{-1}	**	-	-5°C/15min; 8wt% NaOH, 1.6wt% ZnO

* intrinsic viscosity of the pulp according to ISO 5351_2010 test method.
** no activation due to low intrinsic viscosity.

Commercial dissolving grade softwood TCF sulphite pulp, delivered by Domsjö Fabriker AB, was used as a standard material due to its consistent quality and a highly studied background. Other defined raw materials were chosen based on availability, and outlined to three different materials: cotton, AlkOx cooked dissolving pulp (origin from birch wood chips) and organosolv cooked dissolving pulp (origin from birch wood chips). Cotton fibres were chemically purified prior to enzymatic treatment with hot alkaline extraction, that was used to remove impurities, such as silica, and acid washed for which the aim was to reduce the intrinsic viscosity value of fibres and also, remove disturbing heavy metals. The variation between different viscosity values was aligned during the activation procedures in which the viscosities of all raw materials were adjusted as close as possible to target level of 250 mL g^{-1}.

8.1.1 Cellulose concentration

Aimed cellulose content for the dopes with intrinsic viscosity of 250 mL g^{-1} was set to 6 wt% according to Vehviläinen et al. (2015). Cellulose content in viscose dope was 8.9 wt% to imitate a typical viscose production. Because the intrinsic viscosities of all different raw materials was difficult to set to a certain desired level with varying activation methods and starting materials acting differently, the cellulose contents of the raw materials in dissolutions altered according to activated raw materials' intrinsic viscosity values. Aimed cellulose contents in dissolutions were determined according to Figure 5, which was prepared as an educated guess to imitate similar end-solutions prepared of raw materials with varying viscosities (Vehviläinen 2010). Viscosity values of raw materials differentiated between 187 and 300 mL g^{-1} and solubility was estimated to be higher with lower DP values.

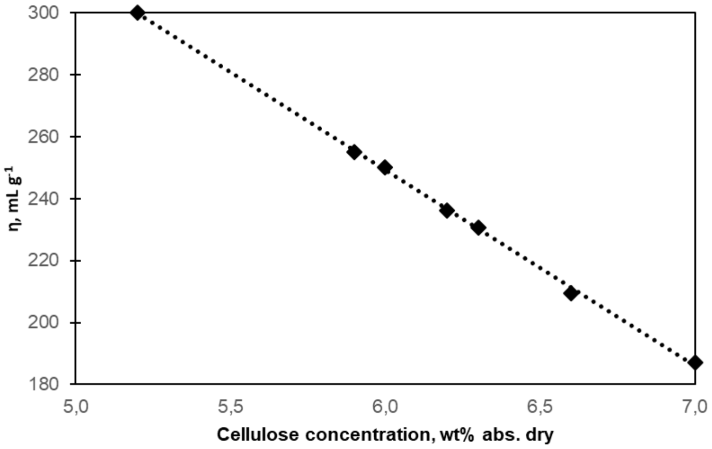

Figure 5. Scheme to select targeted cellulose content of dope based on intrinsic viscosity of raw material.

8.2 Preparation of the cellulose solutions

Viscose preparation process through xanthation was performed by Scitech-Service Oy (subcontractor) to ensure a typical, consistent procedure for the comparison. Viscose sample was frozen (-20 °C) immediately after preparation. Nevertheless, stability and quality analyses of viscose solution were performed by the undersigned.

The cellulose solutions, hereinafter referred to as dope samples, of all process and raw material combinations was prepared in a standard procedure according to US 8066903. In the first part, two different stock solutions A and B with varying ZnO/NaOH ratios were used, the other one complementing enzyme-treated samples (ZnO/NaOH=5), while the other one carbamated (ZnO/NaOH=8).

Stock solution A was a commercial solution provided by Algol Oy. Stock solution B was prepared by weighing solid NaOH (1800 g) and ZnO (360 g) reagents and dissolving them in deionized water, overall solution amount being 10 litres. Results and the final NaOH concentrations of solutions are presented in Table 2.

Table 2. NaOH and ZnO concentrations of stock solutions and dissolution conditions with solution used.

	NaOH	**ZnO**	**NaOH/ZnO ratio**	**Dissolution conditions**
Stock solution A	17.66 wt%	2.20 wt%	8.03	8.0 wt% NaOH / 1.6 wt% ZnO
Stock solution B	17.43 wt%	3.43 wt%	5.08	8.5 wt% NaOH / 1.1 wt% ZnO

Prior to the dissolution, the reactor vessel was precooled to -7 °C, ZnO/NaOH stock solution was stored overnight in -20 °C and deionized water was cooled as cold as possible but yet above its freezing point. First, entire water and portion of overall stock amount was added to the reactor, forming NaOH concentration of approximately 3.5 wt%. Moist cellulosic material (5.2-7 wt%) was added into the reactor and mixture was heavily mixed for 2 minutes for homogenizing the alkaline pulp. The moisture and purity content of cellulose material was taken into consideration when weighing the mass, thus the cellulose concentration indicated the absolute dry cellulose concentration in the mixture. The homogenization step is vital because it allows cellulosic fibres to swell and, thus, induces a wider bath for the more concentrated ZnO/NaOH-solution to penetrate into the pores in the latter stage. After homogenization, the speed was lowered to medium and rest of the stock solution was poured into the reactor, increasing the total NaOH concentration to 8 or 8.5 wt% (depending on dissolution conditions based on the stock solution used). After pouring rest of the stock solution, speed was dropped to low and solution was mixed for 15 minutes to dissolve the cellulose. Temperature of the mixture was -3 °C during dissolution.

8.3 Characterization

The dopes were characterised by determining their solubility and stability. All prepared dopes went through a similar protocol of the following characterization methods and analyses. The analyses were chosen to investigate the effects of the defined activation procedures and raw materials.

The laboratory tests used for the evaluation of quality, solubility, stability, and gelling phenomenon are presented in Table 3. The quality of the solution was evaluated by means of image analysis of polarized microscopic pictures. Processability and stability of the solutions were studied based on changes in viscosities and monitored by means of ball-drop viscosity measurements. Gelation point of the dissolved material is determined through the cross point of G' and G'' obtained from the rheometer.

Table 3. Laboratory tests performed for the dopes to evaluate the solubility and stability.

Measure	**Characterization method**	**Timing**
Cellulose content	**Cellulose** determination by precipitation	Immediately after dissolution
Solubility of the solution	**Image analysis** with light microscopy, analyzed by a quantitative Python-based program	Immediately after dissolution
	Cellulose determination of filtered sample by precipitation	Immediately after dissolution
	Transmittance of films	After dissolution, before gelling
Processability, stability, gelling phenomenon	**Ball-drop viscosity** as a function of temperature	Immediately after dissolution
	Ball-drop viscosity as a function of time	Once a day until the solution sets
	Cross-point of G'/G'' as a function of time, measured with rheometer	After 6, 24 and 52 hours of ageing

8.3.1 Cellulose content

Total amount of cellulose in the dopes was determined in order to verify the actual cellulose content compared to the aimed content. Cellulose contents of dopes were determined by spreading 2-3 g (the exact weight was recorded) of dope between two glass plates. The glass plates were first squeezed to spread the solution evenly and then pulled apart by carefully sliding and then placed into 10% sulphuric acid bath. Coagulated films were first washed with cold tap water for 10 minutes to remove the acid and washing was finished with boiled de-ionized water to remove any salts resulting from washing with tap water. Washed films were dried overnight at 105 °C to a constant weight. The results were calculated as cellulose percentage as a total weight of the dry sample. Three parallel films were prepared per dope sample to verify the reproducibility.

8.3.2 Image analysis

Quality of the prepared sample dopes and the amount of undissolved fibre residual was determined by monitoring the microscopic images with GWB Olympus BH-2 microscope equipped with HDMI camera with high sensitivity CMOS sensor and computer interface (program: ToupTek ToupView version *64, 3.7.7892). Images were furthermore analysed in a quantitative matter with a Python-based algorithm.

Glass slides and cover slips were washed with soap and deionized water prior to the sample placement to remove disturbance of the background. Sample size was kept constant and cover slips were gently pressed onto specimen prior to the imaging with a non-dusting paper tissue. Images were taken by using 10x 160/0.17 objective with phase contrast mode and at least 15 images of each sample was taken for image analysis for quality assurance. Images taken were aimed to cover the entire sample on the glass slide, excluding the border districts as well as possible dirt that were not considered as part of the sample.

Quantitative analysis of images was based on counting the pixels of the image. Each pixel is a combination of three numbers from 0 to 255 (values of these three numbers meaning the intensity of blue, green and red). A threshold was applied in order to distinguish a clear difference in colours (e.g. light grey versus dark grey) by replacing every shade having a value lower than the value of threshold (e.g. 50) to 0 (black) and each value higher than the threshold, was replaced by 255 (white). These numeric values transformed the image form completely of only black and white pixels. Pixels were calculated providing a dissolution rate according to the equation (3):

$$dissolution(\%) = 100 \cdot \left(\frac{1-\Sigma_i \Sigma_j M}{255\, N}\right) \tag{3}$$

where $\Sigma_i\, \Sigma_i M$ sum of the matrix of pixels

N number of pixels

In addition to quantitative method, visual classification of images was performed. Classification of the dopes remotely followed the protocol designed by Navard's research group (Navard & Cuissinat 2006; Sainila 2015, 42-43). Visual evaluation of the images was followed by categorizing the quality of the dope into one of five different classes, 1-2 meaning sufficient solubility, class 3 meaning moderate and classes 4-5 presenting insufficient solubility of the fibres. Evaluation was done based on the number of undissolved fibre residuals and other solvent impurities instead of concentrating on the mechanism of the dissolution.

8.3.3 Cellulose content of filtered samples

Amongst microscopic images, solubility of the solutions was evaluated by filtering the solution through a membrane. The solution was diluted in 8 wt% aqueous NaOH with a factor from two to three (by weighing), factor depending on the solution filterability. Diluted solution was then pressed through a membrane of 5 µm pore size. 2-3 g of filtered sample was then spread on a round glass plate and the film was precipitated in 10% sulphuric acid bath, washed, and dried overnight in 105 °C to a constant weight. The results were calculated as cellulose percentage as a total weight of the dry sample. Three parallel films were prepared per dope sample to verify the reproducibility. The amount of filtered content was compared to non-filtered content and the difference between results indicated the amount of non-dissolved fibres.

8.3.4 Films and their light transmittance

Films were prepared to demonstrate the performance in coating activity. The films were prepared as a coating on a glass plate and the equipment used was Erichsen Film Application coater. Even thickness of the prepared films was ensured by using Erichsen Film Applicator system (Wasag model 288) with 400 µm slot for all samples and a coating speed of 10 m s^{-1}. Films were precipitated in mild sulphuric acid bath (10% H_2SO_4). Coagulated films were let to wash in cold tap water for 10 minutes and thereafter in hot tap water (app. 60 °C) to remove any residual acid. Washed films were left to air-dry between blotting papers that were replaced with new, dry ones once a day, until the samples were fully dried.

Light transmittance of the films was measured with assistance of ultraviolet-visible spectroscopy (UV/VIS/NIR Spectrometer, Lambda 900 by Perkin Elmer). Wide spectrum of wavelengths 200-800 nm was used to determine the transmittance of the film at visible light wavelength (400-800 nm). Device was set to measure the transmittance every 10 nm.

8.3.5 Ball-drop viscosity

The stability and fluidity (processability) of the prepared solutions were monitored with ball-drop viscosity measurements. The method was used to measure kinematic viscosities of the solutions in a simple but precise matter. The measurement was performed according to the modified standard procedure ASTM D1343-95. A measuring glass with a total volume of 100 mL and a height of 25 cm was filled with a sample solution. A stainless-steel ball (diameter 1/8”, weight 130 mg) was dropped to the solution and the elapsed time for the ball to drop a 20 cm fall was recorded with an accuracy of seconds. To minimize the effect of oxygen drying the sample, the solution was covered with Parafilm between each measurement having more than a 10 minutes break.

Measurements were first taken every 5-10 minutes until the solutions reached room temperature (20±1°C). These measurements were recorded in a function of temperature. After that, viscosities of the solutions were measured daily until the solutions reached their gelling points (balls were no longer moving in the solutions). Ball-drop measurements were not proceeded after three days of ageing with samples that were considered as insufficiently dissolved (classes 4-5 in microscopy image evaluation, see 8.3.2 Image analysis). Temperatures of the solutions were monitored prior to each measurement.

8.3.6 Rheology tests

The viscoelastic properties of the dope were studied by using a specific rotational oscillation test. The equipment used was Anton Paar Physica MCR 301 with measuring cone CP50-2/TG. The sample was applied on the plate and let to rest before each measurement for 5 minutes. Gap between cone and plate was set to 1 mm and Peltier hood was used to minimize the effect of evaporation of the sample and additionally, to reduce the effect of airflow nearby affecting the results. Temperature of the device was set to 20 ºC because according to Vehviläinen (2015, 64), the dissolved solution of cellulose gone through an enzyme-aided extrusion is thermally the most stable between 18 - 21 ºC. When the temperature exceeds 22 ºC the enzyme-treated cellulose molecules in ZnO/NaOH-solution start to aggregate increasing the viscosity of the solution (Vehviläinen 2015, 64). Additionally, in Sainila’s (2015, 65) work, the gelation temperature, of carbamated cellulose solutions with varying ZnO/NaOH-concentrations, was observed approximately at 21 ºC and elevated temperatures.

Oscillatory tests with increasing frequency and amplitude were performed to evaluate time-dependent viscoelastic behaviour of the dopes. The storage (G') and the loss moduli (G'') were measured as a function of strain (γ). Frequency was gradually increased from 0.1 Hz to 100 Hz. Low frequency measurements serve the purpose of describing the time-dependent behaviour of a sample in a non-destructive deformation range, thus, there was no shearing of the solution compromising the test result. Higher frequencies were used to determine the shear stress stage at which the sample starts to solidify, thus indicating the force level limiting, for example, for filtering. Amplitude increased gradually from 0 to 100% at each frequency level and 5 minutes of rest was allowed for the sample between the measurements of each level. Examination was carried out overall three times for each sample, after 6, 24 and 52 hours of ageing (counting from the ending time of dissolution mixing) with an automated program. Fresh sample was applied for each measurement and between each measurement, sample was stored in room temperature.

Additionally, extremely high frequency (ramp in from 0 to 9000 Hz in 20 steps with interval time 120 seconds) was applied to simulate fast motion in short timescales as in terms of a sweep test. Sweep tests were applied in both increasing and decreasing directions and two sequential measurements were carried out to evaluate the effect of high shear stress on the sample.

9 Results

9.1 Cellulose solution samples

Prepared solution sample compositions are presented in Table 4. Part I consisted of comparing different activation methods with two different stock solutions having varying NaOH/ZnO ratios (5.08 or 8.03). Whereas, part II followed with comparing different raw materials and having enzyme-aided extrusion as an activation (conditions optimized for each material separately to reach intrinsic viscosity close to 250 mL g^{-1}) and consistent dissolution procedure. As said, organosolv cooked birch pulp was not activated with enzymes due to its low initial intrinsic viscosity (187 mL g^{-1}), however the dissolution procedure followed the same path as for the other samples. Targeted cellulose content of each sample was determined according to their intrinsic viscosity values (see Figure 5).

Table 4. Prepared samples with their cellulose, NaOH and ZnO contents. Standard deviation was determined based on three sequential replicates.

	Sample number and ID		Dissolution conditions	SCAN-visco*	Targeted cellulose content	Determined cellulose content	Std. dev.
Part I	1	Viscose	5.6 wt% NaOH	230 mL g^{-1}	-	8.77%	1.42%
	2	Enzyme-extruded softwood dissolving pulp	A	250 mL g^{-1}	6.0%	5.90%	0.59%
	3	Enzyme-extruded softwood dissolving pulp	B	250 mL g^{-1}	6.0%	5.94%	0.71%
	4	Carbamated softwood dissolving pulp **	A	210 mL g^{-1}	6.6%	6.63%	0.5%
	5	Carbamated softwood dissolving pulp **	B	210 mL g^{-1}	6.6%	6.64%	2.51%
	6	Peroxide-extruded softwood dissolving pulp	A	240 mL g^{-1}	6.2%	6.24%	0.09%
	7	Peroxide-extruded softwood dissolving pulp	B	240 mL g^{-1}	6.2%	-	-
	8	HefCel-treated softwood dissolving pulp	A	230 mL g^{-1}	6.3%	6.28%	0.56%
Part II	9	Enzyme-extruded cotton	A	255 mL g^{-1}	5.9%	5.88%	0.22%
	10	Enzyme-extruded AlkOx cooked birch	A	300 mL g^{-1}	5.2%	5.11%	0.46%
	11	Organosolv cooked birch	A	190 mL g^{-1}	7.0%	5.21%	0.18%

* intrinsic viscosity of the pulp according to ISO 5351_2010 test method.

** degree of substitution: 1

A = 8.0 wt% NaOH / 1.6 wt% ZnO

B = 8.5 wt% NaOH / 1.1 wt% ZnO

Viscose sample (prepared by Scitech-Service Oy) was defrost in 20 °C water bath for one hour and sample was considered as fully molten when solution was clear and viscous. Stage of viscose maturation was determined by titration (20 g of sample and 30 mL of deionized water was added into a glass, and titration was carried out with NH_4Cl until the solution started to solidify). Consumption of ammonium chloride (NH_4Cl) was 8.4 mL indicating a fresh sample for spinning activity.

Solution samples 2-5 were transparent and clear once the dissolution time (15 minutes) had passed. Sample 6 was observed as a semi-clear solution. Sample 7 formed immediately a gel after dissolution and it was discarded as an improper solution, and no analyses were performed for the sample in question. Samples 8-11 were all more or less non-transparent, samples 9 and 10 being extremely non-transparent. Sample 8 had a milky colour and high amount of perceivable non-soluble cellulose matter.

9.2 Solubility of the samples

Microscopic images presented in Figure 6 and Figure 7 were used to evaluate the solubility of the prepared dopes.

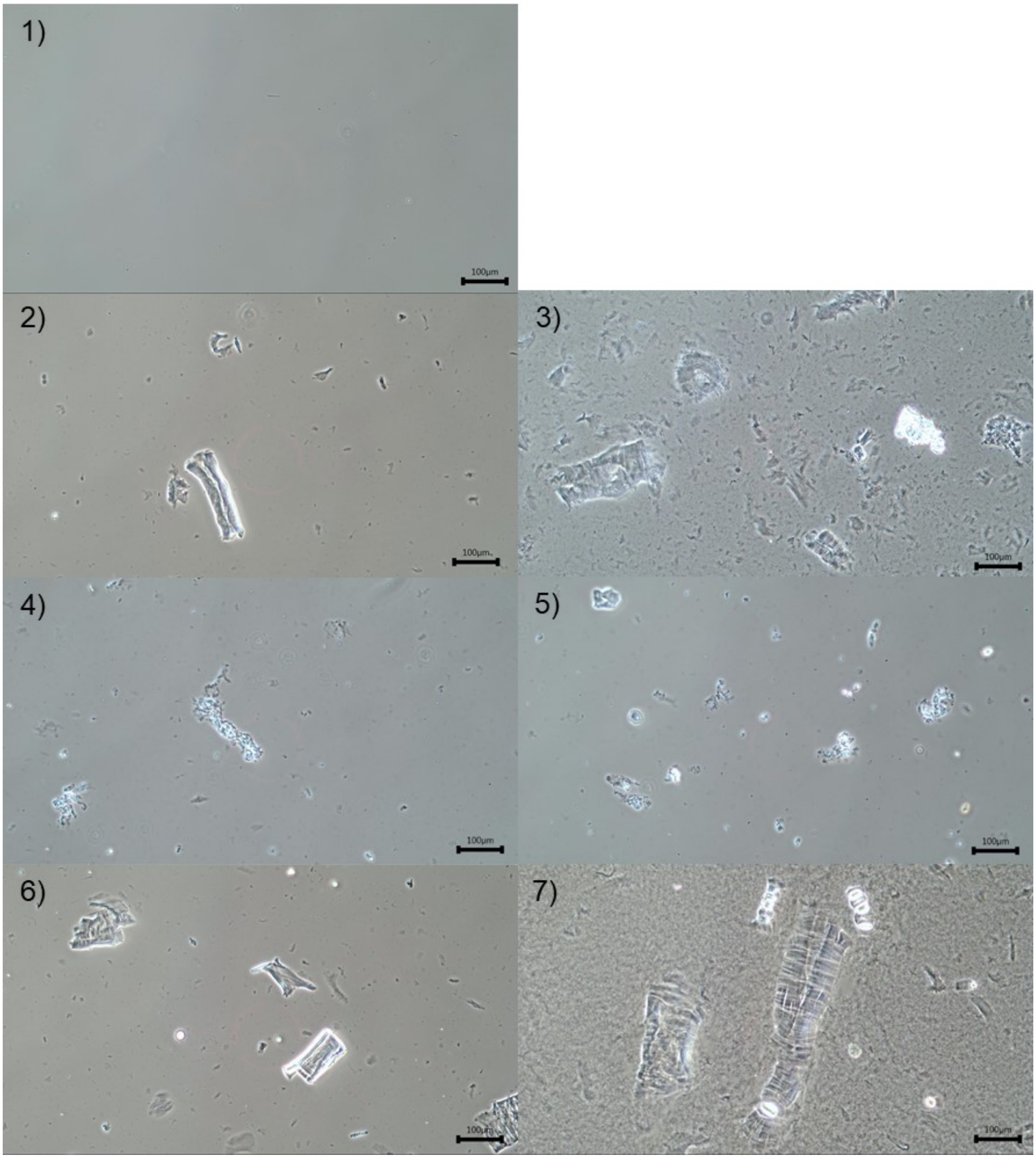

Figure 6. Microscopic images of dopes. Graph numbering corresponds to the sample names in Table 4: 1) viscose, 2-3) enzyme-extruded softwood dissolving pulp with ZnO/NaOH=5 and 8, 4-5) carbamated softwood dissolving pulp with ZnO/NaOH=5 and 8, and 6-7) peroxide-extruded softwood dissolving pulp with ZnO/NaOH=5 and 8.

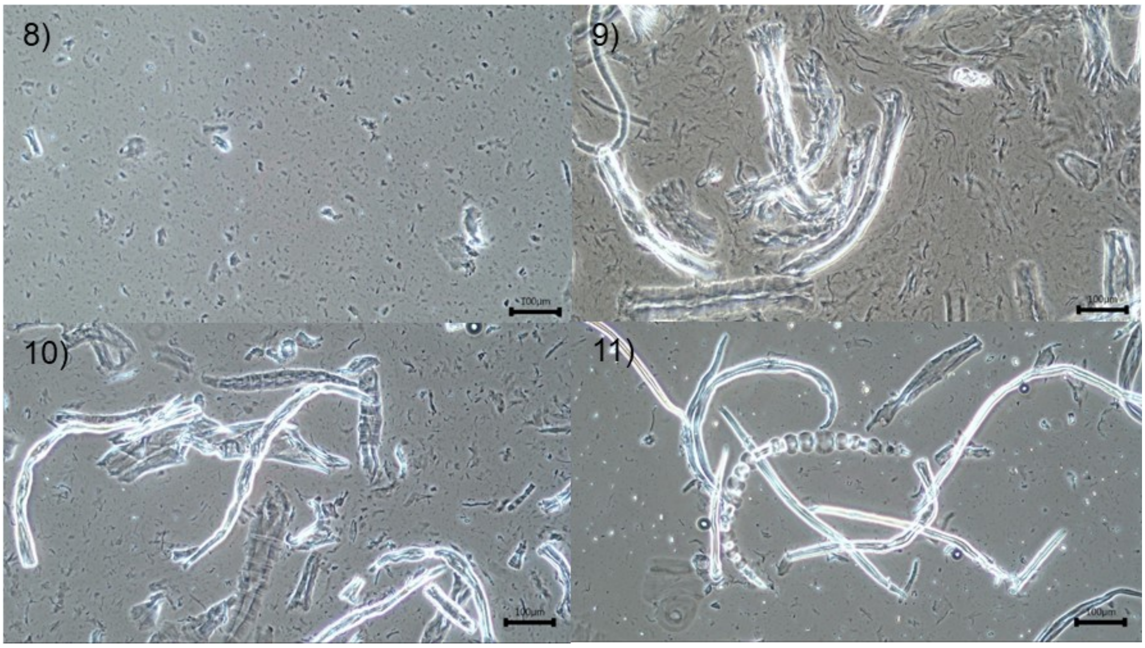

Figure 7. Microscopic images of dopes. Graph numbering corresponds to the sample names in Table 4: 8) HefCel-treated softwood dissolving pulp, 9) enzyme-extruded cotton, 10) enzyme-treated AlkOx birch pulp, and 11) organosolv birch pulp.

Based on the microscopic images (Figure 6 and Figure 7), the solubilities of solutions were classified remotely according to Navard & Cuissinat (2006) and Sainila (2015, 42) into five different solubility classes, classes 1-2 indicating sufficient solubility, class 3 for moderate, and classes 4-5 indicating insufficient solubility. Variation in solubilities is illustrated in Figure 8.

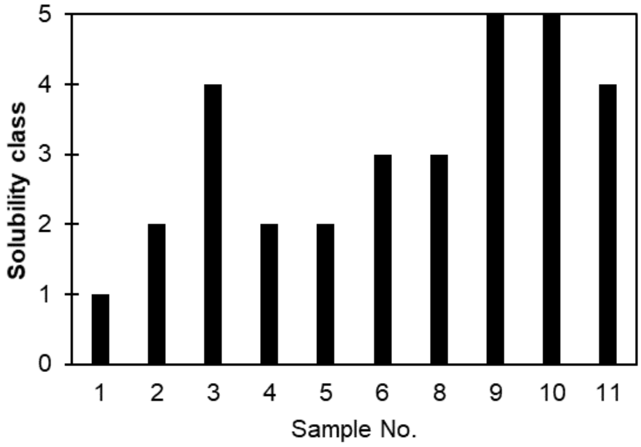

Figure 8. Solubility classes of samples 1-6 and 8-11. Graph numbering corresponds to the sample names in Table 4.

In addition to visual estimation, solubility of the dopes was analysed with a Python based method to quantify the extent of dissolution as well as by filtering the dopes and analysing the cellulose contents of the filtered samples. Results of both these methods are presented in Table 5.

Table 5. Solubility results analysed with a Python based method to quantify the extent of dissolution and by filtering the dopes and then comparing cellulose contents of filtered and non-filtered samples. Graph numbering corresponds to the sample names in Table 4.

Sample	Microscopy				Filtered* vs. non-filtered	
	Level of dissolution	**Std. dev.**	**Number of images**	**Threshold**	**Level of dissolution**	**Std. dev.****
1	99.8%	0.2%	18	180	99.5%	2.1%
2	96.8%	1.5%	31	165	100.2%	1.2%
3	94.5%	1.9%	17	180	101.0%	4.9%
4	97.0%	1.7%	17	165	99.8%	3.3%
5	98.7%	0.5%	16	180	100.5%	8.9%
6	95.4%	1.8%	17	165	100.0%	1.2%
8	95.7%	0.9%	18	175	100.3%	1.1%
9	75.4%	1.7%	18	165	100.2%	0.6%
10	81.5%	1.7%	18	165	103.%	25.7%
11	84.4%	5.5%	15	165	98.4%	2.8%

* pore size of the filter membrane was 5 µm. Samples were diluted with a factor from two to three, depending on the solution filterability.

** standard deviation determined based on three sequential replicates.

9.3 Light transmittance of the films

Light transmittance curves of the prepared films are presented in Figure 9.

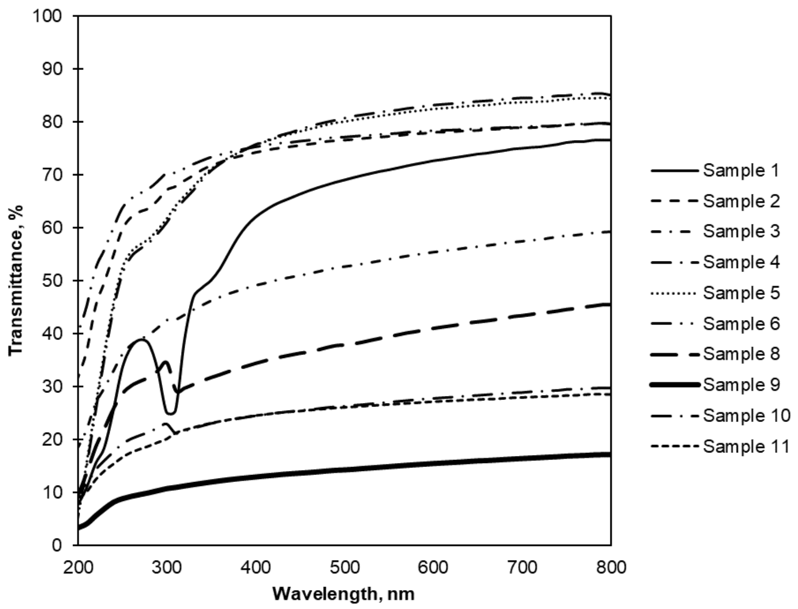

Figure 9. Light transmittance curves of the prepared films at wavelengths 200-800 nm. Graph numbering corresponds to the sample names in Table 4.

9.4 Stability of the dopes

Gelation and open-times were evaluated in terms of ball-drop viscosity measurements. Initial ball-drop values in seconds (measured at the moment of time, when solutions reached room temperature) of all samples are presented in Table 6.

Table 6. Initial ball-drop times the moment of time when solutions reached room temperature (20 °C). Graph numbering corresponds to the sample names in Table 4.

Sample composition			**Ball-drop time, s 20 cm^{-1}**
Part I	1	Viscose, 8.8 wt% cellulose / 5.6 wt% NaOH	38
	2	Enzyme-extruded softwood dissolving pulp, 5.9 wt% cellulose / A	56
	3	Enzyme-extruded softwood dissolving pulp, 5.9 wt% cellulose / B	853
	4	Carbamated softwood dissolving pulp, 6.6 wt% cellulose / A	29
	5	Carbamated softwood dissolving pulp, 6.6 wt% cellulose / B	24
	6	Peroxide-extruded softwood dissolving pulp, 6.2 wt% cellulose / A	48
	7	Peroxide-extruded softwood dissolving pulp, 6.2 wt% cellulose / B	-
	8	Hefcel-treated softwood dissolving pulp, 6.3 wt% cellulose / A	439
Part II	9	Enzyme-extruded cotton, 5.9 wt% cellulose / A	492
	10	Enzyme-extruded AlkOx cooked birch, 5.1 wt% cellulose / A	311
	11	Organosolv cooked birch, 5.2 wt% cellulose / A	16

A = 8.0 wt% NaOH / 1.6 wt% ZnO
B = 8.5 wt% NaOH / 1.1 wt% ZnO

Figure 10 represents the slow gelling phenomenon of the samples at room temperature as a function of time. Lightest colour (30%) represents the samples closest to their initial states at room temperature and, thus, samples are most processable before their increasing aggregation towards their individual gel points. Decrease in processability is illustrated as an increase in colour thickness. White illustrates how many days sample stayed stable before its viscosity changed 30% compared to its initial viscosity at room temperature. 50% represents the time taken by the sample for the viscosity to change from 30% to 50%. 100% bar represents the time how long it took for the viscosity to be doubled compared to initial viscosity of the sample. Viscous illustrates the time when the sample was still liquid but viscosity had doubled compared to initial. Black colour represents the sample in its elastic gelling state.

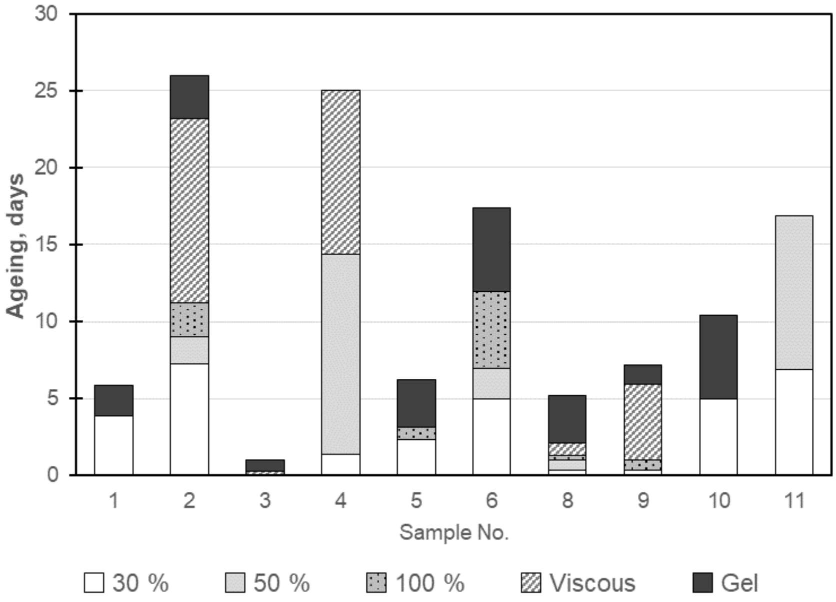

Figure 10. Changes in solution viscosities based on ball-drop measurement results. Graph numbering corresponds to the sample names in Table 4.

9.5 Dynamic viscosity of dopes

Results of rheology tests with constant low frequency (0.1 Hz) and strain amplitude (10%) are presented in Figure 11 as a function of time.

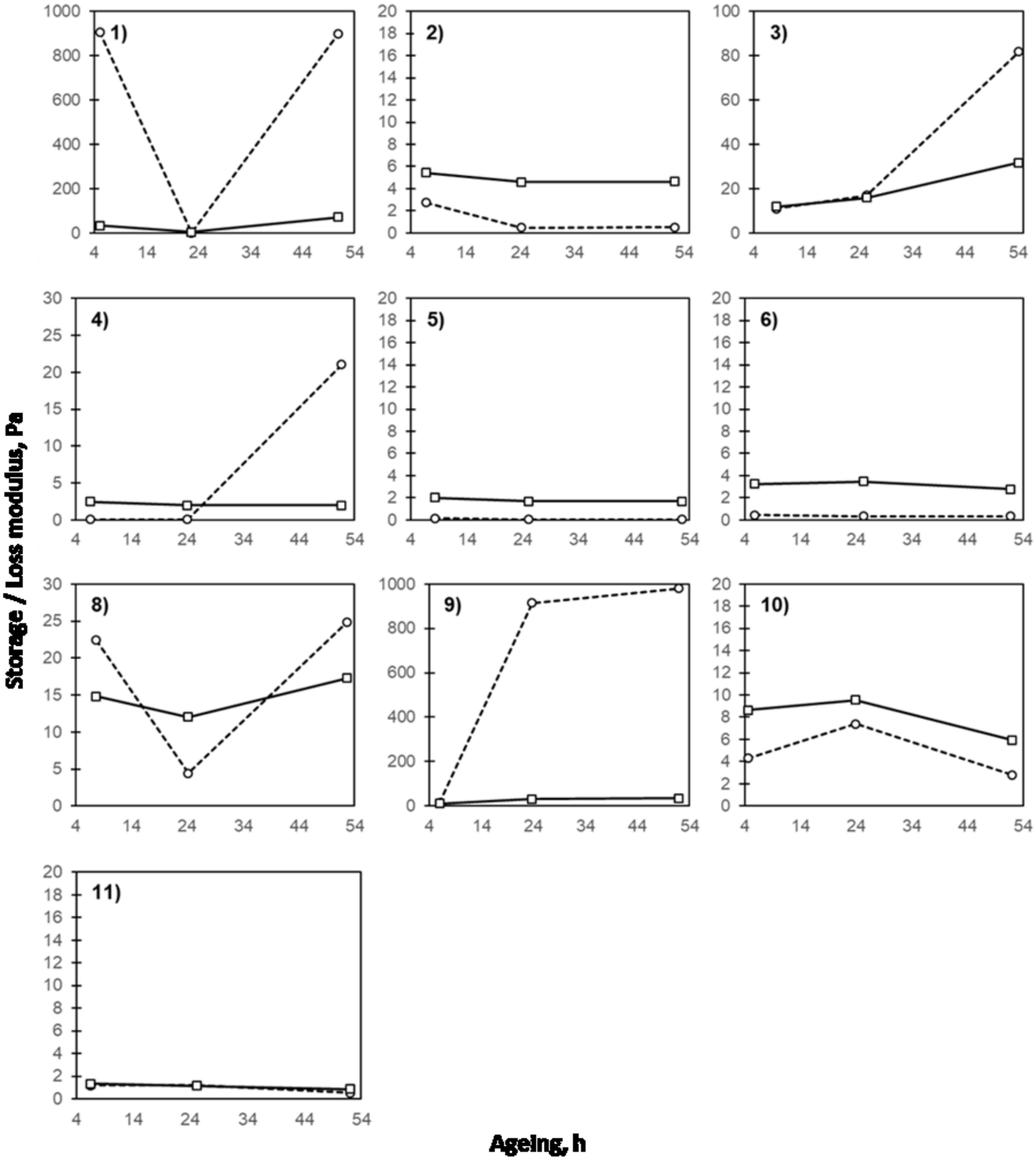

Figure 11. Rheology tests results with constant low frequency (0.1 Hz) and strain amplitude 10%. Dash line presents the change in storage modulus as a function of time, whereas the solid line the change in loss modulus as a function of time. Graph numbering corresponds to the sample names in Table 4.

Results of sweep tests for evaluation of maximum possible shear stress are presented in Figure 12.

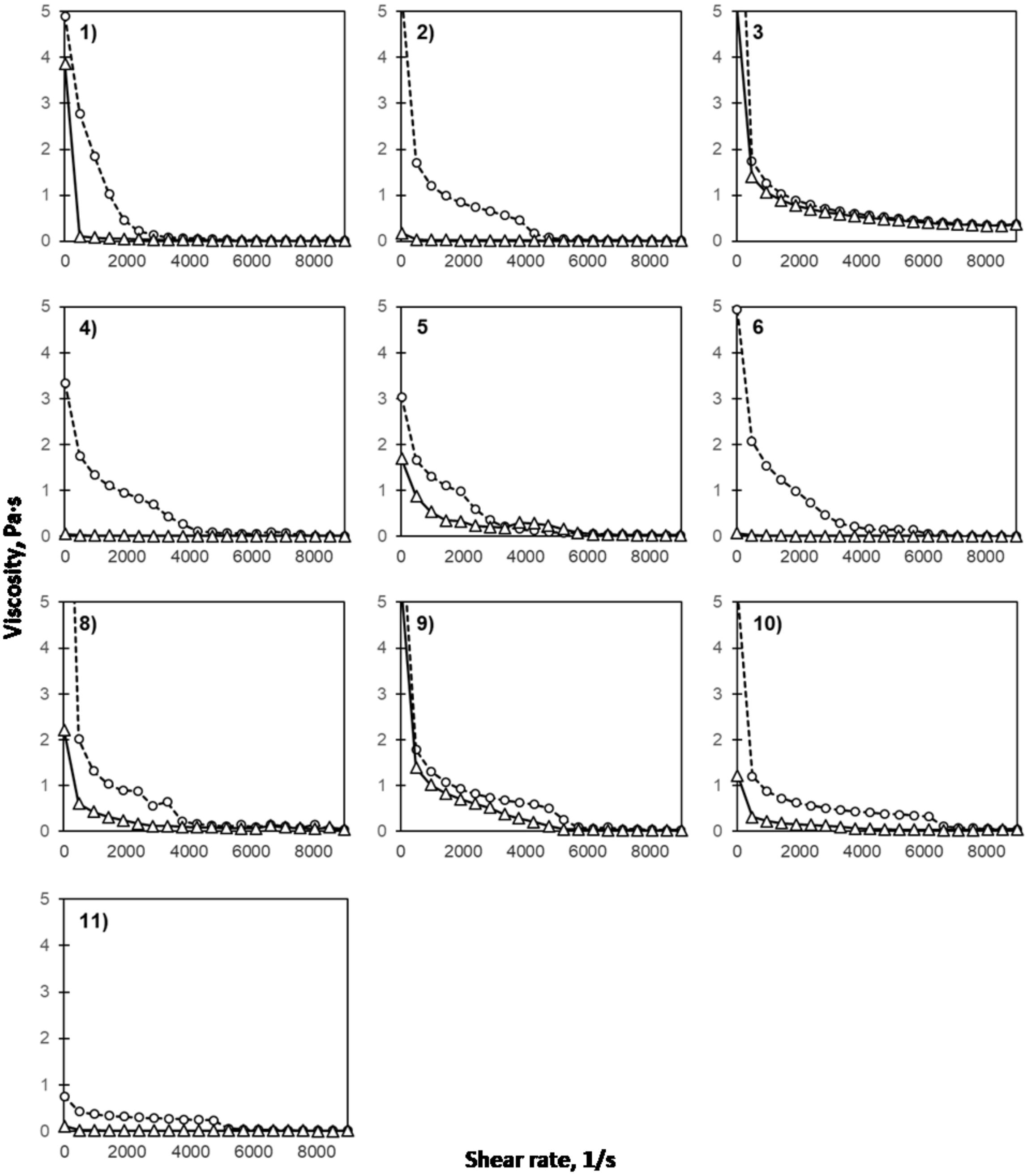

Figure 12. Sweep test results for determination of maximum shear stress. Dash line with round symbol presents the change in viscosity with increasing shear rate, whereas the solid line with triangle symbol the change in viscosity with decreasing shear rate. Graph numbering corresponds to the sample names in Table 4.

10 Discussion

Enzymatic treatment and carbamation prior to dissolution in aqueous NaOH were examined to determine the effect of activation method on solution solubility and stability. These methods were compared to viscose process, which is the most utilized dissolution process applying wet-spinning, but is also dependent on hazardous chemicals.

Hydrogen peroxide is commonly used in bleaching for removing residual lignin (PPG Industries Inc. 1965; Zeronian & Inglesby 1995; Ziaie-Shirkolaee 2008), but it is also an effective chemical for lowering DP of cellulose pulp even in small concentrations (Veness & Evans 1989; Su et al. 2016). Research group of Li et al. (2018) studied the chemical and microstructural changes of alkaline hydrogen peroxide pretreated corn stover and discovered that H_2O_2 treatment increased the accessibility of cellulose through a six-fold increase of the pore volume and doubling of the surface area of cellulose. For this reason, H_2O_2 treated cellulose was examined here as an alternative for cellulose activation. Peroxide treatment was compared to enzymatic activation because both were carried out with assistance of twin-screw extruder.

Cotton was chosen for the examination due to its nearly pure cellulose consistency, thus, no lignin or hemicellulose would exist in the material to compromise the results. Birch was examined both as in AlkOx cooked and organosolv cooked to study the effect of the wood source. Organosolv cooked birch was aimed to play as a reference material for AlkOx cooked birch enabling the comparison of the different cooking methods, but due to unfortunately low intrinsic viscosity value, organosolv cooked was examined to study the effect of low DP.

Prepared samples were successful in means of achieving cellulose contents close to the targeted contents. For samples 2-6 and 8-10 the difference between determined cellulose contents and target was maximum of 0.1 wt%. Difference between target and determined cellulose content for sample 7 was 1.79 wt% (Table 4).

10.1 Solubility of the samples

Based on microscopic images, sample 1 was evaluated as completely dissolved, thus, representing solubility class 1 of sufficient solubility. Samples 2, 4 and 5 had small amounts of undissolved particles and were rated into class 2, also reflecting sufficient solubility.

Solutions 6 and 8 had slightly higher amounts of insoluble particles for which they were rated to class 3 of moderate solubility. Samples 3, 7, 9, 10, and 11 were adjudicated to classes 4 and 5, both indicating insufficient solubility.

Enzyme-treated softwood dissolving pulp dissolved better in 1.6 wt% ZnO / 8.0 wt% NaOH, than in 1.1 wt% ZnO / 8.5 wt% NaOH, indicating that higher ZnO content is needed to dissolve enzyme-treated cellulose efficiently, simultaneously enabling lower NaOH content in dissolution. However, carbamated softwood dissolved sufficiently in both ZnO/NaOH concentrations, suggesting that carbamation activates cellulose structure more efficiently than enzyme-treatment.

Peroxide-treated softwood with 1.1 wt% ZnO / 8.5 wt% NaOH resulted as an immediate gelling of the sample, whereas peroxide-treated softwood with 1.6 wt% ZnO / 8.0 wt% NaOH was sufficiently dissolved and maintained its viscous state. The result was surprising and may indicate that with optimized conditions, cellulose could be fully dissolved in aqueous NaOH if it is first treated with H_2O_2 to increase the accessible surface area. This also may indicate that ratio of ZnO/NaOH is crucial in order to maintain a proper stability of solution with low NaOH content whilst achieving sufficient solubility with correct amount of ZnO.

HefCel was only moderately dissolved in 1.6 wt% ZnO / 8.0 wt% NaOH despite that its deconstructed structure lacks amorphous regions. Nevertheless, the remaining undissolved particles that were visible in the microscopic images were relatively small (compared to other samples) because of microcrystalline structure. Lower level of dissolution might indicate that enzymes used in HefCel treatment are not as effective in means of activation as the enzymes used in Biocelsol process, but it is difficult to draw conclusions because dissolution conditions were not fully optimized for the material in question. Further research is needed, because one of the preliminary tests gave promising results in means of dissolution rate but cellulose content in solution was only 5.2 wt%, due to false dry matter content, and no further examination was conducted. HefCel may require an additional mercerisation step for a complete dissolution.

Surprisingly, cotton did not dissolve in 1.6 wt% ZnO / 8.0 wt% NaOH sufficiently despite the successful enzymatic treatment that set the intrinsic viscosity to the target level, and nearly pure cellulose composition. Additionally, cotton and softwood dissolving pulp had comparable initial viscosity values before activation (see Table 1), yet, cotton required greater enzyme dosage to decrease its intrinsic viscosity to the target level. Reluctance of cotton towards modification may be due to its four-layered cell wall structure (Flint 1950), whereas usual wood-based cells consist of only three-layered structures (Sixta 2006, 41). This demonstrates that despite the intrinsic viscosity value of pulp, varying cellulose raw materials behave differently both in enzymatic activation and the following dissolution. The dissolution conditions need to be optimized for each raw material individually for a consistent comparison.

AlkOx pulp was even more resistant towards enzyme-treatment, although it had lower initial intrinsic viscosity value (compared to both softwood and cotton). Enzyme dosage was higher than for softwood pulp and yet, it resulted higher intrinsic viscosity after activation. The reasoning for low effect might be because of the hardwood source (birch) or because of the differing pulping method. Also, low DP value (190 mL g^{-1}) for birch pulp does not lower the diffusion hindrance enough for enabling sufficient dissolution (organosolv cooked birch) and this is most probably due to hardwood source.

Rough conclusion could be that softwood dissolving pulp has the best reacting ability towards enzyme-treatment (when compared to cotton and birch based AlkOx pulp). The birch based AlkOx pulp has the lowest reactivity towards enzyme-treatment (when compared to cotton and softwood dissolving pulp). Structures with higher dissolution hindrances, such as cotton and birch, may be beneficial to treat with H_2O_2 prior to enzyme-treatment (Li et al. 2018) to open the cell wall structures and increase the accessible surface area for enzymes to enter.

10.1.1 Comparison of methods determining solubility

Solubility results of three evaluation methods (solubility from microscopic images by qualitative evaluation, solubility from microscopic images by quantitative evaluation, and cellulose content of filtered samples) do not fully correlate. Both quantitative analyses (by microscopy and via filtering) gave high solubilities for all samples (81.5 - 99.8% and 98.4 - 103.1%, respectively), but these results cannot be considered reliable and representing the overall levels of dissolution. For example, quantitative method shows higher level of dissolution for peroxide-treated softwood than for enzyme-treated softwood, in contrast to the qualitative evaluation. Also, method via filtering shows highest level of dissolution for AlkOx cooked birch, despite that it was one of the most insufficiently dissolved samples according to qualitative evaluation. Low correlation between the results of the three separate analyses can be observed (Figure 8 and Table 5).

Standard deviations in quantitative determination were low (< 2%), except for organosolv cooked birch pulp (5.5%). Based on this, the replicability of the imaging method of a specific sub-sample was good, but it does not necessarily represent the overall sample. Standard deviation of the cellulose content of filtered samples was large, up to 8.9 % (and 25.7 % for AlkOX cooked birch). This indicates of low reproducibility rate of the method.

One of the reasons for low correlations could be the sample amount used for determination. Sample amount in both quantitative analyses for determining solubility is small (one drop for microscopy and 2-3 g of diluted sample for filtering with three replicates) and may not be representative for 2-3 litres of overall amount of dope, in neither of the analyses. In microscopy, fifteen or more images were taken of each sample, but these were all imaged from one drop of the dope. To increase the reproducibility of the method, the number of samples used for imaging should be increased, but this may not be feasible due to the increased processing time.

For the filtered samples, the dope had to be diluted with a factor of two or three, depending on the filterability. This additional factor could have influenced the viability of the results gained via filtering. Also, the time taken for the sample to be filtered varied greatly. Varying time consumption under vacuum causes differences in amounts of sample evaporation when analysing water-based solutions, which is difficult or even impossible to be prevented. Filtering time should be harmonized in order to increase reliability of the method. Addition of multiple steps with differing membrane pore sizes could be an option to speed up the filtering step but it might simultaneously reduce reliability of the method by increasing number of steps.

One promising option for determination of solution’s level of dissolution might be via reject amount determination. In such method, a recorded amount of sample is filtered but instead of determining the cellulose content of filtered sample, option would include determining the amount of reject. However, weakness of such method might be that the reject needs to be fully washed and dried, yet redeem all the solid content without further dissolution of degradation of the sample.

10.1.2 Light transmittance of the films

As expected, samples 1, 2, 4, 5 and 6 (viscose, enzyme-treated softwood in 1.6 wt% ZnO / 8.0 wt% NaOH, both carbamated softwoods and peroxide-treated softwood in 1.6 wt% ZnO / 8.0 wt% NaOH) showed the highest transmittance, varying between 72.8-83.3% at 600 nm (Figure 9). Surprisingly, viscose did not exhibit the highest transmittance, but this might be due to non-optimized precipitation conditions. Drop in transmittance curve of viscose at around 300 nm is most probably due to a bubble occurring in the film. Samples 8 and 3 (HefCel treated softwood and enzyme-treated softwood in 1.1 wt% ZnO / 8.5 wt% NaOH) set at the middle of the curve, which was due to moderate and insufficient solubilities (Figure 8). Samples 9, 10 and 11 (cotton, AlkOx and organosolv cooked birch) exhibited the lowest transmittances (15.5-27.8%), as was expected due to insufficient solubility (Figure 8).

10.2 Rheology of the samples

Stability and gelling phenomenon of the dope samples was examined in terms of ball-drop viscosity measurements and storage, and loss moduli analyses.

10.2.1 Initial viscosity of the dopes

Initial ball-drop times of the samples varied greatly which may indicate that not all samples had the optimum amount of cellulose to be dissolved in them. For example, cellulose carbamate samples most probably could have tolerated higher cellulose concentration in the solution due to low initial ball-drop time (see Table 6) with cellulose content of 6.6 wt% (with intrinsic viscosity of 210 mL g^{-1} and DP of 267). Sainila (2015, 56) discovered in her work that carbamated cellulose (with DP of 227 and degree of substitution of 0.19) can be dissolved in 1.1 wt% ZnO / 8.0 wt% NaOH to the extent of 10 wt% of cellulose. However, some initial ball-drop times may have been high because of aggregation. For example, the large difference in ball-drop time between samples 2 and 3 (enzyme-treated softwoods) is more likely to be due to gelation instead of cellulose content, as the latter was the same but the ZnO/NaOH contents differed. Variance in initial ball-drop times increases uncertainty to the stability comparison and, for example, differences in stabilities of enzyme-treated and carbamated softwoods should be evaluated with caution.

10.2.2 Stability of the dopes

Analysis (ball-drop) performed for the examination of sample stabilities can be assessed to be reliable due to good correlation of gelation point of viscose (reference material) compared to the result in literature. Irklei et al. (1986) performed a similar stability measurement for viscose with similar specifications, and determined the gelation point to occur after 5.8 days of ageing. Viscose sample in this study performed as was expected (Irklei et al. 1986; Strunk et al. 2012) and reached its final gelatine state after around 5 days of ageing (Figure 10). Nevertheless, viscosity of viscose increased 30% already after 92 hours of ageing which may be a crucial increase for spinning activity (Vehviläinen 2015, 28.). After this, viscosity of the solution increased rapidly and 50% or 100% changes in viscosity were not registered.

Enzyme-treated softwood reached its gelatine state between 556 and 623 hours of ageing. However, although enzyme-treated and carbamated softwoods with lower NaOH contents showed similar results with final gelling points (app. 25 days and 30 days, respectively), enzyme-treated softwood stayed the longest at its initial state (app. 7 days). Figure 10 clearly indicates that enzyme-treated softwood dissolving pulp, with defined activation/dissolution conditions, performed the best stability for further processing as a function of time. Also worth mentioning is that stabilities were tested in normal room temperature. Lower temperature is noticed to have a positive effect on cellulose-NaOH solution stabilities (Roy et al. 2003), thus, decreased temperature for the experiment set-up may have been able to prolong the stability times.

Surprisingly, carbamated samples did not exhibit gelling, on the contrary, they became less viscous as a function of time. This may be if carbamate groups hydrolysed in aqueous NaOH and degraded into sodium carbonate and amines, and celluloses were left with only hydroxyl groups (Moidoveanu & David 2002; Harlin 2019). The smell of ammonia releasing from the sample was also distinguished as it aged, which may support the conclusion. Another possible reasoning may also be the early stage of gelation, in which only few molecules are first attached to each other (increasing viscosity) before the increased networking (gelling). This could be supported by the other carbamated cellulose sample with higher NaOH content (sample 5), which first exhibited decreasing viscosity prior to sudden gelling. Interestingly, the same viscosity decrease phenomenon was not reported for solutions in Sainila’s (2015, 67) work. However, this may be due to many reasons, for example, different cellulose concentration, degree of substitution or other differing conditions. However, it may be concluded that in this work, enzyme-treatment prolonged the stability of cellulose in aqueous

NaOH when stored in room temperature, probably because it works by increasing the accessible surface area, not by substituting functional groups in the structure. Carbamated sample 4 (6.6 wt% cellulose / 1.1 wt% ZnO / 8.0 wt% NaOH) never reached a gelatine state and actually, it was the only sample for which the viscosity decreased instead of increasing, but 30% decrease in viscosity was noticed already after 33 hours of ageing, which may be crucial for spinning activity (Figure 10).

All samples with higher NaOH contents, samples 3, 5 and 7 (enzyme-treated, carbamated and peroxide-treated softwoods), aggregated rapidly (in less than five days, see Figure 10). Shorter stability time occurred as expected and is most likely due to higher NaOH contents, a conclusion that is supported by the literature (Roy et al. 2003; Cai & Zhang 2006). Peroxide-aided softwood (in 1.1 wt% ZnO / 8.0 wt% NaOH) performed well in means of stability (gelling between 12-17 days of ageing) but did not outperform enzyme-treated or carbamated softwoods.

HefCel (in 1.1 wt% ZnO / 8.0 wt% NaOH) showed aggregation activity with the extent of 50% already after 24 hours and became fully solid at some point between 50 and 124 hours. Reasoning for this may be if microcrystalline cellulose has a higher self-tendency to aggregate (according to Ghasemi et al. (2018) nanocellulose usually has a gel-like medium). This strong aggregation may have been prevented with lower cellulose content but further studies should be conducted.

Stabilities of samples 9, 10 and 11 (cotton, AlkOx and organosolv cooked birch pulps) are not considered interesting due to insufficient solubilities. And for example, organosolv cooked birch (with low DP) did not aggregate to the extent of gelling within this study framework but this was due to low solubility.

10.2.3 Dynamic viscosity of the samples

Relations between G'/G'' results and ball-drop viscosity measurements were only somewhat accurate. Some papers in literature suggest that gelling point of a solution can be identified by the cross-over point of storage and loss moduli (Tung & Dynes 1982). However, some papers question this (Winter 1987) and the results have been slightly contradictory regarding this matter.

Storage and loss moduli curves (Figure 11) of samples 2, 5 and 6 (enzyme-treated softwood with lower NaOH content, carbamated higher NaOH content and peroxide-treated softwood with lower NaOH content) exhibit the solutions to be in their viscous state at least for 54 hours after dissolution, as their loss moduli are greater than the storage moduli. Ball-drop analyses support the results as their gelling points were not determined to occur before 54 hours of ageing in any of these samples. Also for sample 3 (enzyme-treated softwood with higher NaOH content), the G’/G’’ curve exhibits gelling point to set at 16 hours of ageing, which can be supported by ball drop measurement (indicating gelation between 0.3-1.05 days).

G’/G’’ curve of the sample 4 (carbamated softwood with lower NaOH content) exhibit a change in the solution rheology (as the storage modulus crosses over loss modulus) at around 24 hours, whereas ball-drop measurement indicated decrease in viscosity as a function of time. The reasoning for the contradiction is unclear, but may be due to an error in rheology measurement at 54 hours measurement point (Figure 11).

In case of HefCel, the drop in storage modulus may indicate that cellulose in the sample continued dissolving (Figure 11). However, storage modulus was restored and ball-drop viscosity results support that the sample did not form a gel before at least 50 hours of ageing.

For the viscose the G’/G’’ curve exhibits the sample to be in its gel state already after 5 hours of ageing (storage modulus is greater than loss modulus), but in reality, this was not the case and it also is not supported by the ball-drop measurement. The reasoning for this phenomenon is unclear but one possible explanation might be, if the temperature of the water bath, that was used to defrost the sample, was too high. Too high temperature may have accelerated the gelling of the viscose.

Samples 9, 10 and 11 (cotton, AlkOx and organosolv cooked birch) exhibited non-correlative G’/G’’ curves, as was expected due to their insufficient solubilities (Figure 8). For example, cotton had a 30% increase in its viscosity after 0.35 days (based on ball-drop measurement), but G’/G’’ curve exhibits the sample to be in its gelation state already after 5 hours of ageing. Thus, these results may not be considered reliable due to insufficient solubilities of the samples.

Shear thinning can be observed to happen before 4000 Pas viscosity (Figure 12) for all samples as the viscosities decrease by increasing shear rate. Also, shear rates between 2000-3000 s^{-1}

may be correlated to fast pressure increase, for example in filtering, and high viscosity (e.g. > 1 Pas) at this shear rate stage may be challenging to work with. For example, enzyme-treated and carbamated softwoods (in 1.1 wt% ZnO / 8.0 wt% NaOH) may be difficult to filter, whereas viscose probably will not be that difficult. Hysteresis loop can also be observed in for samples 1, 2, 4, 5, 6 and 8 (Figure 12). This loop indicates a thixotropic behaviour of the solution. Thixotropy is a phenomenon related to solution gelling and means that solution becomes fluid when agitated but exhibits solid-like behaviour in rest (Barnes 1997).

As can be seen with a wide variety of samples prepared in the study in question, cross-over of loss and storage moduli does not unquestionably define materials' gelling point, with the method used in this study and results should be assessed with caution or verified with another analysis.

10.2.4 Other uncertainties

Deaeration of the dope prior to rheology measurements was not performed, because the bubbles generated while mixing had mostly broken down by the beginning of initial rheology measurement (after six hours ageing). Additionally, despite the former plan, deaeration of variable samples with SpeedMixer DAC 1100.1 VAC-P (speed set to 1600 rpm and the vacuum to 100 %) resulted differently between the variable samples, some of them being sensitive towards gelling in speed mixing while some not. Therefore, deaeration of the samples was considered to possibly alter the rheology results in an inconsequential way.

Deaeration of the samples was practiced in preliminary tests, but was decided to be undone in case of the actual test samples. Optimization of deaeration conditions, which would be consistent for all versatile samples, was not considered as a viable task in this study and would have required an extreme amount of more testing. Thus, smaller microbubbles might have a disturbing effect on some rheology results.

10.3 Research questions

Research frame of the study aimed to examine whether defined pre-treatment and activation methods (derivatization/control of DP) of different raw materials affect the solubility and rheology of alkaline solutions prepared from the modified cellulosic raw materials. The solubility was examined in means of microscopy imaging and cellulose content determination and viscosity change of the prepared solutions was studied over time. This chapter discusses whether explanations for the predefined research questions were found.

How does the defined activation (derivatization/control of DP) and dissolution conditions affect the solution viscosity and rheology over time?

Activation method applied prior to dissolution has a great impact on cellulose stability, as do the dissolution conditions. In order to produce a solution with a sufficient solubility, yet maintaining the prolonged stability and processability, balancing between delicate changes in dissolution conditions needs to be carried out. Increased sodium hydroxide content increases cellulose dissolution, but simultaneously decreases the solution stability. Additionally dissolution conditions, such as agitation and temperature control influences solution rheology highly.

How does the defined activation (derivatization/control of DP) and dissolution conditions affect the amount of undissolved material?

All examined activation methods (xanthation, enzyme-aided extrusion, carbamation and peroxide-aided extrusion) with a consistent dissolution conditions did result solutions of sufficient solubilities, when processes were applied for softwood dissolving pulp. However, in order to do so, process needs to be an optimized composition of additional pretreatments, activation method and dissolution, all with material-specific conditions.

What is the time dependency of solution rheology based on cellulose source?

Aim in part II was to examine whether the raw material has an effect on the solubility and stability, when the intrinsic viscosities of all material are set on a predetermined level which is equal to all material alternatives. However, intrinsic viscosities of all cellulosic raw materials were not managed to be set on the exact level, and some of the materials had a rather high difference between their intrinsic viscosity values, for example the difference between enzyme-treated softwood dissolving pulp and AlkOx cooked birch dissolving pulp was as high as 50 mL g^{-1} (Table 1). For this reason, the raw material comparison cannot be oversimplified and correlation between raw material source and solution stability has to be evaluated with caution.

Experimental solution combinations with activation and dissolution procedures that were not optimized for other raw materials than softwood dissolving pulp, such as enzyme-treatment for cotton, were not sufficiently dissolved. This unfortunate event indicates that it might be safe to state that the raw material source used for the dissolution, cannot be altered without optimizing conditions for that specific cellulosic raw material, despite the known optimal activation and dissolution conditions for another source of raw material. Though, for example in case of cotton, which is nearly pure cellulose with no hemicelluloses or lignin disturbing the dissolution, and the activation step proceeded as planned in terms of receiving cellulose with the closest to the desired intrinsic viscosity value (255 mL g^{-1} vs. 250 mL g^{-1}), yet it dissolved imperfectly and resulted a solution with high amount of undissolved particles.

How does the defined cellulose material source affect the amount of undissolved material? Varying raw materials were studied because the structure and properties of different raw materials vary and they have different diffusion hindrances, which affect the solubility of cellulose. However, each of the defined raw material had different preliminary structures and properties, which determine how the material alters in enzymatic modification. Some of the materials also required additional chemi-mechanical treatments (such as alkali-acid treatment of cotton), and these pretreatments also might have an effect on the material solubility as well as on diffusion hindrance. Thus, cellulose material source affects how it behaves in the activation step prior to dissolution, and what additional pretreatments it may need for a sufficient dissolution.

10.4 Recommendations for further research

Highest possible achievable cellulose content also was not in the scope of this study. Nevertheless, possibility to increase cellulose content of the solution, without jeopardizing spinning quality or solution stability, decreases the economic cost of the overall processing. This should also be further looked into and to determine the highest achievable cellulose content for the dissolution.

HefCel solution exhibited fast aggregation but due to rheology measurements and previous research conclusion of Hagman et al. (2017), dissolution of fibres into the solution is expected to have happened to some extent. A study of Hagman et al. (2017) showed that 1 wt% of microcrystalline cellulose is able to be dissolved in NaOH-solution but the concentration in paper was greatly less than in this study with 6.3 wt%. Further examination towards HefCel dissolution could be a promising alternative to invest in.

Lastly, due to low reliability of solubility results via filtering, it would be highly necessary to invent a method to determine the amount of undissolved cellulose in solution for *in-situ* purposes that is time and cost-efficient to perform on site.

11 Conclusions

It was assumed that clear differences between raw materials in enzymatic treatment and alkali dissolution processes could be observed. Differences are because of fibre wall structure, for example, cotton has multiple fibril layers and efficiency of different pulping methods differs. The formed alkali solutions have different tendencies to form gels and several means are needed to stabilize the system. Preliminary hypotheses for the study were that dissolution in sodium zincate, produces as good or better solutions for wet-spinning as their improved stability properties over the viscose process.

Our reference material viscose method through cellulose xanthate derivative exhibits solution with the highest solubility rate. Nevertheless, images of enzyme-treated and carbamated softwoods illustrated almost as good results in solubility. Despite the higher solubility of viscose, process applies the use of strongly hazardous chemicals that should be kept in mind. In addition to use of hazardous chemicals in the processing, performance of viscose in means of stability fell behind when compared to stability results of enzyme-treated softwood.

Reason for xanthates low stability should be related to lack of stabilization. With carbamate and enzyme-treated solutions zinc shows very efficient stabilization due complexity with hydrophobic site in cellulose. Carbamate improves solubility even if it starts to decay immediately with alkaline contact. Poor solubility causes unexpected anomalies on rheological behaviour. Good solution tolerates high shear without shock gelation.

At first glance, results indicate similar stability performance of both enzyme-treated and carbamated cellulose in aqueous NaOH/ZnO, but unpredictably, cellulose carbamate does not outperform enzyme-treated cellulose in means of solution stability due to carbamate solution's rapid decrease in viscosity. Results of the study designate that enzyme-treated cellulose solution is the most stable in its maturation time before its viscosity starts to increase to the extent of hindering spinning activity or other processing. Additionally, peroxide-treatment exhibited a surprisingly positive effect on dissolution level of cellulose, resulting a sample of sufficient solubility.

It can be stated that cellulose solutions exhibited different properties when activation and dissolution conditions are altered, and so does the source of cellulosic material affect solution solubility. In addition to cellulose source of option, degree of polymerization affects greatly solution solubility and stability as well. Thus, further research of different cellulose solubilities is required for a consistent comparison of cellulose hindrance factors. Rheological studies revealed that in alkali system the build-up of elasticity over viscosity was not pronounced. The reason might be that the consistency of solutions are only modest, below 8%.

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Appendices

Appendix 1. Specification table of the raw materials used. 1 page.

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Sample		**Softwood dissolving pulp for viscose (from Domsjö)**	**Softwood dissolving pulp (from Domsjö)**	**Cotton before acid-alkali washes**	**Cotton after acid-alkali washes**	**Birch before treatments (for AlkOx)**	**Birch dissolving pulp (organosolv cooked)**
Cleanliness	**Num/kg**	90	-	-	-	-	-
Brightness (ISO 2470)	**% ISO**	92,1	-	-	-	-	-
R18, insoluble fraction in 18% NaOH (ISO 692)	**%**	>94	-	-	-	-	-
R10, insoluble fraction in 10% NaOH (ISO 692)	**%**	88	-	-	-	-	-
Viscosity (ISO 5351)	**ml/g**	545	-	-	-	-	-
Visco 388	**kg/t**	1	-	-	-	-	-
Viscosity	**cP**	18	-	-	-	-	-
Degree of polymerization		780	-	-	430	-	-
Dry matter content	**%**	93,07	-	96,2	23,2	35,2	17
Ash (525 °C; ISO 1762)	**%**	0,08	-	0,24	0,05	< 0,01	< 0,01
SiO2 (SCAN-C)	**mg/kg**	45	-	-	-	-	-
Ca (SCAN-CM)	**mg/kg**	35	28,5	153	1,5	4,2	20,5
Co	**mg/kg**	-	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5
Cu	**mg/kg**	-	0,58	< 0,5	< 0,5	< 0,5	< 0,5
Fe (SCAN-CM)	**mg/kg**	1,5	3,4	23,4	2,0	16,2	27,7
Mg (SCAN-CM)	**mg/kg**	220	175	42,9	< 1	2,4	42,7
Mn (SCAN-CM)	**mg/kg**	0,2	< 0,3	< 0,3	< 0,3	0,4	0,31
Si	**mg/kg**	-	< 10	42,6	11,7	19,3	< 10
Acetone extractives (SCAN-CM)	**%**	-	-	-	-	< 0,05	0,2
Total lignin	**%**	-	-	-	-	< 0,5	0,14
Klason lignin	**%**	-	-	-	-	< 0,4	-
Dissolving lignin	**%**	-	-	-	-	0,2	0,14
Arabinose	**%**	-	-	-	-	< 0,3	-
Galaktose	**%**	-	-	-	-	< 0,3	-
Glucose	**%**	-	-	-	-	97,0	98,3
Xylose		-	-	-	-	2,1	1,72
Mannose	**%**	-	-	-	-	0,9	< 0,5
Total carbohydrates	**mg/100mg**	-	-	-	-	103	105
Xylan	**%**	-	-	-	-	-	1,7
Glucomannan	**%**	-	-	-	-	-	0
Alpha cellulose (TAPPI 203)	**%**	-	-	-	-	-	98