Dissolution of cellulose pulp using molten salt hydrates

CAISY KADER, Master Thesis Report (Materials Chemistry and Nanotechnology master program, CTH)

Department of Chemical and Biological Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

Cellulose is the world's most abundant polymer and has through centuries been applied into different aspects of life. In the search for developing new sustainable materials for future applications cellulose has become an exciting green material and today have much research devoted towards finding new use of the biopolymer such as in the textile industry. However, due to the low solubility of the cellulose structure in common solvent systems, such as water and many organic solvents, it has proven to be a challenge to dissolve and process cellulose in solvent systems featuring low environmental impact and low cost. Among some solvent systems which have been successful in dissolving cellulose are ionic liquids and alkali-based solvent systems. In this thesis work, main focus will be dedicated towards finding the underlying dissolution mechanisms that take place when cellulose is dissolved in concentrated aqueous salt system using different anions and cations. For all of the concentrated salt aqueous solutions, the cation and the water content of the aqueous salts are of high importance and affect the dissolution efficiency of the specific hydrated salt systems upon dissolving cellulose. The concentrated salt aqueous solutions chosen for this project were inspired by the Hofmeister series and could be categorized into zinc hydrated salts and chloride hydrated salts. Dissolution trials with varying conditions were designed to give the optimum dissolution of the microcrystalline cellulose (MCC) where analytical testing methods such as rheology measurement and degradation methods were applied to analyze the solvent–cellulose interactions and the state of cellulose dissolved in the hydrated salt systems and provided analytical data for each dissolution condition. Through observations from dissolution trials and results gained from analytical tests it was concluded that the aqueous salt systems $ZnCl_2$:H_2O and ZnI_2:H_2O provides good dissolution of cellulose whereas the remaining molten salts provided no dissolution of cellulose. Observations which could be made suggested a better dissolution of MCC upon using higher stirring rate during the dissolution process. Moreover, it could also be noted that concentrated salt aqueous solutions which contains the Zn^{2+} cation had a higher degree of dissolution compared to the aqueous salts containing Cl^-, which gave indications of having a higher contribution given by the Zn^{2+} cation upon dissolution. A better correlation in regards of the dissolution efficiency can be given for salt hydrates containing the Zn^{2+} cation compared to the Cl^- anion which provides little correlation upon dissolving MCC for the different hydrated salts. Upon comparing the hydrated salt systems $ZnCl_2$:H_2O and ZnI_2:H_2O both solvent systems provided good dissolution of cellulose but showed minor differences in rheological behavior.

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1. Introduction

1.1 Aims and objectives

In all aspects of modern industries, sustainable developments are taking place to encourage forth new technology. Especially, in the development of new sustainable materials, research has become highly dedicated towards finding new bio-based polymers for different applications. For instance, cellulose derived from wood has become of high interest in regards of producing new sustainable alternatives for bio-based materials. It is an exciting green material that can be applied in many different areas such as the textile industry. However, due to special intra- and inter-molecular interactions cellulose has a very unique solubility pattern; it is a very challenging compound for processing and reshaping into new materials. As a result of the low solubility of the cellulose in common solvents, it is often required to use environmentally hazardous and/or costly systems to dissolve cellulose. Therefore, finding environmental friendly and economically feasible solvent systems, such as concentrated inorganic salt aqueous solutions, is extremely important. In this thesis the main focus will be dedicated towards finding the underlying dissolution mechanism for dissolving cellulose in different aqueous salt systems and how these mechanisms correlate when using different anion and cation compositions at different ratios of water.

2. Background

2.1.1 Cellulose and applications

Cellulose is the most abundant organic biopolymer existing on Earth and exists in the cell wall of all green plants. The function of the cellulose is to ensure the structure of the cell wall and provide mechanical stability to the species. With a high annual rate of growth and an already large existing volume, cellulose is today used in either its native or derivate form in a wide range of industries of which pharmaceuticals and the textile industry is a growing sector. Considering that the cellulose molecule is a renewable, biodegradable and environment-friendly biomaterial, a major interest in the use of the biopolymer for different applications is today under development where industries in different areas are showing an increased interest in its future applications. For instance, the fuel and energy sectors have more recently begun to utilize cellulose for energy purposes whereas other components of the wood, such as hemicellulose and lignin, have become of great interest for producing the biofuels bioethanol and biodiesel (1).

2.1.2 The cellulose structure

Cellulose is a homo polysaccharide based on the monomer anhydroglucopyranose unit (AGU) with the molecular formula $C_6H_{10}O_5$ (1). The AGU monomers are connected together by the β-(1→4)-glycosidic bonds which are formed between carbon atom C_1 and the C_4 of an adjacent unit, see figure 1(1).

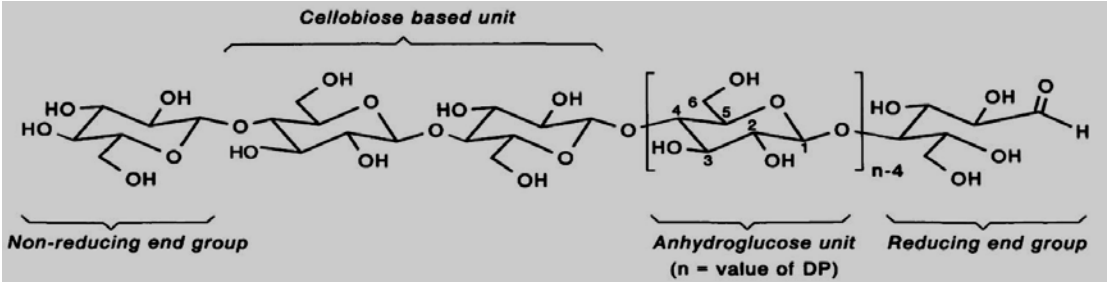

Figure 1. The molecular structure of cellulose (adapted from Klemm et al. 2001b) (1)

This biopolymer has a 2-fold screw axis along the chain direction (3) resulting in the 180° rotation of every second AGU in order to adjust the desired bond angles of the β-(1→4) glycosidic bond (1). The cellobiose, consisting of a dimer of AGUs monomers, can be regarded as the basic unit of the cellulose molecule. Through this analysis it is possible to refer to the cellulose macromolecule as a linear and unbranched polymer with the same monomer as repeating unit (1).

It has previously been derived from X-ray diffractions and NMR measurements that each AGU monomer in the cellulose chain is assumed to have a $^4C_1$ chair conformation (1) resulting in the hydroxyl groups (OH) and the hydrogen atoms becoming situated at the equatorial and axial plane, correspondingly. Given this structure, cellulose will have an intrinsically structural anisotropy, with major differences in polarity for each side of the molecule; while the equatorial direction of a glucopyranose ring has a hydrophilic character because all three hydroxyl groups are located on the equatorial positions of the ring, the axial direction of the ring is hydrophobic since the hydrogen atoms of C–H bonds are located on the axial positions of the ring. This is believed to result in the intricate interactions taking place in the cellulose structure in the form of special intra and intermolecular interactions but foremost has contributed to the cellulose structure´s amphiphilic nature governed mainly by hydrophobic interactions (1,2).

The degree of polymerization (DP) of the cellulose macromolecule can vary from 100 to 20,000 depending on the origin of the cellulose. Also depending on the source and the preprocessing of the cellulose, different degree of crystallinity can be obtained from different cellulose samples. Cellulose, in its native form, possesses a highly crystalline structure due to the presence of extensive intra- and intermolecular hydrogen bonding network existing between the layers of cellulose chains (figure 2).

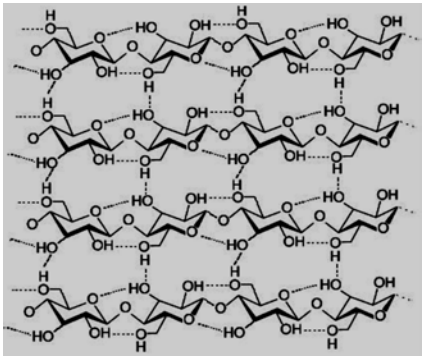

Figure 2. The intra- and intermolecular bonds within the cellulose structure (University of Cambridge 2011) (1)

These intra- and intermolecular interactions illustrated in figure 2 and hydrophobic interactions cause the unique solubility pattern of cellulose. For full dissolution to occur both the intra- and intermolecular hydrogen bonds have to effectively become disrupted and the hydrophobic interactions have to be weakened by a proper solvent system (3).

2.2 Different solvents for cellulose

As previously mentioned, due to the close packing of numerous inter- and intramolecular hydrogen bonds it becomes rather difficult to dissolve cellulose in water and in most of the conventional organic solvents. Until today, only a limited number of solvent systems have successfully been implemented into an industrial scale and often suffer from various environmental problems as well as energy and safety issues (4).

The dissolution of cellulose can take place in different types of solvent systems and these can be categorized as a "derivatizing solvent system" and "non-derivatizing solvent systems". The derivatizing solvent system uses chemical modification (formation of soluble modified cellulose intermediate) whereas in the latter category no chemical modification is done of the cellulose chemical structure (3).

2.2.1 Derivatizing solvent systems

The method for dissolving cellulose using prior chemical modification of the macromolecule is common and used to a large extent. The main objective is to functionalize the hydroxyl groups of the cellulose structure and cause a disruption of the intra- and intermolecular hydrogen bondings with minimal chain degradation (see figure 3) (3). The advantages of chemical functionalization reactions of cellulose are the complete availability of hydroxyl groups which further enhances the control of the degree of substitution (DS) and the distribution of functional groups along the separated cellulose chain (5). Types of functionalization reactions of the cellulose structure include nitration, xanthation, esterification and etherification. However, the solubility of the derivatized cellulose depends on the type of derivatization and the extension of the derivatization process (3).

A traditional technology which is often used for dissolving cellulose is the so called "viscoseprocess" which involves derivatization of cellulose (formation of cellulose xanthate) but has several serious environmental drawbacks (1,2). Most of the polar solvents used for dissolving cellulose often retain certain drawbacks such as high cost, high toxicity, and difficulty in solvent recovery or extreme processing conditions. Therefore, it has become of high desire to develop less energy consuming and more environmentally friendly solvent systems with high efficiency for dissolving cellulose (1,2). Since the aim of this thesis is to focus on the dissolution mechanism involving non-derivatizing solvent systems, detailed descriptions of derivatizing processes are beyond the scope of this review and will not be further discussed. Nevertheless, some examples of derivatizing solvent systems can be found in table 1.

2.2.2 Non-derivatizing solvent systems

As suspected, the non-derivatizing solvent systems consist of solvents which are capable of dissolving cellulose without prior chemical modification. These solvent systems often include ionic liquids, organic solvents in the presence of an inorganic salt, amine oxides, aqueous alkali solutions, aqueous complex solutions, and inorganic molten salt hydrates (3).

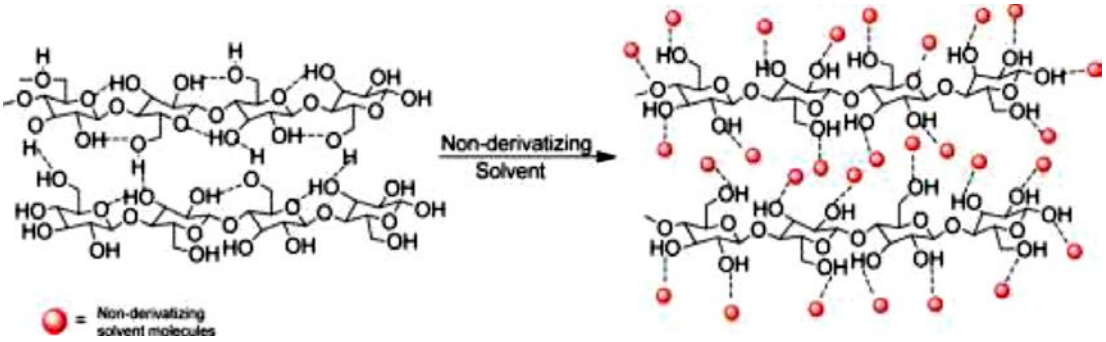

Figure 3. The generic dissolution mechanism when using a non-derivatizing solvent system (3)

It has been shown in previous studies that the dissolution of cellulose in non-derivatizing solvents does not lead to an extensive degradation of the polymer (5). In figure 3, the breakage of the intermolecular hydrogen bondings can be viewed with minimal hydrolysis (decomposition) along the cellulose chain indicating no breakage of hydrogen atoms along the equatorial plane of the macromolecule giving no degradation.

2.3 Aqueous salt solutions and molten salts solvent systems

The solvent systems used in this project derives from the molten salt systems inspired by the Hofmeister series, however instead of using pure molten salt with no water content this work has been dedicated towards finding the underlying dissolution mechanisms of dissolving MCC using concentrated aqueous solutions. As the aqueous salt solutions are related to the molten salt systems, it is important to provide valuable background information regarding different molten salt solvent systems.

Definition of the term inorganic molten salt hydrates is needed in order to understand the overall scope of this thesis. Inorganic molten salt are an important class of cellulose solvent which uses a water to salt molar ratio close to the coordination number of the strongest hydrated cation with the water molecules being tightly bound to the inner coordination sphere of the cation (3). The concentration of the molten salt system can vary between solid hydrates to aqueous salt solutions where a "molten salt hydrate" is designated towards a liquid with water to salt molar ratio close to the coordination number of the strongest hydrated ion, most often the cation in the ionic complex. The concentration range which is used for dissolving cellulose often features properties such as low vapor pressures, extreme acidities, etc (6).

During previous investigations it has become apparent that molten salt hydrates are able to dissolve cellulose without chemical pretreatment or activation of the cellulose. However, not all inorganic molten salts are able to dissolve cellulose and have to be categorized into different groups depending on the observed interaction with cellulose. The inorganic molten salts can be divided into the following categorizes of solvent systems (6):

- no reaction
- fine dispersion
- decomposition
- strong swelling
- dissolution

The solvent systems which can be used for dissolving cellulose will in turn influence the properties of the regenerated polymer directly and cause varieties in properties such as macroscopic morphology or crystallinity and is believed to be a consequence of using different dissolution conditions for dissolving the cellulose in the hydrated solvent melts (6).

The advantages over using inorganic molten salt hydrates over other existing solvent systems are many. For instance, inorganic molten salt hydrates are considered less expensive and easier to prepare compared to other non-derivatizing cellulose solvents. Furthermore, the inorganic molten salts provide an environmentally cautious alternative to dissolving cellulose as no toxic or volatile organic (although not completely inert) compounds are required for preparing the different solvent systems. During the process of regenerating cellulose from the inorganic molten salt solutions most often water is sufficient for regaining the cellulose, however regular alcohol solutions such as methanol and ethanol can also be used for precipitating the cellulose. In addition, there exists the factor of recycling when using inorganic molten salts during the dissolution process. After the regeneration process of cellulose the inorganic salts can be recovered by low pressure distillation of the simple coagulation agent (water, ethanol, etc) present in the solvent system and can hence be recycled for further use, effective in large scales. In this thesis, no work regarding recycling of the solvent systems took place.

Taken into consideration the overall benefits of using inorganic molten salts over other solvent systems there exist a clear argument for implementing these type of solvent systems to a larger extent for dissolving cellulose and a augmented attention towards its applicability in cellulose processing can be seen in today's research (3).

Table 1. Examples of derivatized and non-derivatized solvents

Solvent systems	**Nomenclature**
Derivatized solvents	DMAc/LiCl, (*N*,*N*-dimethylacetamide) DMSO/TBAF, (Dimethyl sulfoxide/ Tetrabutyl ammonium fluoride) DMF/N_2O_4, (*N*,*N*-dimethylformamide) $LiClO_4 \cdot 3\ H_2O$, and $LiSCN \cdot 2\ H_2O$ (4)
Non derivatized solvents Solid molten salt hydrates	$MgCl_2 * 6\ H_2O$ $LiCl * 5\ H_2O$ $LiClO_4 * 3\ H_2O$ $ZnCl_2 * 4\ H_2O$ (6)

2.3.1 Factors of dissolution and regenerated cellulose

As previously mentioned, the properties of the solvent system strongly influence the properties of the regenerated polymer (6). Hence, the dissolution of cellulose and the regeneration of the polysaccharide from different salt aqueous solution systems can be used to modify and control the properties of the final product. Properties such as morphology, crystallinity and the dimensions of the crystallite units depends on the composition of salt and water in the solvent system and is thought to be a consequence of the interactions taking place between the dissolved polymer and the species of the solvent system as well as the conditions of the solvent solution.

Important factors which influence the dissolution process are the following (11, 6):

- salt composition (Li^+ or Zn^{2+}-ions usually necessary)
- salt/water molar ratio in solvent system
- the hydration deficiency of the coordination sphere
- acidity of the solvent system

2.4 Hofmeister series

The Hofmeister series can be used as a guideline for choosing different aqueous salt solutions to focus on for dissolving cellulose.

The Hofmeister series classifies and rank different ions based on their effect on the solubility of proteins (7). Ions can be classified as kosmotropic or chaotropic, depending on their effect in water structuring and/or water structure-disrupting. The series has previously been used for designing kosmotropic salts for given ionic liquids and can also be used to inspire the development of molten salts solvent systems for dissolving cellulose (8).

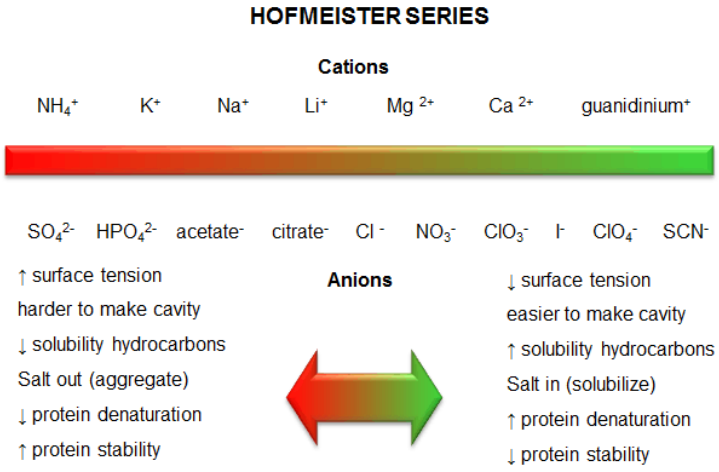

Figure 4. Classification and properties of ions present in the Hofmeister series (9)

The ions of these salts found on the left side of the Hofmeister series show a tendency towards forming water structuring solutions whereas the salts remaining on the right side (chaotropic) of

the series show the opposite characteristics (2,9). Note that figure 4 only demonstrates the most common anions and cations present in the Hofmeister series; several others could be included.

It has been shown in previous studies that especially anions in the Hofmeister series have had a favorable effect in the dissolution of the cellulose. For example, the molten salt lithium perchlorate $LiClO_4$ which contains the perchlorate anion (ClO_4^-) is presented to the right side of the Hofmeister series and show high salting-in effect and has been proven highly effective for dissolving cellulose in previous studies. The same is valid for several lithium base solvents. Overall, it has been observed that the addition of lithium salts significantly increases the solubility of the cellulose. Examples of certain lithium based molten salts are LiCl, LiBr, $LiNO_3$ and $LiClO_4$ (4). We should note however that not all lithium salt systems are able to dissolve cellulose; where $LiClO_4$ is able to give full dissolution of cellulose LiCl is only able to give swelling of the macromolecule (10) which will be discussed further throughout this thesis.

The different aqueous salt solutions which are able to dissolve cellulose are very different in composition. They vary in their composition of cation and anion and in their water content. This raises the question: Which factors determine the dissolving ability of the molten salt hydrates? It can be inferred in some research that salts combining small hard cations with soft polarizable anions have the best dissolving power for cellulose. However, the good dissolving ability of lithium perchlorate melts contradicts this statement, as do several other hydrated melts which contains lithium with different anions which do not show any dissolving ability of cellulose, for instance LiCl (10). Since there exists no definite correspondence between the dissolution of cellulose and the ions present in the Hofmeister series, many studies have been devoted towards finding direct interactions between the cellulose molecule and the molten salts which through comparison can provide indication of how salts in the series relate to each other upon dissolution (11).

All the aqueous salt solutions chosen for this thesis work were inspired by the Hofmeister series and can be divided into the following groups:

Zinc hydrated salt systems: $ZnCl_2$ and ZnI_2
Chloride hydrated salt systems: LiCl and $MgCl_2$

Note! Even though $ZnCl_2$ solvent system also contains the chloride anion, the salt will be categorized as zinc hydrated salt system in order to compare with the ZnI_2 hydrated salt. This way, a correlation for the Zn^{2+} cation and its dissolution ability can be discussed.

3. Materials and methodologies

3.1.1 Methodology

The basic experimental procedure consisted in dissolution trials of the microcrystalline cellulose (MCC) using different experimental conditions such as: different temperatures, stirring rates and molar ratios of water in the aqueous salt solutions. The effect of dissolution for each solvent system depended on which conditions were being used during the dissolution trials and hence provided different results for each set of condition. The aim of the experimental procedure was

to find the more favorable conditions for which an aqueous salt solution system is able to provide the best dissolution of the model cellulose system (MCC). Additionally, the experimental procedure was believed to provide a basis for a hypothesis regarding which dissolution mechanisms take place in each solvent system. This was done through the use of different conditions for dissolving the cellulose and comparing the dissolution efficiency of each dissolution trial. For the solvent systems which could not provide a successful MCC dissolution, extreme conditions consisting of high temperature and high salt concentration were tested. By applying these extreme conditions it became possible to observe how the cellulose fibers had been affected by the aqueous salt solution and functioned as an overall guideline for detecting good solvent systems for dissolving cellulose. The data gathered from the dissolution trials was further extended with the investigation via different analytical testing methods which will be described in a later section.

In order to assure the best dissolution conditions were found for each respective solvent system it was important to test the dissolution efficiency changing several parameters during the dissolution process. Previous to starting the dissolution trials it was also important to gather valid information regarding the different dissolution conditions already available in literature; input from previous dissolution trials, scientific articles and patents functioned as a guideline for designing the dissolution conditions.

3.1.2 Materials

Chemicals and suppliers:
Micro crystalline cellulose (solid powder; PH Avicel 101. Sigma Aldrich (Dry content 96.77%, 50 μm particle size)
$ZnCl_2$ (purity 98% Sigma Aldrich; solid powder)
ZnI_2 (purity 98 % Acros Organics; solid powder)
LiCl (purity 99% Alfa Aesar; solid powder)
$MgCl_2$ (pure, Acros Organics; solid powder)
Deionized water (purity 100 %)
Acetone (95%)

3.1.3 Experimental procedure

All the experiments were conducted using non-activated (i.e. without pre-treatment) micro crystalline cellulose at 96.77 % dry content with a number average degree of polymerization of roughly 200 (12). A fixed amount of microcrystalline cellulose was added to the solvent system and the dissolution experiments were performed in a closed flask with a magnetic stirrer. After the preparation of the fresh MCC/solvent solution, cellulose could be regenerated through the coagulation in a non-solvent solution (ethanol 95%). The salt residues and the non-solvent medium were then removed by extensive washing of the regenerated material with deionized water in an ultra-sonic bath.

For all the dissolution trials the same total batch volume of 30 ml were used for preparing the cellulose dopes. Maintaining the content of cellulose at a constant value of MCC/H_2O (2%) of the total batch volume, the solvent concentration could be tuned using different molar ratios of salt and water. This procedure was repeated for all the dissolution trials conducted with different ratios of salt and water in the solvent system. During the dissolution of cellulose, changes in viscosity, transparency and color were under close monitoring. Details on the calculations regarding the preparation of cellulose dopes are provided in the Appendix section.

3.1.3.1 Dissolution trial - General procedure

The general dissolution procedure for all the different solvent systems was similar and essentially consisted of the following steps:

- Prepare solvent solutions at different concentrations of salt and water
- Add a fixed amount of microcrystalline cellulose to the solvent solution once temperature was stabilized.
- Dissolve MCC through stirring for 30 minutes under a constant desirable temperature.
- In case of the trial being successful in dissolving MCC, the clear and viscous solution is coagulated in a non-solvent solution (95% ethanol) for collecting the regenerated cellulose fibers.
- The coagulated samples are then putted in an ultrasonic bath for one hour in order to rinse the remainders of solvent system and ethanol from the previous coagulation step.
- Finally, the wet coagulated samples are air dried overnight and stored for future analytical testing.

4. Analytical methods

Different analytical methods are generally applied throughout the studies of cellulose dissolution in different molten salts. These analytical tests are complementary methods for providing an overall picture of the dissolution efficiency using different solvent systems at different experimental conditions.

Analytical methods which are often used for the examining the dissolution efficiency of solvent systems are light microscopy, rheology measurements, intrinsic viscosity measurements and nuclear magnetic resonance (NMR) measurements. In this project, light microscopy, rheology measurements and a specific degradation measurement are used; all of which will be further discussed in the report.

4.1 Light microscopy measurements

After the dissolution process, fresh samples were examined under the light microscopy to detect the amount of undissolved cellulose left in the solvent solution. Complete dissolution of cellulose would provide a clear image with no visible residues of MCC fractions whereas no dissolution (or only partial dissolution) would produce a cluttered image with major residues of undissolved cellulose present in the sample. In figure 5 and 6, MCC is "dissolved" in water and as expected no dissolution is obtained.

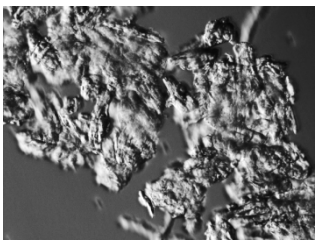

Figure 6. MCC (2%) left in the pure water solution.

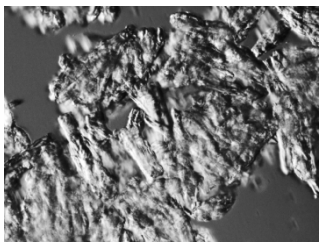

Figure 5. MCC (2%) left in the pure water solution.

The figures demonstrate the inability of water to dissolve cellulose resulting in major residues of slightly swollen undissolved crystalline cellulose.

By comparing the features of the light microscopy images for the different solvent systems it became possible to verify information gained during the dissolution trials for each hydrated salt solvent system. In order to avoid degradation (by hydrolysis) of the cellulose and maintaining good quality of MCC/solvent samples it was important to keep the samples at a low temperature (below 4 C) to reduce the kinetics of degradation. However, to ensure that there would not be any changes in the fresh and the aged samples, both samples were measured for the same condition.

4.1.1 Light microscopy measurements – General procedure

The general procedure for sample preparation was similar for all MCC/solvent systems and included the following general steps:

- Liquid sample solutions were prepared using the pre-determined conditions for each hydrated salt solvent system (conditions optimized during the initial dissolution trials).

- A small sample drop were kept between cover slips and illuminated with linearly polarized light and analyzed through a crossed polarizer. Images were captured and analyzed using proper software.

Through analysing both the fresh and the aged samples it became possible to examine the stability of the samples over a period of time. The results from the light microscopy measurements will be provided in the results section.

4.2 Rheological measurements

Rheometry is an analytical method used for studying the deformation of matter. From a practical point of view, rheology often refers to the flow and deformation of non-ideal materials such as rubber, molten plastics and polymer solutions. In particular, the rheology of polymer solutions and melts have been extensively studied and resulted in considerable progress in developing new polymer materials for different applications (13). The cellulose dopes can be classified as non-ideal solutions. Here, rheology was used for characterization of fresh and aged MCC/solvent

solutions with focus on changes in properties such as shear viscosity, elastic modulus (G´) and viscous modulus (G´´) upon applying varying frequency and temperature.
Polymers are, in general, polydisperse. Polydispersity index (PDI) can be used as a measurement for estimating the distribution of molecular weights within a sample; the larger the polydispersity index, the broader distribution of molecular weights (15). The polydispersity index will have an effect on rheological behavior of the solution (16), this since the rheological measurements are based on the diversities within the sample and are designed to give average properties based on the properties of the molecular mass distribution within the sample (14). Most of the properties of a polymeric material are related to its molecular weight distribution (MWD) (17), especially viscosity is one of the rheological characteristic that is strongly correlated to the polymer molecular mass (14). In the present case we expect not only our raw material to be polydisperse, but also that the solvent system influences the degradation of cellulose, giving rise to higher polydispersity of the final product. The viscosity of a fluid material can be defined as its resistance towards flowing or changing shape. Viscosity can also be described as an internal friction upon applying an external force within the sample which derives from the movement of molecules in the sample and their interactions with each other (see figure 7).

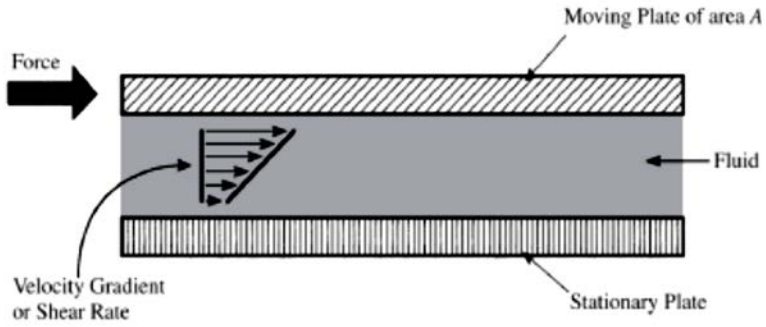

Figure 7. A liquid material´s internal friction and resistance towards flowing upon applying an external force (Lecture 3, Polymer Technology Course (2013). Literature: A Brent Strong, Plastics: Materials and processing 3rd edition, Chapter 4 "Mechanical properties")

Liquids and gases can be classified as Newtonian fluids which are typically characterized by a non-dependence of the viscosity with the applied stress (or strain). Sample solutions obtained through the dissolution of MCC are believed to belong to Newtonian for diluted and semi diluted regimes. As the MCC content increases we expect deviations from the Newtonian behavior. Therefore, in our samples, the cellulose concentration is an important parameter to consider.

Different types of rheological measurements were used such as flow curves, stress and frequency sweeps and temperature ramps. The rheology experiments were performed on a Physica MCR 300 rheometer (Gothenburg, Sweden) using a cone-and-plate measuring geometry (1°, 50 mm diameter). The instrument was equipped with an automatic gap setting and a temperature control unit which was used to ensure minimal temperature variation in the sample chamber from the set value of 20°C. The shear viscosity of the samples was determined in nonlinear rotational measurements, see figure 8.

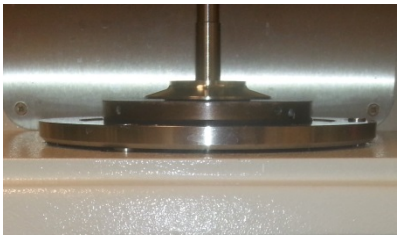

Figure 8. Sample solution put on plasma coated bottom plate. The different rheological information was accessed while applying different stress, frequency and temperature (Physica MCR 300 rheometer)

4.2.1 Rheology measurements – General procedure

Since both light microscopy and rheology performs measurements on liquid sample solutions the sample preparations were similar. Fresh sample solutions were prepared using the pre-determined conditions during the dissolution trials. A certain amount of sample was transferred to the rheometers and the test was performed. In some cases, the samples were aged for a certain period and then re-measured. This particular test allows one to study the stability of the sample with time.

4.2.2 Flow curve analysis – Fundamentals

As previously mentioned, rheology is the study of flow properties of a certain liquid sample. The nature of the sample will determine the geometry of the measuring system and type of measurements. In figure 9, different types of measuring geometries are illustrated depending on the nature of the sample.

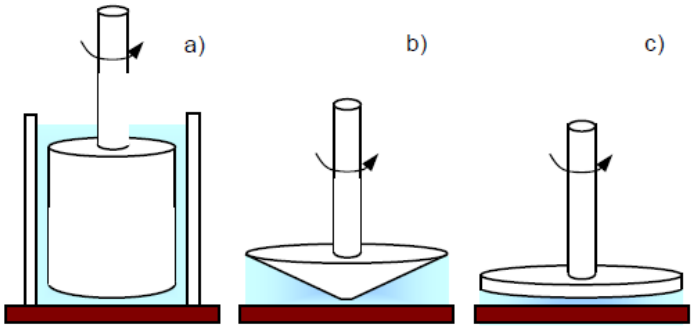

Figure 9. Different top-plates used for rotational rheometers (18)

In figure 9 a) and 9 b) the measuring geometries are used for low viscosity material where a large surface area provides sensitivity at lower shear rates. For the sample solutions, which exhibits a higher viscosity, a cone-and-plate geometry (9b) is used which is the general geometry used for high viscous sample solutions (18). A plate-plate configuration (9C) is useful for high viscous materials where the gap may be adjusted. In this work, a cone and plate geometry was used (1°, 50 mm diameter).

4.2.3 Flow curve analysis – Experimental

The general flow curve analysis was used to study the flow behavior of the liquid sample upon either increasing or decreasing shear rates. For each value of shear rate a corresponded value for the shear viscosity is determined and plotted resulting in different shapes of flow curves depending on the rheological properties of the sample (18). In figure 10 the general different flow behaviors are exhibited with four different figures corresponding to the possible outcomes of the flow curve test.

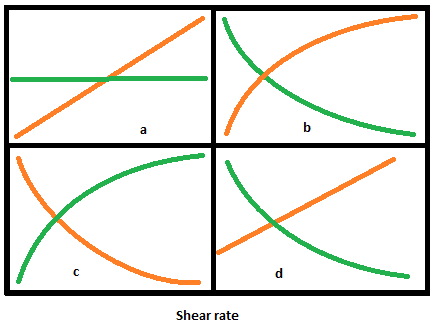

Figure 10. Different types of flow behaviors. Green line represents viscosity and orange line represents shear stress (18)

Depending on the interactions between the different species in the liquid samples different flow behaviors can be observed.

a) **Newtonian Fluid**: Viscosity is constant over the entire shear rate range indicating no dependency between viscosity and shear rate. A typical example of a Newtonian fluid is water; regardless the applied stress, the viscosity of water is constant.

b) **Shear thinning**: In a shear thinning material, the viscosity decreases as shear rate is increased. This is the typical flow curve behavior found for the MCC/solvent sample solutions.

c) **Shear thickening**: The viscosity of the sample solution increases as the shear rate is increased.

d) **Bingham plastic**: Until a certain shear stress is achieved the viscosity of the solution appears to be infinite. In other words, the material needs a critical minimum stress to start flowing.

4.2.4 Dynamic measurements (Oscillatory tests)

Elasticity is a property which foremost is shown for solid materials and describes the tendency of the material to return to its original form after the cessation of the applied stress (or strain). The viscous property can be regarded as the quite opposite of elastic behaviour where the fluid material show low tendency to return to its original form and dissipates energy. The term viscosity is used as a measurement of a fluid´s resistance to flow. A highly viscous liquid will show a greater resistance towards deformation than a low viscous solution (for instance, compare honey with water). Polymers are classified as viscoelastic materials which mean the materials exhibit both elastic and viscous properties (19).

The reasons why viscoelastic properties appear for polymer solutions are due to the entanglements existing between the polymers and the surroundings. Therefore, the cellulose concentration is an important parameter: while at low concentrations the polymers don't "see" each other and thus the viscosity is low, at higher concentration (above the critical concentration, C*) polymer start to interact and entangle contributing to an increase of the viscosity of the system (see figure 11).

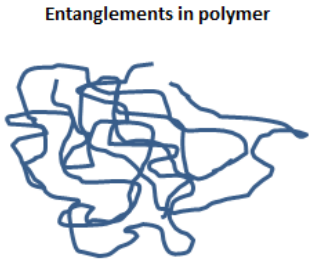

Figure 11. Viscoelastic properties of a liquid sample depend on the interactions between different species within the solution (20)

Different rheology testing methods can be used to determine the viscoelasticity of sample solutions. Among the possible tests, one method uses the oscillation frequency sweep tests and oscillation-temperature ramps (20).

4.2.4.1 Oscillation measurements - Frequency sweep

Oscillation methods using frequency sweep provide information regarding properties which are time dependent. The oscillation measurements can be used to determine the viscoelastic properties of a liquid sample through subjecting the sample to an oscillatory load consisting of either stress or strain (19). A sinusoidal stress or strain is applied to the sample causing an induced response of the sample which follows (or not) the same sine wave, as can be seen in figure 12 (19,20).

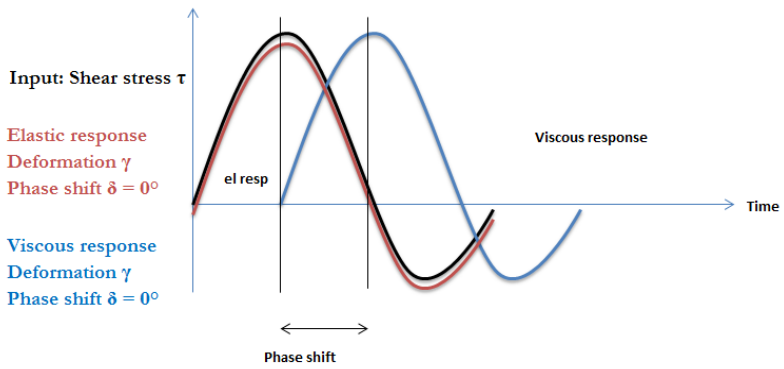

Figure 12. The sample is subjected to sinusoidal stress σ causing an induced response of the sample which follows the same sine wave (20)

Depending on the nature of the sample different outcomes of the oscillation measurement can be obtained. A pure Hooke elastic material would provide a response completely in phase with the applied oscillation. On the other hand, a pure Newtonian viscous material would provide 90º out of phase response. Since most materials show intermediate properties, one expects polymer solutions to show a mixture between the viscous and the elastic properties; a viscoelastic material will provide a phase shift angle between 0º and 90º (21).

An important issue in these measurements is the previously determination of the linear viscoelastic region, the so called LVR, in order to ensure that the measurements are carried out without changing the structure of the material. In order to determine the LVR, a stress (or strain) sweep test is performed where the maximum stress or strain is registered in the area of which the viscoelastic properties are still constant. Above the determined maximum, the material properties changed with the applied stress or strain and thus, microscopically, the structure of the polymer-solvent network is being altered. While maintaining the sample structure the complex modulus remains constant. However, upon exceeding the limit for applied stress a breakdown of the sample structure take place causing the modulus to decrease.

In figure 13, a typical oscillation curve analysis is shown for two samples.

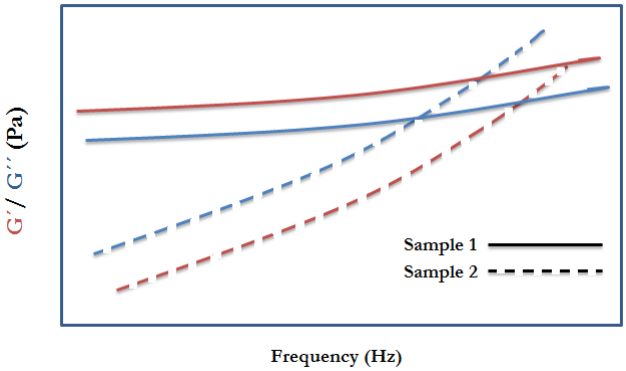

Figure 13. Storage modulus (G´) and loss modulus (G´´) are plotted to give information regarding the liquid and solid behavior in the sample solution upon increasing frequency (20)

In figure 13, the storage modulus (or elastic modulus) G´ and the loss modulus (or viscous modulus) G´´ are plotted as a function of frequency. Upon observing the behaviors of the different sample solutions in figure 13, a distinct difference between sample 1 and sample 2 can be made. Sample 1, represented by the solid lines, shows both moduli frequency independent and exhibit a behavior for which the storage modulus G´ (elastic modulus) is higher over the entire frequency range. This is the typical behavior of a gel-like solid system. On the other hand, the second sample shows both moduli to be highly dependent of the applied frequency and is noted as clearly frequency dependent providing a higher loss modulus (viscous modulus) throughout the entire frequency range. The interpretation which can be made from the latter case is that there exist little internal network or interactions between the species providing low stability of the material (20). The conclusion which could be for the second samples is that it behaves much more as a liquid material than compared to the first sample.

The storage modulus (G´) and the loss modulus (G´´) can be determined through the determination of complex shear modulus, G*(ω) and are shown in the following equations (21):

$G' = G^* \cdot \cos\delta$ (Storage modulus G, elastic property) (Equation 1)

$G'' = G^* \cdot \sin\delta$ (Loss modulus G´´, viscous property) (Equation 2)

The complex shear modulus, G*, can be used for measuring the relative importance of viscous to elastic contributions for a material at a given frequency and can be defined as the following (21):

$$G^* = \frac{\text{complex stress amplitude}}{\text{complex strain amplitude}} = \frac{\sigma_0}{\gamma_0}\text{Cos}\,\delta + \frac{\sigma_0}{\gamma_0}\,j\,\text{Sin}\,\delta \quad \text{(Equation 3)}$$

so that:

$G^* = G' + j\,G''$ (Equation 4) $\quad\quad$ $\text{Tan}\,\delta = G''/G'$ (Equation 5)

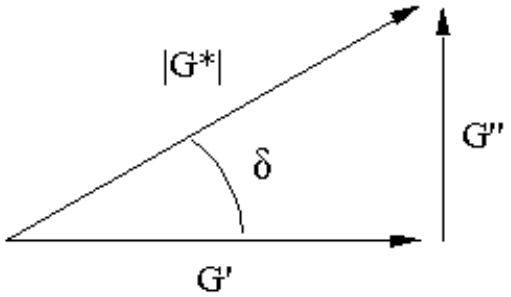

Figure 14. A vectorial representation of the moduli representing both the viscous and elastic modulus (21)

In this study the frequency sweep analysis was used to measure the behaviour of the MCC/solvent solutions upon increasing frequency. By subjecting the sample to an increasing frequency, the liquid (G") and the solid (G') contributions for the viscoelastic behaviour of the solution could be measured. Additionally, a higher liquid behaviour would give an indication towards less cellulose becoming dissolved in the solvent system contributing to a lower viscosity of the MCC/solvent solution. On the other hand, a higher solid behaviour would give an indication towards more MCC becoming dissolved in the solution contributing to a higher viscosity of the sample.

4.2.4.2 Oscillation curve – Temperature ramp

Additional rheology measurements can be used for providing information regarding temperature dependent properties. Through applying constant frequency and constant amplitude during the analysis, temperature dependent properties such as aging, gelation, curing and crosslinking or degradation (hydrolysis) within the sample material can be estimated (20).

In this project, temperature ramps at constant amplitude and frequency were used to infer on the changes in viscosity and the liquid/solid behaviour with increasing temperature from room temperature (20 C°) to 60 C°. Through plotting the temperature dependent properties against the increasing temperature it becomes apparent whether any gelation with temperature takes place for the MCC/solvent solution. If the liquid behaviour (G´´) of the sample remains higher than the solid behaviour (G´) there would be an indication of having no gelation in the MCC/solvent system. However, if the solid behaviour prevails over the liquid behaviour the opposite occur resulting in gelation of the sample. The kinetics of the gelation process were monitored through the observation of the solid (G´) and liquid (G´´) behaviour over a fixed range of period. The parameters frequency (ω =1 Hz) and shear stress (1 Pa) were set as constant over the entire temperature range.

4.2.4.3 Advantages of oscillatory testing methods

There are many advantages of using oscillatory testing methods for obtaining information regarding rheological properties of a certain material. Few have already been discussed previously and can be summarized into the following (20):

- Great extension of measuring range
- Non-destructive method
- Provide information regarding the material structure
- Provide information regarding the properties which are time or temperature-dependent.

4.3 Degradation measurements

In order to measure potential degradation of the cellulose after the dissolution process it was important to study the changes of the molecular weights due to the effect of the solvent.
Viscosity measurements are mentioned in literature research to provide valuable indications regarding degradation of cellulose. By estimating the degree of polymerization, DP, for both native and regenerated MCC it becomes possible to draw a conclusion regarding the effects of the different solvent systems.

For a polymer the degree of polymerization, DP value, is often defined as the number of monomeric units existing in the whole polymer unit or molecule. For homopolymers which consist of only one specific type of monomeric unit, as in the case of cellulose, the average number for the degree of polymerization can be given by the following equation (19):

$$DP_n = X_n = M_n/M_0 \quad \text{(Equation 6)}$$

Where M_n represents the average number of the molecular weight and M_0 represents the molecular weight of the repeating monomer unit in the polymer molecule.

However, due to lack of time and delay in receiving the capillary viscometer, the intrinsic viscosity measurements could not be performed. Instead, a simple method was used comparing the content of cellulose for the fresh dope and dried coagulated samples to detect the differences in cellulose mass weight. The method was based on comparing the theoretical value of cellulose weight towards the weight of the dried coagulated sample which in its dry form was assumed to contain no solvent or non-solvent, only cellulose.

4.3.1 Degradation measurement analysis – Procedure

After each successful dissolution trial, coagulated samples were prepared by weighing dope sample solutions on petri dishes and coagulated in non-solvent (ethanol 95 %). The wet coagulated samples were then washed in deionized water in ultra-sonic bath and dried overnight in open air atmosphere. The air dried coagulated samples were then put for high temperature drying in furnace set for 105 °C (2 hours) to remove moist from the coagulated samples.

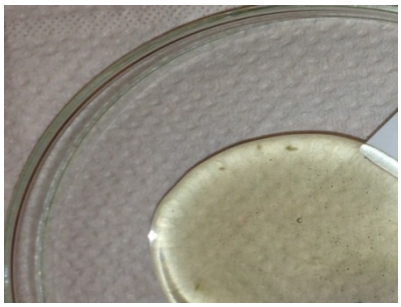

Figure 15. $ZnCl_2$:H_2O Dope sample (1:4, 40 °C, 400 rpm) prepared for coagulation in non-solvent solution

The known amounts of cellulose which was added to the solvent systems were compared to the mass of the dried coagulated samples which is assumed to contain no moist and only cellulose. Two coagulated batches from the same dissolution condition were selected to give an overall estimation of the cellulose lost during the dissolution trial.

The solvent systems which had not been able to dissolve the MCC where discarded for this particular test. Information regarding the non-success dissolution trials is only provided in the light microscopy analysis. The specific conditions used for each solvent system as well as the results are provided in the result and discussion part of the report.

5. Results and discussion

The concentrated salt hydrate systems which had been decided to be focus on were inspired by the Hofmeister series and were divided into zinc hydrated salts ($ZnCl_2$ and ZnI_2) and chloride hydrated salts (LiCl and $MgCl_2$, $ZnCl_2$). A comparison of the dissolution efficiency for the different salts will be made for each analytical trial.

5.1 Dissolution trials

5.1.1 Zinc hydrated salts

As mentioned, the zinc based hydrated salt systems consisted of zinc-chloride salt ($ZnCl_2$:H_2O) and zinc-iodide hydrated salt (ZnI_2:H_2O). Keeping the same cation (i.e. zinc cation Zn^{2+}) and changing the anions (Cl^- and I^-) make it possible to gain information regarding effects of the cation on the dissolution.

5.1.1.1 $ZnCl_2$:H_2O hydrated salt

$ZnCl_2$:H_2O as a concentrated hydrated salt solution for dissolving cellulose is an already well-documented system in the cellulose world and has in this project provided a reference for designing and testing the dissolution trials for the remaining solvent systems. The initial literature research show that the best dissolution conditions for this system are found to be at the molar ratio 1:4 ($ZnCl_2$:H_2O) (3,10). We have followed these conditions and tested dissolution at 40 °C at a 400 rpm stirring rate.

The outcome of the dissolution was observed to correlate well to the results found in the literature research. A successful dissolution of the MCC powder was noted resulting in a transparent and viscous liquid solution with little residues of MCC left in the solvent system (see figure 16). The increase in viscosity gave an indication towards increasing intermolecular interactions between the dissolved cellulose molecules which was believed to be the effects of increased entanglements (figure 11). This confirmed that the condition (1:4, 40 °C, 400 rpm) is sufficient for dissolving MCC when using the molten salt $ZnCl_2$ as a solvent system.

To confirm the specific molar ratio range effective for dissolving MCC in $ZnCl_2$:H_2O solvent system, other molar ratios were tested. It could be concluded that the molar ratio 1:4 gave the best dissolution performance of cellulose with less residues of MCC left in the solvent system as well as produced a clear and viscous solution. From the dissolution trials it could also be concluded that lower molar ratio of water (1:2) gives a non-viscous and foggy solution with much undissolved MCC left in the solvent system; giving a clear indication that lower molar ratios of water are not sufficient for dissolving MCC. On the other hand, trials conducted at higher molar ratios (1:5-6) resulted in the similar outcomes; very little increase in the viscosity, low transparency and most MCC powder left undissolved in the solvent solution.

A comparison between the molar ratio 1:3.5 and 1:4 under the same condition (40 °C, 400 rpm) was made to detect the effects of using slightly higher concentration of molten salt in the solvent system. It could be concluded that both the molar ratio 1:3.5 and 1:4 (40 °C, 400 rpm) gave good results in terms of viscosity and transparency for the MCC/solvent solution. However, the 1:4 molar ratio sample results in less MCC residues left in the solution after the dissolution trial giving indication that using molar ratio below 1:4 (40 °C, 400 rpm) lowers the solvent performance. The viscosity of the MCC/solvent solution however increased more for the 1:3.5 molar ratio compared to the 1:4 molar ratio indicating that a slightly higher salt concentration in the molten salt system has a promoting effect on the dissolution of MCC in the $ZnCl_2$:H_2O hydrated salt system. Figure 16 and 17 demonstrates outcomes of using different molar ratios for the dissolution trial.

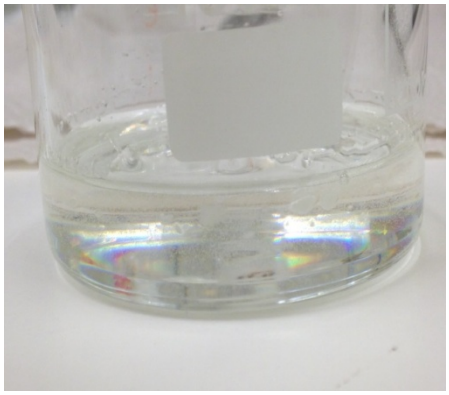

Figure 16. $ZnCl_2$:H_2O (1:4, 40 °C, 400 rpm)

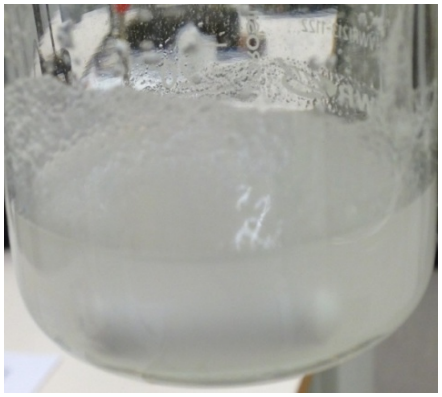

Figure 17. $ZnCl_2$:H_2O (1:2, 40 °C, 400 rpm)

The figures 16 and 17 illustrate how different dissolution conditions result in different dissolution efficiency; figure 16 show good dissolution of MCC whereas figure 17 show poor dissolution of MCC. For all the different dissolution trials both higher and lower stirring rates were used to see the influence in the dissolution efficiency. It could be noted that for the successful ratio 1:4 ($ZnCl2/H_2O$) at 40 °C, cellulose dissolution is enhanced at a higher stirring rate of 600 rpm. This was indicated through the observations of an increasing viscosity and clarity of the MCC/solvent solution after dissolution. Hence a higher stirring rate was believed to give an overall higher efficiency of the dissolution process leaving less MCC residues left in the system, see figure 18 and 19.

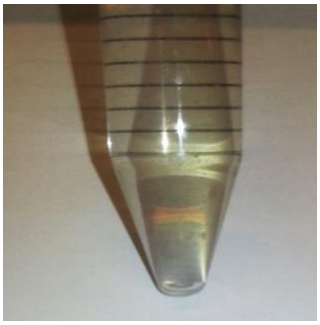

Figure 18. $ZnCl_2$:H_2O (1:4, 40 °C, 600 rpm)

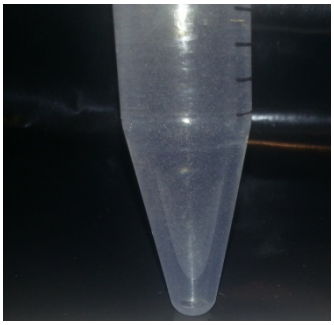

Figure 19. $ZnCl_2$:H_2O (1:4, 40 °C, 400 rpm)

In figures 19 (1:4, 40 °C, 400 rpm) greater MCC residues can be observed when compared to figure 18 (1:4, 40 °C, 600 rpm), indicating a higher dissolution efficiency upon using higher stirring rate.

In addition, the regenerated cellulose from the two samples prepared with different stirring rates presents differences in the consistency and appearance of the air dried coagulated samples; the sample prepared at 400 rpm appeared more brittle and hard while the sample prepared at 600 rpm appeared more porous (see figure 20 and 21). Coagulation medium was 95% ethanol (room temperature).

Figure 20. Dried coagulated sample $ZnCl_2$:H_2O (1:4, 40 °C, 400 rpm)

Figure 21. Dried coagulated sample $ZnCl_2$:H_2O (1:4, 40 °C, 600 rpm)

One hypothesis based on the dissolution trials was that the dissolution at higher strain rate suffers from some kind of mechanical degradation and this manifest with a more porous material. This suggestion however has to be verified in more tests which access to the molecular structure.

Additional investigation regarding the effective range of dissolution for $ZnCl_2$:H_2O hydrated salt was also done using a lower temperature for dissolving MCC (30 °C). The dissolution profile was comparable to when using the regular temperature of 40 °C. In any case, for the higher temperature conditions it is believed that the dissolution of MCC occurred to a larger extent than for the 30 °C since the sample solution prepared at lower temperature contained larger residues of undissolved MCC after the dissolution trial. Therefore, the chosen condition for the $ZnCl_2$:H_2O solvent system was set at (1:4, 40 °C, 600 rpm).

5.1.2 ZnI_2:H_2O hydrated salt

As no experimental conditions for the effective dissolution of cellulose had been provided in the literature research for a system containing ZnI_2, the dissolution conditions found for the $ZnCl_2$ system were used as a reference starting point. Using the conditions (1:4, 40 °C, 400 rpm) for the ZnI_2 hydrated solvent system; the first dissolution trial gave an extremely high viscous solution with major residues of undissolved MCC left in the solvent system. In order to improve solubility, the molar ratio of the molten salt was lowered to 1:6. The result of the dissolution was a rather transparent sample solution with small residues of MCC, but that had still maintained a relatively high viscosity.

By increasing the temperature, stirring rate and the content of salt in solvent system the condition for dissolving MCC could be optimized and it was found that the 1:5-6 ratio, 60 ºC, 600 rpm (30 min) produced a highly viscous transparent solution with little residues of MCC left, see figure 22. Upon comparing the 1:5 and the 1:6 molar ratio there appeared to be a higher extent of undissolved MCC residues left in the solvent system when using the molar ratio containing less molten salt (1:6).

Figure 23. ZnI_2:H_2O (1:5, 60 °C, 600 rpm)

Figure 22. ZnI_2:H_2O (1:6, 60 °C, 600 rpm)

When comparing the different dissolution systems there appears to provide better dissolution for the 1:5 molar condition (figure 22) than for the 1:6 molar condition (figure 23) indicated by less MCC residues and higher viscosity.

ZnI_2 is a highly light sensitive compound and therefore it was important to expose the sample to as little light as possible during the dissolution process since interactions with light could cause chemical instability within the sample (34). Thus, during the preparation of the MCC/solvent solution the beakers containing the ZnI_2 salt had to be covered with protective alumina foil in order to minimize the light exposure. Since there appeared to be no color changes upon adding the MCC to the solvent system there appeared to be no visible degradation of the cellulose within the given dissolution conditions. However, this speculation needs to be further confirmed.

After the coagulation process, yellow areas appeared in the center of the regenerated wet coagulated samples (figure 24) but could be removed through extensive washing in overnight in deionized water bath and ultrasonic bath. Most likely, the yellow parts in the wet coagulated samples derived from trapped residues of ZnI_2 in the coagulated polymer matrix.

Figure 24. Coagulated cellulose obtained from the ZnI_2:H_2O molten salt

After the wet coagulated samples had been put for overnight air drying, the air dried coagulated samples showed major differences when compared with the air dried $ZnCl_2$. The dried coagulated samples had become severely brown colored, as can be seen in figure 26.

To protect from any exposure of light during the drying process the wet coagulated samples were covered with alumina foil, but, unfortunately the same result was obtained. One prediction was that small residues of ZnI_2 salt were still present in the coagulated samples resulting in reaction with light causing the changes in appearance of the dried coagulated samples.

Figure 25. Wet coagulated samples ZnI_2:H_2O (1:5, 60 °C, 600 rpm)

Figure 26. Air dried coagulated samples ZnI_2:H_2O (1:5, 60 °C, 600 rpm)

Based on the dissolution trials of the ZnI_2:H_2O solvent systems, the overall conclusion gained from the trials was that the experimental conditions (1:5, 60 °C, 600 rpm) were the most suitable for dissolving cellulose.

5.1.3 Chloride hydrated salts

The chloride based molten salts used were lithium chloride (LiCl) and magnesium chloride ($MgCl_2$). The same procedure for finding the best dissolution condition consisted of initiating the experimental procedure with research articles to find previous trials and conditions for dissolving cellulose. However, the information from the literature research suggested that neither LiCl nor $MgCl_2$ molten salts can be used as a direct solvent system for dissolving cellulose. LiCl is documented to only cause swelling to the cellulose whereas the $MgCl_2$ is suggested to cause the cellulose to decompose (hydrolysis). To be sure of the information gained from the literature research, dissolution trials for each hydrated salt system were designed to include extreme conditions which consisted of high temperature and high salt concentrations for a longer period attempting to dissolve MCC in the solvent system. The high salt concentration was accommodated to fit the highest solubility of each respective molten salt in water. In order to avoid degradation of cellulose, the temperature was set to not exceed 60 °C.

5.1.3.1 LiCl:H_2O hydrated salt

The literature research suggested swelling rather than dissolution of cellulose. The conditions which had been described in the literature confirmed that the molar ratios 1:2-1:5 (LiCl:H_2O) only causes swelling of the cellulose structure whereas the highest salt concentration 1:2 was suggested to give the most swelling. The molar ratios which were tested for the LiCl:H_2O molten salt system were 1:3-1:7 (60 °C, 600 rpm, 1 hour) which all gave the same result ; no dissolution of MCC (see figure 27). The MCC remained as an undissolved powder in the solvent. The information gained from the dissolution trials corresponded with what the literature had suggested; no dissolution of cellulose.

5.1.3.2 $MgCl_2$:H_2O hydrated salt

As for the previous molten salt system, the literature suggested no full dissolution of cellulose for the $MgCl_2$:H_2O hydrated salt system. Instead, decomposition or degradation by hydrolysis of the cellulose chains was reported to occur. As previously mentioned the dissolution conditions were designed to include extreme conditions of high temperature and high concentration of salt in the hydrated salt system in order to observe the effects of degradation of cellulose in the solvent

system and included the conditions 1:10-1:18 (60 °C, 600 rpm, 1 hour). The observation for all the trials using $MgCl_2$:H_2O solvent conditions were similar and showed no increase in viscosity or transparency of the sample solution indicating no dissolution of MCC (see figure 28). After 40-50 minutes of stirring, there appeared to be a slight change in color for the sample solution which might indicate a possible degradation of the cellulose. The degradation of cellulose in the solvent system was further examined in the analytical trials.

Figure 27. LiCl:H_2O (1:3, 60 °C, 600 rpm)

Figure 28. $MgCl_2$:H_2O (1:10, 60 °C, 600 rpm)

In figures 27 (LiCl:H_2O, 1:3, 60 °C, 600 rpm) and 28 ($MgCl_2$:H_2O, 1:10, 60 °C, 600 rpm) both conditions provide low viscous and opaque sample solutions indicating no dissolution of cellulose.

5.2 Light Microscopy – Results and discussion

In the polarized light microscopy studies, micrographs were obtained for every sample with a constant magnification of 20X**.**

5.2.1 Zinc Chloride – Light Microscopy Results

From both the dissolution trials and the literature research it could be concluded that the dissolution condition 1:4 molar ratio ($ZnCl_2$:H_2O) at 40 C was the optimum condition. Since the $ZnCl_2$:H_2O solvent system has been concluded to have a high dissolution efficiency of cellulose the light microscopy were expected to provide clean images with nonexistent or only little residues of cellulose left in the solvent system. In order to obtain a wider background towards the possible dissolution mechanisms, different conditions including different temperatures were compared, for both fresh and aged samples.

5.2.1.1 Fresh $ZnCl_2$:H_2O treated MCC

It could be noted based on the increased viscosity and the fewer residues of MCC in the solvent system, that a higher stirring rate had an enhancing effect on the dissolution of MCC in the solvent system.

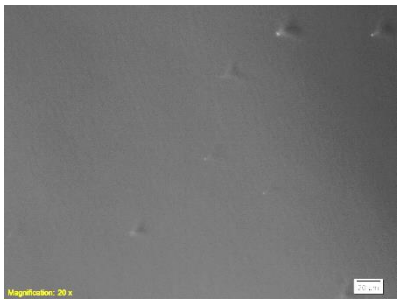

Figure 29. The dissolution efficiency of the condition $ZnCl_2$:H_2O (1:4, 40 °C, 400 rpm)

Figure 30. The dissolution efficiency of the condition $ZnCl_2$:H_2O (1:4, 40 °C, 600 rpm)

In figure 29 and figure 30 however it can be seen that both the conditions for using lower and higher stirring rate provided a good dissolution of MCC and little change between the light microscopy images can be observed.

5.2.1.2 Aged $ZnCl_2$:H_2O treated MCC

The light microscopy micrographs on the aged samples (8 days) prepared under the same condition (1:4, 40 °C, 600 rpm) appeared to have become phase separated during the storing process.

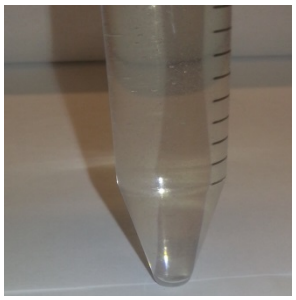

Figure 31. Fresh sample ; $ZnCl_2$:H_2O (1:4, 40 °C, 600 rpm)

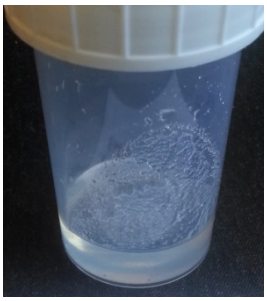

Figure 32. $ZnCl_2$:H_2O Aged 8 days; (1:4, 40 °C, 600 rpm)

Figure 31 and figure 32 illustrate the difference in sample solution before and after ageing for 8 days. For the aged sample the solution appears to have become phase separated and show less clarity when compared to the fresh sample.

Light microscopy micrographs were taken for both the liquid phase and the solid phase in order to observe the potential differences due to the phase separation process. Although the generic image for the liquid aged sample (figure 33) remained the same as for the fresh, other features appeared in the liquid sample which appeared more extensively in the solid phase sample (figures 34 and 35).

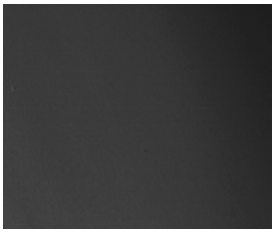

Figure 34. PLM $ZnCl_2$:H_2O; Generic image, Aged liquid sample

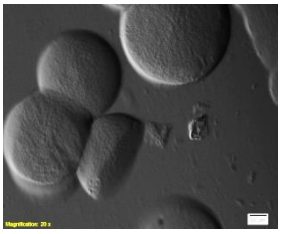

Figure 33. PLM $ZnCl_2$:H_2O; Generic image, Aged solid sample

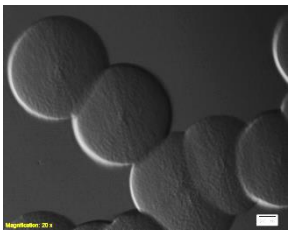

Figure 35 PLM $ZnCl_2$:H_2O, Aged liquid sample

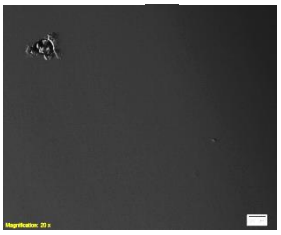

Figure 36. PLM $ZnCl_2$:H_2O, Aged liquid sample

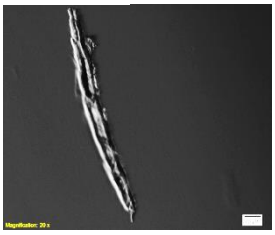

Figure 37. PLM $ZnCl_2$:H_2O, Aged liquid sample

As it can be seen in figure 33, the typical polarized light microscopy (PLM) micrograph for both the aged liquid sample and the fresh liquid sample appeared similar, showing no residues of undissolved cellulose. However, for the remaining images other features appeared in the liquid and, especially, in the solid phase of the sample (figure 34). For instance, in figures 34 and 35 there appears to be spherical shaped objects present in the solution whereas in figure 36 and figure 37 there appear to be undissolved cellulose left in the solvent system. Figure 37 illustrates a single fiber strand of cellulose that has remained undissolved in the solvent system, whereas figure 36 illustrates a smaller fraction of undissolved micro crystalline cellulose present in the sample solution. The undissolved MCC however only appeared to very little extent in the generic image of the liquid solution and was considered negligible. Nevertheless, the same assumption could not be made for the spherical shaped objects due to their frequent appearance in the solid phase of the aged sample (figures 34 and 35).

There are several possible explanations for these features. The first explanation is that the circular features were due to trapped air bubbles in the liquid sample. Another explanation is that the spherical structure are residues of undissolved MCC or cellulose fragments which had failed to become dissolved in the solvent system during the dissolution trial and become swollen or gelled during the aging process. A final suggestion to this phenomenon is that the cellulose had become degraded to smaller fragments and surrounded by the solvent systems hence resulting in the spherical objects, see figure (38).

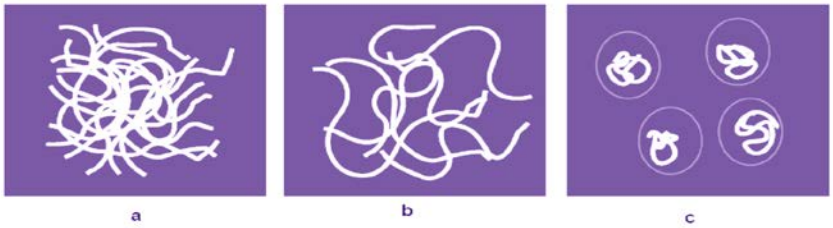

Figure 38. Cellulose structure fragmented down to smaller pieces and then surrounded by the solvent system forming a gel like material (2)

Since the structures formed in the sample are presumably metastable it was suggested that one could eliminate these structures through extensive centrifugation, which would cause bursting of these objects. Therefore, the aged samples were exposed to high speed centrifugation and new PLM micrographs were taken in order to detect the effect of centrifugation in the aged sample.

5.2.1.3 Aged $ZnCl_2$: H_2O treated MCC; centrifuged

When comparing the centrifuged aged samples with the non-centrifuged aged samples it appeared that the spherical shaped objects had become dispersed and could not be found throughout the entire light microscopy image. This supports the idea of the spherical shaped features being less stable and thus disappearing with centrifugation.

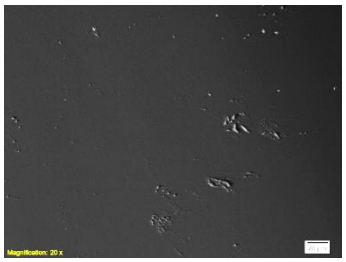

Figure 40. Generic image 1, Aged Centrifuged (1:4, 40 °C, 600 rpm)

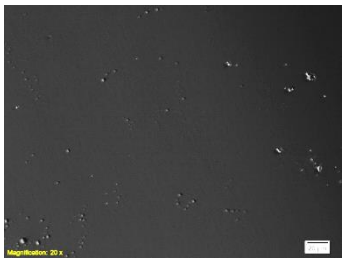

Figure 39. Generic image 2, Aged Centrifuged (1:4, 40 °C, 600 rpm)

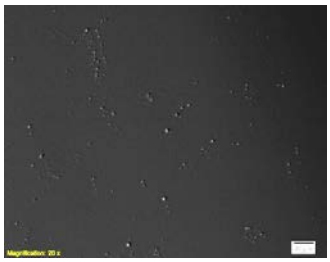

Figure 41. Aged Centrifuged (1:4, 40 °C, 600 rpm)

All the PLM images shown in figures 39, 40 and 41 provide similar results containing no spherical shaped objects in the light microscopy sample. A possible explanation to the slightly more cluttered images is related to the breakage of the cellulose "bubbles" causing fragments of cellulose by the extensive centrifugation. In order to obtain more information regarding the bubble shaped features it was important to do additional light microscopy measurements. Two different conditions were examined under the light microscopy comparing fresh and aged samples with and without centrifugation. First, to verify the effects on ageing a second fresh sample prepared at the condition (1:4, 40 °C, 600 rpm) was aged for a week without any exposure to centrifugation and examined under the light microscopy.

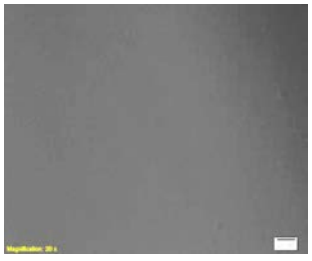

Figure 44. $ZnCl_2$:H_2O Generic PLM ; Fresh liquid sample (1:4,40 °C, 600 rpm)

Figure 43. $ZnCl_2$:H_2O Generic PLM ; 7 days aged liquid sample (1:4, 40 °C, 600 rpm)

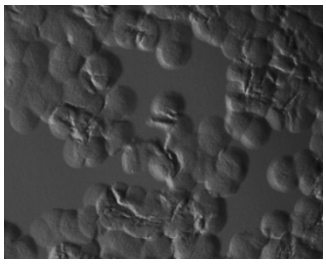

Figure 42. $ZnCl_2$:H_2O Generic PLM ; 12 days liquid aged sample (1:4, 40 °C, 600 rpm)

In figure 44 it can be seen that a longer ageing promotes the gelation of the fresh liquid MCC/solvent solution. The 7 days aged sample (figure 43) appeared to give no major change compared to the fresh sample indicating a stable MCC/solvent solution (figure 42) whereas a prolonged ageing gave a full change in the PLM micrograph containing swollen spherical objects (figure 44).

Since the phase separation took place for both the aged samples, the solid phase of each sample was compared under the light microscopy to give a verification towards which had become most gelled during the aging process.

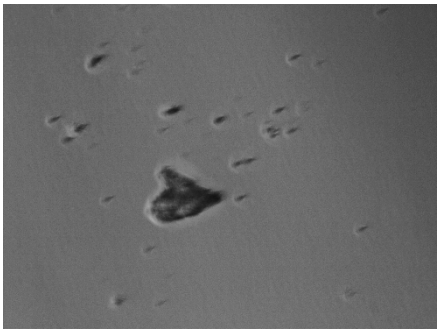

Figure 45. $ZnCl_2$:H_2O Generic image, 7 days aged solid phase (1:4, 40 °C, 600 rpm)

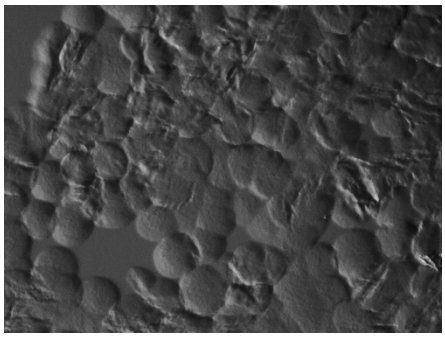

Figure 46. $ZnCl_2$:H_2O Generic image, 12 days aged solid phase (1:4, 40 °C, 600 rpm)

Figures 45 and 46 illustrate the generic light microscopy image for the solid phase of the sample aged for 7 days and 12 days. It can be observed that the gelation of the MCC/solvent solution took place for the most aged sample furthermore confirming the fact that gelation is due to aging.

A second condition using a lower temperature (1:4, 30 °C, 600 rpm) during the dissolution process was used for comparing the aged and the fresh sample under the light microscopy. The aim of this study was to obtain information regarding if the use of a different temperature would produce the same changes for the light microscopy images as it had previously been observed.

Figure 48. $ZnCl_2$:H_2O Fresh sample; Condition (1:4, 30 °C, 600 rpm)

Figure 47. $ZnCl_2$:H_2O 7 days aged sample; Condition (1:4, 30 °C, 600 rpm)

As for the previous condition, there were signs of phase separation after aging for 7 days for the condition (1:4, 30 °C, 600 rpm) (figure 48). Through the light microscopy images it could be

Figure 49. $ZnCl_2$:H_2O, Fresh liquid sample (1:4, 30 °C, 600 rpm)

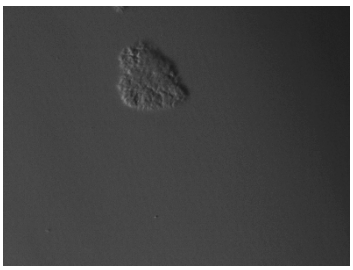

Figure 50. $ZnCl_2$:H_2O Aged sample, liquid phase (1:4, 30 °C, 600 rpm)

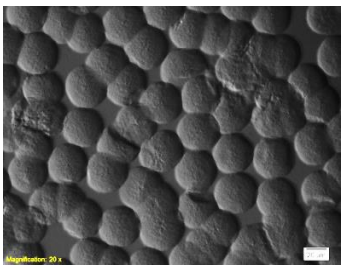

Figure 51. $ZnCl_2$:H_2O Aged sample, solid phase (1:4, 30 °C, 600 rpm)

confirmed that the major gelation had given rise to similar spherical structures in both the solid and liquid phase (more extensive in solid phase, see figure 51) furthermore verifying the effects of ageing. The dissolution of MCC appeared to be fully successful resulting in almost no residues of undissolved crystalline cellulose left in the solution (figures 49 and 50). The examination of the aged samples under the light microscopy began to target a possible physical crosslinking of cellulose which seemed to occur during the aging process. The formation of a 3D network with time was expected to result in a higher viscosity.

Both the literature research and the dissolution trials had suggested the molar condition 1:4 (40 °C, 600 rpm) to give the best performance in dissolving cellulose for the $ZnCl_2$:H_2O hydrated salt system. In the polarized light microscopy, changes in the mixing temperature (30 ºC and 40 ºC) appeared to provide similar results resulting in full dissolution and no perceptible differences in the micrographs.

Figure 52. $ZnCl_2$:H_2O Generic image; Fresh sample (1:4, 30 °C, 600 rpm)

Figure 53. $ZnCl_2$:H_2O Generic image; Fresh sample (1:4, 40 °C, 600rpm)

On the other hand, when comparing the aged samples there appeared to be a gelation for the experimental conditions (1:4, 30 °C, 600 rpm) indicating a network formation which can be inferred from figure 51.

Given that there had been an indication during the dissolution trials towards 40 °C providing a more extensive dissolution of MCC compared to 30 °C a suggestion was made that the more extensive gelation at 30 °C aged sample was due to a higher content of undissolved cellulose left in the solvent solution after dissolution, see figures 54 and 55.

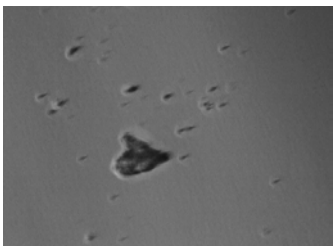

Figure 54. $ZnCl_2$:H_2O, 7 days aged liquid sample; Condition (1:4, 40 °C, 600 rpm)

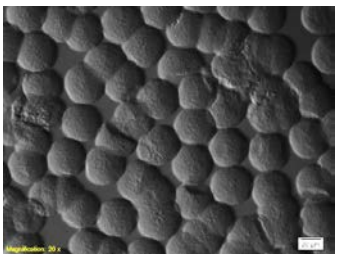

Figure 55. $ZnCl_2$:H_2O, 7 days aged liquid sample; Condition (1:4, 30 °C, 600 rpm)

Upon centrifugation of the aged samples it could be seen that the meta-stable structures of cellulose formed in the aged samples (figure 55) were eliminated due to the high speed centrifugation (see figures 56 and 57). Nevertheless, the full nature of these spherical objects remains unclear and further studies are needed to fully understand this intriguing phenomenon.

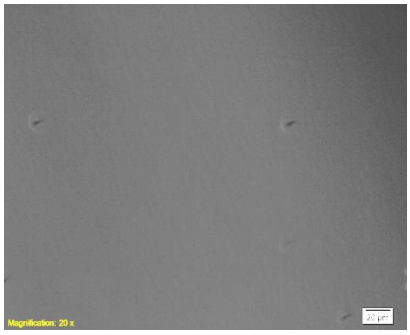

Figure 57. $ZnCl_2$:H_2O Aged (7 days) centrifuged sample (1:4, 40 °C, 600 rpm)

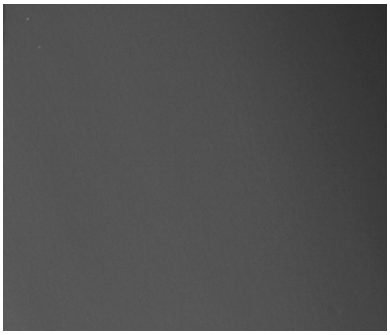

Figure 56. $ZnCl_2$:H_2O Aged (7 days) centrifuged sample (1:4, 30 °C, 600 rpm)

The overall conclusion from the light microscopy analysis was that the experimental condition (1:4, 40 °C, 400/600 rpm) was sufficient for dissolving MCC in the $ZnCl_2$:H_2O hydrated salt system. This agrees well with the information obtained from the dissolution trials as well as the information found in the available literature.

5.2.2 Zinc Iodide – Light microscopy results

As for the $ZnCl_2$ solvent system, the light microscopy images gave similar results which consisted of clear images with insignificant undissolved residues of MCC left in the solvent solution, see figure 58.

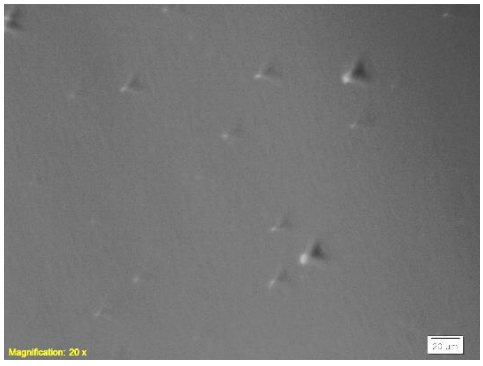

Figure 58. ZnI_2:H_2O Light microscopy image, Aged 6 days (1:5, 60 °C, 600 rpm)

The light microscopy image in figure 58 show no residues of undissolved MCC left in the solvent system (background interferences represented by white dots). When comparing the light microscopy images for aged sample solutions prepared with the $ZnCl_2$:H_2O and ZnI_2:H_2O solvent system there appeared to be a greater stability of the ZnI_2:H_2O sample solution. However, both the hydrated salt complexes appeared to give full dissolution of the MCC in the solvent system. Aging the samples for an even longer period (figure 59) appears to produce no changes, which gave indication of high stability of the dope prepared with ZnI_2:H_2O solvent system.

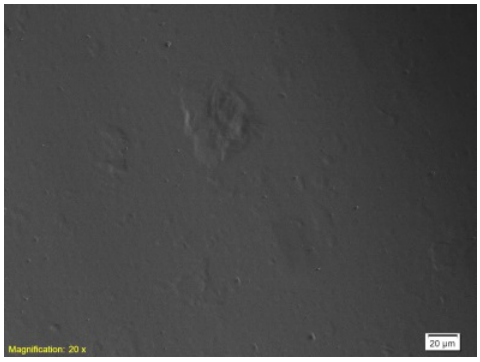

Figure 59. ZnI_2:H_2O (Aged >20 days) Light microscopy image, (1:5, 60 °C, 600 rpm)

The overall conclusion regarding the dissolution efficiency for dissolving cellulose in the ZnI_2:H_2O concentrated hydrated salt system was that the condition (1:5, 60 °C, 600 rpm) had been successful, furthermore verifying the information gained from the dissolution trials which gave indication towards ZnI_2:H_2O being an effective solvent for dissolving cellulose.

5.2.3 Lithium chloride - Light microscopy results

In the initial stages of the dissolution trials it could be concluded that the LiCl:H_2O solvent system was not a successful hydrated salt for dissolving cellulose. This indication was verified by both literature research and experimental dissolution trials. Since the literature research only suggested swelling of the cellulose rather than dissolution, the aim for the LiCl:H_2O solvent system became to focus on how the cellulose is affected by the hydrated salt. As suspected, the light microscopy images showed no full dissolution of cellulose (figure 60).

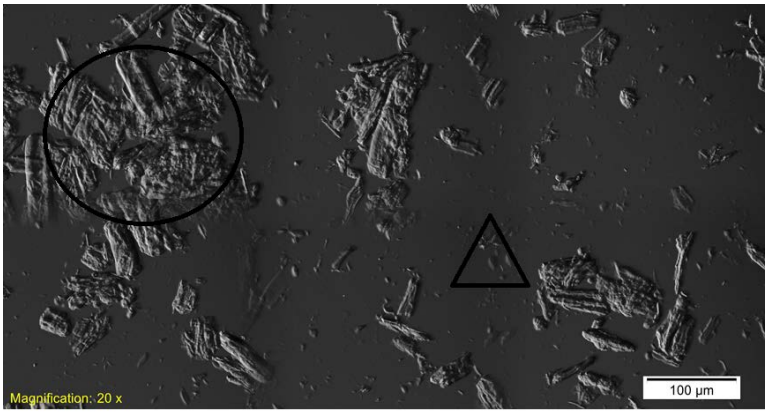

Figure 60. LiCl:H_2O Light microscopy image, Aged 6 days (1:3 ,60 °C, 600 rpm)

The figure 60 demonstrates large areas of undissolved MCC present in the solvent system. Major residues of possibly minor swollen MCC fragments (ring marked) and undissolved crystalline cellulose (triangle marked) appeared under the light microscopy, which corresponded with the previous conclusion of having no dissolution of MCC in the LiCl:H_2O hydrated salt system. Using a higher concentration of molten salt, higher temperature or having a longer ageing effect are all factors which could have contributed to a greater swelling, however the figure illustrates the overall mechanism of LiCl treated MCC which is dispersion and decomposition by hydrolysis of the cellulose. Hydrolysis is suggested since there seems to be less residues of MCC left in the sample solution compared to having no solvent at all (see figure 5; 2 % MCC/H_2O).

5.2.4 Magnesium chloride- Light microscopy results

In previous literature studies the $MgCl_2$:H2O hydrated salt had been suggested to cause decomposition (hydrolysis) of cellulose. The condition which was focused on for the dissolution trials was (1:10, 60 °C, 600 rpm). The effects of the $MgCl_2$:H_2O molten salt on the treated MCC under the light microscopy is illustrated in figure 61 and show great resemblance with the light microscopy images of the LiCl:H_2O treated MCC. Great areas of undissolved cellulose gave indications of no fully successful dissolution of cellulose, however the reduced amount undissolved cellulose compared to MCC dispersed in pure water with no solvent (figure 5) gave indications of hydrolysis or possibly partial dissolution of MCC.

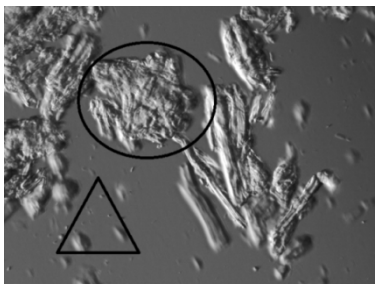

Figure 61. $MgCl_2$:H_2O Generic Light microscopy image (1:10, 60 °C, 600 rpm)

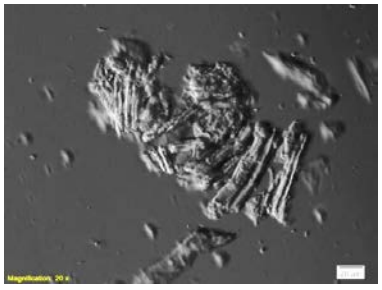

Figure 62. $MgCl_2$:H_2O Light microscopy image (1:10, 60°C, 600 rpm)

The overall conclusion based on the light microscopy images are that both $MgCl_2$:H_2O and LiCl:H_2O solvent systems had failed to dissolve cellulose and cannot be regarded as successful solvents for dissolving cellulose. In the following pictures (figures 63-67) one is able to compare the differences in light microscopy images and correlate the visible dissolution efficiency for using different hydrated salts as solvent systems.

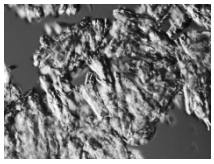

Figure 67. MCC/H_2O (2%) No solvent

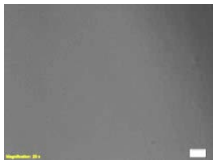

Figure 66. $ZnCl_2$:H_2O (1:4, 40 °C, 600 rpm)

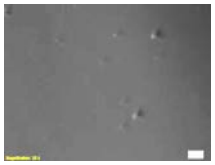

Figure 65. ZnI_2:H_2O (1:5, 60 °C, 600 rpm)

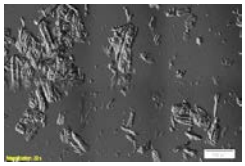

Figure 64. LiCl:H2O (1:3, 60 °C, 600 rpm)

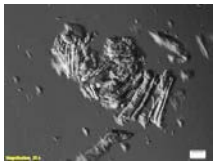

Figure 63. $MgCl_2$:H_2O (1:10, 60 °C, 600

Full dissolution of cellulose could be observed for the $ZnCl_2$:H_2O (1:4, 40 °C, 600 rpm) and ZnI_2:H_2O (1:5, 60 °C, 600 rpm) conditions, whereas no full dissolution, rather partial hydrolysis or minor swelling could be obtained from the latter hydrated salt systems LiCl:H_2O and $MgCl_2$:H_2O.

5.3 Rheology measurements – Results and discussion

As mentioned earlier, only homogenous sample solutions were selected to be measured by rheology measurements. Since LiCl:H_2O and $MgCl_2$:H_2O molten salt were not able to provide any dissolution of the MCC, these systems were discarded regarding the rheology measurements. On the other hand, the successful dissolution trials using $ZnCl_2$:H_2O and ZnI_2:H_2O as hydrated salt for dissolving cellulose were able provide good homogenous dopes and could be used to measure the rheological properties. Different rheological measurements, previously described in the theory section of the report, were applied. For all the rheology measurements 2% (v/w%) MCC was added to the solvent solution and remained constant for all dissolution trials.

5.3.1 $ZnCl_2$:H_2O hydrated salt– Rheology results

Fresh and aged sample solutions were measured by the different rheological tests such as simple flow curve and frequency sweep analysis.

5.3.1.1 Flow curve analysis

In figure 68 and figure 69 the flow curve analysis measurements are shown for the fresh melt prepared at the dissolution conditions (1:4, 40 °C, 400 rpm) and (1:4, 40 °C, 600 rpm). Upon comparing the rheological patterns for increasing shear rate for both samples there seemed to be a decrease in the shear viscosity with increasing shear rate which indicates the typical fingerprint of a shear thinning behaviour; the initial entanglements and interactions between the cellulose molecules are gradually disrupted by the applied shear causing an alignment of molecules in the flow direction resulting in a lower dynamic viscosity. For the experimental conditions of using a higher stirring rate (figure 69) it appeared that the viscosity of the liquid MCC/solvent dope is slightly higher, possibly indicating that the dissolution was more efficient and thus more cellulose is available in the solution contributing to a higher viscosity.

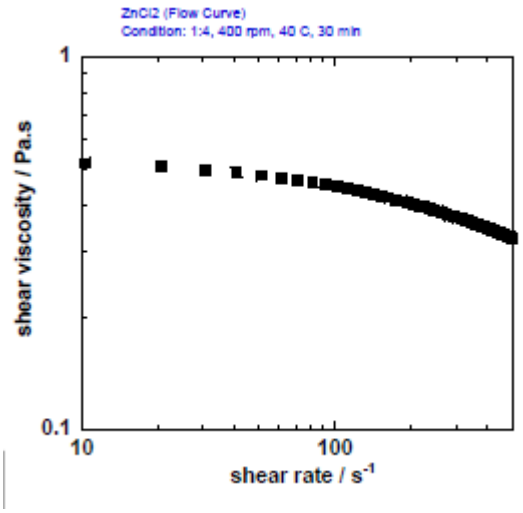

Figure 68. Flow curve analysis, $ZnCl_2$:H_2O fresh sample (1:4, 40 °C, 400 rpm)

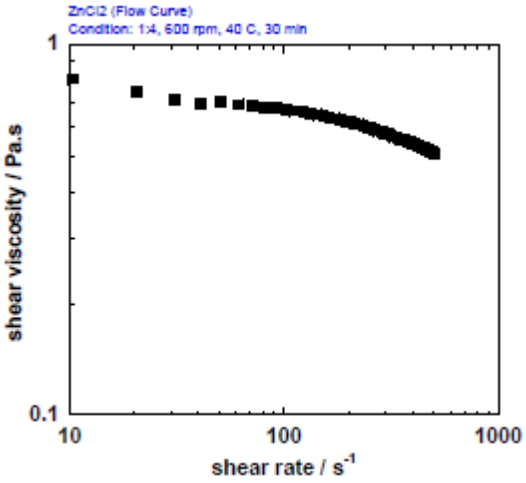

Figure 69. Flow curve analysis, $ZnCl_2$:H_2O fresh sample (1:4, 40 °C, 600 rpm)

Similar behaviour for the aged samples could be observed where an increase in shear rate resulted in the decrease in shear viscosity (see figure 70). However, it was observed for the aged sample that the viscosity was much higher than for the fresh sample regardless the stirring rate. The increase in viscosity (progressive gelation) was believed to be due to self-aggregation of the cellulose chains in the solution with time and/or at elevated temperatures. The progressively increased number of more hydrophobic junction zones between the cellulose chains in the solution makes the physical entanglements highly viable.

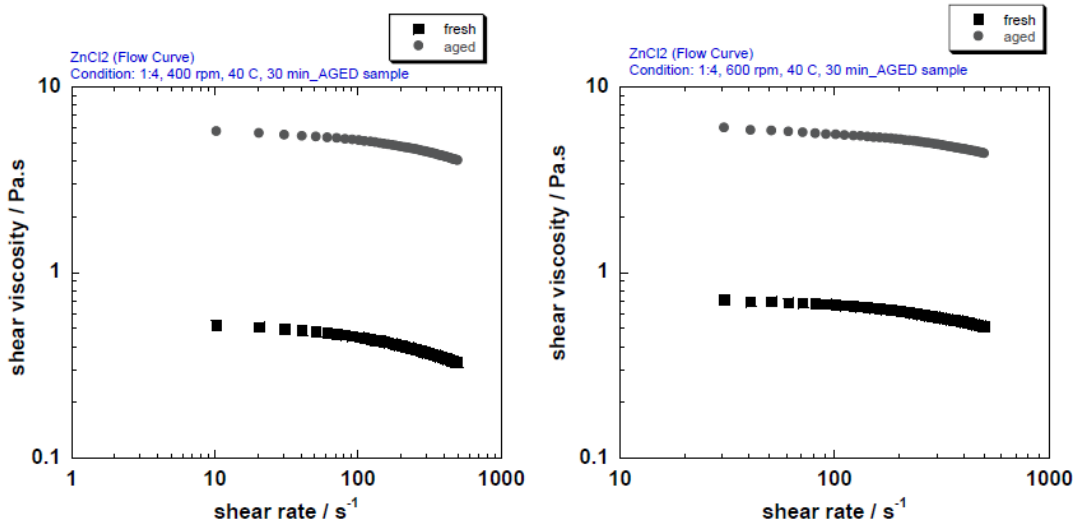

Figure 70. Flow curve analysis, $ZnCl_2$:H_2O fresh vs. aged samples (1:4, 40 °C, 400/600 rpm)

For easier comparison, the flow curves of the sample prepared at different stirring rates were compared to the pure solvent.

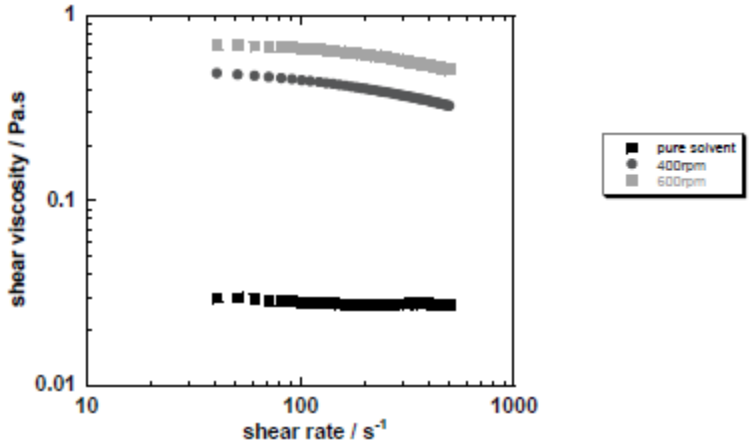

Figure 71. Flow curve analysis, $ZnCl_2$:H_2O Pure solvent vs. fresh samples prepared at 400 and 600 rpm (1:4, 40 °C)

Figure 71 show the changes in viscosity with increasing shear rate for pure solvent containing no cellulose as well fresh samples prepared at different stirring rates (400 vs. 600 rpm). Samples prepared at 400 rpm and 600 rpm showed decreasing viscosity upon shearing whereas the pure solvent solution showed little change.

For both samples containing cellulose there is a decreasing viscosity with increasing shear rate indicating the breakage of existing interactions between the cellulose molecules and species of the solvent. On the other hand, the pure solvent (without cellulose) behaves as a Newtonian fluid and the viscosity does not change with the applied stress, indicating no entanglements between different species of the MCC/solvent system.

5.3.1.2 Frequency sweep analysis ($ZnCl_2$:H_2O)

In figure 72 it can be seen that for both the 400 rpm and the 600 rpm there appears to be a higher liquid behaviour (G´´) with increasing the frequency. Additionally, it can be observed that for the sample prepared at 600 rpm the G´´ is higher than for the sample prepared at 400 rpm, which gave the indication that the former condition using higher stirring rate during dissolution had a higher viscous modulus due to more extensive dissolution of cellulose.

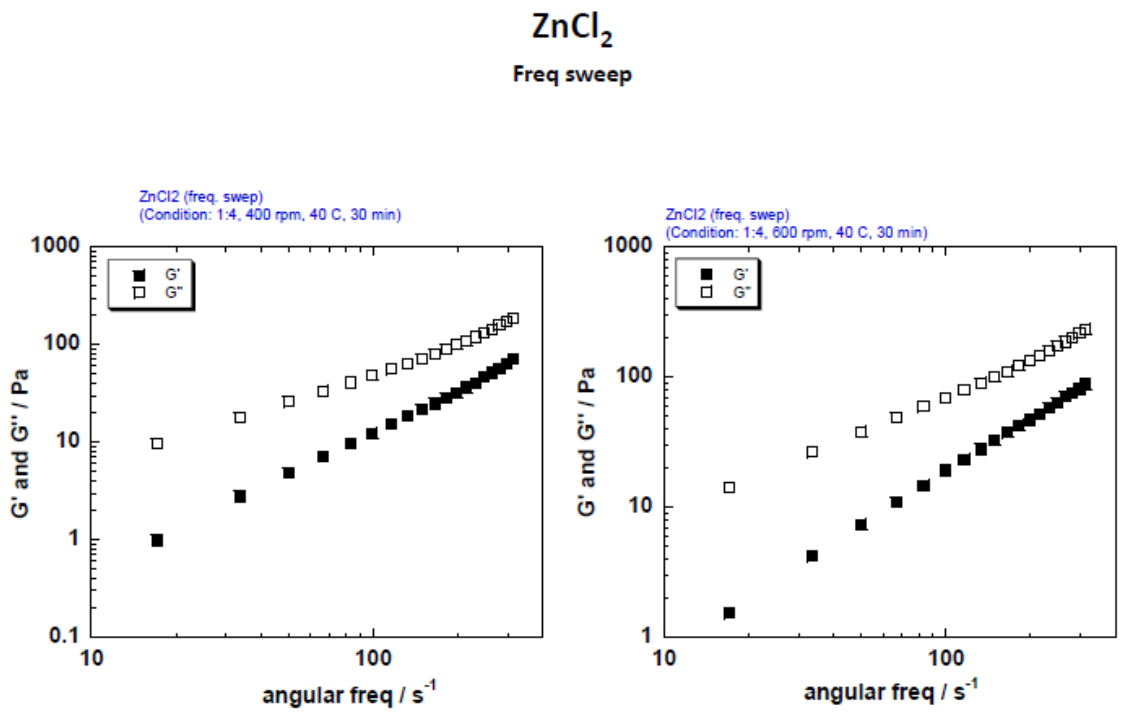

Figure 72. Frequency sweep analysis $ZnCl_2$:H_2O ; Solid (G´) and liquid (G´´) properties of the MCC/solvent solution prepared at 400 rpm resp. 600 rpm

As previously mentioned, the temperature ramp analysis was used to provide information regarding the changes in viscosity and liquid/solid behaviour upon increasing temperature. Through the analysis (figure 73 and 74) it can be observed whether any gelation of the sample occured for higher temperatures or not.

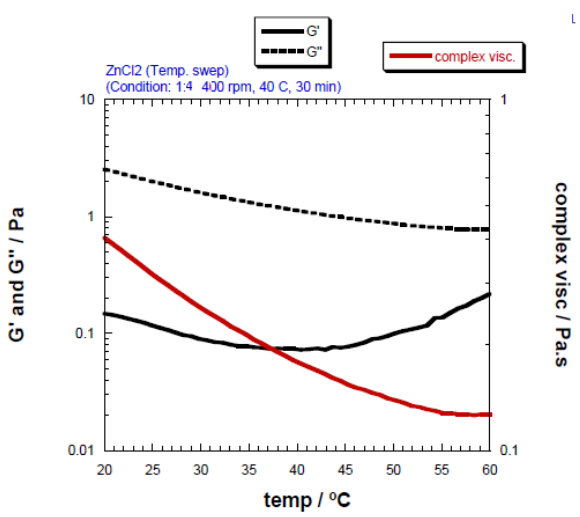

Figure 74. Temperature sweep analysis, $ZnCl_2$:H_2O. Variations in viscosity and solid/liquid behavior (G´/G´´) upon increasing temperature (1:4, 400 rpm, 40 °C, 30 min)

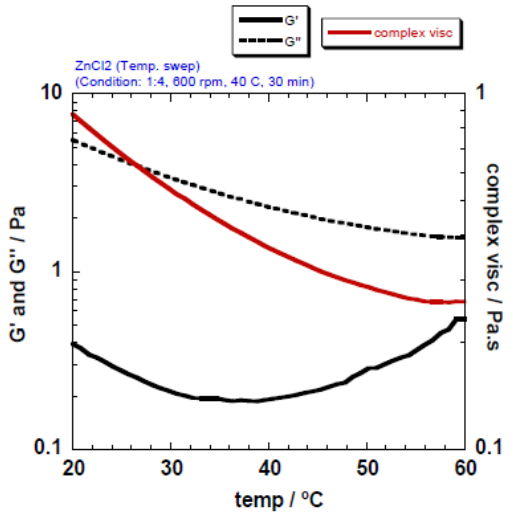

Figure 73. Temperature sweep analysis, $ZnCl_2$:H_2O Variations in viscosity and solid/liquid behavior (G´/G´´) upon increasing temperature (1:4, 600 rpm, 40 °C, 30 min)

Figures 73 and 74 show the variations in viscosity and solid (G´)/liquid (G´´) properties upon increasing temperature for samples prepared at different stirring rates. Comparing the behaviours of the solid and liquid properties for the samples prepared at 400 rpm and 600 rpm, there was a clear pattern of the initial decrease in viscosity with increasing temperature, as expected since the kinetics and molecular motions are enhanced at higher temperatures. Moreover, it could also be noted for both samples, a similar behaviour of the solid and liquid properties taking place indicating no gelation upon increasing the temperature since the liquid behaviour (G´´) constantly remained higher than the solid behaviour (G´) indicating relatively high stability of both sample solutions. However, the data indicated that above 40-45ºC the G' modulus starts to increase and might be a sign of initial gelation. Regarding the tendency of G' and G", one thus speculated that both samples might gel for higher temperatures above 60 ºC being the sample prepared at 400 rpm is more susceptible for gelation.

5.3.2 ZnI_2:H_2O hydrated salt– Rheology results

The same rheology measurements were conducted for the ZnI_2:H_2O hydrated salt systems.

5.3.2.1 Flow curve analysis - ZnI_2:$H_2$0 (1:5 vs. 1:6, 60 °C, 600 rpm)

Similar behaviour for the flow curve analysis can be observed for the ZnI_2:H_2O molten system.

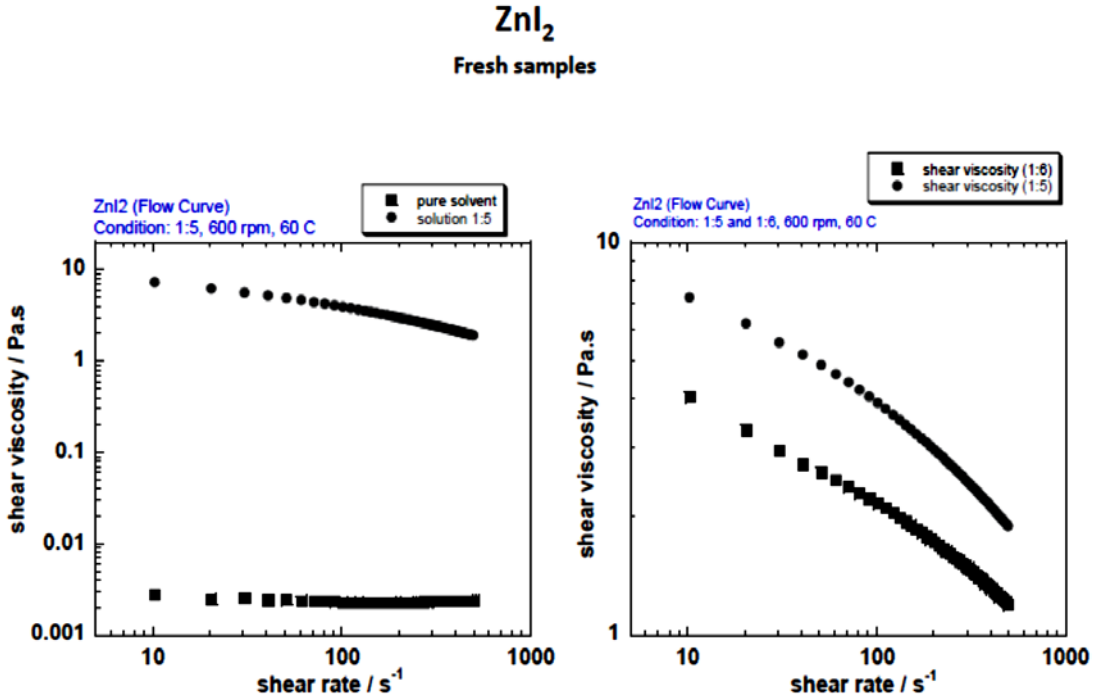

Figure 75. Flow curve analysis ZnI_2:H_2O solvent vs. sample solution (1:5 /1:6, 60 °C, 600 rpm)

In figure 75 the viscosity of the pure solvent solution and the MCC/solvent sample was measured to show the influence of the polymer addition. As expected, the pure solvent behaved

as a Newtonian fluid while the cellulose dope appeared shear thinning with a clear decrease in its high viscosity upon increasing shear rate (left figure). When comparing the changes in viscosity for the samples prepared for different molar ratios 1:5 and 1:6 (right figure) it became apparent that the higher molar ratio of molten salt (1:5) demonstrated a higher viscosity, indicating a better dissolution of MCC. This information is in perfect agreement with the dissolution trials which also had suggested as greater dissolution of cellulose for the condition containing higher molar ratio of the ZnI_2:H_2O hydrated salt.

Upon comparing the changes in viscosity for the conditions (1:5, 60 °C, 600 rpm) respective (1:6, 60 °C, 600 rpm) for both fresh and aged sample the same trend appeared as for the previous hydrated salt ($ZnCl_2$:H_2O), showcasing a decrease in viscosity upon increasing shear rate (figures 76 and 77). Additionally, similarities of aging the MCC/solvent samples could be found showing an increased viscosity with time (see figure 77).

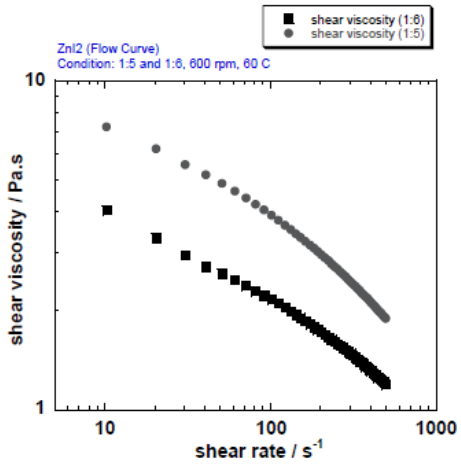

Figure 77. Flow curve analysis ZnI_2:H_2O, Fresh sample (1:5 vs. 1:6, 60 °C, 600 rpm)

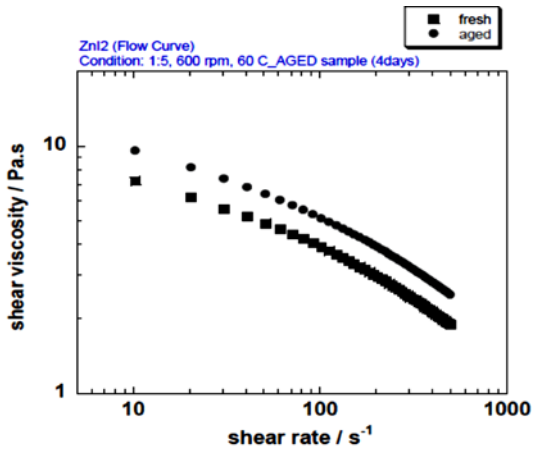

Figure 76. Flow curve analysis ZnI_2:H_2O, Aged sample (1:5 vs. 1:6, 60 °C, 600 rpm)

Figure 76 and figure 77 demonstrates the decrease in viscosity upon increasing shear rate for both fresh sample and aged sample prepared in the conditions (1:5 & 1:6, 60 °C, 600rpm).

5.3.2.2 Frequency sweep analysis; ZnI_2:H_20 (1:5 vs 1:6, 60 °C, 600 rpm)

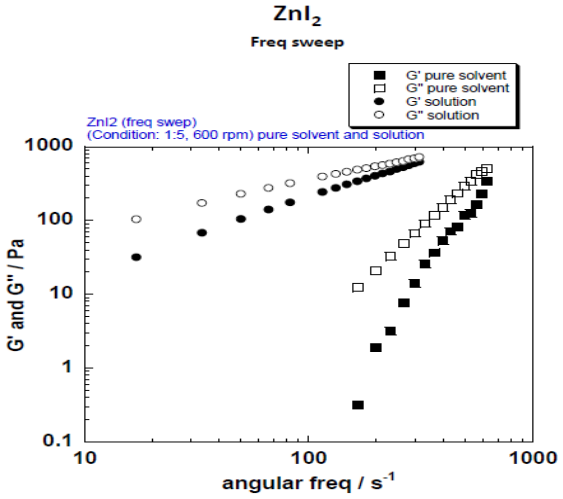

Figure 78. Frequency sweep analysis for pure solvent and MCC/solvent sample solution prepared at condition (1:5, 60 °C, 600 rpm); Fresh sample

Figure 78 illustrates the solid behaviour (G´) versus the liquid behaviour (G´´) for pure solvent and fresh MCC/solvent sample solution prepared at condition (1:5, 60 °C, 600 rpm). In this figure, similar patterns could be seen for the ZnI_2 solvent as for the previous solvent system which suggested a higher liquid behaviour than solid behaviour. This indicates that the cellulose dope, in these conditions, behaves as a liquid material. As expected, both moduli were much higher when cellulose was present.

Also for this solvent system, the temperature ramp analysis was used to provide information regarding the changes in viscosity and liquid/solid behaviour upon increasing temperature.

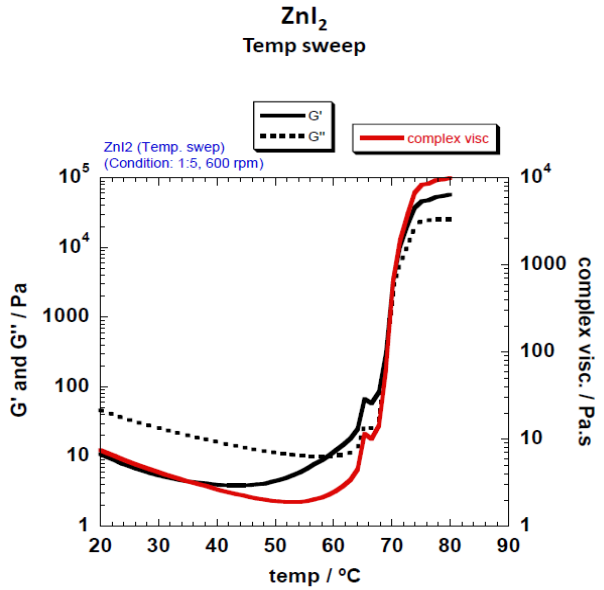

Figure 79. Temperature sweep analysis, ZnI_2:H_2O Variations in viscosity and solid/liquid behavior (G´/G´´) upon increasing temperature (1:5, 600 rpm, 60 °C, 30 min)

As for the temperature ramp analysis of the $ZnCl_2$:H_2O sample solution there existed a predominant liquid behaviour at lower temperatures. However, the solid behaviour of the ZnI_2:H_2O sample increased radically close to 60 °C resulting in the gelation of the sample at temperatures higher than 60 ºC (see figure 79). At the same time that we observe the crossing between both moduli, the complex viscosity follows the trend and increases abruptly. Comparing the two molten salts, $ZnCl_2$:H_2O and ZnI_2:H_2O, a more rapid gelation for the latter molten salt system can be observed giving the indication that a greater stability of cellulose dope is achieved in the $ZnCl_2$:H_2O system.

5.4 Degradation measurements

These highly concentrated salt solutions are typically present a low pH, causing the solvents to behave as a Lewis acid. Therefore, it was important to include studies regarding the possible degradation which occur during dissolution trial. By determining the difference in sample weights of cellulose before and after the dissolution trial attempts were made to estimate the loss of cellulose due to degradation. Nevertheless, we should highlight that these tests need support from other techniques such as the DP (degree of polymerization) determination via intrinsic

viscosity measurements. Calculations for the degradation measurements can be found in Appendix.

The conditions chosen for measurements were the following:

$ZnCl_2$:H_2O hydrated salt

- (1:4 40 °C, 400 vs. 600 rpm)

ZnI_2:H_2O hydrated salt

- (1:5, 60 °C, 600 rpm)

The yield (%) was calculated via the following equations:

$$m(\text{cellulose in dope}) = m(\text{dope}) \cdot \%(\text{cellulose}) \quad \text{(equation 7)}$$

$$\text{Yield (\%)} = [m(\text{coagulated})/m(\text{cellulose in dope})] \cdot 100\ \% \quad \text{(equation 8)}$$

Where,

m(dope)= mass of entire dope (30 gram)
%(cellulose) = cellulose content in dope (constant 2% of total batch volume)
m(cellulose in dope) = mass of cellulose in dope
m(coagulated) = mass of cellulose in dried coagulated cellulose (100% cellulose content)

The resulted yields are presented in the following table and are the average value of each condition.

Table2. Average yields of cellulose from dried coagulated samples calculated from dissolution trials

Dissolution Conditions	**Average Yield (%)**	**Observations**
$ZnCl_2$:H_2O (1:4, 40 °C, 400 rpm)	112%	No sign of degradation, however uptake of moist in the air.
$ZnCl_2$:H_2O (1:4, 40 °C, 600 rpm)	111 %	No sign of degradation, however uptake of moist in the air.
ZnI_2:H_2O (1:5, 60 °C, 600 rpm)	101 %	No sign of degradation

Since the furnace dried coagulated samples were extremely sensitive towards moist in the air there existed a high chance of moist uptake during the process of weighing the dried coagulated sample. Hence, it was possible that the water uptake from the surrounding air could have influenced the measurements resulting in the increase average yield. It has been reported in previous studies of dissolving cellulose in $ZnCl_2$:H_2O hydrated salt systems that major degradation of the polymer takes place. Hence having no weight loss, as showed in this degradation measurement, was not consistent with information gained from previous studies.

There are several reasons behind the results gained from the degradation method, besides the uptake of water. For instance, even though degradation of the cellulose polymer takes place there is the risk of having smaller degraded fragments of cellulose present in the regenerated cellulose during the coagulation process (95% ethanol). This leads to no loss of degraded cellulose into the solvent system and the total mass of the regenerated material is virtually the same as before dissolution. Additionally, there is also the risk of having solvent ions from salt trapped in the in the 3 dimensional structure of cellulose, which even upon washing has not successfully become removed. This also leads to weight gain and results in inaccurate results. Therefore, taking all aspects into consideration, there seemed to be a low reliability of the methods for providing information regarding degradation (hydrolysis) of cellulose in different solvent systems. In conclusion, other methods are needed for determining the degree of degradation, such as intrinsic viscosity and nuclear magnetic resonance (NMR).

6. Discussion

Based on the observations gained from the dissolution trials, the hydrated salt systems $ZnCl_2$:H_2O (1:4, 40 °C, 600 rpm) and ZnI_2:H_2O (1:5, 60 °C, 600 rpm) appeared to provide good dissolution of cellulose resulting in high viscous and rather transparent sample solutions. The results remained consistent with the results gained from the light microscopy measurements and rheology measurements which both showed good indications of full dissolution. The results gained from the $ZnCl_2$:H_2O (1:4, 40 °C, 600 rpm) condition correlated with results gained from previous studies in literature studies. However, not much information in literature research could be found for the ZnI_2:H_2O hydrated salt regarding the dissolution of cellulose; hence no conformational information could be found in previous studies. From the rheological measurements, same indications was given as both sample solutions showed decrease in viscosity upon increasing shearing indicating the breakage of existing interactions between the species of the solvent system and the cellulose polymer. However, upon comparing the results gained from the temperature ramp there seemed to be a higher stability of the sample derived from the $ZnCl_2$:H_2O sample solution compared to the ZnI_2:H_2O sample solution as a more rapid gelation of the latter sample solution occurred around 60 °C. Although, the overall conclusion which could be made for the zinc based hydrated systems was that both systems provides a good dissolution, indicating that the Zn^{2+} cation has a favourable effect on dissolution. For both of the zinc based hydrated salt systems there appeared to be a greater dissolution upon using a higher stirring rate.

For the hydrated salts $LiCl:H_2O$ (1:3, 60 °C, 600 rpm) and $MgCl_2:H_2O$ (1:10, 60 °C, 600 rpm), neither of the solvent systems seemed able to dissolve cellulose upon using extreme conditions of high temperature and high molar ratio of salt. In literature studies it was suggested that $LiCl:H_2O$ acts as a swelling agent upon dissolving cellulose, this information however could not be fully confirmed as the light microscopy measurements only gave indications of dispersion and potential major degradation by hydrolysis of the cellulose polymer. The same results were obtained for the $MgCl_2:H_2O$ solvent system which partially corresponded to what is suggested in the literature research; decomposition by hydrolysis of the cellulose polymer. There existed the chance of partial dissolution of cellulose for both solvent systems since the light microscopy images showed less residues of MCC in the solvent system after dissolution. However, since no indication of increased viscosity could be observed during the dissolution trials for neither of the hydrated solvent systems, no immediate conclusion could be made. As for the previous zinc based solvent systems, more analytical methods have to be included.

7. Conclusion

The overall conclusion gained from this study is that the Zn^{2+} based hydrated salt systems, $ZnCl_2:H_2O$ and $ZnI_2:H_2O$, are able to provide good dissolution of cellulose indicated by high viscous and transparent sample solutions after dissolution process. This was also further confirmed with both light microscopy measurements and rheological measurements, both which showed indications of good dissolution. The optimal conditions for dissolving MCC, based on the observations from the completed analytical measurements, were found at $ZnCl_2:H_2O$ (1:4, 40 °C, 600 rpm) and $ZnI_2:H_2O$ (1:5, 60 °C, 600 rpm). The results gained for the $ZnCl_2:H_2O$ (1:4, 40 °C, 600 rpm) condition corresponds with previous trials provided in literature research. However, for the $ZnI_2:H_2O$ hydrated salt system, additional analytical tests are needed to provide with better conformation since none could be found in literature research. Upon comparing the hydrated salts, there appeared to be a lower stability of the sample solution prepared with $ZnI_2:H_2O$ hydrated salt due to faster gelation at temperature above 60 °C. However, overall it appears that the Zn^{2+} cation has a favourable effect on dissolving cellulose. Little correlation could be given for dissolution effects of Cl^- anion since different hydrated salts containing the anion provided with different outcomes; $ZnCl_2:H_2O$ (successful dissolution), $LiCl:H_2O$ and $MgCl_2:H_2O$ (non-successful dissolution).

The conclusion which could be made for the chloride based hydrated salt systems was that no complete dissolution could be observed for any conditions using the concentrated aqueous salts $LiCl:H_2O$ and $MgCl_2:H_2O$ as solvent systems. However, considering that $ZnCl_2:H_2O$ has proved successful for dissolving cellulose little correlation could be obtained regarding the dissolution effects of the Cl^- anion. More studies are needed to provide with a better understanding regarding the effects of dissolution using different hydrated salt complexes containing Zn^{2+} and Cl^- ions.

The final conclusions based on the analytical trials are the following:

- **The Zn^{2+} based hydrated salt systems**, $ZnCl_2$: H_2O and ZnI_2:H_2O, were successful in dissolving cellulose and can be used as effective solvents for MCC. This gives the indication that Zn^{2+} has a favourable effect on dissolving cellulose.
- **The Cl^- based hydrated salt systems**; $ZnCl_2$:H_2O, LiCl:H_2O and $MgCl_2$:H_2O provided with different results indicating little correlation for the dissolution effect of the Cl^- anion. The hydrated salt $ZnCl_2$:H_2O, as previously mentioned, provided with good dissolution, whereas the two last hydrated solvent systems showed poor dissolution abilities.

8. Future work

For all the hydrated systems, additional analytical tests are needed to provide better understanding of the underlying mechanisms which takes place during dissolution of cellulose in different solvent systems. For instance, qualitative analytical tests can be used to provide with better correlations for the Cl^- based solvent systems and how the cellulose structure is affected in each solvent. Examples of qualitative analytical tests are nuclear magnetic resonance (NMR) and intrinsic viscosity measurements (IV) which can be used for providing further characterization of the cellulose sample solution and detect possible degradation or change in cellulose structure after dissolution.

Moreover, it would also be interesting to include a wider range of concentrated aqueous salts containing the Cl^- anion and Zn^{2+} cation in order to draw a more firm conclusion regarding to their effects on dissolution process. The Zn^{2+} cation has previously been documented for having a favourable effect on dissolution, which also has been confirmed by experimental and analytical procedures in this project. Research should hence include additional hydrated salts containing the I^- anion since the ZnI_2:H_2O hydrated system also had been successful in providing good dissolution and can give valuable information towards whether the cation Zn^{2+} or the I^- anion has the most favourable effect on dissolution. Moreover, by including additional hydrated salt systems containing these specific cations and anions one will be able to provide with a hint of how these ions act in a salt complex and affect the solubility of cellulose.

9. Acknowledgement

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I owe sincere gratitude to my supervisor Alberta Mok (SP) who has given me much help and assistance throughout my diploma work. Her guidance and excellent introduction to the underlying science behind cellulose and cellulose dissolution has indeed brought me a better understanding of the field. I would also like to thank Dr. Bruno Medronho, prominent cellulose researcher at University of Algarve, for his valuable feedback during the entire project and for providing me with a good revision of the final thesis report. Furthermore, I would like to give my sincere appreciation to Mats Westin (SP), Åsa Östlund (SP) and Hanna de la Motte (SP) who all have functioned as mentors throughout the thesis work and provided me with good insight of

the scientific background and experimental procedures of the project. Finally, I would also like to express thanks to my examiner, professor Krister Holmberg at the division of Applied Chemistry (Chalmers), for giving me appreciated guidance and support throughout the project as well.

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