Rheological study of cellulose dissolved in aqueous ZnCl$_2$

- Regenerated cellulosic fibers for textile applications

Reologisk undersökning av cellulosa upplöst i vattenhaltig ZnCl$_2$
- Regenererad cellulosa för textilapplikationer

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ABSTRACT

The most known regenerated cellulosic fiber is viscose, produced in a wet spinning process, but due to cost and environmental issues other processes has been developed. Lyocell fibers, produced in air-gap spinning, have superior dry and wet strength and a lower environmental impact compared to viscose. Research in different cellulose solvent has increased significantly the last decades, due to an increased cotton price and a decreased paper production, providing more wood pulp to production of regenerated cellulosic fibers.

Inorganic molten salt hydrates, have the ability of dissolving cellulose for production of textile fibers. Aqueous zinc chloride was investigated at Swerea IVF from dissolution of cellulose to fiber spinning.

Aqueous zinc chloride has a dissolving capacity of up to at least 13.5 % cellulose, possibly much higher. Dissolving concentration ZnCl₂/water range from 65-76% and lowest possible ZnCl₂ concentration increases as the cellulose concentration increases. Above around 68 % ZnCl₂ results in a significantly increased viscosity due to a polymeric structure formed by zinc chloride, creating a network of cellulose-zinc chloride complexes and causing a gel behavior of the dope difficult to use in spinning processes. The dissolving capacity of 68 % ZnCl₂ is only about 8 % cellulose, which is very low compared to other solvents used today e.g. Lyocell and ILs.

Additions of 0.3 % CaCl₂ or 0.05-0.1 % NaOH is used to decrease degradation of cellulose. The addition causes an increased viscosity, which either is a result of less degradation or the interaction of the added molecules to zinc-cellulose complexes. Addition of NaOH results in a temperature dependent gelation at increased temperatures (75°C and 80°C), which also might be an effect of the interaction.

Highest tensile strength was reached for wet spun fibers coagulated in ethanol of 9.5 % cellulose with 0.1 % NaOH addition, with tenacity of 13-15 cN/tex, elongation of 10-12 % and wet strength 30% of dry strength. Because of many disadvantages of zinc chloride as a solvent, e.g. degradation of cellulose, corrosivity and the high viscosity and gel behavior at cellulose concentrations of 9.5 % and 13.5 % cellulose, a future possibility of a conventional production of textile fibers appears to be quite limited.
SAMMANFATTNING

Den mest kända regenererade cellulosafibern är viskos, producerad i en våtspinningsprocess, men på grund av kostnads- och miljöproblem har andra processer utvecklats. Lyocell-fibrer, producerade i ”air-gap”-spinning, har överlägsen torr- och våtstyrka och en lägre miljöpåverkan än viskos. Forskning av olika cellulosa lösningsmedel har ökat betydligt de senaste årtiondena, på grund av ett ökat pris på bomull och en minskad pappersproduktion, vilket ger mer trämassa tillgängligt för produktion av regenererade cellulosafibrer.

Oorganiska smälta saltshydrater har förmåga att lösa upp cellulosa för produktion av textilfibrer. Vattenhaltig zinkklorid undersökes på Swerea IVF från upplösning av cellulosa till fiberspinning.

Vattenhaltig zinkklorid har en upplösningskapacitet av minst 13.5 % cellulosa, möjlichen mycket högre. Koncentration ZnCl₂/vatten för upplösning sträckte sig från 65-76% och lägsta möjliga zinkkloridkonzentration ökade vid högre koncentration av cellulosa. Över ungefär 68 % ZnCl₂ resulterar i en stor ökning av viskositet p.g.a. en polymerisk struktur formad av zinkkloriden. Strukturen underlättar formationen av ett nätverk av zinkklorid-cellulosakomplex och skapar hög-viskös gel, vilket är svårt att använda i en spinningsprocess. Upplösningskapaciteten av 68 % ZnCl₂ är bara runt 8 % cellulosa, vilket är väldigt lågt i jämförelse med vissa andra lösningsmedel som används idag, t.ex. Lyocell och joniska vätskor.

Tillsats av 0.3 % CaCl₂ eller 0.05-0.1 % NaOH används för att sänka nedbrytning av cellulosa eftersom ZnCl₂ är ett surt salt. Tillsatsen ökar viskositeten, vilket antingen kan bero på en minskad nedbrytning eller en interaktion mellan de tillsatta molekylerna och zinkklorid-cellulosakomplex. Tillsats av NaOH resulterar i en temperaturberoende gelning vid höga temperaturer (75°C and 80°C), vilket också kan vara en effekt av interaktionen.

Högsta uppnådda dragstyrka erhölls för fibrer våtspunna och koagulerade i etanol av 9.5 % cellulosa med 0.1 % NaOH tillsats, med dragstyrka på 13.15 cN/tex, elongation på 10-12 % och våtstyrka på 30 % av torrstyrka. På grund av många nackdelar med zinkklorid som lösningsmedel, t.ex. nedbrytning av cellulosan, korrosivitet och den höga viskositeten och gel-beteendet vid cellulosakoncentrationer på 9.5 % och 13.5 %, så ser framtida möjligheter för en konventionell produktion av textilfibrer ut att vara ganska små.
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1. INTRODUCTION

1.1 About Swerea IVF

This laboratory work was executed at the textile and polymer division of the research institute Swerea IVF in Gothenburg. During the last couple of years, they have investigated several cellulose solvents for wet spinning and air-gap spinning. To increase their knowledge in different solvents for production of textile fiber, the inorganic molten salt hydrate ZnCl$_2$ was studied in this work.

1.2 Categorizing and accessibility of textile fiber

Textile fibers can be divided into two main categories; natural or man-made fibers, see Figure 1. Man-man fibers consist of both oil-based fibers and cellulose-based fibers (1). Regenerated cellulose fibers will be described further in Section 2.2.

![Textile fibers divided into subgroups depending on origin and production method.](image)

Regenerated cellulose fibers have a great advantage compared to ordinary cotton fibers in an environmental aspect. Ordinary cotton needs large arable lands to grow and uses pesticides and fertilizers. As the population increases in the world, these arable lands will be needed for food production, limiting the cotton production as well as increasing the price of cotton fibers (2, 3). Also, during production of cotton fibers, a large amount of water is required, see Figure 2. For production of regenerated fibers, none of the above mentioned requirements are needed (2). Instead of cotton, wood and plants are used as base material, which is appropriate as the paper production is currently decreasing, leaving more wood pulp for production of regenerated cellulose fiber (4).
Figure 2. Average cotton price from year 2000-2012 (left) "A-index" - a proxy for the world price of cotton, data collected from (3). Amount of water required for production of different fibers (right), data collected from (2).
2. CELLULOSIC REGENERATED FIBERS

2.1 Cellulose

Cellulose is the most abundant renewable material on Earth and is generated in almost 700 billion tons annually. The biodegradable raw material has large potential in replacing fossil oil fibers and cotton fibers (5). Cellulose is found in plants, wood and cotton, containing 30%, 50% and 90% cellulose respectively. It is mainly used for paper production; around $10^8$ tons pulp annually, which only corresponds to a small fraction of all cellulose (6).

Cellulose is a polysaccharide with $\beta$ 1,4-anhydroglucose linkages, see Figure 3 (7). The cellulose chain consists of many glucose units (C$_6$H$_{12}$O$_5$) each having reactive sites C$_1$-C$_6$ and three hydroxyl groups at carbon atoms C$_2$, C$_3$ and C$_6$. Due to the twisted backbone of cellulose intramolecular and intermolecular hydrogen bonds can be formed (8). These bonds strengthen and order the chains into a crystalline structure. The OH-group forms a hydrogen bond to an oxygen atom either at one molecular chain (intramolecular) or as a linkage to an adjacent chain (intermolecular) (9), see Figure 4-5. The cellulose chain consists of both amorphous and crystalline regions, with chains often passing several regions of both types. This structure can affect the dissolving capacity of cellulose, as crystalline regions are more difficult to dissolve than amorphous (7).

When cellulose forms derivatives, a solvent reacts with one or more hydroxyl groups on the cellulose chain. The number of hydroxyl group on each glucose unit reacted with the solvent is described as the degree of substitution (DS). DS is detected through spectroscopy and can be a measurement of how effective the solvent is (8).

![Figure 3. Molecular structure of cellulose and its repeating glucose units.](image-url)
Figure 4. Intramolecular bonding between reactive sites a) OH3 to O5 and b) OH2 to O6.

Figure 5. Intermolecular bonding between reactive sites a) OH6 to O3 and b) O3 to OH6 according to the 180° rotated glucose units.

The length of a cellulose molecular chain differs depending on the cellulose source. It is measured by the number of anhydroglucose units and referred to as degree of polymerization (DP). DP of wood pulp is 300 to 1700 whereas DP of cotton and other plants can be 800 to 10,000 (9). When using wood as a source of cellulose for production of regenerated fibers, the raw material needs to be processed and purified, which will cause a decreased DP. DP of cellulose is also decreased when processed at temperature above 65°C. In terms of ability to dissolve cellulose and spin the solution into fibers, a cellulose with high DP is more difficult to dissolve, but relatively high DP is favored in the spinning process because it can produce high strength fibers. A great decrease in DP due to processing can lead to non-cohesive fibers (8).

Solvents with capability to dissolve cellulose are separated into two main groups, derivatizing and non-deriatizing, which in turn can be divided into subgroups of aqueous and non-aqueous solutions. If dissolution of cellulose occurs through reaction with cellulose hydroxyl groups to form an intermediate compound, e.g., cellulose xanthate in viscose process, the solvent is classified as derivatizing. A non-deriatizing solvent only creates a temporary interaction with cellulose molecules, e.g., Lyocell, leading to a less complicated dissolving process (10).
2.2 Fiber spinning processes

The possibility of dissolving cellulose and form cellulosic fibers was discovered around the 17th Century. Many different solvents have been investigated since, and research in the field has increased during the last decades. This section will describe some of the solvents available today.

2.2.1 Viscose process

The most famous regenerated cellulosic fiber, viscose, was introduced in 1891 and is still today the most used artificial fiber around the world. Viscose is manufactured through several steps to transform cellulose from wood pulp into textile fiber. Wood pulp is treated with dilute sodium hydroxide (NaOH) to enable swelling of cellulose, converting it into alkali cellulose. The alkali cellulose is reacted with carbon disulphide (CS₂) vapor to produce sodium cellulose xanthate and then dissolved in dilute NaOH to produce a spinnable dope. Filaments are extruded through a spinneret in a wet spinning process and coagulated in sulphuric acid (H₂SO₄) and salts (11).

Since the 1970's, production of viscose fiber has been reduced because of increased use of cheaper oil-based synthetic fibers. The viscose process is both expensive and polluting. The recovery of the toxic carbon disulphide vapor is only around 50% in the viscose process; the rest becomes waste chemicals that will damage the environment. As an objective to make more cost/performance effective and environmentally friendly fibers, new processes were investigated. Despite this, the viscose process still produces almost 3 million tons annually (12).

2.2.2 NMMO – Lyocell

In 1939 the first patent of cellulose dissolved in amine oxide was published. The new regenerated cellulose fiber named Lyocell (also called Tencel) is produced from wood pulp dissolved in N-methyl morpholine oxide (NMMO). The process has, unlike the viscose process, a possibility of recovering over 99% of the solvent for reuse and uses renewable raw material. Also, Lyocell enables cellulose to dissolve directly in an organic solvent, without creating the intermediate compound as in the viscose process. Lyocell has superior wet and dry strength to the previously produced fibers (11). The Lyocell process creates a high viscosity dope with cellulose concentration of 10-18% and must be held at a high temperature (80-130°C) to ensure a spinnable solution. Due to the high temperature process, the NMMO can reduce DP of cellulose, which is undesirable. It can also form colored oxidation and be explosive if temperature is not controlled (12). The dope is spun through an air gap before entering the coagulation bath to stretch and increase molecular orientation before regeneration, which increase strength of the fibers. Air gap-spinning processes allow a greater cellulose
concentration, but also require a more homogenous dope with no undissolved particles or air bubbles, along with difficulty of fibers sticking together (11).

Lyocell is primarily spun into yarn and used as textile fiber, but it has great potential in other areas as nonwovens (e.g. wipes or filters) and paper production. Defibrillation behavior of Lyocell is negative for fiber production, but positive in nonwovens and paper production (9). Fibrillation of the fibers is created during wet treatment, where fibrils are partially removed from the fibers and enable contact with neighboring fibers creating hydrogen bonds throughout the structure (11).

2.2.3 Ionic Liquids

A lot of research has been done lately in the area of ionic liquids (ILs), which is seen as an environmentally friendly solvent for cellulose. It is a direct solvent, like Lyocell, and does not create any intermediate compound as viscose (9). There is still some challenges to overcome; increase the dissolution efficiency and recoverability of ILs. ILs are salts with low melting point (<100°C) and have useful properties as high thermal and chemical stability, no flammability and great solubility with organic compounds. Examples of ILs are imidazolium based BMIMCl and EMIMAc. Solubility of cellulose in BMIMCl has been measured up to 14.5% and in EMIMAc up to 20% (12, 9). Ionic Liquids can, due to their high viscosity, be spun in an air-gap spinning process similar to Lyocell (13).

2.2.4 Inorganic molten salt hydrates – Zinc chloride (ZnCl₂)

Next group of direct solvents can dissolve cellulose without pretreatment or activation and have high acidity levels. It is a liquid with a molar water-salt ratio close to the coordination number of the strongest hydrated ion, i.e. the number of closely bonded atoms to each centered ion (14). Molten salt hydrates can be classified into four groups depending on their effect on cellulose; dissolve, swell, decompose or show no effect on cellulose. Factors affecting the dissolving capacity of salt hydrates are the acidity, the water concentration and the properties of the coordination sphere of the cations in the melt (15). Examples of molten salt hydrates are ZnCl₂, LiClO₄, Zn(NO₃)₄ and FeCl₃, all mixed with a certain amount or a range of water content. Dissolving 2-3 % cellulose in different molten salt hydrates, ZnCl₂ showed higher crystallinity than LiClO₄, but a lower viscosity than the other salt hydrates tested (14). The reduction of DP was slightly higher in ZnCl₂ than in LiClO₄, which did not show any reduction at all compared to pure cellulose (15).
2.2.4.1 Aqueous zinc chloride

Zinc chloride is non-toxic and easy recoverable for reuse in a cellulose dissolving process. It is corrosive, which puts high demands on the equipment used (16). Zinc chloride is highly soluble in water and must be held in a dry environment otherwise it can attract water molecules from the surrounding air. It is found that cellulose dissolves in aqueous zinc chloride (65-76 % ZnCl₂, 35-24 % water w/w) without any pretreatment or activation, but if the water concentration is above or below this molar concentration, only swelling occurs (17). Density of zinc chloride is 2.907 g/cm³ compared to water 1 g/cm³. Therefore, a 500g mix of ZnCl₂*4H₂O result in only 287ml, see Figure 6.

![Figure 6](image)

**Figure 6.** Highly dense ZnCl₂/water mix. 500g equals only 287ml. (175g water, 325g ZnCl₂)

The first spinning trials of cellulose dissolved in ZnCl₂ led to weak non-cohesive fibers, only possible to be extruded into a coagulation bath but not spun into fibers. In a patent from 1991, fibers were spun from a zinc chloride/cellulose solution in a wet spinning process with water and alcohol as a coagulation bath, using microcrystalline cellulose with DP of 100-300 (16). More recent trials with cellulose dissolved in ZnCl₂ can be found in literature. Wet spun fibers from 8.5% cellulose have reached a tensile strength of around 15 cN/tex and elongation of 15-20% and elastic modulus of 450-1100 cN/tex (linear density of filaments: 3,6-11 dtex) (17). Pre-wetting of cellulose has been found to increase the effectiveness of the dissolving capacity, either with water or with >79% ZnCl₂ slowly adding water until a dissolving concentration is reached (16, 17).

Concentration below 65% ZnCl₂ is less effective due to the water molecules competing with the hydroxyl groups in cellulose to create interactions with zinc chloride. At low concentrations of ZnCl₂, the reactive sites are saturated with water and can therefore not dissolve, but only swell cellulose (18). For increased concentrations of cellulose, also requiring increased concentration of zinc chloride, it is also more difficult to get a homogenous solution. Molecule chain
entanglement and higher viscosity of the solution makes it harder for the solvent to be evenly distributed and therefore, the dissolving capacity can be different at different places in the solution (19).

When the concentration of ZnCl₂ increases in the solution, it becomes more viscous and gelled. This might be due to a polymeric structure formed by ZnCl₂, which can interact with the cellulose chain through hydrogen bonding and cause a more stable zinc-cellulose complex (20). As more water is added to zinc chloride, lowering the concentration, the water molecules can substitute some chlorides leading to a decreased size of the ZnCl₂ polymeric structure. This will in turn lead to fewer possibilities to interact with cellulose molecules resulting in a less viscous solution. It is showed that elevated temperature can rupture the ZnCl₂ polymeric structure. Trials with only 3 % cellulose has shown that zinc chloride concentration of 74% compared to 64% exhibit a significantly higher difference in viscosity from 65°C to room temperature. This behavior is explained by an increased interaction at higher concentrations of zinc chloride existing at lower temperatures, but ruptured at higher temperatures (20).

Dissolving cellulose in zinc chloride is found to be most effective at 60-80°C. Wet spinning has been preferred prior to air-gap spinning due to non-uniform fibers in air-gap trials (16,17). After coagulation, zinc is still present (around 15% w/w) which allow stretch before washing the fibers in water to eliminate the zinc content. When allowing stretch prior to crystallization, molecule orientation is increased and inter-molecular hydrogen bond is formed, causing an increased tensile strength (21).

Zinc chloride among other metal salts has been found to effectively degrade cellulose, a negative effect for fiber spinning but positive for biomass-use for fuels. A cellulose-zinc chloride solution used for fiber spinning should not be processed at 70-80°C more than 3h, otherwise it starts degrading (17). At 200°C, cellulose becomes significantly degrading after only 150 s. The proposed degradation mechanism for cellulose treated with zinc chloride is that ZnCl₂ will affect the oxygen atom holding two glucose units together. The oxygen-zinc coordination will lower the activation energy needed for further breakdown of cellulose into D-glucose used for fuel (22), see Figure 7.
Additions of substances of neutral salts e.g. CaCl₂ (0.2-0.5 % of ZnCl₂ weight) have been found to decrease the degrading effect of cellulose dissolved in zinc chloride (17). The addition of CaCl₂ can increase the viscosity of the solution. A theory explaining this behavior is that a more rod-like and rigid structure might be formed in the zinc-cellulose complex (23).
3. PROJECT DESCRIPTION

This master thesis is a rheological study of cellulose dissolved in aqueous zinc chloride. This includes dissolving trials with variation of cellulose concentration, ZnCl$_2$/H$_2$O concentrations and additives. The trials were characterized and evaluated using e.g. rheology measurement, polarizing light microscope and tensile measurement of spun filaments.

3.1 Aim of study

- Define a method for dissolving cellulose in ZnCl$_2$ aqueous solution and determine rheology for different cellulose concentrations.
- Investigate how additives can affect rheology of ZnCl$_2$/cellulose-solutions.
- Study how rheology affects the spinnability of solutions and fiber properties obtained.
4. EXPERIMENTAL PART

In this section, the laboratory work is described from dissolution of cellulose to fiber forming methods and characterization of structure and properties. In addition to this section, more detailed descriptions of the laboratory work are available in Appendix 1-3.

4.1 Dissolution of cellulose

Dissolution of cellulose, dependent on the particular solution used and the laboratory equipment at Swerea IVF, is explained in the following section. The laboratory equipment used is specified in each section.

4.1.1 Preparing cellulose dope

Forming a liquid that will dissolve cellulose, zinc chloride and water was mixed at a concentration of 65/35% weigh to weight (molar ratio of ZnCl₂*4H₂O), according to previous literature. Zinc chloride was added slowly to the water to avoid a too heavy exothermic reaction and blending continues until the white zinc chloride powder is no longer visible.

To investigate solubility of possible additives, 1% of CaCl₂, NaOH, CaO and ZnO respectively, were added to four 50 g samples of the zinc chloride solution by using magnetic blender and heat when required.

The cellulose used for dissolution was Buckeye dissolving pulp, with a cellulose purity of 99 % and DP of 775 (viscosity of 534). Swelling of cellulose was done by placing the cellulose sheet in large amount of water, separating the structure by hands and with a mixer, see Figure 8. Water was removed by squeezing the cellulose pulp by hand to approximately 30% cellulose content and some residual water. The exact water content in the squeezed cellulose was determined by placing a sample in a vacuum oven 2h at 100°C removing all water, weighing before and after.

![Figure 8. Process of swelling cellulose a) A cellulose sheet was separated into pieces. b) Cellulose pieces were wetted with a large amount of water and mixed. c) Excess water was removed by the swelled cellulose was stored in sealed bag in refrigerator.](image-url)
Aqueous zinc chloride was added to swelled cellulose and blended in a cup. In this step, an extra amount of water was always present due to water content of around 70% in swelled cellulose. The extra water decreases the concentration of zinc chloride (lower than 65%), acting only as swelling agent but not dissolving cellulose. During this swelling, zinc chloride can be homogenously distributed in the cellulose pulp to allow equally strong reaction at all areas when enough water is evaporated.

4.1.2 Kneading of cellulose dope

Kneader used in this work was a Coperion kneading machine LUK 20515813. The cellulose dope was placed in a kneader for intensive mixing with the ability of changing temperature and using vacuum to remove air bubbles. The excess water in the dope was also removed with vacuum as the temperature increases above room temperature (RT). The vacuum pump used, Mini laboratory pump VP86 Type PM20405-86, had an ultimate vacuum of 100mbar to enable kneading at elevated temperatures. Higher vacuum pressure (1000mbar) evaporates water too fast already at 55°C resulting in a high ZnCl₂/water concentration of >80-90% after only a few minutes, giving no time for dissolution. The evaporation of water was controlled afterwards by placing a small sample of the kneaded dope in a vacuum oven at 100°C over night, weighing before and after, see Figure 9. Vacuum oven used was Gallenkamp SG97/09/555.

![Figure 9. a) Dissolved sample of zinc chloride/water-cellulose before vacuum oven and b) sample dried in vacuum oven, only containing zinc chloride and cellulose/sugar.](image)

To measure the amount of evaporated water during kneading, measuring glasses were connected to the outlet of the vacuum pump. Each glass was filled with a starting level of water and a layer of paraffin oil on top of the water, measuring the evaporated water as it cools down and increases the level in the glass, see Figure 10.
As the measured evaporated water did not completely correspond to the actual amount controlled afterwards in the vacuum oven (only 80-90% accurate), the method was developed by adding a short evaporation in vacuum oven prior to kneading. The dope was spread out on a large sheet and placed in the vacuum oven, weighing before and after. By several trials optimal temperature/time dependence was formed for a certain amount of cellulose dope. When placing the dope in the kneader, the concentration of ZnCl₂ was known and with only a few milliliter of water evaporating in the kneader, the measure glasses gave more accurate results. The dope was kneaded until a thinner, more transparent structure was formed, after approximately 60-200min depending on % cellulose and size of batch. A sign of dissolved cellulose was that long treads could be formed when slowly drawing parts of the dope with a spoon, see Figure 11.

Figure 10. a) Cellulose/aqueous zinc chloride mix. b) Kneader used for dissolving cellulose c) vacuum pump and glasses to measure water evaporation. d) Measuring glass with a layer of paraffin oil for more accurate measurement.

Figure 11. Dissolving 9.5 % cellulose in kneader a) Start of kneading after vacuum oven b) 50min c) 75min d) 90min e) 90min, tread forming.
4.2 Structure and property characterization

When the kneaded cellulose solution formed the more transparent structure, it was investigated using laboratory equipment listed below.

4.2.1 Microscopy

Light microscope used was Nikon SMZ1500. To determine if the cellulose fibers are dissolved or not, a small sample from the kneader was pressed between two thin glasses with approximate size of 1 cm$^2$. The sample was placed in a light microscope and by using polarizing glasses where the crystalline particles like cellulose fibers showed as light particles on the screen. When no cellulose fibers were longer visible, the cellulose was dissolved, see Figure 12. Several stops in the kneading process were made to control if the cellulose was dissolved or not. All microscope images in this work are shown in 10x zoom.

![Figure 12. a) Light microscope b) Sample between two polarizing glasses c) Undissolved sample and d) Almost completely dissolved sample.](image)

4.2.2 Rheology

Rheology measurement was made to characterize the dissolved dope before continuing to fiber forming processes. Each rheology measurement could be compared to previous ones to determine e.g. if the sample was degraded and how different cellulose/additives concentration affected the dope. A Bohlin rheometer BR CSM 01:01 was used in this work.

For non-Newtonian materials, viscosity cannot be defined as a single value, but depends on parameters e.g. temperature and shear rate, possible to map by rheology measurements. When dissolved cellulose dope was achieved, a small sample was placed on a fixed flat circular plate and an upper rotational conic circular plate was pressed down into the sample, see Figure 13.
Two types of measurement were done, oscillation and stress viscometry. The oscillation rheology determines viscosity, loss modulus and elastic modulus. As shown in Figure 14, L is the vertical length between the upper and lower plate and δ is the circular movement of the upper plate back and forth. Shear, δ, of the upper plate is determined as a function of the calibrated length L from a fixed value of 0.01. Shear value equals δ/L=0.01.

Pre-determined frequencies of 30-0.01 Hz was run from high – low – high corresponding to fast movement at high frequencies and slow movement at low frequencies, always the same shear distance, and response of the cellulose dope is recorded. Depending on the dominating modulus, the dope is either more liquid-like (loss modulus) or gel-like (elastic modulus) alternatively a cross over corresponding to a sol-gel transition can be seen at certain frequencies and temperatures. A dominating loss modulus, corresponding to a solution, is favorable in a spinning process because of easier conformation of dope and greater ability of stretching fibers without breakage.

![Figure 14. Shear of dope in a rheology measurement.](image)

Stress viscometry register shear rate of the material as a function of applied shear stress. The upper plate turns with selected applied forces and the response of the material is recorded. The viscosity was plotted as a function of shear stress and the slope of the curve was determined to compare different cellulose solutions, where a steeper slope is more difficult to spin into fibers.
4.3 Fiber formation

When a successful dissolution of cellulose was reached according to previous steps, the cellulose dope was ready to be formed into fibers. Two different methods were used in this work: extrusion in a capillary rheometer and spinning (wet and air gap). The rheology extrusion was used as a trial method to control if the dope was fiber forming in coagulation baths as well as the appropriate extrusion speed and temperature. After extrusion in the capillary rheometer, next step was to set up the spinning equipment. Set up of spinneret is presented in Appendix 2.

4.3.1 Capillary rheometer extrusion

A less complicated method to form fibers than the spinning processes was to extrude fibers by using a Bohlin Rheoscope 1000. Instead of the ordinary setup of the capillary rheometer, where a polymer is extruded through one small hole in a circular plate, a spinneret was attached to the lower part of the extruder, making it possible for many thin filaments to be extruded. Cellulose dope was placed in a valve with regulated temperature, pushed though the spinneret and the extruded fibers fell down into a cup filled with ethanol or water as a coagulation bath. Because the fibers were not stretched in this method, they did not gain any specific strength. Mainly, this extrusion gave information of which solutions that was able to form cohesive fibers. After coagulation, the fibers were washed out from zinc chloride and dried. A sketch and photo of the extrusion are shown in Figure 15. Varying parameters are presented in Table 1.

Table 1. Varying parameters in capillary rheometer extrusions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulation bath</td>
<td>Ethanol/Water</td>
</tr>
<tr>
<td>Distance: spinneret to coagulant</td>
<td>0 = wet spinning/ 1-10cm = air-gap</td>
</tr>
<tr>
<td>Temperature of dope/spinneret</td>
<td>40-80°C/25-60°C</td>
</tr>
<tr>
<td>Spinneret (number of holes x size f holes)</td>
<td>80 x 100µm, 31 x 150µm</td>
</tr>
</tbody>
</table>
4.3.2 Wet spinning and air-gap spinning

The dissolved cellulose dope was filtered prior to spinning to remove undissolved particles. The dope was then carefully placed in a cylinder for spinning, avoiding air bubbles being captured and ruin the fiber formation during extrusion. The metal pipe was placed upside down above the extruder using applied pressure from a pump to force the dope down into the spinneret at a defined flow rate. A glass pipe was vertically connected to the spinneret and the lower part of the glass pipe was submerged in a coagulation bath. Using a manual air pump, the bath level was increased in the pipe to desired level. In this way, the level of the coagulation bath could create either wet spinning or air-gap spinning using the same experimental setup. The dope was pressed through the capillaries forming thin threads leaving the spinneret either immediately down into the coagulation bath or through an air-gap of 1-3cm before entering the coagulation bath. The fibers fell continuously, due to gravity, down through the glass pipe and were collected at the end of the pipe. To increase the strength of fibers, they were drawn onto one or two rolls, circulating at a speed corresponding to the flow rate of the extrusion. Before the second roll, the fibers were drawn through an additional warm bath for washing and stretching. Bundles of fibers were collected from the first alternatively from the second collective roll for washing. A sketch of spinning line and a photo from the first part of the spinning line is shown in Figure 16. The varying parameters in the spinning trials are presented in Table 2. Spinning equipment used in this work is not specified.

Figure 16. Spinning line and a sketch of the spinning line enabling both wet spinning and air-gap spinning. (1) Cylinder with dope. (2) Spinneret. (3) Coagulation bath. (4) First collective roll. (5) Hot water bath for additional stretching and washing of fibers. (6) Second collective roll.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulation bath</td>
<td>Ethanol/Water</td>
</tr>
<tr>
<td>Distance: spinneret to coagulant</td>
<td>0 = wet spinning/ 1-3 cm = air-gap</td>
</tr>
<tr>
<td>Stretch 1st to 2nd collective roll</td>
<td>60-120%</td>
</tr>
<tr>
<td>Spinneret (number of holes x size f holes)</td>
<td>150 x ø80μm, 80 x ø100μm, 31 x ø150μm</td>
</tr>
</tbody>
</table>
4.3.3 Washing and drying of fibers

The collected fibers from the spinning line were washed for 3h, changing water 3 times. Some fiber bundles were stretched during washing, others were not, see Figure 17.

![Figure 17. a) 30cm long fiber bundles washed in water for 3h b) fibers drying while hanging vertically to avoid shrinkage.](image)

The washed fibers were then dried for 4 days at 24°C, while stretched. To investigate how drying affects the fiber properties, all bundles were split in half. One half was dried in an oven at 100°C for 1h, while the other half of all bundles were left in room temperature.

4.3.3 Fiber measurement

Tensile tests were performed by using a Lezing Technic Vibroscope 427 and Vibrodyn 369. From each bundle of filament, 10-20 tests were performed to ensure the quality of the result. The tensile test provides information of tenacity (cN/tex), elongation (%) and young’s modulus (cN/tex) The tensile test was based on the linear mass density of each filament. The linear mass density was measured by attaching a clamp of 500-3000mg at the end of each filament and by an applied frequency investigate its oscillation. It is measured in dtex (decitex) and corresponds to mass in grams per 10,000 meters.

![Figure 18 a) Tensile test and linear density measurement b) Tensile test of single filament c) Linear density of single filament.](image)
5. RESULT

The result is divided into five parts: dissolution method, additives, rheology, fiber formation and fiber characterization.

5.1. Dissolution method

Evaporation of water in vacuum oven (70-80°C in dope) and approximate kneading time for kneading speed of 75rpm (75°C of dope) until the dope was dissolved is presented in Table 3.

Table 3. Dissolving time for 13.5, 9.5, 8 and 7% cellulose and the lowest zinc chloride concentration for dissolution. *Dope separated into two halves, placed one at a time in vacuum oven, for a more efficient evaporation.

<table>
<thead>
<tr>
<th>Cell</th>
<th>ZnCl₂/H₂O</th>
<th>Dissolution time for capillary rheometer batch (14g cell)</th>
<th>Dissolution time for spinning batch (28g cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oven</td>
<td>Kneader</td>
</tr>
<tr>
<td>13.5%</td>
<td>74-76%</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>9.5%</td>
<td>69-70%</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>8%</td>
<td>67-68%</td>
<td>45</td>
<td>90</td>
</tr>
<tr>
<td>7%</td>
<td>65-66%</td>
<td>45</td>
<td>90</td>
</tr>
</tbody>
</table>

As the total time heated (oven + kneader) of the spinning dope is over 3h, the cellulose will be degraded. Additives with ability to lower the degradation are presented in Section 5.2 and their effects on the cellulose dope are investigated in different rheology measurements in Section 5.3. Most rheology measurements are made from capillary rheometer batches with the shorter dissolving time.

Cellulose dope of 13.5 % cellulose results in a highly viscous gel. At 9.5 % the structure is more honey-like but still very viscous, see Figure 19. At 7 and 8 % cellulose the dope the viscosity is lowered even more and is easier to dissolve and process.

![Figure 19. Cellulose dope of a) 13.5 % cellulose, 76 % ZnCl₂ and b) 9.5 % cellulose, 69 % ZnCl₂.](attachment:figure19.png)
Temperature dependence of dissolution shows that dissolving capacity is very limited at 35°C, but very effective at 75°C, see Figure 20. Time dependence of dissolution at 75°C is showed in Figure 21.

![Figure 20](image1.png)

**Figure 20.** Temperature dependence of dissolving cellulose, no pre-heating. a) 90min at 35°C b) 120min at 35°C c) 40min at 75°C d) 75min at 75°C.

![Figure 21](image2.png)

**Figure 21.** Dissolving 9.5 % cellulose with 0.1 % NaOH additive at 75°C after a) 25min b) 55min c) 80min and d) 90min.

_Dissolution method:_ The lowest possible zinc chloride concentration for dissolution increases with increased cellulose concentration, ranging from 65-76%. As the cellulose concentration increases, up to 13.5 %, the dope becomes more and more viscous. Dissolution is effective at 75°C and the dissolution time increases with increasing cellulose concentration.
5.2. Additives

Solubility of additives in an aqueous ZnCl₂ solution is presented in Table 4. CaCl₂ and NaOH were further used as additives to aqueous zinc chloride for cellulose dissolution.

Table 4. Solubility of additives in aqueous zinc chloride solution. Specified for each additive if it was further used in cellulose dissolution or not: ✓ = YES ✗ = NO

<table>
<thead>
<tr>
<th>Additive</th>
<th>Addition % of ZnCl₂·H₂O</th>
<th>Temp. (°C)</th>
<th>Comment</th>
<th>OK to use</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>&gt; 1 %</td>
<td>25</td>
<td>Easily dissolved at room temperature.</td>
<td>✓</td>
</tr>
<tr>
<td>NaOH</td>
<td>&gt; 1 %</td>
<td>50-100</td>
<td>White liquid-like precipitations. Required temperatures above 50°C to dissolve.</td>
<td>✓</td>
</tr>
<tr>
<td>CaO</td>
<td>&lt; 0.5 %</td>
<td>&gt;100</td>
<td>Turbid mix. Required temperatures above 100°C, dissolved very slowly and became saturated after 0.5% addition.</td>
<td>✗</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;0.08%</td>
<td>100</td>
<td>White crystal-like precipitations. Required temperatures around 100°C, but became saturated after 0.08% addition.</td>
<td>✗</td>
</tr>
</tbody>
</table>

13.5 % cellulose was dissolved in aqueous zinc chloride with addition of CaCl₂ and NaOH up to 1% of the ZnCl₂ weight respectively. Additions of 1% of CaCl₂ and 0.3-1 % NaOH led to a very gelled, hard dope challenging for the kneader to process. The dissolving capacity was also difficult to examine in microscopy due to the gelled and hard structure, see Figure 22. The addition was then lowered until a less gelled structured was formed, see Table 5.

Figure 22. Dissolving 13.5 % cellulose. a) 0.1 % NaOH, after pre-heating in oven prior to kneading b) 0.1 % NaOH, dissolved after 100min kneading at 75°C c) no addition, dissolved cellulose after 100min d) 1 % NaOH, not fully dissolved.
**Table 5.** Additives of CaCl$_2$ and NaOH at 13.5 % cellulose.

- $\times$ = Gelled and hard, ✓ = Dissolved, - = Not done.

<table>
<thead>
<tr>
<th>Addition</th>
<th>CaCl$_2$</th>
<th>NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 %</td>
<td>$\times$</td>
<td>$\times$</td>
</tr>
<tr>
<td>0.3 %</td>
<td>✓</td>
<td>$\times$</td>
</tr>
<tr>
<td>0.1 %</td>
<td>-</td>
<td>✓</td>
</tr>
<tr>
<td>0.05%</td>
<td>-</td>
<td>✓</td>
</tr>
</tbody>
</table>

*Additives:* Additions of 0.3 % CaCl$_2$ or 0.05-0.1 % is possible, higher additions leads to gelled and hard samples difficult to process.
5.3 Rheology

Rheology measurements in this section present how viscosity of a cellulose/zinc chloride solution depends on temperature, time, cellulose concentration and additives. As an effective temperature for dissolving cellulose with zinc chloride was found to be around 75°C, rheology measurements were performed from 60 to 80°C. The first oscillation measurement with 13.5 % cellulose without additive shows how viscosity depends on the temperature, the lowest temperature of 60°C giving the highest viscosity, see Figure 23. Viscosity decreases with frequency, typical shear thinning behavior. All rheology measurements are presented in logarithmic scales.

![Oscillation: 13.5% cell, temperature dependence](image)

**Figure 23.** Temperature dependence of 13.5 % cellulose, no additive. Highest viscosity at 60°C and lowest at 80°C. Kneaded for 2h, no pre-heating in oven.

Measurements above 100°C resulted in burned samples and measurements from 90-100°C did not differ from the temperature pattern of 60-80°C. Further measurement were therefore mainly performed at 60 and 80°C.

Complete oscillation diagrams show viscosity, total modulus $G^*$, elastic modulus $G'$ and loss modulus $G''$. Elastic modulus $G'$ dominates for all dope of 13.5 % and 9.5 % cellulose, with and without additives, at frequencies 0.01-30 Hz. (80°C and 60°C), indicating a gel structure instead of a solution. Mainly viscosity curves from the oscillation measurements is presented in this section, complete oscillation diagrams and stress viscometry diagrams are presented in Appendix 3.
5.3.1 Degrading effect at elevated temperatures

An aqueous zinc chloride/cellulose solution should not be processed at 70-80°C for more than a few hours, otherwise it becomes significantly degraded. To investigate the degrading effect, oscillation measurements were made after 2h and 4h of kneading at 75°C. Viscosity was significantly decreased after 4h (about 4.6 times at 60°C) and less temperature dependent, see Figure 24.

![Oscillation: 13.5% cell, time dependence, no additive](image)

*Figure 24. Kneading of 13.5 % cellulose at 75°C for 2h and 4h respectively, no pre-heating in vacuum oven.*

An early spinning trial with 13.5 % cellulose heated for 4h (due to non-efficient pre-heating), with similar viscosity as 4h showed in Figure 24, led to non-cohesive fibers due to severe degradation. This was therefore prevented by separate the larger spinning-batches in two during pre-heating to decrease the total time processed at elevated temperature. According to this result, viscosity was further used to approximate degradation of a dope, relatively to other dopes with similar cellulose content. To investigate how additives and cellulose concentration affect viscosity, the smaller capillary rheometer-batches was compared, with similar heating and kneading times.

5.3.2 Structure difference after rest in refrigerator

Dissolution of cellulose and spinning it into fibers is a time consuming process, therefore the ability to store the dissolved cellulose dope in refrigerator over night was studied. After storage, the cellulose dope had turned into a mealy/gel structure rather than the viscous solution from the day before. When reheating the dope at 50°C, the structure returned into a more viscous structure after a few seconds, see Figure 25. For dope of 8 % cellulose, the viscous structure returned even at RT when kneading it by hands.
To investigate how properties of the cellulose/zinc chloride dope change along with storage time, rheology measurements were made directly after dissolution and again after 15h at 5°C. Viscosity after storage was decreased (about 2.6 times at 60°C) compared to viscosity before storage, see Figure 26. The lowered viscosity is due to continued degrading of cellulose, even when stored at low temperature, because of the degrading effect caused by zinc chloride.

![Figure 25](image_url)

**Figure 25.** Dope of 9.5 % cell with 0.1 % NaOH addition. 15h at rest in 5°C (left) and after reheating at 50°C (right).

![Figure 26](image_url)

**Figure 26.** Difference in viscosity for 9.5% cell A) directly after kneading and B) after rest at 5°C for 15h.
5.3.2. Additives

Additions of CaCl₂ or NaOH result in higher viscosity than a sample without additive, NaOH giving the highest viscosity and but with difference between 60°C and 80°C. The difference at 9.5 % cellulose with NaOH is about 2.1 times, with CaCl₂ 3.2 times and without additive 4.3 times, see Figure 27.

![Figure 27](image1)

**Figure 27.** Differences between 0.1 % NaOH, 0.3 % CaCl₂ and no additive. All heated for 160 min including pre-heating and kneading.

Addition to 13.5 % cellulose resulted in less difference between the two temperatures for all additions, see Figure 28. Also, addition of 0.05-0.1 % NaOH did not differ much in viscosity and both had higher viscosity than addition of 0.3 % CaCl₂. Both 0.05 % and 0.1 % NaOH was further used.

![Figure 28](image2)

**Figure 28.** Differences with additions of 0.05 %-0.1 % NaOH and 0.3 % CaCl₂. All heated for 180 min including pre-heating and kneading.
5.3.4 Cellulose concentrations

The viscosity increases with increased cellulose concentration. At 13.5 % and 9.5 % cellulose oscillation measurement shows a gel behavior instead of a solution. But when cellulose concentration is lowered to 7 % the oscillation measurement shows that viscosity is lowered, the viscosity curve is flatter and loss modulus is dominating, corresponding to a solution. Most noticeable is the large gap in viscosity of 7 % to 9.5 %, see Figure 29, which is an indication that not only the cellulose concentration affects the viscosity.

![Oscillation: 0.3 % CaCl$_2$, cellulose concentration](image)

**Figure 29.** Difference in viscosity of different cellulose concentrations with addition of CaCl$_2$.

Also with addition of NaOH at different cellulose concentrations, the large gap can be seen, see Figure 30. Even comparing 8 % cellulose to 9.5 % results in a large difference in viscosity, indicating that not only the cellulose concentration affects the viscosity. Another phenomena seen only for addition of NaOH is the sudden increase in viscosity at 80°C compared to 60°C, particularly visible for the lower cellulose concentrations, e.g. 8 %. This is the opposite behavior of the previously measured viscosities, which is lowered with increased temperature.
Figure 30. Viscosity of different cellulose concentrations with addition of NaOH. Large gap between 8% cell and 9.5% cell at 60°C, but increased viscosity for 8% cellulose at 80°C due to temperature dependent gelation.

Complete oscillation graph shows that at 60°C loss modulus, $G''$, is dominating corresponding to a solution, similar to the behavior of CaCl$_2$ addition. But at 80°C, the elastic modulus, $G'$, is dominating corresponding to a gel behavior, see Figure 31. This indicates that a NaOH addition leads to a temperature dependent gelation at high temperatures, not seen for addition of CaCl$_2$ or without additive.

Figure 31. Complete oscillation graphs for 8% cellulose with addition of 0.05% NaOH. At 60°C (right) loss modulus $G''$ is dominating corresponding to a solution, while at 80°C elastic modulus is dominating corresponding to a gel behavior.
Closer examination at temperatures 80, 75, 70, 65, 60, 50, 40, and 30°C showed that the temperature dependence gelation starts between 70-75°C. From 60°C down to 30°C the cellulose dope is a solution. The same behavior can also clearly be seen in stress viscometry measurement, where 80 and 75°C result in slopes of about -1 corresponding to a gel structure, while 60 and 40°C results in a flatter curve corresponding to a solution, see Figure 32.

![Stress viscometry: 8 % cell 0.05 % NaOH](image)

**Figure 32.** Stress viscometry shows a gel behavior at 75 and 80°C, but a solution at 60°C and 40°C.

Rheology: Viscosity decreases with increased temperature but increases with increased cellulose concentration. Additives of CaCl₂ or NaOH result in a higher viscosity than without addition. NaOH addition gives the highest viscosity even though NaOH addition is lower than CaCl₂ addition. Both with and without additives at 9.5 and 13.5 % cellulose result in a gel structure rather than a solution, but at 7 and 8 % viscosity is lowered and results in a liquid-like solution. A large gap between viscosities of 7 and 8 % cellulose to 9.5 % cellulose indicates that not only the cellulose concentration affects the viscosity. Cellulose concentrations of 7 and 8 % with NaOH addition result in a temperature dependent gelation at 75 and 80°C, while it is a solution at temperatures at 70°C and lower.
5.4 Fiber formation

Fibers were formed either through capillary rheometer extrusion or spinning. The capillary rheometer extrusion trials gave information of appropriate temperature, extrusion speed and coagulation bath, as well as the ability of air-gap spinning compared to wet spinning. During spinning trials, the same parameters could be changed and also give fibers possible to measure tensile strength and elongation.

5.4.1 Capillary rheometer extrusion

Cellulose dope of 13.5 % and 9.5 % cellulose, with additions of 0.1 % NaOH, 0.3 % CaCl and no additive, were extruded into a cup filled with coagulation media. Varying parameters and their fiber forming ability are presented in Table 6. It should be mentioned that “fiber forming” in these extrusion trials does not mean that the fibers are ok to use, but only that extrusion of separated filaments and coagulation is possible. Almost all fibers in the extrusion are somewhat curled and mixed with occasional clumps. Due to small difference between additions they are not specified in the table. A more detailed result of the extrusions is discussed in Section 6.4.1.

Table 6. Capillary rheometer extrusion of 13.5 % and 9.5 % cellulose with different additives. Result presented describe if fiber formation was possible or not. ✓=YES ✗=NO - =NOT DONE

<table>
<thead>
<tr>
<th>Cellulose</th>
<th>Coagulant</th>
<th>Spinneret type</th>
<th>Extrusion method</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>100 x Ø80μm</td>
<td>31 x Ø150μm</td>
<td>Wet</td>
</tr>
<tr>
<td>13.5 %</td>
<td>Ethanol</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>13.5 %</td>
<td>Water</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>9.5 %</td>
<td>Ethanol</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>9.5 %</td>
<td>Water</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

5.4.2 Spinning

Spinning trial with 13.5 % cellulose without addition was difficult due to the viscous structure and gave incoherent fibers in both ethanol and water, due to degradation of cellulose after long kneading times at high temperature (4-5h).

Spinning trials with 9.5 % cellulose with 0.1 % NaOH addition and 8 % cellulose with 0.05 % NaOH addition succeeded to form cohesive fibers. Operating temperature of both dope and coagulant was 50°C. Varying parameters and the ability of collecting fibers or not for tensile strength measurement with 9.5 % cellulose is presented in Table 7.
Table 7. Fibers spun from 9.5 % cellulose with 0.1 % NaOH addition. Summarizes fibers possible to collect for tensile strength measurement. ✓ = YES X= NO

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Spinneret type</th>
<th>Spinning method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>✓ 100 x Ø80 µm</td>
<td>✓ 64 x Ø100 µm</td>
</tr>
<tr>
<td>Water</td>
<td>✓ 100 x Ø80 µm</td>
<td>✓ 64 x Ø100 µm</td>
</tr>
</tbody>
</table>

Spinning trial with 8 % cellulose also formed cohesive fibers and was performed with ethanol as a coagulant and with spinneret 64 x Ø100 µm, based on the preferred parameters from trial with 9.5 % cellulose.

5.5 Fiber Characterization

Tensile test of 9.5 % cellulose fibers coagulated in ethanol are presented in Table 8. All fibers presented in the table were dried in oven for 1h and then continued dried in air for 4 days. All results are average values from 10-20 filaments of each fiber type. The highest tenacity for a single filament was 14.6 cN/tex from fiber 1a.

Table 8. Coagulated fibers from 9.5 % cellulose and 0.1 % NaOH additive. 1a) Fibers dried while hanging vertically with a weight at the end. 1b) Fibers dried while hanging with no stretching weight. 2a) Fibers from second collective roll in spinning line, 10-15% stretch. 2b) Fibers from first collective roll.

<table>
<thead>
<tr>
<th>Type of fiber</th>
<th>1a</th>
<th>1b</th>
<th>2a</th>
<th>2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear density (dtex)</td>
<td>15.6</td>
<td>20.7</td>
<td>47.6</td>
<td>75.1</td>
</tr>
<tr>
<td>Tenacity (cN/tex)</td>
<td>13.4</td>
<td>8.9</td>
<td>10.9</td>
<td>7.6</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>12.4</td>
<td>38.0</td>
<td>24.0</td>
<td>26.8</td>
</tr>
<tr>
<td>Young’s modulus (cN/tex 1%)</td>
<td>585</td>
<td>365</td>
<td>400</td>
<td>242</td>
</tr>
</tbody>
</table>

Difference in tenacity and elongation of fibers dried 1h in oven compared to fibers only dried in air is shown in Figure 33 and 34.

Figure 33. Shows an increased tensile strength of fibers dried in oven for 1h.
Figure 34. A slightly decreased elongation for all fiber types except 1a.

Wet strength was studied for fiber 1a with the highest tensile strength. The difference in tenacity and elongation is presented in Figure 35. Highest tensile strength achieved of a single filament from fiber 1a was a dry strength of 14.6 cN/tex and a wet strength of 4.9 cN/tex.

Figure 35. Average tensile strength and elongation were lower for wet fibers than dry.

Trials of wet strength showed very weak fibers. Filaments were unfortunately often ruptured at the lower attachment of the tensile equipment, leading to weaker fibers than actual value. Though, a low Young’s modulus at the beginning of each tensile test indicates that the wet strength was not more than possibly 30-40% of dry strength.

Fibers spun from 8 % cell with 0.05 % NaOH was stretched between 1st and 2nd collective roll to investigate how stretch affected the fiber strength for these fibers. 0 % stretch corresponds to fibers collected from 1st roll. 50 % and 120 % stretch corresponds to an increased speed of 2nd roll compared to 1st roll. Increased stretch increases fiber strength and decreases elongation with a maximum tenacity of 11.7 cN/tex, see Figure 36.
A comparison of conventional Viscose and Lyocell to the experimental fibers of 9.5 % cellulose with 0.1 % NaOH from this laboratory work is presented in Figure 37. Properties of experimental zinc chloride fibers are more similar to viscose fibers due to the low wet strength.

**Fiber Characterization:** Fibers can be spun from 8 % and 9.5 % cellulose, with 9.5 % cellulose giving the strongest fibers. Strength can be increased by stretch during spinning and while washing, as well as by drying fibers in oven. Ethanol is better than water as a coagulant and spinneret 64 x Ø100μm gives the most favorable extrusion with less die swell than 31 x Ø150μm and less clogging than 100 x Ø80μm. Due to low wet strength of the experimental fibers using a wet spinning process they are more similar to viscose fibers than Lyocell. No air-gap trials have succeeded.
6. DISCUSSION

This section is divided into four sections: dissolution method, rheology, fiber formation and fiber characterization.

6.1 Dissolution method

Dissolving concentration of zinc chloride/water increases with increased cellulose concentration, ranging from 65-76% ZnCl₂. This laboratory work showed that a dissolving zinc chloride concentration could range from e.g. 69-70 % for 9.5 % cellulose and 74-76 % for 13.5 % cellulose. This corresponds to cellulose competing with the water molecules for interaction with zinc chloride, where increased water content leads to zinc chloride reactive sites saturated with water molecules. Because a higher zinc chloride concentration, along with an increased cellulose concentration, contributes to a higher viscosity, it is desirable to use the lowest possible concentration of each range (e.g. 69 % for 9.5 % cell and 74 % for 13.5 %). One method found in literature to reach a dissolving concentration has been to start with ZnCl₂ of >76 % (swelling cellulose) and then add water to decrease the ZnCl₂ concentration to reach a dissolving concentration (17). The method developed in this laboratory work was instead to start with a lower concentration of zinc chloride (swelling) and evaporate the excess water until a dissolving concentration was reached. With this method, the excess water in the beginning facilitates a homogenous distribution of the solvent. Also, with controlled evaporation it could be stopped, i.e. stop the vacuum outlet when the lowest concentration of zinc chloride is reached, giving the lowest possible viscosity for each cellulose concentration.

As the collected evaporation of water in the kneading process did not give accurate results, it was difficult to establish a functioning method to investigate similar trials with for instance different additives. Evaporation of water in vacuum oven prior to kneading proved therefore to be an efficient way to control the concentration of zinc chloride in the dope. Using this method, the dissolving trials resulted in a greater repeatability, because the evaporation during kneading had a lower deviation. Evaporation of spinning dope (double batch) in vacuum oven was very slow and needed to be split in two separate evaporations otherwise the dope was exposed to elevated temperatures for too long, risking degradation of cellulose.

Dissolution of extrusion dope (14g cellulose) was a relatively quick process of 150-180 min for 9.5-13.5 % cellulose, including pre-heating and kneading. Dissolution of spinning dope (28g cellulose) was more time consuming (200-240 min), which led to more degraded cellulose. To decrease the degradation, more trials with additives as well as developing the method used for
spinning dope should be further investigated. Possibilities of future work can be to reduce the excess water in the dope by squeezing the cellulose to a higher dry content, which will decrease the time for pre-heating. If there is no excess water when zinc chloride/water is mixed with cellulose, there might be problems with uneven dissolution. Another possibility can be to increase the temperature in vacuum oven when pre-heating and develop a new temperature time/dependence, but higher temperatures at shorter time might also lead to more degradation.

*Dissolution method:* Dissolving capacity is effective around 75°C, limited at lower temperature and causes cellulose degradation at higher temperatures. It also causes degradation when processed at 75°C for more than 3-4h. Evaporating excess water was a functioning method to investigate the lowest possible dissolving concentration of zinc chloride for each cellulose concentration.

### 6.2 Rheology

#### 6.2.1 Additives and degradation

It has been shown that degradation of zinc chloride-cellulose dope can be reduced with small additions of e.g. CaCl₂ (17, 20). Aqueous zinc chloride is an acidic salt with low pH and the additions described are mainly neutral salts. Along with CaCl₂, the strong bases CaO and NaOH and the amphoteric ZnO (either acid or base) was investigated as additions, all currently existing in different cellulose processes. Solubility of additives in aqueous zinc chloride was studied up to 1% of the zinc chloride weight. Lower additions were mostly used in further cellulose dissolution, but because the solubility was only studied by eye with reasonable accuracy, a higher solubility than later used was a requirement. Only CaCl₂ and NaOH were soluble up to 1%. Because NaOH is an alkali salt and CaCl₂ a neutral salt, additions of NaOH could possibly be lower than CaCl₂ with the same effect on the acidic ZnCl₂/water solution.

Additives of CaCl₂ or NaOH to zinc-cellulose dope result in a higher viscosity than without addition. Additions of 1% of CaCl₂ or NaOH to 13.5 % cellulose increased the viscosity significantly and resulted in a hard and gelled dope, which was difficult to process in the kneader and examine in microscopy. It has been shown in literature that addition of CaCl₂ (0.2-0.5 %) can increase viscosity of the solution. A possible explanation to this behavior was that it might be due to how the additives interact with the zinc-cellulose complex.

Additions of 0.3 % CaCl₂ or 0.05-0.1 % NaOH in this laboratory work resulted in similar structure as solutions without additive, but with a slightly higher viscosity. The increased
viscosity with additive compared to without additive could either be a result of the interaction of the additive on the zinc-cellulose structure, or a result of a less degraded sample. At higher additions up to 1 %, where the hard and gelled structure was clearly visible by eye and did at all not look similar to the dope without additive, the interaction of added molecules probably have a large effect on the viscosity. The increase in viscosity at lower amount of addition, e.g. 0.05 % NaOH of ZnCl₂ weight, is more likely a result of a less degraded sample. It seems more difficult for the small amount of addition to interact with zinc-cellulose complexes changing the structure enough to create a higher viscosity. NaOH addition gives the highest viscosity even though NaOH addition is lower than CaCl₂ addition. If the increase in viscosity is due to a less degraded sample, it is reasonable that NaOH as a strong base require less addition to affect the acidity level in the dope and thereby decreasing the degradation.

The trials using rheology to determine degradation of the samples were relatively rough estimations. It could only be applicable for comparison of a specific cellulose concentration, zinc chloride concentration and additive. The method was most useful to investigate if viscosity of the larger spinning batches had decreased a lot compared to the smaller capillary rheometer batches, which indicated that dope was significantly degraded and would not form cohesive fibers. Decreased viscosity of a degraded dope is partially a result of shorter cellulose chains, facilitating movement of chains relatively to each other with less entanglement and interactions.

6.2.2 Cellulose concentration

To reach a high tensile strength of fibers produced from cellulose dope, cellulose concentration needs to be high (favorable 15-20 % cellulose), which also creates an efficient process because less amount of solvent is needed. Therefore, dissolution trials started at 13.5 % cellulose with the aim to increase the cellulose concentration in further trials. 13.5 % cellulose resulted in a gel behavior rater than a solution, both with and without additions, and there were problems with degradation due to long kneading times. Decreasing the cellulose concentration to 9.5 %, viscosity was lowered, but it still resulted in a gel behavior. At 7 % and 8 % cellulose the dope resulted in a solution rather than a gel behavior, which is favored in a spinning process. The significant decrease in viscosity of 7 % and 8 % cellulose compared to 9.5 % and 13.5 % indicates than not only the cellulose content and degradation affect the viscosity, but also the zinc chloride concentration. Because of longer heating times of 13.5 % cellulose (approximately 30min longer than 9.5 %) it might be more degraded, i.e. the difference in viscosity between the 13.5 % and 9.5 % should maybe be somewhat larger. Taken the degradation into account, the difference between 7 % and 8 % to the higher concentrations is still major. The reason for this large gap in viscosity is probably due to the change in zinc chloride concentration.
6.2.3. Zinc chloride polymeric formation

It has been discussed in literature (20) that zinc chloride might be forming a polymeric structure in the cellulose dope, creating zinc chloride-cellulose complexes with a rigid structure. This can lead to increased viscosity as well as more gel behavior as cellulose molecular can interact with each other with zinc chloride polymeric structures between two chains, creating a temporary network of hydrogen interactions. When the zinc chloride concentration is decreased, water molecules tend to break up the zinc chloride polymeric structure, destroying the network and result in a solution instead of a gel behavior. The rheology results from this laboratory work indicate that the break up has a large effect at zinc chloride concentrations of around 68 % and lower (seen for 8 % and 7 % cellulose). To reach a spinnable solution at higher cellulose concentrations it would require a zinc chloride concentration of no more than 68 %. The problem then arises with the water molecules competing with cellulose molecules leading to some saturated reactive sites of zinc chloride by water molecules, which prevents higher cellulose concentrations than around 8 % to be fully dissolved.

It could be interesting to investigate if high cellulose content could be dissolved a high zinc chloride concentration and thereafter be diluted with water to decrease the polymeric structure formed by zinc chloride. But because water function as a coagulant for zinc-cellulose, it is possible that the temporary interactions between zinc chloride and cellulose will be ruptured by stronger interactions between zinc chloride and water.

Cellulose concentrations of 7 and 8 % with NaOH addition result in a temperature dependent gelation at 75 and 80°C, while it is a solution at temperatures at 70°C and lower. The behavior might also exist at 9.5 % and 13.5 % cellulose, but only less visible because they result in a gel behavior at 60°C as well. This is probably not the same polymeric structure formed by zinc chloride as seen for the higher cellulose content, but rather an accelerated interaction of cellulose-cellulose complexes or cellulose-zinc chloride-cellulose complexes. The reason why this behavior only is seen for addition of NaOH might be because the NaOH either acts as attraction between the complexes, facilitate hydrogen interaction (cellulose-cellulose or cellulose-zinc-cellulose) or by repulsion forcing molecular chains apart and creates a more rigid structure. Regardless what cases this behavior, the gelation at 75°C and 80°C is not a problem as spinning of the dope is done at around 50°C.

*Rheology*: Additions of 0.3 % CaCl₂ or 0.05-0.1 % NaOH is used to decrease degradation of cellulose. The addition causes a small rise in viscosity, which either is a result of less degradation or the interaction of the added molecules to zinc-cellulose complexes. Addition of
NaOH results in a temperature dependent gelation at increased temperatures (75°C and 80°C), which also might be an effect of the interaction.

Aqueous zinc chloride has a dissolving capacity of up to at least 13.5 % cellulose, possibly much higher. Dissolving concentration ZnCl₂/water range from 65-76% and lowest possible ZnCl₂ concentration increases as the cellulose concentration increases, e.g. 65-66 % ZnCl₂ for 7 % cellulose and 74-76 % ZnCl₂ for 13.5 % cellulose. Zinc chloride concentrations exceeding around 68 % results in a significantly increases viscosity due to a polymeric structure formed by zinc chloride, creating a network of cellulose-zinc chloride complexes and causing a gel behavior of the dope difficult to use in spinning processes. The dissolving capacity of 68 % ZnCl₂ is only about 8 % cellulose, which is very low compared to other solvents used today e.g. Lyocell and ILs.

6.3 Fiber formation

6.3.1 Capillary Rheometer Extrusion
To investigate qualities of a cellulose dope before preparing the entire spinning equipment, extrusion with a spinneret, connected to a capillary rheometer, was made to ensure coagulation and fiber formation. For highly viscous 13.5 % cellulose solutions temperatures of 80°C was required to lower the viscosity enough for extrusion through the spinneret. For an even heat distribution, the extruder was heated to around 100°C and then slowly cooled to operating temperature. For 9.5 % cellulose the temperature could be held much lower, around 45-55°C. Higher temperatures resulted in a too low viscosity for extrusion to work properly and the dope got stuck on the outside of the spinneret, especially when extruding into air. Temperature for wet extrusion was not as sensitive; filaments could be extruded at any temperature between 40-60°C. Wet extrusion led to fibers curling and twisting on their way down in the coagulant due to lack of stretching. When extruding into air, speed was of great importance. The highest extrusion speed possible of 200mm/min was required for dope to extrude as separated filaments. Problems with clogging of spinneret holes and uneven dope led to only around 5cm filament extrusion interrupted by lumps of dope falling down in the cup.

13.5 % dope was easier to use in the extruded because of the less sticky behavior when placing it in the pipe. Capillary rheometer extrusion could be a convenient trial method for even higher cellulose concentration for investigation of fiber formation and coagulation. Especially in studies of air-gap spinning, the extruder can provide easy and fast trials of a high viscous dope, with natural stretch of filament as they fall through air before entering the coagulation bath. It
should be noted that no accurate results can be obtained from this method, but only give an indication of what might be functioning or not in further spinning trials in terms of cellulose concentration, additives, temperature, extrusion speed and coagulant.

6.3.2 Spinning

Fibers were wet spun from 9.5 % cellulose dope with 0.1 % NaOH and 8 % cellulose with 0.05 % NaoH. As addition of NaOH to zinc-cellulose was not found in any literature, it was more interesting to study than the previous investigated addition of CaCl₂ (16, 17, 20).

During spinning trials with zinc-cellulose dope the main parameters are coagulant, spinneret type and extrusion speed. It is shown in literature that alcohols and water can be use as coagulant, ethanol often favored. Trials with ethanol gave more cohesive fibers than water and they were not as sensitive when drawn to the first collective roll. Ethanol was also more suitable for the vertical spinning method used, as the fibers in water became curled and did not fall down as easily in the pipe due to higher density of water compared to ethanol.

Air-gap spinning trials of 9.5 % cellulose had some of the same problems as in capillary rheometer extrusion trials. Filaments were extruded for a few seconds but interrupted of lumps of dope clogging or sticking to the outside of spinneret. Air-gap spinning normally requires high cellulose concentration and high viscosities e.g. Lyocell and ILs, but the main problem for zinc chloride as a solvent is the gel behavior at 9.5 % and 13.5 % cellulose leading to uneven extrusion and clogging of spinneret holes. 8 % cellulose concentration results in a solution rather than a gel, which is favored in spinning processes, but air-gap spinning did still not succeed. Wet spinning trials with 8 % cellulose had a much more homogenous extrusion than 9.5 % and almost no holes got clogged. Functioning air-gap spinning would require a very homogenous dope without air-bubbles, which is challenging when the concentration of cellulose is increased along with the viscosity. Filtration of the dope removes non-homogenous particles, but this is also difficult with a gel-like dope. Air-gap spinning trials in this laboratory work do not result in any definite conclusion of the possibility of air-gap spinning for zinc-cellulose dope. When air-gap spinning did not succeed after some variation of parameters, the main focus was changed from comparing air-gap spun fibers with wet spun fibers to instead collect only wet spun fibers of different variations.

Stretch will be limited for a gel-like dope, because the network of hydrogen interactions will be ruptured, i.e. the filaments will be ruptured more easily than the more flexible molecular structure of a solution. This phenomenon could be observed in wet spinning trials where
filaments of 9.5 % cellulose (gel behavior) could only be stretched around 10-15 % between 1st and 2nd collective roll before breakage, while 8 % cellulose (solution) could be stretched up to 120 % before breakage.

A significant die swell could be detected for 9.5 % cellulose when using spinneret with Ø 150μm holes, as the pump frequency and extrusion rate was much higher than the possible collective speed. Die swell leads to a thicker filament than the spinneret hole, see Figure 35, but could have been decreased if fibers were stretched more before drying. Die swell is decreased as the length/diameter ratio of each capillary is increased and the angle of the inlet decreases. If air-gap spinning is possible, die swell can be reduced as filaments are drawn in the air-gap before entering the coagulation bath.

![Figure 38. Die swell after extrusion of a single filament.](image)

Fiber formation: Zinc chloride-cellulose dope was wet spun at cellulose concentrations of 9.5 % and 8 %. Due to the gel behavior of 9.5 % cellulose, it causes clogging of spinneret holes and did not allow stretch more than 10-15 % before breakage of filaments. With 8 % cellulose, resulting in a solution, the extrusion was much more homogenous and filaments could be stretched up to 120 %. It requires further trials to make any conclusion of the possibility of air-gap spinning for zinc-cellulose dope.

6.4 Fiber characterization

Fibers collected from spinning trials were characterized by linear density and a tensile test giving data of tenacity, elongation and young's modulus. Mainly three parameters were found to affect the fiber properties in this study: spinneret, stretch of filaments and type of drying. The spinneret of Ø 150μm holes with significant die swell, lead to fibers with higher linear density than expected. The elongated molecular structure created when forcing the dope though the spinneret is ruined directly after extrusion due to swelling of dope creating a less oriented compressed structure. Fibers with large die swell can therefore achieve high elongation but with
lack of tensile strength. As the elongation exceeds around 30 %, the cross section of the fiber is decreased, resulting in a lower tensile strength than the actual value.

Stretch during/after spinning is vital to increase the tensile strength of the fiber. Especially when sufficient stretch is not achieved in the spinning line, additional stretch should be applied during washing prior to recrystallization of the cellulose molecules, when some residual zinc chloride is still left. Stretch while drying of fiber is also of great importance to avoid shrinkage and entanglement. An additional drying of fibers in oven is showed to increase tensile strength and elongation, as least for fibers without die swell.

Normally, a higher cellulose content results in higher tensile strength of filaments. As spinning trials of 8 % cellulose had a more homogenous extrusion with significantly higher ability of stretching filaments compared to 9.5 %, it was still expected that tensile strength of 8 % should be higher than 9.5 %, but it was not. Even more surprising was that stretch of 120 % compared to 0 % did not affect the tensile strength that much. 8 % cellulose only had 0.05 % NaOH addition, while 9.5 % cellulose had 0.1 % NaOH. The addition was decreased to lower the viscosity as much as possible and get rid of the gel behavior as much as possible. It is not yet clear if the higher addition of 0.1 % to 9.5 % had any affect on the increased strength of fibers, or if other factors had a larger effect.

It should be noted that linear density of filaments was around 10-18 dtex, which is higher than expected for the spinneret holes used. This can partially be dependent on die swell, but it is more likely a result of 2-4 filaments sticking together. This does probably not affect the measured tenacity and elongation, as the measurements are made based on each linear density. Wet strength also requires further investigation, because more then half of the filaments tested were ruptured right above the lower clamp of the test equipment. The expected wet strength is might be up 40% of dry strength. The fiber properties are more similar to Viscose fibers than Lyocell, especially due to the low wet strength. But also, the wet spinning method probably has a large impact on the low tensile strength of the experimental fibers, compared to air-gap spun Lyocell fibers often reaching a higher tensile strength.

**Fiber characterization:** Highest tensile strength was reached for wet spun fibers coagulated in ethanol of 9.5 % cellulose with 0.1 % NaOH addition (gel behavior), with tenacity of 13-15 cN/tex, elongation of 10-12 % and wet strength 30% of dry strength. Wet spun fibers from 8 % cellulose only reached a tenacity of 10-12 cN/tex with elongation of 6-8 %, despite a more homogenous extrusion of filaments and with significantly higher stretch.
6.3 Future outlook of zinc chloride as a solvent

Zinc chloride is said to be a relatively cheap solvent and is used as a direct solvent without any intermediate compounds. These types of direct solvents are favored compared to e.g. Viscose, by creating an effective process from dissolution to fiber formation. But there are a lot of problems regarding zinc chloride as a solvent that needs to be considered before more research is done. First of all, zinc chloride is very corrosive putting high demands on the equipment used, but it can also create problems when using the same equipment for a zinc chloride-cellulose dope as for other dopes that are more sensitive to contaminations. The zinc chloride-cellulose solution itself is not sensitive for contaminations, which definitely is an advantage, but residual zinc chloride can affect other sensitive dopes even if the equipment is carefully washed between each use. Zinc chloride has also been found degrade cellulose, at high temperatures the degradation is higher in a zinc chloride-cellulose dope compared to pure cellulose (15). Other molten salt hydrates e.g. LiClO₄ does not show increased degradation compared to pure cellulose and might therefore be a more favorable solvent for this particular reason.

The main problem of zinc chloride as a solvent is the gel behavior and the sudden increase in viscosity from 8 % to 9.5 % cellulose, which probably is dependent on a polymeric structure formed by zinc chloride especially above 68 % ZnCl₂. The dissolving capacity of 68 % ZnCl₂ (and lower) was limited to maximum around 8 % cellulose, even though the dissolving capacity is much higher if the zinc chloride concentration is increased. This limitation of cellulose concentration is a major drawback compared to other solvents possible to dissolve and spin fibers from 15-20 % cellulose (e.g. Lyocell and ILs). Even though fibers could be spun from 9.5 % cellulose dope with a gel behavior in this laboratory work, this should not be favored in a conventional process due to the problems of uneven extrusion and clogging of spinneret holes.

In addition to the limited cellulose concentration, it is difficult to hold the zinc chloride concentration at a specific level, as the dope is processed at high temperatures causing evaporation of water by just opening the cover in the kneader for examination. Even though 8 % cellulose can be dissolved in 68 % zinc chloride, it can also be dissolved just as good at higher zinc chloride concentrations up to 76 % zinc chloride, which causes higher viscosity and a gel behavior also for 8 % cellulose.

Future outlook of zinc chloride as a solvent: Because of the many disadvantages of zinc chloride as a solvent, the possibility of using it in future conventional production of textile fibers appears small, especially because of the wide range of solvents existing today.
7. CONCLUSION

Aqueous zinc chloride has a dissolving capacity of up to at least 13.5 % cellulose, possibly much higher. Dissolving concentration ZnCl₂/water range from 65-76% and lowest possible ZnCl₂ concentration increases as the cellulose concentration increases. Above around 68 % ZnCl₂ results in a significantly increased viscosity due to a polymeric structure formed by zinc chloride, creating a network of cellulose-zinc chloride complexes and causing a gel behavior of the dope difficult to use in spinning processes. The dissolving capacity of 68 % ZnCl₂ is only about 8 % cellulose, which is very low compared to other solvents used today e.g. Lyocell and ILs.

Additions of 0.3 % CaCl₂ or 0.05-0.1 % NaOH is used to decrease degradation of cellulose. The addition causes an increased viscosity, which either is a result of less degradation or the interaction of the added molecules to zinc-cellulose complexes. Addition of NaOH results in a temperature dependent gelation at increased temperatures (75°C and 80°C), which also might be an effect of the interaction.

Highest tensile strength was reached for wet spun fibers coagulated in ethanol of 9.5 % cellulose with 0.1 % NaOH addition, with tenacity of 13-15 cN/tex, elongation of 10-12 % and wet strength 30% of dry strength. Because of many disadvantages of zinc chloride as a solvent, e.g. degradation of cellulose, corrosivity and the high viscosity and gel behavior at cellulose concentrations of 9.5 % and 13.5 % cellulose, a future possibility of a conventional production of textile fibers appears to be quite limited.
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APPENDIX: Film making for DP measurement

For future DP measurements, cellulosic films were made, see Figure 36-38. A sample of the dissolved solution was pressed between two petri glasses, coagulated in ethanol, removed from the glasses and washed in water. The films were dried in air and saved for eventual use together with some spun fibers for an eventual DP measurement after this thesis had ended.

Figure 39. Film pressed between two petri dishes, coagulating in ethanol bath. Approximate size ø7mm

Figure 40. Thickness 1-2mm

Figure 41. Coagulated films removed from the petri dish, washed in a water bath. Dried in air saved for future DP measurement.
APPENDIX 2: Spinneret setup

The spinneret nozzle setup used in capillary rheometer extrusion and spinning is showed in Figure 42. It contains textile filters, metal filters, sealing, capillaries and finally the spinneret.

![Figure 42. Spinneret setup.](image)
APPENDIX 3: Rheology graphs - oscillation and stress viscometry

A.3.1 Oscillation graphs of 13.5% cellulose

Figure 43. Rheology of 13.5% cellulose at 80°C and 60°C. Dope kneaded for 2h at 75°C. Storage modulus $G'$ is dominating at both temperatures.

Figure 44. Rheology 13.5% cellulose with addition of CaCl at 80°C and 60°C. Pre-heated 80min and kneaded for 100min. Dominating storage modulus $G'$ at both temperatures.

Figure 45. Rheology 13.5% cellulose with addition of NaOH at 80°C and 60°C. Pre-heated 80 min and kneaded for 100min. Dominating storage modulus $G'$ at both temperatures, but crossover at 0.015 Hz at 60°C
A.3.2 Oscillation graphs of 9.5 % cellulose

**Figure 46.** Rheology of 9.5 % cellulose with addition of CaCl at 80°C and 60°C. Pre-heated 60min and kneaded for 90min. Dominating storage modulus $G'$, but small crossover at 0.4 Hz at 60°C.

**Figure 47.** Rheology of 9.5 % cellulose with addition of NaOH at 80°C and 60°C. Pre-heated 60min and kneaded for 90min. Dominating storage modulus $G'$ for both temperatures.
A.3.3 Stress viscometry graphs of 13.5 % and 9.5 % cellulose

**Figure 48.** Stress viscometry of 13.5 % cellulose with addition of CaCl₂ gave no consistent measurement, possible slope of -1. With NaOH addition instead resulted in a slope of -1/2 60°C and 80°C, corresponding to a gel.

**Figure 49.** Stress viscometry of 9.5 % cellulose with addition of CaCl₂ resulted in a slope of -1 for 60°C and 80°C. With NaOH addition did also result in slope of -1 for 60°C and 80°C.
A.3.4 Oscillation graph of 8 % cellulose

Figure 50. 8% cellulose with addition of 0.05 % NaOH. At 75 and 80°C a temperature dependent gelation is formed resulting in a steeper viscosity curve and a domination elastic modulus (green solid line) corresponding to a gel.

Figure 51. 8% cellulose with addition of 0.05 % NaOH. Results in a low viscosity and a dominating loss modulus (blue stacked line) corresponding to a solution at 60 and 70°C.

Figure 52. 8% cellulose with addition of 0.05 % NaOH. Results in a low viscosity and a dominating loss modulus (blue stacked line) corresponding to a solution even down to 50 and 30°C.
A.3.5 Oscillation graphs of 7 % cellulose

**Figure 53.** 7 % cellulose with addition of 0.3 % CaCl. Results in a low viscosity with a flatter curve and a dominating loss modulus (blue stacked line) corresponding to a solution at both 60 and 80°C.

**Figure 54.** 7 % cellulose with addition of 0.05 % NaOH. Results in a low viscosity and a dominating loss modulus (blue stacked line) corresponding to a solution at 60°C. At 80°C a temperature dependent gelation is formed resulting in a steeper viscosity curve and a domination elastic modulus (green solid line) corresponding to a gel.