



## **RHEOLOGICAL MEASUREMENTS OF CELLULOSE DERIVATIVES**

Lappeenranta–Lahti University of Technology LUT

Master's programme in chemical engineering, Master's thesis

2022

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## ABSTRACT

Lappeenranta–Lahti University of Technology LUT

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### **Rheological measurements of cellulose derivatives**

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Because the need for textiles in the world has increased, so has the need for textile fibres. There are different processes which produce textile fibres from pulp, which depending on the type has their own downsides and upsides. Cold alkali dissolved pulp is an important field for the environment, as the process can be done in a sustainable way, with decent fibre properties. The problem with cold alkali dissolved pulp is the temperature stability of the dissolved pulp, as they tend to gel in room temperatures. Gelling of dissolved pulp during the process leads to fibre breakup and bad fibre quality. Therefore, it is detrimental to the process that good quality, stable pulps are identified for the process.

The aim of the experiments is to give insight on how this dissolved pulp can be characterized and compared, to give an indication whether the pulp used is stable. The research is based on the rheological properties of pulp and evaluating the differences between different pulps. By determining gelling times, and temperatures, pulps can be characterized whether they are storage and process stable after dissolution. A flow sweep was used to determine change in viscosity under shear, frequency sweep for evaluating gelling times, and temperature hysteresis for gelling temperatures.

The results of the experiments were as expected, Brookfield viscosity giving the best indication of stability and sample behaviour. Temperature hysteresis and frequency sweep tests gave contradicting results regarding sample stability, though flow sweep measurements were in line with temperature hysteresis results. The results of these experiments can be used to further refine the process of evaluating the required dissolved pulp quality.

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### **Selluloosajohdannaisten reologiset määritykset**

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Jatkuvan tekstiilien kulutuksen kasvun takia myös tekstiilikuitujen tarve kasvaa. Erilaisia prosesseja on olemassa tuottamaan sellusta tekstiilikuituja, tekniikasta riippuen tuoden omia ongelmiaan ja etujaan esiin. Kylmään emäkseen liuotettu sellu on ympäristön kannalta hyödyllinen tutkinnan kohde, sillä prosessi on itsessään toteutettavissa ympäristölle turvallisella tavalla uusiutuvista materiaaleista, saavuttaen kohtuullisia kuituominaisuuksia. Suurin ongelma kylmällä emäksellä liuotetulle sellulle on sen stabiilisuus. Liuotetut sellut geeliiytyvät helposti lämpötilan vaikutuksesta, joka ei ole prosessin kannalta toivottua, sillä se aiheuttaa kuitujen katkeilua ja huonolaatuisuutta. Tämän takia on tärkeää löytää selluja, jotka ovat tarpeeksi stabiileita niin säilytykseen, kuin itse prosessiin.

Työn tarkoituksena on antaa tietoa, miten selluja voidaan arvioida, vertailla, ja päätellä onko se stabiili. Tutkimus perustuu reologisten ominaisuuksien tarkasteluun ja arviointiin sellumassojen välillä. Tutkimalla selluille ominaisia geeliiytymislämpötiloja ja geeliiytymisaikoja, voidaan todeta, onko käytetty sellu tarpeeksi stabiili säilytykseen ja prosessiin. Määrittelemällä selluille ominaisia geeliiytymisaikoja ja lämpötiloja, voidaan selluja vertailla jo liuotusvaiheen jälkeen. Virtaustestillä (flow sweep) saatiin aineen viskositeetin muutos leikkauksen vaikutuksesta, taajuustestillä (frequency sweep) aineen geeliiytymisaika ja lämpötilahystereesillä geeliiytymislämpötila.

Suoritettujen kokeiden tulokset olivat odotettavia, viskositeetin todettiin antavan indikaation sellun stabiilisuudesta ja käyttäytymisestä. Lämpötilahystereesin ja taajuustestien tuloksissa huomattiin risteävyyksiä sellun laadun arvioimisessa, vaikkakin virtaustestien tulokset tukivat lämpötilahystereesin tuloksia. Kokeiden tulokset antavat pohjaa tulevien sellujen laadun tutkimusten suorittamiselle.

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## Abbreviations

AGU	Anhydroglucose unit
HCL	Hydrochloric acid
NaOH	Sodium hydroxide
MMCF	Man-made-cellulosic fibres
ILs	Ionic liquids
Dope	Dissolved pulp
DP	Degree of polymerization

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Appendix 3. Frequency sweep test results, gelling times.

# 1. Introduction

Due to the exponential growth of human population, demand for new process options for sustainable production is at an all-time high. Businesses are looking more into environmentally sound options, such as utilizing recycled or bio-based materials to replace other fossil-based materials. As the population in the world increases, so does the need for textiles. Man-made-cellulosic fibres (MMCF) as a raw material for textile production are under extensive research, where some, such as Rayon and Lyocell regenerated fibres, are well established processes.

Here, alkali dissolved cellulose is discussed and studied. Previous studies have found that alkali soluble cellulose are potentially unstable and may turn into gel quickly in either elevated temperatures or under high shear. These challenges are discussed in chapter 2.

The aim of this study is to introduce new ways of evaluating dissolved pulp, stability, and to be able to predict the stability of such. This dissolved pulp is henceforth called in this work as dope. This thesis includes a literature review of previous studies of evaluating dope performance, and how further tests are to be conducted.

Previous studies have yet to consider temperature variation in frequency sweep measurements, so an attempt in dope stability evaluation via temperature stability is an interesting area to investigate, as temperature stability is an always relevant problem in alkali dissolved pulps. Previously other rheology methods such as temperature hysteresis and flow sweeps have been studied by other researchers (Vehviläinen, 2015; Lue and Zhang 2009) and they will act as a reference for a new measurement method.



## 2. Cellulose

In this chapter, cellulose and its derivatives will be introduced and discussed.

### 2.1 Cellulose as a material

Cellulose, a biopolymer able to form durable structures for trees and green plants, is the most readily available polymer occurring in nature. Cellulose as a raw material is practically endless in supply, and therefore perfect for the ever-growing needs of sustainable processes. It is present in wood, cotton linters, certain bacteria, and other woody plants, to name a few, illustrated in Figure 1.

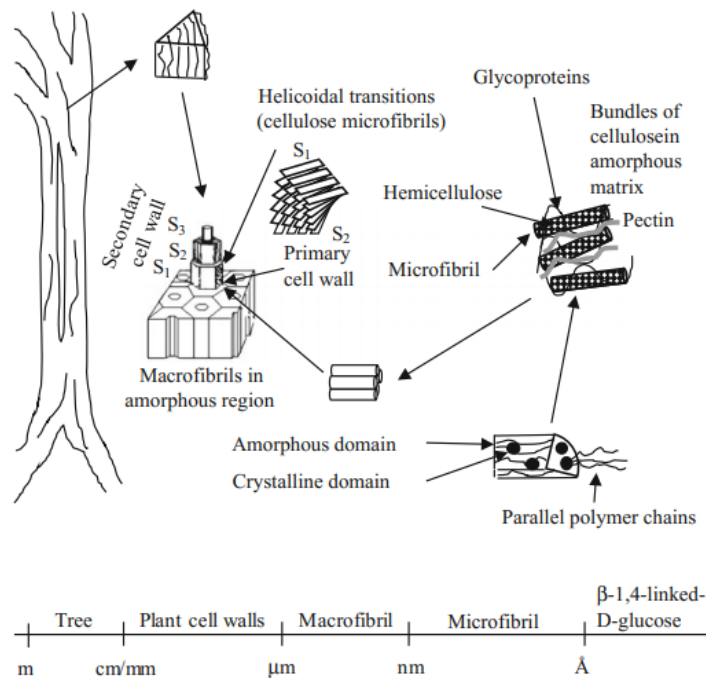


Figure 1 Cellulose in wood (Heinze and Seoud, 2018)

#### 2.1.1 Cellulose structure

The structure of cellulose was first discovered by a French agricultural chemist Anselme Payen in 1837, with the French Academy naming the newly discovered carbohydrate as cellulose. A cellulose molecule consists of  $\beta$ -(1 $\rightarrow$ 4)-glycosidically linked glucose units,

displayed in Figure 2. The anhydroglucose unit (AGU) is the base unit of cellulose. A unit consisting of two anhydroglucose units is called cellobiose. These AGU units create a linear chain consisting of numerous AGU units whose length is expressed as the degree of polymerization (DP). The DP of natural cellulose can be over 20 000, while the shortest chains can be as short as 160 (Chami Khazraji and Robert, 2013) The AGU units exist as a D-glucopyranose ring in  ${}^4C_1$ -chair configuration, as it is the lowest energy conformation with  $\beta$ -linkages resulting in a cellulose chain axis turn of  $180^\circ$  of each second AGU. A cellulose chain has a non-reducing end-group and a reducing end-group. The end groups themselves do not affect the properties of cellulose, or their derivatives, but they may be used for selective modification, for example by reductive amination.(Heinze and Seoud, 2018)

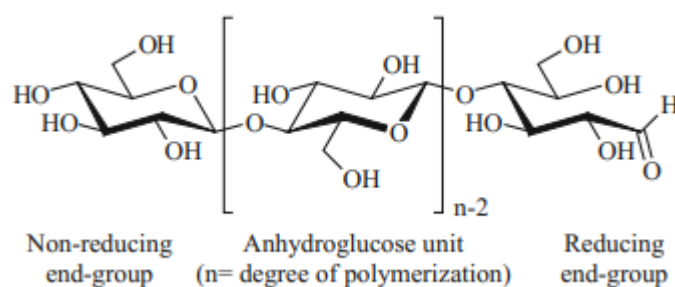


Figure 2 Chemical structure of cellulose (Heinze and Seoud, 2018)

Cellulose is a major component in lignocellulosic biomass, usually making up 40-73% of wood, depending on the species (Heinze and Seoud, 2018; Phanthong *et al.*, 2018). AGU units can form strong hydrogen bonds with adjacent glucose units in the same and different chains, so called intramolecular and intermolecular bonding networks. These hydrogen bonding networks are strong and packed in the crystalline sections of cellulose fibrils. This structure is also the reason why cellulose fibrils are insoluble in water and highly resistant to organic solvents (Phanthong *et al.*, 2018). This insolubility is what limits the use of cellulose and its derivatives. To utilize cellulose different methods are available, derivatizing methods and non-derivatizing methods help dissolve the cellulose for further processing.

Cellulose also displays different allomorphs, as orientation of glucose molecules and hydrogen bonding networks have wide orientation. These allomorphs are generally divided into four types, I, II, III, IV, depending on the source of lignocellulosic biomass and method

for treatment. Type I cellulose allomorph is the most typical allomorph, displaying a parallel packing hydrogen-bond network. Type I also appears in two distinct crystal phases:  $I_\alpha$  and  $I_\beta$ . The difference between each crystal phase is that  $I_\alpha$  has a triclinic unit cell, which contains one chain and  $I_\beta$  has a monoclinic unit cell with two parallel chains. Type II is derived from irreversible chemical regeneration of type I cellulose from dissolving in a solvent or swelling in acid or alkaline solution and the reaction is considered to be irreversible (Habibi, Lucia and Rojas, 2010). As cellulose is regenerated, type II cellulose is comprising of different arrangements of hydrogen-bond network antiparallel packing. Type III is ammonia treated type I cellulose and type IV is heat modified type III cellulose in 260°C in glycerol. Type III and IV cellulose also have two forms, depending whether it is derived from cellulose I or II. (Nishiyama *et al.*, 2003; Tongye *et al.*, 2009; Heinze and Seoud, 2018; Phanthong *et al.*, 2018)

## 2.2 Cellulose dissolution

Cellulose dissolution is difficult to achieve due to strong intra- and intermolecular bonds and crystalline structure (Figure 3), which is resistant to hydrolysis by weak acids and bases. Interest in new ways of dissolving cellulose has increased, and studies of cellulose dissolving mechanisms are plenty, but speculative. Dissolution can be divided into two categories, derivatizing and non-derivatizing dissolutions. The latter retaining the cellulose structure, the former forming new derivatives of cellulose, enabling different end products. For cellulose in this work, non-derivatizing dissolution is used in aqueous alkali solution. (Carlos and Alves, 2015)

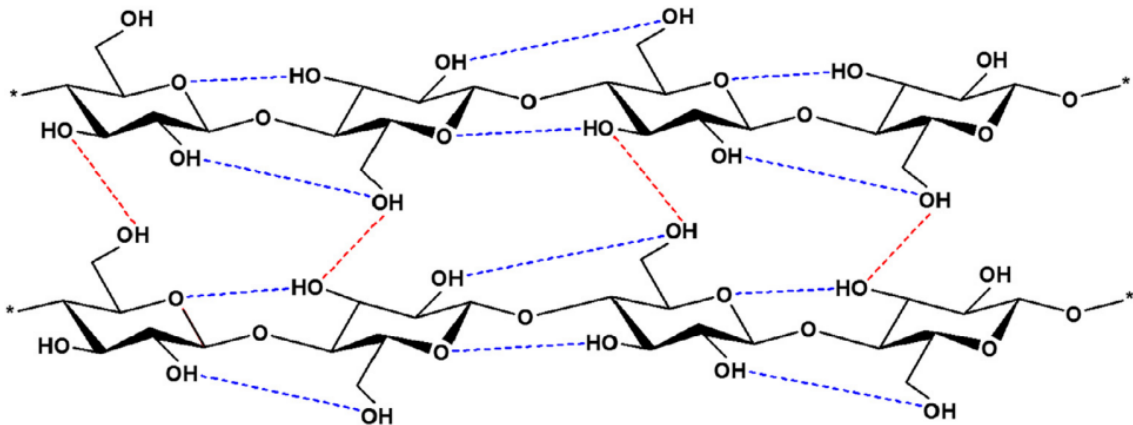


Figure 3 Intra- and intermolecular hydrogen bonding networks in cellulose (blue line and red lines respectively). (Phanthong *et al.*, 2018)

Aqueous alkali hydroxides can be used to dissolve cellulose as it causes swelling of cellulose in water. This is the general route of dissolution. Fibres swell when in contact with a solvent, changing the structure, volume, and physical properties of the biopolymer. The crystalline network of cellulose is gradually destroyed when the cellulose-solvent interactions are stronger than the intra- and intermolecular interactions of cellulose. As the individual chains gain their own conformational chain movement, their activity in the solution increases, and fibres start to swell to a gel-like medium. From this swelling the chains start to disintegrate into the solution. An ideal state is a complete dissolution, where no interchain bonds remain. (Väisänen *et al.*, 2021)

Certain additives can also help in the dissolution process, increasing the amount of cellulose dissolved, or the stability of the solution (Vehviläinen, 2015). The mechanism of additives is often debated, often referencing water-binding abilities and intermolecular hydrogen bond breaking, preventing association and therefore stabilize the system.

The process of dissolution itself is temperature critical, and only low amounts of cellulose can be dissolved at once. Lower temperatures result in increased swelling and increases dissolution. An explanation of why lower temperatures aid dissolution was done by Medronho *et al.*, who suggests that the O-CH<sub>2</sub>-CH<sub>2</sub>-O segments with conformational freedom around the C-C bonds can change their conformations with temperature from a less polar state at high temperatures to more polar states at lower temperatures. This way when temperature is lowered, more polar states are populated and attractive interactions with the polar solvent are favoured, leading to dissolution. (Medronho *et al.*, 2012)

One important factor is also the degree of polymerization (DP) of the selected cellulose. Too long a polymer chain is difficult to dissolve, and therefore short (200-300 DP) chain cellulose should be used for dissolving. The chain length depends on the pre-treatment of the material. (Heinze and Seoud, 2018)

Thermodynamically observing the dissolution, the free energy of the dissolution process must be negative for it to happen spontaneously,  $\Delta G_{Dissolution} < 0$ . Therefore, the dissolution only occurs when the mixed state corresponds to a lower free energy than two separate phases. To achieve this, a negative enthalpy term or a positive entropy term, or both are required. As stated by Heinze et al. and Medronho et al. (2018), essential requirements of solvents include the following: adequate stability of the electrolyte/solvent complex, cooperative action of the solvated ion pair on hydrogen bonding of cellulose, sufficient basicity (density or hardness of charge) of the anion, and adequate volume of the electrolyte/solvent complex. Stability of the electrolyte/solvent complex is important due to complexes that are too stable, or unstable do not dissolve cellulose. (Medronho *et al.*, 2012; Heinze and Seoud, 2018)

The crystalline regions of cellulose display a lower free energy than amorphous regions of cellulose, and therefore dissolution is thought to begin at the amorphous regions. This is also likely, as hydroxyl groups in the amorphous regions are more accessible to reagents than in the crystalline regions. (Heinze and Seoud, 2018)

### 2.2.1 Cold dissolution of cellulose

This work focuses on cold alkali dissolved cellulose dopes. The method of cold alkali dissolved cellulose is conducted initially in low temperatures of -5 to -12°C, balancing out at near 3°C, at low quantities, with cellulose content of less than 10 m-% due to low solubility. To achieve dissolution, cold alkali is added to the cellulose mass and mixed in a stirring vessel until all cellulose in the sample has dissolved. Cold alkali dissolution has a narrow area where it is possible to dissolve pulp, as can be seen in Figure 4.

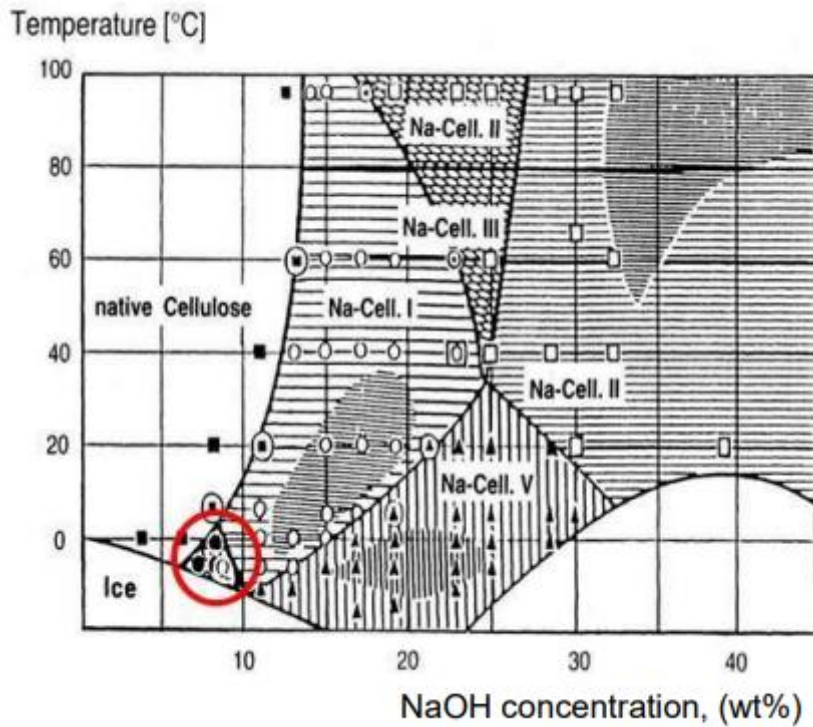
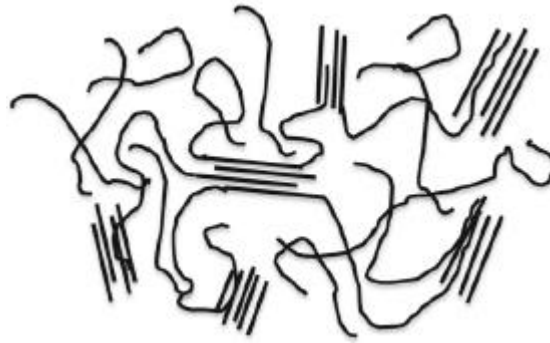


Figure 4 Pulp dissolution in cold alkali has a narrow are where dissolution is possible. (Budtova and Navard, 2016b)

Additives, such as zinc oxide, thiourea, and urea can help in this dissolution process. The dissolution process is temperature sensitive and freezing of the pulp is to be avoided. (Lue and Zhang, 2009; Vehviläinen, 2015)

### 2.3 Gelation of dope

The mechanism of gelling in dope is still a debated matter, and the most important one regarding its' stability. The gelling time of course being directly related to the storage time and processing time. Gelling also weakens the physical properties of regenerated fibres and films. A sketch of the possible structure of gelling is presented in Figure 5.



*Figure 5 Hypothetical sketch of gel structuring, where crystallites work as junction points to form a 3D cross linked network. (Pereira et al., 2018)*

Gelation is mostly thought to be irreversible, though using certain methods, reversible gels have been studied, as mentioned by Vehviläinen (Vehviläinen, 2015). Gelation determination via rheometry (see chapter 3 for reference) is often done via storage ( $G'$ ) and loss moduli ( $G''$ ) crossover point analysis, where the crossover point is thought to be the point of gelling. This cross-over point can be moved with temperature control. Increasing temperatures have been found to decrease the gelling time exponentially, initial gelling times decreasing from several hours in room temperature to a couple of minutes in 30°C (Pereira et al., 2018).

Using the cross-over point of storage and loss moduli as a way of determination of the gelling point is likely a somewhat false statement, as gelling begins to occur at minimum  $G'$  values, as described in Thomas Mezger's Applied Rheology book. Though when considering the material, the crossover point of  $G'$  and  $G''$  can still be thought of as the point when the matter has formed into a gel.

The gelation process usually begins from aggregated fibres, and the gelation time decreases with increasing temperatures and increased concentration/molecular weight of cellulose in the solution (Vehviläinen, 2015). Via turbidity tests by Pereira et al., the irreversibility of cellulose aggregation can be determined, as the viscosity and turbidity were retained after cooling the sample back to room temperature after heating to 45°C. This structural irreversibility has also been tested via temperature hysteresis, where the sample did not return to its initial form after slow temperature ramp, where storage and loss moduli measurements were done at constant frequencies and strain (Figure 6).

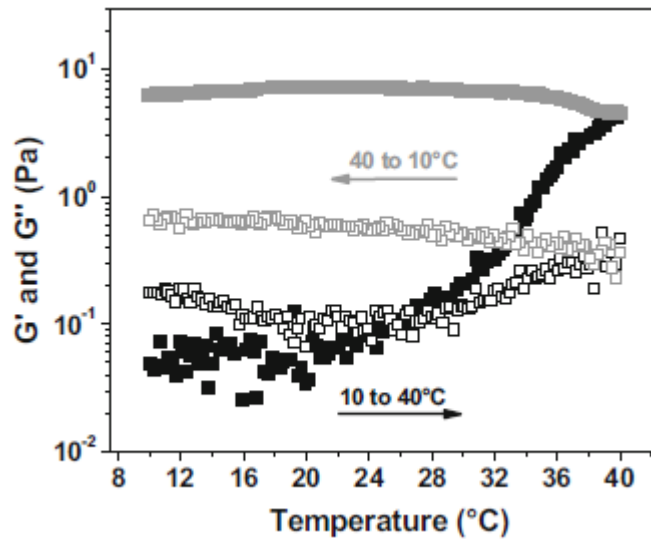


Figure 6 Example temperature hysteresis from 10°C to 40°C, at constant frequency of 1 rad/s and a strain of 0.1% with a constant heating/cooling ramp of 1°C/min. Black squares and squares with outer black layers indicate the rising temperature ramp, while the grey ones indicate the decreasing temperature ramp. (Pereira et al., 2018)

From Figure 6 we can see that the heating causes gelling, and roughly at 26°C the crossover of  $G'$  and  $G''$  occurs, indicating the gelling point, though an even earlier point of the initial gelling could be determined via more accurate data, as will later be discussed in the experimental work. Other key elements affecting the gelling is contact with air, which has to be minimized to avoid inaccurate results.

## 2.4 Additives and pre-treatments

As solubility of cellulose is quite poor, certain pre-treatments and additives can be used to help in the dissolution process. Pre-treatment methods can be divided into three categories, chemical, physical and biological. Here, main pre-treatment methods are introduced.

### 2.4.1 Chemical and biological pre-treatment

Chemical pre-treatment methods aim to remove chemicals and polymers harming the dissolution process, mostly lignin and some hemicellulose. A popular technique for pre-treatment is with alkali solutions, where cellulosic materials swell, and hemicellulose dissolves, restructuring the material, affecting the pore structure or crystallinity, which in



turn influences the accessibility of cellulose chains to solvents. Alkali hydrolysis is often used in conjunction with enzymatic and mechanical treatments, and the most popular alkali used in pre-treatment is sodium hydroxide for its cheapness and efficiency. (Rahikkala, 2013; Budtova and Navard, 2016a)

Hydrolysis is the most used chemical pre-treatment of cellulose, where alkali or acid catalysts are used to decrease cellulose chain length, lowering the degree of polymerization. In hydrolysis long chains are chopped into smaller components. (Rinaldi and Schüth, 2009)

Examples of acids used in acid hydrolysis are sulfuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ), hydrochloric acid ( $\text{HCl}$ ) and phosphoric acid ( $\text{H}_3\text{PO}_4$ ), though the use of acids has a negative trait of challenging recycling, corrosiveness and toxicity. (Rahikkala, 2013)

Other chemical pre-treatments include steam method and organosolv method, which both help dissolve hemicellulose and lignin. Water pre-treatment and biological methods. Biological methods work by utilizing micro-organisms in order to break down lignin and hemicellulose, with the main downside being its slowness. (Rahikkala, 2013)

#### 2.4.2 Physical and mechanical pre-treatment

As described by Vehviläinen (Vehviläinen, 2015), physical methods of cellulose pre-treatment include mechanical treatment, drying, irradiation or thermal processing. The overall objective of these methods is to increase cellulose porosity and surface area, decrease the particle size and chain length, and break hydrogen bonds.

The most popular method of physical pulp pre-treatment is steam explosion, or autohydrolysis method, where pulp is handled with saturated steam in a high pressure where the steam begins the autohydrolysis. Using this method, hemicellulose is separated, and lignin is altered under high temperature, increasing the chance of cellulose hydrolysis. Steam explosion method is an inexpensive method for hardwood trees. The pulp must be dry for the steam to be able to penetrate the material. Other limitations for the method include partial degradation of xylene fraction, incomplete breakdown of the lignin-carbohydrate matrix and the formation of inhibitor compounds. Steam explosion method requires no recycling, the resulted product is more susceptible for enzymatic hydrolysis, and the amount of energy required is less than in mechanical pre-treatment methods. Other such methods include Ammoniac explosion method, and  $\text{CO}_2$  explosion method. (Rahikkala, 2013)

As for mechanical pre-treatment, it is usually done in order to mechanically lower crystallinity of the pulp, either using grinding or chipping. The achieved particle size depends on the used instruments. The biggest downside of mechanical pre-treatment is its energy consumption. (Rahikkala, 2013)

### 3. Rheology

Rheology is the science of studying the flow and deformation of matter, as the name itself is derived from the Greek word “rhei”, meaning “to flow”. With different geometries of measurement different substances may be studied, such as food stuffs, paint, gels, cosmetics or even solids. For different samples and objectives, the measurement can be done either with rotational, or oscillating movement. This work will focus mainly on rotational rheology measurements with a concentric cylinder geometry (also known as a bob and cup geometry), and a 50mm parallel plate geometry.

#### 3.1 Geometries of measurement

The geometry of measurement is chosen on the basis of the sample’s properties and measurement type. Correct geometry usage is important, as to avoid wall slippage and wall depletion effects. In Figure 7 are presented the most common rheological measurement geometries. A cone-and-plate geometry is often used as a more advanced tool to evaluate sample properties over a plate-and-plate system, offering the same flow rates across the whole measuring head. On a plate-and-plate geometry the flow rate of the sample is dependent on the distance from the centre. The cone-and-plate counteracts this with a slight angle of 2 degrees. As for a concentric cylinder (bob-and-cup) geometry, it is used to evaluate more liquid substances, as the sample is in a measuring cup.

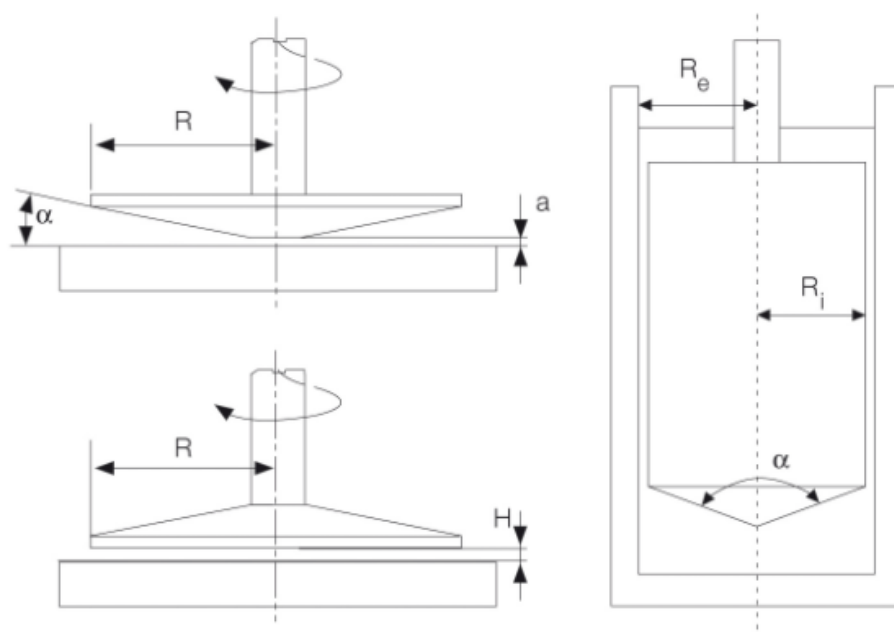


Figure 7 Different measurement geometries, cone-and-plate (top left), parallel plate (bottom left) and concentric cylinder geometry (right) (from: <https://wiki.anton-paar.com/en/basics-of-rheology/>)

In oscillatory measurements, the sample is stimulated with an angular deflection or torque at a given oscillation frequency. The response oscillates with the same frequency and is characterized by a phase shift and an amplitude. The measured data can be used to calculate parameters to characterize the viscoelastic behaviour of the matter. The parameters are storage modulus  $G'$  (elastic modulus), loss modulus  $G''$  (viscous modulus), loss factor  $\tan \delta$ , and the absolute complex viscosity value. (ISO 3219)

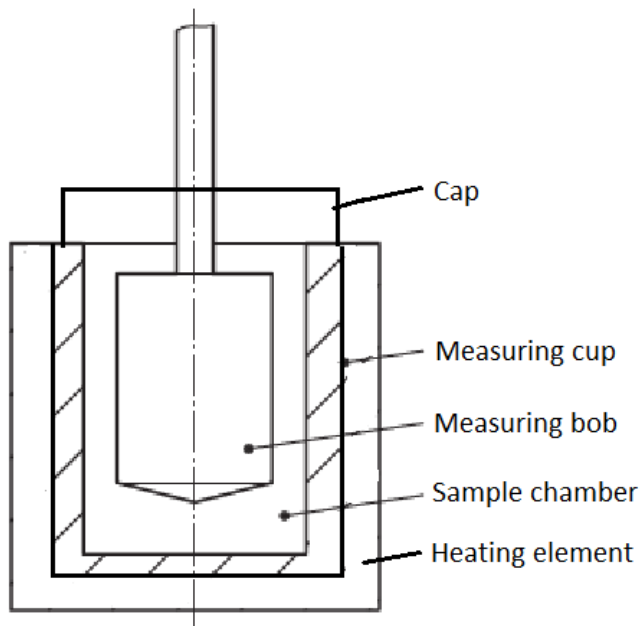
Previous studies have used these storage- and loss moduli to evaluate the gelling of cellulose dopes evaluate the stability of the matter. The cross-over point of  $G'$  and  $G''$  are thought to tell the gelling of the material, though this is false in a sense. The gelling begins to occur before the cross-over point in pseudoplastic substances, such as dope. In simple terms, the sample starts to lag less behind the measuring head as the value of  $G'$  starts to rise. If the sample would keep losing viscosity, the sample would lag behind the measuring head more, giving a higher  $G''$  result. As  $G''$  reaches its lowest point, the gelation begins, as described in Thomas Mezger's Applied Rheology book (2018). Dope itself is shear-thinning, and with added shear, viscosity decreases along with temperature increase. At some point in studies of temperature hysteresis, the viscosity sees an increase in value after time and added temperature, exhibiting the point at which the gelling process begins. The cross-over point

of the loss- and storage moduli can be thought of the point when it is mostly gelatinous. The gelling point and mechanism are still a disputed and unknown subject in cellulose dopes.

Rotational rheometry is a more basic measurement type, where the sample is subjected to either constant, or variable loading in one direction, from which shear viscosity can be calculated. Different geometries help with different problems, choosing the right geometry for the right substance, is important to minimize the error in the results. For testing viscosity, the geometry cannot allow the substance to escape the measuring geometry, for example a bob-and-cup geometry would be viable for low- to medium viscosity samples, while for higher viscosity samples with higher viscosity can be measured using a cone-and-plate, as the sample will not escape the measuring head. A sample may also have additional requirements, such as heat, moisture or air flow.

To choose the correct measuring geometry, the sample and data required to evaluate the sample's properties must be considered. Cellulose dope is a viscous substance, viscosity increasing as time passes and in increasing temperatures as gelling initiates. Moisture and excess airflow on the sample surface may also lead to possible structural changes and gelling, if water droplets get in contact with the sample. Due to prior investigation of temperature and time on dopes (Vehviläinen, 2015; Väisänen 2021; Tatiana, 2017), the effect of shear rate and a constant temperature will be used to try and evaluate and predict the stability of it.

Minimization of wall-slip and wall-depletion should be considered, as normal parallel plate (plate-and-plate) geometry often causes different flows between the measuring head and lower plate. Temperature control is vital when analysing temperature sensitive samples. As dope is temperature sensitive, low viscosity substance, and requires a closed environment for accurate data, concentric cylinder geometry is chosen with a Peltier heating element for temperature control. Moisture and airflow control is achieved with a cap on the cup. A concentric cylinder geometry is best suited for the low viscosity dope samples, as in rotational measurements the low viscosity sample tends to escape the measuring geometry. The geometry used is displayed in Figure 8.



*Figure 8 Used geometry for rotational tests of cellulose dope*

Due to lack of instrument resources, another type of geometry was used, a 50mm parallel plate geometry (for reference, see Figure 7) with a heating element to keep the temperatures constant, though a cone-and-plate would have been a better alternative due to more the geometry having the same flow across the measuring geometry. Measurements conducted in this thesis with this geometry were oscillatory since it was deemed unfit for rotational measurements due to sample slippage. Parallel plate geometries are problematic due to different velocities within the measuring area, leading to inaccurate results, slippage, and wall depletion effects. Parallel plate geometry also allows airflow from the sides, decreasing gelling times for the samples. A plate size of 50mm was chosen purely due to the smaller 25mm plate being unable to accurately measure samples with low viscosities. Generally, a parallel plate geometry is to be avoided in rheometry, and a cone-and-plate geometry be used instead due to the flow rate being the same across the whole measuring geometry. This was not possible in this work, as a cone-and-plate geometry was not readily available.

## 3.2 Rheological measurements

Rheology has many types of measurements, which are used to describe the substances properties and behaviour. This work mainly focuses on two types of rheological measurements, rotational flow sweep measurements and oscillating frequency sweep measurements.

### 3.2.1 Flow sweep

Flow sweep measurements are rotational measurements conducted to show how the sample behaves under shear, e.g., flow behaviour. This is done via inspecting the sample in low shear rates, to determine the sample's zero-shear viscosity (the highest point of viscosity in the measurement) and high shear rates to determine how shear thinning the sample is in the case on pulp samples. Shear thinning is as the name implies, an event where in added shear rates, the sample thins as viscosity decreases. (Thomas Mezger, 2018).

These measurements can be conducted on all measurement geometries, though using a parallel plate geometry is to be avoided as the difference in flow rate depends on the distance from the centre of the geometry, which is mitigated in a cone-and-plate geometry by the angle of the geometry. An example of a flow sweep is presented below, in Figure 9.

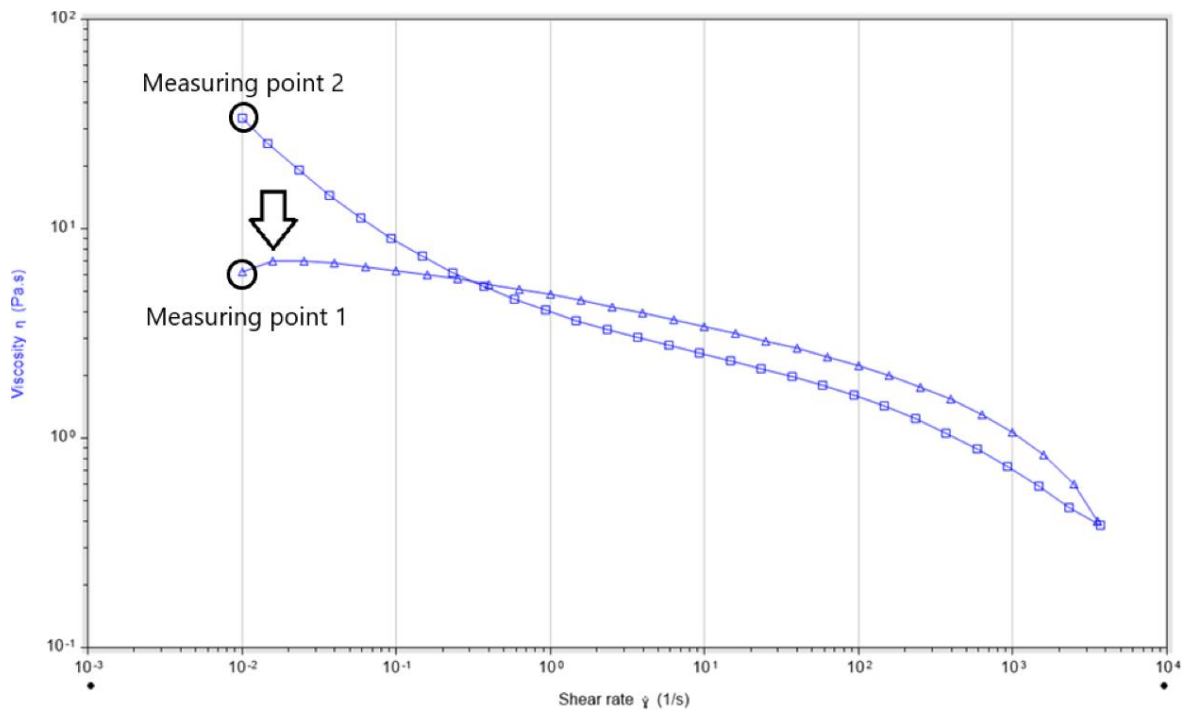


Figure 9 Example of a flow sweep measurement. The highest point of the flow curve down (triangles) is the point at which the sample begins to flow and is called the sample's zero-shear viscosity, marked with an arrow.

In this experiment, data is gathered from the beginning of the experiment, as to find the initial viscosity of the sample, and the end point from the measurement, as to determine how much the sample's viscosity changes under high shear rates.

### 3.2.2 Frequency sweep

Frequency sweeps are utilized to evaluate the sample's structural stability, and how fluid, or solid the sample is. Frequency sweeps are oscillatory measurements, where the instrument evaluates how much the sample lags behind the measuring head, and outputs the samples properties as loss- ( $G''$ ) and storage ( $G'$ ) moduli. When storage modulus values are higher than loss modulus values, the sample behaves more like a solid, than a liquid, which is used in this thesis as an evaluation tool when a sample turns into gel in a set temperature. An example of a frequency sweep is presented below, in Figure 10.

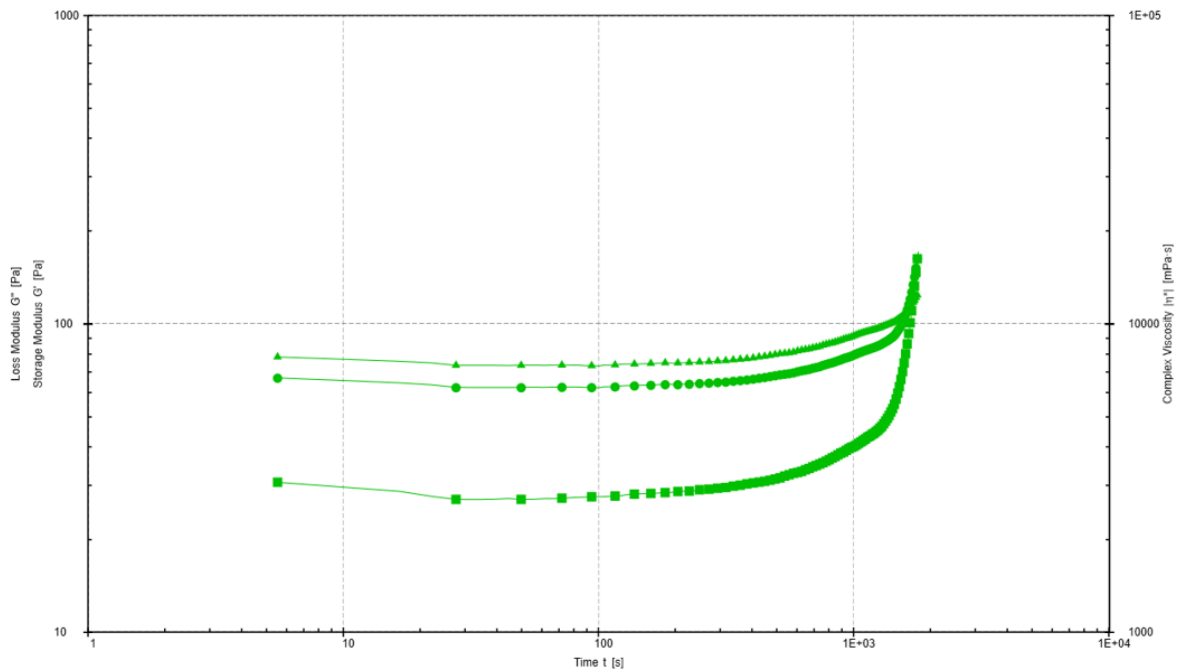


Figure 10 Example of a frequency sweep. Triangles represent the sample's loss modulus, squares represent the sample's storage modulus, and the circles represent the complex viscosity. From the cross-over point of  $G'$  and  $G''$  can be found the gelling point of the sample.

Another type of oscillating measurement can also be utilized by introducing a heat loop to create a temperature hysteresis. In this hysteresis, all measurement conditions are kept constant except for temperature, which is first gradually increased to a certain point with point intervals, and then decreased back to the starting point. This measurement is used to determine the gelation point of a sample in one measurement. The slow, increasing heat allows the sample to assume the temperature of the measuring geometry giving a good indication when the gelling occurs. The points that we are most interested in are the lowest value of storage modulus, viscosity, and the cross-over point of  $G'$  and  $G''$ , as they all correlate to the gelling of the selected dope. An example of a temperature hysteresis is presented below, in Figure 11.



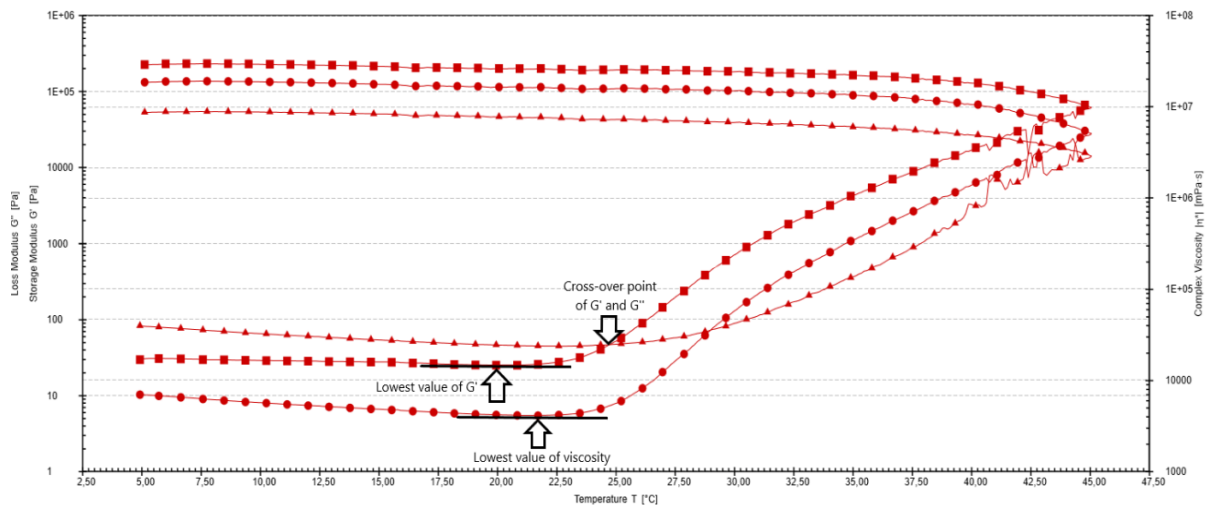


Figure 11 Temperature hysteresis with a point interval of 1°C/minute from 5 to 45°C. The triangles represent the loss modulus,  $G''$  and the squares represent the storage modulus. The circles represent complex viscosity.

This experiment gives good, clear points of data when the sample begins to gel, and eventually forms a gel.

## 4. Experimental work

Here the experimental part of this thesis is laid out and discussed.

### 4.1 Materials and methods

The materials chosen in this work was based on previous experimental work on the pulps provided. Previous on-site tests were used to determine two pulp samples, one that was previously determined stable, and one that was unstable. Then for reference, a new, modified pulp was used. It is to be kept in mind, that dope stability, and performance are highly dependent on the dissolution step, and results may vary even using the same cellulose, which has been a previously known problem. A table of sample properties can be found below, in Table I.

*Table I Sample properties. Sample 1 has previously been easy to dissolve, while sample 2 gelled in testing. Samples 3 and 4 were modified cellulose pulps.*

Sample code	Sample type	Consistency
Sample 1	Good stability	Low consistency
Sample 2	Bad stability	High consistency
Sample 3	Improved stability	High consistency
Sample 4	Improved stability	Low consistency

Pulp was dissolved with four different cellulose contents per sample, 7.0 m-% to 7.6 m-% with an increment of 0.2 m-% in an alkali system. After this, solid impurities were removed and the sample was divided into three parts, two of which for inspecting viscosity changes over time in different conditions (refrigerated and room temperature samples) to see the difference in the MMFCs under different storage conditions, and the final part being the actual sample. This sample would be kept cold until measurement.

Four different pulp materials were used, Sample 1 being a previously well-behaved sample, Sample 2 being a previously worse behaving sample, and Samples 3 and 4 being a new, modified sample. Samples 1 and 4 had low cellulose consistencies prior to dissolution, while samples 2 and 3 had higher consistencies. Unfortunately for samples 3 and 4, the amount of sample received was low, therefore only two tests of each could be conducted, with the cellulose consistencies chosen being 7.0% and 7.6%.

#### 4.2 Brookfield viscosity

An initial viscosity of all samples were measured right after dissolution, the second measurement was done after 24h, after which it was measured after 5 days, 10 days, etc. until the sample had gelled. No sample was measurable after 10 days, most gelling before 5 days. All Brookfield viscosity measurements were conducted on a Brookfield DV1 viscometer. The Brookfield viscometer had an error margin of 60 mPa·s.

#### 4.3 Rheological measurements

All oscillating measurements (temperature hysteresis and frequency sweeps) were conducted on an Anton Paar MCR 72 rheometer, and all rotational measurements (flow sweeps) were conducted on a TA Discovery HR 1 rheometer. For rheological measurements, the same sample was used for both Anton Paar rheometer and TA rheometer. Ideally, only

the TA instruments rheometer would have been utilized, but due to low instrument resources, the Anton Paar rheometer was used. The TA instruments' rheometer would have been the more suitable choice for measurement, as it is more accurate with its air bearing system, and had all the required geometries for measurements, that were not available for the Anton Paar rheometer. The only geometries available for Anton Paar rheometer were a 25, and 50mm parallel plate geometry, which both were non-ideal for oscillatory experiments with low to medium viscosity samples. The Anton Paar rheometer also has a more inaccurate, ball bearing system, which causes the rheometer to misrepresent low viscosity sample viscosity measurements.

The loading of samples was done with a plastic spoon for both rheometers. For the Anton Paar rheometer, as a parallel plate geometry requires the sample to be within the measuring geometry, excess dope had to be wiped from the sides before initiating the measurement. For the concentric cylinder geometry, sample loading was easier, as the measuring geometry had to be submerged into the sample for measurement. For both instruments, the samples were loaded gently, as to avoid formation of bubbles, which could harm the results.

#### 4.3.1 Flow sweep

For the flow sweep, the fresh dope sample was loaded into the measuring cup, and the measuring head was lowered to a set height. The measuring range was 0,01 – 3700 1/s, as this is the maximum shear rate range for the TA rheometer. The measurement consists of a ramp up from 0,01 1/s to 3700 1/s and ramp down from 3700 1/s to 0,01 1/s. This data is then combined, and the resulting difference of viscosity implies the state of gelling for the sample. Lower shear rates help determine the sample's properties at rest, e.g., zero shear viscosity and higher shear rates are used to emulate conditions the dope experiences in a spinneret and in dissolution.

#### 4.3.2 Temperature hysteresis and frequency sweep

Temperature hysteresis range was from 5°C to 45°C with an increment of 1°C/min. This measurement is used to determine approximate gelling temperature for each dope. From the hysteresis, an increase in  $G'$  can be found, which is to be interpreted as the point where initial gelling begins, and soon after  $G'$  starts increasing, viscosity follows. The point at which  $G'$  and  $G''$  cross, is also marked as a point of the sample being a gel. The sample is loaded onto the parallel plate geometry, and the head is then lowered. Excess sample is shaved off the

sides and the measurement is initialized. First, the sample is cooled down to the desired temperature before the experiment is ran. After reaching the desired temperature of 5°C, a waiting period of one minute is started, after which the measurement begins to avoid any stresses to the material before the measurement.

A frequency sweep was conducted in four different set temperatures for all samples, and the sample loading was the same as in the temperature hysteresis. Compared to the temperature hysteresis, the measuring temperatures were the constant for the duration of the measurement. The temperatures, and settings are listed below in Table II.

*Table II Flow sweep measurement settings, the strain was chosen by utilizing previous measurements of linear viscoelastic region, and frequency was chosen to be low, as to avoid sample slippage.*

Measurement	Temperature, °C	Frequency, Hz	Strain, %
First measurement	20	2	5
Second measurement	25	2	5
Third measurement	30	2	5
Fourth measurement	35	2	5

From these frequency sweeps, a gelling point is determined from the cross-over point of  $G'$  and  $G''$ . The gelling times are then gathered and compared. This reflects the temperature sensitivity of the dope.

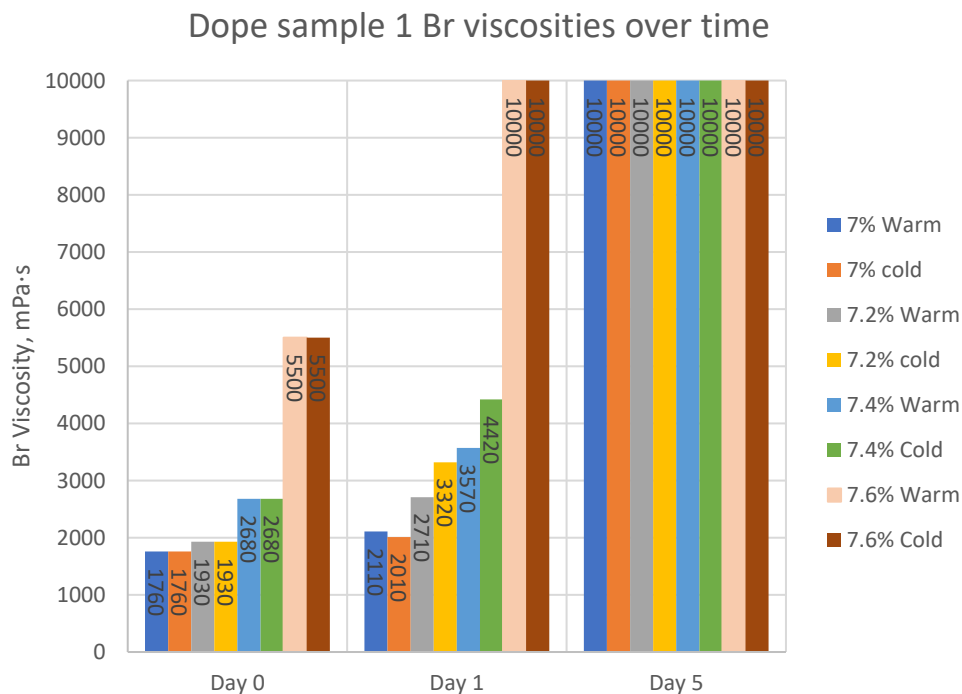
## 5. Results

In this section findings and results of each measurement will be discussed. The conclusions of the measurements are discussed in chapter 6.

### 5.1 Brookfield viscosity

Brookfield viscosity was measured from all samples right after dissolution, after which they were measured on day 5, 10, 15 etc. until gelling. All samples were measured at room temperature (approximately 23°C) to avoid inaccurate results, as cold samples inherently

display higher viscosities in fluids. The results from the Brookfield viscosity measurements for samples 1 and 2 are presented below in Figure 12 and 13, and the results for samples 3 and 4 in Figures 14 and 15. A Brookfield viscosity of over 10000 represents the sample being a gel, as the measuring instrument can only measure samples with viscosities of up to 10000 mPa·s. Identical viscosity results for day 0 are due to them being the same sample until separation for storage.



*Figure 12 Brookfield measurements of pulp sample 1 over time. The warm samples were kept in room temperature, 23°C, and cold samples were kept in a refrigerator, in 4°C.*

All samples behave as expected, with rising viscosities over time, samples with higher cellulose content displaying the highest viscosities. Cold stored samples saw more increase in viscosity than warm stored samples, even though both samples were measured in room temperature. All samples gelled before reaching 10 days.

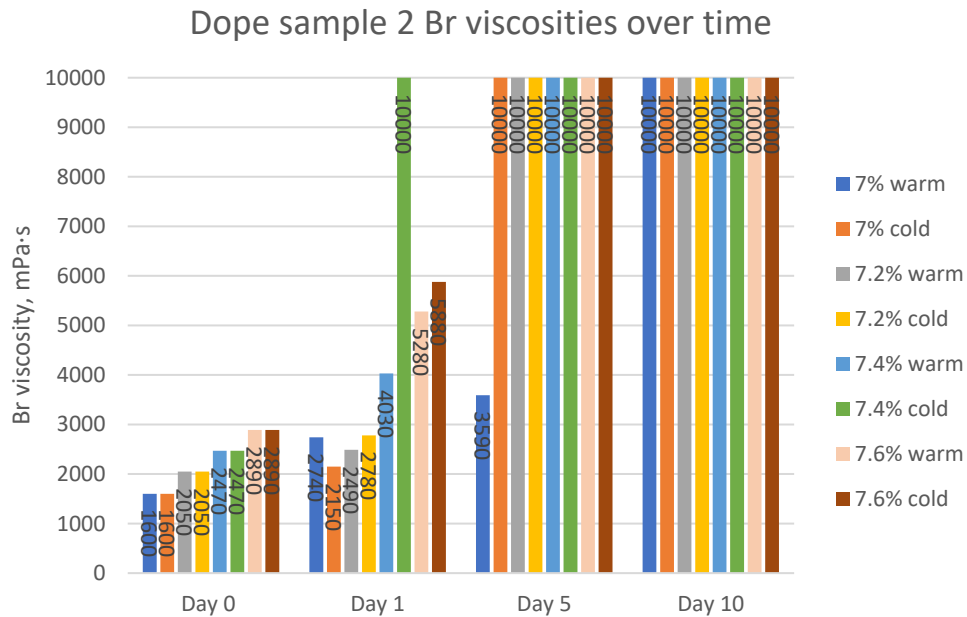


Figure 13 Brookfield measurements of pulp sample 2 over time. The warm samples were kept in room temperature, 23°C, and cold samples were kept in a refrigerator, in 4°C.

As for sample 2, viscosities behaved as expected, with the outlier of the refrigerated sample at 7.4% cellulose content, which gelled after just one day. The sample at 7.0% cellulose content was the only sample that had not gelled 5 days after dissolution. Below are presented the Brookfield viscosities of samples 3 and 4 in Figures 14 and 15.

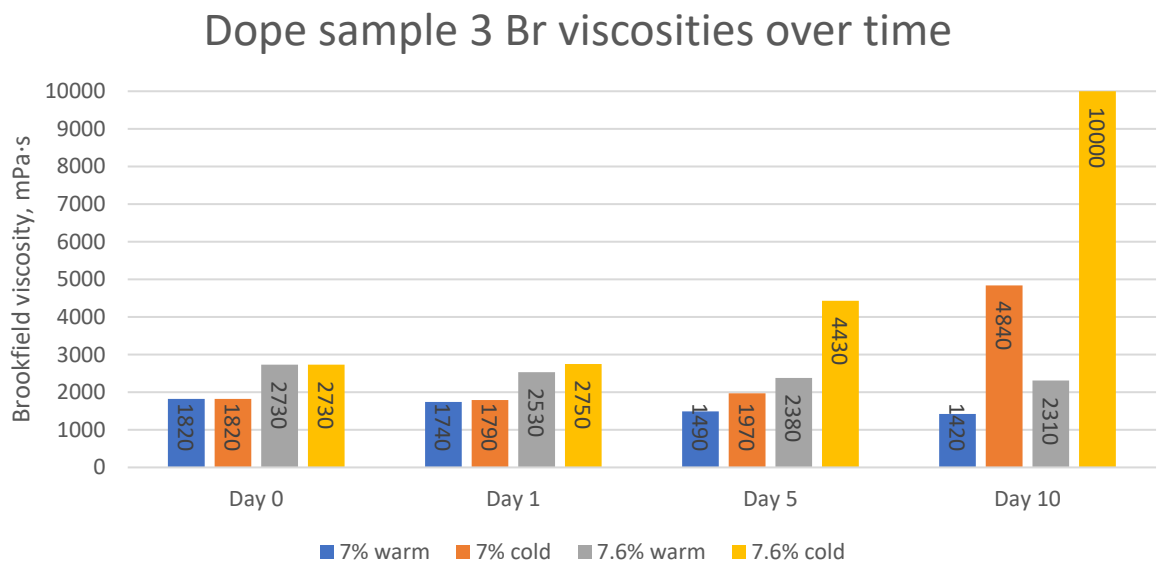
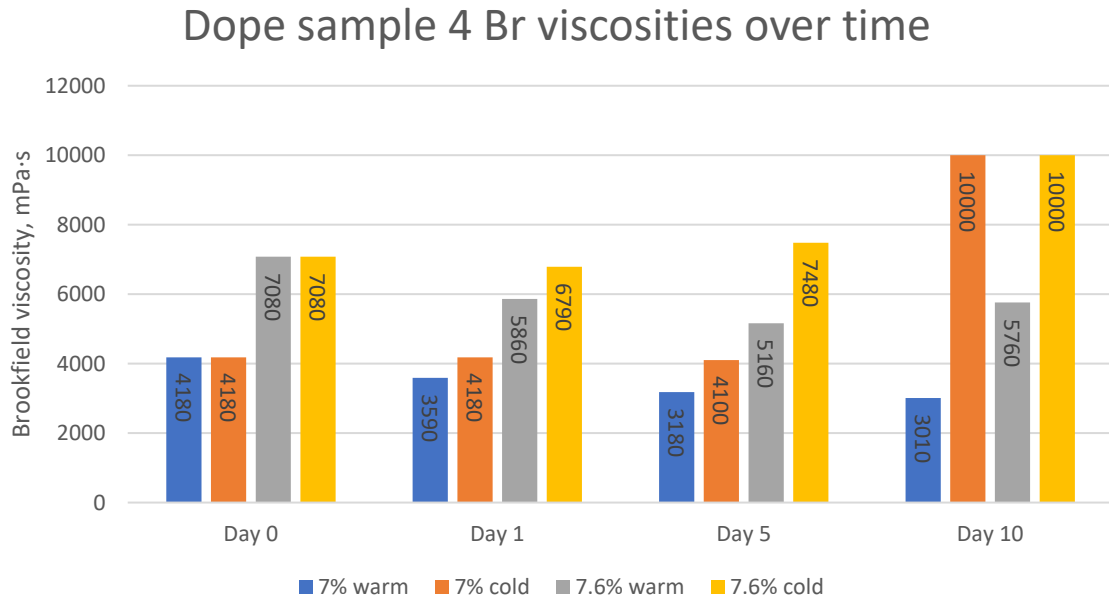


Figure 14 Brookfield measurements of pulp sample 3 over time. The warm samples were kept in room temperature, 23°C, and cold samples were kept in a refrigerator, in 4°C.

From Figure 14 we can see that dope samples with 7% and 7.6% cellulose content stored in room temperature did not have noticeable changes in Brookfield viscosity, while samples that were stored in cold started to see a rise in Brookfield viscosity.



*Figure 15 Brookfield measurements of pulp sample 4 over time. The warm samples were kept in room temperature, 23°C, and cold samples were kept in a refrigerator, in 4°C.*

Sample 4 had interesting results, with the samples retaining their viscosity, and in the case of room temperature stored samples, they lost viscosity over time. Unfortunately, due to time constrictions, follow up measurements after day 10 were not possible.

## 5.2 Temperature hysteresis

A temperature hysteresis was conducted on each sample on the same day as the dissolution. The quicker the sample starts to gel, the worse the temperature stability of the sample. The gelling points, and  $G'$  and  $G''$  cross-over points, and viscosity increase temperatures gathered from the temperature hysteresis are shown in Tables III and IV.

*Table III Sample 1 temperature hysteresis results for each dope.*

Sample 1	T(Gelling), °C	T( $G' = G''$ ), °C	T(Viscosity increase), °C
7,00 %	25,23	29,32	26,24
7,20 %	24,92	28,9	25,01

7,40 %	22,28	26,56	22,28
7,60 %	18,30	24,15	20,95

From Table III we can see that the more cellulose the sample contains, the lower the gelling temperature. The sample containing the highest amount of cellulose starts to gel at a temperature 7°C lower than the least cellulose containing sample. Also, the viscosity increase follows this point of gelling closely. The sample with the highest cellulose content becomes a gel at a temperature 5°C lower than the one with the lowest cellulose content.

*Table IV Sample 2 temperature hysteresis results for each dope.*

Sample 2	T(Gelling), °C	T(G' = G''), °C	T(Viscosity increase), °C
7,00 %	23,91	29,54	25,80
7,20 %	21,84	25,89	22,28
7,40 %	20,08	24,70	21,27
7,60 %	15,55	20,74	18,10

From Table IV we can see similar results to sample 1, the sample with the highest cellulose content starts to gel at a temperature 8°C lower than the one that has the least cellulose content. Viscosity follows the point of gelling closely. The sample with the highest cellulose content becomes a gel at a temperature 9°C lower than the one with the lowest cellulose content. The results for samples 3 and 4 are presented below in Tables V and VI.

*Table V Sample 3 temperature hysteresis results for each dope*

Sample 3	T(Gelling), °C	T(G' = G''), °C	T(Viscosity increase), °C
7,00 %	27,55	33,37	29,63
7,60 %	25,02	29,54	26,11

*Table VI Sample 4 temperature hysteresis results for each dope*

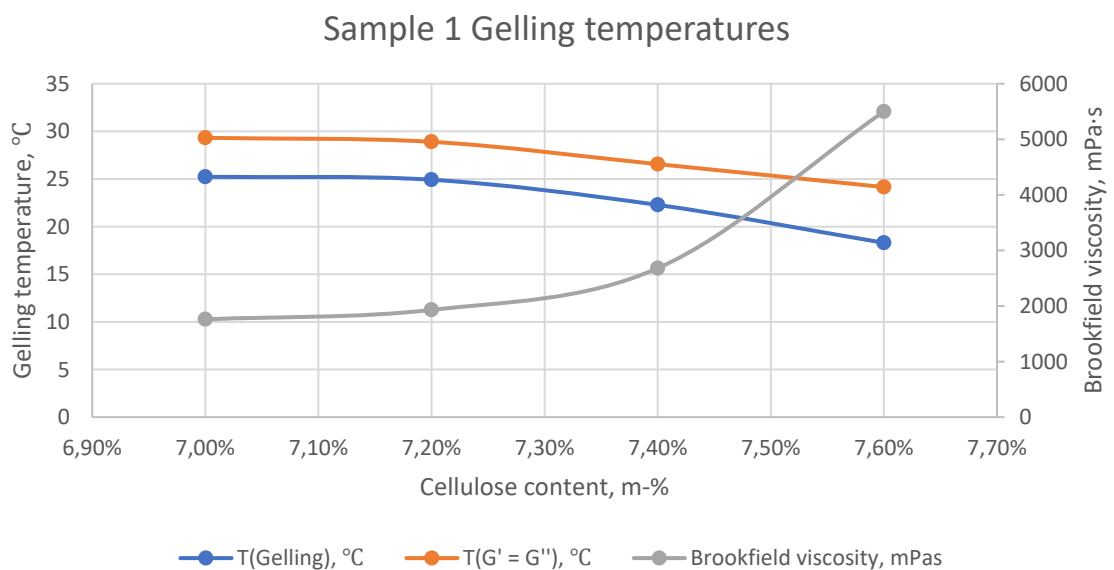
Sample 4	T(Gelling), °C	T(G' = G''), °C	T(Viscosity increase), °C
7,00 %	34,47	38,33	34,59



7,60 %	26,78	32,61	28,88
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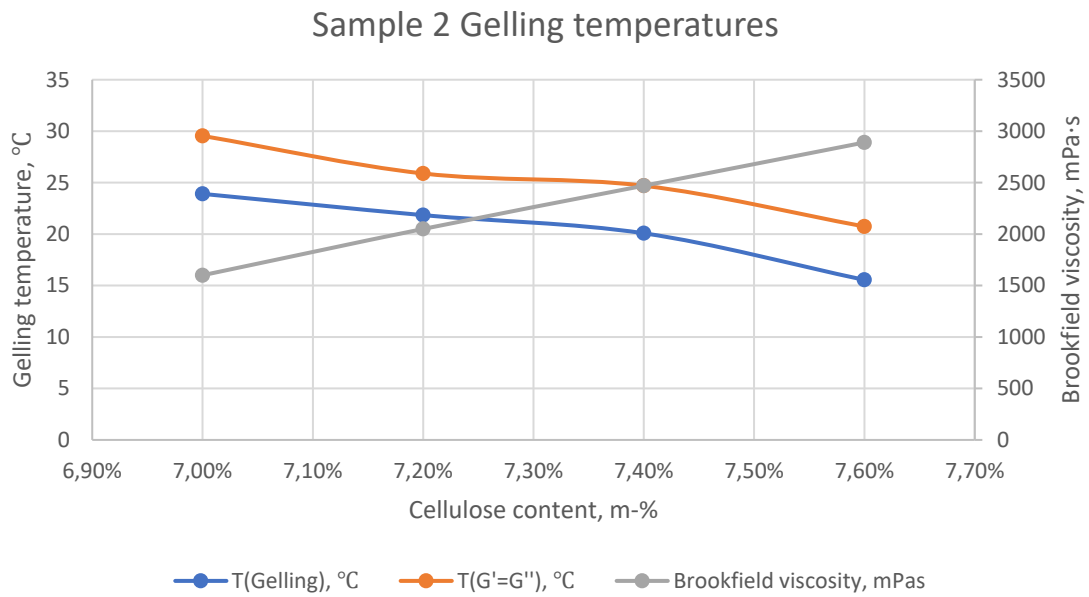
Samples 3 and 4 exhibit a vastly higher gelling temperature compared to the other two, non-modified samples.

As can be seen from the temperature hysteresis results, the temperature activated gelling is linear in most cases, as shown in Figure 16-19. The gelling and cross-over points of  $G'$  and  $G''$  were compared to the Brookfield viscosity of the sample.



*Figure 16 Sample 1 gelling temperatures, blue line representing the start of gelling, orange line representing the point at which the sample is a gel. The grey line is the sample's Brookfield viscosity.*

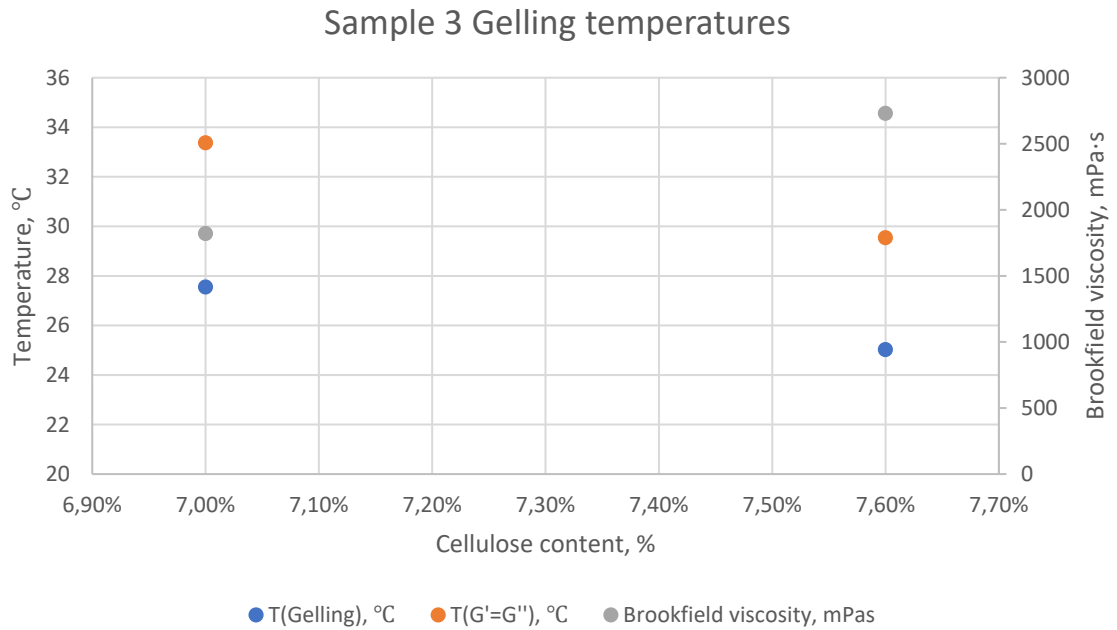
Sample 1 had a steady decline in gelling temperature, which correlated well with the rising Brookfield viscosity of the sample. These results were expected, with gelling temperature decreasing with increased viscosity and cellulose content.



*Figure 17 Sample 2 gelling temperatures, blue line representing the start of gelling, orange line representing the point at which the sample is a gel. The grey line is the sample's Brookfield viscosity.*

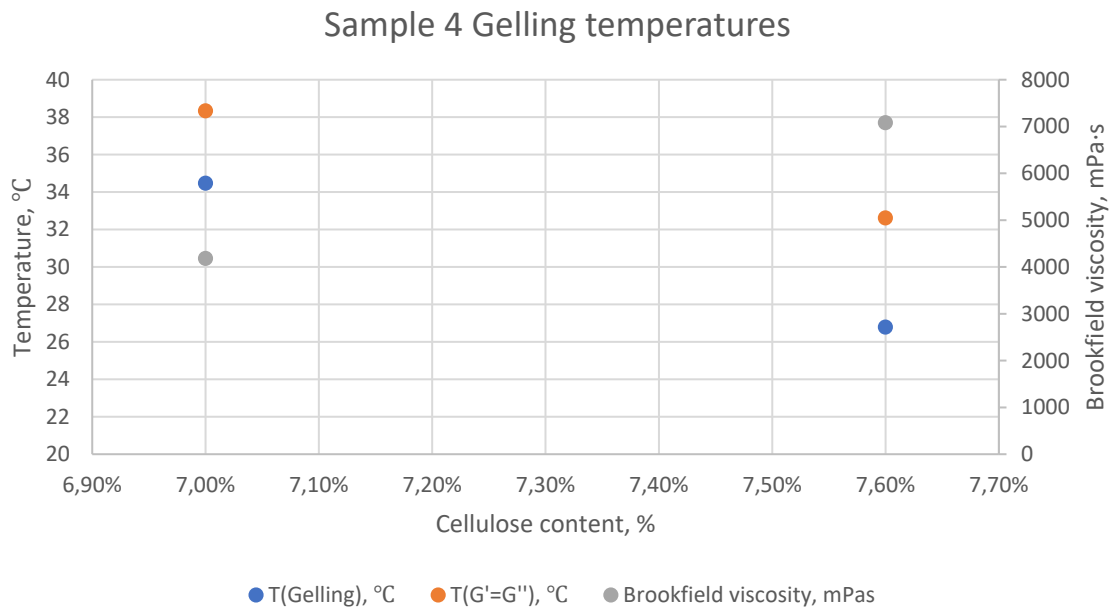
The same can be seen for sample 2, as for sample 1, the gelling temperature decreased as Brookfield viscosity increased. Sample 2 did not perform as well as sample 1, gelling at lower temperatures.

Sample 1 had higher gelling temperatures than sample 2, despite sample 1 having a higher viscosity in the 7.6% dope by 2610 mPa·s. Usually, a vastly higher viscosity would indicate more temperature instability, but this was not the case. Sample 1 is therefore more temperature stable than sample 2.



*Figure 18 Sample 3 gelling temperatures, blue line representing the start of gelling, orange line representing the point at which the sample is a gel. The grey line is the sample's Brookfield viscosity.*

With sample 3 we see a noticeable improvement in gelling temperatures, along with logical results that gelling temperature decreases along with rising Brookfield viscosity. The gelling temperatures also see a vast improvement of over 4 °C over previous samples in the same viscosity region.



*Figure 19 Sample 4 gelling temperatures, blue line representing the start of gelling, orange line representing the point at which the sample is a gel. The grey line is the sample's Brookfield viscosity.*

Sample 4 exhibited the highest Brookfield viscosities, but also the highest gelling temperatures. This indicates that sample 4 is the most temperature stable despite the high Brookfield viscosity.

### 5.3 Frequency sweep

In frequency sweep measurements, measurement conditions were kept constant and gelling times for each sample with different cellulose content was measured and compared. Examples of frequency sweeps of sample 1 and 2 in 7.6% cellulose content are presented in Figures 20-23. You can find all measurement results in the appendix 3.

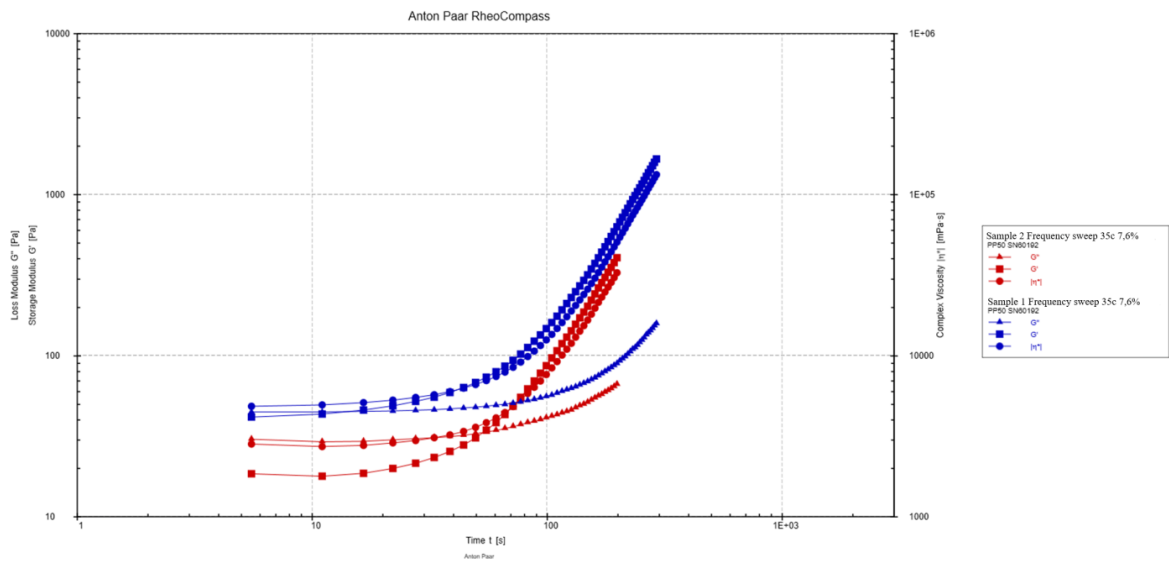


Figure 20 Frequency sweep of both sample 1 (blue) and 2 (red) in 7,6% cellulose content in 35°C. Sample 1 gels faster, as expected, due to higher initial viscosity.

From the curves in 35 °C we can see the cross-over point of  $G'$  and  $G''$  for Sample 1 (10 s) is lower than that of Sample 2's (50 s), indicating that the sample is less stable in high temperatures. Higher initial viscosity is often a good indicator of a less temperature stable sample, leading to faster gelling. This is based on the DP of the sample, and the concentration of cellulose in the sample. A higher concentration leads to a higher viscosity, and this leads to lower stability. (Vehviläinen, 2015)

This can also be seen in other frequency sweeps, Figures 20-22.

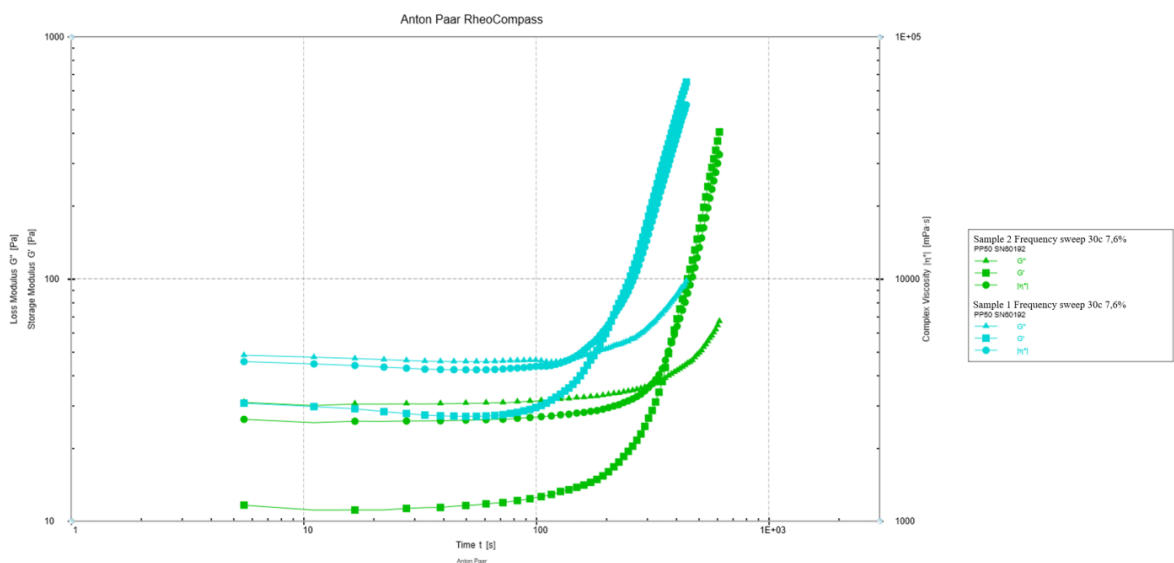


Figure 21 Frequency sweep of both sample 1 (cyan) and 2 (green) in 7,6% cellulose content in 30°C. Sample 1 gels faster, as expected, due to higher initial viscosity.

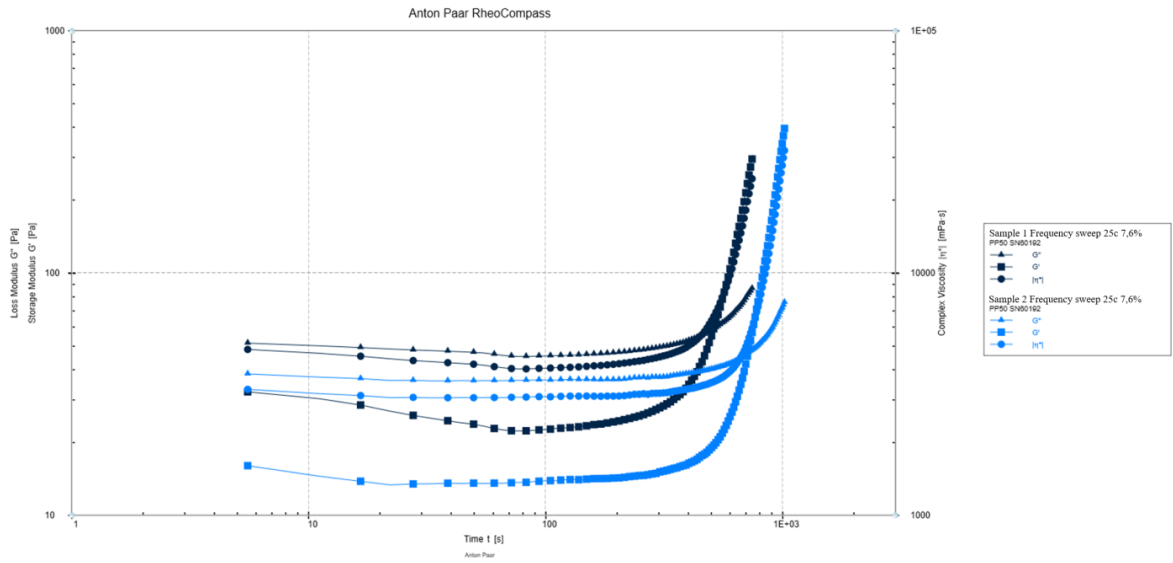


Figure 22 Frequency sweep of both sample 1 (black) and 2 (blue) in 7,6% cellulose content in 25°C. Sample 1 gels faster, as expected, due to higher initial viscosity.

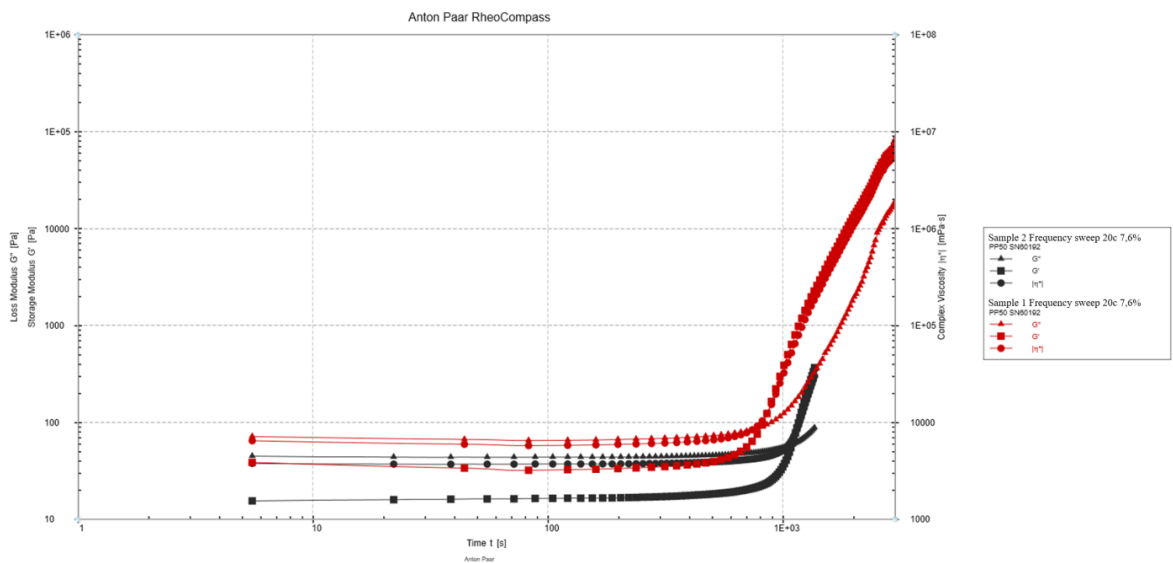
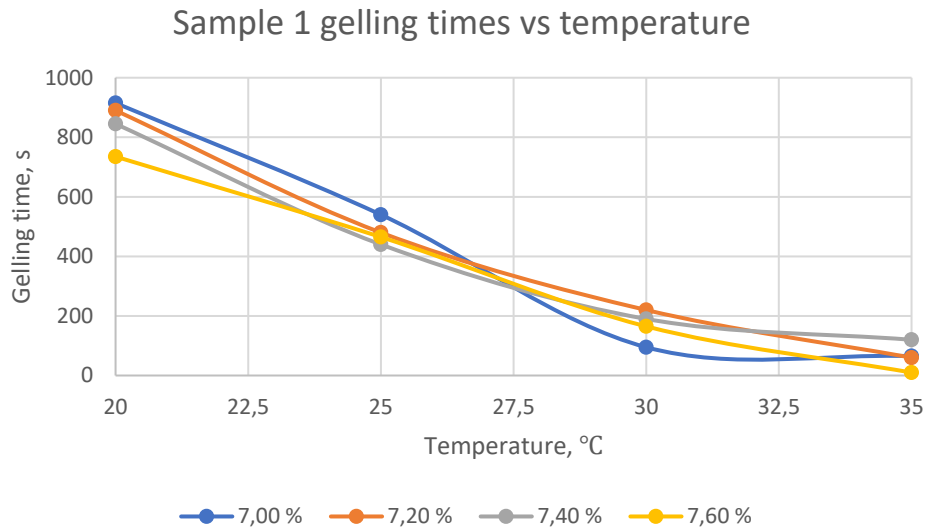
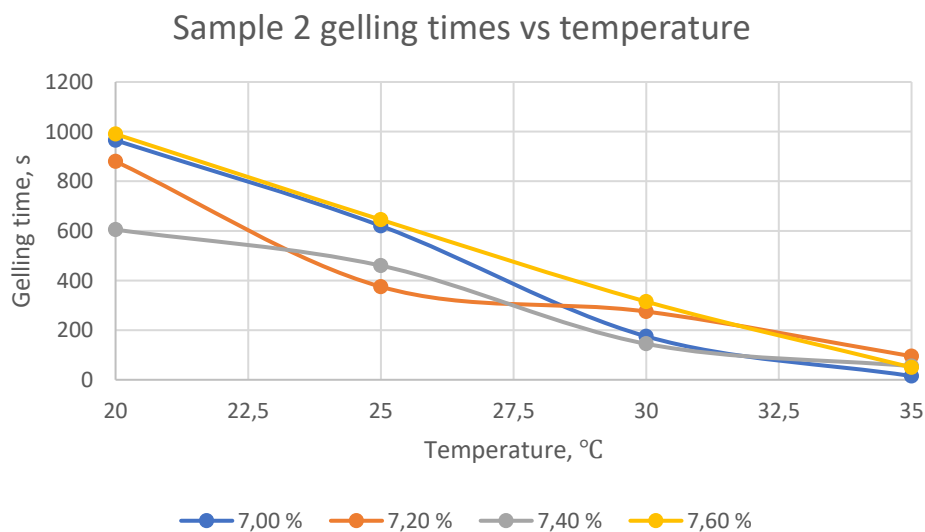


Figure 23 Frequency sweep of both sample 1 (red) and 2 (black) in 7,6% cellulose content in 20°C. Sample 1 gels faster, as expected, due to higher initial viscosity.

As can be seen from Figures 20-23, Sample 1 is less stable than Sample 2 in all temperatures. Below in Figures 24 and 25 are presented all the gelling times of samples with their correlating cellulose content.



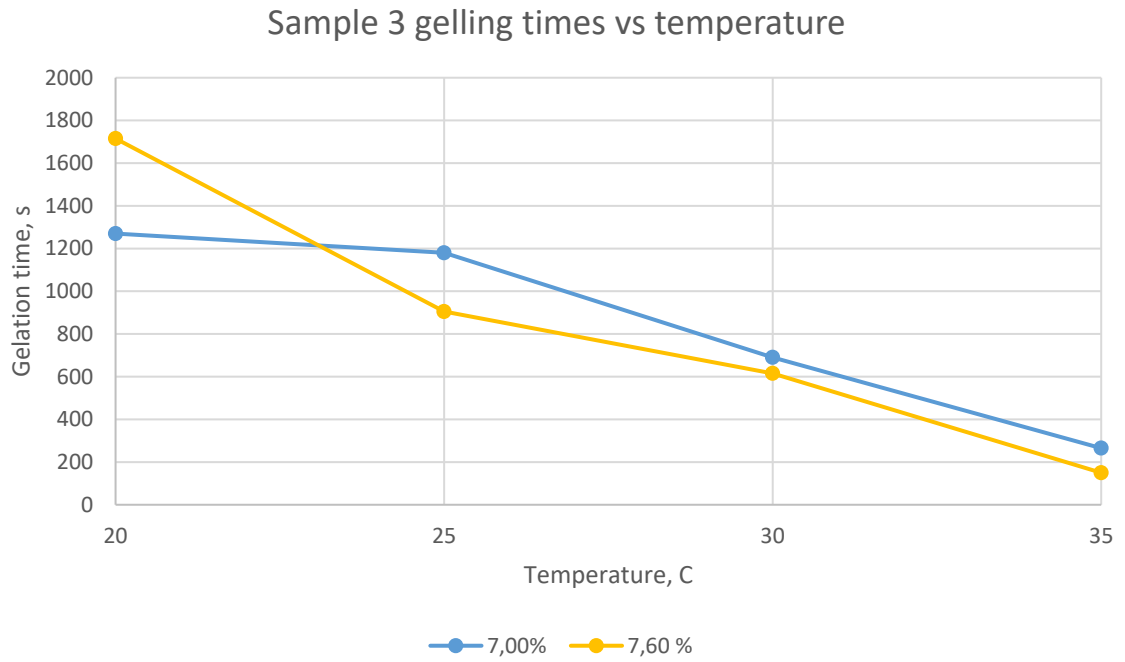
*Figure 24 Sample 1 gelling times as a function of temperature gathered from frequency sweep experiments.*



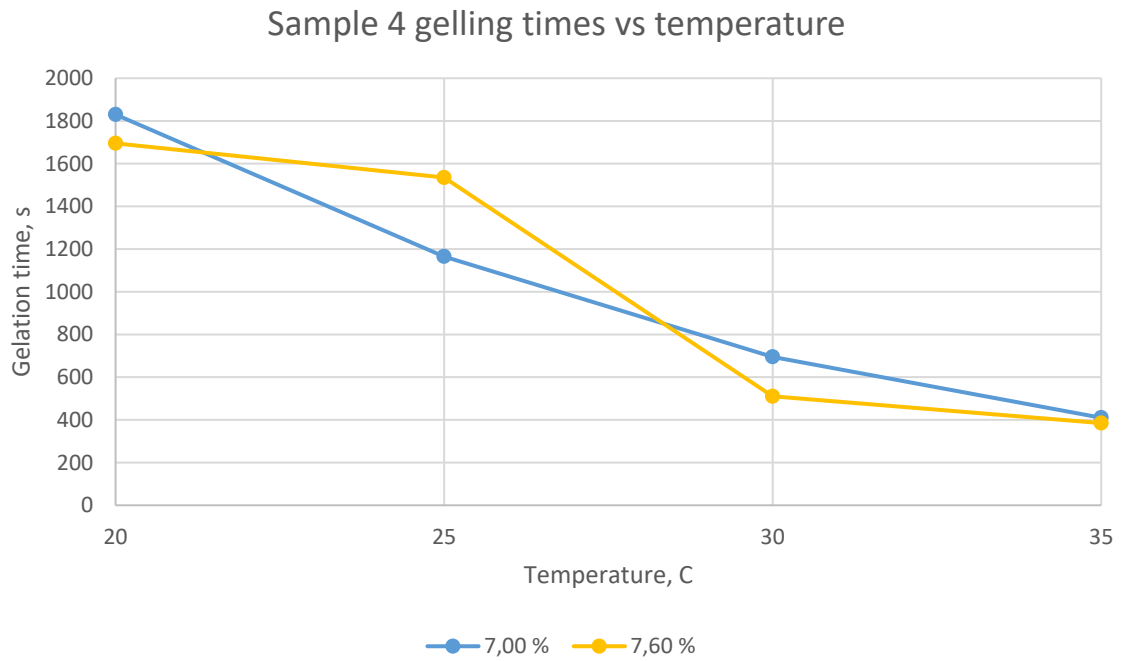
*Figure 25 Sample 2 gelling times as a function of temperature gathered from frequency sweep experiments.*

From these gelling times, we can see that Sample 2 is more temperature stable than Sample 1. The only sample that exhibited lower temperature stability for Sample 2 was the 7.4% cellulose content sample, which may be a result of a measuring error, problems in dissolution, or the sample handling was poor.

For samples 3 and 4, the gelling times are presented in Figures 26 and 27.



*Figure 26 Sample 3 gelling times as a function of temperature gathered from frequency sweep experiments.*



*Figure 27 Sample 4 gelling times as a function of temperature gathered from frequency sweep experiments.*



The results of samples 3 and 4 are vastly superior to samples 1 and 2, with sample gelling times being multiple times higher in some temperatures. These results are further analysed in chapter 6.2.

#### 5.4 Flow sweep

For evaluating dope performance under high shear, a flow sweep with a ramp up from 0,01 to 3700 1/s and ramp down from 3700 to 0,01 1/s was used, and the difference in viscosity calculated. An example of a flow sweep is presented in Figure 28.

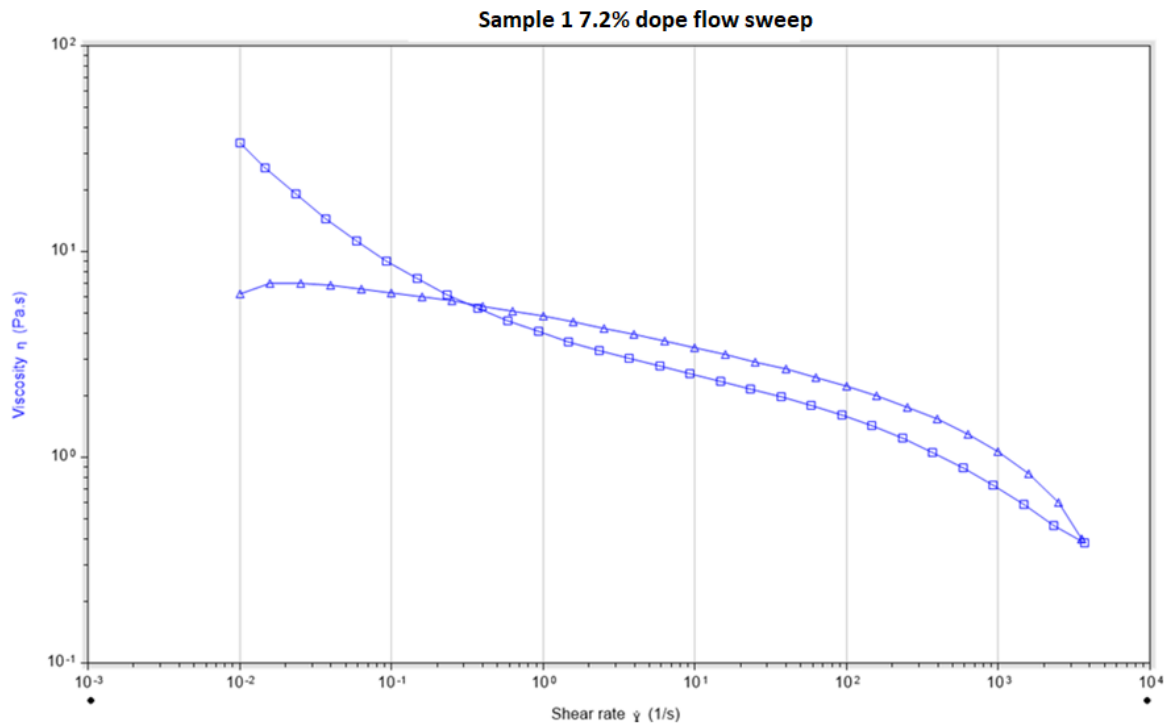


Figure 28 Example of a flow sweep measurement on sample 1, 7.2% dope. The measurement points with triangles are the ramp down from 3700 1/s to 0,01 1/s, and squares represent the ramp up.

The measurement was conducted in 15°C to avoid the effect of temperature on gelling. Below, in Figures 29 and 30 is presented the results for samples 1 and 2.

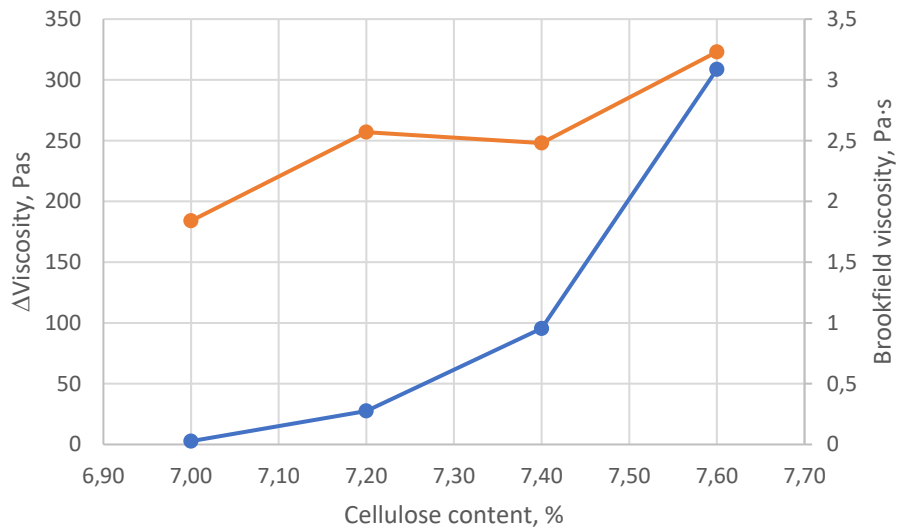


Figure 29 Flow sweep results for Sample 1, blue line represents the change in viscosity after measurement, orange line represents the sample's Brookfield viscosity.

From Figure 29 we can see that Brookfield viscosity of the sample does not necessarily match with the outcome of the test. Brookfield viscosity of the sample is affected by the dissolution phase in sample preparation, and cellulose content.

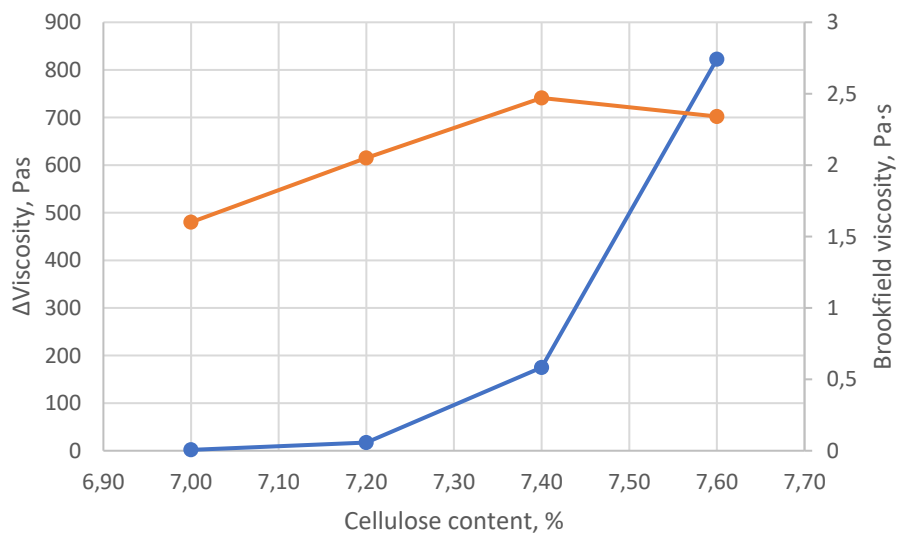


Figure 30 Flow sweep results for Sample 2, blue line represents the change in viscosity after measurement, orange line represents the sample's Brookfield viscosity.

From Figure 30 we can see that the growth in difference in viscosity is exponential. This could be seen from the samples, with 7.6% dope being a stiff gel, and other samples still being fluid.

For samples 3 and 4, the results are presented below in Figures 31 and 32.

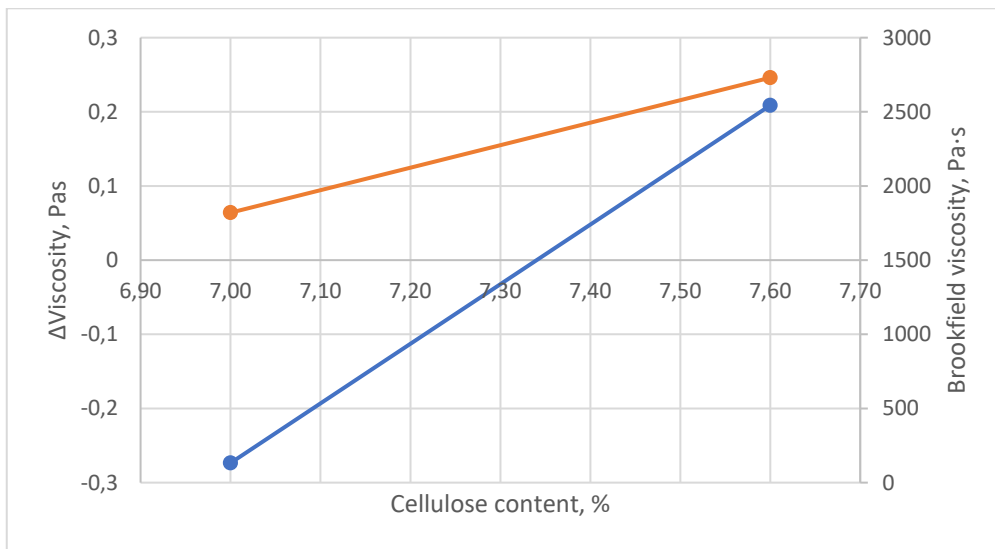


Figure 31 Flow sweep results for Sample 3, blue line represents the change in viscosity after measurement, orange line represents the sample's Brookfield viscosity.

From Figure 31 we can see that the sample 3 had minimal, if any change in structure after the flow sweep measurement, the 7% dope exhibiting a lower viscosity than in the beginning. The lower viscosity means that the sample's structure did not change during measurement.

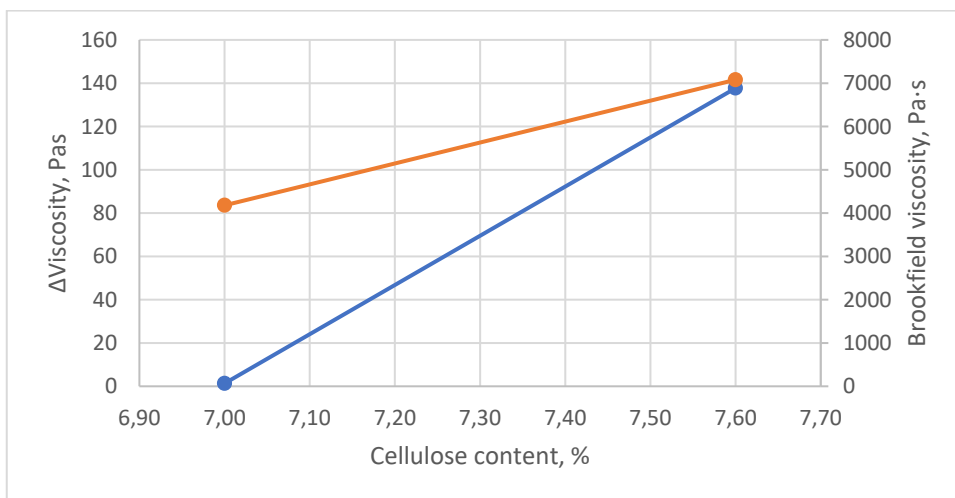


Figure 32 Flow sweep results for Sample 4, blue line represents the change in viscosity after measurement, orange line represents the sample's Brookfield viscosity.

From Figure 32 we can see that the sample did not gel as much as the non-modified samples 1 and 2 but had worse performance than sample 3. In comparison to samples 1 and 2 the change in viscosity was much lower, indicating less gelling.

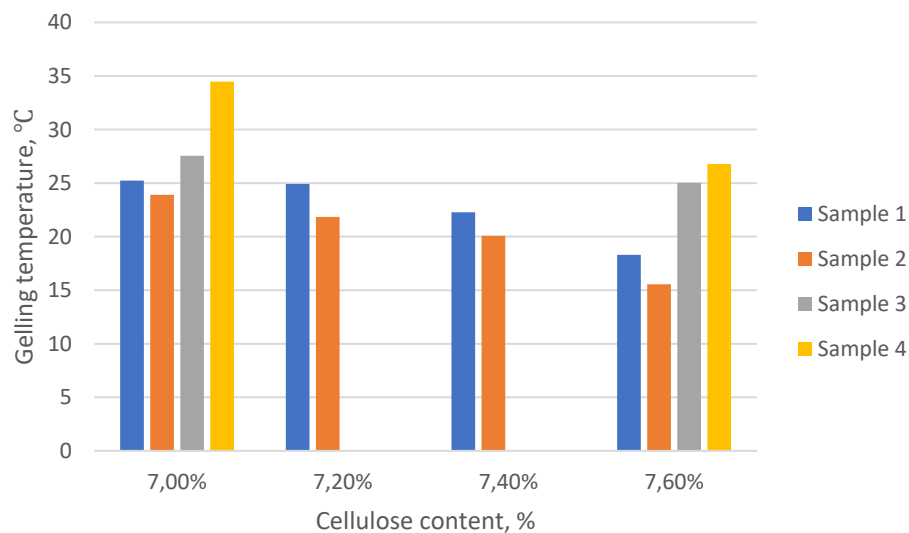
## 6. Results and discussion

Here, all results from experiments are discussed and the suitability of the measurement is evaluated whether it is a good indicator of dope stability.

### 6.1 Temperature hysteresis

Temperature hysteresis is a good, single measurement tool to evaluate stability of dope and it was successfully used to move the gelation point via increasing, or decreasing the cellulose content of the sample, exhibiting a good predictor when the sample gels with previous measurements, as the increase or decrease of the gelling point was linear. Though keeping in mind, that different flow rates in a parallel plate geometry give approximate results. The samples also display faster gelling from the edges, as they are exposed to air, and as the measurements are long, approximately 90 minutes long, the gelling influences the results. Still, a comparison of the two samples did show differences that were a bit contradictory to

the results from frequency sweeps. Below the results of the temperature hysteresis are presented in Figure 33, where the beginning of gelling is displayed for each sample.



*Figure 33 Temperature hysteresis gelling temperatures*

From Figure 33 we can see that in all cellulose contents, Sample 1 is the most stable. This is contrary to the results gathered from frequency sweeps at different temperatures, where Sample 2 outperformed Sample 1 in almost all temperature categories. Samples 3 and 4 were in their own league compared to the other samples, displaying a much higher gelling temperature with sample 4 performing the best. In Figure 34 is displayed the temperature of cross-over point of  $G'$  and  $G''$  and in Figure 35 the point of viscosity increase.

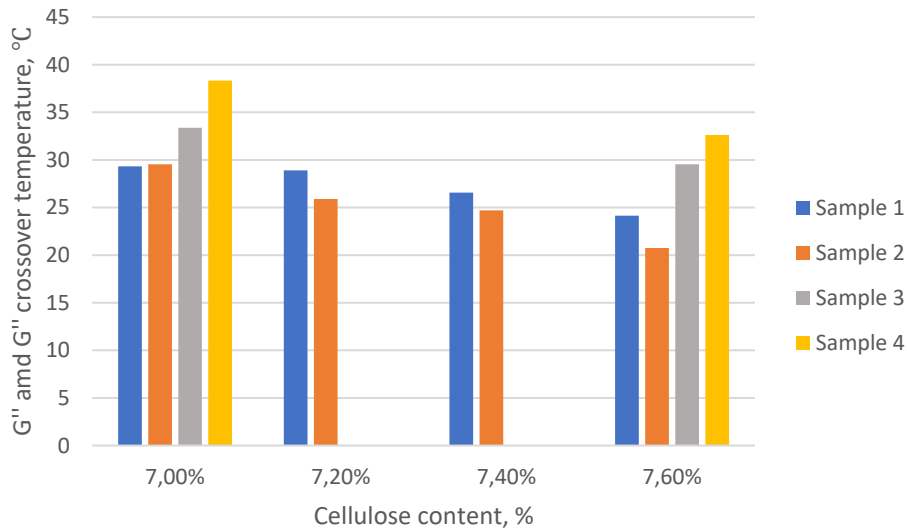


Figure 34 Cross-over points of  $G'$  and  $G''$  for all samples. Samples with modified cellulose, samples 3 and 4, are the most stable, gelling long after the other samples.

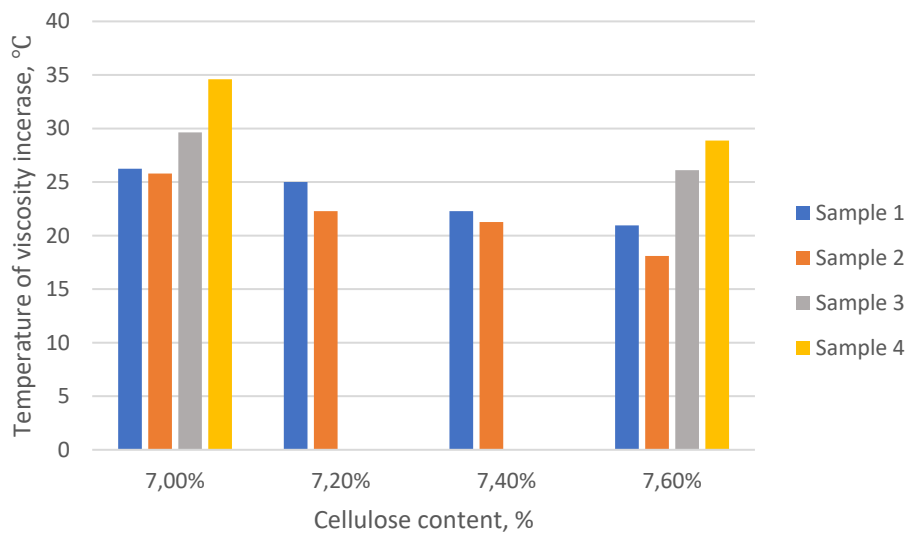


Figure 35 Temperature of viscosity increase for all samples. The increase in viscosity is in line with other results of temperature hysteresis, with the samples with modified cellulose displaying higher temperature requirement for an increase in viscosity (indicating gelling).

Below in Table VII is presented the comparison of samples 1 and 2, and in Table VIII is presented the comparison of samples 3 and 4. Differences of gelling temperatures, cross-over point of  $G'$  and  $G''$ , and temperature of viscosity increase are compared to each other with negative values indicating worse performance compared to the other.

*Table VII Differences of temperature required for gelling, viscosity increase, and cross-over point of  $G'$  and  $G''$ . Positive values indicate Sample 1's better performance, in degrees Celsius, over Sample 2.*

Cellulose content	$\Delta T(\text{Gelling}), ^\circ\text{C}$	$\Delta T(G' = G''), ^\circ\text{C}$	$\Delta T(\text{Viscosity increase}), ^\circ\text{C}$
7,00 %	1,32	-0,22	0,44
7,20 %	3,08	3,01	2,73
7,40 %	2,2	1,86	1,01
7,60 %	2,75	3,41	2,85

Sample 1 would be more temperature stable according to the temperature hysteresis by a few degrees, the biggest differences being in 7.2% and 7.6% cellulose content samples.

*Table VIII Differences of temperature required for gelling, viscosity increase, and cross-over point of  $G'$  and  $G''$ . Positive values indicate Sample 3's better performance, in degrees Celsius, over Sample 4.*

Cellulose content	$T(\text{Gelling}), ^\circ\text{C}$	$T(G' = G''), ^\circ\text{C}$	$T(\text{Viscosity increase}), ^\circ\text{C}$
7,00 %	-6,92	-4,96	-4,96
7,60 %	-1,76	-3,07	-2,77

Sample 4 outperformed sample 3 in all categories by a significant margin, indicating a better overall temperature stability.

## 6.2 Frequency sweep

From this experiment it can be seen that initial viscosity is a good indicator of temperature stability, as samples with higher initial viscosity gelled faster. This type of measurement was quick to conduct, as the longest measurements lasted close to 1000 seconds, with the shortest being mere seconds. The fact that the measurements are short, means that the sample does not have time to form a gel on the outer rim, which would harm the results.

In Table IX is presented the difference in gelling times between Sample 1 and 2. The results are the difference between Sample 1 and Sample 2, negative values indicating that Sample 1 gelled that number of seconds faster than Sample 2.

*Table IX Frequency sweep results between samples 1 and 2. Negative values indicate faster gelling of Sample 1 compared to Sample 2.*

Comparison	20°C	25°C	30°C	35°C
7,00 %	-50 s	-80 s	-80 s	50 s
7,20 %	10 s	105 s	-55 s	-35 s
7,40 %	240 s	-20 s	45 s	65 s
7,60 %	-255 s	-180 s	-150 s	-40 s

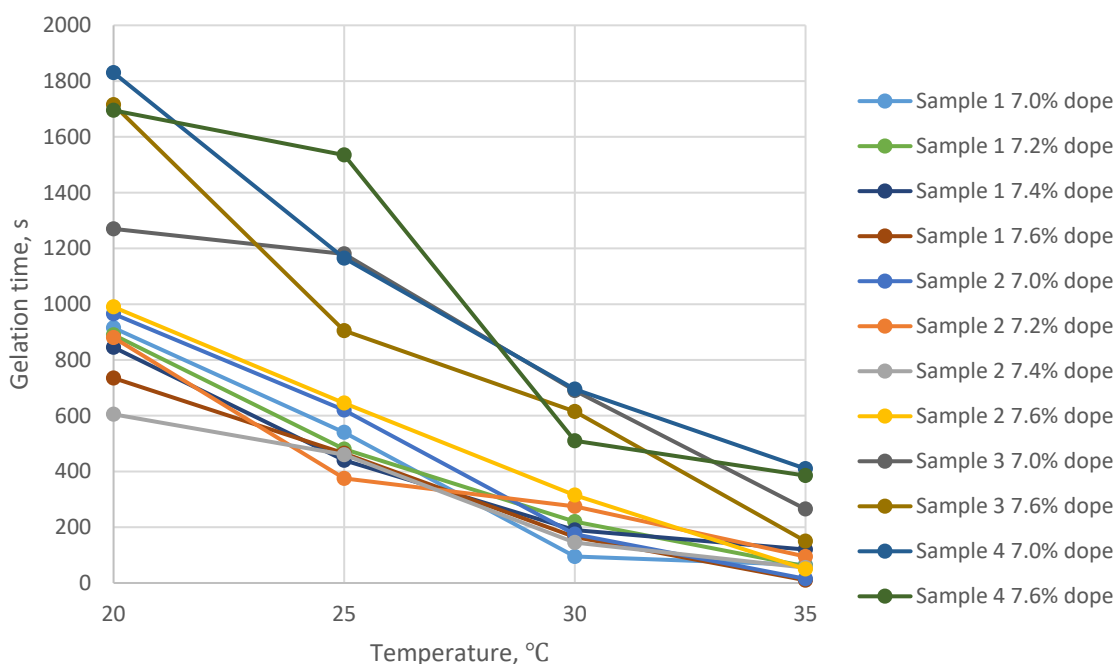
From Table IX we can see that Sample 1 is less temperature stable in almost all temperatures, though in 7,4% cellulose content Sample 1 seems to behave better than Sample 2. In the case of 7,4% must be noted, that initial viscosity of both samples was close to each other, and all results were close to each other, drawing a conclusion that the first measuring point was not successful. In Table X are presented the frequency sweep results between samples 3 and 4.

*Table X Frequency sweep results between samples 3 and 4. Negative values indicate faster gelling of Sample 3 compared to Sample 4.*

Comparison	20°C	25°C	30°C	35°C
7,00 %	-560 s	15 s	-5 s	-145 s
7,60 %	20 s	-630 s	105 s	-235 s

Sample 4 performed vastly better in almost all temperatures, indicating a better stability. Compared to samples 1 and 2, they both outperformed their stability clearly, this is illustrated below in Figure 36.





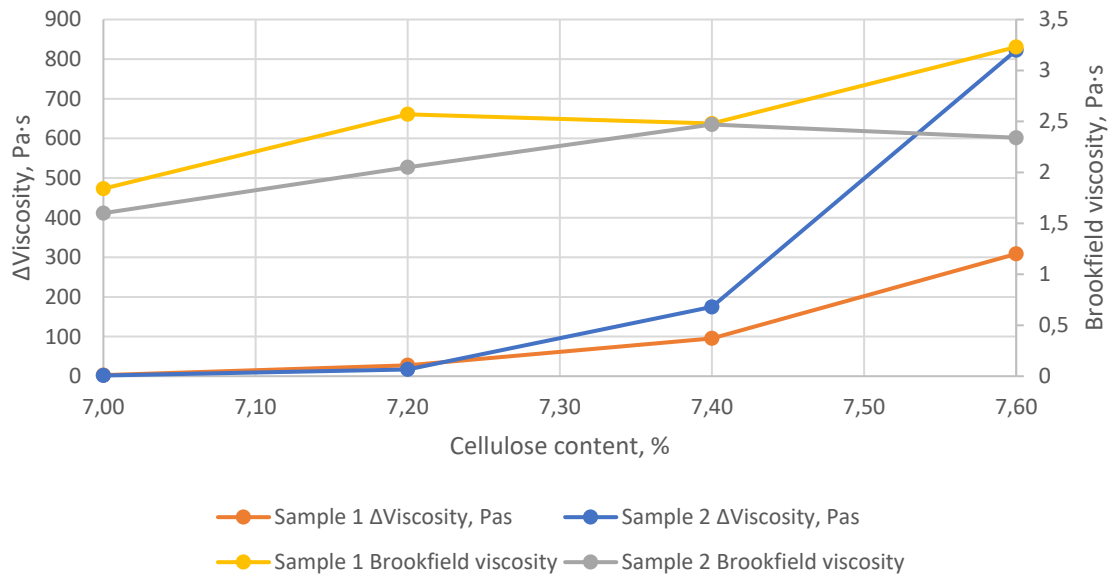
*Figure 36 Dope gelation times in seconds as a function of temperature.*

The tool itself serves its purpose well in helping to predict the sample gelation times, as in temperature hysteresis. The data gathered is mostly linear, with gelling time decreasing with rising temperatures. This tool can be used to predict when at which temperature a sample will start to gel. The gelling point can be moved by adjusting either the temperature, or cellulose content. The long measurement times for samples 3 and 4 were problematic, as gelation from the edges due to contact with air would have more time to affect the results, and the measurements could not be replicated due to insufficient amount of material provided for reference. The main takeaway from these results is that the modified cellulose was more stable, and this measurement was able to detect that.

### 6.3 Flow sweep

The purpose of the flow sweep measurements was to evaluate dope performance under high shear by subjecting it to high shear rates and measuring the viscosity difference at the end of the measurement. As the measurement was conducted in 15°C, the effect of temperature on the gelling was minimized. From the results of the measurements, we can see an exponential growth in viscosity when moving from 7.0% to 7.6% cellulose content dope. This shows, that in increasing cellulose content samples, the dope gels more. The increased amount of

cellulose increases the interaction between the chains, forming a gel faster than with lower amounts of cellulose, along with heat caused by internal friction. Even in the case of sample 2, where the 7.6% dope exhibited lower initial Brookfield viscosity, the viscosity increase from the measurement was vastly different. The comparison of Samples 1 and 2 is presented below in Figure 37.



*Figure 37 Flow sweep comparison of Sample 1 (orange line) and Sample 2 (blue line). Sample 2 exhibits a very large difference in viscosity compared to Sample 1 at higher cellulose contents. Sample 1 (yellow line) displayed a higher Brookfield viscosity, and better performance under high shear than sample 2 (Gray line).*

From Figure 37 can be seen that Sample 1 behaves much better under high shear, keeping its fluid form, whereas Sample 2 gelled completely into a stiff gel, displayed in Figure 38.



Figure 38 Picture of Sample 1 (left) and 2 (right) after flow sweep tests.

The results indicate that the sample's Brookfield viscosity does not directly correlate with its performance in high shear conditions. Sample 1 had higher Brookfield viscosities than Sample 2 in all measurements. Below in Figure 39 is presented the flow sweep comparison of samples 3 and 4.

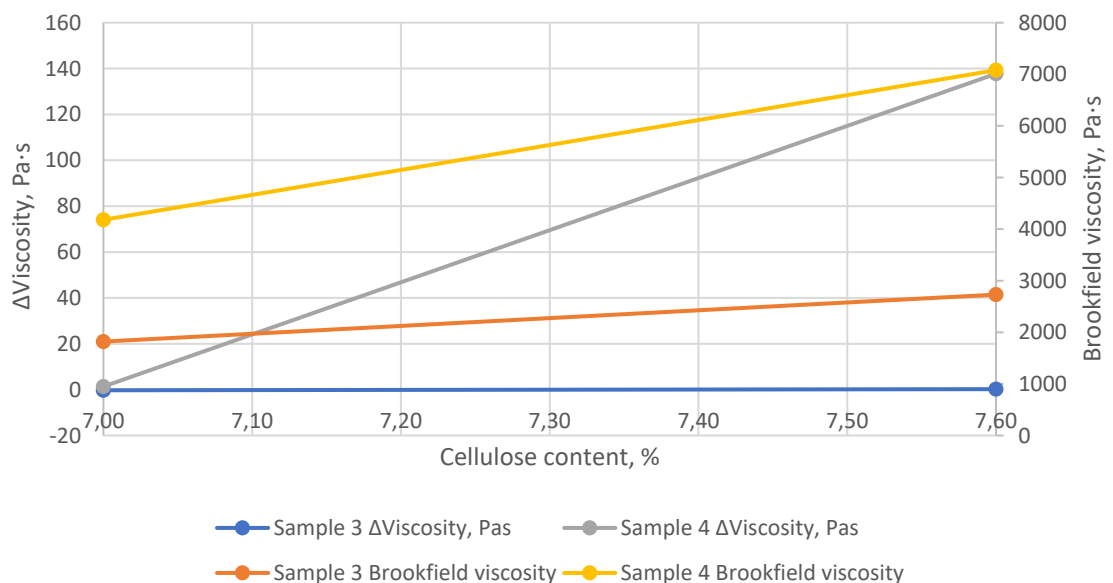


Figure 39 Flow sweep comparison of Sample 3 (blue line) and Sample 2 (grey line). Sample 4 exhibits a very large difference in viscosity compared to Sample 3 at higher cellulose contents, with Sample 3 having almost no change in viscosity after measurement. Sample 3 (orange line) displayed a lower Brookfield viscosity than sample 4.

From Figure 39 we can see that sample 3 did not gel at all during measurement, while sample 4 exhibited a growth in viscosity similar with samples 1 and 2. This unaffected viscosity implies that sample 3 does not gel under high shear.

## 7. Conclusions

The purpose of this thesis was to find methods of evaluating dissolved pulp (dope) stability. Three different methods were tested, temperature hysteresis, frequency sweep and flow sweep. All chosen measurement types succeeded in evaluating dope stability. As a prediction tool, the gelling could be adjusted by either reducing cellulose content or adjusting temperature in the system. Though, flow sweep tests only succeeded in evaluating dope performance, and cannot be used as a prediction tool. From these tests, you could predict the gelling times in different temperatures due to linearity of data. In temperature hysteresis tests, by changing the pulp content in the dope the gelling points could be moved, and were linear, as seen in chapter 5.2. Additionally, to other methods tested the Brookfield viscosity and the gelling points were correlative, with increasing viscosity the sample's gelling point was lowered.

Frequency sweep results had interesting results. Samples with higher initial viscosity, and higher cellulose content, with non-modified pulp dope had faster gelling times than lower viscosity samples as expected. In the case of modified pulp samples, sample 4 performed better than sample 3 despite having a higher Brookfield viscosity, indicating better stability. Unlike previous samples where high, 4000, and 7000 mPa·s Brookfield viscosities were recorded, the sample exhibited the most time until gelling.

Temperature hysteresis results were contradictory with frequency sweep results regarding samples 1 and 2 and had a few contradicting measurement points for samples 3 and 4. The reason for these different results is up to debate. The only difference between the measuring type was the way temperature was handled. In frequency sweeps, the temperature was constant, and started higher, 20°C at the lowest, while in temperature hysteresis, the temperature started as low as 5°C. The difference in temperature in the measurements may indicate that samples may have better stability in higher temperatures, and others in lower temperatures, which would explain the two contradicting results. To study this, further studies of different storage conditions should be studied, in conjunction with these measurements, whether they reflect dope stability well while also confirming the results gathered.

The flow sweep tests also showed interesting results. Non-modified pulp dope showed that the sample with a higher Brookfield viscosity, sample 1, performed better than the lower Brookfield viscosity sample 2. In the case of modified pulp dope the results were as expected, and sample 3 with lower Brookfield viscosity performed well, displaying no change in viscosity after flow sweep experiments, while sample 4 exhibited a slight rise in viscosity, but still lower than non-modified samples. Previously Brookfield viscosity has been a good indicator for stability in dope, with lower viscosities indicating higher stability, but in this case a higher viscosity sample performed better under shear with non-modified samples, and worse with modified pulp dopes. Once again in this experiment, modified pulp dope performed better than non-modified samples.

One other observation was the obvious significance of the Brookfield viscosity of each sample, which already gave a clear indicator whether the sample was temperature stable, and how the viscosity increases in time, i.e., how fast the sample gels. It is to be noted, as previously mentioned that even if a dope displays lower viscosity, it does not mean that it will not gel under high shear slower than dopes with higher viscosity. Brookfield viscosity by itself can be used as a reference in dope shelf-life stability comparison, as samples with high viscosity will reach a gel-like state sooner. It also was well correlating with the other results, a higher Brookfield viscosity for the same sample by adjusting the amount of cellulose in the dope resulted in a more unstable dope, decreasing gelling times and temperatures.

Sample's 3 and 4 modified cellulose dopes performed better than conventional cellulose samples outright, with better temperature stability in all three experiments, flow sweep, frequency sweep and temperature hysteresis. Their viscosity in storage was unchanged, performance under high shear excellent, and gelling temperatures were much higher.

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Appendix 1. Results from Temperature hysteresis tests

Sample 1	T(Gelling), °C	T(G' = G''), °C	T(Viscosity increase), °C
7,00 %	25,23	29,32	26,24
7,20 %	24,92	28,9	25,01
7,40 %	22,28	26,56	22,28
7,60 %	18,3	24,15	20,95

Sample 2	T(Gelling), °C	T(G' = G''), °C	T(Viscosity increase), °C
7,00 %	23,91	29,54	25,8
7,20 %	21,84	25,89	22,28
7,40 %	20,08	24,7	21,27
7,60 %	15,55	20,74	18,1

Sample 3	T(Gelling), °C	T(G' = G''), °C	T(Viscosity increase), °C
7,00 %	27,55	33,37	29,63
7,60 %	25,02	29,54	26,11

Sample 4	T(Gelling), °C	T(G' = G''), °C	T(Viscosity increase), °C
7,00 %	34,47	38,33	34,59
7,60 %	26,78	32,61	28,88



Appendix 2. Brookfield viscosity measurement results and temperatures.

Storage	Sample 1	Day 0	Day 1	Day 5
Warm	7,00 %	1760(20,2c)	2110(23,2c)	GEL
Cold			2010(22,1c)	GEL
Warm	7,20 %	1930(21c)	2710(22c)	GEL
Cold			3320(20c)	GEL
Warm	7,40 %	2680(20,4c)	3570(22,1c)	GEL
Cold			4420(21,9c)	GEL
Warm	7,60 %	5500(12c)	GEL	
Cold			GEL	

Storage	Sample 2	Day 0	Day 1	Day 5	Day 10
Warm	7,00 %	1600(20c)	2740(19,6c)	3590(22,1c)	GEL
Cold			2150(20,3c)	GEL	
Warm	7,20 %	2050(19,6c)	2490(20,4c)	GEL	
Cold			2780(20c)	GEL	
Warm	7,40 %	2470(21,7c)	4030(23,1c)	GEL	
Cold			GEL		
Warm	7,60 %	2890(22c)	5280(22,2c)	GEL	
Cold			5880(22c)	GEL	

Storage	Sample 3	Day 0	Day 1	Day 5	Day 10
Warm	7,00 %	1820(21,1c)	1740(22,8)	1490(22,5c)	1420(23,1c)
Cold		1820(21,1c)	1790(22,1c)	1970(21,3c)	4840(21,5c)
Warm	7,60 %	2730(21,7c)	2530(22,1c)	2380(22,4c)	2310(23,1c)
Cold		2730(21,7c)	2750(22,1c)	4430(22,1c)	GEL

Storage	Sample 4	Day 0	Day 1	Day 5	Day 10
Warm	7,00 %	4180(23,2c)	3590(22,3c)	3180(22,1c)	3010(22,1c)
Cold			4180(21,8c)	4100(21,4c)	GEL
Warm	7,60 %	7080(21,1c)	5860(21,3c)	5160(21,9c)	5760(22,3c)
Cold			6790(20,6c)	7480(20,4c)	GEL

Appendix 3. Frequency sweep test results, gelling times.

Sample 1	20°C	25°C	30°C	35°C
7,00 %	915 s	540 s	95 s	65 s
7,20 %	890 s	480 s	220 s	60 s
7,40 %	845 s	440 s	190 s	120 s
7,60 %	735 s	465 s	165 s	10 s

Sample 2	20°C	25°C	30°C	35°C
7,00 %	965 s	620 s	175 s	15 s
7,20 %	880 s	375 s	275 s	95 s
7,40 %	605 s	460 s	145 s	55 s
7,60 %	990 s	645 s	315 s	50 s

Sample 3	20°C	25°C	30°C	35°C
7,00 %	1270 s	1180 s	690 s	265 s
7,60 %	1715 s	905 s	615 s	150 s

Sample 4	20°C	25°C	30°C	35°C
7,00 %	1830 s	1165 s	695 s	410 s
7,60 %	1695 s	1535 s	510 s	385 s