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Wet-Spinning of Cellulosic Fibres from Water-Based Solution Prepared from Enzyme-Treated Pulp

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Abstract

The demand for textile fibres is increasing constantly due to the growing population and improving standard of living. Currently, 64 % of the fibres produced globally are synthetic man-made fibres from oil-based raw materials, 29 % is cotton and the rest are man-made cellulosic fibres, wool and other natural fibres. The production of synthetic fibres and cotton cannot be increased in the future, thus creating a gap between the fibre demand and the production. One candidate to fill the gap is the viscose fibre which production covers currently 96 % of the man-made cellulosic fibres. However, the viscose process is challenging due to the occupational health and environmental issues relating to the use of carbon disulphide.

As a consequence, there is a need of such fibres that are made from the renewable resources (vs. oil), do not compete with the food production (as cotton) and do not need hazardous chemicals (as viscose).

This work introduces a new cellulosic fibre process which attempts to respond the need described. In the process, a dissolving grade wood pulp is treated with enzymes, dissolved in water-based solvent and regenerated to fibres using a wet spinning method. Thus the raw material is renewable, which growth does not use arable land, and the carbon disulphide needed in the viscose process is here replaced with enzymes.

Dissolution of the enzyme-treated pulp into aqueous sodium zincate and the regeneration of the solution into cellulosic fibres were demonstrated first. Thereafter, the preparation of the spin dope and the wet spinning of the fibres were studied in more detailed. The enzyme-treated cellulose was dissolved either by mixing-procedure or by freezing-thawing cycle. Both methods resulted in high quality solution for the spinning trials. However, the alkali ratio of the solution prepared by freezing-thawing cycle was lower (1.1 vs. 1.3) thus requiring less sulphuric acid during the coagulation. The spinneret draw ratio and the stretching ratio during the spinning exhibited negative correlation. This was due to the rapid coagulation of the solution. The coagulation rate decreased significantly when the sulphuric acid spin bath was replaced with an acetic acid bath. Equally, the stretching ratio of the fibres increased, but unexpectedly the tenacity of the fibres did not increase. It was found that the acetic acid spun fibres shrunk during the drying and thus the orientation gained during the stretching was lost.

Another route to modify the fibre properties was explored through the chemical modification of enzyme-treated cellulose with allyl glycidyl ether. The treatment resulted

in the pulp with low amount of 3-allyloxy-2-hydroxypropyl groups (DS_A 0.05) which had higher solubility in aqueous sodium zincate than the un-substituted enzyme-treated pulp. The 100 % solution from the modified pulp did not form fibres in acidic bath, thus the fibres were spun from the solutions containing 25 % and 10 % of the modified pulp. The 3-allyloxy-2-hydroxypropyl groups provide reactive C=C double bonds in the fibre structure, thus allowing the further functionalization to gain new properties for the fibres.

It was shown that the production of regenerated cellulosic fibres in an environmental manner is possible, thus providing one option to fill the gap between the fibre demand and the production in the following decades.

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Preface

This thesis was carried out in the Department of Materials Science at Tampere University of Technology. It is a fruit of interesting work which started already in 1990's. Part of the work was done in the EUFP6 financed Biocelsol (NMP2-CT-2003-505567) project (2004-2007) and part in the TEKES financed FuBio Cellulose program of the Finnish Bioeconomy Cluster FIBIC (2011-2014).

I would like to express my gratitude to my supervisor Professor Pertti Nousiainen for his guidance, patience and support throughout these years. I am extremely grateful to my colleague and co-author Taina Kamppuri for her friendship, enthusiasm, feedback and many conversations when we puzzled over various issues of this work. I warmly thank Maija Järventausta for her friendship and expert assistance in the laboratory with many suggestions to improve the practises. I also want to thank my third team mate Esa Leppänen for his skills in fibre spinning and in creating the devices needed for the practical work.

I would like to thank all my co-authors abroad and in Finland for pleasant cooperation and for their contribution in papers. I also want to thank the personnel of the Department of Materials Science for an enjoyable and inspiring working atmosphere. I am grateful to Maritta Suoniemi for her assistance in the practical concerns.

Finally, I wish to express my gratitude to my family for their support.

Tampere, August 2015

Marianna Vehviläinen

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List of Symbols and Abbreviations

AFEX	ammonia freeze-explosion
AGE	Allyl glycidyl ether
AGU	Anhydroglucose unit
AHP	3-allyloxy-2-hydroxypropyl
bar	atmospheric pressure on Earth at sea level, equal to 10 000 Pa
CBH	cellobiohydrolase
CH_3COOH	Acetic acid
CP/MAS	cross polarization magic angle spinning
CS_2	carbon disulphide
DMAc	dimethylacetamide
DP	degree of polymerisation
DP_n	number average degree of polymerisation
DP_v	viscosity average degree of polymerisation
DP_w	weight average degree of polymerisation
DS_A	degree of 3-allyloxy-2-hydroxypropyl substitution
dtex	deci tex, linear density of fibre, mass (g) / 10 000 m
EC	Enzyme Commission
EG	endoglucanase
FESEM	field-emission scanning electron microscope
FTIR	Fourier transform infrared spectroscopy
H_2SO_4	sulphuric acid

HWM	high wet moulus
IUPAC	International Union of Pure and Applied Chemistry
LiCl	lithium chloride
LiOH	lithium hydroxide
MCC	microcrystalline cellulose
Mt	Million tonnes
M_w	weight average molecular weight
M_n	number average molecular weight
NaOH	sodium hydroxide
Na_2SO_4	sodium sulphate
NH_3	ammonia
NMMO	N-methylmorpholine-N-oxide
NMR	nuclear magnetic resonance
P	primary wall
PDI	polydispersity index, M_w/M_n
PEG	polyethylene glycol
tBuOH	tert-butanol
S	secondary wall
S1	outer layer of secondary wall
S2	middle layer of secondary wall
S3	inner layer of secondary wall
SAXS	small angle x-ray scattering
T	titre, linear density of fibre

TCF	total chlorine free
WAXS	wide-angle x-ray diffraction
ZnO	zinc oxide
$Zn(OH)_4^{2-}$	tetrahydroxozinc complex ion

List of Publications

I. Vehviläinen M, Kamppuri T, Rom M, Janicki J, Ciechanska D, Grönqvist S, Siika-aho M, Elg Christoffersson K and Nousiainen P (2008) Effect of wet spinning parameters on the properties of novel cellulosic fibres, Cellulose 15:671-680

II. Vehviläinen M, Kamppuri T, Nousiainen P, Kallioinen A, Siika-aho M, Elg Christoffersson K, Rom M and Janicki J (2010) Effect of acid and enzymatic treatment of TCF dissolving pulp on the properties of wet spun cellulosic fibres. Cellulose Chem.Technol., 44(4-6), 147-151

III. Vehviläinen M, Kamppuri T, Grönqvisti S, Rissanen M, Maloney T, Honkanen M and Nousiainen P (2015) Dissolution of enzyme-treated cellulose using freezing-thawing method and the properties of fibres regenerated from the solution. Cellulose 22(3), 1653-1674, doi:10.1007/s10570-015-0632-0

IV. Vehviläinen M, Kamppuri T, Setälä H, Grönqvist S, Rissanen M, Honkanen M and Nousiainen P (2015) Regeneration of fibres from alkaline solution containing enzyme-treated 3-allyloxy-2-hydroxypropyl substituted cellulose. Cellulose 22(4), 2271-2282, doi: 10.1007/s10570-015-0647-6

Author’s contribution

The author planned all the experiments, and participated the practical work as a team member. The author digested and interpreted the results and prepared the manuscripts. The co-authors delivered enzyme-treated and chemically substituted pulps (VTT, Finland), characterised the samples and commented the manuscripts.

1 Introduction

1.1 Background and research environment

The global population is growing steadily which causes increasing demand for food and consumables (Malik et al. 2014). It is estimated that in 2050 the global production should be 60 % higher than in 2007 to be equal with the consumption (Alexandratos and Bruinsma 2012). Textiles are an important group of consumables. Currently, 64 % of the fibres produced globally are synthetic man-made fibres, 35 % are cellulose-based fibres including cotton and man-made cellulosic fibres, and the rest consists of wool and other natural fibres (CIRFS 2015). The advantages of the cellulosic fibres over the synthetic oil-based fibres are their high hydrophilicity and breathability, comfortable touch, biodegradability and the use of renewable resources. Cotton fibres cover the major part (89.5 % in 2011) of the textiles made from the cellulose-based fibres (Kranthi et al. 2011).

Besides the growth of population, the other driving force for the increasing demand of textiles is the improving standard of living in the developing countries. Since 1960, the per capita fibre consumption is increased from 4.9 to 12.7 kg (CIRFS 2015; PRB 2013). Following the same trend it is estimated that the consumption exceeds 15.5 kg per capita by 2030 with the global fibre production of 135.4 million tons (Figure 1). The production of synthetic fibres has increased dramatically since the end of 1990’s, and seems currently to response the best for the total fibre demand. The production of cotton has fluctuated from year to year and has increased only moderately. The production of man-made cellulosic fibres has started to increase during the past ten years after a steady decrease since the mid 1970’s. Even though the share of synthetic fibres from the total production has increased constantly, it is not likely that the growth can continue with the same pace. This is due to the declining oil resources which increases the prices, and the lack of sustainable recycling of the synthetic polymers which is an environmental issue (Tsoskounoglou 2008; Moore 2008). The limited production of synthetic fibres will increase the demand for other fibres. With the growth index derived from the production figures of cotton fibres from the period 1920–2013, it is predicted the production will be 34 million tons in 2030. This is 31 % more than cotton was produced in 2014 (USDA 2014). However, the cotton production has serious obstacles; the area of arable land used for the cultivation cannot be increased due to the equally increased demand for food. Moreover, the land area is constantly decreasing due to the urbanization and soil erosion, and due to the farmers that switch to the more profitable food production (Hämmerle 2011). Thus, the only way to increase the production of cotton is to increase the yield (kg/hectare). In 2014, the average yield was 801 kg/ha (USDA 2014). It is predicted that in 2030 the yield could be 925 kg/ha due to the cultivation of genetically modified cotton (Hämmerle 2011). However, even with the increased yield and the current area (32.7 million hectares) (USDA 2014) the production of cotton will only be 30.2 Mt and could not be increased from that in the future.

Currently, the cellulosic man-made fibres fulfil the requirement of utilising the renewable resources the best. Thus it is foreseen that their production increases even more rapidly than estimated based on the development during the past 13 years.

The industrially produced man-made cellulosic fibres include viscose, lyocell and cupro. The global production of these fibres was 5.7 million tons in 2013 (CIRFS 2015). The production capacity of lyocell fibres increased to 0.22 million tons at the end of 2014 (Guldt 2014) covering now 3.9 % of the cellulosic man-made fibres produced annually. The share of cupro fibres is only marginal, thus the viscose fibres are the most important man-made cellulosic fibres at the moment.

Industrial production of the viscose fibres started in the early 1900’s. The first 30 years included process development, IPR protection, business arrangements and price agreements between the players. After the expiry of the first patents in the 1930’s the production volumes began to increase rapidly (Woodings 2001). The steady growth lasted until 1973 when the production reached 3.9 million tons. However, due to the emerging production of the synthetic fibres, the demand for the viscose fibres started to decline. It had also come evident that the viscose process suffers from the occupational health and environmental issues. These are due to the use of carbon disulphide (CS_2) and the formation of its toxic degradation and reaction products which are harmful to humans even at low exposure rates (Tolonen et al. 1975; Kuo et al. 1997; Newhook and Meek 2002). The dangerous nature of carbon disulphide had led to the tighten legislation of the workers' exposure rates and of the recovery systems of the factories.

The predicted decline in the production of synthetic fibres, stagnating production of cotton fibres and the downside issues of the viscose process have boosted the research in the field of man-made cellulosic fibres. However, there is still the need to produce cellulosic fibres in an economic and environmentally viable manner. This work introduces a process, which attempts to fulfil the requirements for the new cellulosic fibre process.

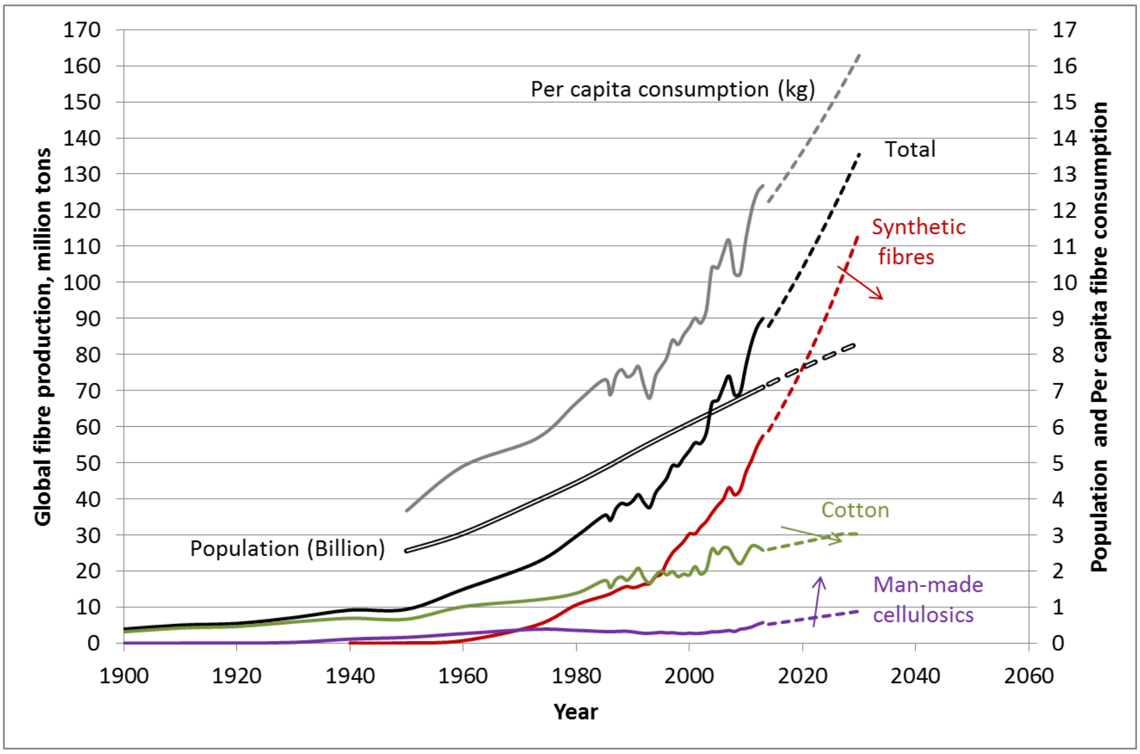


FIGURE 1 Global production of textile fibres, population and per capita fibre consumption. Dotted lines indicate estimated values derived from realised period and arrows indicate predicted change of course (CIRFS 2015; International Data Base 2013).

1.2 Objectives and scope

The research problem identified is '*How to produce cellulosic fibres in an economic and environmentally acceptable manner*?' The objective of the work was to study a process for manufacturing cellulosic fibres that would be capable to contribute part of the future demand for the textile fibres.

The process is based on the enzymatic treatment of cellulose and the dissolution of treated cellulose in a water-based solvent. The dissolved cellulose is shaped into the cellulosic fibres using a wet spinning method. The process does not use any environmentally harmful chemicals nor produces any such kind of by-products. Figure 2 outlines the main process steps of the method.

The research questions in this work were:

1. Is it possible to dissolve cellulose in a water-based solvent in a way the fibre forming process is successful using a wet spinning method?
2. How to increase the cellulose concentration of the spin dope?
3. Is it possible to decrease the alkali concentration of the spin dope?
4. How to increase the tenacity of the fibres?
5. How to modify the properties of the fibres?

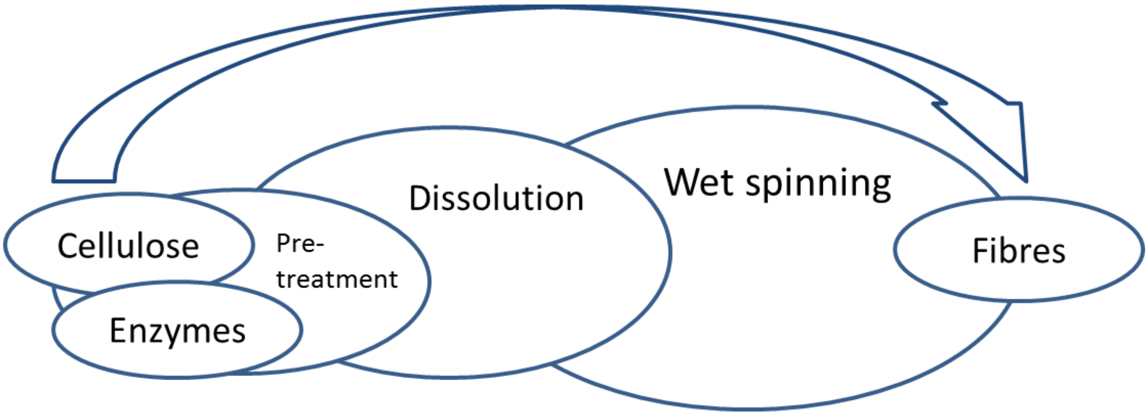


FIGURE 2 Main process stages for producing fibres from enzyme-treated cellulose.

1.3 Research process and dissertation structure

This work is part of the long-term co-operation between the Finnish (prof. Nousiainen) and Polish (prof. Struszczyk) research groups in which the author joined in early 1990's. The origin of the research was a discovery made in late 1980's that cellulose became directly alkali soluble after the enzymatic treatment (PL 167519, FI 107335). The discovery was remarkable since it is well known that cellulose is difficult to process because of its limited solubility in common solvents. The early experiments were done by using an experimental enzyme mixture from *Aspergillus niger* strain. In this work the commercial cellulase mixtures secreted by e.g. *Trichoderma reesei* have been used.

Besides the bilateral co-operation between the Finnish and Polish groups, a large EU funded research project under FP6 (NMP2-CT-2003-505567) was carried out in 2004–2007. The name of the project was Biocelsol – *Biotechnological process for manufacturing cellulosic produts with added value*. Since the project, the name 'Biocelsol' is established for the fibres prepared from the enzyme-treated cellulose, as well as for the process to prepare these fibres.

The enzymatic treatment of cellulose is a crucial step in the entire process as it determines the degree of polymerisation and the shape of the molecular weight distribution curve of the treated cellulose. These raw material properties along with the type of the solvent and the dissolution conditions play the major role in controlling the properties of the cellulose solution. Providing these prior stages result in a solution that is stable during the filtration and deaeration one can continue for the spinning trials.

The work comprises four publications that focused on the research questions. The theoretical background includes basics of cellulose, enzymes, cellulose dissolution and wet spinning. The cellulose dissolution in aqueous NaOH-based solvents is reviewed in more detail. The special considerations regarding the method studied here are also briefly enlightened. The Experimental section summarises the materials and methods that relate to the results presented in the next chapter. The procedures used for preparing the cellulose solutions are given in more detail. The Results section provides the main results of each publication concerning the research questions. The results are discussed based on the theoretical implications, additionally some practical implications are suggested, the reliability and validity of the results appraised, and the future research recommended.

2 Theory

2.1 Cellulose

Cellulose is a semicrystalline glucan homopolysaccharide consisting of glucose units linked together through the 1 and 4 carbon atoms with a β-glucosidal linkage (Figure 3). Each glucose unit has three hydroxyl groups which have different polarities (Kamide 2005). The number of the glucose units (AGU) per molecule may vary over a wide range from 100 up to 10000 depending on the source of the cellulose (Ward 1946). The molecular weight of one AGU is 162.15 g mol^{-1}.

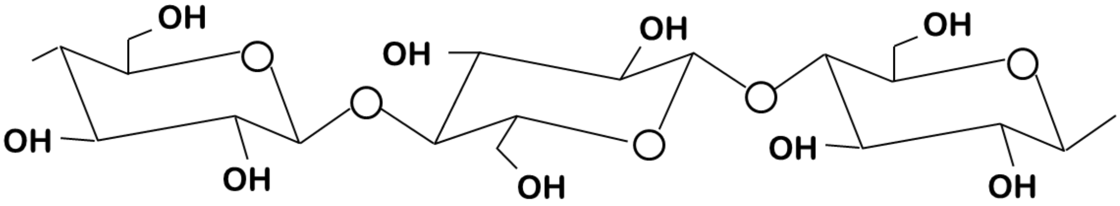


FIGURE 3 Chemical structure of cellulose.

In native cellulose the glucan chains are packed parallel to each other forming the Cellulose I crystal structure with two crystal allomorphs, Iα and Iβ (Nishimura et al. 1991; Focher et al. 2000; Nishiyama et al. 2002). The allomorphs differ from each other in unit cell sizes being either a one-chain triclinic (Cell Iα) or a two-chain monoclinic unit cell (Cell Iβ) (Nishiyama 2009). The higher plants, such as wood cellulose is composed of both allomorphs. The hydroxyl groups are situated in equatorial position relative to the chain, thus enabling the formation of hydrogen bonds within the chain (intramolecular) and between the adjacent chains in the same sheet (intermolecular), but not in between the sheets (intersheet). The forces holding the cellulose sheets together are hydrophobic interactions, weak C-H…O bonds and van der Waals forces (Nishiyama et al. 2002; Bergenstråhle et al. 2010; Gross and Chu 2010). The energy of intermolecular hydrogen bonds in cellulose is estimated to be 207.0 kJ mol^{-1} (Bochek 2003).

The various chemical treatments of native cellulose change the position of the chains and produce different polymorphic lattice structures known as Cellulose II, III, IV (Stipanovic and Sarko 1976; Krässig 1993). The most common crystal structure of the modified cellulose is Cellulose II in which the chains are packed in an antiparallel order (Stipanovic and Sarko 1976). The Cellulose II is forming e.g. due to the sodium hydroxide treatment of Cellulose I. The intermediate structures found during the complete conversions from Cellulose I to Cellulose II are the Na-Cellulose I, II, III, IV, V and Q crystal forms (Calkin 1935; Sobue 1940; Nishimura et al. 1991). Change from the Cellulose I to the Cellulose II polymorph is permanent, thus the crystalline form of the regenerated fibres is Cellulose II.

Cellulose is synthesised by the all higher plants and a wide variety of other organisms (Klemm et al. 1998). *C*ommercially the most important source of cellulose is wood which contains 40-50 % of cellulose as the dry weight. The other compounds of wood are lignin and non-cellulosic polysaccharides (hemicellulose) (Alén 2000). The cellulose molecules are packed tightly to each other in the form of fibrils with the diameters of 30-35 Å. The fibrils are the subunits of the microfibrils, whose diameter is about 250 Å (Hult et al. 2001). The microfibrils are organised in layers in the cell wall of a wood fibre. The outermost layer is called the primary wall (P) in which the microfibrils form a rather loose structure. Underneath the primary wall is the secondary wall with three distinct layers (S1, S2 and S3). In each layer the microfibril lamellas are organized in a woven or felted texture (Wardrop 1957) such as the angle between the lamellas and the cell axis is smaller in the S3 layer than in the S2 layer. Furthermore, the S1 layer shows a different pattern. (Roelofsen and Houwink 1953; Houwink and Roelofsen 1954; Alen 2000)

Lignin is located between the microfibrils in the cell wall (Wardrop 1957), and between the cells in the wood material where it forms a matrix to cement the cells together (Gullichsen 2000).

2.1.1 Separation of cellulose from wood

In order to utilise cellulose from native wood fibres the lignin and other non-cellulosic materials must be removed from it. Purification is carried out in the chemical pulping process which results in degradation, chemical modification and dissolution of the non-cellulosic substances (Holzer 1954; Gullichsen 2000). Most of the lignin, 70 - 80 %, is located in the secondary wall of wood fibre, which is the thickest of the cell wall layers (Donaldson 2001). The delignification proceeds preferentially from the different parts of the cells, which causes changes in the lignin distribution in the pulped fibre compared to the original wood fibre. The parameters of the pulping process determine the mechanism of the lignin removal as well as the properties of the purified cellulose fibres. The kraft pulping process with the mixture of sodium hydroxide and sodium sulphide is a dominant method for producing paper grade pulps, while the acid sulphite process with bisulphide as the delignifying medium, and the prehydrolysis kraft process are used for producing the dissolving grade pulps. (Sihtola 1977; Gullichsen 2000; Sixta et al. 2013)

The final step for producing high quality chemical pulp is the bleaching. For the papermaking fibres it is important to obtain high brightness while preserving the strength of the fibres. Instead, for the dissolving grade pulp the primary objective is to remove contaminants and hemicellulose, and to set the degree of polymerisation of cellulose within the desired range.

2.1.2 Structure of pulped cellulose fibres

The effect of pulping on a single cell is a reduction in both the inner and the outer perimeters of the cell, thus, the inner perimeter shrinkage is notably larger than the outer one. This results in a significant growth in the cell wall thickness during the pulping process. This expansion is caused by a delayed movement of the peripherally located fibrils toward the lumen, and simultaneously the new pore volume is created in the cell wall (Stöckmann 1971). The primary wall of the fibres is removed almost completely during the dissolving pulp process, thus uncovering the secondary wall S1 (Jurbergs 1960). The hemicellulose, about 3 – 10 %, in the dissolving pulp fibres is placed mainly in the middle layer of the secondary wall (S2) (Meier 1961; Marchessault et al. 1967). However, pronounced amount of xylan is precipitated on the surface of pulped fibres as revealed by the enzymatic peeling method (Sjöberg et al. 2005).

2.1.3 Reactivity of cellulose fibres

The raw material and the conditions during the pulping process determine the supermolecular structure of the cellulose fibres and their reactivity towards the chemicals used in the further processes. The reactivity is defined as the accessibility of the functional hydroxyl groups of cellulose, thus the more available the hydroxyl groups the more reactive the cellulose (Krässig 1993). In the most cases, cellulose must be pretreated to increase its reactivity. Factors affecting the reactivity include porosity, surface area, particle size, structure of fibrils, crystallite size variation, the extent of the different hydrogen bonds, lignin content and the extractives content (Tsao 1978; Schleicher and Kunze 1988; Krässig 1993; Klemm et al. 1998).

The pore volume and the shape of the pores determine the cellulose accessibility for the different reagents. The accessibility increases with the increasing pore volume. Splitting of the hydrogen bonds between the fibrils is a common effect of most of the activation processes and causes the improved transport of the substances and the more homogeneous reactions. A decrease of the degree of crystallinity of the cellulose has a positive effect for many cellulose reactions. A connection has been found between the degree of crystallinity and the enzymatic degradation of cellulose. The enzymatic degradation increased with decreasing degree of crystallinity. (Schleicher and Kunze 1988).

2.2 Enzymes

An enzyme is a large molecule made up of a folded amino acid chain. There are all together 20 different amino acids (residues), whose arrangement and number in the chain, and the three-dimensional structure due to the cross-linking of the chain, determine the function of the enzyme (Phillips 1966). The enzymes are substrate-specific catalysts which means they act mainly on the one type of substrate. The enzymes are divided into the six main classes according to the reaction they catalyse (IUPAC). All enzymes which initiate hydrolysis on the substrates belong to the Class 3 (Hydrolases) which is further divided into 13 subclasses based on the type of the bond the enzyme is specialised for.

The enzymes that are capable of hydrolysing cellulose by breaking the β-1,4-linkage between the glucose units are called cellulases. According to IUPAC classification they belong to the EC 3.2.1 subclass (Glycosidases) and more specifically to two sub-subclasses depending on their mode of action. The exoglucanases, which release sugar units from the chain end belong to the EC 3.2.1.91, and the endoglucanases that are capable of breaking the bond in the middle of the chain belong to the EC 3.2.1.4 sub-subclass. (Hildén and Johansson 2004)

Another classification of enzymes is based on their three-dimensional similarities, together with the specific features of sequences, substrate specificity and the reaction mechanism (Henrissat 1991; Henrissat and Davies 1997). It has been possible to identify the amino acid residues which are responsible for the catalytic action, as well as their location in the protein. Most of the cellulases have a large domain with the catalytic residues, and a smaller domain which binds to the substrate (Tomme et al. 1988). The shape of the catalytic domain varies according to the reaction to which it is specialised. There are several different shapes including e.g. a cleft, which is found in the endoglucanases and a tunnel, which is found in the exoglucanases (Davies and Henrissat 1995; Alzari et al. 1996).

2.2.1 Enzymatic action on cellulose

Degradation of the plant biomass in nature is based on a synergistic action of several different types of enzymes, which are secreted by the fungi and bacteria. A filamentous fungus *Trichoderma reesei* is one of the most studied cellulolytic fungi, which produces at least six genetically different cellulases and two β-glucosidases. These are cellobiohydrolases (CBH) I and II (EC 3.2.1.91), endoglucanases (EG) I, II, III and V (EC 3.2.1.4) and β-glucosidases (BGL) I and II (EC 3.2.1.21) (Knowles et al. 1987; Kleywegt et al. 1997; Häkkinen et al. 2012). The other *T.reesei* enzymes except the EG III have a bi-functional domain structure with a large catalytic domain and a smaller cellulose binding domain (CBD). EG III does not have the CBD (Sandgren et al. 2001).

According to a simplified model the enzymatic degradation of cellulose is started by the endoglucanases which randomly cut the internal glucosidic bonds within an unbroken glucan chain. The newly created non-reducing chain ends then become the substrate for the cellobiohydrolases, which cleave the cellobiose dimers from the glucan chain and release them into the solution. The hydrolysis of cellulose into the glucose end product is completed by the β-glucosidase, which splits the cellobiose into the glucose monomers. (Reese 1955)

Adsorption of the cellulases on a solid substrate is necessary for the effective enzymatic action (Medve et al. 1994). The relatively large size of the enzymes and the compact structure of the cellulose restrict the adsorption, and thus slow down the action of enzymes (Grethlein 1985; Gama et al. 1994). In order to enhance the adsorption of the enzymes the cellulosic material is subjected to different kinds of pretreatments. It has been found that the pretreatment which affects only the molecular structure of cellulose, e.g. irradiation (Focher et al. 1981), is not effective to improve the kinetics of the hydrolysis reaction. Instead, the treatment which causes structural modification of the cellulose, e.g. mechanical agitation (Mooney et al. 1999; Grönqvist et al. 2014, 2015a and 2015b; Virtanen et al. 2015), steam explosion (Wong et al. 1988) or swelling (Focher et al. 1981) are beneficial for the enzymatic action. Thus, the key factor to the rapid and complete enzymatic hydrolysis of the cellulose is the pretreatment which opens up the cellulose structure and increases the surface area accessible to the enzymes (Saddler et al. 1982; Schleicher and Kunze 1988)

2.3 Dissolution

Dissolution is kinetic process where the forces that hold the crystalline structure are overcome and results in the disintegration of the structure to the molecules (Burchard 2003). The forces include the hydrogen bonds within the chain (intramolecular) and between the neighbouring chains (intermolecular), as well as the van der Waals forces and hydrophobic forces. The dissolution occurs when such a solvent is introduced to polymer which is able to disturb the mutual interaction of the polymer molecules. The solubility of polymer depends on the thermodynamic energies involved, such as a change in enthalpy (ΔH) and a change in entropy (ΔS) of the system. The remainder of ΔH - T ΔS at constant pressure and temperature is equal to the free energy change, (Gibbs energy, ΔG) which shows a negative value when the dissolution takes place. The negative value means that the reaction happens thermodynamically spontaneously, if the value is positive, no reaction (dissolution) occurs (Miller-Chou and Koenig 2003). The change in enthalpy corresponds to the interaction between the polymer and the solvent molecules, and the change in entropy relates to the changed molecular organisation due to the dissolution. The dissolution can occur only at the area where the solid and the solvent are in contact with each other. The parameters that affect this contact include mixing, the specific surface area of polymer, concentrations of the solid and solvent, molecular mass of polymer, temperature and catalysts (Burchard 2003).

2.3.1 Cellulose solvents in general

The cellulose solvent systems can be categorised to three groups that are 1) Dissolution of cellulose after chemical modification, 2) Dissolution into aqueous systems, and 3) Dissolution in non-aqueous, non-derivatising media (Liebert 2010). Commercially the most important cellulose dissolving system, the viscose method, belongs to the first group. It utilises the chemical modification of alkali treated cellulose with carbon disulphide (CS_2). The reaction results in cellulose xanthate which is an intermediate product in the viscose process. The cellulose xanthate is dissolved in sodium hydroxide and the solution regenerated in acidic bath to the cellulosic products. (Wilkes 2001) The first aqueous non-derivatising solvent for cellulose (Group 2), cuprammonium hydroxide, was discovered already in 1897 (Liebert 2010). It is still used for the production of cupro fibres and dialysis membranes. However, the production volumes are low due to the high cost of the raw materials (Kamide and

Nishiyama 2001). The other Group 2 solvents include complexes of transition metal (e.g. cadmium, cobalt, zinc or nickel) with amines, ammonia or tartaric acid; ammonium hydroxides; *alkali hydroxides*; inorganic salts; inorganic molten salt hydrates and thiocyanate-containing systems (e.g. ammonia/ammonium thiocyanate) (Liebert 2010; Heinze and Koschella 2005). The non-aqueous, non-derivatising media (Group 3) include molten organic salts (ionic liquids) and amine oxides (N-methylmorpholine-N-oxide, NMMO) as well as polar, aprotic and organic liquids and salts (Liebert 2010).

Apart from the viscose, cuprammonium hydroxide and NMMO methods, the chemicals that dissolve cellulose the best are not used in industrial scale (Hergert et al. 1978; Turbak 1984; Cuculo et al. 1994; Sakamoto 1994; Saalwächter et al. 2000; Hattori et al. 2004; Fisher et al. 2003). This is due to the heavy metals, amines and toxic chemicals which make the recovery and recycling difficult. Thus, the methods are unattractive for industrial utilisation. Contrary, *the alkali hydroxides* are simple and cheap chemicals without environmental issues. However, the complete dissolution of cellulose in alkali hydroxides without prior modification and/or use of additives is limited to the low molecular weight or low cellulose concentration. To overcome these limitations, lot of studies have been carried out to understand the cellulose dissolution mechanism in aqueous environment, and to optimise the system for industrialisation.

2.3.2 Interaction of cellulose and alkali hydroxides

The treatment of cellulose with aqueous sodium hydroxide to form alkali cellulose is one of the oldest and most important commercial reactions of cellulose. Depending on the concentration and temperature of NaOH the cellulose undergoes both physical and chemical changes. The physical changes include swelling (Nicoll and Conaway 1946) and partial dissolution (Davidson 1936), and the chemical change includes the transformation of the crystal lattice form (Calkin 1935; Sobue 1940; Sisson and Saner 1941; Sarko and Muggli 1976; Nishimura et al. 1991; Nishiyama et al. 2000). The swelling is accompanied by the absorption of preferential amount of sodium hydroxide which extent depends on temperature. This can be visualised by plotting the curves of alkali absorption in the function of NaOH concentration at different temperatures. The absorption curves of regenerated cuprammonium cellulose had maxima which occurred at NaOH concentrations between 10-12 %. The maximum absorption tripled when the temperature decreased from 40 ºC to 5 ºC. The extent of cellulose swelling was the highest at the same sodium hydroxide concentration at which the maximum absorption occurred (Nicoll and Conaway 1946; Davidson 1934). The same applied in dissolution; Davidson (1934) showed that the proportional dissolution of acid hydrolysed cellulose at different temperatures varied in the function of NaOH concentration. The highest solubility (94.6 %) was obtained in 9.7 % NaOH at -5 ºC.

The swelling behaviour of cellulose in different sodium hydroxide concentrations is due to the type of interaction (inter- or intra-micellar) between the cellulose and sodium hydroxide. The x-ray pattern was shown to change gradually from Cell I (native cellulose) to Na-Cell I (alkali cellulose) when the sodium hydroxide concentration increased from 10.3 % to 14.4 % (Calkin 1935; Kamide et al. 1990). As a consequence, the swelling of cellulose in aqueous sodium hydroxide below 12 % takes place merely between the micelles, whereas with higher than 12 % NaOH the solution absorbs also inside the micelles. If native cellulose (Cell I) is treated with more concentrated aqueous sodium hydroxide (>23 %) at 60-100 ºC a new x-ray pattern (Na-Cell II) is obtained (Nishiyama et al. 2000). A reversible transformation of Na-Cell I to Na-Cell III occurs due to drying and rewetting. Moreover, Na-Cell IV, Na-Cell V, Na-Cell VI and Na-Cell Q were obtained with different procedures (Nicoll and Conaway 1946; Krässing 1993). Sobue (1940) combined the effects of temperature and sodium hydroxide concentration regarding the cellulose lattice changes and derived the cellulose – NaOH – water ternary phase diagram (Figure 4). Interestingly, the narrow area named Na-Cell Q coincides with the conditions under which the cellulose dissolves, found previously by Davidson (1934, 1936 and 1937).

The change in x-ray pattern due to the alkali treatment is caused by the changes in the cellulose chain packing (from parallel to antiparallel) and in the unit cell dimensions. (Stipanovic and Sarko 1976; Nishimura et al. 1991; Nishiyama et al. 2000; Lagan et al. 2001).

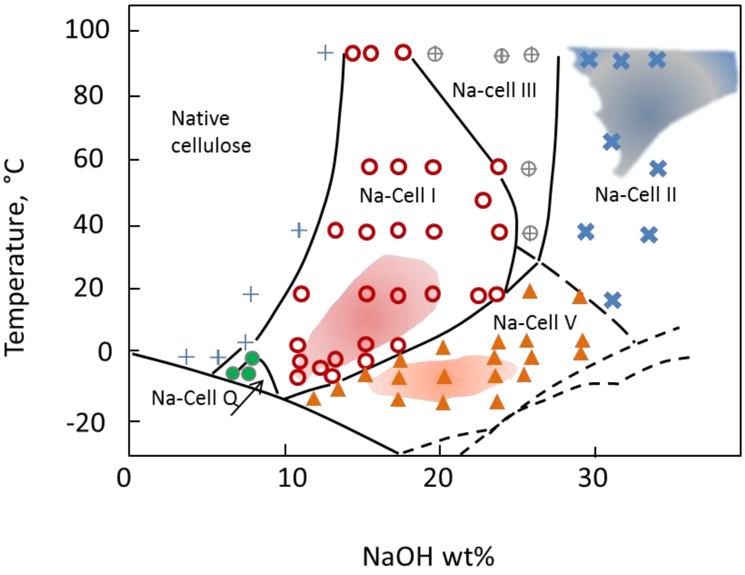


FIGURE 4 Changes in alkali cellulose crystal lattice form due to temperature and concentration of alkali in solution (Sobue 1940) .

2.3.3 Dissolution of cellulose in aqueous systems

The solubility degree of cellulose in an aqueous environment is controlled by the characteristics of the cellulosic material, properties of the solvent, temperature and mechanical agitation. The most important inherent property is the DP of cellulose. It is the main obstacle when preparing high quality cellulose solution for further processes (Klemm et al. 2005; Le Moigne and Navard 2010). The long linear molecular chains that are attached to each other by hydrogen bonds and hydrophobic stacking forces are difficult to separate to form homogeneous solution. Often a compromise between the DP of cellulose and its concentration in an aqueous solution is required. Moreover, the stability of the alkaline solution towards gelation is challenging in most cases.

The alkali hydroxides which are capable of dissolving cellulose are based on sodium hydroxide and lithium hydroxide (Davidson 1934; Yamashiki et al. 1988; Kamide et al. 1992; Xiong et al. 2013). The optimal NaOH concentration was found to be 9 wt% and LiOH concentration 5.8 wt%, both having the same molarity, 2.5 M (Yamashiki et al. 1988). The anion OH^- was shown to break the intra- and intermolecular hydrogen bonds of cellulose (Yamashiki et al. 1988), which was suggested to follow by the accumulation of Na^+ and Li^+ cations on the negatively charged cellulose chains (Xiong et al. 2013) resulting in the dissolution of cellulose.

Kamide et al. (1984) obtained a clear correlation between the increased solubility of cellulose in sodium hydroxide and decreased molecular weight of cellulose. They showed by the deuteration IR and ^{13}C NMR studies that the destruction of the intramolecular hydrogen bonds of cellulose had significant contribution in the dissolution. Kamide and Okajima (1987) developed a steam explosion method which was claimed to break the intramolecular hydrogen bonds especially between the O3H and O5 and thus produced cellulose which dissolved in sodium hydroxide without any other modification (Yamashiki et al. 1990a; 1990b; 1990c; Kamide et al. 1992). The authors also pointed out that if cellulose I is treated to obtain cellulose II and the both have the same amount of intramolecular hydrogen bonds, the cellulose I dissolves more. This is due to the denser three dimensionally structure of the cellulose II solid as compared to the cellulose I, which thus would require larger number of intramolecular hydrogen bonds to be destructed for the solubilisation. Laszkiewicz and Cuculo (1993) confirmed the relationship between the amount of intramolecular hydrogen bond and the solubility in NaOH using samples having the cellulose I and III crystalline forms. Further, Isogai and Atalla (1998) proved that the crystal type or degree of crystallinity of the cellulose sample did not affect its solubility in aqueous NaOH, providing the DP was around the levelling-off value (200). With increasing DP the solubility of differently treated samples varied from each other. However, the dominant factor in the dissolution was the long-ranged order of the structure not the DP. For example, cotton linters either mercerised with 17.5 wt% NaOH or dissolved in cuen and regenerated from that had the same crystal form (cellulose II), the same crystallinity index (50) and the same DP_v (800 and 750). However, the mercerised sample had the solubility degree of 32 % while the regenerated sample dissolved completely (if not previously dried). The authors concluded that this was due to the decreased long-range order of the structure which was a result of the prior dissolution in a media which dissolved cellulose completely and regeneration from that. They also speculated that if the length of the units is less than 100 nm which corresponds to the length of a cellulose chain having 200 anhydroglucose units, the cellulose is soluble. Instead, when the units are larger they have a long-range order, which restricts the solubility. The order must be destructed before cellulose dissolves.

Thus it is evident that the dissolution efficiency of aqueous sodium hydroxide and lithium hydroxide is limited to cellulose with low DP and low concentration. In order to enhance the dissolution, certain additives are used in aqueous solvents.

2.3.3.1 Additives

The additives that are used to enhance the solubility of cellulose include zinc oxide (Davidson 1937), urea (Cai and Zhang 2005; Cai et al. 2008; Cuissant and Navard 2006; Egal et al. 2008), thiourea (Zhang et al. 2002; Cai and Zhang 2005), and poly(ethylene glycol) (PEG) (Yan and Gao 2008).

The effect of zinc oxide depends on the concentration of sodium hydroxide and on the ZnO/NaOH molar ratio. Below the NaOH concentration of 2.5M (8.9 %) the effect of ZnO was insignificant, whereas above that the solubility of cellulose increased rapidly (Davidson 1937). The optimum ZnO/NaOH molar ratio was found to be 0.229 in 2.75 M NaOH (equal to ca. 4.6 wt% ZnO / 9.9 wt% NaOH). The solubility had maximum value which increased and shifted to higher sodium hydroxide concentrations with increasing amount of zinc oxide (Davidson 1937). The enhanced solubility of cellulose in the presence of zinc oxide was explained by the formation of hydrogen bonds between the zincate ion ($Zn(OH)_4^{2-}$) and cellulose which are stronger than those between the hydrated NaOH and cellulose (Yang et al. 2011). However, this reasoning does not consider the hydrophobic stacking forces that attach the cellulose molecular sheets firmly together (Nishiyama et al. 2002). The all-atom molecular dynamics simulations showed that the contribution of intersheet forces in cellulose crystals is much stronger than the contribution of hydrogen bonds. Moreover, the strength of the hydrogen bonds reduced significantly when the chains were exposed to water (Gross and Cu 2010). It has been highlighted that the low solubility of cellulose in polar solvents might be due to the hydrophobic interactions (Lindman et al. 2010; Medronho et al. 2012; Medronho and Lindman 2014a; Medronho and Lindman 2014b). Kihlman et al. (2013) showed that the addition of amphiphilic surfactant in NaOH/cellulose or NaOH/ZnO/cellulose solution improved the dissolution rate of cellulose and the stability of the solution. The authors suggest that ZnO charges up the cellulose and the surfactant weakens the hydrophobic interactions.

Addition of urea in aqueous sodium or lithium hydroxide has shown to enhance the dissolution of cellulose. The optimum contents were found to be 7 % NaOH / 12% urea and 4.2 % LiOH / 12% urea (Cai and Zhang 2005). The authors found that LiOH/urea dissolved cellulose with higher molecular weight, thus being better solvent than NaOH/urea. This was confirmed by Xiong et al. (2013) who found by NMR studies that Li^+ hydration ions stabilised cellobiose more than Na^+ hydration ions. Based on the DSC studies urea was not found to have strong interaction with cellulose when added in NaOH (Cai and Zhang 2005; Egal et al. 2008; Isobe et al 2013; Xiong et al. 2014) or in LiOH (Isobe et al. 2013). In spite of that, it clearly increased the crystal swelling as shown by x-ray diffraction, and facilitated the dissolution of cellulose (Isobe et al. 2013). Moreover, Isobe et al. (2013) found that cellulose/LiOH/urea solution was thermally stable at 30 ºC for at least 8 h, whereas the reference solution without urea started to form gel less than one hour. It was suggested that the effect of urea is related to its amphiphilic property which allows it to self-assemble on the nonpolar sites and in that way reduces the hydrophobic interactions (Xiong et al. 2014).

Thiourea has proved to be more powerful additive than urea to increase the alkaline solubility of cellulose. Zhang et al. (2002) found that the optimum solvent composition was 1.5 M NaOH / 0.65 M thiourea (equal to ca. 5.6 wt% NaOH / 4.6 wt% thiourea). The authors suggested based on the NMR analyses that NaOH would break the intermolecular hydrogen bonds of cellulose molecules and thiourea would prevent the association between the molecules thus stabilising the system.

Polyethylene glycol (PEG) is claimed to significantly increase the solubility of cellulose into NaOH. Yan and Gao (2008) were able to dissolve 13 wt% of cellulose into 9 wt% aqueous NaOH containing 1 wt% PEG-2000. The effect of PEG is most likely related to the weakening of the hydrophobic interactions in the system (Lindman et al. 2010).

2.3.3.2 Effect of temperature on dissolution of cellulose

The dissolution temperature of cellulose / aqueous alkali hydroxide has a crucial effect on the solubility of cellulose. It has been shown that the low temperature (from 4 ºC to -20 ºC) facilitates the solubility of cellulose (Davidson 1936; Davidson 1937; Yamashiki et al. 1988; Laszkiewicz and Cuculo 1993; Isogai and Atalla 1998; Cai and Zhang 2005). Moreover, the low temperature of the solution improves its stability towards gelation (Roy et al 2003).

Yamashiki et al. (1988) studied the effect of temperature on the structure of aqueous sodium hydroxide without and with cellobiose. They found many features which showed that the properties of aqueous sodium hydroxide were unique in the concentration range 9 – 12 % compared to the lower or higher concentrations, and at temperatures below 4 ºC compared to the higher temperatures. The findings included plateau in electrical conductivity, which indicated the presence of a metastable state that restricts to some extent the ionic transportations. The changes in proton chemical shift suggested rapid interaction between NaOH and cellulose, as well as the high number of water molecules dissolved in NaOH at the specific concentration range (9 – 12 %) and at low temperature. Furthermore, based on the ^{23}Na chemical shift it was evident that Na^+ ion does not have crucial effect on the dissolution of cellulose, although it was suggested the cellulose interacts strongly with both cationic and anionic species in the solution. Raman spectroscopy showed that the strength of hydrogen bonds was the weakest in the range of 9 - 12% NaOH, and the sudden change in specific rotatory angle of the cellobiose/aqueous alkali solutions suggested that cellobiose might take a specific conformation when the alkali concentration was 9 – 12 % (Yamashiki et al. 1988).

Later on it has been suggested (Lindman and Karlström 2009; Medronho et al. 2012; Kihlman et al. 2013) that the reason for the beneficial effect of lowered temperature in cellulose dissolution is due to the conformational change in molecular structure of cellulose. The hypothesis is based on the bi-functional behaviour of oxyethylene oxide based surfactants which exhibit strongly decreased solubility in water with increasing temperature while at the same time their solubility in hydrocarbons increases. The behaviour is due to the conformational changes of ethylene oxide chains in non-ionic surfactant. Low temperature favours such conformation of $O\text{-}CH_2\text{-}CH_2\text{-}O$ segments around the C-C bond that makes the ethylene oxide more polar and thus solubility in polar solvent is enhanced. Lindman’s group suggest that similar kind of conformational change due to temperature could apply to cellulose also, thus explaining the improved solubility at low temperature

Isobe et al. (2013) studied the dissolution of cellulose in static system containing cellulose/LiOH/urea. They found that cellulose started to dissolve rapidly when the temperature decreased below 10 ºC, i.e. four times more cellulose dissolved at 0 ºC compared to the amount dissolved at 10 ºC. The result clearly shows that the dissolution was driven only by the decreased temperature as no stirring was used.

The structure of alkaline cellulose solutions at low temperature was studied with DSC based on the principle of eutectic mixture (Roy et al. 2001; Egal et al. 2007; Wang et al. 2015). Roy et al. (2001) showed that 20 % aqueous NaOH produced only one melting peak at -35 ºC, whereas the solutions with lower NaOH concentrations (1-15 %) produced two peaks; one at the same temperature as 20 % NaOH (i.e. melting of eutectic mixture) and another one at higher temperature (from -1.2 to -14.1 ºC, melting of ice). This confirmed that the pseudo eutectic model was valid for the NaOH hydrates. The DSC curves of cellulose/NaOH/water mixtures with 5 % cellulose and various NaOH (3-11 %) contents were identical with the corresponding curves of aqueous NaOH without cellulose (Roy et al. 2001). Thus, undissolved cellulose did not have any effect on the melting behaviour of the cellulose/NaOH/water mixture. Instead, when the cellulose/NaOH/water solutions with various cellulose contents (0.5-7.5 %) were studied, it was found that the enthalpy of the eutectic peak decreased with increasing cellulose content (Roy et al. 2001; Egal et al. 2007). Thus, there was a clear interaction between the dissolved cellulose and sodium hydroxide. Based on the decreased enthalpy the minimum amount of NaOH molecules per one anhydroglucose (AGU) that was required to dissolve cellulose was concluded to be four (Egal et al. 2007). The same relationship was found when cellulose/NaOH/urea solutions were studied with the same experimental setup (Egal et al. 2008). However, in both studies unusual correlation between the amount of bound NaOH and the concentration of cellulose was found. It was apparent that much higher amount of NaOH was bound to cellulose at low cellulose concentration compared to the high concentration. The authors (Egal et al. 2007) recalculated the results of Kuo and Hong (2005) and found those to coincidence with their own results. Egal et al. (2007) speculated that the behaviour might be due to the steric hindrance at higher cellulose concentration or due to the complex interaction between the bound and unbound NaOH hydrates in the presence of cellulose which prevents NaOH to participate in the crystallisation of the eutectic mixture. One possible reason for the contradictive NaOH/AGU ratio which the authors did not discuss is the amount of undissolved cellulose in the sample. It is plausible, when considering the reported sample preparation procedure, that the solutions have contained undissolved cellulose which share had increased with increased cellulose concentration. As the undissolved cellulose did not make any change in the enthalpy of eutectic peak as shown by Roy et al. (2001), the recalculation may change the NaOH/AGU ratio of the cellulose/NaOH/water solutions to be more consistent.

The resent results of Wang et al. (2015) with low-substituted hydroxyethyl cellulose (HEC) showed that it was not possible to derive the NaOH/AGU solubility limit from the changes in eutectic enthalpy peaks. They found that the enthalpy of eutectic peak decreased to zero already with 1 % HEC concentration even though the highest concentration dissolved was 7 %. The authors suggested that the phase diagram might be more complicated than considered up to now, since a third peak below the temperature of eutectic peak has occasionally been found, but not included in the studies.

Nevertheless the ratio between NaOH/AGU needs some further research, the thermal studies of cellulose/NaOH/water samples confirmed that there is a clear interaction between cellulose and NaOH. Moreover, the interaction involves NaOH hydrates at eutectic mixture as active compounds to penetrate into the cell wall layers. This is the reason why the solubility of cellulose in aqueous NaOH is favoured by the lowered temperature.

2.3.3.3 Stability of the cellulose solution

Stability of the solution is generally understood as unchanged rheological properties at constant conditions. Gelling means the increase in viscosity until network of different kind of associations restricts the flow of material. Gelling can be reversible (Nyström et al. 1995) or irreversible (Roy et al. 2003; Weng et al. 2004), and it can be induced by time, temperature or chemical agent. The strength of gel is dependent on the molecular structure and concentration of the polymer, as well as total ionic strength, pH and temperature of the system (Mathur 2011). The reversible gel is formed by physical junction which activity can be controlled by e.g. temperature. Thermal gelation and possible phase separation are connected to hydrophobic interaction, which increase with increasing temperature (Lindman and Karlström 2009). An example of cellulosic material exhibiting reversible temperature induced gelation is aqueous solution of ethyl(hydroxyethyl)cellulose (Nyström et al. 1995). Chemical gelling is characterised by covalent cross-links, thus being irreversible. However, irreversible gels can be formed also through physical association. The gelling phenomena is utilised widely e.g. in food industry (Saha and Bhattacharya 2010), pharmaceuticals (Jones et al. 1996) and aerogel processing (Gavillon and Budtova 2008). On the other hand, the gelling of a polymer solution might be adverse if occurring in a too early stage of the process e.g. in fibre spinning.

The alkaline cellulose solutions are very prone to form gel at elevated temperature or with the passage of time, only. The instability is greatly increased with increasing cellulose concentration of the solution and / or increasing molecular weight of cellulose (Roy et al. 2003; Weng et al. 2004; Cai and Zhang 2005; Gavillon and Budtova 2008). This is due to the increased interaction of the molecular chains as the linear molecules tend to have a folded or a random-coil conformation in the solution (Mathur 2011).

The gelation process of solutions is studied by determining the rheological properties of the solutions. The steady-state flow curves show the basic nature of the solution, while gelation is usually studied by the dynamic measurements which involve the effect of time, temperature and sinusoidal strain and stress waves (Mathur 2011). The storage modulus (G') represents the elasticity of the sample and the loss modulus (G'') the viscosity of the sample. The ratio between G''/G' is equal to the tanδ (loss tangent) in which the δ is the phase lag between the sinusoidal strain and stress waves formed in the oscillatory shear test (Pal 2006).

The aqueous solution of 5 % microcrystalline cellulose in 9 % NaOH formed irreversible gel already at 10 ºC with sufficiently long duration. With increased temperature (to 30 ºC) the gelation time decreased rapidly (Roy et al. 2003). The authors suggested that both the hydrogen bonding and hydrophobic associations were involved in gelation. The slight turbidity of the formed gels indicated that the phase separation has also occurred. The thermal gelation of cellulose/NaOH/thiourea aqueous solutions (Weng et al. 2004) was found to proceed through a partial aggregation of cellulose chains that occurred before the gel point, to a formation of an elastic gel network that occurred after the gel point (T>50 ºC). No plateau was observed in G' value indicating the gelation was not caused by chemical cross-links. This was further confirmed by NMR studies where no chemical shifts or peak shapes different from the solution were observed. The WAXD studies showed no crystalline structures, which proved the gelation was due to the random junction between the molecules. ESEM and AFM studies of gels revealed they have phase separated structure with nanoparticles. The authors concluded that the gelation was caused by the destruction of inter- and intramolecular hydrogen bonds of solution leading to the self-association of cellulose chains.

In the case of aqueous alkaline cellulose solution that is prepared for the fibre spinning, it is essential that the solution does not form gel in a too early stage of the process. It has been found that the same additives that increase the solubility of cellulose (ZnO, urea, thiourea), enhance the stability of the solution, as well (Kihlman et al. 2013; Cai et al. 2004; Cai et al. 2007; Jin et al. 2007). Moreover, it is well demonstrated that controlling of the temperature is crucial when preventing premature gelation.

2.3.4 Pretreatment of cellulose

Due to the complex supermolecular structure of cellulose, the material is usually subjected to various physical and/or chemical pretreatments in order to enhance the desired reactions. The physical methods include mechanical treatment, drying, irradiation or thermal processes of cellulose. These methods increase the porosity and the surface area of the cellulose, decrease the particle size (Millet et al. 1975 and 1976; Krässig 1993), decrease the chain length and break the hydrogen bonds (Schleicher and Philipp 1980; Alvira et al. 2010; Henniges et al. 2012; Henniges et al. 2013). The chemical treatments include swelling and degradation processes with strong acids or bases such as sulphuric acid or sodium hydroxide or with other cellulose swelling / dissolving agents or with enzymes (Warwicker 1971; Philipp et al 1977; Krässig 1993; Klemm et al. 1998; Nousiainen et al. 1991).

Irradiation of pulp samples was studied with plasma, electron beams and gamma-rays (Henniges et al. 2012). Plasma treatment was not found to affect the molecular mass of cellulose, whereas the e-beam and gamma radiation degraded the material. The degradation occurred preferentially in high molar mass area. It was apparent that the carbonyl content of the pulps increased with increasing irradiation dose.

Steam-explosion process involves both physical and chemical aspects (Kamide and Okajima 1987; Alvira et al. 2010). Mixture of cellulose and a hydrogen bond-cleaving agent is subjected to a pressure of 10 to 250 atmospheres at high temperature. When the pressure is suddenly released, the water evaporates rapidly and the fibres separate from each other. The hydrogen bond-cleaving agent can be water or different kinds of aqueous solutions. The treatment weakens the intramolecular hydrogen bonds of cellulose, which results in increased reactivity (alkali solubility) of the treated cellulose. In the ammonia freeze-explosion (AFEX) technique (Dale and Moreira 1982) the lignocellulosic material is contacted with a volatile liquid at temperatures less than which degrade sugars (less than in the steam explosion process). After a given contact time, the pressure is released and the volatile liquid evaporates. If the liquid is also chemically active against the cellulose the overall effect of the treatment on cellulose would be enhanced.

The pretreatment of cellulose prior to acetylation can be carried out for example with 85% formic acid in the room temperature or with glacial or aqueous acetic acid, either alone or in the presence of part or all of the esterification catalyst, at 60^{o}C. Treatment causes swelling of the cellulose and correspondingly the intermolecular hydrogen bonds are partly destroyed (Haney and Martin 1945; Rogovin and Kostrov 1968).

Nousiainen et al. (1991) discovered that the solubility of cellulose in NaOH was significantly improved when the cellulose was treated by cellulolytic enzymes. Although, the main detectable effect of the enzymes was the degradation of cellulose, it was shown that the increased solubility in NaOH was not entirely due to a decrease in molecular weight (Vehviläinen et al. 1996). The DP_w of hardwood dissolving pulp decreased only by 12 % (from 690 to 604) in the enzymatic treatment while the alkaline solubility increased by 47 % (from 32 % to 47 %). Moreover, the solubility of mechanically, chemically and enzymatically treated pulp was significantly higher (80 %) as compared to the mechanically and chemically treated pulp (61 %), even though its DP_w was slightly higher (420 and 393, respectively). It was recently proved that the mechanical shredding of pulp increases the amount of accessible sites for the enzymes (Grönqvist et al. 2014). This facilitates the penetration of the enzymes in the cellulose, thus enhancing their action. It has been shown that the enzymatic treatment of cellulose broke a considerable amount of intermolecular hydrogen bonds while only a marginal change in intramolecular hydrogen bonds and free OH-groups was detected (Janardhnan and Sain 2005).

2.3.5 Enzyme-aided dissolution of cellulose

Enzymatic treatment of cellulose has proven to be beneficial for enhancing the dissolution of cellulose into aqueous sodium hydroxide (Struszczyk et al. 1995; Rahkamo et al. 1996, 1998a, 1998b, 1998c; Vehviläinen et al. 1996; Cao and Tan 2002a, 2002b and 2006). Mechanical shredding of pulp prior to enzymatic treatment, lowering the dissolution temperature below zero, and incorporation of zinc oxide to sodium hydroxide further increase the solubility of enzyme modified cellulose (Vehviläinen et al. 1996; Grönqvist et al. 2014).

Rahkamo et al. (1996) found that the effect of purified *Trichoderma reesei* cellulases on the solubility of hardwood dissolving pulp varied significantly due to the enzyme considered. At the same hydrolysis level the endoglucanases (EG I and EG II) proved to be more efficient in increasing the solubility than the cellobiohydrolases (CBH I and CBH II), and among the endoglucanases, EG II was the most efficient. The effect of EG II was not improved when the cellulose was first subjected to purified *Trichoderma reesei* hemicellulases or other cellulases. The simultaneous hydrolysis with hemicellulases or with different purified cellulases did not affect the solubility of cellulose either (Rahkamo et al. 1998b). As a consequence, the endoglucanases are preferred type of enzymes for increasing the alkaline solubility of cellulose, and cellobiohydrolases should be avoided to minimise the yield loss.

The mechanical treatment prior to enzymes and the addition of zinc oxide to sodium hydroxide had pronounced effects on the extent of alkaline solubility (Vehviläinen et al. 1996; Nousiainen and Vehviläinen 2001). Vehviläinen et al. (2009) discovered that by subjecting alkaline cellulosic slurry containing enzyme-treated cellulose, NaOH and ZnO to sub-zero temperature (i.e. freezing), it was possible to dissolve cellulose with significantly lower NaOH concentration than without freezing.

The method studied in this work is based on the enzymatic activation of cellulose with a specific enzyme combination.

2.4 Wet spinning

In the wet spinning process, the polymer solution (dope) is pumped with a predetermined rate through a spinneret with numerous small holes, which is completely immersed into a coagulation bath. The solution coagulates instantly when it emerges from the spinneret hole to the bath. The coagulated, nascent fibres are next pulled from the bath with aid of a godet and guided through the stretching zone and washing baths (Wilkes 2001). The fibres are collected either in continuous filament form or in staple fibres when the filament tow is cut to the desired length. The fibres are finished and dried as final steps.

Wet-spinning technology is applied in the production of viscose and cupro fibres, acryl and modacryl (Bahrami et al. 2003), aramid and para-aramid (Hongu and Phillips 1997), elastane (Singha 2012), various alginate (Kong and Ziegler 2011; Qin 2008) and polylactide fibres (Gupta et al. 2007; Rissanen 2010).

Depending on the reactions between the dissolved polymer and the chemicals in the coagulation bath the fibre forming comprises coagulation due to neutralisation, dehydration, ion exchange and/or desolvation, and regeneration e.g. in the case of viscose fibres (Irklei et al. 2005; Fink et al. 2001; Shahzadi et al. 2015).

2.4.1 Coagulation

Coagulation means a phase-separation process in which the single-phase polymer solution is separated to the solid polymer and solvent components. It starts instantly when the solution emerges from the spinneret orifice to the coagulation bath. In the first phase the surface of the fluid jet is solidified to give appropriate mechanical strength for the as-spun fibre. The membrane formed acts as an interface between the solvent in the dope and the non-solvent in the bath, and thus regulates their mutual diffusion. Another driving force for the diffusion is the difference in concentrations of the dope chemicals and of the coagulation bath chemicals (Oh et al. 1996). The diffusion is accompanied by neutralisation and dehydration, respectively provided that acid-base reactions and a high salt content in the bath are involved during the coagulation process (von Bucher 1968).

The molecular chains of the solution are subjected to multiple forces which include shear stress due to the hydrodynamic flow in the spinneret channel, phase transition due to the coagulation and due to the stretching during taking-up of the filaments (Ziabicki 1967). The level of shear stress depends on the rheological properties of the dope, the flow rate and the dimensions of the spinneret. Qin et al. (2001) found that with lower dope concentration the increased flow rate and thus increased shear stress induced orientation for the polyethersulfone molecules whereas similar kind of behaviour was not observed with the higher concentration. In addition, the uniaxial stretching due to the velocity difference between the taking-up rate of the fibres to the first godet and the extrusion velocity (i.e. spinneret draw ratio) aligns the molecular chains. Finally, the balance between the visco-elastic properties of the dope and the coagulation kinetics determine at which extent the shear stress relaxes and the stretch orients the molecules before the skin is formed for the nascent fibres (Ziabicki 1967).

Miyamoto et al. (2009) simulated the regeneration of cellulose by molecular dynamics and found that the sheets were preferentially stacked with van der Waals forces. Isobe et al. (2012) confirmed the simulated model by following the regeneration of cellulose/LiOH/urea solution with synchrotron x-ray diffraction. The results indicated that the cellulose molecules attached first in sheets by hydrophobic associations and thereafter the sheets were organised by hydrogen bonding.

2.4.2 Spinneret draw ratio

The spinneret draw ratio is a parameter which is usually adjusted experimentally such as the fibres do not break (too high spinneret draw ratio) nor form any kind of instabilities (too low spinneret draw ratio) in the coagulation bath (von Bucher 1968). The spinneret draw ratio is calculated according to Equation 1 (Götze 1967).

$$spinneret \cdot draw \cdot ratio = V_I \times \frac{\left(\frac{\pi}{4}\right) \times D^2 \times n}{Q}, \qquad \text{[Equation 1]}$$

where

V_I = velocity of first godet, m min^{-1}

D = diameter of orifice capillary, mm

n = number of orifices

Q = flow rate of dope, ml min^{-1}

The flow rate of the dope (Q) is fixed according to the desired linear density of the fibres (Equation 2) and the velocity of the first godet by the maximum stretching ratio of the fibres (Equation 3). Thus, the type of the spinneret has major effect on the spinneret draw ratio, and must be selected such as the behaviour of the as-spun fibres in the coagulation bath is within the limits.

2.4.3 Linear density

The linear density of the fibres (T) is fixed by adjusting the ratio between the spinning velocity (V_{III}) and the flow of the dope (Q) to the desired value according to Equation 2 (Götze 1967).

$$T = \frac{Q \times \rho_{dope} \times \frac{\alpha}{100} \times 10000}{n \times V_{III}}, \qquad \text{[Equation 2]}$$

where

T = linear density, dtex

Q = flow rate of dope, ml min^{-1}

V_I = velocity of first godet, m min^{-1}

ρ_{dope} = density constant of dope, 1.4 g mL^{-1} for cellulose

α = dry content of dope

n = number of orifices

V_{III}=spinning velocity, m min^{-1}

The effects of fibre shrinkage during the drying and the moisture regain during the conditioning are taking into account by the empirical density constant. The unit of the linear density, dtex, is equal to the mass in grams of a filament fibre with a length of 10 000 m.

The maximum stretching of the fibres is adjusted by decreasing the velocity of the first godet. In this way, the linear density of the fibres is not changed, instead the spinneret draw ratio is decreased. The more the fibres stretch, the lower the spinneret draw ratio, i.e. the extensibility of the fibres determines the value for the spinneret draw ratio.

$$stretching \cdot ratio = \frac{V_{III}}{V_I}, \qquad \text{[Equation 3]}$$

where

V_{III} = velocity of third godet (i.e. spinning velocity), m min^{-1}

V_I = velocity of first godet, m min^{-1}

2.4.4 Orientation

Orientation of the molecular chains in the fibre structure is the most important factor affecting the fibre tenacity. Stretching of the as-spun fibres between the godets contributes most on orientation, although, the effect of spinneret draw ratio might be observed at experimental scale. The structure of the gel developed in the coagulation bath determines the extensibility of the fibres. It is aimed that the gel is soft with non-permanent bonds that allow the molecules to be aligned effectively during the stretching. A soft gel is obtained when the coagulation rate is sufficiently slow (von Bucher 1968). The more the molecules are aligned with the fibre axis the higher the orientation, and consequently the higher the tenacity. (McGarry and Priest 1968; Moncrieff 1970).

Theoretically the orientation is defined as a mean angle between the chain molecules and the fibre axis. The degree of orientation can be measured by the polarised infra-red radiation using infra-red dichroism or by birefringence (Morton and Hearle 1993; Fouda and Seisa 2007). The orientation of the crystals can be measured by wide-angle x-ray diffraction (Chen et al. 2006).

2.4.5 The viscose process

The viscose process is the most common commercial method for producing regenerated cellulosic fibres. In the process, the cellulose is treated with sodium hydroxide and carbon disulphide (CS_2) to obtain cellulose xanthate which is then dissolved into sodium hydroxide. The cellulose xanthate solution is ripened, filtered and finally extruded through the spinneret into an acid coagulating bath to form filaments. (Mitchell and Dual 1990; Wilkes 2001)

Control of the coagulation and regeneration rates of the cellulose xanthate is the key parameter in the viscose method. The stream of solution extruded into the spin bath forms initially a gel of which structure must be adequate for further stretching. If the gel is too soft it does not give permanent alignment of the molecules, if it is too rigid the stretching is impossible. The coagulation and regeneration reactions are controlled by the dope additives and by the composition of acidic bath, as well as by the properties of the dope. Sodium sulphate is formed through the neutralisation during the coagulation of cellulose xanthate. Its function is to dehydrate the cellulose xanthate stream causing the filament to shrink and precipitate (Wilkes 2001). Normal amount of sodium sulphate is 120-200 g/l. Another salt, that can be used for higher dehydrating is ammonium sulphate with the dose of 230-350 g/l (Turbak 1990). However, it is not used commercially. The degree of xanthate substitution (gamma-value), the $NaOH/H_2SO_4$ concentrations and the concentration of inorganig ($ZnSO_4$) and organic modifies (eg. Mi07) determine the extents of the coagulation and regeneration, and the structure of the formed gel (McGarry and Priest 1968).

Properties of the viscose fibres can be adjusted by modifying the spinning process; e.g. Modal fibres are produced by using high DP cellulose at low dope concentration (high alkali ratio, high gamma value) and a low sulphuric acid concentration in the spin bath with high amount of zinc sulphate and organic modifiers. The Japanese improved the fibre properties by using very high-DP cellulose and high concentrations of carbon disulphide (without zinc). These parameters enabled high stretching and consequently high tenacity. The fibres were called polynosic, but they are not currently produced commercially. (Turbak 1990)

2.5 Special consideration regarding the spinning of aqueous dopes

The NaOH-based cellulose solutions are an attractive alternative for the preparation of regenerated fibres, because they can be processed by the wet spinning technique using the same machinery as in the viscose fibre production. Few spinning trials have been done using cellulose/NaOH dopes without any additive (Yamashiki et al. 1990; Vehviläinen et al. 1996; Yamane et al. 1996). However, the mechanical properties of the fibres were very low. The addition of urea (Cai et al. 2004; Cai et al. 2007; Chen et al. 2007; Qi et al. 2008a), thiourea (Ruan et al. 2004; Chen et al. 2006), urea/thiourea (Zhang et al. 2009) zinc oxide (Vehviläinen et al. 1996) or polyethylene glycol (PEG) (Zhang et al. 2010) enhanced the solubility of cellulose and improved the properties of the fibres obtained.

The most important dope-related factors affecting the properties of regenerated cellulosic fibres are the DP of cellulose and the quality of the spin dope. The increased DP of cellulose increases the tenacity of the fibres (Morton and Hearle 1993). However, already a small amount of high-DP cellulose increases the viscosity of the dope significantly (Fink et al. 2001) and hinders the solubility of cellulose in a water-based environment (Isogai and Atalla 1998; Qi et al. 2008b). As a consequence, it is necessary to find a suitable DP for the cellulose which produces dope with sufficiently high concentration and low viscosity enabling the production of fibres with adequate mechanical strength.

The NaOH and cellulose concentrations of the dope contribute to the consumption of non-solvent in the coagulation bath, and thus determine the economy of the process and the amount of by-products evolved. In most of the experimental cases the ratio between NaOH and cellulose (alkali ratio) has been above 1.3 (Cai et al. 2004; Cai et al. 2007; Chen et al. 2007; Zhang et al. 2010) which causes high consumption of sulphuric acid and high formation of salts during the coagulation compared to the amount of fibres obtained. As a reference the alkali ratio in the regular viscose fibre process is 0.55-0.60.

The viscosity of the dope affects its filtration and deaeration efficiency. The filtration is an important process step because the undissolved fibre fragments and/or gel particles deteriorate the spinning by clogging the spinneret orifices. If the dope is not stable over time and temperature changes, the viscosity increases during the deaeration and restricts the movement of the air bubbles. This has detrimental effect on spinning since air bubbles enter the spinneret orifices which in turn opens a path for the non-solvent to flow through the orifice inside the spinneret. This results the as-spun filament to break, and the dope to coagulate premature which clogs the orifice.

The temperature during the deaeration determines which amount of dissolved air is possible to remove from the dope. As the solubility of air increases with decreasing temperature (Henry’s law), a solution subjected to low temperature during the dope preparation contains considerable volume of air in dissolved form. In order to avoid the formation of air bubbles during the spinning (due to their decreased solubility), it is important to have equal or higher dope temperature in the deaeration than in the spinning. This is challenging with the NaOH-based solutions as they tend to form gel at ambient temperature (Yamashiki et al. 1990; Jin et al. 2007; Qi et al. 2008b; Zhang et al. 2010).

It was possible to improve the alkali ratio of the cellulose/ZnO/NaOH dope when an enzyme-treated pulp was subjected to a freezing-thawing cycle (Vehviläinen et al. 2009). In this method, the pulp and sodium zincate (ZnO/NaOH) are mixed at the room temperature and thereafter frozen. A cellulose solution is obtained upon thawing. By applying this method the NaOH content of the dope was decreased from 7.8 wt% to as low as 5.5 wt% with the same amount of pulp (6 wt%).

The dopes that are prepared without derivatisation of cellulose coagulates very rapidly because there is no chemical reaction happening during the fibre forming. The lyocell fibres prepared from the N-methylmorpholine-N-oxide/cellulose dopes coagulate also fast. Orientation of the molecules is achieved by using an air gap between the spinneret and the coagulation bath. However, the processing window is very narrow and the process requires carefully adjusted viscoelastic properties of the dope (Fink et al. 2001). The inadequate rheological properties of the aqueous cellulose solutions restrict the use of an air gap during the spinning. Thus, the coagulation must be controlled with the additives both in the dope and in the spin bath (Kotek 2007). The modifiers in the viscose process are usually organic compounds which form an acid-resistant barrier on the surface of the as-spun fibre (McGarry and Priest 1968). As the function of the commercial modifiers is based on the retardation of the chemical reaction it is not expected the same effect would be achieved if used in a NaOH-based cellulose solution.

3 Experimental

This chapter summarises the materials and methods that relate to the results presented in the next chapter. More comprehensive information of the different characterisation methods can be found from the relevant publication. However, as the high quality cellulose solution is the most critical prerequisite for the spinning trials, and as the two different procedures for dissolving the enzyme-treated cellulose were used, these procedures are presented here in more detail.

3.1 Pulp materials and treatments

The starting materials of the experiments were low and medium viscosity dissolving grade softwood sulphite pulps. The characteristics of pulps and treatments prior to dissolution are given in Table 1.

TABLE 1 Pulp raw materials and treatments.

	Paper I	**Paper II**	**Paper III**	**Paper IV**
Pulp raw material	commercial dissolving grade softwood TCF sulphite pulp delivered by Domsjö Fabriker AB, Sweden			
Pulp SCAN*	405 ml/g		405 ml/g and 558 ml/g	558 ml/g
Mechanical treatment	Wet pulp (dw 20 wt%) was shredded mechanically for five hours using a Baker Perkins shredding machine (size 6-1 Universal mixer S/N 44777).			
Enzyme	commercial endoglucanases (AB Enzymes Oy, Finland and Genencor International, Netherlands)		a) Ecostone N400 (AB Enzymes Oy, Finland) b) Fibercare R (Novozym CGP20048)	Fibercare R (Novozym CGP20048)
Enzymatic treatment: conditions and enzyme dosage	5 wt%, pH 5, 50ºC for 3 hours, 250 nkat/g		5 wt%, pH5, 50°C, 2 - 3h, a) 1.9 mg/g b) 1 mg/g	5 wt%, pH5, 50 °C for 2 hours, 1 mg/g
Dissolved sugars (DNS method)	3 %		a) 3 %, b) 1.8 %	1.8 %
Pulp SCAN* after enz.tr.	270 ml/g		a) 260 ml/g b) 245 ml/g	240 ml/g

* intrinsic viscosity of the pulp according to SCAN-CM 15:99 test method

3.2 Preparation of cellulose solutions

The cellulose solutions were prepared according to two procedures. In publications I and II the enzyme-treated pulp was dissolved by adding it to cold sodium zincate and stirring the mixture in the cooling bath until the cellulose dissolved (Procedure I). In publications III and IV the enzyme-treated pulp was dissolved by mixing it with sodium zincate at ambient temperature and freezing the obtained mixture. The cellulose dissolved during the freezing-thawing cycle (Procedure II).

In both procedures the pulp was added into sodium zincate in wet form. The pulp can be dried (in air, not oven) after the enzymatic treatment and this is recommended if the pulp is stored for a longer period. However, prior to the dissolution the dry pulp must be activated in water and the dry weight of the wet pulp adjusted to the desired range as indicated later. There have been several slightly different methods to activate the dry pulp: the use of excess hot or cold water with later separation, or the use of exact amount of water at once. In each case, the wet pulp was stirred until homogeneous slurry without any hard particles was obtained. The activation was done at least one day before the dissolution and the wet pulp was stored in a refrigerator.

Preparation of the high quality sodium zincate with optimum zinc oxide and sodium hydroxide concentrations was critical in both procedures. Zinc oxide was first dissolved in concentrated sodium hydroxide (stock solution), which was then diluted prior to use.

3.2.1 Dissolution procedure I, stirring in cooling bath

3.2.1.1 Preparation of sodium zincate stock solution I

2 wt% ZnO / 18.5 wt% NaOH, 1000 g

Solid sodium hydroxide (185 g) and solid zinc oxide (20 g) were weighed into a beaker (1000 ml, with known empty weight). Ion exchanged water (ca. 200 ml) was added by stirring with a glass rod. The mixture was heated (gently bubbling) with magnetic stirrer until all the zinc oxide was dissolved (i.e. no tiny rods were observed against the light, but the solution was completely clear). The solution was let to cool (important) and the rest of water was added to adjust the total weight of solution to 1000 g. In this stage the solution warmed and turned opaque, however it cleared upon cooling. The final ZnO concentration was 2 wt% and NaOH concentration 18.5 wt%.

3.2.1.2 Preparation of cellulose solution I, 200 g

The sodium zincate stock solution (84.3 g) was diluted with ion exchanged water (68.7 g) to obtain 153 g solution with 1.1 wt% ZnO / 10.2 wt% NaOH. The solution was cooled to -5 ºC in a cooling bath.

Dry pulp (12 g) was activated with water and its weight was adjusted to 47 g (dw 25.5 wt%). The wet pulp (47 g) was added into cold sodium zincate (153 g) and the mixture was stirred at 1000 rpm until the cellulose was dissolved (1-3 h). Note; all the pulp was added first and the stirring started after that. Temperature of the solution was monitored during the dissolution and maintained at or below 3 ºC.

The final concentrations of the solution were 6 wt% cellulose, 0.84 wt% ZnO and 7.8 wt% NaOH.

3.2.2 Dissolution procedure II, freezing-thawing

3.2.2.1 Preparation of sodium zincate stock solution II

<u>8 wt% ZnO / 40 wt% NaOH, 1000 g</u>

Solid sodium hydroxide (400 g) and solid zinc oxide (80 g) were weighed into a beaker (1000 ml, with known empty weight). Ion exchanged water (520 ml) was added by stirring with a glass rod. The mixture was heated (gently bubbling) with magnetic stirrer until all the zinc oxide was dissolved (i.e. no tiny rods were observed against the light, but the solution was completely clear). The solution was let to cool down at RT, the weight was checked and ion exchanged water added to obtain 1000 g. The concentrated solution was stored in a refrigerator.

3.2.2.2 Preparation of cellulose solution II, 200 g

The sodium zincate stock solution (32.5 g) was diluted with ion exchanged water (87.5 g) to obtain 120 g solution with 2.2 wt% ZnO / 10.8 wt% NaOH. Temperature of the solution prior to pulp addition was 20-22 ºC.

Dry pulp (12 g) was activated with water and its weight was adjusted to 80 g (dw 15 wt%). The wet pulp (80 g) and diluted sodium zincate (120 g) were mixed to obtain a slurry-like sample. The alkaline cellulose slurry was frozen in a freezer at -40 °C for at least 12 h. The sample was thawed to obtain cellulose solution.

The final concentrations of the solution were 6 wt% cellulose, 1.3 wt% ZnO and 6.5 wt% NaOH.

3.3 Spinning parameters

The solutions prepared for the fibre spinning trials were filtered and placed in a spin reservoir. The pressure inside the reservoir was lowered to below 0.88 bar for removing the air bubbles. The dope was characterised by measuring the dry content, amount of gel particles and fluidity. The fibres were spun using a laboratory wet spinning machine with a gear pump of 0.3 mL/r. The spinning parameters are collected in Table 2.

TABLE 2 Spinning parameters.

	Paper I	**Paper II**	**Paper III**	**Paper IV**
Spin baths	5% H_2SO_4 + 10% Na_2SO_4 15% H_2SO_4 + 10% Na_2SO_4 T 15 ºC	5% H_2SO_4 + 10% Na_2SO_4 15% H_2SO_4 + 10% Na_2SO_4 20% H_2SO_4 + 10% Na_2SO_4	10% H_2SO_4 + 10% Na_2SO_4 5% CH_3COOH	10% H_2SO_4 + 10% Na_2SO_4 20% H_2SO_4
Spinneret	100 x 51µm	100 x 51µm	100 x 51µm	100 x 51µm
Spinneret draw ratio	0.4 -1.1	0.7, 1.0	0.78-1.04	0.62-0.95
Stretching ratio	1.17-1.42	1.07-1.3	1.29-1.53	1.16-1.42
Stretching bath	Hot water	Hot water	Hot water	Hot water
Washing bath	Water (RT)	Water (RT)	Water (RT) 10% H_2SO_4	Water (RT)

3.4 Characterisation

3.4.1.1 Mechanical properties

The fibres were conditioned at a relative humidity of 65±5 % and temperature of 20±2 °C for at least 24 hours. The mechanical properties were determined using a Vibroskop and Vibrodyn testing machines (Lenzing AG) (Publications I and II) or a Favigraph testing machine (Textechno GmbH) (Publications III and IV). The rate of elongation was 20 mm/min and the gauge length 20 mm. The yield point and yield stress were measured from the stress-strain curve according to the Meredith's method (Morton and Hearle 1993).

3.4.1.2 Crystallinity and size of crystallites

Crystallinity degree and crystallite size of the fibres were analysed by Wide-angle X-ray diffraction (WAXS) at University of Bielsko-Biała, Poland. Measurements were carried out in the reflection mode at ambient temperature using a Seifert URD-6 diffractometer with a scintillation counter connected to a computer.

3.4.1.3 Average molecular weights and molecular weight distributions

The weight average degree of polymerisation (DP_w) and the molecular weight distributions of samples were measured either in Institute of Biopolymers and Chemical Fibres, Poland (Publication I) or at Domsjoe Fabriker Ab, Sweden (Publication II). The samples were dissolved in LiCl/DMAc without derivatisation.

3.4.1.4 Rheological properties of cellulose solutions

The viscoelastic properties of the cellulose solution were measured with Anton Paar MCR 301 rotational rheometer using a concentric cylinder geometry. Temperature of the cylinders was first allowed to settled, and thereafter a fresh sample (stored in a refrigerator at 6 °C) was applied. The shear stress was measured at the constant temperatures (18 °C, 22 °C and 30 °C) with two or three shear rate cycles. The storage (G') and the loss moduli (G'') were measured in the function of temperature from 10 °C to 60 °C, and at the constant temperature (22 °C and 30 °C) in the function of time until the cross-over of the curves.

3.4.1.5 Orientation of fibres

Birefringence of the fibres was measured with Leitz 662098 polarised microscope equipped with a Berek compensator. The objective used was 25/0.50. The diameter of the fibre was measured with Leitz Laborlux D microscope.

3.4.1.6 FTIR of fibres

The FTIR-spectra of the fibres were analysed with Bruker Optics Tensor 27 FTIR spectrometer at 4 cm^{-1} resolution with 32 scans per sample. The samples were air-dried and mounted directly in the sample holder. The total crystallinity index (TCI) and the lateral order index (LOI) were calculated as described by Nelson and O’Connor (1964).

4 Results

This section gives the main results of each publication thereby addressing the research questions. The third publication is divided into two parts, thus answering two of the posed questions.

4.1 Effect of wet spinning parameters on the properties of novel cellulosic fibres, Publication I

Is it possible to dissolve cellulose in a water-based solvent in a way the fibre forming process is successful using a wet spinning method?

The production of fibres by means of wet spinning method from the enzyme-treated pulp comprises multiple steps that are the mechanical and enzymatic treatments of the pulp, dissolution of enzyme-treated pulp, filtration and deaeration of the cellulose solution and finally coagulation of the solution to the fibre form. The wet spinning method is the most multivariated technique among the fibre spinning processes. The solution is forced through the spinneret orifices with a diameter of 51 microns into a non-solvent. The polymer must be dissolved homogeneously with appropriate concentration and rheological properties.

The challenge here was to develop the treatment conditions such that the cellulose does not degrade too much, dissolves at sufficient concentration resulting in low enough viscosity which allows efficient filtration. The solution must also be stable during the filtration and deaeration. This concept was studied in Publication I including the characterisation of the fibres.

4.1.1 Mechanical and enzymatic treatment

The pulp (dw) was shredded mechanically for five hours using a Baker Perkins shredding machine (size 6-1 Universal mixer S/N 44777) and thereafter treated with commercial endoglucanase-rich enzyme preparations. The treatments dissolved circa 3% of the cellulose as soluble sugars. As the enzyme preparations used were commercial products it is likely that they contained some activity against hemicellulose also. Thus, all the material dissolved was not cellulose and the yield (approx. 97%) obtained after enzymatic treatment is comparable with the yield of the viscose process after mercerisation.

4.1.2 Preparation of the dope

The enzyme-treated pulp was added to the precooled aqueous sodium zincate in wet form and thereafter mixed at high shear rate until all the cellulose was dissolved. The temperature during the mixing was maintained at approximately 3 ºC. The dope comprised 5.9-6.1 wt% cellulose, 7.8 wt% NaOH and 0.84 wt% ZnO. Several dopes were prepared which falling ball viscosities (fluidity) ranged from 82 s to 159 s. This variation was concluded to be due to the small changes in cellulose concentration. The dopes were filtrated through a filter felt using a vacuum pump and thereafter subjected to the lowered pressure (0.88 bar) at 0 ºC for removing the air bubbles.

4.1.3 Spinning trials

The spin baths contained sulphuric acid (5 % and 15 %) and sodium sulphate (10 %), which are typical chemicals used in the viscose process. As a result of neutralisation reaction between NaOH in the dope and H_2SO_4 in the bath some sodium sulphate was generated and dissolved in the bath during the spinning. The schematic presentation of the spinning line is presented in Figure 5. It consists of three godets, one stretching bath with hot (> 90ºC) demineralised water, two washing baths with cold (22 ± 2 °C) demineralised water and a fibre collector. Solution of sodium lauryl sulphate (0.1 %) was used to lubricate the godets during the spinning.

The effects of the spinneret draw ratio, stretching ratio and the constitution of the coagulation bath on the properties of the fibres were elucidated. The fibres spun with the spinneret draw ratio below 0.6 withstood stretching higher than 30 %, whereas the maximum stretching of the fibres spun with the higher spinneret draw ratios ranged from 17 % to 27 %. The sulphuric acid concentration of the coagulation bath (5 % or 15 %) did not affect the stretching ratio at the different spinneret draw ratios applied.

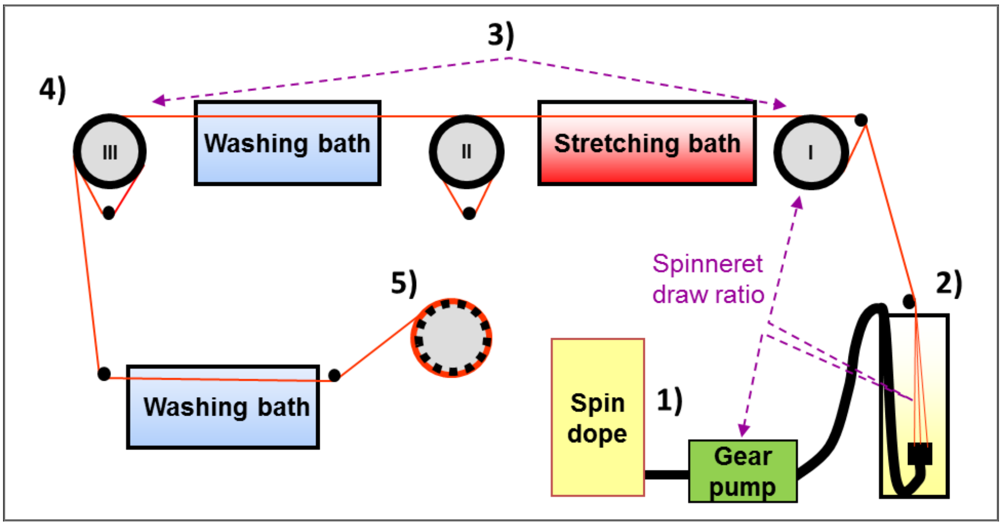


FIGURE 5 Schematic presentation of wet spinning line.

The mechanical properties of the fibres were measured in conditioned state. The strongest fibres obtained with 5 % sulphuric acid concentration in the spinning bath had tenacity of 1.6 cN dtex^{-1} and with 15 % sulphuric acid concentration of 1.8 cN dtex^{-1}. The determined tenacities of the reference viscose fibres were 2.1 - 2.2 cN dtex^{-1}. The stress-strain curves of the fibres spun here (Biocelsol) and of the commercial viscose fibres have identical shapes with clear yield points as shown in Figure 6.

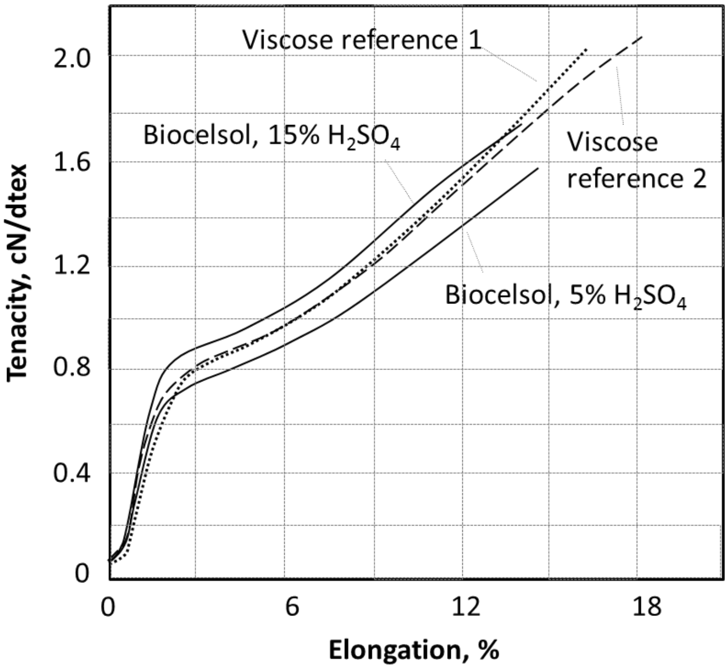


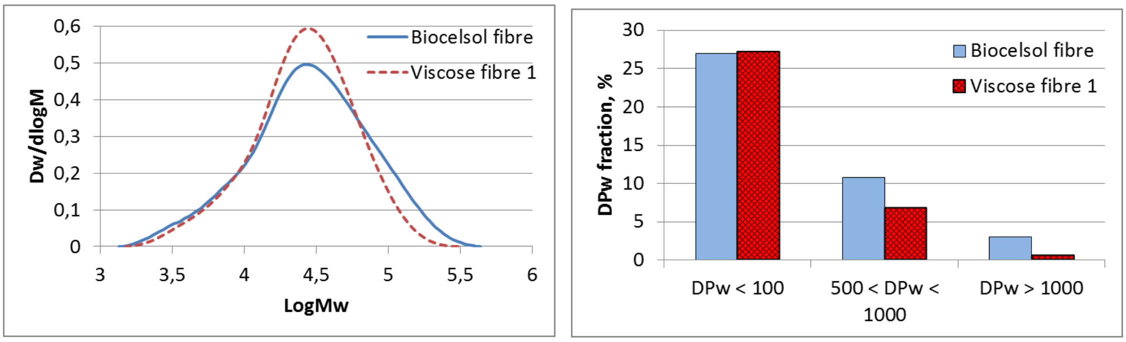
FIGURE 6 Stress-strain curves of Biocelsol and viscose fibres.

4.1.4 Fibre morphology

The Biocelsol fibres spun here had equal average size (in directions perpendicular to planes 101, $10\bar{1}$ and 002) of crystallites (42 Å) but clearly higher average degree of crystallinity (42 %) than the commercial viscose fibres (34 %). Porosity of the Biocelsol fibres measured by SAXS was twice as high as of the viscose fibres (1160 vs. 540 m^{2} cm^{-3}, respectively). The cross sections of the Biocelsol fibres were circular and the surface structure either smooth or furrowed depending on the coagulation conditions.

4.1.5 Average degree of polymerisation

Molecular weight distribution curves of the Biocelsol and viscose fibres revealed that the Biocelsol fibres had clearly higher amount of the high-DP cellulose than the viscose fibres (Figure 7a). The share of DP$_{w}$-fraction higher than 1000 was 3 % in the Biocelsol fibre compared to 0.5 % in the viscose fibre (Figure 7b). The high-DP fraction resulted in relatively high viscosity of the Biocelsol spinning solutions regarding to the cellulose concentration used. In spite of that, it can be stated that the enzymatic treatment of the dissolving pulp depolymerises the cellulose in a manner which produces molecular weight distribution curve closely similar to that of an alkaline ageing in the viscose process.



a)

b)

FIGURE 7 a) Molecular weight distribution curves, and b) Share of DPw-fractions of Biocelsol and viscose fibres.

4.2 Effect of acid and enzymatic treatment of TCF dissolving pulp on the properties of wet spun cellulosic fibres, Publication II

How to increase the cellulose concentration of the spin dope?

One disadvantage of the NaOH-based cellulose solutions is the low cellulose concentration compared to the NaOH concentration. This consumes high amount of non-solvent due to the neutralisation reaction and produces high amount of salts as by-products during the regeneration. The cellulose degree of polymerisation is the main obstacle to increase the cellulose concentration. Already small amount of high-DP cellulose increases the viscosity of the solution to a too high level for an efficient filtration. The stability of the solution towards the temperature and time impairs when the concentration increases.

The results presented in Publication I showed that the fibres prepared from the enzyme-treated pulp had a higher average DP and a higher share of long chain molecules than the commercial viscose fibres. Due to this it was not possible to increase the cellulose concentration (6 wt%) of the dope. The effect the cellulose degree of polymerisation on the concentration of cellulose in the spin dope, and the combined effect of decreased DP and increased cellulose concentration on the fibre tenacity were studied in the Publication II.

4.2.1 Effect of pulp treatments on average degree of polymerisation

Cellulose was treated mechanically and thereafter degraded by enzymes and further by acid at 80 °C or at 100 °C for 30 minutes. The enzymes decreased the average molecular weight by 38 % and the following acid treatments further by additional 21 % (80 °C) and 39 % (100 °C). The polydispersity (PDI= M_w/M_n) of the samples decreased from 6.8 to 4.8 (Table 3) indicating that the treatments made the molecular weight distribution curve narrower. However, the M_w-distribution curves (Figure 8) revealed that the acid treatment at higher temperature (100 °C) produced significant amounts of low molecular weight cellulose; seen as a shoulder in the curve.

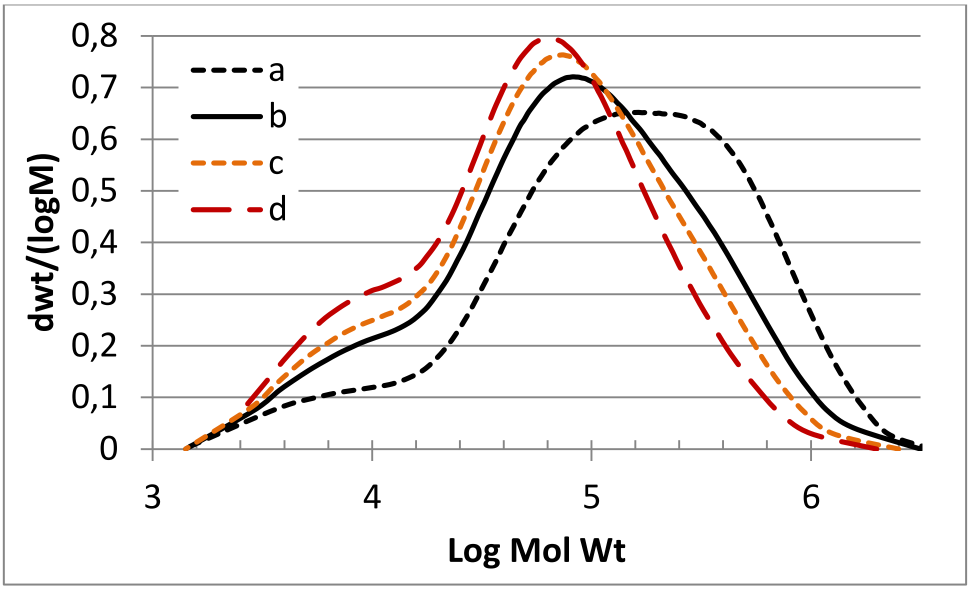


FIGURE 8 Molecular weight distribution curves of a) Mechanically treated dissolving pulp, b) Mechanically and enzymatically treated dissolving pulp (= Reference pulp), c) Reference pulp treated with acid at 80 °C, and d) Reference pulp treated with acid at 100 °C.

4.2.2 Effect of average degree of polymerisation on cellulose concentration

The decreased DP_w enabled to increase the cellulose concentration of the dope from 6 wt% to 7.2 wt% without extensive effect on fluidity (viscosity) of the dope. Instead, when the concentration increased further from 7.2 to 7.5 wt% the fluidity increased very sharply from 31 s to 360 s (Table 3). This indicates that the limit for processability at decreased DP_w was approached. The fluidity of the solutions was sensitive for temperature e.g. fluidity of the 7 wt% solution at 20 ºC was lower than of the 6.7 wt% solution at 18 ºC; 16 s and 41 s, respectively.

TABLE 3 Characteristics of samples.

Treatment	***Sample code***	***Mw***	***PDI***	***Cell.conc. wt%***	***Fluidity, s/20 cm***	***Temperature, ºC***
Mechanically treated	a	276160	6.8			
Mechanically + enzyme-treated	b	170384	5.9	6.0	73	20.6
Mechanically + enzyme-treated + acid treated at 80°C for 30 min	c	134154	5.3	5.7	33	19.5
Mechanically + enzyme-treated + acid treated at 100°C for 30 min	d	103153	4.8	6.0	8	20
				6.1	6	22.2
				6.5	13	20.0
				6.7	41	18.3
				7.0	16	20.0
				7.2	31	19.3
				7.5	360	20.0

4.2.3 Effects of cellulose concentration of the dope and average degree of polymerisation on fibre tenacity

Three spinning dopes with increasing cellulose concentration were prepared from the most degraded pulp (enzymes + acid 100 ºC), one from the moderately degraded pulp (enzymes + acid 80 ºC) and one from the reference pulp (enzymes). The increased cellulose concentration of the acid 100 ºC -treated pulp had positive effect on the fibre tenacity as seen from Figure 9 (code d). However, the highest tenacity was significantly lower than of the fibres prepared from the reference pulp (code b). The concentration of the solution prepared from the moderately degraded pulp (code c) was slightly lower than of the solution from the reference pulp. This might had some contribution to the lower tenacity, although it is probably mostly due to the lower DP_w.

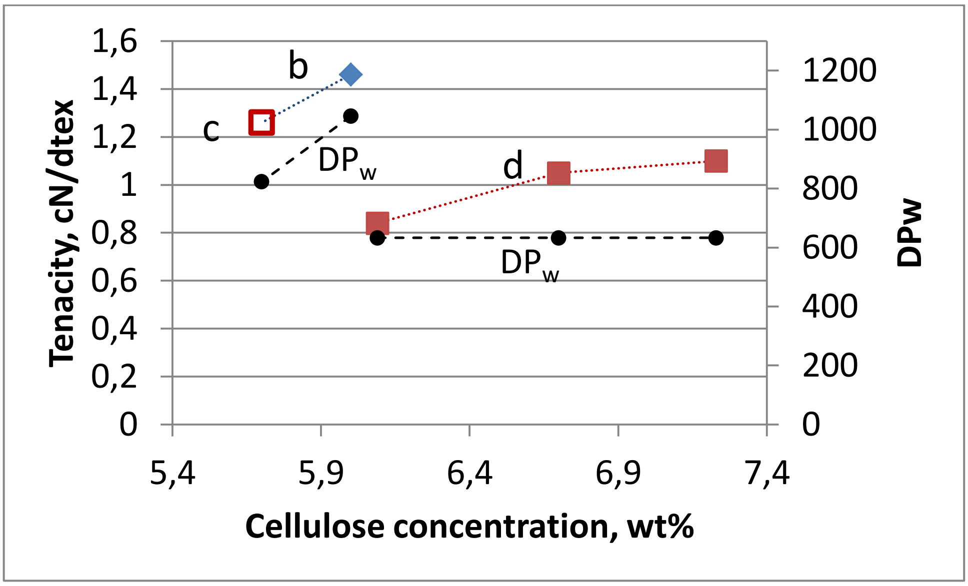


FIGURE 9 Combined effect of DP_w of differently treated cellulose and cellulose concentration in dope on tenacity of regenerated fibres. b= Mechanically and enzymatically treated reference pulp, c= reference pulp treated with acid at 80 ºC, d= reference pulp treated with acid at 100 ºC. Square- and diamond-symbols indicate tenacity, circles indicate DP_w. Standard deviation of tenacity values were in the range 0.07-0.13.

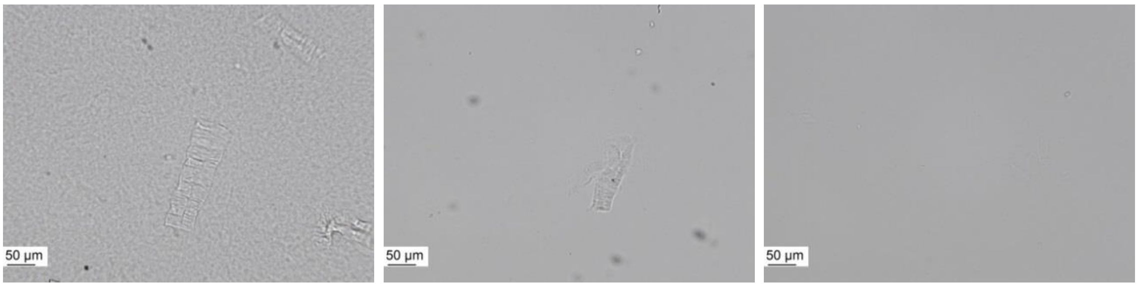
4.3 Dissolution of enzyme-treated cellulose using freezing-thawing method and the properties of fibres regenerated from the solution, Publication III, part 1

Is it possible to decrease the alkali concentration of the spin dope?

Apart from the increased cellulose concentration through the reduced DP another way to improve the economy of the process is to decrease the ratio between alkali and cellulose in the dope (i.e. alkali ratio). When studying this option it was found that by freezing the enzyme-treated cellulose/ZnO/NaOH mixture the cellulose dissolved with significantly lower amount of NaOH than without freezing. The effect of zinc oxide and sodium hydroxide concentrations on the solubility of cellulose were optimised for a spinning dope and presented in the Publication III.

4.3.1 Optimisation of ZnO and NaOH concentrations

The solubility of cellulose was clearly affected by both the zinc oxide and sodium hydroxide concentrations of the sample. Some dissolution occurred without zinc, and its extent increased when the NaOH content increased from 4 wt% up to 6.5 wt%. However, the zinc oxide was needed for higher/complete dissolution. Microscope images of the solutions prepared with varying sodium zincate contents are presented in Figure 10. The solution with 0.84 wt% ZnO / 5.5 wt% NaOH contained gel-like partly dissolved cellulose and large swollen fibres (Figure 10a), with higher ZnO and NaOH contents (1.3 wt% / 6.0 wt%) almost all the fibres were dissolved (Figure 10b), and with 1.3 wt% ZnO /6.5 wt% NaOH no undissolved fibres were observed (Figure 10c).



a) b) c)

FIGURE 10 Cellulose solutions (6 wt%) from low viscosity enzyme-treated dissolving pulp with a) 0.84 wt% ZnO/ 5.5 wt% NaOH, b) 1.3 wt% ZnO/ 6.0 wt% NaOH and c) 1.3 wt% ZnO / 6.5 wt% NaOH.

4.3.2 Rheological properties of spinning dope

The steady-state flow curves (Figure 11) of the solution containing 5.5 wt% cellulose, 1.3 wt% ZnO and 6.5 wt% NaOH show that the solution is shear thinning. The behaviour is due to the linearity of the cellulose molecules which allow them to align in the direction of the flow (Mathur 2011). The increasing shear rate at 18 °C induced significant increase in viscosity, which is seen as a yield point in the curve. The viscosity forms a hysteresis loop with the shear rate cycle at 18 °C which indicates the solution is thixotropic (Barnes 1997). Similar kind of loop did not occur at 22 °C, while at 30 °C it is again observed. Even though, the viscosity was lower at higher temperatures, the results indicate the instability of the solution was increased with increasing temperatue.

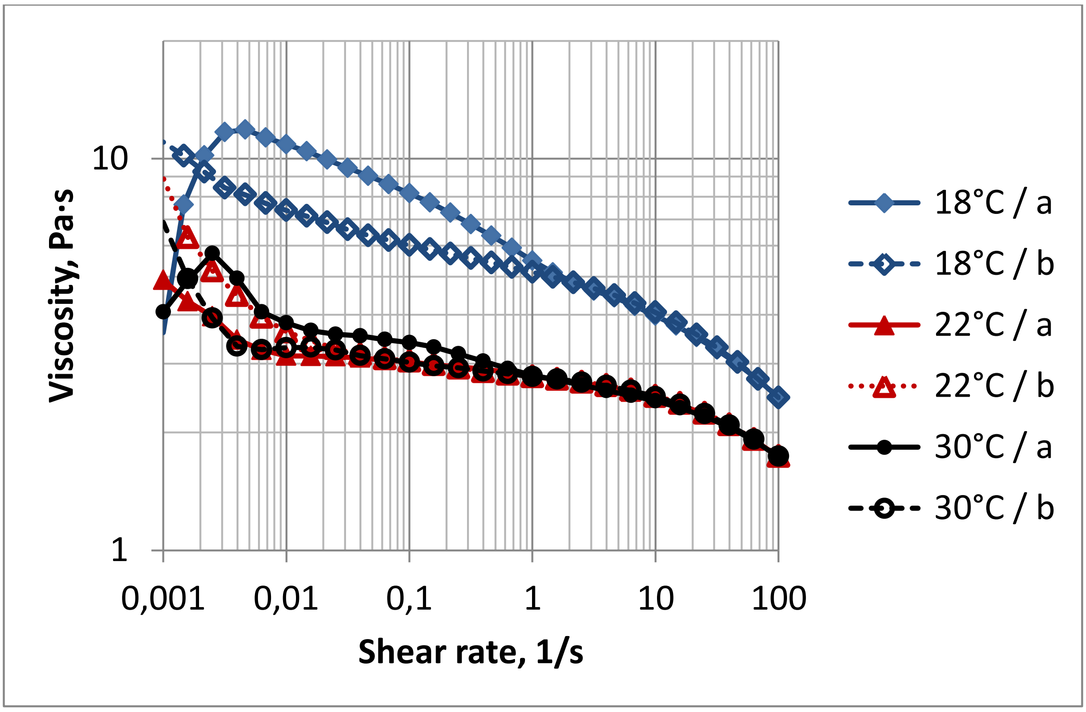


FIGURE 11 Steady-state flow curves of cellulose solution containing 5.5 wt% medium viscosity enzyme-treated pulp, 1.3 wt% ZnO and 6.5 wt% NaOH at 18 °C, 22 °C and 30 °C. Curves a with increasing shear rates and curves b with decreasing shear rates.

The effect of temperature was further studied with dynamic measurements at low angular frequency (1 rad s^{-1}). The storage modulus (G’) represents the elasticity of the sample and the loss modulus (G’’) the viscosity of the sample. The ratio G’’/G’ is equal to the tanδ (loss tangent), thus the higher the tanδ the higher the viscosity (Pal 2006). The G’ and G’’ of the cellulose solution had two cross-over points, the first at 16.3 °C and the second at 42.5 °C (Figure 12). In between these temperatures, at the studied angular frequency, the sample is liquid-like. The decrease of G’ at temperatures below 21 °C indicates the microstructure of the sample breaks effectively. The microstructure is probably formed due to the entanglement of the cellulose molecules, and the entanglement density decreases due to the Brownian motion with increased temperature (Barnes 1997). The viscous character (tanδ) reaches the maximum value at 28 °C, where after it declines first moderately and above 37.5 °C more rapidly. The gel point is reached at the second cross-over point of the G’ and G’’ at 42.5 °C. The G’ increased steadily after the gel point without any plateau, which indicates the gelation was not caused by any chemical cross-links (Weng et al. 2004). The decreased viscose character before the gel point suggests that cellulose chains start to aggregate (Weng et al. 2004). The aggregation is driven by the hydrophobic stacking of cellulose chains as proven by Isobe et al. (2012). In the next stage the stacked crystals are attached to each other by hydrogen bonds forming an elastic gel network (Roy et al. 2003).

Even though, the viscous character of the solution was the highest at 28 °C (Figure 12), the solution was stable at 22 °C only for 157 minutes. The results confirmed the importance of controlling the temperature during the processes towards the fibre spinning.

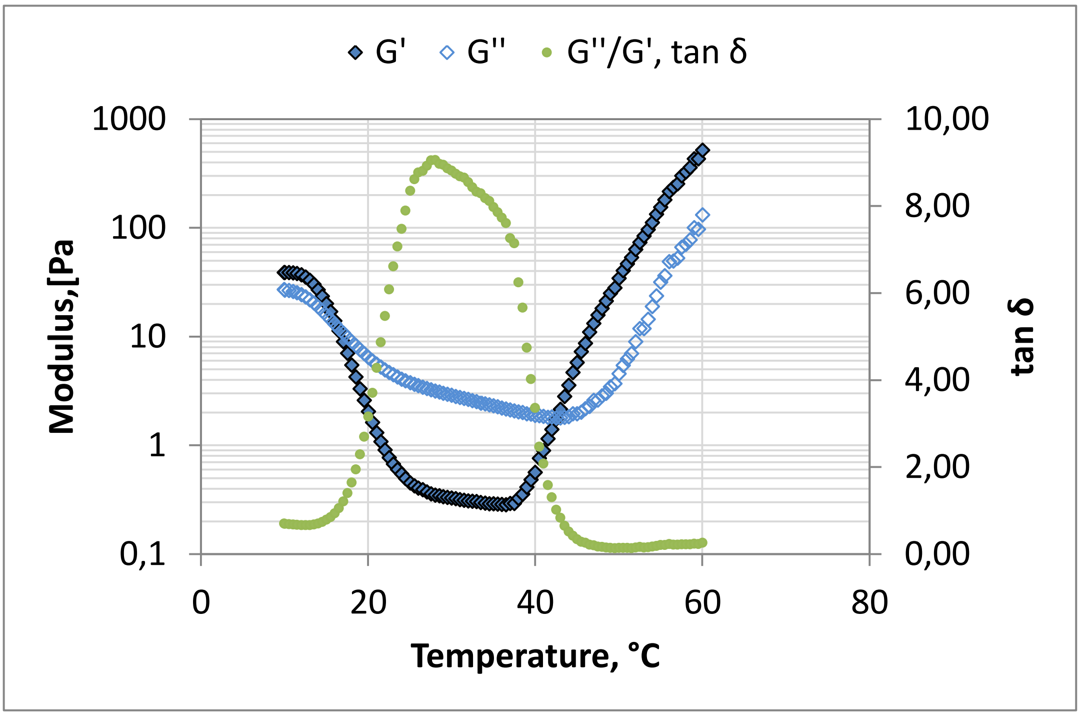


FIGURE 12 Dynamic viscoelasticity of 5.5 wt% cellulose solution (medium viscosity enzyme-treated pulp) in function of temperature.

With the freezing-thawing cycle the alkali ratio of the cellulose solution decreased from 1.3 to 1.1 which consumes 15% less sulphuric acid during the coagulation, thus providing significant improvement for the economy of the process.

4.4 Dissolution of enzyme-treated cellulose using freezing-thawing method and the properties of fibres regenerated from the solution, Publication III, part 2

How to increase the tenacity of the fibres?

Tenacity of the fibres and the orientation of the molecules relative to the fibre axis exhibit a positive linear correlation. The more the fibres are stretched between the godets, the higher the orientation, and consequently, the higher the tenacity (McGarry and Priest 1968). Thus the key factor to increase the fibre tenacity is to increase the stretching of the fibres. The main obstacle restricting the stretching is the formation of rigid bonds between the molecules during the coagulation. As a consequence it is essential to slow down the formation of permanent bonds at the too early stage. In the viscose process the sufficient stretching is ensured by using the spin dope modifiers and the spin bath additives which retard the regeneration of cellulose xanthate (Kotek 2007). As the coagulation of the NaOH-based cellulose solution does not involve any chemical reaction, it is not expected that viscose modifiers would slow the coagulation. Thus, the other means must be considered. The effect of coagulation bath composition, namely the type of acid, on the coagulation rate was studied in the Publication III. It was assumed that the solution coagulates slower in the acetic acid spin bath than in the sulphuric acid bath, and thus the higher stretching ratio would be achieved. This was expected lead to higher tenacity of the fibres.

In the experimental setup the fibres were spun into acetic acid (5 %) and sulphuric acid (10 %) using the same spinneret draw ratio and spinning velocity. All the fibres were stretched with the maximum stretching ratio in the bath containing hot water (90 ºC). The following washing bath contained cold water (22 ºC) or 10% sulphuric acid (for acetic acid spun fibres). All the fibres were washed to neutral in water prior to drying.

4.4.1 Effect of coagulation bath on stretching ratio and fibre tenacity

The acetic acid spun fibres stretched circa 10 % more between the godets than the sulphuric acid spun fibres. This indicates the coagulum formed in acetic acid was softer than the one formed in sulphuric acid. Unexpectedly, the higher stretching ratio of the acetic acid spun fibres did not produce higher tenacity for the air-dried fibres. Instead, the tenacity was much lower than that of the sulphuric acid spun fibres. Moreover, the tenacity of the acetic acid spun fibres increased slightly with increasing spinneret draw ratio, whereas the tenacity of the sulphuric acid spun fibres had opposite relationship with the spinneret draw ratio (Figure 13).

The composition of the washing bath of the acetic acid spun fibres (water vs. sulphuric acid) did not have significant effect on the fibre tenacity. Instead, the acetic acid spun fibres guided through the sulphuric acid bath had lower elongation at break than the fibres guided through the water bath (Figure 14). This indicates some further bonds between the molecules were created due to the sulphuric acid wash.

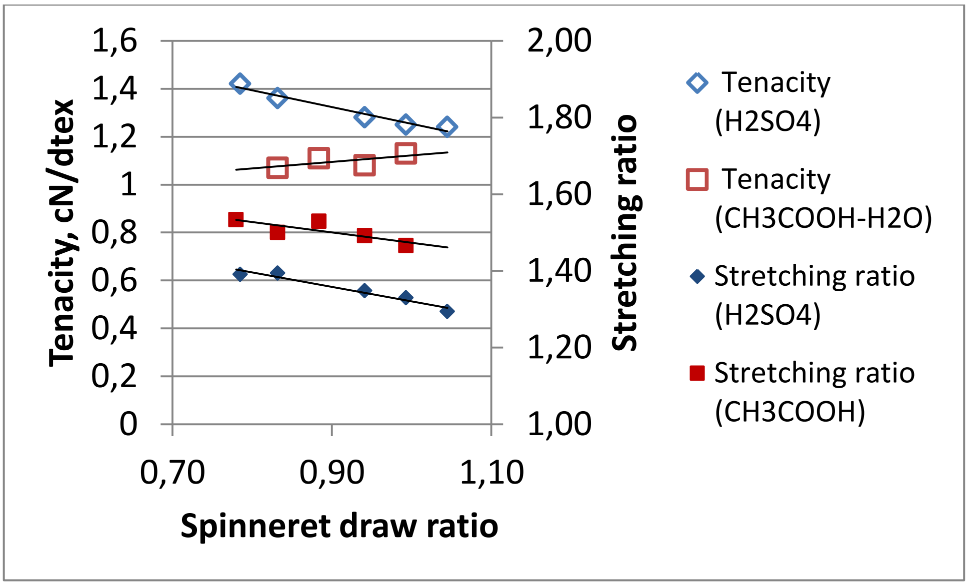


FIGURE 13 Relationship between spinneret draw ratio, tenacity and stretching ratio of sulphuric acid (H_2SO_4) and acetic acid (CH_3COOH-H_2O) spun fibres. Standard deviation of tenacity values were 0.03-0.06 in sulphuric acid spun fibres and 0.09-0.18 in acetic acid spun fibres.

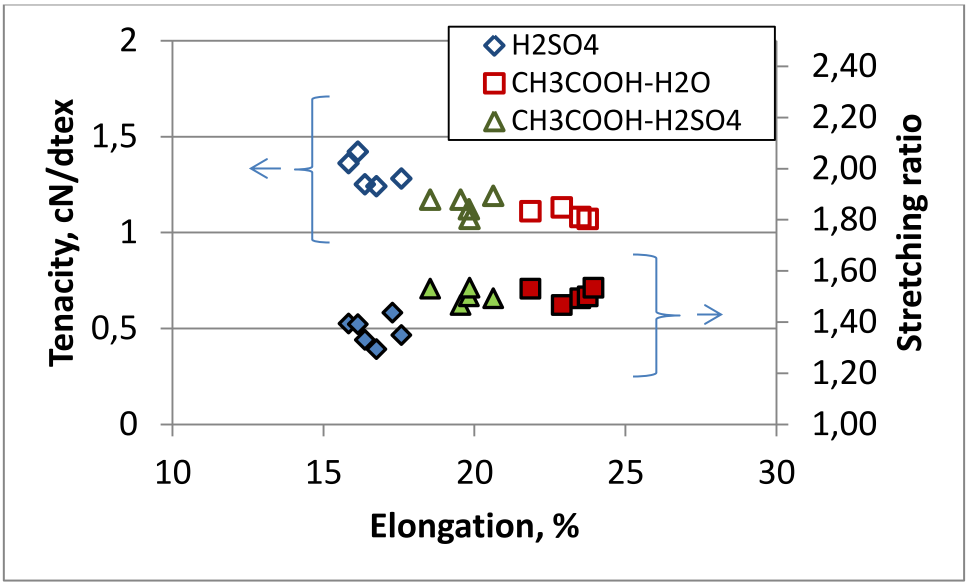


FIGURE 14 Relationship between elongation at break, tenacity at break and stretching ratio of sulphuric acid (H_2SO_4) and acetic acid (CH_3COOH-) spun fibres. CH_3COOH-H_2O-fibres were washed with water and CH_3COOH-H_2SO_4 with sulphuric acid. The filled symbols indicate stretching ratio and the open symbols tenacity of fibres. Standard deviation of tenacity values were 0.03-0.06 in sulphuric acid spun fibres, 0.09-0.18 in acetic acid-water washed and 0.08-0.10 in acetic acid-sulphuric acid washed fibres.

4.4.2 Characteristics of fibres

The birefringence of the fibres spun into acetic acid at maximum stretching ratio (1.5) was very low and at the same range (0.009) as of the fibres spun into sulphuric acid without stretching (i.e. stretching ratio 1.0). Instead, the birefringence of the fibres spun into sulphuric acid at maximum stretching ratio (1.4) was higher (0.025) and equal to commercial viscose fibres (Morton and Hearle 1993). In spite of the low birefringence of the acetic acid spun fibres their elongation at break and lateral order index (LOI) measured from the FTIR spectra were significantly lower than those of the fibres spun without stretching (Figure 15). These indicate the acetic acid spun fibres had more ordered structure than the fibres spun into sulphuric acid without stretching. It was concluded that the acetic acid spun fibres did orient due to the stretching, but most of the orientation was lost due to the shrinkage of the fibres during the drying.

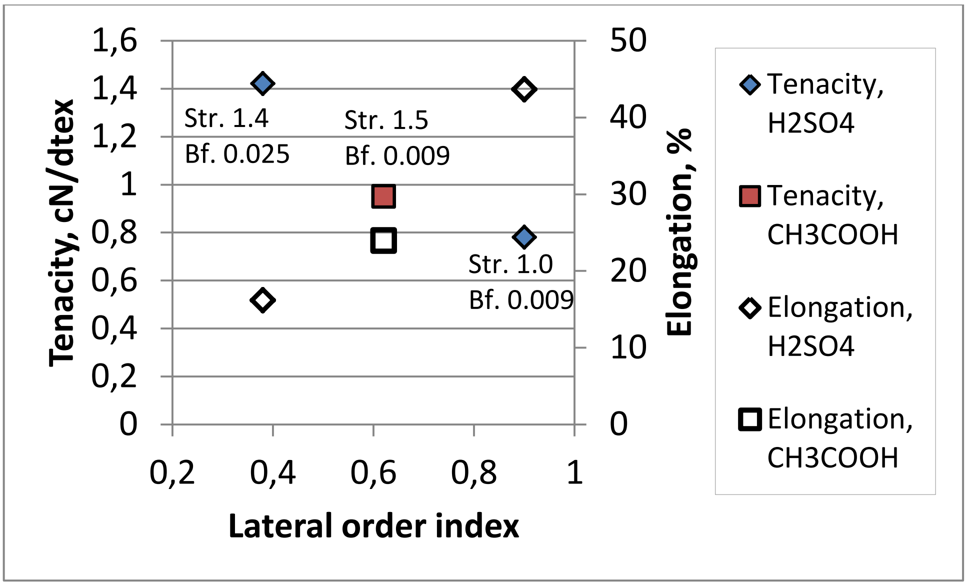


FIGURE 15 Relationship between lateral order index, tenacity at break and elongation at break of sulphuric acid (H_2SO_4) and acetic acid (CH_3COOH) spun fibres. Stretching ratios (Str.) and birefringence (Bf.) of fibres as indicated in Figure. Standard deviation of tenacity values were 0.04-0.05 in sulphuric acid spun fibres and 0.14 in acetic acid spun fibre.

4.5 Regeneration of fibres from alkaline solution containing enzyme-treated 3-allyloxy-2-hydroxypropyl substituted cellulose, Publication IV

How to modify the properties of the fibres?

The mechanical properties of the fibres regenerated from the NaOH-based solution are sufficient, but not superior, for the further textile processes. The introduction of new functionality for the fibres would make them interesting option for the special applications. The incorporation of the reactive double bonds in the cellulosic fibres through the 3-allyloxy-2-hydroxypropyl substituents was studied in the publication IV.

4.5.1 Spinning of mixture fibres

Enzyme-treated cellulose was modified in alkaline aqueous tert-butanol (tBuOH) using allyl glycidyl ether (AGE) as the modification reagent. The treatment resulted in cellulose with 3-allyloxy-2-hydroxypropyl substituents (AHP) with rather low degree of substitution (DS_A), 0.05, which implied that cellulose was not soluble in water. Instead, the solubility into sodium zincate was increased compared to the un-substituted reference pulp.

In spite of the low amount of substituents, the spinning solutions containing 100 % or 50 % of the AHP-pulp did not coagulate into fibres. The solutions containing 25 % or 10 % shares of the AHP-pulp formed fibres, but they required lower velocity of the spinning line compared to the reference dope from the un-substituted enzyme-treated pulp. The tenacity of the fibres ranged from 1.0 to 1.5 cN dtex^{-1} and the elongation from 18 to 26 %. Rather similar maximum tenacity was achieved for each types of the fibres as shown in Figure 16.

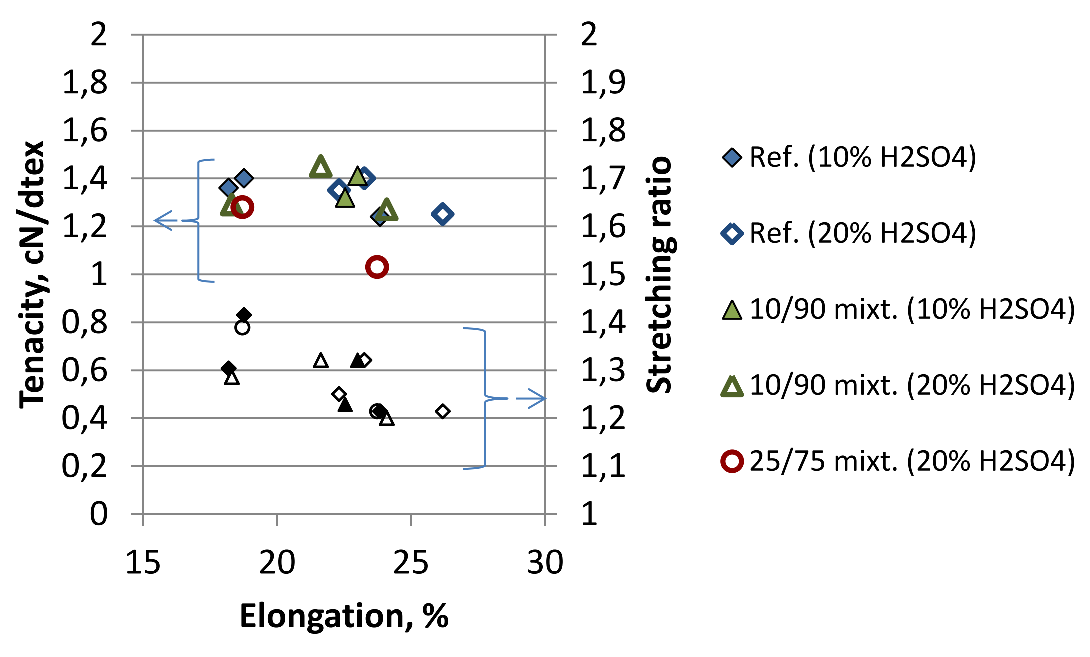


FIGURE 16 Relationship between stretching ratio, tenacity and elongation of reference fibres and mixture fibres containing 10% or 25% of AHP-pulp. Fibres coagulated either in 10% or 20% H_2SO_4 as indicated in legend. Coloured symbols indicate tenacity and respective black symbols indicate stretching ratio. Standard deviation of all tenacity values were below 0.09.

The stress-strain curves of the strongest fibres had identical shapes with the clear yield points (Figure 17). Elongation of the reference fibre was clearly higher when spun into 20 % sulphuric acid compared to 10 % sulphuric acid. The same effect was not seen in 10/90 mixture fibres, suggesting the small amount of substituents compensated the effect of acid. With higher amount of substituents (25/75 mixture fibres) the elongation was lower probably due to the lower tenacity.

The 10 % and 25 % shares of the 3-allyloxy-2-hydroxypropyl substituted cellulose in the fibres increased their water holding ability by 12 % and 33 %, respectively. This is most likely due to the loosen structure of the fibres induced by the 3-allyloxy-2-hydroxypropyl side chains (Klemm et al. 2005).

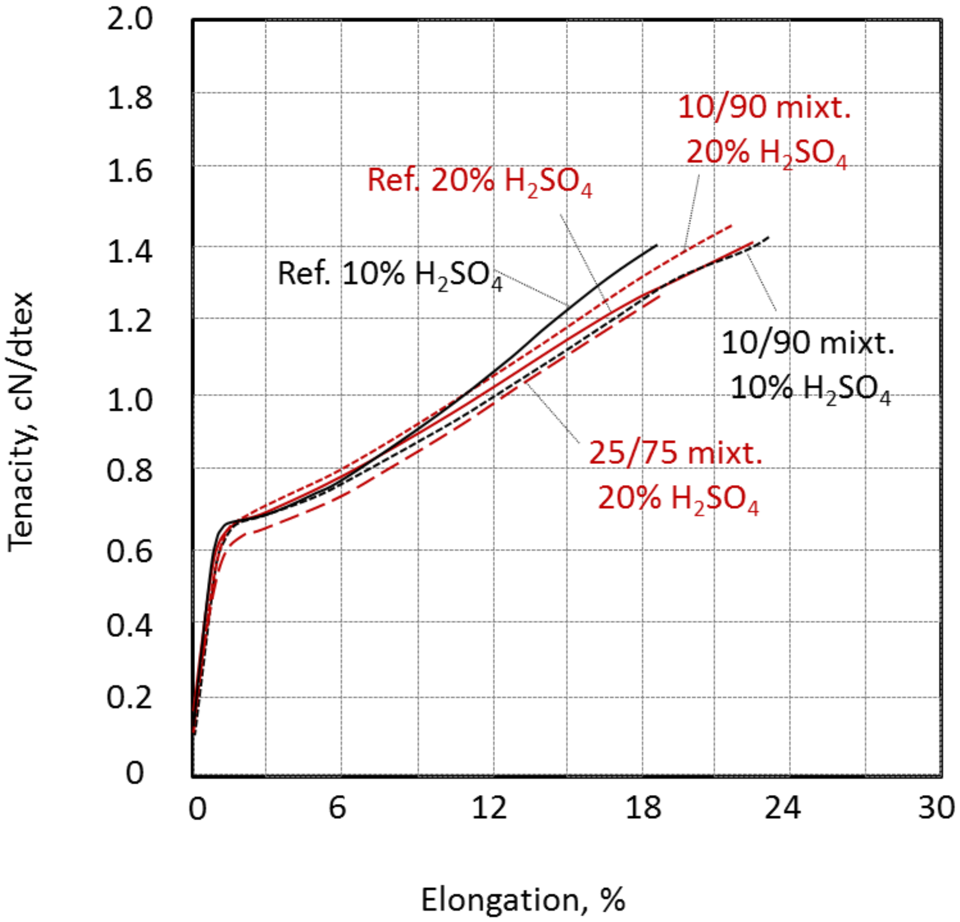


FIGURE 17 Stress-strain curves of reference fibres and mixture fibres containing 10% or 25% of AHP-pulp. Fibres coagulated either in 10% or 20% H_2SO_4 as indicated in figure.

4.5.2 Reactivity of fibres with 3-allyloxy-2-hydroxypropyl substituents

Reactivity of the C=C double bond in the 3-allyloxy-2-hydroxypropyl substituents was confirmed by the colorimetric method using bromine (Sepersu 2012). Small amount of fibres (ca. 0.1 g) was soaked in water (10 ml) and small amount of bromine was added. The sample with reference fibres was stained yellow and with 10/90-mixture fibres pale yellow. The sample with 25/75 mixture fibres did not change the colour due to the addition of bromine (Figure 18). This is due to the bromination of the double bonds, which confirm the fibres are reactive and can be further functionalised to gain new properties.

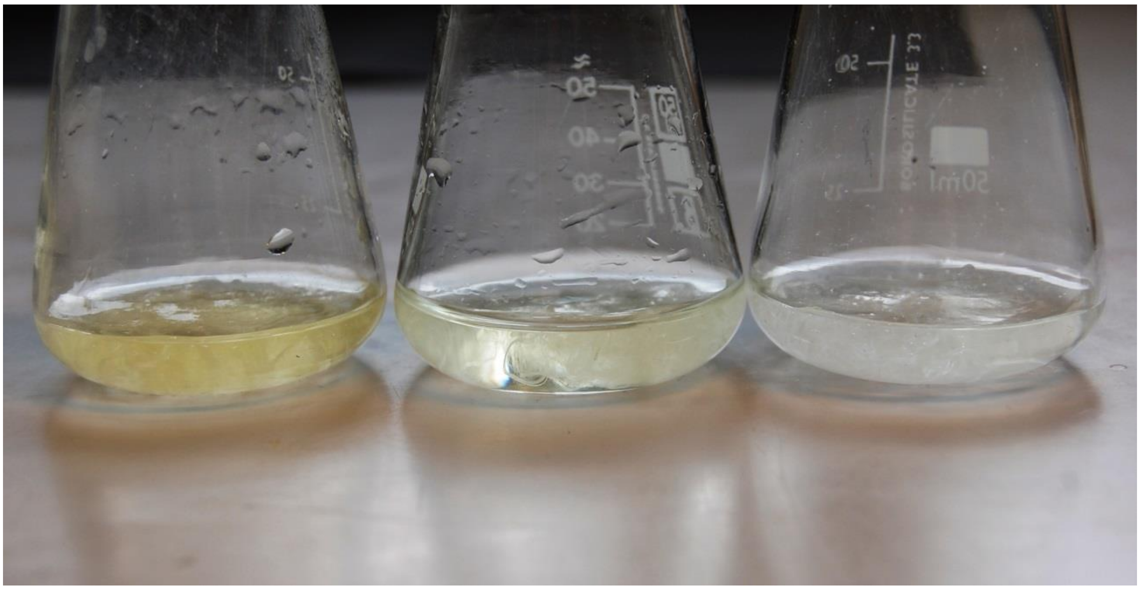


FIGURE 18 Reaction of fibres with bromine. Samples from left to right: reference fibres, 10/90-mixture fibres and 25/75-mixture fibres.

4.6 Results summary

The research problem identified is *a lack of procedure to produce cellulosic fibres in an economic and environmentally acceptable manner*. The objective of this work was to study the process that could offer a solution for the research problem. In this process the cellulosic fibres are manufactured from the enzyme-treated pulp by utilising commercial dissolving grade pulp and the known wet spinning method.

The entire process comprises multiple factors, thus it was not possible to cover all of them in this work. The contribution selected here included the proof of concept (Publication I), studies to improve the properties of cellulose solution (Publications II and III-part 1) and studies to modify the properties of fibres (Publications III-part 2 and IV).

The key factor of the process is the enzymatic treatment of cellulose. It results in cellulose that is soluble in NaOH-based solvent without use of hazardous chemicals. Thus, the cellulose treatment fulfils the requirement for the environmental acceptance.

However, to produce regenerated fibres from NaOH-based cellulose solution is not self-evident. The major challenge is the stability of the solution required for the filtration and deaeration steps. Thus, the first research question was:

1. *Is it possible to dissolve cellulose in a water-based solvent in a way the fibre forming process is successful using a wet spinning method?*

The results of several spinning trials are presented in the Publication I, thus showing that the concept works. Thereafter, it was possible to tailor the process towards the economical aspect. The next two research questions deal with the consumption of the chemicals:

2. *How to increase the cellulose concentration of the spin dope?*
3. *Is it possible to decrease the alkali concentration of the spin dope?*

In the Publication II it was shown that by decreasing the average degree of polymerisation of cellulose it was possible to increase the cellulose concentration from 6.0 wt% to 7.2 wt%. With the NaOH-concentration of 7.8 wt% the alkali ratio decreased from 1.3 to 1.1, thus decreasing the consumption of NaOH per produced fibre (kg/kg) by 17 %. From the neutralisation reaction between sodium zincate and sulphuric acid [$2NaOH + ZnO + 2H_2SO_4 \rightarrow Na_2SO_4 + ZnSO_4 + 3H_2O$] it can be calculated the consumption of sulphuric acid (kg) per produced fibre (kg) decreases also by 17 % when the cellulose concentration increased to 7.2 wt%. The figures are convincing, however, the degradation of cellulose deteriorated the fibre properties and other means to improve the economy were needed.

The new dissolution method utilising freezing-thawing cycle of cellulose/sodium zincate mixture was introduced in the Part I of Publication III. The optimal parameters found to be 6 wt% cellulose /1.3 wt% ZnO / 6.5 wt% NaOH. Compared to the parameters used in the Publication I (6 wt% cellulose /0.8 wt% ZnO / 7.8 wt% NaOH) the alkali ratio decreased from 1.3 to 1.1 and the consumption of sulphuric acid per produced fibre by 10 %. This procedure did not affect negatively to the fibre properties and the economy of the process was clearly improved regarding the consumption of chemicals.

When launching the new fibre, its properties are of utmost importance. As a consequence the next two studies focused on the mechanical strength and the functionality of the fibres. The research questions were:

4. *How to increase the tenacity of the fibres?*
5. *How to modify the properties of the fibres?*

There was a justified approach to increase the stretching ratio and consequently the tenacity of the fibres as reported in the Part 2 of Publication III. However, it turned out that in spite of the significantly increased stretching ratio the tenacity of the fibres was not increased. Reason for that was found to be the shrinkage of the fibres during the drying. Some corrective actions are suggested in paragraph 5.4 Recommendations for further research.

Chemical modification of cellulose prior to the dissolution was an interesting option to bring inherent properties for the regenerated fibres. It was possible to modify the enzyme-treated cellulose using allyl glycidyl ether and dissolve the cellulose containing 3-allyloxy-2-hydroxypropyl substituents. In spite of the low amount of substituents in the spinning solution they had profound effect on the coagulation behaviour of the solution. The same settings as used for the reference dope prepared from the un-substituted enzyme-treated pulp did not work for the mixture dopes. However, with adjusted settings the mechanical properties of the mixture fibres were comparable with the reference fibres. Moreover, it was shown that the mixture fibres contained reactive C=C double bonds which makes it possible to further functionalise the fibres.

5 Discussion

5.1 Theoretical implications

Almost complete dissolution of cellulose in aqueous sodium zincate and the following removal of the undissolved fraction are a prerequisite to fulfil the research problem: ‘*How to produce cellulosic fibres in an economic and environmentally acceptable manner*?’ The entire enzyme-aided process comprises a large number of variables which have been investigated over the years. The main steps of the process are 1) Cellulose pretreatment, 2) Dissolution of treated cellulose, 3) Filtration and deaeration of the cellulose solution, and 4) Wet spinning of the cellulose solution.

The types of cellulose and enzymes, as well as the treatments done for cellulose determine the properties of the solution obtained. The aim of this work was to produce regenerated cellulosic fibres from the dissolving grade chemical pulp similar to utilised in the viscose process. The mechanical shredding of cellulose prior to the enzymatic treatment was needed to decrease the average DP of cellulose at a level sufficient for the efficient dissolution. The shredding alone does not affect the DP, but it increases the porosity of the pulp (Grönqvist et.al. 2014) which in turn provides more accessible sites for the enzymes. As the enzyme requires direct contact with the substrate its efficiency increases due to the larger surface area (Medve et.al. 1994). Different kinds of mechanical treatments prior to the enzymatic treatment, and also a combined mechanical and enzymatic treatment have been studied in connection with the enzyme-assisted process (Grönqvist et al. 2015). However, in this work the shredding using a Baker Perkins type machine before the enzymatic treatment was set as a constant parameter.

The selection of optimal type of enzymes for the treatment is crucial for preventing too extensive degradation of cellulose and to obtain narrow molecular weight distribution.

The commercial enzyme preparations are mixtures, thus they always have more or less side activities besides the main activity. Rahkamo et al. (1996) studied the effect of purified *Trichoderma reesei* cellulases (EG I, EG II, CBH I and CBH II) on the alkaline solubility of cellulose. The endoglucanases were clearly more efficient than the cellobiohydrolases, and among the endoglucanases the EG II was superior in increasing the solubility of cellulose. As a consequence, the commercial enzyme preparations that have proven to work best are enriched with the endoglucanases and more preferable with the endoglucanase II. Such kinds of preparations are e.g. Ecostone N400 and Biotouch C29 produced by AB Enzymes, Finland, Fibercare R produced by Novozymes, Denmark, and IndiAge RFW produced by Genencor International B.V., The Netherlands. All of these enzyme preparations were used in this work.

The slight variations of the cellulose concentration in the alkaline solution had rather high effect on the fluidity of the solution as shown in Publication I. This was most likely due to the small fraction of high-DP cellulose, whose contribution to the viscosity increases with increasing concentration. This phenomenon is related to the volume occupancy of the large linear molecules in the solution (Mathur 2011). This emphasizes the importance to adjust the molecular weight distribution of cellulose to be as narrow as possible.

The adjustment of the average molecular weight of the enzyme-treated cellulose was studied with the aid of additional acid treatments (Publication II). The molar mass decreased rapidly which enabled to increase the cellulose concentration of the spinning solution. Also the molecular weight distribution of the cellulose became narrower due to the acid treatments. However, the treatment at higher temperature (100 ºC) led to an accumulation of short-chain molecules, which was seen as a shoulder formation in the molar mass distribution curve. As the DP of cellulose and the tenacity of cellulosic regenerated fibres exhibit positive correlation, the shorter the molecules the lower the tenacity of the fibres (Morton and Hearle 1993; Sixta et al. 2004). Apart from the lower tenacity of the fibres it was observed that the cellulose concentration of the spin dope and the fibre tenacity exhibited a slight positive correlation. This suggests that there is an optimum ratio between the molar mass of cellulose and its concentration in the spin dope which results in adequate mechanical properties for the fibres. By optimising this ratio it is expected to improve the economy of the process.

Freezing-thawing cycle of solid cellulose in aqueous sodium zincate is another way to improve (i.e. decrease) the alkali ratio of cellulose solution (Publication III, Part 1). By applying this method the enzyme-treated cellulose dissolved in significantly lower NaOH-concentration than without freezing (6.5 vs. 7.8 wt%). The beneficial effect of lowered temperature during the dissolution relates to the formation of eutectic mixture of NaOH hydrates (Egal et al. 2007). The eutectic crystals penetrate effectively into the cellulose fibre and interact with cellulose breaking the intermolecular and intramolecular hydrogen bonds (Yamashiki et al. 1988). A conformational change of the cellulose molecule due to the decreased temperature decreases the hydrophobic associations in cellulose crystal (Lindman and Karlström 2009) leading to solubilisation of cellulose. Moreover, the hydrogen bond network of the cellulose is most likely suitably weakened by the enzymes, which favours the dissolution, and on the other hand the new hydrogen bonds are created between the cellulose and zinc hydrate which prevents the chains to attached each other (Yang et al. 2011).

The rheological studies of the cellulose solution revealed that temperature, time and shear rate have a profound effect on the viscosity of the solution. At higher temperature (22 ºC vs. 18 ºC) the thixotropic behaviour disappeared and the share rate dependent viscosity decreased. However, the stability towards time at 22 ºC was less than three hours; the elasticity (G’) started to increase rapidly indicating the gel formation. The gelation is irreversible and is due to the aggregation of the cellulose molecules (Cai and Zhang 2006). In the first stage the cellulose sheets are stacked together by hydrophobic forces to form crystals, which are next attached to each other by hydrogen bonds (Isobe et al. 2012). The lower viscosity due to the increased temperature would be beneficial for the filtration and deaeration of the cellulose solution. However, in such a case one must consider the duration of operations and be able to monitor the development of viscosity.

The last step of this enzyme-aided process after the successful prior steps is the fibre forming using a wet spinning method. Publication I reports the results from several spinning trials of the cellulose solutions which were prepared by the mixing procedure, and Publication III of solutions prepared through a freezing-thawing cycle. Both methods proved to produce high quality dopes for the fibre spinning. In both studies the spinneret draw ratio is one parameter studied. In Publication I the term ‘compressive spinneret draw’ was used for the values below 1, whereas in Publication III a better term as ‘spinneret draw ratio’ was adopted. The spinneret draw ratio is not such a critical parameter in wet spinning if the formation of the permanent bonds between the molecules during the coagulation can be easily controlled. This is the case in the viscose process, where the fibre forming is controlled by neutralisation, salting out and regeneration of the cellulose xanthate (McGarry and Priest 1968). However, when the coagulation of the solution does not involve any chemical reaction its rate is more difficult to control. The coagulation tends to occur very fast with the formation of more permanent bonds. This result in coagulum which does not extend much between the godets, thus the effective orientation of the polymer chains is restricted. In the spinning trials done in this work, the spinneret draw ratio and the stretching ratio exhibit always negative correlation. This indicates that at least some of the bonds formed at low spinneret draw ratio are less permanent than the bonds formed at high spinneret draw ratio, thus allowing higher stretching. This might be connected to the diameter of the as-spun filament, which is larger at low spinneret draw ratio and therefore requiring longer time for the non-solvent to diffuse through the fibre (Radishevskii and Serkov 2005). As a consequence, the formation of rigid bonds in the fibre matrix is delayed allowing the fibres to stretch more between the godets. Generally, the tenacity and the stretching ratio of the fibres should coincidence with each other, which is the case with the sulphuric acid spun fibres. However, with an acetic acid spin bath (Publication III) the fibres stretched more but had yet lower tenacity than the comparable sulphuric acid spun fibres. Moreover, the tenacity and stretching ratio exhibited slight negative correlation. This was concluded to be due to the shrinkage of the acetic acid spun fibres during the drying. The shrinkage in turn, indicates that the structure was not fixed by permanent bonds until the fibres dried. Thus, some other means to fix the oriented structure and to prevent the shrinkage during the drying are needed. With the corrective actions it is expected that the fibre tenacity increases significantly.

Besides the composition of the spin bath, the properties of the spin dope determine the characteristics of the regenerated fibres. An etherification of the enzyme-treated cellulose using allyl glycidyl ether resulted in low degree of 3-allyloxy-2-hydroxypropyl substitution (DS_A 0.05) of cellulose (Publication IV). The solubility of modified pulp (AHP) in sodium zincate was significantly higher than of the un-substituted enzyme-treated pulp. The intrinsic viscosity of the pulp did not decrease during the etherification, instead it was slightly increased, which indicates that the low molar mass fraction was dissolved during the treatment. The improved solubility was suggested to be due to the increased entropy of the cellulose chains and the disturbed hydrogen bond network caused by the relatively large 3-allyloxy-2-hydroxypropyl groups which act as a spacer (Klemm et al. 2005, Spurlin 1946). The molar mass distribution might also have narrowed during the etherification, which in turn enhances the properties of the solution especially regarding the viscosity.

In spite of the very low DS_A the alkaline solution prepared from the substituted cellulose did not form fibres. This was probably due to the large substituents which restricted the close packing of the cellulose molecules, and thus the bonds required for the linear fibre structure were not formed. A decreased amount of substituents in the spin dope enabled fibre forming, although a lowered spinning velocity was required. Tenacity of the 25/75-fibres was slightly lower than that of the reference fibres, instead the 10 % share of the substituted cellulose did not affect the fibre properties too much. The presence of 3-allyloxy-2-hydroxypropyl groups brings reactive C=C double bonds in the structure, which enable the attachment of the functional groups to the fibres. The functional groups can be attached by grafting or by thiol-ene reaction. The graft copolymerisation of acrylic acid would lead to the superabsorbent fibres (Kaur et al. 2010) and of poly-N-isopropylacrylamide to the temperature-sensitive hydrogel fibres (Xie and Hsieh 2003; Carillo et al. 2008). The thiol-ene reaction would allow the attachment of polyethylene glygol (PEG) which also results in hydrogel fibre (Sepersu 2012) or of poly(ε-caprolactone) (PCL) which results in hydrophopic fibres (Zhao et al. 2010). The double bonds could also be used for cross-linking the fibres (Shen et al. 2006) to decrease e.g. shrinkage.

5.2 Practical implications

It was shown that the dissolving grade pulp dissolves into cheap and common aqueous sodium zincate after the appropriate mechanical and enzymatic treatments. The dissolution was conducted either by mixing the enzyme-treated pulp in precooled aqueous sodium zincate at cooling bath or by freezing the mixture of cellulose and sodium zincate. The mixing-procedure requires higher sodium hydroxide concentration than the freezing-procedure, moreover the temperature control during the mixing is challenging because of the evolved heat due to the friction. Incomplete dissolution due to the rapidly dissolved cellulose which forms a gel layer on the surface of particles was also observed.

Thus, the freezing-thawing cycle is a preferred practice to dissolve cellulose. The initial mixing is done at ambient temperature when the cellulose is not yet dissolved and a homogeneous mixture is easy to obtain. An efficient freezing unit which ensures the temperature of the cellulose/sodium zincate mixture to decrease at sufficiently high rate is required. However, this kind of units are in every-day use in food industry e.g. freezing tunnel or plate freezer used in freezing the fishes. A freezing tunnel was also tested in practice to freeze 60 kg of cellulose/sodium zincate mixture and found to work perfect. Otherwise, the machinery needed for the mechanical and enzymatic treatments are trivial and the conditions used moderate. The practices and machines needed for the filtration and deaeration of the cellulose solution, and for the regeneration of the solution to fibres are known from the viscose process.

As a result the machinery needed for realising the process exists and can be combined to a continuous process line for producing cellulosic fibres. It is foreseen, this could be an industrial process in the future, although a pilot scale line as an intermediate step would be needed to further optimise the operations.

Agents who could benefit this work include the pulp producers who are interested in adding the value of the pulp by enzymatic and/or chemical treatments, the viscose fibre producers who would like to tune their process towards the more susceptible practices or a new player who has courage to invest this process by establishing a pilot plant and reserving a share for the future fibre demand. The fibres prepared from the enzyme-treated pulp would be ideal for medical applications where the sulphuric impurities present in the viscose fibres are not allowed. Besides fibres, the alkaline cellulose solution could be applied for preparing films or coatings e.g. for sausage casings.

5.3 Reliability and validity

This work includes only part of the knowledge gained during the past 20 years in the subject. The results presented here are carefully studied and reproducible, and are thus reliable. However, lot of issues remain still to be studied in more detail in order to optimise the different steps of the process.

5.4 Recommendations for further research

The studies recommended here as further research include the approaches to optimise the process economy or the properties of the fibres, and also the scientific studies to gain more understanding of the mechanisms behind the certain behaviour.

Price of the raw material is identified to be one of the factors affecting the most the price of the regenerated fibres. Here, the raw material was dissolving grade pulp, which is the most expensive among the pulp materials. Some studies with cheaper paper grade pulp were done already in the 1990’s. Thereafter, the mechanical and enzymatic treatments as well as the dissolution procedure have been extensively developed and modified, thus it would be worth of thoroughly study the suitability of other cellulosic materials in the enzyme-assisted process.

The freezing-thawing method to dissolve cellulose was optimised in Publication III. However, more scientific approach to explain e.g. the effect and mechanism of ZnO/NaOH ratio on the dissolution ability is still lacking. Thus, investigation of the eutectic behaviour of different cellulose/NaOH/ZnO solutions according to Egal et al. (2008) should be carried out.

The rheological studies of the spin dope reported in the Publication III revealed the sensitivity of the solution towards temperature, time and prior shear. Nice correlation between the properties measured and the behaviour observed in practice was possible to draw. Thus, it would be rather useful to study the effect of different spin dope additives on the rheological properties of the solution. It should be possible to select the optimal additives and dosages regarding the stability of the dope towards temperature and time. The additives to be tested first are those known from the viscose process (e.g. different kinds of polyoxy ethylene glycol additives), and also the effect of small amount of 3-allyloxy-2-hydroxypropyl substituted pulp on the rheology would be interesting to elucidate.

In spite of the high stretching ratio of the fibres spun into acetic acid their mechanical strength was lower than of the fibres spun into sulphuric acid (Publication III). The reason was found to be the shrinkage of the fibres during the drying. Thus, the shrinkage must be prevented by fixing the orientation before drying. The effect of different chemicals in washing bath and/or stretching bath should be studied. The fibres can also be subjected to some physical treatment e.g. heat setting during the drying under controlled stress. A compromise between the elongation and tenacity of the fibres might be necessary to accept.

The coagulation conditions are crucial when using the NaOH-based cellulose solutions. It would be of utmost importance to be able to control the diffusion rates of the solvent and non-solvent during the coagulation. The effects of the dope properties (additives, rheological properties), fluid velocity and the composition of the spin bath on the properties of the as-spun fibres could be investigated by e.g. coagulating the solution without any drawing. The extent of die swell frozen in the fibres should correlate with the relaxation of the shear stress, and thus enlighten the effect of the coagulation chemicals on the diffusion rates. The recently proven crystallisation mechanism (Isobe et al. 2012) of cellulose molecules during the coagulation should also be fully considered.

Functionalisation and characterisation of the fibres having the C=C double bonds due to the 3-allyloxy-2-hydroxypropyl substituents belong also to the recommended further research.

Conclusions

An enzyme-assisted method to produce cellulosic regenerated fibres was introduced in this work. The wet spinning of the fibres was studied in more detailed, but as the successful fibre spinning requires high quality cellulose solution, and as the prior steps of the process affect the fibre properties the procedures related to the pulp treatment and preparation of the dope were also considered.

The mechanical shredding of pulp prior to the enzymatic treatment was needed in order to achieve high enough solubility for cellulose. This was due to the increased porosity of the pulp which provided more sites for the enzymes. The spinning dopes were prepared either by mixing the enzyme-treated pulp into precooled aqueous sodium zincate or by freezing the mixture of enzyme-treated pulp and sodium zincate. The freezing procedure is preferred because of easier temperature control, lower alkali ratio and higher stability at low temperature.

The rheological studies of the solution prepared through the freezing-thawing cycle with optimal content (1.3 wt% ZnO/6.5 wt% NaOH) revealed the solution was shear thinning, thixotropic and thermally the most stable between 18 - 21 ºC. When the temperature exceeded 22 ºC the cellulose molecules started to aggregate increasing the viscosity of the solution.

The coagulation rate decreased and the stretching ratio of the fibres increased when the sulphuric acid spin bath was replaced with an acetic acid bath. In spite of that the tenacity of the fibres did not increase. It was found that the acetic acid spun fibres shrunk during the drying and thus the orientation gained during the stretching was lost.

Fibres with inherent ability for functionalization due to the reactive C=C double bonds were prepared through the slight etherification of the enzyme-treated pulp with allyl glycidyl ether. Due to the rather large size of the substituents already small degree of substitution affected the properties of the dope. The fibres were prepared with 25 % and 10 % shares of the substituted pulp. The fibres can be further modified by grafting or thiol-ene reactions to obtain e.g. super absorbent fibres or temperature-sensitive hydrogel fibres. The fibres were shown to have the reactive bonds, however further functionalisation of the fibres remained to be done as the future research.

It was shown in this work that the production of regenerated cellulosic fibres in an environmental manner is possible, thus providing one option to fill the gap between the global demand of cellulosic fibres and the predicted supply by cotton and man-made cellulose fibres in the following decades.

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ORIGINAL PAPERS

I

EFFECT OF WET SPINNING PARAMETERS ON THE PROPERTIES OF NOVEL CELLULOSIC FIBRES

by

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Effect of wet spinning parameters on the properties of novel cellulosic fibres

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Abstract Novel cellulose fibres (Biocelsol) were spun by traditional wet spinning technique from the alkaline solution prepared by dissolving enzyme treated pulp directly into aqueous sodium zincate (ZnO/NaOH). The spinning dope contained 6 wt.% of cellulose, 7.8 wt.% of sodium hydroxide (NaOH) and 0.84 wt.% of zinc oxide (ZnO). The fibres were spun into 5% and 15% sulphuric acid (H_2SO_4) baths containing 10% sodium sulphate (Na_2SO_4). The highest fibre tenacity obtained was 1.8 $cNdtex^{-1}$ with elongation of 15% and titre of 1.4 dtex. Average molecular weights and shape of molecular weight distribution curves of the celluloses from the novel wet spun cellulosic fibre and from the commercial viscose fibre were close to each other.

Keywords Biocelsol · Cellulases · Cellulosic fibres · Directly alkaline soluble cellulose · Dissolving pulp · Enzymatic treatment of cellulose

Introduction

Most of the wet spun cellulosic fibres are currently produced using the viscose method, in which the chemical pulp is treated with sodium hydroxide (NaOH) and carbon disulphide (CS_2) to form an alkali soluble cellulose xanthate derivative. The derivative is thereafter dissolved in dilute NaOH and spun into fibres usually at acidic pH using a wet spinning technique. The CS_2 bound in the cellulose structure is liberated during the regeneration, and thus an efficient recovery system due to the hazardous nature of the CS_2 is required. In spite of a high recovery level, part of the CS_2 and some newly formed hydrogen sulphide (H_2S) emissions are liberated into the atmosphere. This is sensed as bad odours in the vasinity of the viscose factory (Mitchell and Daul 1990; Wilkes 2001).

The enzyme-assisted method to dissolve chemical pulp could be one solution to eliminate the environmental load caused by the viscose process. In this method, the sodium hydroxide and carbon disulphide

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treatments used in the viscose process are replaced with the cellulase treatment (Struszczyk et al. 1995; Matero et al. 1996; Rahkamo et al. 1996). The cellulase treated chemical pulp dissolves directly into alkaline solvent, which enables the production of cellulosic fibres without the use of carbon disulphide. The first fibres (Celsol) utilising the enzyme-treated pulp were produced from dopes containing 3–5 wt.% of cellulose, 9 wt.% of NaOH and 0 wt.% or 1.8 wt.% of zinc oxide (ZnO), the maximum tenacity of the fibres was 1.2 cNdtex^{-1} with an elongation of 13% (Matero et al. 1996; Vehviläinen and Nousiainen 1997).

In this paper we present the results from the spinning trials of second generation cellulosic fibres (Biocelsol) from enzyme-treated pulp and discuss the effect of spinning parameters on the fibre properties. Some properties of commercial nonwoven type viscose fibres are presented as reference.

Materials and methods

Enzymatic treatment

The starting material was a commercial dissolving grade softwood TCF sulphite pulp delivered by Domsjö Fabriker AB, Sweden. The pulp was first shredded mechanically for 5 h with a Baker Perkins Mixer at a cellulose consistency of 20 wt.%, and thereafter treated with a commercial endoglucanase-rich enzyme preparation at pH 5, 50 °C for 3 h. The enzymes were delivered by AB Enzymes Oy, Finland and Genencor International, Netherlands. The enzyme-dosage used was based on the endoglucanase activity of the preparations, being 250 nkat/g (IUPAC 1987). The enzyme treatment released about 3% of the pulp as soluble sugars measured using the DNS method (Bernfeld 1955) and decreased the viscosity from 405 mL/g to 270 mL/g as measured by the SCAN-CM 15:88 method.

Preparation of spin dope

The enzyme-treated pulp was dissolved into alkaline solvent according to the previously described method, except no urea was used (Struszczyk et al. 2001). The targeted solution content was 6 wt.% cellulose, 7.8 wt.% NaOH and 0.84 wt.% ZnO. The temperature of the cellulose mixture during the dissolution was maintained at approximately 3 °C by altering both the setting of the cooling agent and the rate of mixing. The solution obtained was filtrated through two AMN 546 K filter felts using a Diaphragm MZ 2C vacuum pump (Vacuubrand Gmbh+Co KG, Germany), and thereafter deaerated by lowering the pressure to 0.88 bar and leaving under vacuum throughout the following day. The temperature was maintained at approximately 0 °C during the filtration and deaeration.

The viscosity of the dope was measured using the modified Ball-Drop Method (ASTM D 1343-86) using stainless steel balls (1/8″, 130 mg) and a measuring distance of 20 cm. The filtrated and deaerated dope was collected from the gear pump into a measuring cylinder and the falling ball viscosity recorded at ambient temperature. The result was given as the average of three measurements.

Cellulose content (alpha) was measured by weighting the films casted from the filtrated solution into 10% H_2SO_4.

Spin baths

Spin baths with 5% and 15% of sulphuric acid (H_2SO_4) containing 10% of sodium sulphate (Na_2SO_4) were used. Temperature of the baths was set at approximately 15 °C.

Spinning

The fibres were spun using a laboratory wet spinning machine. The spin dope was pushed from a sealed reservoir (0 °C) to a Zenith BPB-4391 gear pump (0.30 mL/r) by nitrogen gas (1.5–2 bar). The spinning head with one spinneret was immersed in a vertical spin bath tank of 13 l, 35 cm from the surface. The spinneret used had 100 orifices of 51 μm and was made of a gold/platinum mixture by Wetzel Gröbzig Micro Products.

The spinning line consisted of three godets, one stretching bath with hot (>90 °C) demineralised water, two washing baths with cold (22 ± 2 °C) demineralised water and a fibre collector (Fig. 1). A solution of sodium lauryl sulphate (0.1%) was used to lubricate the godets during the spinning.

The desired initial speed of the spinning pump was calculated according to Eq. 1 (Götze 1967):

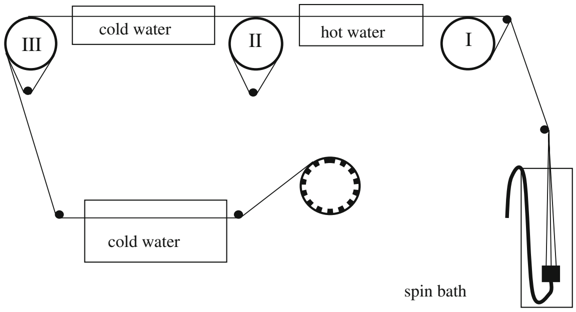

Fig. 1 Schematic presentation of the spinning line

$$Q = \frac{T \times n \times v_{\mathrm{III}}}{\rho_{\mathrm{dope}} \times \frac{\alpha}{100} \times 10000}, \tag{1}$$

where Q = capacity of pump, mL/min; T = desired titre of fibres = 1.7 dtex; n = number of spinneret orifices; v_{III} = speed of III godet = 20 m/min; ρ_{dope} = density constant of spin dope = 1.4 g/mL; α = cellulose concentration of spin dope, %

Additionally, the spinneret draw applied for the as-spun fibres was calculated as a ratio between the speeds of the first godet (V_1) and that of the spinning dope through the spinneret (V):

$$V = \frac{Q_1}{(\pi/4) \cdot D^2},$$

$$\begin{aligned} \Longrightarrow \text{spinneret draw} &= \frac{V_1}{(V)} \\ &= \frac{V_1}{\frac{Q/n}{(\pi/4) \cdot D^2}} = V_1 \cdot \frac{(\pi/4) \cdot D^2 \cdot n}{Q} \end{aligned} \tag{2}$$

where Q_1 = volumetric flow rate per orifice, mL/min; D = capillary orifice diameter, mm.

Several dopes were prepared for the spinning trials. The velocity of the spinning dope through the spinneret holes (V) varied from 20 to 72 m min^{-1} depending on the spinneret draw applied (0.4–1.1) and the spinning speed used (22–76 m min^{-1}). The maximum stretch ratio of the fibres ranged from 1.17 to 1.42. The fibres were collected in wet continuous form and thereafter cut into 5 cm lengths by hand. The fibres were washed with demineralised water until free of salts (measured with a conductivity meter) and finished by exchanging water to ethanol in order to minimise the fibre attachments during the drying. The drying was carried out at room temperature (22 ± 2 °C).

The obtained fibres (Biocelsol) were studied by measuring the mechanical properties, crystallinity, average size of crystallites and internal surface as a function of porosity, as well as, the structure of surface and cross sections. Additionally, the molecular weight of the cellulose from a Biocelsol fibre spun into 15% sulphuric acid and from a reference viscose staple fibre were analysed.

Reference viscose fibres

Reference viscose fibres (Viscose 1 and Viscose 2) were commercial nonwoven type fibres obtained from Suominen Nonwovens Ltd., Finland, where fibres are used as raw material for hydroentangled products. The fibre properties given by Suominen for Viscose 1 were titre 1.72 dtex, length 40 mm, tenacity 2.28 cNdtex^{-1} and elongation 19.3%, and for Viscose 2; titre 1.65 dtex, length 38 mm, tenacity 2.31 cNdtex^{-1} and elongation 19.7%.

Mechanical properties

The fibres were conditioned at a relative humidity of 65 ± 5% and temperature of 20 ± 2 °C for at least 24 h. The mechanical properties were determined as an average of 20 or 50 measurements according to the ISO 1973 and ISO 5079 standards using a Vibroskop and Vibrodyn testing machines (Lenzing AG). The tests included titre, tenacity, elongation, Young's modulus at 1% elongation and work of rupture. The rate of elongation was 20 mm min^{-1} and the gauge length 20 mm.

Average molecular weights and molecular weight distributions

The weight average degree of polymerisation ($\mathrm{DP_w}$) and the molecular weight distributions of selected samples were measured with Hewlett-Packard HP1050 HPLC apparatus and GPC method. The fibre sample was dissolved according to the previously developed method (Matero 1991) in which the air dried sample (25 mg) is immersed in dimethylacetamide (DMAc, 2 mL), heated in a microwave oven at 600 W for 2 min and cooled at ambient temperature for 5 min. Thereafter, the DMAc is poured off and 4.5 mL of 8% LiCl/DMAc added. The sample is rotated until it dissolves or heated at 105 °C for 10–30 min to enhance the dissolution. After complete dissolution the solution is diluted with 4.5 mL of DMAc, filtrated through 0.45 µm PTFE filter and analysed by HPLC.

Here, the GPC system consisted of a pump (Hewlett-Packard, HP 1050), a manual injector (Rheodyne Inc., model 7125), three Plgel Mixed A 300 mm columns (Polymer Laboratories, Ltd.) and a refractive index detector (Hewlett-Packard, HP 1047 A). Mobile phase, 0.5% LiCl/DMAc (vacuum filtrated through 0.45 µm PTFE filters), was pumped at a flow rate of 1.0 mL min^{-1}, and the sample injection volume was 100 µL. Calibration was carried out with the polystyrene standards (M_w 3200–5000000, Polymer Laboratories, Ltd.). The data was collected and processed by PL Caliber GPC/SEC Software Version 5.1 (Polymer Laboratories, Ltd.). Weight (M_w) and number (M_n) average molecular weights, and the average degree of polymerisation (DP_w) were calculated.

The Mark-Houwink constants used in the calculation were:

$$\text{for}\quad \text{polystyrene: } a = 0.65, K = 17.3 \times 10^{-5}\ \text{cm}^3\text{g}^{-1}$$
$$\text{cellulose: } a = 1, K = 12.78 \times 10^{-5}\text{cm}^3\text{g}^{-1}$$

Crystallinity and size of crystallites

Crystallinity degree and crystallite size of the fibres were analysed by Wide-angle X-ray diffraction (WAXS). Measurements were carried out in the reflection mode at ambient temperature using a Seifert URD-6 diffractometer with a scintillation counter connected to a computer. Ni-filtered CuK$_\alpha$ radiation ($\lambda = 1.542$ Å) was used, the X-ray diffraction patterns were registered between 2θ values from 2° to 60° with the step of 0.1°. Samples were powdered using a microtome in order to avoid the effect of orientation. The crystalline peaks in the patterns were indexed based on the cellulose unit cell parameters given by Ellefsen et al. (1964). Using this data, the interplanar spacings d(hkl) and the related angular positions of reflections were calculated. Crystallinity was calculated using a modified Hindeleh & Johnson method (Hindeleh and Johnson 1971, 1978) and a computer program *Waxsfit* (Rabiej 2002).

Porosity and nanostructure

Porosity of the fibres was obtained by measuring the interface area between the cellulose and pores (internal surface area) by Small angle X-ray scattering (SAXS). The measurements were carried out with a compact Kratky camera, equipped with the SWAXS optical system of Hecus-Mbraun (Austria). The Cu target X-ray tube, operated at 40 kV and 30 mA (PW1830 Philips generator), was used as the radiation source ($\lambda = 1.542$ Å). The primary beam was monochromatised by Ni filter and the scattered radiation was detected by a linear position sensitive detector. Samples were powdered using a microtome. The internal surface area was calculated based on the scattering model from the multiphase system (Goodisman and Brumberger 1971) using the method proposed by Brumberger (Brumberger et al. 1986).

Surface and cross section

The surface and cross section structures of the fibres were studied with a scanning electron microscope (JEOL JSM 5500 LV). Samples were cut to obtain cross sections and examined after coating with gold in the Jeol JFC 1200 ionic evaporator machine. Images were obtained using a secondary electrons detector.

Results and discussion

Enzymatic treatment

The loss of pulp during the enzymatic treatment was 3% at the maximum. In this study we did not analyse the composition of sugars released, however, as the enzyme preparations used were commercial products it is likely that they contained some activity against hemicellulose also. Thus, all the material lost was not cellulose and the yield (approx. 97%) obtained after enzymatic treatment is comparable with the yield of the viscose process after mercerisation.

Spin dope properties

The falling ball viscosity of the spin dopes prepared for the spinning trials varied from 82 s to 159 s. This was mainly due to small changes in cellulose concentration; viscosity increased with increasing concentration (Fig. 2). The source of endoglucanase, among the preparations used, was not found to affect the dope properties.

Mechanical properties

Spinneret draw, stretch ratio and the constitution of coagulation bath are among the most important spinning parameters affecting the fibre formation and the final fibre properties. Usually, the spinneret draw is higher than 1.0 and the values below that stand for compression. Here, most of the fibres were spun with compressive spinneret ‘draw’, because it worked better than the real drawing. The spinneret draws applied ranged from 0.4 to 1.1. Additionally, the fibres were stretched as much as possible between the first and the second godets. The fibres spun with the spinneret ‘draw’ below 0.6 withstand stretching higher than 30%, whereas the maximum stretching of the other fibres ranged from 17% to 27%. The sulphuric acid concentration of the coagulation bath (5% or 15%) did not affect the stretch ratio at the different spinneret draws applied (Fig. 3).

Generally, the tenacity of wet spun fibres increases with the increasing stretch of the fibres. Here, the trend is also seen in spite of the deviation of fibres spun into 15% sulphuric acid and stretched by 26–27% (Fig. 4). The deviation can be explained by the spinneret draw applied, as seen in Fig. 5; the tenacity of fibres (stretched by 26–27%) increases with increasing spinneret draw following a polynomial curve. The relationship between fibre tenacity, stretch ratio and spinneret draw was further studied at constant spinneret draws of 0.7 and 1.0 (Fig. 6). It was found that the increasing stretch ratio did not affect the fibre tenacity if the spinneret ‘draw’ was compressive (0.7). However, at the spinneret draw 1.0 the tenacity of the fibres increased clearly with the increasing stretch. Eventhough, we did not measure the orientation factor of the fibres, we

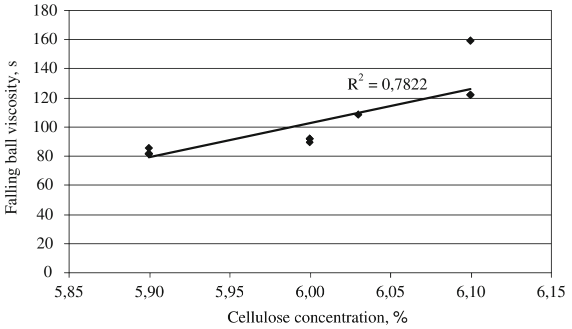

Fig. 2 Falling ball viscosity of the spin dopes as a function of cellulose concentration

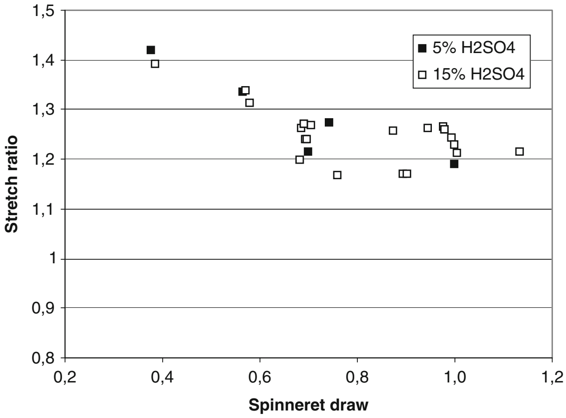

Fig. 3 Stretch ratio of the fibres as a function of spinneret draw

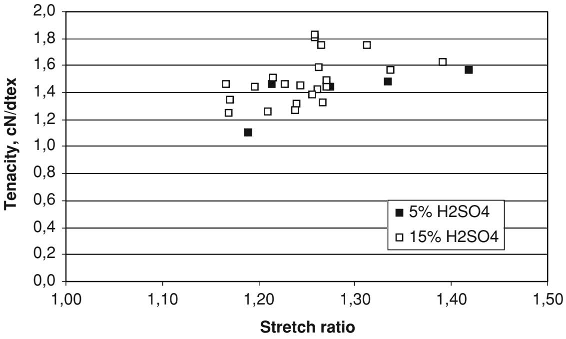

Fig. 4 Tenacity of the fibres spun into 5% and 15% sulphuric acid as a function of stretch ratio

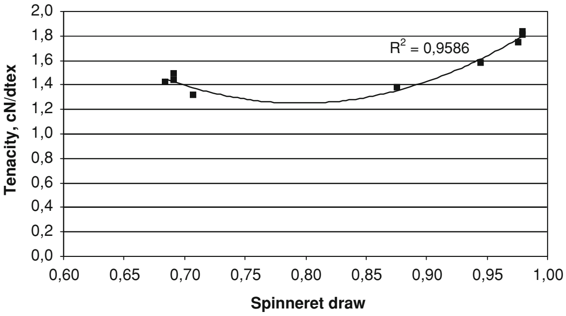

Fig. 5 Tenacity of the fibres spun into 15% sulphuric acid and stretched by 26–27% as a function of spinneret draw

propose that the fibres spun with spinneret draw 1.0 have higher orientation than the fibres spun with spinneret draw 0.7 (compression). This is based on the fact that without drawing the molecular chains cannot straighten up effectively in the spin bath but coagulate more or less a curly arrangement. Additionally, the structure of fibres fix so tightly that they do not stand very high stretching between the godets. Here, the small stretching applied was not enough to increase the chain orientation of the fibres spun with compressive spinneret 'draw', thus no effect on the fibre tenacity was achieved. Instead, with spinneret draw 1.0 even the small stretching increased the tenacity of fibres, which is most likely due to further orientation of the molecular chains (Fig. 6).

Tenacity and breaking extension of all the Biocelsol fibres spun into 5% and 15% sulphuric acid baths and of the reference viscose fibres are shown in Fig. 7. The strongest fibres obtained with 5% sulphuric acid had a tenacity of 1.6 cNdtex^{-1}, and with 15% sulphuric acid of 1.8 cNdtex^{-1}. The tenacity of reference viscose fibres (measured with the same equipment as the Biocelsol fibres) were 2.1 cNdtex^{-1} (Viscose 1) and 2.2 cNdex^{-1} (Viscose 2). Examples of the stress–strain curves of the Biocelsol and viscose fibres are given in Fig. 8. The shape of all the curves is identical with clear yield points; the yield strain is about the same for both types of fibres, but the yield stress of the Biocelsol fibre spun into 15% sulphuric acid is higher than that of the viscose fibres. This indicates that the Biocelsol fibres (spun into 15% sulphuric acid) have better elastic recovery than the viscose fibres (Morton and Hearle 1993).

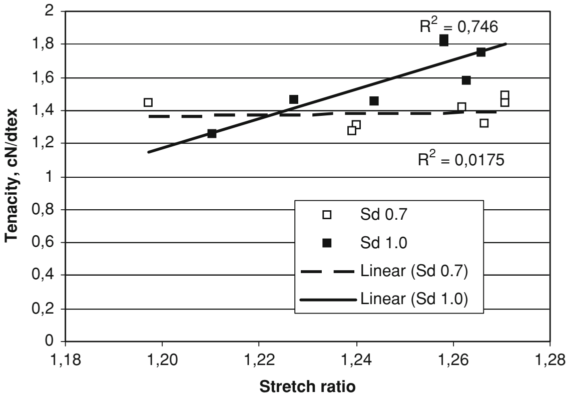

Fig. 6 Tenacity of the fibres spun into 15% sulphuric acid at spinneret draw 0.7 and 1.0 as a function of stretch ratio

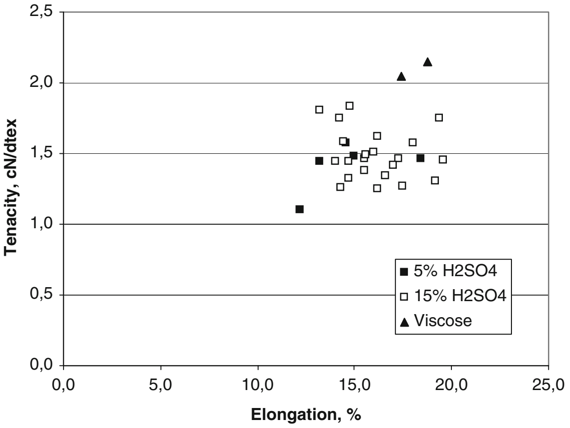

Fig. 7 Breaking tenacity and extension of the Biocelsol fibres spun into 5% or 15% sulphuric acid and of the commercial viscose fibres

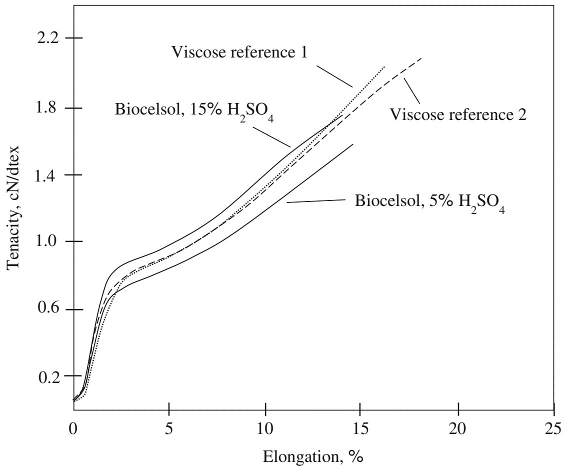

Fig. 8 Stress–strain curves of Biocelsol and reference viscose fibres

Fibre morphology

The crystallinity degree of the Biocelsol fibres varied from 38% to 47% and the average size of the crystallites from 40 Å to 43 Å. No clear trend between the crystallinity degree and tenacity of the fibres was found. Variation in the average crystallite size was small, however the fibres spun into 5% sulphuric acid had slightly larger crystallites than the fibres spun into 15% sulphuric acid. The crystallinity degree of the commercial viscose fibres differed considerable from each other being 28% for Fibre 1 and 39% for Fibre 2. The average size of the crystallites of both viscose fibres was 42 Å. The

Biocelsol fibres have a clearly higher average crystallinity degree (42%) than the viscose fibres (34%), which might be due to the more rapid coagulation of the Biocelsol spinning solution in the acidic bath compared to the coagulation rate of the fibres in the viscose process (Table 1).

The spinneret draw and the sulphuric acid concentration of the coagulation bath had clear effects on the porosity (internal surface) of the Biocelsol fibres as measured by SAXS (Fig. 9). The porosity decreased with increasing spinneret draw, and at the equal spinneret draw the fibres spun into 15% sulphuric acid had a clearly higher porosity than the fibres spun into 5% sulphuric acid. The effect of spinneret draw on porosity might be due to the fibre orientation; with higher spinneret draw the chains are packed less curly and there are fewer empty spaces between the chains, thus porosity decreases. The effect of the sulphuric acid concentration on the porosity is most probably due to differences in the diffusion rates of the solvent (ZnO/NaOH) and non-solvents (5% and 15% H_2SO_4) during the coagulation. The diffusion occurs faster in the higher non-solvent concentration (15% H_2SO_4) resulting in faster coagulation of the fibre structure and thus more developed pore structure than in the lower (5% H_2SO_4) non-solvent concentration. Additionally, it was found that the average porosity of the Biocelsol fibres (1140 m^2 cm^{-3}) is considerably higher than that of the reference viscose fibres (543 m^2 cm^{-3}). This indicates that the Biocelsol fibres might have a higher absorption capacity than the viscose fibres, which would be an important parameter in hygiene applications, for example (Table 1).

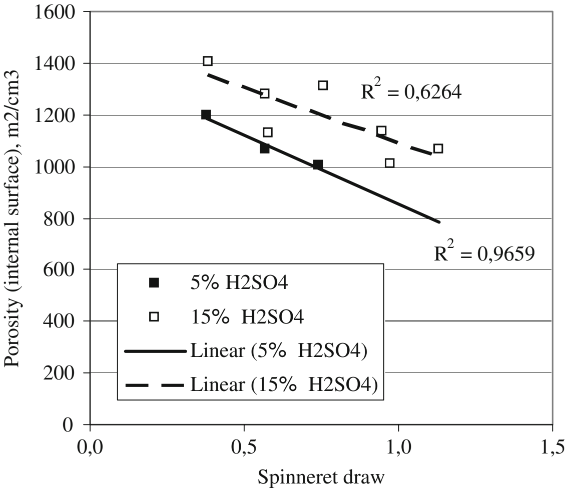

Fig. 9 Porosity of the Biocelsol fibres spun into 5% or 15% H2SO4 as a function of spinneret draw

Surface and cross-section of the fibres

Biocelsol fibres have circular cross section more like lyocell than viscose fibres (Fink et al. 2001), which is logical due to the rapid precipitation of cellulose without any chemical reaction. The surface structure of the fibres spun into 5% sulphuric acid was smooth and the shape of the cross section slightly angular as

Table 1 Crystallinity degree, size of crystallites and porosity of Biocelsol fibres and reference viscose fibres

Fibre	Coagulant H_2SO_4 (%)	Spinneret draw	Stretch ratio	Titre (dtex)	Tenacity (cN/dtex)	Crystallinity degree (%)	Average size of crystallites (Å)	Porosity (m^2/cm^3)
1	15	0.4	1.39	3.7	1.6	38	42	1406
2	15	0.6	1.34	2.3	1.6	42	41	1282
3	15	0.8	1.17	2.0	1.5	39	42	1315
4	15	0.9	1.26	1.5	1.6	42	41	1133
5	15	1.1	1.22	1.4	1.5	42	41	1068
6	15	1.0	1.23	1.4	1.5	45	41	
7	15	0.6	1.31	2.7	1.8	41	40	1131
8	15	1.0	1.27	1.8	1.8	47	40	1008
9	5	0.4	1.42	3.1	1.6	38	43	1196
10	5	0.6	1.33	2.2	1.5	44	42	1064
11	5	0.7	1.27	1.8	1.4	42	42	1002
Viscose reference 1, commercial				1.9	2.1	28	42	428
Viscose reference 2, commercial				1.7	2.2	39	42	658

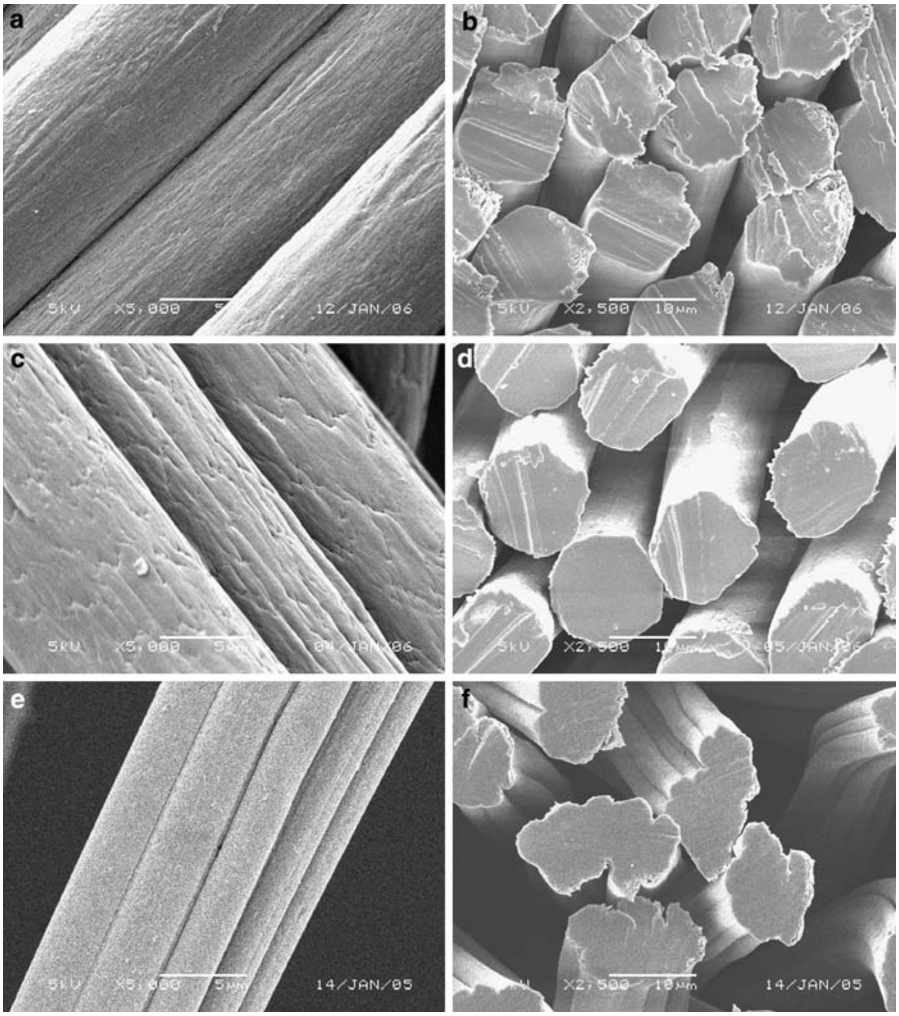

Fig. 10 (**a**) Surface and (**b**) cross section of the Biocelsol fibre spun into 5% H_2SO_4, (**c**) surface and (**d**) cross section of the Biocelsol fibre spun into 15% H_2SO_4, (**e**) surface and (**f**) cross section of the reference viscose fibre

compared to the fibres spun into 15% sulphuric acid. The deep furrows developed on the surface of the fibres in 15% sulphuric acid are probably due to the very rapid solidification of the solution without any relaxation of the structure. Surface and cross section images of the Biocelsol fibres are presented in Figs. 10a–d and the reference viscose fibres in Figs. 10e and f.

Molecular weights

The weight average polymerisation degree (DP_w) of cellulose from the Biocelsol fibres spun into 15% sulphuric acid was 268, and of the cellulose from the reference Viscose fibres (1) 220 (Table 2). The most significant difference in molecular weight distribution curves is the larger fraction of high DP cellulose in the Biocelsol fibre as compared to the Viscose fibre (Fig. 11). This can be the reason for the relatively high viscosity of the Biocelsol spinning solutions regarding to the cellulose concentration used (Fig. 1). However, it can be stated that the enzymatic treatment of dissolving pulp depolymerises the cellulose in a manner closely similar to that of an alkaline ageing in the viscose process.

Conclusions

The second generation cellulosic fibres from the enzyme-treated pulp were successfully spun with a

Table 2 Molecular weight determination of cellulose from the Biocelsol fibre and from a commercial viscose staple fibre

Sample	M_n	M_w	M_w/M_n	DP_w	Content of DP_w fraction (%)		
					$200 > DP_w$	$200 < DP_w < 550$	$DP_w > 550$
Biocelsol fibre	17436	43685	2.5	268	55	33	12
Viscose reference fibre 1	17000	35000	2.1	220	61	33	6

M_n = Number average molecular weight, M_w = Weight average molecular weight, DP_w = Weight average degree of polymerisation

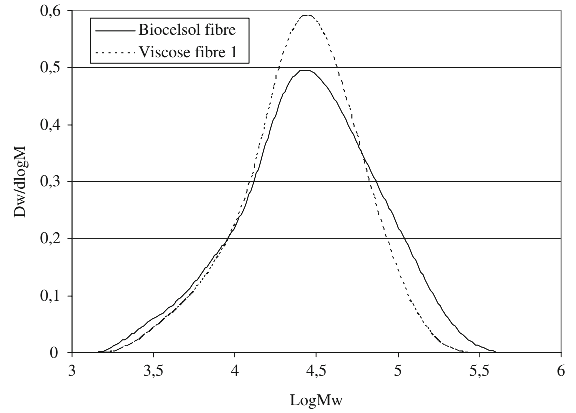

Fig. 11 Molecular weight distribution curves of cellulose from Biocelsol fibre and from a commercial viscose fibre

laboratory wet spinning machine. The fibre formation worked better with the compressive than the actual spinneret draw. The spinneret draw applied affected the stretching, tenacity and porosity of the fibres. With the compressive spinneret ‘draw’ the stretching did not affect the fibre tenacity, whereas with spinneret draw 1.0 the tenacity increased with the increasing stretch. The porosity of fibres decreased with the increasing spinneret draw, which is supposed to be due to the increased orientation of the fibres.

The concentration of the coagulation bath (5% or 15% H_2SO_4) affected tenacity, porosity, average size of crystallites, shape of cross section and surface structure of the fibres. The tenacity and porosity of the fibres spun into 15% sulphuric acid were higher and average size of crystallites was smaller than that of the fibres spun into 5% sulphuric acid. The cross section of the Biocelsol fibres was more like lyocell than viscose with circular shape. The surface structure of Biocelsol fibres spun into 15% sulphuric acid was more furrowed than that of the fibres spun into 5% acid. The differences in the porosity, cross section, average size of crystallites and morphology are probably due to the faster solidification of fibres in the higher spin bath concentration.

The Biocelsol fibres have more cellulose with high DP than the viscose fibres. This fraction is most likely the reason for the relatively high viscosity of the spin dopes regarding to the cellulose concentrations. The similar kind of molecular weight distribution curves of the cellulose from Biocelsol and from viscose fibres suggests that the depolymerisation caused by the enzymes is comparable to the alkaline ageing in the viscose process. Thus, the enzyme-assisted method could be a potential option for replacing the viscose method because the raw material (dissolving pulp) and the fibre forming method are identical. The clear advantage would be the elimination of carbon disulphide, which consequently completely eliminates the bad odour emissions into the air.

The second generation cellulosic fibres from enzyme-treated pulp (Biocelsol) were spun from the dopes with a lower alkali to cellulose ratio (7.8%/6%) than the first generation (Celsol) fibres (3–5%/9%). With improved procedures and optimisation of the spinning process the fibre tenacity increased from 1.2 $cNdtex^{-1}$ (Celsol) to 1.8 $cNdtex^{-1}$ (Biocelsol) with the elongation increase from 13% to 15%, respectively. Studies to further improve the fibre properties will be continued.

Acknowledgments The research was carried out in the EU FP6 project Biocelsol—Biotechnological Process for Manufacturing Cellulosic Products with Added Value, with contract number of NMP2-CT-2003-505567. The authors wish to thank European Commission for partly financing the work. The authors wish also to thank Teija Jokila and Nina Vihersola, VTT Biotechnology, for their excellent laboratory work related to the enzymatic treatments, Maija Järventausta and Esa Leppänen, Tampere University of Technology, for their excellent contribution in fibre spinning trials and fibre testing and Dr Ryszard Kwiatkowski of the University of Bielsko-Biała for valuable discussion on structural parameters. The text reflects only the authors’ views and the Community is not liable for any use that may be made of the information contained therein.

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II

EFFECT OF ACID AND ENZYMATIC TREATMENTS OF TCF DISSOLVING PULP ON THE PROPERTIES OF WET SPUN CELLULOSIC FIBRES

by

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EFFECT OF ACID AND ENZYMATIC TREATMENTS OF TCF DISSOLVING PULP ON THE PROPERTIES OF WET SPUN CELLULOSIC FIBRES

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Dissolving-grade softwood pulp was treated with EG-rich enzymes and hot diluted sulphuric acid, to decrease the molecular weight of cellulose. The treated samples were dissolved in aqueous sodium zincate and spun into cellulosic fibres by a wet spinning method. The effects of cellulose concentration in the spinning solution and of cellulose molecular weight on the fibre properties were studied. The molecular weight (M_w) of the treated cellulose decreased by 38 to 63%, depending on the treatment parameters. The falling ball viscosity of the alkaline solution prepared from the differently treated pulps correlated linearly with the M_w of the treated cellulose. At constant M_w of cellulose, the tenacity of the obtained wet spun fibres correlated positively with the cellulose concentration of the spinning solution. However, a higher cellulose concentration could not compensate the lowered M_w as to the fibre properties.

Keywords: enzymatic treatment of cellulose, cellulosic fibres, wet spinning

INTRODUCTION

Native cellulose fibres have a complex physical structure, due to their different layers, composed of oriented microfibril lamellas.[1] The microfibrils are built up from aggregated elementary fibrils formed of cellulose molecules attached to each other by intermolecular hydrogen bonds. The molecules also have large intramolecular hydrogen bondings, which makes the structure rigid.[2] The cellulose fibres as such are considered to be insoluble in aqueous solutions. Consequently, derivatisation with carbon disulphide is used in the viscose process to dissolve and convert them into variously shaped articles. However, carbon disulphide is a highly toxic chemical, which requires special care in handling and recovery.[3] Therefore, an ecological method to dissolve cellulose in an aqueous environment is still being sought.

Enzymes have proved to be powerful biocatalysts that modify the cellulosic material into an alkaline soluble form.[4-6] In nature, the synergistic action of different cellulases leads to the degradation of native crystalline cellulose into glucose monomers.[7] However, when using specially tailored enzymes with a controlled ratio of different cellulases, it is possible to obtain alkali-soluble cellulose with a reasonable degree of polymerisation.[4,5]

The first alkaline solutions prepared from enzyme-treated cellulose for fibre spinning[5,8] had relatively low cellulose (3-5 wt%), and high sodium hydroxide (9 wt%) and zinc oxide (1.9 wt%) concentrations. Thereafter, cellulose concentration increased to 6 wt%, while the sodium hydroxide and zinc oxide concentrations decreased to 7.8 wt% and 0.84 wt%, respectively.[9] The ratio between sodium hydroxide and cellulose in the spinning solution determines the amount of sulphuric acid needed for regeneration, as well as the amount of sodium salt formed as a by-product. Thus, the ratio is critical for the economy of the wet spinning process and it should desirably be below 1.

In the present investigation, the molecular weight of enzyme-treated cellulose was lowered prior to dissolution, which permitted to increase the cellulose concentration of the spinning solution. Degradation was carried out by dilute acid hydrolysis. The effects of cellulose molecular weight and cellulose concentration of the spinning solution on the properties of wet spun fibres are discussed.

MATERIALS AND METHOD

The raw material used was a commercial dissolving-grade sulphite pulp produced from a mixture of pine and spruce, by a total chlorine-free process. The pulp was delivered by Domsjoe Fabriker Ab, Sweden.

The starting pulp was first treated mechanically and with enzymes, as previously described,[9] then subjected to 0.1 M H_2SO_4 for 30 min at 80 °C or at 100 °C. Finally, the pulp was washed with demineralised water until an acid-free condition was reached. The reference samples prepared represented mechanically shredded pulp without further treatments, with enzymatic treatment only or with acid treatment (100 °C) only (Fig. 1).

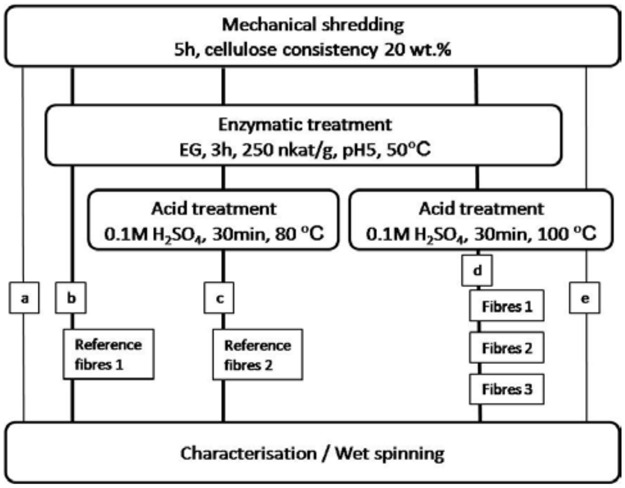

Figure 1: Schematic presentation of the treatments

The molecular weights of the differently treated samples were measured with an HPLC at Domsjoe Fabriker Ab.

The treated pulps were dissolved into aqueous sodium zincate, according to a previously described method,[10] the only exception being that no urea was used. Viscosity of the obtained alkaline cellulose solutions was measured by the modified Ball-Drop Method (ASTM D 1343-86) with stainless steel balls (1/8”, 130 mg), at a measuring distance of 20 cm. Viscosity was measured immediately after dissolution and then again on the next day, in the solutions applied for fibre spinning. The cellulose content (alpha) of the alkaline solution was measured by weighing the dried films prepared by casting the solution into 10% H_2SO_4.

The cellulosic fibres were spun from the selected alkaline solutions by the wet spinning method.[9] Two types of reference fibres were prepared, one from the mechanically and enzyme-treated pulp without acid treatment, and another one with subsequent acid treatment, at 80 °C. Three fibre samples were prepared from the mechanically and enzyme-treated pulp with subsequent acid treatment, at 100 °C, to study the effect of dope cellulose concentration on the fibre properties. The coagulation bath had either a low (50 g/L) or a high (168-246 g/L) amount of sulphuric acid. The mechanical properties of the fibres were determined as described previously.[9]

RESULTS AND DISCUSSION

The acid treatment at 100 °C decreased the molecular weight of the mechanically shredded pulp by 52%, while the enzymatic treatment decreased it by 38%. The acid treatments of the enzyme-treated pulp further decreased the M_w by 39 or 21%, as depending on the temperature the acid treatment was carried out at: 100 or 80 °C (Table 1). Each treatment decreased the polydispersity of molecular weight distribution, as compared to that of the sample treated only mechanically. The acid treatment of the mechanically shredded pulp at 100 °C produced a nearly identical shape of the molecular weight distribution curve with that obtained after the acid treatment of the mechanically and enzyme-treated pulp at 80 °C. The acid treatment of the mechanically and enzyme-treated pulp at 100 °C degraded cellulose to a higher extent, and increased clearly the share of low molecular weight cellulose – compared to the other samples (Fig. 2).

The molecular weight of the differently treated pulps correlated linearly with the falling ball viscosity of the alkaline solution, at constant cellulose concentration (Fig. 3). On the other hand, at constant M_w, falling ball viscosity increased very fast above a certain cellulose concentration, indicating a rapid gelling behaviour of the alkaline solution at a higher cellulose content (Fig. 4).

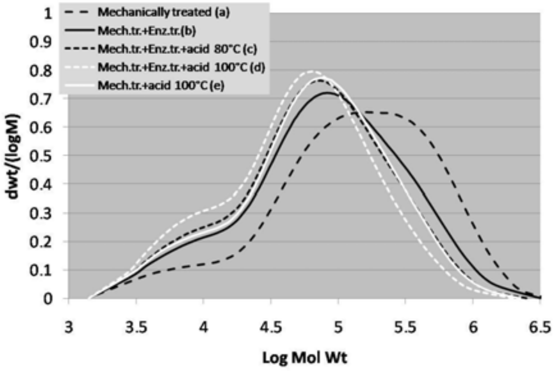

Figure 2: Average molecular weight distribution curves of differently treated pulp samples

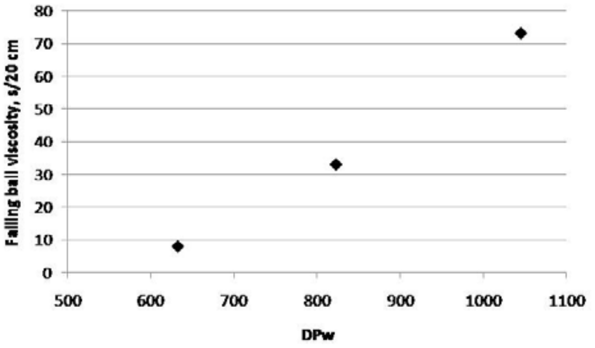

Figure 3: Falling ball viscosity of alkaline cellulose solution at constant cellulose concentration (~6 wt%)

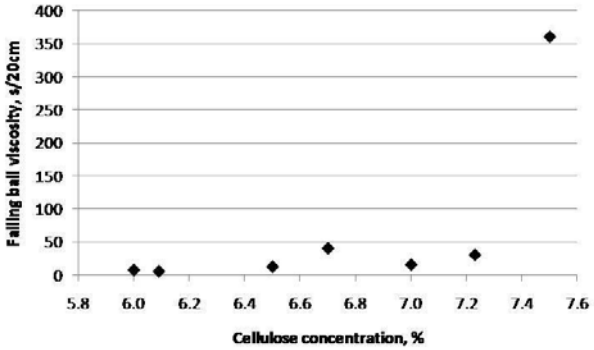

Figure 4: Falling ball viscosity of alkaline cellulose solution at constant weight average molecular weight (103153)

Table 1

Weight average (M_w) and number average (M_n) molecular weights of the samples
(Pd = polydispersity, DP_w = weight average degree of polymerisation)

Sample		Mw	Mn	Pd	DP_w
A	Mechanically treated	276160	40445	6.83	1694
B	Mechanically + enzyme-treated	170384	28843	5.91	1045
C	Mechanically + enzyme-treated + acid-treated at 80 °C	134154	25446	5.27	823
D	Mechanically + enzyme-treated + acid-treated at 100 °C	103153	21729	4.75	633
E	Mechanically treated + acid-treated at 100 °C	132810	26028	5.10	815

M_w was shown to have a positive linear correlation with the tenacity of the obtained fibres (Fig. 5). However, the slightly weaker fibres, with lower M_w, have the extensibility equal (~16%) to that of the fibres with higher M_w (Fig. 6). At the same molecular weight, the cellulose concentration of the spinning solution was nearly linearly correlated with fibre tenacity (Fig. 7), but did not present an equally clear correlation with elongation (Fig. 8). Instead, the high sulphuric acid concentration of the spin bath seemed to increase fibre elasticity (Fig. 9), while the effect on tenacity was not so obvious (Fig. 10).

At the same M_w and spin bath acid values, a higher cellulose concentration of the spinning solution produced stronger and more elastic fibres than those produced at a lower cellulose concentration (Table 2). As tenacity increased without any extensibility loss, the fine structure of the fibres was improved,[11] as due to an increased cellulose concentration. However, it was shown that the higher cellulose concentration of the spinning dope could not compensate the lowered M_w of cellulose (Fig. 7), which is most likely due to a too severe degradation of cellulose during the acid treatment.

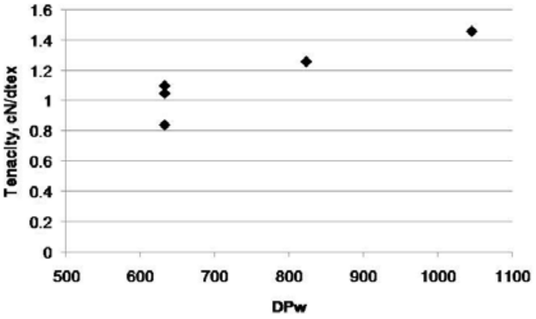

Figure 5: Tenacity of fibres as a function of the average degree of cellulose polymerisation (DP_w)

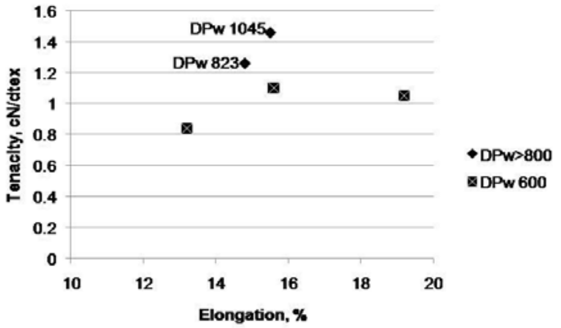

Figure 6: Mechanical properties of wet spun cellulosic fibres

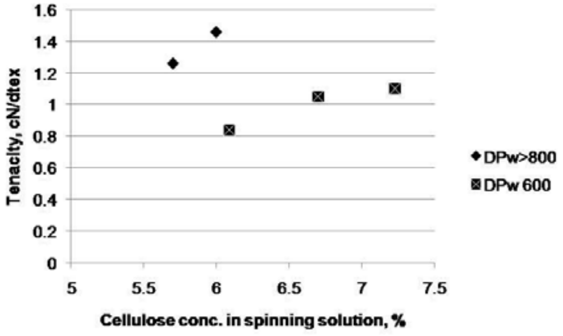

Figure 7: Tenacity of fibres as a function of cellulose concentration in the spinning solution

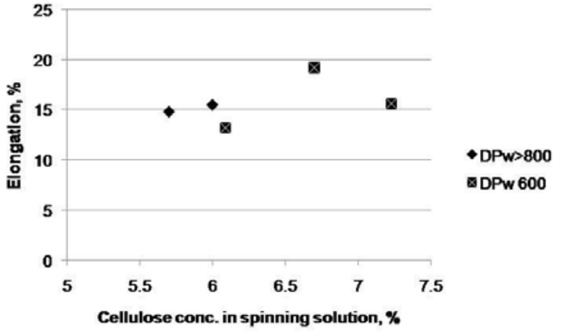

Figure 8: Elongation of fibres as a function of cellulose concentration in the spinning solution

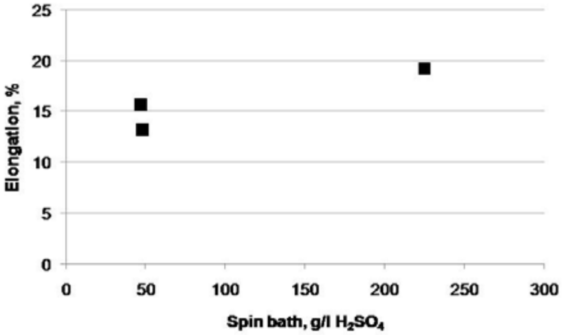

Figure 9: Elongation of fibres as a function of spin bath sulphuric acid concentration (DP_w 600)

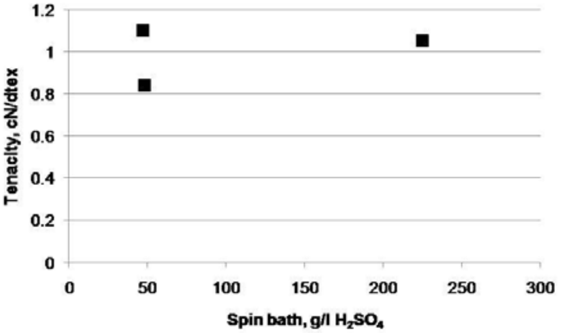

Figure 10: Tenacity of fibres as a function of spin bath sulphuric acid concentration (DP_w 600)

Table 2
Wet spinning parameters

Fibre sample	Acid treatment		Alkaline solution		Spinning	Mechanical properties of fibres	
	Temperature, °C/time, min	M_w	Cellulose concentration, wt%	Falling ball viscosity*, s/20 cm	H_2SO_4, g/L	Tenacity, cN/dtex	Elongation, %
Reference 1	0/0	170384	6.0	83	168	1.46	15.5
Reference 2	80/30	134154	5.7	27	246	1.26	14.8
Fibre 1	100/30	103153	6.1	6	48	0.84	13.2
Fibre 2	100/30	103153	6.7	33	225	1.05	19.2
Fibre 3	100/30	103153	7.2	50	47	1.10	15.6

*the next day, prior to spinning

CONCLUSIONS

The cellulose concentration of the spinning solution can be raised from 6 wt% up to 7.2 wt% by decreasing the molecular weight of cellulose. Even in such a case, the fibre properties were better at a higher cellulose concentration while, at the same M_w, a higher concentration could not compensate for the reduced M_w, because molecular weight had degraded too much. However, fibre properties might be improved by optimising the values within the limits applied in the present work.

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III

DISSOLUTION OF ENZYME-TREATED CELLULOSE USING FREEZING–THAWING METHOD AND THE PROPERTIES OF FIBRES REGENERATED FROM THE SOLUTION

by

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ORIGINAL PAPER

Dissolution of enzyme-treated cellulose using freezing–thawing method and the properties of fibres regenerated from the solution

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Abstract The rapid coagulation of NaOH-based cellulose solution during the wet spinning process leads to a low stretching ratio and, consequently, the low mechanical properties of the fibres. The aim of this work was to slow down the coagulation by replacing the sulphuric acid spin bath with an acetic acid bath. The spin dope was prepared by dissolving the enzyme-treated dissolving pulp in aqueous sodium zincate using a freezing–thawing method. The optimal zinc oxide and sodium hydroxide concentrations were studied first. The most thermally stable cellulose solution contained 6.5 wt% NaOH and 1.3 wt% ZnO with 6 wt% enzyme-treated dissolving pulp. The spin dope was prepared accordingly. Coagulation of the cellulose solution slowed down in the acetic acid bath, resulting in a significantly higher stretching ratio for the fibres than with the sulphuric acid bath. However, the acetic acid spun fibres shrunk strongly during drying, and the possibly aligned order of the molecular chains due to the high stretch was partly lost. As a consequence, the high stretch was not transferred to high tenacity of the fibres in this study. However, the result suggests attractive potential to develop processing conditions to increase fibre tenacity.

Keywords Cellulose dissolution · Dissolving pulp · Enzymatic treatment · Wet spinning · Regenerated fibres · Biocelsol

Introduction

The cell wall of a cellulose fibre is composed of microfibril bundles organised in compact layers (Jurbergs 1960; Wardrop 1969). The microfibrils are built up of cellulose chains attached to each other by intermolecular hydrogen bonds and stiffened by intramolecular hydrogen bonds (Kamide et al. 1992; Krässig 1993; Klemm et al. 2005). The morphological structure of the cellulose fibre and the average length of the cellulose molecules [degree of polymerisation (DP)] determine the long-range order of the fibre and its reactivity towards different chemicals (Isogai and Atalla 1998; Le Moigne and Navard 2010). If the DP of the cellulose is below or close to the levelling-off DP, it dissolves easily in aqueous NaOH, whereas the coherent structure of higher-DP cellulose hinders its dissolution.

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Egal et al. (2007) studied the eutectic behaviour of aqueous NaOH at subzero temperatures. They found that a minimum of four NaOH molecules are needed per anhydroglucose unit (AGU) to dissolve low-DP cellulose. They presumed that entropic reasons would hinder dissolution of higher-DP cellulose, thus requiring more than four NaOH molecules per AGU for dissolution.

Enzymatic hydrolysis treatment of dissolving-grade pulp has proved to be beneficial for its dissolution in aqueous sodium hydroxide (Rahkamo et al. 1996, 1998; Vehviläinen et al. 1996; Cao and Tan 2002a, 2002b, 2006). Mechanical shredding of the pulp prior to enzyme treatment, lowering the dissolution temperature below zero and incorporation of zinc oxide into the sodium hydroxide solution further increase the solubility of enzyme-modified cellulose (Vehviläinen et al. 1996; Grönqvist et al. 2014). The beneficial effects of low temperature and zinc on the swelling and dissolution of cellulose in sodium hydroxide were found already in the late 1800s by John Mercer. These phenomena were intensively studied in the early 1900s by several researchers (Marsh and Wood 1942). Davidson (1934) showed that the solubility of chemically modified cotton cellulose reached a maximum at a certain sodium hydroxide concentration, and with decreasing temperature this maximum both shifted to lower alkali concentration and increased significantly (from 10 to above 80 %). Later, Davidson (1937) showed that, with sodium zincate, the solubility of cellulose depends on the amount of zinc oxide in the sodium hydroxide (molar ratio), the concentration of sodium hydroxide and the temperature. With an increase of molar ratio at constant temperature, the maximum solubility increased significantly, but shifted only slightly, and this time to higher sodium hydroxide concentration. With decreasing temperature (at the studied molar ratio) the maximum solubility did not increase, instead it was reached with a wider range of sodium hydroxide concentrations starting from a significantly lower value than at higher temperature. Besides zinc oxide, also urea, thiourea, dicyandiamide, guanidine, and their derivatives, and urethanes, added to sodium hydroxide have been found to increase the solubility of modified cellulose at low temperature (Lilienfeld 1930).

The mechanism behind the temperature effect in the NaOH/urea/cellulose system is suggested to be associated with the interaction between the NaOH hydrates and cellulose, and the self-assembly of urea hydrates (Cai et al. 2008). Lindman and Karlström (2009), on the other hand, suggested that the temperature effect is due to the conformational change in the molecular structure of cellulose. They base this hypothesis on results obtained with oxyethylene-based surfactants. With increasing temperature, the solubility of the surfactants decreased strongly in water, while in hydrocarbons the solubility increased. This behaviour is due to the conformational changes of the ethylene oxide chains in a non-ionic surfactant. Low temperature favours a conformation of O–CH_2–CH_2–O segments around the C–C bond that makes the ethylene oxide more polar, thus enhancing the solubility in polar solvent. The authors suggested that similar kinds of temperature-induced conformational changes could apply also to cellulose, thus explaining the improved solubility at low temperature.

The enhanced dissolution of cellulose in sodium zincate has been explained by the formation of hydrogen bonds between $Zn(OH)_4^{2-}$ and cellulose which are stronger than those between hydrated NaOH and cellulose (Yang et al. 2011). However, Kihlman et al. (2013) disagree and suggest that $Zn(OH)_4^{2-}$ would act as an anionic co-solute that promotes dissolution by forming a charged complex with cellulose. This is based on their previous review (Lindman et al. 2010) which emphasized that polyelectrolytes dissolve better than nonionic polymers due to the entropy of the counterions.

NaOH-based cellulose dissolution systems are an attractive alternative for preparation of regenerated fibres, because they can be processed by the wet spinning technique using the same machinery as in viscose fibre production. Fibres have been prepared at experimental level from cellulose/NaOH (Yamashiki et al. 1990; Vehviläinen et al. 1996; Yamane et al. 1996), cellulose/NaOH/urea (Cai et al. 2004, 2007; Chen et al. 2007; Qi et al. 2008a), cellulose/NaOH/thiourea (Ruan et al. 2004; Chen et al. 2006), cellulose/NaOH/ZnO (Vehviläinen et al. 1996, 2008, 2010), cellulose carbamate/NaOH/ZnO (Fu et al. 2014a, 2014b) and cellulose/NaOH/polyethylene glycol (PEG) (Zhang et al. 2010) solutions. Thus, the properties of NaOH-based cellulose solutions (dopes) have been proven to be sufficient for regenerating fibres by the wet spinning technique.

In the wet spinning process, the solution is pumped at a predetermined rate through a spinneret which has numerous small orifices. The spinneret is immersed in a coagulation bath facing upward. The solution coagulates instantly when it emerges from the spinneret orifice into the bath. The coagulated, nascent fibres are next pulled from the bath with the aid of a godet and guided through the stretching and washing baths. The velocity difference between the taking-up rate of the fibres to the first godet and the flow rate of the dope through the spinneret orifices is called the spinneret draw ratio. The velocity difference between the second godet and the first godet is called the stretching ratio (Wilkes 2001).

The most important factors affecting the properties of regenerated cellulosic fibres include:

1. DP of cellulose

Increasing the DP of the cellulose increases the tenacity of the fibres to a certain value, whereafter it levels off (Morton and Hearle 1993). However, it is not possible to take full advantage of the high DP (in a large-scale process), because even a small amount of high-DP cellulose increases the viscosity of the dope significantly (Fink et al. 2001). Additionally, high DP hinders the solubility of cellulose in a water-based environment (Isogai and Atalla 1998; Qi et al. 2008b). As a consequence, it is necessary to decrease the DP of the starting cellulose to increase the cellulose concentration of the dope, while at the same time maintaining the viscosity of the dope at a low enough level.

2. Quality of spin dope

Even though a decreased DP enhances the solubility of cellulose in an aqueous solvent, complete dissolution is not achieved. The solution contains undissolved fibre fragments and/or gel particles, which must be removed by filtration to increase the quality of the dope. The dope also contains a lot of air dissolved during the processing. The amount of dissolved air increases with decreasing temperature (Henry's law), which means that a solution subjected to low temperature during dissolution has a considerable volume of air in dissolved form. To avoid the formation of air bubbles (due to their decreased solubility) during spinning, it is crucial to carry out deaeration of the dope at a temperature that is the same or higher than that to which the solution is warmed during spinning. This might be challenging if the solution tends to form gel at ambient temperature, which is the case with most NaOH-based solutions (Yamashiki et al. 1990; Jin et al. 2007; Qi et al. 2008b; Zhang et al. 2010).

3. Orientation of molecules

Orientation of the molecular chains develops in the wet spinning process due to the multiple kinetic steps through which the dissolved polymer is transferred to a solid fibre. The steps that determine the orientation include: hydrodynamic flow in the spinneret channel, phase transition in the coagulation bath and uniaxial stretching of as-spun fibres (Ziabicki 1967). In the hydrodynamic flow, the dope is subjected to shear stress due to the flow within the walls of the spinneret capillary. The shear stress depends on the rheological properties of the dope, the flow rate and the dimensions of the spinneret. The relationship between these parameters determines the orientation of the molecular chains in the flow (Qin et al. 2001). In the phase transition step, the dope emerges from the spinneret orifice into the coagulation bath. Instantly, the shear stress relaxes, and a skin is formed for the nascent fibres. The balance between the visco-elastic properties of the dope and the coagulation kinetics determines which happens first. If the dope coagulates faster than the shear stress relaxes, some of the molecular orientation is fixed, whereas for slower solidification, the stress is relaxed first and the orientation is lost. In the stretching step, the as-spun fibres are subjected to elongation forces, first in the coagulation bath due to the spinneret draw ratio and second in between the godets due to the stretching ratio. All these steps determine the relative molecular arrangement in the final fibre structure and thus affect the fibre properties. The more the molecules are aligned with the fibre axis, the higher the orientation, and consequently the higher the tenacity (McGarry and Priest 1968; Moncrieff 1970).

Usually, the linear density of fibres is fixed to a certain value (e.g. 1.7 dtex) by adjusting the ratio between the spinning velocity (=second and third godets) and the flow of the dope (pump capacity) to a desired value (Eq. 1). The maximum godet stretching is then adjusted by decreasing the velocity of the first godet. In this way, the linear density of fibres is not affected, but the spinneret draw ratio is decreased. The more the fibres stretch, the lower the spinneret draw ratio; i.e. the extensibility of the fibres determines the spinneret draw ratio. However, there are certain limits for acceptable spinneret draw ratio values, which must be measured experimentally. The value is adequate when the as-spun fibres do not break (too high spinneret draw ratio) nor form any kind of instabilities (too low spinneret draw ratio) in the coagulation bath (von Bucher 1968). If these limits are exceeded, either the desired linear density of the fibres or the diameter of the spinneret orifices must be changed (Eqs. 1, 2). In spinning processes where it is possible to slow down the coagulation (and regeneration) of the fibres (e.g. the viscose process), it is only the godet stretching ratio that determines the properties of the fibres; the effect of the spinneret draw ratio, when within the limits, is insignificant (von Bucher 1968). In contrast, in spinning processes where no chemical reaction is involved (e.g. NaOH-based solutions), it is difficult to slow down the coagulation, which is very fast, and the effect of the spinneret draw ratio increases. In experimental work, it has been found that the spinneret draw ratio and the tenacity of the fibres exhibit a positive correlation when the spinneret draw ratio exceeds a certain value (Vehviläinen et al. 2008).

Even though rather high mechanical properties have been reported for fibres prepared from experimental-scale NaOH-based dopes, the ratio between the alkali and cellulose content of these dopes (alkali ratio) has typically been above 1.3 (Cai et al. 2004, 2007; Chen et al. 2007; Zhang et al. 2010). This causes high consumption of sulphuric acid and high formation of salts during coagulation, thus burdening the economy of large-scale processes. To overcome this disadvantage, we have developed a dissolution method which is based on a freezing–thawing cycle of an enzyme-treated pulp (Vehviläinen et al. 2009). In this method, the pulp and sodium zincate are mixed at room temperature and thereafter frozen to solid. A cellulose solution is obtained upon thawing. With this method, a significant improvement in the dissolution of the enzyme-treated cellulose was obtained. Without a freezing step, the NaOH content of the dope was 7.8 wt% (Vehviläinen et al. 2008), while as little as 5.5 wt% NaOH dissolves the same amount of pulp (6 wt%) when freezing is included.

Besides low cellulose content, another disadvantage of NaOH-based cellulose solutions is the very rapid coagulation during fibre production. This leads to a lower stretching ratio during spinning and consequently lower mechanical strength of the fibres compared with commercial viscose fibres (Vehviläinen et al. 2008). In the viscose process, sufficient stretching is ensured by using spin dope modifiers and spin bath additives which retard the regeneration of the cellulose xanthate (Kotek 2007). Such modifiers are usually organic compounds which form an acid-resistant barrier on the surface of the as-spun fibres (McGarry and Priest 1968). As the function of commercial modifiers is based on retardation of the chemical reaction, it is not expected that the same effect would be achieved if used in NaOH-based cellulose solutions.

In this paper, we first demonstrate how the NaOH and ZnO concentrations affect the solubility of the enzyme-treated pulp in the freezing–thawing method. Thereafter, we give details of the spin dope preparation with the selected parameters, and describe in depth the spinning trials. Our goal was to slow down the coagulation of the fibres, thus we used two spin baths with different coagulation power: 10 % sulphuric acid and 5 % acetic acid. Sulphuric acid is a traditional spin bath adopted from the viscose process. However, as it coagulates the directly dissolved cellulose very fast, it does not allow proper stretching of the as-spun fibres. Acetic acid is a weak acid, thus it was expected to coagulate the solution more slowly, consequently enabling higher stretching of the fibres between the godets. We studied the effects of different spinning parameters on the fibre properties, and discuss the results in this paper.

Materials and methods

Pulp treatments

The starting materials were low-viscosity (405 mL g^{-1}) and medium-viscosity (558 mL g^{-1}) dissolving-grade softwood [totally chlorine-free (TCF)] pulps produced by Domsjö Fabriker AB, Sweden. The wet pulp (dw 20 wt%) was first shredded mechanically for 5 h using a Baker Perkins shredding machine (size 6-1 Universal mixer S/N 44777) and thereafter treated with Ecostone N400 (AB Enzymes Oy, Finland) or Fibercare R (Novozym CGP20048) enzyme preparation (5 wt%, pH 5, 50 °C, 2 or 3 h, as indicated in the text). The Ecostone N400 enzyme dosage was 1.9 mg, and the Fibercare R enzyme dosage was 1 mg protein/g pulp. The enzymes were inactivated by increasing the temperature above 90 °C for 15 min. Thereafter, the sample was filtrated and washed with cold water. The filtrate was collected for analyses.

Preparation of concentrated sodium zincate

Solid sodium hydroxide (20 g) and solid zinc oxide (Table 1) were weighed into a beaker. Ion-exchanged water was added to obtain a total weight of 50 g and NaOH concentration of 40 wt%. The mixture was heated (gently bubbling) with magnetic stirring until all the zinc oxide had dissolved (2–3 h). The solution was cooled down at room temperature (RT), the weight was checked, and ion-exchanged water added if necessary. The concentrated solution was stored in a refrigerator.

Preparation of small-scale samples for selecting the spin dope parameters

Twenty small-scale samples (series 1) containing 6 wt% enzyme-treated pulp and different amounts of sodium hydroxide and zinc oxide as given in Table 1 were prepared as follows: the enzyme-treated dry pulp was activated by adding ion-exchanged water (15 wt% pulp, 85 wt% water) with mixing and thereafter left in a refrigerator for the next day. The concentrated sodium zincate (RT) was diluted with the desired amount of ion-exchanged water (Table 1). The wet pulp and sodium zincate were mixed for 5 min at 1000 rpm to obtain a slurry-like sample. The sample (series 1) was frozen solid in a Lauda Ecoline RE107 cooling bath at −35 °C and thereafter thawed in the same bath at 10 °C. The duration of the freezing–thawing cycle was 24 h. The temperature during the cycle was followed with a thermocouple. The freezing rate (°C min^{-1}) was calculated from the data from 0 to −30 °C. Three additional samples (series 2) were prepared accordingly, but frozen solid in a freezer at −40 °C. Moreover, one additional sample was prepared accordingly to series 2, except the cellulose content was 5.5 wt%.

Table 1 Preparation and characteristics of small-scale samples

Concentrated sodium zincate, 50 g 20 g NaOH + ZnO		Preparation of sample; 40 g of wet cellulose mixed with diluted concentrated ZnO/NaOH		Characteristics of the samples		
Sample	ZnO (g)	Conc. ZnO/ NaOH (g)	Water (g)	NaOH (wt%)	ZnO (wt%)	Measured cellulose content (wt%)
1	0	10.0	50.0	4.0	0	Samples did not form cohesive films in sulphuric acid
2	2.5	10.0	50.0	4.0	0.5	
3	4.2	10.0	50.0	4.0	0.8	
4	6.5	10.0	50.0	4.0	1.3	6.1
5	0	13.8	46.2	5.5	0	5.9
6	1.8	13.8	46.2	5.5	0.5	5.9
7	3.1	13.8	46.2	5.5	0.8	6.0
8	4.7	13.8	46.2	5.5	1.3	5.9
9	1.7	15.0	45.0	6.0	0	5.8
10	2.8	15.0	45.0	6.0	0.5	5.9
11	4.3	15.0	45.0	6.0	0.8	6.1
12	1.5	15.0	45.0	6.0	1.3	5.9
13	2.6	16.2	43.8	6.5	0	5.9
14	4.3	16.2	43.8	6.5	0.5	5.9
15	1.5	16.2	43.8	6.5	0.8	5.9
16	2.6	16.2	43.8	6.5	1.3	5.7
17	4.0	17.5	42.5	7.0	0	Samples did not form cohesive films in sulphuric acid
18	1.4	17.5	42.5	7.0	0.5	
19	2.4	17.5	42.5	7.0	0.8	5.9
20	3.7	17.5	42.5	7.0	1.3	6.1

Preparation of spin dope

The wet pulp and sodium zincate were mixed to obtain a slurry-like sample containing 6 wt% pulp, 6.5 wt% NaOH and 1.3 wt% ZnO. The slurry was frozen in plastic boxes in a freezer at −40 °C. The temperature during freezing was followed with a thermocouple. The freezing rate (°C min^{-1}) was calculated from the data from 0 to −30 °C. The frozen sample was broken into pieces and placed in a sealed tank, whose temperature was set to 18 °C. The melted sample was a solution. The solution was filtered twice by forcing it from the tank through a filter cartridge using nitrogen gas (2 bar). The first filter had a wound structure with nominal porosity of 10 µm (Aquator MS97PP10), and the second filter had a melt-blown structure with nominal porosity of 1 µm. The material of both filter types was polypropylene. The filtrated solution was placed in a spin reservoir (18 °C), and the pressure inside the reservoir was lowered to below 200 mbar to remove air bubbles. The dope was characterised by measuring the dry content, amount of gel particles and fluidity.

Wet spinning

The fibres were spun using a laboratory wet spinning machine (Fig. 1). The gear pump used (Zenith BPB-4391) had capacity of 0.3 mL per revolution, and its speed was set to 13.1 rpm. The spinneret used (Wetzel Gröbzig Micro Products) had 100 orifices of 51 µm. The spinneret was made of a gold/platinum mixture with *L*/*D* ratio of 2.94 ($L = 0.15$ mm, $D = 0.051$ mm).

The desired settings of the machine as well as the parameters realised were calculated according to Eqs. 1, 2 and 3 (Götze 1967).

$$T = \frac{Q \times \rho_{\mathrm{dope}} \times \frac{\alpha}{100} \times 10000}{n \times V_{\mathrm{III}}}, \qquad (1)$$

where T is the desired linear density of fibres (dtex), i.e., the mass (g) of a filament fibre of length 10,000 m, Q is the capacity of the pump (mL min^{-1}), ρ_{dope} is the constant density of the spin dope (1.4 g mL^{-1}), α is the cellulose concentration of the spin dope (%), n is the number of spinneret orifices, and V_{III} is the velocity of the third godet (m min^{-1}).

$$\text{spinneret draw ratio} = V_{\mathrm{I}} \times \frac{\left(\frac{\pi}{4}\right) \times D^2 \times n}{Q}, \qquad (2)$$

where V_{I} is the velocity of the first godet (m min^{-1}) and D is the diameter of an orifice capillary (mm).

$$\text{stretching ratio} = \frac{V_{\mathrm{II}}}{V_{\mathrm{I}}}, \qquad (3)$$

where V_{II} is the velocity of the second godet (m min^{-1}) and V_{I} is the velocity of the first godet (m min^{-1}).

Two spin baths were used; the first contained sulphuric acid (100 g L^{-1}) and sodium sulphate (100 g L^{-1}), and the second acetic acid (50 g L^{-1}). The temperature of the spin baths was 21 °C. The specific gravity of the sulphuric acid bath was 1.135 and that of the acetic acid bath was 1.008.

The stretching bath contained hot (90 °C) ion-exchanged water, and the first washing bath either ion-exchanged water (21 °C) or 10 % sulphuric acid (21 °C). The second washing bath contained ion-exchanged water (21 °C).

Three series of fibres were spun at the predetermined spinneret draw ratio and the maximum stretching ratio. The spinneret draw ratio was adjusted by setting the velocity of the first godet to the desired value. The maximum stretching ratio was thereafter adjusted by increasing the velocity of the second godet until the fibres broke and then by decreasing the velocity from that point by 1 m min^{-1}. The fibre sample was collected with the obtained settings. The theoretical linear density of the fibres changed according to Eq. 1. Additionally, one fibre sample was spun with the spinneret draw ratio and stretching ratio of 1 (i.e. no stretching applied).

In the first series the fibres were spun into 10 % sulphuric acid, and in the second and third series into 5 % acetic acid. In the second series the washing bath contained water, and in the third series it contained 10 % sulphuric acid.

The fibres were collected in wet continuous form and thereafter cut into 5.5-cm lengths by hand. The fibres were washed with ion-exchanged water until free of salts (measured with a conductivity meter) and finished by exchanging water to ethanol to minimize fibre attachments during drying. Drying was carried out at ambient temperature (22 ± 2 °C).

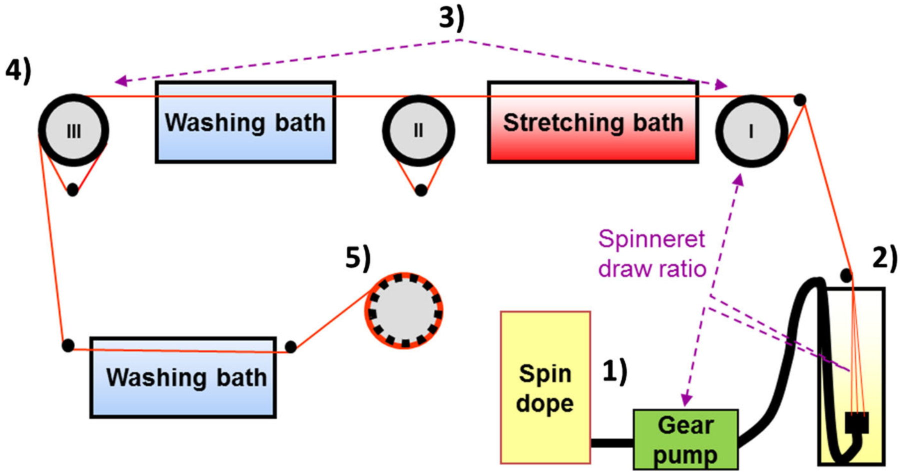


Fig. 1 Schematic of laboratory-scale wet spinning machine. *1* spin dope reservoir, *2* spin bath tank and spinneret, *3* stretching ratio (due to velocity difference of i and iii godets), *4* speed of third godet is also spinning speed, *5* fibre collector

Characterisation

Pulp

Soluble sugars dissolved during the enzyme treatment were measured using the 3,5-dinitrosalicylic acid (DNS) method (Bernfeld 1955). The intrinsic viscosity of the pulp (mL g^{-1}) was measured both before and after enzyme treatment according to the SCAN-CM 15:99 (ISO 5351:2004) method. In this method, the sample is dissolved in cupriethylenediamine hydroxide and the intrinsic viscosity derived from the efflux time of the solution.

Small-scale samples and spin dope

The cellulose content (α) of the solution (gel particles not removed from the small-scale samples) was measured by coagulating films from a known amount of sample into 10 % sulphuric acid. The films were washed, dried at 105 °C, and weighed. The cellulose content was calculated as a weight percentage of the dried films compared with the weighed sample. The result is given as an average of two measurements.

The fluidity and stability of the solution (gel particles not removed from the small-scale samples) were evaluated by the modified ball-drop method (ASTM D 1343-86). A plastic cylinder with measuring distance of 20 cm was filled with a solution. A stainless-steel ball (1/8″, 130 mg) was dropped in the solution, and the falling time of the ball recorded. The result is given in seconds. The properties of the small-scale samples were followed as a function of temperature as they warmed from 10 °C to ambient temperature (20–21 °C). The fluidity of the spin dope was measured from a sample collected at the gear pump just before spinning. The result is given as an average of three measurements.

The samples were studied with an optical light microscope (Leitz Laborlux D) with and without polarisation. Additionally, a 5 g portion of the sample was extruded onto a glass plate and photographed for visual characterisation.

The viscoelastic properties of the cellulose solution were measured with an Anton Paar MCR 301 rotational rheometer using a concentric cylinder geometry. Surface of the rotating inner cylinder (CC17/S) was roughened to prevent slippage. The diameter of the inner cylinder was 16.661 mm, and that of the stationary outer cylinder (C-CC17/T200/SS) was 18.076 mm. The temperature of the cylinders was first allowed to settled, and thereafter a fresh sample (stored in a refrigerator at 6 °C) was applied. The measurement was started when the temperature of the system was steady. The shear stress was measured at constant temperatures (18, 22 and 30 °C) with two or three shear rate cycles, wherein the rate was changed logarithmically from 0.001 to 100 and back to 0.001 s^{-1}. Thereafter, the storage (G') and loss moduli (G'') were measured as functions of temperature from 10 to 60 °C at rate of 0.5 °C min^{-1}, strain of 10 % and angular frequency of 1 rad s^{-1}. Finally, the storage (G') and loss moduli (G'') were measured at constant temperature (22 and 30 °C) as functions of time until cross-over of the curves.

The amount of gel particles was measured from the spinning solution before and after filtration. The solution (10 g) was diluted by adding 50 g of 6.5 wt% NaOH; the sample was mixed carefully by hand and thereafter centrifuged at 3000*g* for 20 min. Supernatant was discharged and the gel part poured onto a glass plate. The film formed from the gel upon drying at ambient temperature was coagulated into 10 % sulphuric acid, washed with ion-exchanged water, and dried at 105 °C. The amount of gel particles was calculated as weight percentage of the dried films compared with the amount of cellulose in the sample.

Fibres

The fibres were conditioned at relative humidity of 65 ± 5 % and temperature of 20 ± 2 °C for at least 24 h. The mechanical properties were determined as an average of 20 measurements according to the ISO 1973 and ISO 5079 standards using a Favigraph testing machine (Textechno GmbH). The tests included linear density (dtex), tenacity (cN dtex^{-1}), elongation (%), Young's modulus at 1 % elongation (cN dtex^{-1}) and work of rupture (cN cm). The rate of elongation was 20 mm min^{-1}, and the gauge length was 20 mm. The yield point and yield stress were measured from the stress–strain curve according to Meredith's method (Morton and Hearle 1993).

Shrinkage of the fibres during drying was analysed by measuring the length of dried individual fibres and calculating the change in length compared with the wet fibre (5.5 cm). The result is given as an average of 10 measurements.

Birefringence of the fibres was measured as follows: the fibre was straightened with the aid of 100 mg weight and attached on a microscope slide at both ends. The diameter of the fibre was measured with a Leitz Laborlux D microscope, and thereafter the retardation of the same fibre with a Leitz polarised microscope equipped with a Berek compensator. The compensation of one fibre was obtained as an average of five measurements, and the birefringence of the fibre sample as an average of five fibres.

Fourier-transform infrared (FTIR) spectra of the fibres were analysed with a Bruker Optics Tensor 27 FTIR spectrometer at 4 cm^{-1} resolution with 32 scans per sample. The samples were air-dried and mounted directly in the sample holder. The total crystallinity index (TCI) and the lateral order index (LOI) were calculated as described by Nelson and O'Connor (1964).

The swelling coefficient (SwC) of the fibres was determined as the amount of water held by the sample. A desired amount of fibres was kept in ion-exchanged water for at least 20 h. The fibre sample was drained through a wetted filter fabric and centrifuged at 3000*g* for 80 s. The sample was weighed prior to and after drying at 105 °C, and the result is given as a percentage of water compared with the dry sample.

The pore size distribution (PSD) of the sample was measured by thermoporosimetry using a Mettler 821 differential scanning calorimeter (DSC). The method is based on the fact that water which is held within a sufficiently small cavity will have a depressed melting temperature. The sample (1–3 mg) was placed in an aluminium sample pan and distilled water added to obtain 2 g water/g solids. The pan was sealed and the sample allowed to condition overnight. The measurement was done with an isothermal step melting method as described previously (Maloney and Paulapuro 2001). In this approach, the frozen sample is melted in equilibrium steps in the range from −33 to −0.2 °C. The resulting enthalpy versus melting temperature data can be used to calculate the cumulative PSD with the aid of the Gibbs–Thomson equation in the form

$$D = \frac{1.22}{\Delta T} + 0.35, \tag{4}$$

where D is the pore diameter (nm), ΔT is the melting temperature depression (°C), 1.22 is the Gibbs–Thomson coefficient for cellulose (°C nm), and 0.35 is the thickness of the non-freezing water layer (nm) (Maloney 2015).

The amount of non-freezing water in each sample was calculated from the difference between the total moisture content measured gravimetrically and the total freezing water measured with the DSC. Three measurements were performed, and the average is reported.

This DSC method is suitable for measuring pores in cellulose samples in the range of about 1–6.5 nm. Larger pores than this are not detected with DSC.

Surface and cross-sectional structures of the fibres were studied with a field-emission scanning electron microscope (FESEM, ULTRAplus, Zeiss). The cross-sectional FESEM samples were prepared as follows: a bundle of fibres was moistened with resin (epoxy embedding, Fluka) followed by hardening in air at 100 °C for 1 h; moulded fibres were then fractured in liquid nitrogen, and the fracture surfaces were studied with FESEM. The surface and cross-sectional samples were carbon-glued onto aluminium stubs followed by carbon coating to avoid sample charging in FESEM studies.

Results and discussion

Pulp treatments

The low-viscosity dissolving pulp was treated with Ecostone N400 enzyme preparation. The treatment decreased the intrinsic viscosity of the pulp by 36 % (to 260 mL g^{-1}) and released about 3 % of the pulp as soluble sugars. The medium-viscosity dissolving pulp was treated with Fibercare R enzyme preparation. The treatment decreased the intrinsic viscosity of the pulp by 56 % (to 245 mL g^{-1}) and released about 1.8 % of the pulp as soluble sugars.

Effect of sodium hydroxide and zinc oxide concentrations on the solubility of enzyme-treated pulp

The pulp used for the solubility studies in the first series was the low-viscosity dissolving pulp treated with Ecostone N400 enzyme preparation. The aim was to study the effect of the NaOH and ZnO contents on the solubility of the enzyme-treated pulp in the freezing–thawing method, and to select the best parameters for the spin dope. The NaOH concentrations in the samples were 4.0, 5.5, 6.0, 6.5 and 7.0 wt%, and the ZnO concentrations were 0, 0.5, 0.8 and 1.3 wt% (Table 1).

In the freezing stage, the temperature of the samples decreased below −33 °C during the first 2 h. The change of temperature (one sample) as a function of time is given in Fig. 2a. The temperature decreased approximately at the same rate (0.51–0.57 °C min^{-1}) in all the other samples, except the ones containing the highest amount of NaOH (7 wt%), which froze slightly more slowly (0.35 °C min^{-1}) (Fig. 2b). The shape of the curve during the thawing was identical in each sample.

Based on the visual characterisation of the samples (Fig. 3), it is clear that the solubility of cellulose increased when the zinc oxide concentration was increased from 0.5 to 1.3 wt% and the sodium hydroxide concentration from 4 to 6.5 wt% NaOH. Surprisingly, the samples containing 7 wt% NaOH lost their fluidity. This is probably due to the partial dissolution of the cellulose before freezing, which was noted as an opaque colour of the sample. The dissolved part formed gel during the freezing, and consequently decreased the fluidity of the whole sample after thawing. A similar kind of gelation due to decreased temperature was found for cellulose/NaOH/urea solutions (Cai and Zhang 2006).

The polarised microscope studies (Fig. 4) revealed that all the samples without zinc oxide had considerable amount of undissolved fibres. With increasing zinc oxide concentration, the amount of undissolved fragments decreased. The samples containing 6.5 wt% NaOH had less insoluble fibres at each zinc oxide concentration than the other samples. It seems that the insoluble fibres in the samples containing 7 wt% NaOH were more swollen compared with the samples

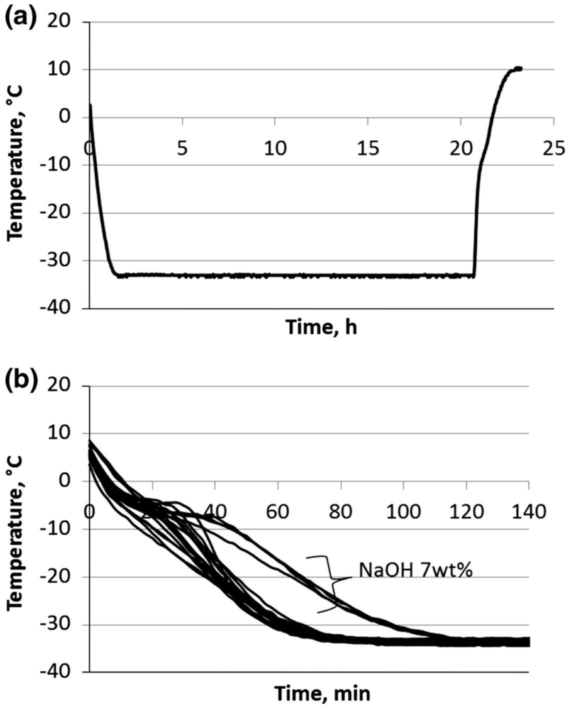


Fig. 2 Temperature change of samples during freezing–thawing cycle. **a** Typical curve of whole cycle. **b** Freezing stage of samples

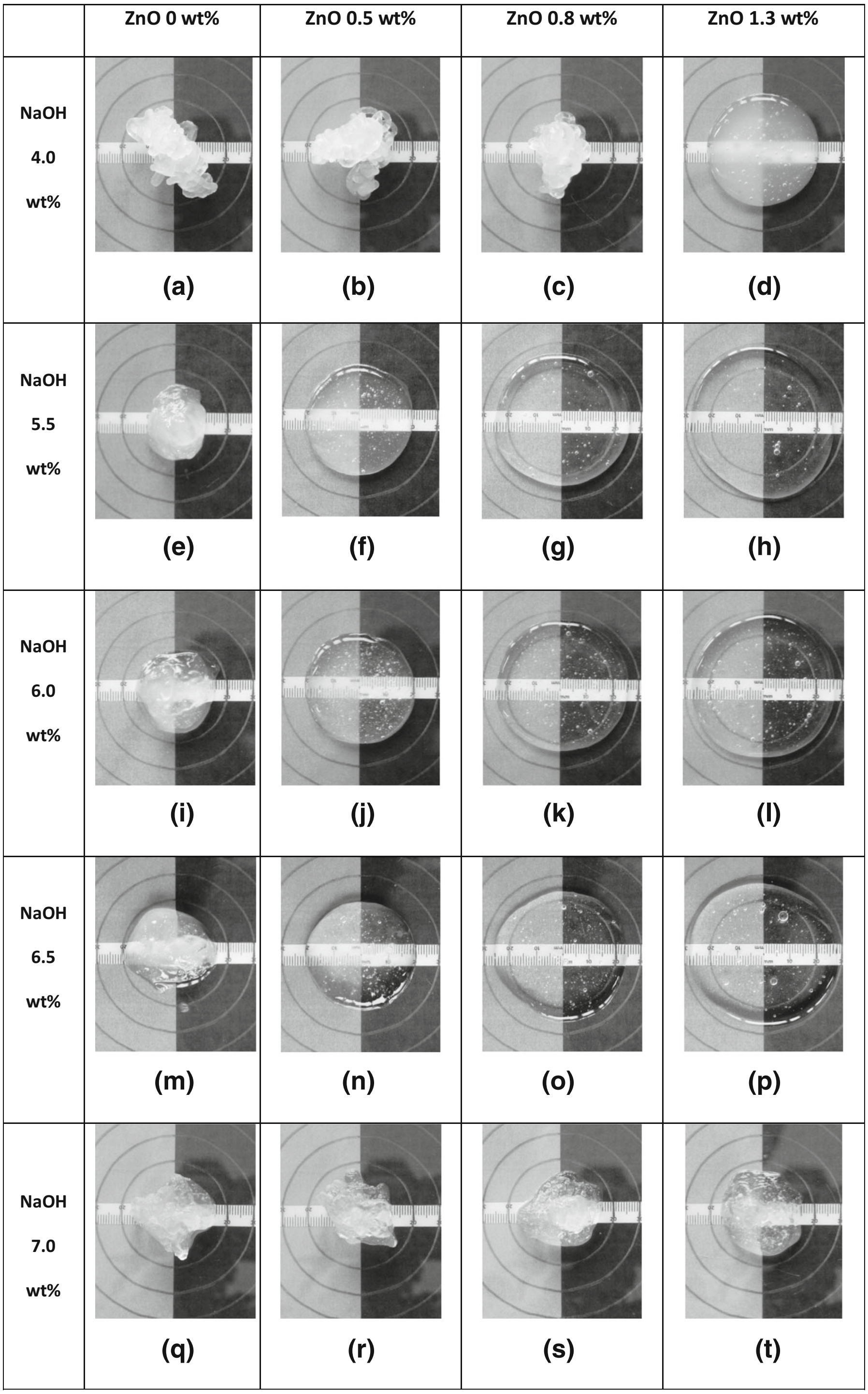


Fig. 3 Photographs of thawed samples extruded onto glass plate. *Two-coloured paper* with measuring scale under glass plate visualises transparency and fluidity of samples. NaOH and zinc oxide contents of each sample as indicated (Vehviläinen et al. 2009)

with lower NaOH concentration. Based on the images, the samples containing 1.3 wt% ZnO and 5.5–6.5 wt% NaOH were the most soluble. The cellulose content of the most fluid samples (with insoluble particles) ranged from 5.7 to 6.1 wt% (Table 1).

The fluidity and stability of the best samples were evaluated by measuring the falling ball times as a

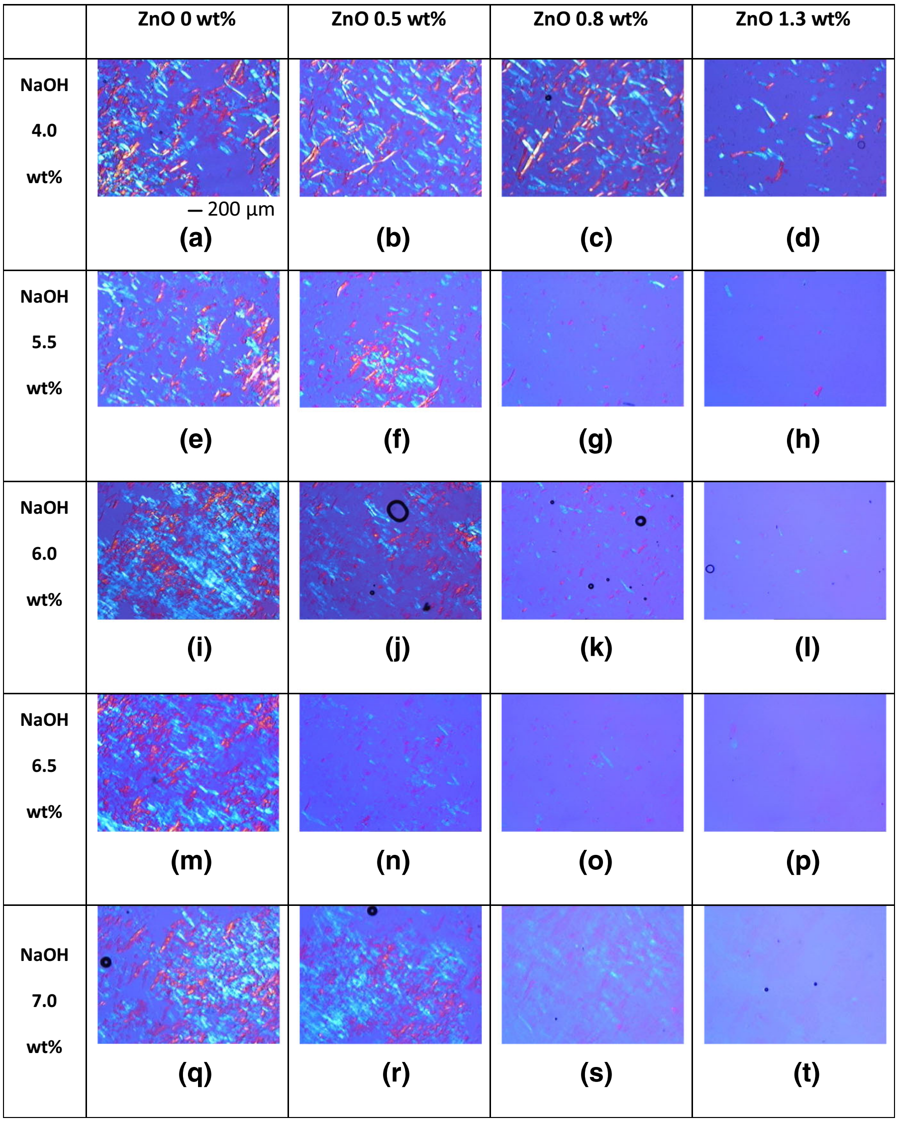


Fig. 4 Polarised microscope images of thawed samples. NaOH and zinc oxide contents of each sample as indicated (Vehviläinen et al. 2009). The same *scale bar* in each image as indicated in (**a**)

function of temperature (Fig. 5). The samples containing 1.3 wt% ZnO and 6.0 or 6.5 wt% NaOH were the only ones that did not form gel due to increased temperature.

Three additional samples were prepared from the medium-viscosity Fibercare R-treated pulps (series 2) with 6 wt% cellulose content. The ZnO and NaOH contents were (a) 0.8/5.5 wt%, (b) 1.3/6.0 wt% and (c) 1.3/6.5 wt%, respectively. None of the samples had whole insoluble fibres when studied under the light microscope (Fig. 6). Some swollen fragments were found from the sample containing 0.8 wt% ZnO and 5.5 wt% NaOH. In the fluidity measurement (Fig. 7), this sample formed gel instantly when the temperature increased above 12 °C. The other two samples behaved similarly to the corresponding Ecostone N400-treated samples; i.e. the 0.5 wt% difference in the NaOH content produced a clear difference in fluidity. With the lower NaOH content (6.0 wt%) the fluidity was significantly higher (i.e. shorter falling ball time) than with the higher (6.5 wt%) NaOH content. However, when the temperature exceeded 20 °C, the sample with lower NaOH became more unstable, which was noted as fluctuated falling ball times.

The rheological properties of the most stable solution containing 1.3 wt% ZnO and 6.5 wt% NaOH

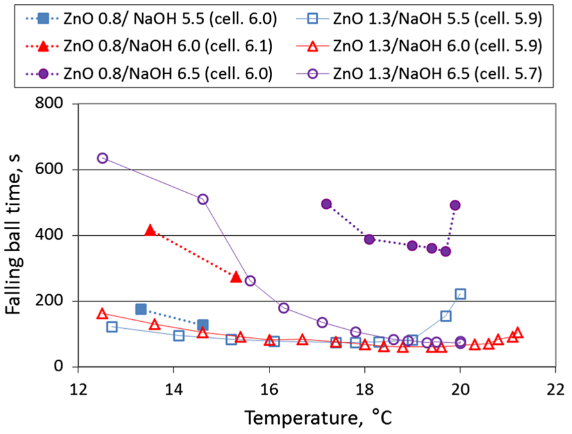


Fig. 5 Fluidity (falling ball time) of cellulose solutions as a function of temperature. Pulp: low-viscosity pulp treated with Ecostone N400 enzyme preparation

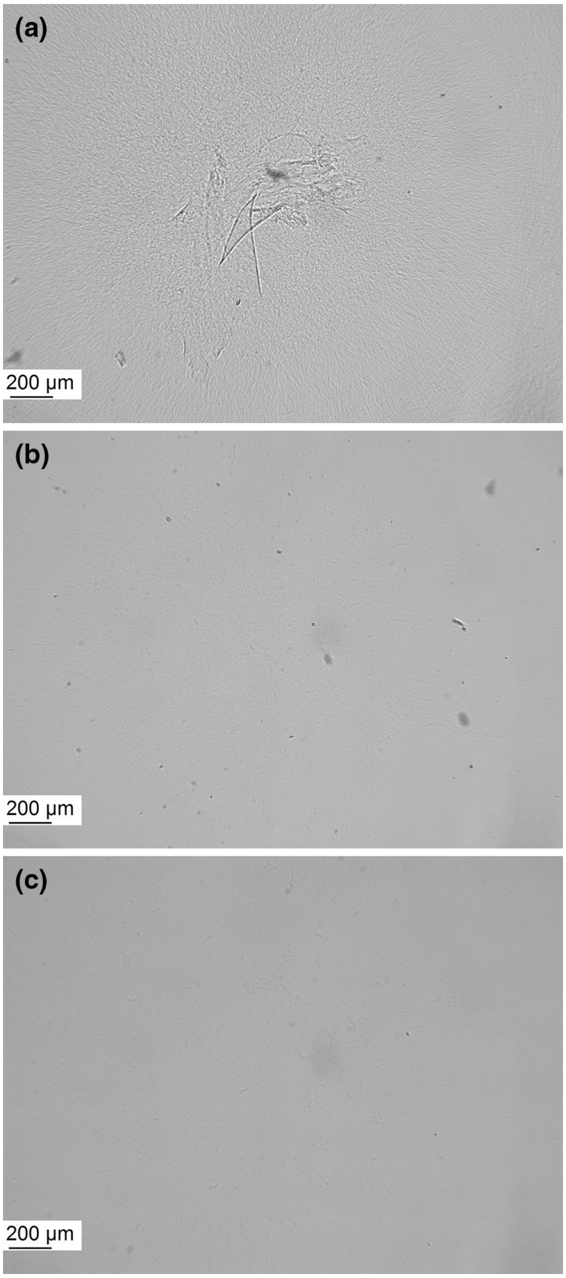


Fig. 6 Microscope images of Fibercare R-treated medium-viscosity pulp dissolved in sodium zincate. **a** 6.0 wt% cellulose, 0.8 wt% ZnO/5.5 wt% NaOH, **b** 6.0 wt% cellulose, 1.3 wt% ZnO/6.0 wt% NaOH, **c** 5.9 wt% cellulose, 1.3 wt% ZnO/6.5 wt% NaOH

was studied with 5.5 wt% cellulose content (medium-viscosity Fibercare R-treated pulp) to minimise the effects of possible insoluble fragments. The steady-state flow curves (Fig. 8) show that the solution is shear thinning. This behaviour is due to the linearity of the cellulose molecules, which allows them to align in the flow direction (Mathur 2011). The first shear rate cycle at 18 °C has a yield point and hysteresis loop, indicating that the solution is thixotropic (Barnes 1997). The loop nearly disappeared during the second cycle at 18 °C. A similar kind of first cycle loop did not occur at 22 or 30 °C, even though the samples were fresh without prior shear history. This indicates that increased temperature induced similar kind of changes in the microstructure of the solution as increased shear. However, the solution was very sensitive at higher temperature, as the shear stress started to build up during the second cycle at the low shear rates at 22 °C and 30 °C. This was probably due to the gelation of the solution which accelerated at higher temperature. The effect of temperature was further studied with dynamic measurements at low angular frequency (1 rad s^{-1}). The storage modulus (G') represents the elasticity of the sample, and the loss modulus (G'') the viscosity of the sample. The G''/G' ratio is equal to tan δ (loss tangent), where δ is the phase lag between the sinusoidal strain and stress waves formed in an oscillatory shear test (Pal 2006). The G' and G'' of the cellulose solution had two cross-over points, the first at 16.3 °C and the second at 42.5 °C (Fig. 9a). In between these temperatures, at the studied angular frequency, the sample is liquid-like. The decrease of G' at temperatures below 21 °C indicates that the microstructure of the sample breaks effectively. The microstructure is probably formed

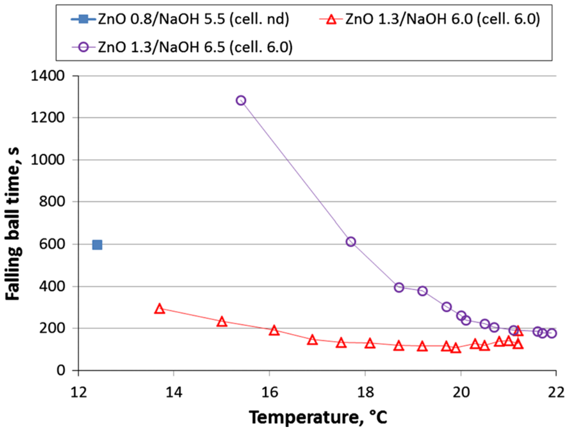


Fig. 7 Falling ball time of cellulose solutions as function of temperature. Pulp: medium-viscosity pulp treated with Fibercare R enzyme preparation

due to entanglement of cellulose molecules, and the entanglement density decreases due to Brownian motion with increased temperature (Barnes 1997). According to the moduli, the viscous character of the sample reached its highest state at 28 °C and remained rather constant up to 37.5 °C. However, at 38 °C, G' started to increase rapidly, and at 42.5 °C the elastic character became dominant. The cross-over of G' and G'' is stated as the gel point of a liquid sample (Cai and Zhang 2006). To study the combined effect of temperature and time, oscillatory measurements were conducted at constant temperatures (Fig. 9b). The times for the G' and G'' cross-over points were 157 min at 22 °C and 75 min at 30 °C. Thus, the stability of the solution at temperatures above 22 °C was rather short-term, which must be considered when processing the spin dope to avoid premature gelation.

The spin dope was prepared based on the results obtained from the solubility studies, i.e. containing 1.3 wt% ZnO, 6.5 wt% NaOH and 6 wt% of cellulose.

Preparation of spin dope

The spin dope was prepared from the medium-viscosity Fibercare R-treated dissolving pulp using the freezing–thawing method. The temperature decreased from 0 to −30 °C at a rate of 0.10 °C min^{-1}. The frozen sample was allowed to melt at 18 °C for 20 h. In the filtration, the solution passed very quickly through the first filter (10 µm) and slowly through the second filter (1 µm). This indicates that only a minor part of the impurities was removed by the first step, thus the selected filter was not optimal. The targeted cellulose content of the dope was 6.0 wt%, whereas 5.8 wt% was obtained. The amount of gel particles in the solution before filtration was 1.19 wt%, and after the two filtration steps 0.14 wt%, from the measured amount of cellulose (5.8 wt%). Thus, the filtration removed 88.4 % of the gel particles from the solution. The amount of impurities in cellulose xanthate solution after the filtration procedure has been reported to be <0.05 wt% (Treiber 1981). The result

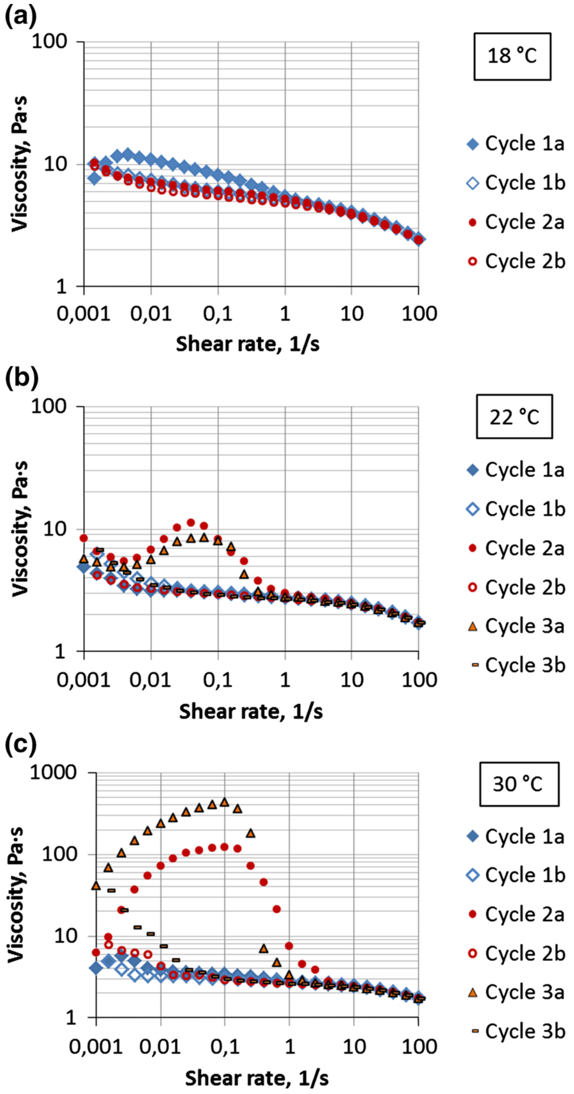


Fig. 8 Steady-state flow curves of cellulose solution containing 5.5 wt% medium-viscosity Fibercare R-treated pulp, 1.3 wt% ZnO and 6.5 wt% NaOH at temperature of **a** 18 °C, **b** 22 °C, **c** 30 °C

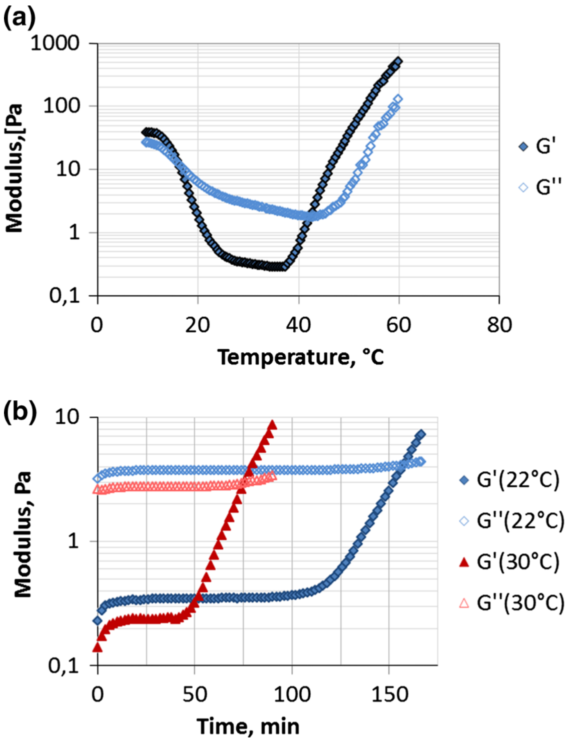


Fig. 9 Dynamic viscoelasticity of 5.5 wt% cellulose solution (medium-viscosity Fibercare R-treated pulp) as a function of **a** temperature and **b** time at 22 and 30 °C

obtained here was thus acceptable at the experimental scale, although it could still be improved. The fluidity of the dope at the gear pump was 38 s, which indicates good processing properties of the dope. The much lower fluidity of the dope as compared with the sample in the solubility test (series 2; 178 s) was due to the slightly lower cellulose concentration of the dope (5.8 versus 6.0 wt%), lower amount of gel particles and most importantly the shear history and shear-thinning nature of the solution. The filtration introduced rather high stress to the solution, which most likely caused irreversible loosening of the intermolecular network of the solution (Ritzoulis 2013). Additionally, the gear pump induced shear strain in the solution, which was not relaxed prior to the falling ball measurement, so the fluidity of the solution increased. The characteristics of the dope are given in Table 2.

Spinning

Three series of fibres with the predetermined spinneret draw ratio and the maximum stretching ratio were spun to study the effect of the spin bath composition on the stretching ratio and on the properties of the fibres.

The correlation between the theoretical (Eq. 1) and obtained linear density of the fibres was studied , because this gives valuable information about the correct setting of the parameters as well as the function of the spinneret during the trial. If the realised linear density deviates significantly from the theoretical value, it is usually due to clogging of the spinneret holes. If this happens, the spinneret draw ratio also changes from the predetermined value (Eq. 2). Figure 10 shows that the linear densities of two fibres deviated much more from the theoretical values than the others. These fibres were excluded from further studies, because the actual spinneret draw ratio of the fibres differed from the predetermined ratio. The linear densities of the fibres spun into the sulphuric acid bath were closest to their theoretical values, whereas the acetic acid spun fibres deviated somewhat systematically from the theoretical values.

The acetic acid spun fibres stretched circa 10 % more between the godets than the sulphuric acid spun fibres. Additionally, for both baths, the maximum stretching ratio increased slightly with decreasing spinneret draw ratio (Fig. 11). Acetic acid is a much weaker acid than sulphuric acid, thus the stretching ratio was higher which is due to the formation of gel-like precipitant (Radishevskii and Serkov 2005). The increased stretching ratio with decreased spinneret draw ratio is most likely connected to the depth of the precipitant's diffusion into the nascent fibre. At the constant pump capacity, the diameter of the flow from the spinneret orifice increases with decreasing spinneret draw ratio. As a consequence, the proportional depth of the precipitant's diffusion compared with the fibre diameter is smaller for lower spinneret draw ratio (Radishevskii and Serkov 2005). Thus, it is suggested that the inner parts of the as-spun fibres were not entirely solidified (in sulphuric acid) or were more gel like (in acetic acid) at the lower spinneret draw ratio, which enabled the higher stretching between the godets.

Unexpectedly, the higher stretching ratio of the acetic acid spun fibres did not produce higher tenacity for the air-dried fibres. Instead, the tenacity was much lower than for the sulphuric acid spun fibres (Fig. 12). The composition of the washing bath of the acetic acid spun fibres (water versus sulphuric acid) did not have a significant effect on the fibre tenacity. Based on the

Table 2 Characteristics of dope preparation

Starting material	Softwood TCF dissolving-grade pulp
SCAN viscosity of starting material	558 mL g^{-1}
Mechanical treatment	Barker Perkins, 20 wt%, 5 h
Enzyme treatment	Fibercare R, 1 mg g^{-1}, 2 h, 50 °C, pH 5
Soluble sugars during enzyme treatment	1.8 %
SCAN viscosity of enzyme-treated pulp	245 mL g^{-1}
Freezing	−40 °C/0.10 °C min^{-1}
Thawing	18 °C/18–20 h (until thawed)
Filtration	2 bar by nitrogen gas
First stage	10 µm/wound structure
Second stage	1 µm/melt-spun structure
Deaeration	200 mbar/20 h/18 °C
Targeted cellulose content of spin dope	6.0 %
Measured cellulose content of spin dope	5.8 %
Amount of gel particles from cellulose	
Before filtration	1.19 %
After filtration	0.14 %
Falling ball time at gear pump	38 s

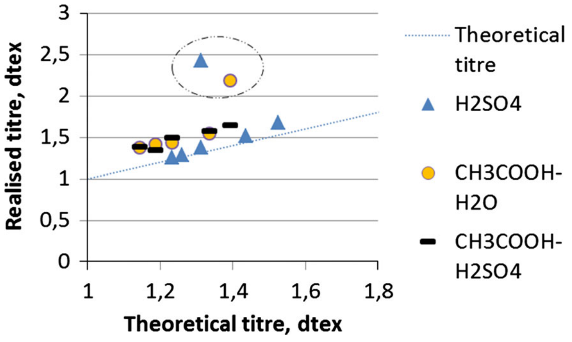


Fig. 10 Correlation between theoretical and realised linear density (titre) of fibres (H_2SO_4, fibres spun into 10 % sulphuric acid; $CH_3COOH–H_2O$, fibres spun into 5 % acetic acid with water in washing bath; $CH_3COOH–H_2SO_4$, fibres spun into 5 % acetic acid with 10 % sulphuric acid in washing bath)

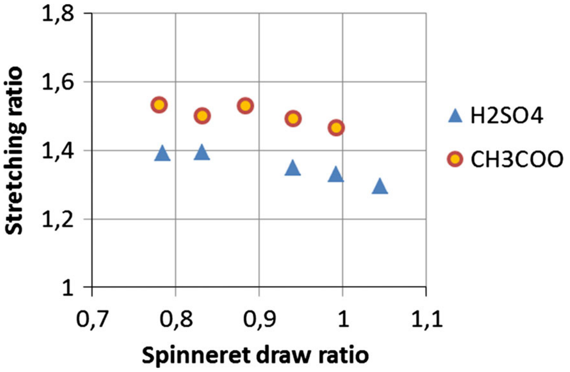


Fig. 11 Effect of spin bath composition on stretching ratio of fibres at predetermined spinneret draw ratio (H_2SO_4, fibres spun into 10 % sulphuric acid; CH_3COOH, fibres spun into 5 % acetic acid)

theoretical and realised linear densities of the fibres at known stretching ratios, it became evident that the acetic acid spun fibres shrank more during drying than the sulphuric acid spun fibres. This was further confirmed by measuring the lengths of the selected dried fibres (Table 3). Both types of fibres spun into the acetic acid spin bath shrank more than the fibres spun into the sulphuric acid bath. The use of sulphuric acid in the washing bath slightly decreased the shrinkage of the acetic acid spun fibres. The elongation at break of the fibres is in line with the shrinkage; i.e. the fibres with higher shrinkage extended more in the stress–strain test (Fig. 13).

The birefringence of the fibres spun into the sulphuric and acetic acid spin baths confirmed that the low tenacity of the acetic acid spun fibres was due to the low orientation of the structure. The birefringence of the acetic acid spun fibres with stretching ratio of 1.5 was equal (0.009) to that of the sulphuric acid spun fibres without stretching (Table 3). Instead, the birefringence of the sulphuric acid spun fibres with stretching ratio of 1.4 was 0.025, which is in the same

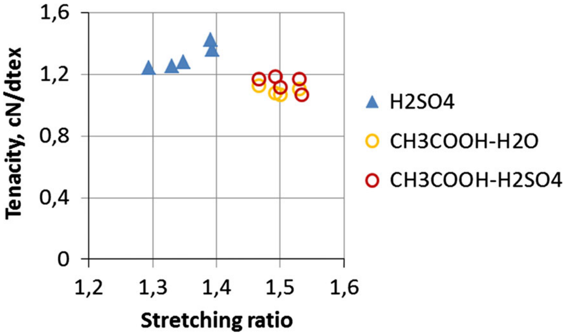


Fig. 12 Effect of spin bath and washing bath compositions on tenacity of fibres (H_2SO_4, fibres spun into 10 % sulphuric acid; $CH_3COOH–H_2O$, fibres spun into 5 % acetic acid with water in washing bath; $CH_3COOH–H_2SO_4$, fibres spun into 5 % acetic acid with 10 % sulphuric acid in washing bath)

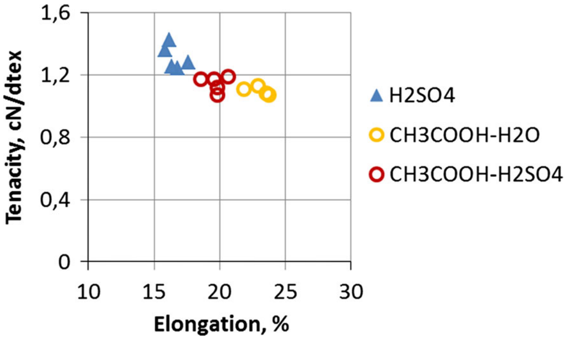


Fig. 13 Tenacity and elongation at break of fibres (H_2SO_4, fibres spun into 10 % sulphuric acid; $CH_3COOH–H_2O$, fibres spun into 5 % acetic acid with water in washing bath; $CH_3COOH–H_2SO_4$, fibres spun into 5 % acetic acid with 10 % sulphuric acid in washing bath)

range as commercial viscose fibres (Morton and Hearle 1993). In spite of the low birefringence of the acetic acid spun fibres, their elongation at break in the stress–strain test was not as high as the elongation of sulphuric acid spun fibres without the stretching, 24 and 44 %, respectively. Moreover, the yield stress of the acetic acid spun fibres was also higher than that of the sulphuric acid spun fibres without the stretch (Fig. 14). These results indicate that the molecular chains of the acetic acid spun fibres are to a certain extent oriented (Moncrieff 1970). Thus, we suggest that the chains did orient during the spinning, but distorted partly due to the shrinkage during drying.

The FTIR spectra were recorded from the fibres spun into the sulphuric acid bath with stretching ratio of 1.4 and also without stretching, and from the fibres spun into the acetic acid bath with water or sulphuric acid washing bath. All spectra were characteristic of the cellulose II crystalline form (Forziati and Rowen 1951; Carillo et al. 2004; Oh et al. 2004) with absorption bands at 893, 1156, 1364, 1420 and 2883 cm^{-1} (Fig. 15). According to Nelson and O'Connor (1964) the crystallinity of cellulose can be estimated by the ratio of absorptions at 1375 and 2900 cm^{-1} (TCI, total crystallinity index), which ranked the samples in the same order as the X-ray diffraction and density measurements. As the

Table 3 Characteristics of selected fibres

Spin bath–washing bath	10 % H_2SO_4 + 10 % Na_2SO_4–H_2O			5 % CH_3COOH–H_2O		5 % CH_3COOH–10 % H_2SO_4	
Spinneret draw	1.04	0.78	0.83	0.78	0.83	0.78	0.83
Stretching ratio	1.00	1.39	1.4	1.53	1.50	1.53	1.50
Theoretical titre, dtex	1.59	1.52	1.44	1.39	1.33	1.39	1.33
Realized titre, dtex	1.88	1.68	1.52	2.19	1.58	1.65	1.55
Tenacity, cN $dtex^{-1}$	0.78	1.42	1.36	0.95	1.07	1.07	1.12
Elongation (%)	44	16	15	24	24	20	18
Shrinkage (%)			7		12		9
Birefringence	0.009	0.025		0.009			
Total crystalline index (TCI)	1.01	1.07		1.08		1.03	
Lateral order index (LOI)	0.90	0.38		0.62		0.66	
Swelling coefficient value (%)			177		192		195
Non-freezing water (g g^{-1})			0.32		0.32		0.42
Total pore volume (mL g^{-1})			1.23		1.17		1.36

Fig. 14 Stress–strain curves of fibres spun into sulphuric acid with and without stretch and into acetic acid (with water washing bath) with stretch. Stretching ratios and birefringence values of fibres as indicated. Yield point and yield stress of each fibre measured as shown for H_2SO_4-spun fibre

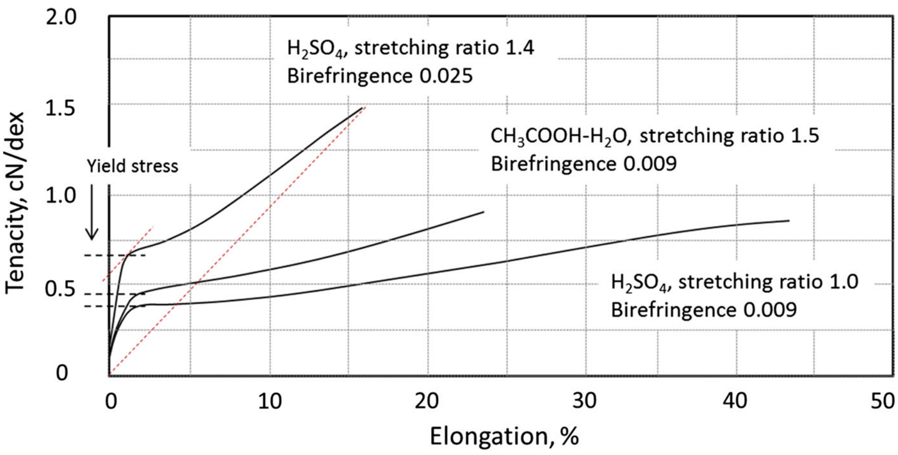
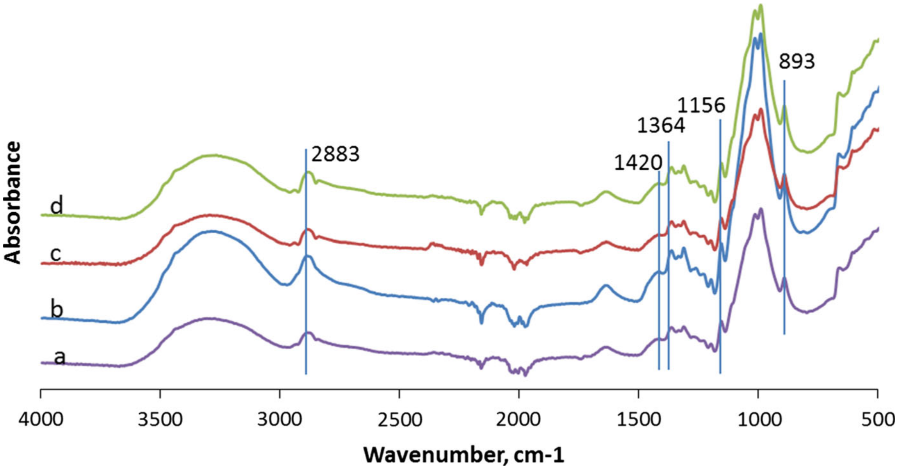


Fig. 15 FTIR spectra of cellulose fibres spun into *a* sulphuric acid without stretch, *b* sulphuric acid with stretch, *c* acetic acid with water washing bath, and *d* acetic acid with sulphuric acid washing bath



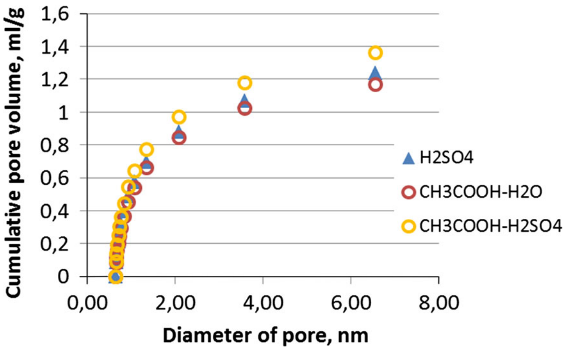


Fig. 16 Cumulative pore volume of fibres (H_2SO_4, fibres spun into 10 % sulphuric acid; CH_3COOH–H_2O, fibres spun into 5 % acetic acid with water in washing bath; CH_3COOH–H_2SO_4, fibres spun into 5 % acetic acid with 10 % sulphuric acid in washing bath)

maximum bands in the spectra were found at 1364 (1375) and 2883 cm^{-1} (2900), these were used for determining the TCI in this work. The total crystallinity indices of the fibres were in the same range around 1 (Table 3). Colom and Carillo (2002) obtained TCI values from 0.68 to 0.74 for commercial lyocell, viscose and modal fibres using the KBr pelleting technique in FTIR sample preparation. According to the data of Röder et al. (2006), attenuated total reflection (ATR) FTIR produced approximately 50 % higher crystallinity values (derived from the TCI) for regenerated cellulosic fibres than KBr FTIR. Thus, the crystallinity degree of the fibres in this work can be regarded as comparable to commercial regenerated cellulosic fibres. The 1420/893 cm^{-1} absorption ratio (LOI, lateral order index) was shown to correlate negatively with the X-ray crystallinity provided the sample contained mainly the cellulose II crystalline form (Nelson and O'Connor 1964). The shift of the band from 1430 to 1420 cm^{-1} confirms that the samples mainly have cellulose II crystalline form (Oh et al. 2005). The fibre spun into the sulphuric acid bath without stretching had the highest LOI (0.90), whereas the fibre spun with stretching ratio of 1.4 had the lowest LOI (0.38). Both the acetic acid spun fibres had LOI values between these two (0.62 and 0.66) (Table 3). Rojo et al. (2013) obtained LOI of 0.60 for viscose fibres, and Carillo et al. (2004) 0.54 for viscose and 0.35 for lyocell fibres. Rojo et al. measured the samples also with X-ray diffraction and concluded that the LOI increased with increase of amorphous regions. Thus, the LOI values support the suggestion that the fibres spun into the acetic acid bath have more ordered structure than the fibres spun into the sulphuric acid bath without stretching.

The water absorption ability measured by the swelling coefficient factor (SwC) gives an indication of the fibre porosity. The acetic acid spun fibres had slightly higher SwC than the sulphuric acid spun fibres (Table 3). This might be due to the disordered structure of the fibres developed during the shrinkage, or due to the changed pore structure caused by the different coagulation media. The pore structure and content of non-freezing water were studied more closely by thermoporosimetry after initial drying and rewetting. No difference in the cumulative pore volumes was recorded between the sulphuric acid and the acetic acid spun fibres when the washing bath contained water (Fig. 16). Thus, the shrinkage is such a powerful change in the structure that it overrides the changes possibly caused by the coagulation. However, when the sulphuric acid washing bath was used for acetic acid spun fibres, slightly increased porosity for the fibres was obtained. These fibres also had higher non-freezing water content compared with the others. This suggests that the hydrated surface area of the fibres was opened up in the process. This could be due to higher swelling, higher accessibility to existing adsorption sites or possibly addition of new adsorption sites e.g. acid groups.

According to the FESEM studies, the cross-section of the fibres was round (Fig. 17). This indicates that coagulation occurred through the whole fibre matrix without any skin formation. The surface morphology of the sulphuric acid and acetic acid spun fibres differed from each other (Fig. 18). The outer surface of the sulfuric acid spun fibres was relatively smooth with localized indentations (Fig. 18a) similar to

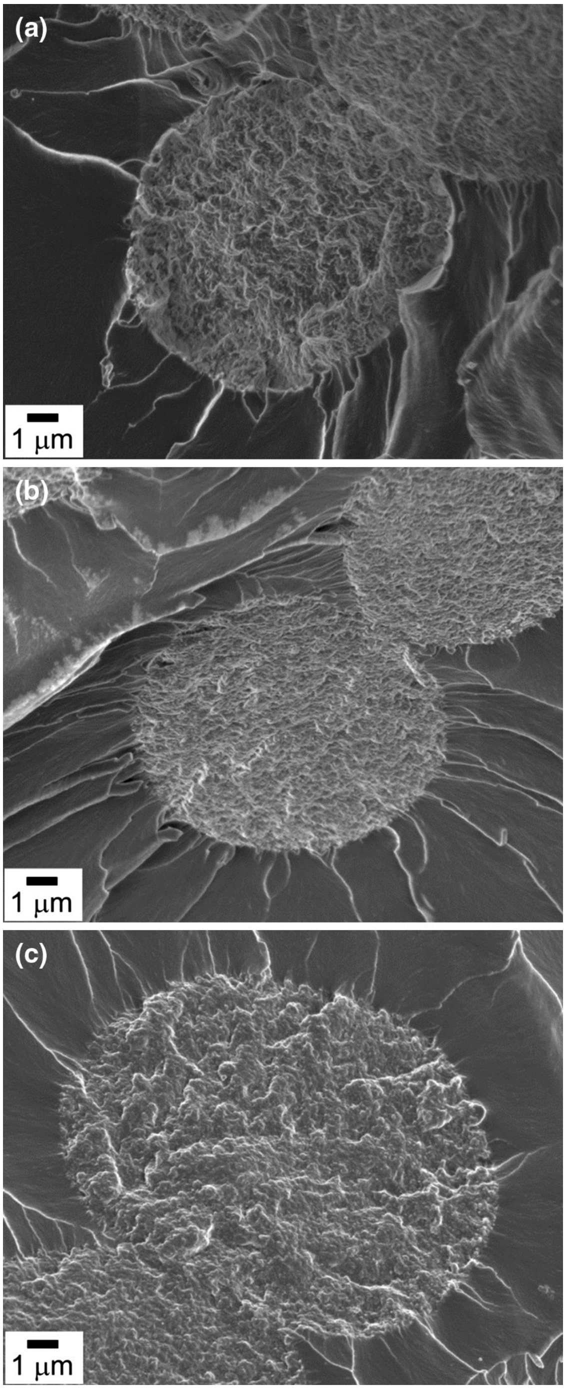


Fig. 17 FESEM images from cross-sections of fibres spun into **a** 10 % sulphuric acid, **b** 5 % acetic acid with water in washing bath, **c** 5 % acetic acid with 10 % sulphuric acid in washing bath

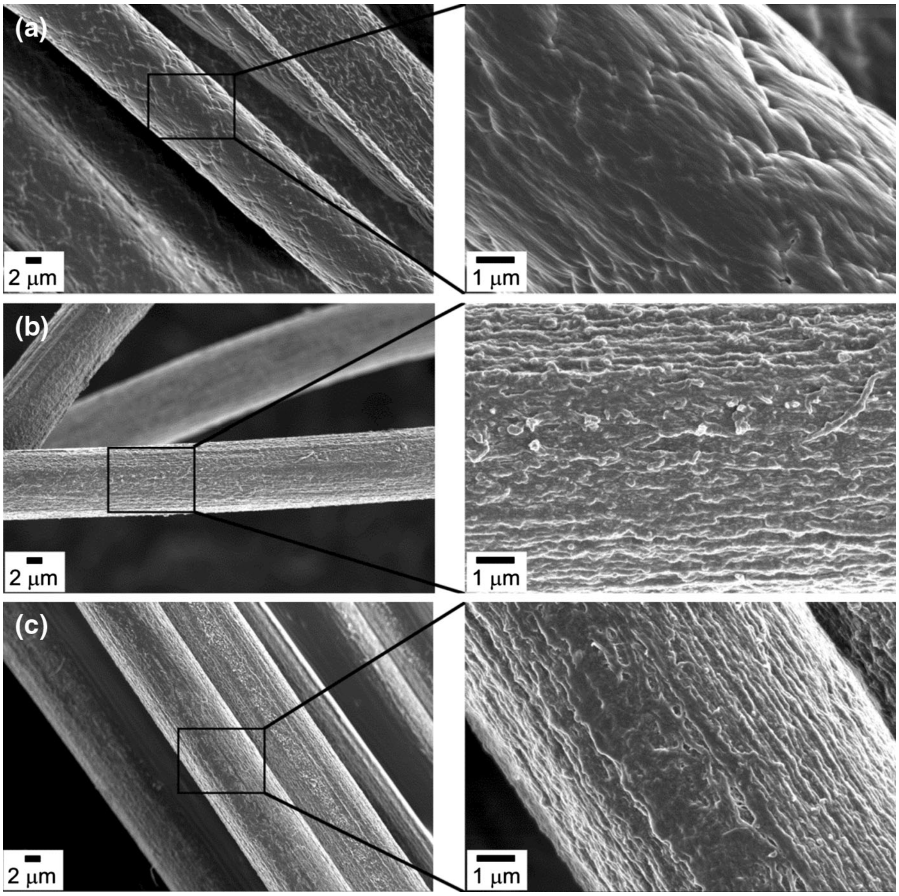


Fig. 18 FESEM images from surfaces of fibres spun into **a** 10 % sulphuric acid, **b** 5 % acetic acid with water in washing bath, **c** 5 % acetic acid with 10 % sulphuric acid in washing bath

previous findings from fibres spun into 15 % sulphuric acid (Vehviläinen et al. 2008). The acetic acid spun fibres, with both water and sulphuric acid washing baths (Figs. 18b, c), had a much higher degree of fine-scale roughness which was organized into a pattern of longitudinal stripes. The indentations on the surface of the sulphuric acid spun fibres might be due to the rapid diffusion of the coagulation chemicals inside the fibres, leaving a point-like pattern on the surface. As the acetic acid has lower coagulating power, the diffusion is slower and no clear points are seen on the surface.

Conclusions

The solubility of enzyme-treated dissolving pulp in the freezing–thawing method was clearly affected by both the zinc oxide and sodium hydroxide concentrations of the sample. Some dissolution occurred without zinc, and its extent increased when the NaOH content was increased to 6.5 wt%. However, the zinc oxide was needed for higher/complete dissolution. Surprisingly, the samples with 7 wt% NaOH formed gel during the freezing stage. This is thought to be due to the partial dissolution of the cellulose before freezing. The most thermally stable sample contained 1.3 wt% zinc oxide and 6.5 wt% NaOH. The rheological studies of this sample with 5.5 wt% cellulose content revealed the solution to be shear thinning, thixotropic and thermally very sensitive. The viscosity at shear rate of 100 s^{-1} decreased from 2.4 to 1.7 Pa s when the temperature was increased from 18 to 22 °C. However, the solution started to form gel at 22 °C during the second measuring cycle. According to dynamic measurements, the viscous character of the solution reached the highest state at 28 °C and the gel point at 42.5 °C. However, at constant temperatures of 22 and 30 °C the solution was stable for only 157 and 75 min, respectively.

Spin dope containing 6 wt% cellulose, 6.5 wt% NaOH and 1.3 wt% ZnO was prepared using the freezing–thawing method. Filtration of the dope removed 88.4 % of the gel particles, decreasing their amount to 0.14 % from the cellulose. The fluidity of the spin dope was significantly higher than the fluidity of the comparable small-scale sample. This was a direct consequence of the rheological characteristics of the solution: both the filtration and the pumping of the spinning solution through the gear pump introduced stress to the solution which was not relaxed prior to fluidity measurement.

The solution was regenerated into fibres using either a sulphuric acid (10 %) or an acetic acid (5 %) spin bath. The acetic acid spun fibres were guided through a washing bath which contained either water or 10 % sulphuric acid. The acetic acid spun fibres stretched circa 10 % more in the spinning line than the sulphuric acid spun fibres. This was due to the weaker coagulating power of acetic acid, which produced softer structure for the as-formed fibres and allowed them to extend more. In spite of the high stretching ratio, the tenacity of the acetic acid spun fibres was clearly lower than that of the sulphuric acid spun fibres. This was due to the shrinkage of the acetic acid spun fibres during drying, which distorted their structure partly.

The birefringence of the acetic acid spun fibres was equal to that of the fibres spun into the sulphuric acid bath without stretching, while the birefringence of the sulphuric acid spun fibres with stretching ratio of 1.4 was equal to values reported for commercial viscose fibres. In spite of the low birefringence and tenacity of the acetic acid spun fibres, their elongation in the stress–strain test was significantly lower and their yield stress slightly higher than for sulphuric acid spun fibres without stress. These results indicate that the structure had some orientation. The lateral order indices (LOI) measured from the FTIR spectra support the suggestion that the fibres spun into the acetic acid bath have more ordered structure than the fibres spun into the sulphuric acid bath without stretching.

Slightly higher water absorption ability was obtained for the acetic acid spun fibres compared with the sulphuric acid spun fibres. However, no difference in the cumulative pore volume between these fibres was recorded when the washing bath contained water. Thus, it was concluded that shrinkage of the fibres destroyed the possible differences in the pore structures caused by the different coagulation media. However, when the acetic acid spun fibres were washed with sulphuric acid, slightly increased porosity and non-freezing water content were obtained. This indicates that there are more water adsorption sites in this sample. This could be due to higher accessibility to existing sites or addition of new adsorption sites, which could be e.g. acid groups originating from the sulphuric acid washing bath.

According to the FESEM studies the shapes of the cross-sections were round for each type of fibre, confirming that coagulation occurred without skin formation. The surface morphology of the sulphuric acid spun fibres indicates that the precipitation chemicals diffused rapidly into the fibres, leaving a point-like pattern on the surface. Similar kind of perforation was not visible on the surface of the acetic acid spun fibres, suggesting slower diffusion.

The aim of this work was to slow down the coagulation of aqueous NaOH-based cellulose solution in order to increase the stretching ratio and consequently the strength of the fibres. The first part of the target (high stretching ratio) was achieved, and reasons for not achieving the second part (high strength) were partly explained (shrinkage). These results motivate further studies to prevent shrinkage of fibres during drying and thus increase fibre strength. Possible means to be studied are the composition, other than sulphuric acid, of the washing bath and controlled drying of the fibres under suitable tension.

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IV

REGENERATION OF FIBRES FROM ALKALINE SOLUTION CONTAINING ENZYME-TREATED 3-ALLYLOXY-2-HYDROXYPROPYL SUBSTITUTED CELLULOSE

by

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ORIGINAL PAPER

Regeneration of fibres from alkaline solution containing enzyme-treated 3-allyloxy-2-hydroxypropyl substituted cellulose

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Abstract The aim of this study was to regenerate fibres from the alkaline cellulose solution containing 3-allyloxy-2-hydroxypropyl substituents. Enzyme-treated cellulose was modified in alkaline aqueous *tert*-butanol (tBuOH) using allyl glycidyl ether (AGE) as the modification reagent. 3-allyloxy-2-hydroxypropyl substituted (AHP) enzyme-treated cellulose with DS_A 0.05 was obtained. Enzyme-treated cellulose without (reference) and with substituents were dissolved in sodium zincate using the freezing-thawing cycle. The reference solution alone and the mixture solutions containing 10 or 25 % of the AHP cellulose were regenerated into cellulosic fibres using the wet spinning technique. The solutions containing 100 or 50 % of the AHP cellulose did not form fibres in acidic bath. The 10 % share of AHP cellulose did not affect the mechanical properties of the fibres (1.5 cN $dtex^{-1}$), while the 25 % share decreased the tenacity slightly (1.3 cN $dtex^{-1}$). Elongation of the fibres ranged from 18 to 22 %. The 10 and 25 % shares of AHP cellulose increased the water holding ability of fibres by 12 and 33 %, respectively. According to FESEM the fibre structures are composed of nanosized fibrils.

Keywords Enzyme-treated cellulose · 3-Allyloxy-2-hydroxypropyl cellulose · AHP cellulose · Wet spinning · Regenerated fibres · Biocelsol · Fibril structure

Introduction

Native cellulose fibre has a complex layered structure, high degree of polymerisation (DP), and strong intra- and intermolecular hydrogen bond network which limit its dissolution and further processing (Klemm et al. 2005). As a consequence, the chemical modifications of cellulose through substitution reactions are important routes for the commercial cellulosic products. The two main reactions used are esterification and etherification of cellulose. Industrially, the most important ester is cellulose xanthate which is an intermediate product in the viscose process. It is formed through a carbon disulphide (CS_2) treatment of mercerized cellulose and it enables the dissolution and subsequent regeneration of the modified cellulose in aqueous environment (Wilkes 2001). The other commercial cellulose esters do not commonly dissolve in water-based solvents (Heinze and Liebert 2001). The industrially important cellulose ethers include methyl cellulose (MC), carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC) (Klemm et al. 2005). Depending on the degree of

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substitution the ethers either swell strongly or dissolve in water. The ethers are important cellulose-based products as additives in the paper, cosmetic, hygiene and food industry. The ethers as such are not suitable for producing textile fibres, however, the properties of existing fibres can be modified by slight surface etherification. For example, carboxymethylation of cotton fibres leads to the increased water sorption of the fibres (Balasubramanian et al. 2013).

Besides, the industrially utilised chemical modification methods, there is a large variety of alternative concepts that have been studied to gain new functionalities for cellulosic materials (Purves 1946; Heinze 2005). Etherification with allyl glycidyl ether (Huijbrechts et al. 2009; Qi et al. 2012) produces interesting derivatives because the substituent has reactive allylic double bond. This enables further modification of the substituted material by grafting (Pohjanlehto et al. 2011) or by click chemistry (Obermeier and Frey 2010). Moreover, entire new functional group such as thiosulphates or thioethers (Wenz et al. 2005) or epoxy groups (Huijbrechts et al. 2010) can be added due to the double bond. Qi et al. (2012) have prepared 3-allyloxy-2-hydroxypropyl (AHP) derivatives by homogeneous etherification of cellulose in NaOH/urea aqueous solution. The AHP celluloses with DS 0.32 and higher were soluble in water, whereas derivatives with DS 0.15–0.21 were only swelling in water and with DS 0.09 they were insoluble in water.

Dissolution of cellulose in alkaline solvents has been studied to find alternative methods for the complex and expensive commercial water-based processes (viscose and cupro) (Wilkes 2001; Kamide and Nishiyama 2001). Depending on the DP and the supermolecular structure of the unmodified cellulose it either swells or dissolves partly in aqueous sodium hydroxide. The solubility increases with decreasing degree of order, decreasing DP and increasing accessibility of cellulose (Schleicher and Lang 1993). The mechanical, chemical and enzymatic modifications are widely studied for increasing the accessibility of cellulose. Kamide et al. (1992) achieved markedly increased solubility in sodium hydroxide using the steam explosion treatment. Isogai and Atalla (1998) found that despite the high DP the decreased coherence of the structure due to the prior dissolution in strong medium and regeneration from that facilitated the dissolution of cellulose. The enzymes are also capable of modifying the cellulose structure such as the alkaline solubility of treated cellulose increases significantly (Nousiainen et al. 1991; Vehviläinen et al. 1996; Rahkamo et al. 1996; Cao and Tan 2002, 2006; Grönqvist et al. 2014). Without mechanical pretreatment the increased solubility of enzyme-treated cellulose correlated linearly with the decreased viscosity (DP) (Rahkamo et al. 1996). However, with mechanical pretreatment the solubility at the same cellulose DP increased clearly (Vehviläinen et al. 1996). It was recently proofed that the mechanical shredding increases the amount of accessible sites for the enzymes, thus facilitating their penetration in the structure (Grönqvist et al. 2014).

Apart from the cellulose-based properties, the type of solvent and the conditions play important role in the dissolution. Davidson (1934, 1936) found already in the 1930's that the solubility of cellulose in sodium, lithium and tetramethylammonium hydroxides was significantly increased when the temperature was lowered from 15 to −5 °C. Moreover, the addition of zinc oxide and beryllium oxide enhanced the solubility (Davidson 1937). Recently, also other additives such as thiourea, urea or PEG in sodium hydroxide and urea in lithium hydroxide have been found to facilitate the dissolution of cellulose (Zhang et al. 2002; Cai and Zhang 2005; Yan and Gao 2008, Yang et al. 2011).

Previously we have dissolved the enzyme-treated cellulose into sodium zincate and produced wet spun regenerated fibres from the solution obtained (Vehviläinen et al. 2008, 2010, 2015). In the current work we studied a novel way to incorporate reactive double bonds in the cellulosic fibres. We carried out a heterogeneous etherification of enzyme-treated cellulose with allyl glycidyl ether. Thereafter, we dissolved the obtained 3-allyloxy-2-hydroxypropyl substituted (AHP) enzyme-treated pulp in the sodium zincate using the freezing-thawing cycle (Vehviläinen et al. 2009). Finally, we regenerated fibres from the solutions containing substituted pulp. Here, we present the results of the etherification, dissolution and spinning trials of the enzyme-treated pulp, as well as, the characteristics of the pulp and regenerated fibres.

Materials and methods

Pulp treatments

The starting material was medium viscosity dissolving grade softwood (TCF) pulp produced by Domsjö

Fabriker AB, Sweden. The pulp was first shredded mechanically for five hours using a Baker Perkins shredding machine (size 6-1 Universal mixer S/N 44777) and thereafter treated with Fibercare R (Novozym CGP20048) enzyme preparation at pH 5, 50 °C for 2 h. The enzyme dosage was 1 mg protein/g pulp. The enzyme treatment dissolved circa 1.8 % of the pulp as soluble sugars measured using the 3,5-Dinitrosalicylic acid (DNS) method (Bernfeld 1955).

One portion of the enzyme-treated pulp was further modified chemically with allyl glycidyl ether (AGE). The modification was done in alkaline aqueous conditions at 45 °C for 20 h. The reaction scheme is presented in Fig. 1. Wet enzyme-treated pulp containing 200 g of cellulose (1.24 mol of anhydroglucose units, AGU) was weighed and added into a reaction flask with 1440 mL of water and with 1730 mL of 90 % aqueous *tert*-butanol (tBuOH). Concentrated aqueous NaOH (10 M NaOH, 240 mL) was added to adjust the molarity of NaOH to 1 M in respect of the total amount of water in the reaction mixture. The NaOH/AGU ratio was 1.9. The reaction mixture was stirred first for 2 h at 65 °C, cooled down to room temperature and stirred overnight for activation with NaOH. Next, the reaction mixture was heated to 45 °C, allyl glycidyl ether (187 mL) was added and the reaction mixture stirred again overnight at 45 °C. Thereafter, the reaction mixture was neutralized with sulphuric acid (10 v/v %) and the substituted cellulose was washed twice with 95 % ethanol, ethanol–water (1:1) and finally with water. The sample was stored in wet form for further processing, except a small portion was freeze-dried for characterisations.

Solubility of 3-allyloxy-2-hydroxypropyl substituted pulp

Solubility of the enzyme-treated 3-allyloxy-2-hydroxypropyl substituted (AHP) pulp was studied at a small scale (30 g). Wet cellulose (dw 15 wt%) and sodium zincate were mixed to obtain a slurry-like sample containing desirable amount of modified cellulose, 6.5 wt% NaOH and 1.3 wt% ZnO. The slurry was frozen in a clear plastic test tube (30 mL) in a freezer at −35 °C. The frozen sample was thawed and the obtained solution studied under a light microscope. The viscosity and the dry content of the solution were measured. Samples from the unsubstituted enzyme-treated pulp were prepared accordingly for reference.

Preparation of spin dopes

The spin dopes were prepared from the enzyme-treated pulp (reference) and from the 3-allyloxy-2-hydroxypropyl substituted enzyme-treated (AHP) pulp. The wet pulp and sodium zincate were mixed to obtain a slurry-like sample containing desirable amount of pulp, 6.5 wt% NaOH and 1.3 wt% ZnO. The reference pulp sample was mixed with an overhead stirrer, whereas the AHP pulp sample was mixed manually in order to prevent the formation of air bubbles. The both slurries were frozen in plastic boxes at −40 °C in a freezer and thawed to obtain solutions. The solution from reference pulp was filtered through a 10 µm wound filter (Aquator MS97PP10) and through a 50 µm melt blown filter (Aquator MB50-10), and the solution from AHP pulp was filtered through a 10 µm wound filter (Aquator MS97PP10).

Besides the 100 % dopes from the reference and AHP pulps, three mixture dopes were prepared having 50/50, 25/75 and 10/90 AHP/reference pulp ratios, respectively. The solutions were placed in the spinning reservoirs and the pressure inside the reservoirs was lowered to below 200 mbar for removing the air bubbles.

Spin baths

Two spin bath compositions were used:

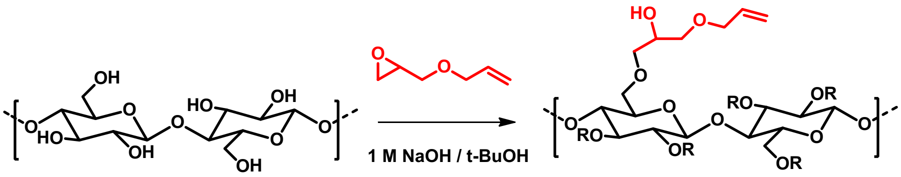


Fig. 1 Synthesis of 3-allyloxy-2-hydroxypropyl A ether derivatives of cellulose. R=H or substituted with A groups

1. 106 g l^{-1} of sulphuric acid (10 % H_2SO_4) and 100 g l^{-1} of sodium sulphate (10 % Na_2SO_4), specific gravity 1.135.
2. 224 g l^{-1} sulphuric acid (20 % H_2SO_4), specific gravity 1.137.

Spinning

The fibres were spun using a laboratory wet spinning machine. The spinneret used had 100 orifices of 51 μm and was made of a gold/platinum mixture by Wetzel Gröbzig Micro Products. The L/D-ratio of the spinneret was 2.94 (L = 0.15 mm, D = 0.051 mm). The gear pump used (Zenith BPB-4391) had capacity of 0.3 mL per revolution.

The fibres were spun with predetermined spinneret draw ratio with varying stretching ratios: the spinneret draw ratio was adjusted to the desired value and the velocities of II and III godets were increased until the fibres broke. The maximum stretching was obtained by decreasing the velocities of II and III godets by 1 m min^{-1} from the breakage velocity. The maximum stretching ratio was explored for the each sample at different spinneret draw ratio values.

The stretching bath contained hot water and the washing baths cold water.

Equations 1, 2 and 3 (Götze 1967) were used to calculate the desired settings of the machine, as well as the parameters realised.

$$T = \frac{Q \times \rho_{dope} \times \frac{\alpha}{100} \times 10000}{n \times V_{III}}, \tag{1}$$

where *T* desired linear density of fibres, *dtex,* mass [g] of a filament fibre which length is 10,000 m, *Q* capacity of pump, mL min^{-1}, ρ_{dope} density constant of spin dope = 1.4 g mL^{-1}, α cellulose concentration of spin dope(%), *n* number of spinneret orifices, 100, V_{III} velocity of third godet, m min^{-1}

$$spinneret \times draw \times ratio = V_I \times \frac{\left(\frac{\pi}{4}\right) \times D^2 \times n}{Q}, \tag{2}$$

where V_I velocity of first godet, m min^{-1}, *D* diameter of orifice capillary, mm

$$stretching \times ratio = \frac{V_{II}}{V_I}, \tag{3}$$

where V_{II} velocity of second godet, m min^{-1}, V_I velocity of first godet, m min^{-1}

The fibres obtained were collected in the wet continuous form and thereafter cut into 5.5 cm lengths by hand. The fibres were washed with demineralised water until free of salts (measured with a conductivity meter) and finished by exchanging water to ethanol in order to minimize the fibre attachments during the drying. The drying was carried out at ambient temperature (22 ± 2 °C).

Characterisation

The intrinsic viscosity of the pulp (mL g^{-1}) was measured before and after the enzyme treatment, and after the chemical modification with allyl glycidyl ether according to the SCAN-CM 15:99 (ISO 5351:2004). In this method, the sample is dissolved in cupriethylenediamine hydroxide and the intrinsic viscosity derived from the efflux-time of the solution.

The degree of substitution (DS) of the 3-allyloxy-2-hydroxypropyl substituted enzyme-treated pulp was characterized using a solid state ^{13}C NMR spectroscopy. The ^{13}C CP/MAS NMR measurements were performed with a Chemagnetics CMX 400 MHz Infinity NMR spectrometer using a 5.0 mm double-resonance MAS NMR probe operating at 100.6 MHz. For all the samples, 30,000 transients were accumulated using a 1 ms contact time, 3 s recycle time and a spinning speed of 7 kHz. The chemical shifts were referenced to hexamethylbenzene (HMB) using the methyl signal (+17.35 ppm) as an external reference. The degree of substitution (DS) was determined by comparing the integrals originating from the substituent (C11–C12) and cellulose C1 signal integral with the aid of signal deconvolution.

The crystalline structures of the pulps and the regenerated fibres were analysed by recording the Fourier transform infrared spectra (FTIR) with Bruker Optics Tensor 27 FTIR spectrometer. The samples were mounted directly in the sample holder.

The viscosity of the small scale solution was measured at ambient temperature by dropping a stainless steel ball (1/8″, 130 mg) in the solution and recording its falling time (s) at 5 cm distance. The time obtained was multiplied by four to be comparable with the viscosity of the spin dope.

The viscosity of the dope was measured at ambient temperature by the modified Ball-Drop Method (ASTM D 1343-86). A plastic cylinder was filled with the dope, a stainless steel ball (1/8″, 130 mg) was dropped in the solution and the falling time of the ball was recorded (s) at 20 cm distance. The dopes were collected from the gear pump. The result is given as an average of three measurements and referred to be the viscosity or falling ball time of the dope.

The cellulose content (alpha) of the solution was measured by coagulating films from the known amount of solution into 10 % sulphuric acid. The films were washed, dried at 105 °C and weighed. The cellulose content was calculated as a weight percentage of the dried films from the weighed solution. The result is given as an average of two measurements.

The regenerated fibres were conditioned at a relative humidity of 65 ± 5 % and the temperature of 20 ± 2 °C for at least 24 h. The mechanical properties were determined as an average of 20 measurements according to the ISO 1973 and ISO 5079 standards using a Favigraph testing machine (Textechno GmbH). The tests included titre (dtex), tenacity (cN dtex^{-1}), elongation (%), Young's modulus at 1 % elongation (cN dtex^{-1}) and work of rupture (cN cm). The testing speed was 20 mm min^{-1} and the gauge length 20 mm.

The swelling coefficient (SwC) of the regenerated fibres was determined as the amount of water held by the sample. Desired amount of fibres were soaked in ion exchanged water for at least 20 h. The fibre sample was drained through a wetted filter fabric and centrifuged at 3000×*g* for 80 s. The sample was weighed prior to and after the drying at 105 °C, the result is given as a percentage of water from the dry sample.

The surface and cross-sectional structures of the regenerated fibres were studied with a field-emission scanning electron microscope (FESEM, ULTRA-plus, Zeiss). The cross-sectional FESEM samples were prepared as follows: bundle of fibres was moistened with resin (epoxy embedding, Fluka) followed by hardening in air at 100 °C for 1 h, the moulded fibres were then fractured in liquid nitrogen and the fracture surfaces were studied with FESEM. The surface and cross-sectional samples were carbon-glued on the aluminium stubs followed by carbon coating to avoid the sample charging in the FESEM studies.

Results and discussion

Changes in degree of polymerisation due to treatments

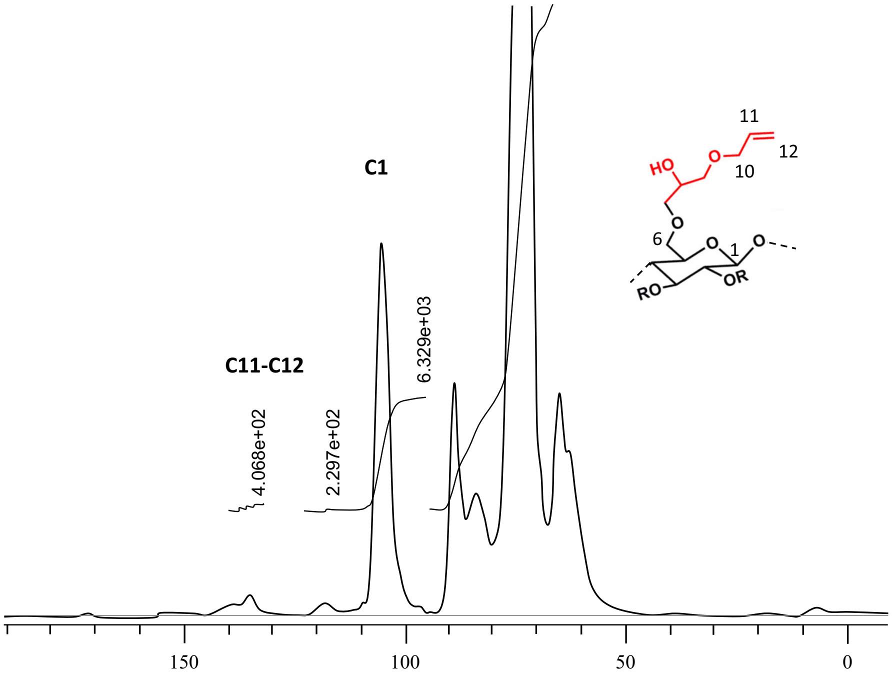
The enzymatic treatment of dissolving grade pulp decreased its intrinsic viscosity from 558 to 240 mL g^{-1}. The following modification of enzyme-treated pulp with allyl glycidyl ether increased slightly the intrinsic viscosity to 252 mL g^{-1}. This indicates that the alkaline conditions in chemical modification treatment dissolved some of the shortest molecules, but did not degrade the pulp.

Solubility of 3-allyloxy-2-hydroxypropyl substituted (AHP) pulp

According to the NMR analyses the DS of the 3-allyloxy-2-hydroxypropyl substituted enzyme-treated (AHP) pulp was only 0.05 (Fig. 2). The modified cellulose with such a low amount of substituents is not soluble in water (Qi et al. 2012).

The alkaline solubility of AHP pulp was studied by dissolving 6.0, 6.5 and 7.0 wt% of pulp in sodium zincate. Duplicate samples were prepared with 6 wt% concentration; the first was mixed with an overhead stirrer and another one manually. The stirrer-mixing induced large amount of air bubbles in the solution indicating the 3-allyloxy-2-hydroxypropyl substituents have high surface activity. As the air bubbles hampered the characterization of the solution (falling ball time and microscopy) and would prolong the deaeration of the spin dope, the other samples were mixed carefully by hand. This decreased the amount of air and enabled the characterization of the samples. No clear difference between the samples with different amounts of pulp (6.0, 6.5, 7.0 wt%) was observed with a light microscope; they all contained few small particles without any larger undissolved fragments (images not shown). The dry contents of the solutions were very close to the targeted values. The reference solutions from the unsubstituted enzyme-treated pulp were prepared with lower cellulose content, as it turned out that its solubility decreased rapidly with higher than 6 wt% content. The viscosity of the solutions from AHP pulp increased only moderately with the increasing cellulose concentration as compared to the reference samples. The result shows that the substitution clearly improves the solubility of the enzyme-treated

Fig. 2 Solid state ^{13}C NMR spectrum of 3-allyloxy-2-hydroxypropyl substituted enzyme-treated cellulose



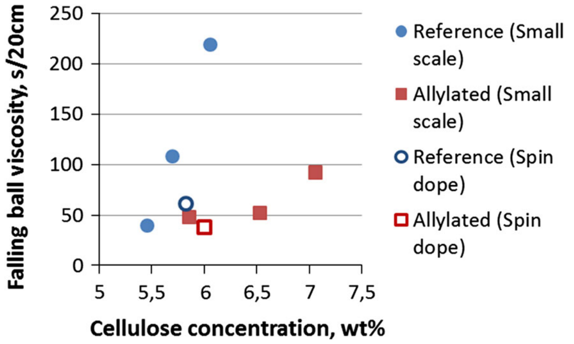


Fig. 3 Effect of dry weight of solution on its viscosity as measured by falling ball time

cellulose in the water-based environment (Fig. 3). As the intrinsic viscosity of the AHP pulp was slightly higher than of the enzyme-treated pulp the average degree of polymerisation did not decrease due to the chemical modification. Thus, the improved solubility can be due to the increased entropy of the cellulose chains and the disturbed hydrogen bond network caused by the relatively large 3-allyloxy-2-hydroxypropyl groups (Klemm et al. 2005; Spurlin 1946).

Spin dopes

Two spin dopes, one from the unsubstituted enzyme-treated pulp (reference) and another one from the 3-allyloxy-2-hydroxypropyl substituted (AHP, DS 0.05) enzyme-treated pulp were prepared at 6 wt% cellulose concentrations. The solutions were filtered and mixed with each other in the desired ratios. The AHP pulp produced solution with lower viscosity than the reference pulp. The viscosity of the AHP dope was in line with the small scale samples, instead the viscosity of the reference dope was clearly lower than of the small scale solutions (Fig. 3). This was due to the thixotropic nature of the reference dope (Vehviläinen et al. 2015). The solution was collected from the gear pump for the viscosity measurement and the shear strain induced by the pumping was not relaxed prior to the viscosity measurement. Consequently, the obtained viscosity was lower than of the small scale samples without similar kind of shear history. Also, the filtration of the spin dope, which removed the gel-like undissolved impurities decreased somewhat the viscosity compared to the small scale samples that were not filtered. The viscosities of the mixture dopes were in line with the ratios between the two dopes. The properties of the spinning solutions are given in Table 1.

Spinning

Spinning trials of the solutions prepared from the AHP pulp and from the 50/50 AHP/reference pulp were not

Table 1 Characteristics of dopes

Code of spin dope	Enzyme treatment	Modification	Ratio of AHP/reference	Measured cellulose content of spin dope (%)	Falling ball time, s/20 cm (T)
Reference	Dose 1 mg g^{-1}, 2 h, 50 °C, pH 5	None	0/100	5.8	61 (21 °C)
AHP	Dose 1 mg g^{-1}, 2 h, 50 °C, pH 5	3-Allyloxy-2-hydroxypropyl substitution (DS 0.05)	100/0	6.0	38 (22 °C)
50/50 Mixture			50/50	6.0	40 (23 °C)
25/75 Mixture			25/75	5.9	46 (22 °C)
10/90 Mixture			10/90	5.9	57 (22 °C)

Fig. 4 Gelled cellulose solution from 100 % AHP pulp on *top* of spinneret

successful. The solutions formed gel layer on the surface of the spinneret in a spin bath containing 10 % sulphuric acid and 10 % sodium sulphate (Fig. 4). Even though, the 50/50 mixture solution contained very low amount of substituents the solution did not form fibres (under the conditions used). The result indicates the 3-allyloxy-2-hydroxypropyl groups disturbed the formation of bonds between the adjacent chains.

The mixture solutions containing 10/90 and 25/75 AHP/reference pulp did coagulate into fibres. However, the solutions needed considerably longer coagulation time than the reference solution. This was seen as a formation of gel lumps at the spinneret which led to the fibre breakages. The situation improved when the spinning speed was decreased. The instant formation of a thin membrane on the surface of the solution jet as it enters into the spin bath is a prerequisite for the fibre development. The membrane keeps the nascent fibres apart from each other, and regulates the following neutralisation and dehydration reactions which lead to the coagulation. The neutralisation proceeds by the diffusion of the non-solvent into the as-formed fibre and of the solvent from the fibre, and the dehydration proceeds by the osmosis as water squeezes out from the fibre (von Bucher 1968). The processes can be controlled by the composition of the coagulation bath. In the commercial viscose process, high sodium sulphate concentration (12–20 %) of the spin bath along with the optimal acid concentration ensure efficient dehydration of the cellulose xanthate solution prior to too extensive regeneration. The properly selected salt and acid concentrations enable sufficient stretching of the formed densified viscose (Turbak 1990). In this study, the coagulation of the mixture dopes enhanced when the 10 % sulphuric acid/10 % sodium sulphate bath was replaced with the 20 % sulphuric acid bath. This is most likely due to the more rapid neutralisation of the as-formed fibres in the bath with higher acid concentration. The 25/75-mixture solution was spun in the 20 % sulphuric acid bath only.

The maximum stretching ratios at the desired spinneret draw values are given in Table 2. The velocities of the second and third godets (=spinning speed) are equal to the velocity of the first godet multiplied by the stretching ratio.

Fibres

Generally, a linear relationship between the realised and theoretical linear density of the fibres confirms

Table 2 Realised spinning parameters

Spin bath[a]	Godet I, m/min	Spinneret draw	Maximum stretching ratio		
			Reference dope	10/90 mixture	25/75 mixture
10 % H_2SO_4	5.3	0.62	1.42	1.32	
10 % H_2SO_4	5.6	0.76	1.30	1.28	
10 % H_2SO_4	7.0	0.95	1.21	1.23	
20 % H_2SO_4	5.3	0.62	1.32	1.32	1.39
20 % H_2SO_4	5.6	0.76	1.25	1.29	1.16
20 % H_2SO_4	7.0	0.95	1.21	1.20	1.21

[a] 10 % H_2SO_4 bath contained also 10 % Na_2SO_4, 20 % H_2SO_4 bath did not contain any added salt

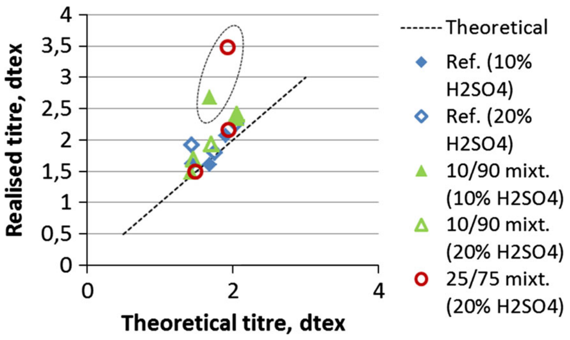


Fig. 5 Realised linear density (titre) of fibres in function of theoretical values. Two samples inside the *circle* are excluded from the further studies

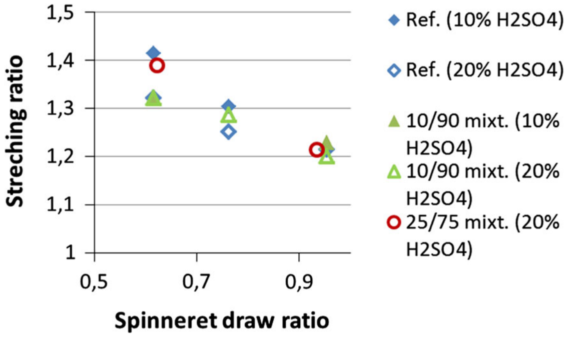


Fig. 6 Stretching ratio of fibres in function of spinneret draw ratio

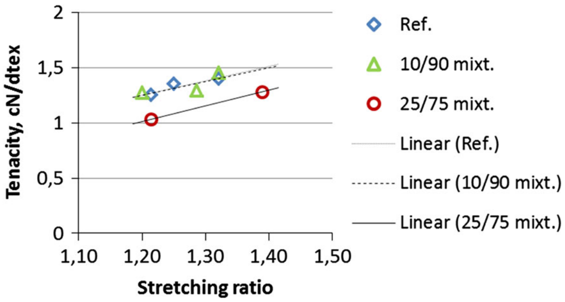


Fig. 7 Correlation between stretching ratio and tenacity of fibres spun into 20 % sulphuric acid

that the machine settings have been correct and that the spinneret has worked without cloggings. Figure 5 shows that the realised linear density of the all fibres except two are close to the theoretical values. This indicates that inspite of some difficulties at the spinnerets, real clogging occurred only during those two samples. Thus, the adjustments done (decreased spinning speed) worked and the samples collected (excluding the two with high deviation) are relevant for the further studies.

The stretching ratio of the fibres and the spinneret draw ratio correlated negatively with each other (Fig. 6) similar to found previously for the fibres spun from the unsubstituted enzyme-treated dopes (Vehviläinen et al. 2008, Vehviläinen et al. 2015). The obtained maximum stretching ratio of the different fibres varied from each other at the low spinneret draw ratio, whereas rather constant stretching ratio (1:2) was realised at the high spinneret draw ratio. The scattered values at the low spinneret draw ratio are most likely due to the rather slow taking up velocity.

The tenacity of the fibres spun into 20 % sulphuric acid increased with increasing stretching ratio, as expected (Fig. 7). Even though, the 10 % share of the AHP pulp caused some disorder in the coagulation it did not affect the fibre tenacity as compared to the reference fibres at the comparable stretching ratios. Instead, the 25 % share of the AHP pulp clearly decreased the tenacity (Fig. 7).

Inspite of the decreased tenacity of 25/75 mixture fibres when studied in respect to the stretching ratios,

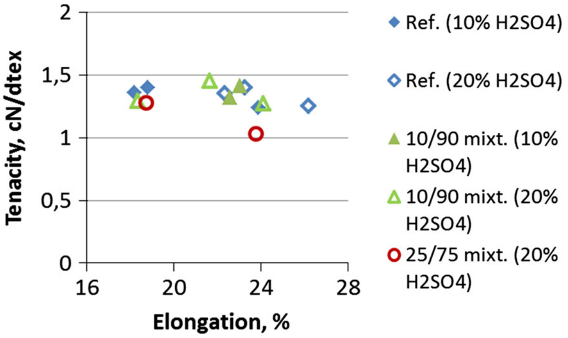


Fig. 8 Tenacity and elongation at rupture of fibres spun at low speed

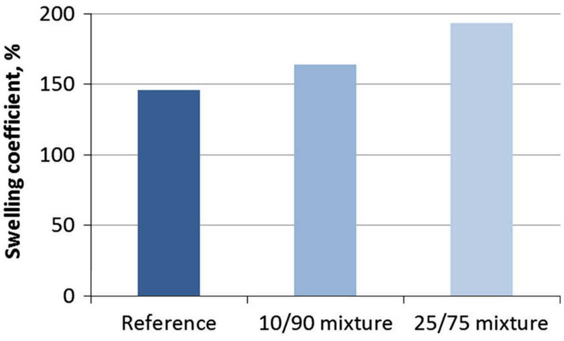


Fig. 9 Swelling coefficient value of fibres spun into 20 % sulphuric acid

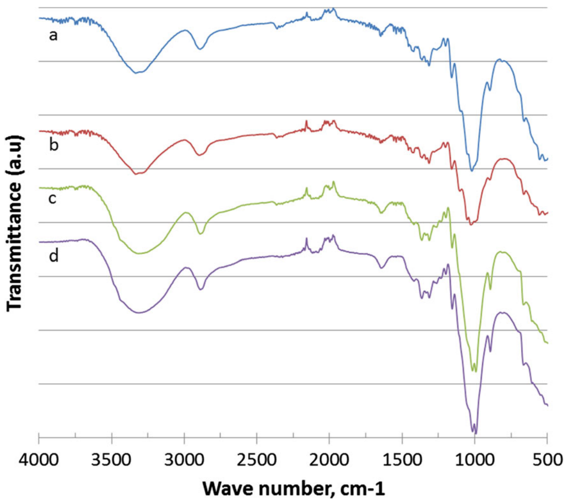


Fig. 10 FTIR spectra of pulp and regenerated fibre samples, **a** Unsubstituted enzyme-treated pulp (Reference pulp), **b** 3-allyloxy-2-hydroxypropyl substituted, DS 0.05, enzyme-treated pulp (AHP-pulp), **c** Regenerated fibre from regerence pulp and **d** Regenerated fibre from 25 AHP/75 reference pulp

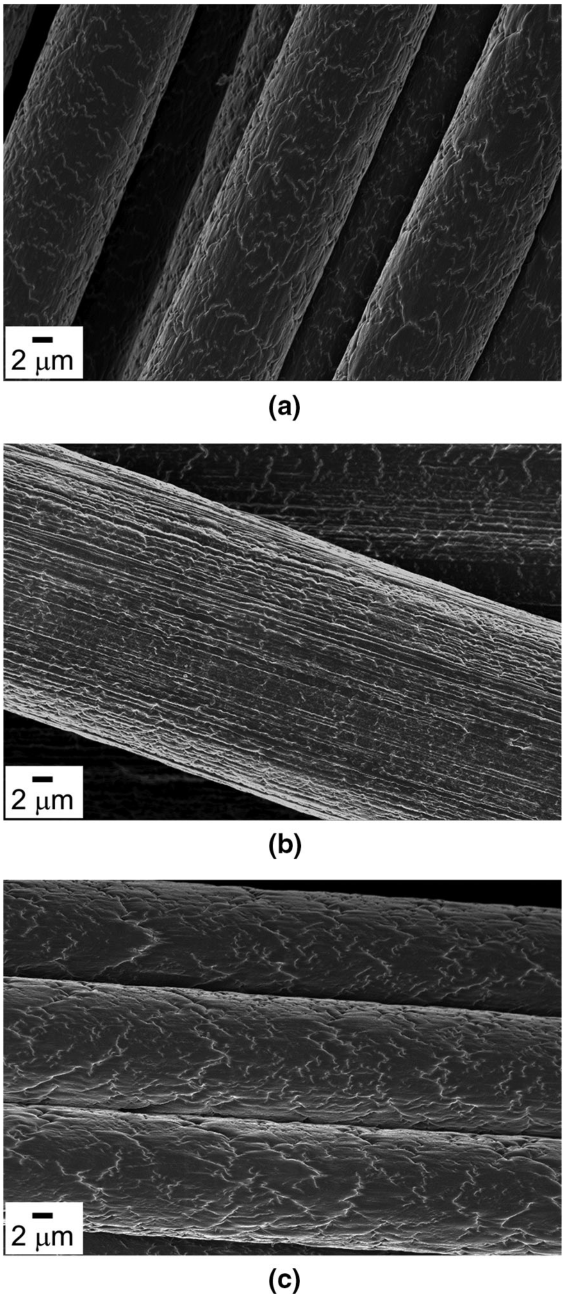


Fig. 11 FESEM images of fibre surfaces **a** Reference fibre regenerated into 20 % H_2SO_4, **b** 10/90 mixture fibre regenerated into 10 % H_2SO_4/10 % Na_2SO_4 and **c** 25/75 mixture fibre regenerated into 20 % H_2SO_4

the maximum tenacity achieved (1.3 cN dtex^{-1}) was close to the 10/90 mixture fibres and to the reference fibres (1.4–1.5 cN dtex^{-1}) (Fig. 8). The elongation of the strongest fibres ranged from 18 to 23 %. This

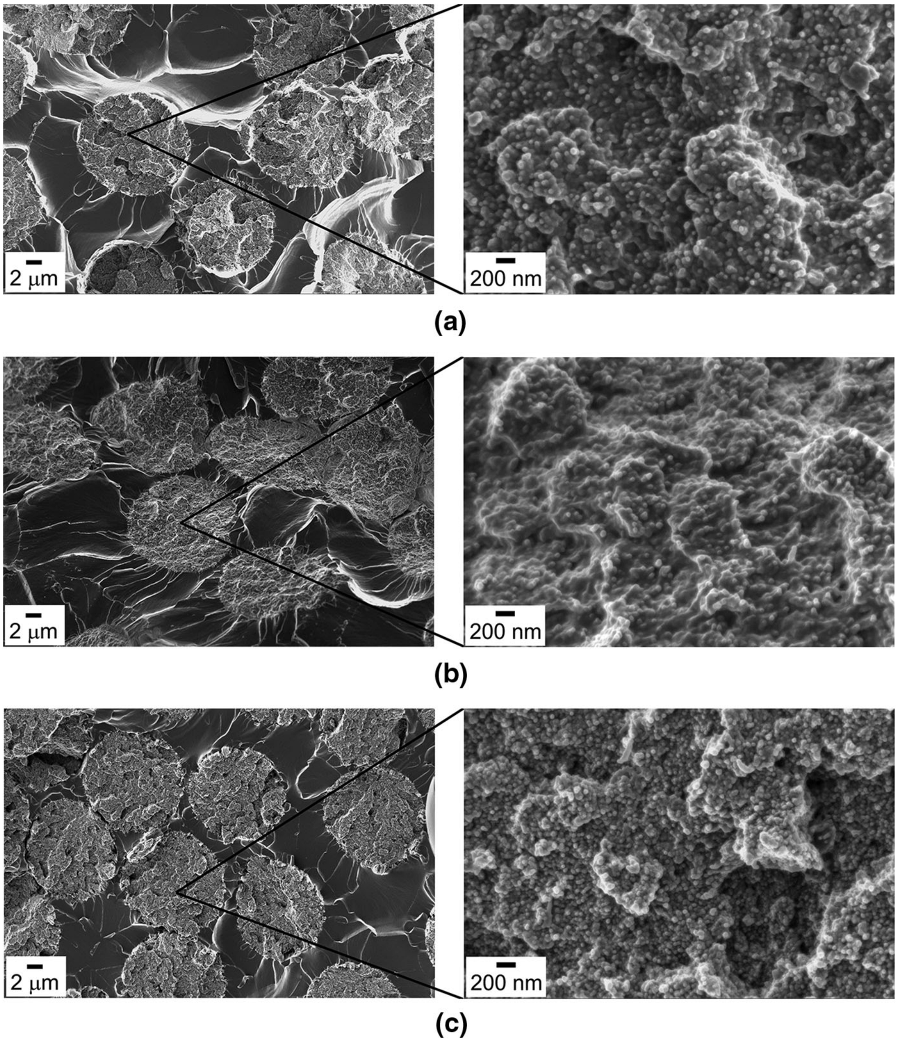


Fig. 12 Cross-sectional FESEM images of fibres **a** Reference fibre regenerated into 20 % H_2SO_4, **b** 10/90 mixture fibre regenerated into 10 % H_2SO_4/10 % Na_2SO_4 and **c** 25/75 mixture fibre regenerated into 20 % H_2SO_4

indicates that by controlling the spinning parameters it is possible to produce fibres with acceptable mechanical properties from the dopes containing 3-allyloxy-2-hydroxypropyl substituents.

The fibres spun into 20 % sulphuric acid were further studied by measuring their water holding ability. The increased share of the APH pulp in the spin dope increased the swelling coefficient value as well (Fig. 9). This is most likely due to the loosen structure of the fibres induced by the 3-allyloxy-2-hydroxypropyl side chains (Klemm et al. 2005).

The selected regenerated fibres, as well as, the reference and AHP pulps were further studied by FTIR. Shape of the large band around 3100–3500 cm^{-1} (–OH stretching of the intramolecular hydrogen bonds) and of the sharp band around 1000 cm^{-1} (C–O stretching) in the FTIR-spectra (Fig. 10a, b) show that the etherification of the enzyme-treated dissolving pulp did not change the cellulose crystalline form from the cellulose I (Carillo et al. 2004). Instead, the both regenerated fibres (Fig. 10c, d) have the cellulose II crystalline form, as expected. The vibrations of the C=C bond at 1570 cm^{-1} (Qi et al. 2012) could not be found from the FTIR spectra of the samples containing the 3-allyloxy-2-hydroxypropyl substituents. This is most likely due to their small amounts.

The surface and cross-sectional structures of the selected fibres were studied with FESEM. The surface of the fibre containing 25 % share of the AHP cellulose (Fig. 11c) shows similar kind of pattern with localized indentations as the reference fibre (Fig. 11a). Instead, the fibre containing 10 % share of the AHP cellulose and regenerated into the 10 % sulphuric acid spin bath (Fig. 11b) does not have such transversal bands, but the pattern is organised longitudinally. The spinneret draw ratio of the studied fibres was the same (0.62) and the stretching ratio of the reference and the 10/90 mixture fibre was also the same (1.32). Thus, the stripes on the surface of the fibre are suggested to be due to the 3-allyloxy-2-hydroxypropyl substituents in the dope which slowed down the coagulation of the dope. The shape of the cross section of each fibre is roundish (Fig. 12). The inner structure of the fibres is clearly formed from the fibrils whose ends are seen in the cross sections. It seems that the 25/75 mixture fibre (Fig. 12c) has smaller fibrils than the reference (Fig. 12 a) and the 10/90 mixture fibre (Fig. 12b). It also seems that the fibrils form bundles that are rather visible on the cross sections of the reference and of the 25/75 mixture fibres.

Conclusions

The enzyme-treated pulp was substituted with ethyl glycidyl ether under the heterogeneous conditions to obtain the 3-allyloxy-2-hydroxypropyl substituted (AHP) pulp with DS 0.05. Despite the rather low degree of substitution, the AHP pulp dissolved better into sodium zincate than the same pulp without the substituents. It was confirmed that the better dissolution was not due to the decreased average degree of polymerisation of the AHP cellulose. The fibres were successfully wet spun from the dopes containing either 10 or 25 % of the AHP pulp. The presence of the AHP groups slowed down the coagulation of the dope in the acidic bath, which made it necessary to slow down the spinning speeds. The 10/90 mixture dope was coagulated both in the 10 % and in the 20 % sulphuric acid baths, whereas the 25/75 mixture dope was coagulated only in the 20 % sulphuric acid bath. The tenacity of the fibres ranged from 1 to 1.5 cN dtex^{-1} and the elongation from 18 to 26 %. Rather similar maximum tenacity was achieved for the each types of the fibres. This proves that it is possible to adjust the spinning parameters such as the regeneration of the dopes containing the 3-allyloxy-2-hydroxypropyl substituents produces fibres with acceptable mechanical properties.

The increased share of the substituted cellulose increased the water holding ability of the fibres. This is suggested to be due to the loosen structure of the fibres induced by the 3-allyloxy-2-hydroxypropyl side chains. According to the FESEM studies the cross sections of the fibres are roundish, and the inner structures of the fibres are formed from the nanosized fibrils.

In this work we demonstrated the unique way to incorporate the 3-allyloxy-2-hydroxypropyl substituents in the regenerated cellulosic fibres. The substituents are expected to have the reactive C=C double bonds, which makes it possible to further attach functional groups to the fibres. In the next phase, we intend to study the functionalisation of the fibres, and the properties of the thus obtained fibres.

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