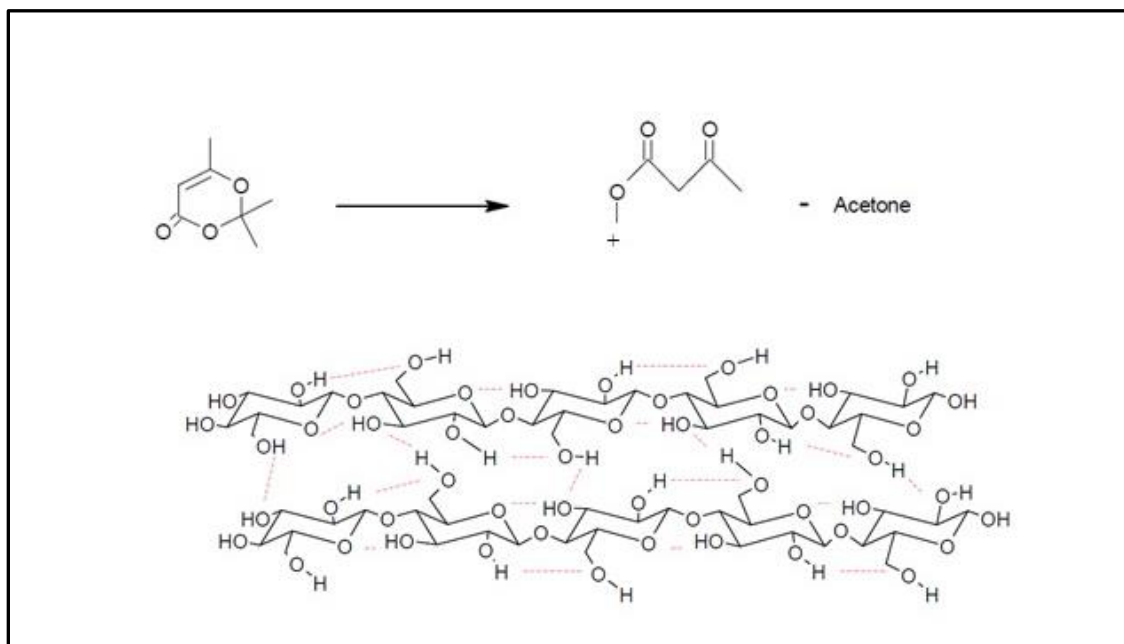




CHALMERS



Cellulose Reinforced Composites

The influence of surface modification

A Bachelor Thesis within Chemical Engineering

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Department of Chemistry and Chemical Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

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Akademisk avhandling för kemiingenjörsexamen på Chalmers tekniska högskola som försvaras offentligt den 5 juni 2018, klockan 17.00 på Kemigården 4, sal KS101 på Chalmers Tekniska Högskola, Göteborg.

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ABSTRACT

The transition from fossil to a renewable and bio-based society is one of our greatest challenges. To deal with this there are many solutions that must be found. One area that shows potential is materials from renewable resources, where composites are of special interest. They have a great application area and can be a combination of fossil and renewable materials that could lighten the fossil dependence during the transition towards 100% renewable competitive materials.

A renewable material that can be utilised for composites is cellulose. With good thermal and mechanical properties and the fact that it is the world's most abundant biopolymer makes it suitable as a reinforcement material in the composites. A strong reinforcement however is dependent on the materials interfacial stress transfer abilities, meaning that there needs to be good adhesion between the surfaces of the materials. If cellulose is to be mixed in a hydrophobic matrix that is plastics polymers, surface modification must be done to reduce its hydrophilic nature. This can be done through esterification reactions where hydroxyl groups on the cellulose molecules are substituted with molecules that are more hydrophobic.

In this thesis, bio-composite materials were created by mixing modified cellulose and the plastic polymer LDPE, where initial studies were made by exploring three different reagents ability to modify the cellulose surface through esterification. The reagent that formed the most successful esters were then used in the compounding of the composites. The composites later went through tensile tests to see if a relationship could be found between the chemical modification and material performance.

Diketene-acetone adduct proved to be the most effective reagent at forming cellulose esters and was thus used as the modifying agent for the composites. Two different cellulose substrates with three degrees of reagent load were studied. Results showed that mechanical properties increase when using cellulose as a composite reinforcement material. However, the results also show that increasing the hydrophobicity does not necessarily seem to improve the composites mechanical properties. When the cellulose is modified with high reagent load the reaction seem to weaken the cellulose polymer. It is suspected that areas of agglomerated cellulose networks make for an un-distributed surface contact with the reagent leading to areas with hydroxyl groups that are more susceptible to esterification reactions. This consequently means that those areas can form less hydrogen bonds which thereby creates mechanical weak spots. A result that signifies that there is no linear correlation between cellulose hydrophobicity and composite

strength meaning that there are more variables that need to be considered when creating bio-composite materials.

SAMMANFATTNING

Inför framtiden är övergången från det fossila till förnyelsebara och biobaserade samhället en av de största utmaningarna. För att klara detta krävs flertalet lösningar på problem. Ett område som visat stor potential är material från förnyelsebara resurser, där kompositer är av stort intresse. Kompositer kan appliceras på ofantligt många områden och kan vara en kombination av fossila och förnyelsebara material, som kan minska behovet av de fossila råvarorna under övergångsperioden mot ett 100% förnyelsebart och konkurrenskraftigt material.

Ett förnyelsebart material som kan användas för tillverkning av kompositer är cellulosa. God termisk förmåga och mekaniska egenskaper, och det faktum att det är världens mest tillgängliga biopolymer, gör den lämplig att armera med i kompositer. En bra armering är beroende av materialens förmåga att överföra spänning över gränssnittsyterna, vilket innebär att god vidhäftning mellan materialen är ett måste. Om cellulosa blandas med en hydrofob matris likt en plastisk polymer bör en yt-modifiering av cellulosan ske för att reducera dess naturliga hydrofila yta. Detta kan göras genom esterifieringsreaktioner där hydroxidgrupper på cellulosamolekylen substitueras med molekyler som är mer hydrofoba.

I detta arbete har biokompositmaterial tillverkats genom att blanda modifierad cellulosa och den plastiska polymeren LDPE, där initiala studier gjordes genom att undersöka tre olika sorters reagens förmåga till att modifiera cellulosans yta genom esterifiering. Det reagens som lyckades skapa tydligast esterifiering användes sedan vid tillverkning av kompositer. Kompositerna gick sedan igenom dragprovstester för att se eventuella samband mellan den kemiska modifieringen och materialets egenskaper.

Diketen-aceton adduct visade sig vara det mest effektiva reagenset för att bilda cellulosaestrar och användes följaktligen som modifieringsagens till komposittillverkningen. Två olika cellulosasubstrat med tre nivåer av reagenstillstånd studerades. Resultaten visade på att de mekaniska egenskaperna ökade med mängden tillsatt cellulosa som armeringsämne i kompositerna. Emellertid, så visade resultaten också på att ökad hydrofobicitet inte nödvändigtvis förbättrade de mekaniska egenskaperna hos kompositerna. Då cellulosan utsätts för hög reagenstillstånd verkar det som att det försvagar cellulosapolymeren. Det antas att områden av agglomererade cellulosanätverk skapar en ojämn fördelning av ytillgänglighet för reagenset, som leder till områden med hydroxidgrupper som är mer mottagliga för förestringsreaktioner. Detta innebär att dessa områden kan bilda mindre vätebindningar, vilket i sin tur skapar mekaniskt svaga punkter. Ett resultat som innebär att det inte finns någon linjär

korrelation mellan cellulosahydrofobicitet och kompositstyrka, vilket medför att det finns fler variabler som måste tas i beaktan vid framställningen av bio kompositer.

LIST OF ABBREVIATIONS

Anhydrous glucose unit – AGU

Alkyl ketene dimer – AKD

Carbon-13 nuclear magnetic resonance – C-NMR

Degree of substitution – DS

Degree of Polymerisation – DP

Diketene-Acetone Adduct – DAA

Fourier transform infrared spectroscopy – FTIR

Low density polyethylene – LDPE

Microcrystalline cellulose – MCC

Proton nuclear magnetic resonance – H-NMR

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1 INTRODUCTION

1.1 Background

As we have become more and more aware of climate change in the latest decades and how the unsustainable use of fossil-based resources is accelerating this, there has been an ever-growing desire to decrease the use- and the reliance of fossil-based resources. To deal with this, different solutions to many areas must be applied. One that has huge potential are materials from a bio-based nature. Though, further research and development must be conducted before these materials fully can compete with the non-renewable ones. Therefore, must new solutions be found where the bio-based resources are utilized better to make the materials more competitive. When it comes to plastics it is seen that in present state most environmentally friendly polymers e.g. poly lactic acid cannot compete economically with plastics derived from fossil-based nature. To work around this problem, to mitigate the environmental impact, one way to approach it is to use inexpensive natural fibres as filler material. It can either be used to reduce the cost of the expensive environmentally friendly ones or to reduce the usage of fossil-based material (*Sumigin, D., et al 2012*). Using natural fibres as a filler also has the potential to work as a reinforcement, turning the material into a composite.

Composites is a type of material that is widely used in industrial manufacturing where its benefits lie in the great versatility of the material. It is composed of two or more different raw-materials whose individual properties are combined. Having this adaptability where the material properties can be changed to the demand of the environment, makes it applicable in many areas. One natural fibre that can be utilised is cellulose. It is the most abundant biopolymer on earth and because of its good thermal and mechanical properties it is suitable to use as a reinforcement material. A reinforced composite material depends on molecular interactions and structural alignments between the different materials for stress to easily transfer between boundary surfaces. For cellulose, having both hydrophobic and hydrophilic properties result in a negative effect on the interfacial adhesion to the hydrophobic matrix of a plastic polymer (*Herrera-Franco, P, J. & Valadez-Gonzalez, A 2005*). This can be improved by chemically modifying the surface properties of the cellulose molecule, making it less hydrophilic. This is however, an extremely complex field to understand and therefore it is also hard to predict how structural modifications and variations will affect the material properties.

To understand the complexity that is surface modification and mixing of polymers, studies are needed on both molecular and material property level.

1.2 Purpose specification and scope

The purpose in this thesis is to create bio-composite materials by using plastic polymer LDPE (Low Density Polyethylene) and cellulose as reinforcement, to study the behaviour of different surface modifications and their influence in the making of the composite.

The cellulose is going to be modified through esterification reactions using three different types of reagents. The first one being a nitrile derivative that is quite unexplored for this purpose. The second, a commonly used substance in the paper industry for improvement of wetting ability. The third, a chemical used for acetoacetylation of different substances. The modification of the cellulose aims to increase the surface adhesion to the plastic polymer and thereby also improve it as a composite material. With the limited time and resources in this thesis not all theories, properties and aspects can be considered, and therefore FTIR will be our main validating device when making decisions on how to proceed forward.

The reagent that forms the most successful esters are the ones that will be used in the composites, and the aim during the study is to find a relationship between chemical modification, surface activity and material performance.

2 THEORY

This section will introduce some theoretical aspects of the experiments, materials and machines that were used during this thesis.

2.1 Wood composition and cellulose

Wood is a good bio-resource material for which mankind have used for a long period of time, but there are still many properties that yet have not been utilised and for which much research and development is done to unravel. Benefits of using wood for applications is that it is a renewable resource that is CO₂ neutral and if used as building material it even can be seen as a way for carbon capture provided that new plants are sown. Wood are in many countries an abundant resource that is easy to transport and can be harvested all year around. The wood in trees is built up by cells that has thick and strong cell walls, known as wood fibres. The fibres are built up by four types of different constituents: lignin, extractives, hemicellulose and cellulose. The composition of these vary between tree species and place of growth but can generally be approximated by the numbers shown in Table 1, where variations within softwood and hardwood is seen. (Henriksson et al.,2008)

Table 1. Typical composition values of softwood and hardwood. (Henriksson et al.,2008)

	<u>Softwood</u>	<u>Hardwood</u>
<u>Cellulose</u>	<u>42±3</u>	<u>45±4</u>
<u>Hemicellulose</u>	<u>27±2</u>	<u>30±5</u>
<u>Lignin</u>	<u>28±3</u>	<u>21±4</u>
<u>Extractives</u>	<u>3±1</u>	<u>4±2</u>

In the pulping process it is possible to separate these constituents from one another by digesting woodchips in a reactor with a water-based solvent containing sodium hydroxide and sodium sulphide, called Kraft pulping process and different types of sulphite-based solutions in the sulphite pulping process. In this process hemicellulose, lignin and extractives are dissolved and hydrolysed yielding a cellulose rich pulp. The hydrolysed and dissolved organic materials are incinerated together with the cooking chemicals in a recovery boiler while the pulp often, depending on application purpose, is further treated through several bleaching steps. This pulp mainly constitutes of cellulose together with some hemicellulose but can also contain small fractions of lignin and can be used in many application areas such as printing paper, packaging and tissue products. Another type of pulp containing mainly cellulose is dissolving pulp. It is either produced by adding a pre-hydrolysis step to the kraft process which enhances hemicellulose removal and delignification reactions, or through sulphite process. Dissolving pulp is used to produce textile fibres. If an acid hydrolysis is performed after the pulping process one can obtain a highly pure cellulose content where also the cellulose chain has been hydrolysed to fragments with low degree of polymerisation, called microcrystalline cellulose. (Battista 1950; Virtanen, Svedström et al. 2012) microcrystalline cellulose has a very high surface area compared to normal pulp fibre and can be used for applications such as hydrogels, composites and films and barriers.

Cellulose is a linear polysaccharide made up of β -D-glucopyranose units commonly referred to as Anhydrous Glucose Units, AGU. These are linked to each other through β -1,4 ether bonds, also called glucosidic bonds. Every second AGU is rotated 180° meaning that one cellulose monomer consists of two AGU: s, see Figure 1. The degree of polymerisation of wood cellulose polymers is about 8000. The polymer chain is said to have one reducing end and one non-reducing end. This is because the reducing end has ability to mutarotate into an aldehyde by

opening its ring structure. This aldehyde in turn can reduce for example the transition metal Cu^{2+} . (Lennholm, H. Blomqvist, K. 2008)

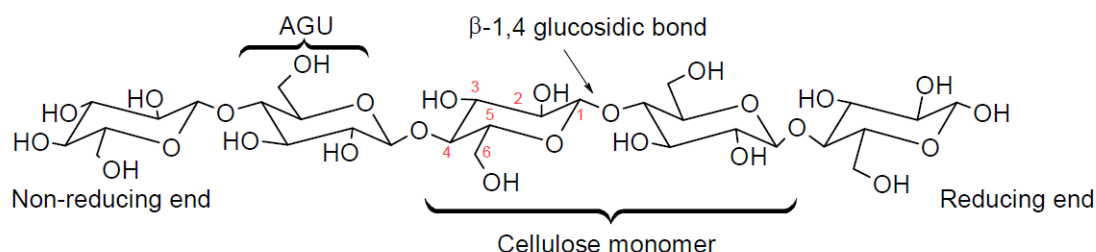


Figure 1. Schematic figure of a cellulose chain

The rotation of the glucose units enables for high amount of intra – and intermolecular hydrogen bonding which results in a configuration that is both linear and planar, schematics can be seen in Figure 2. This further enables the polymer chains to configure them self in a strong ordered sheet like manner. (Lennholm, H. Blomqvist, K. 2008)

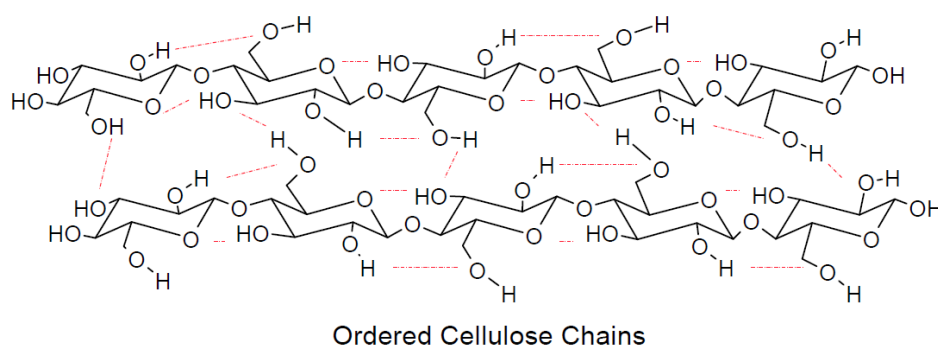


Figure 2. The configuration of ordered cellulose chains showing the hydrogen bond interactions.

The glucose units have a configuration that makes it hydrophilic in the plane because of the hydroxide groups pointing outwards. Above and below the plane however, it is rather hydrophobic due to the chair conformation. These hydrophilic and hydrophobic interactions between units and polymer chains make them organise into microfibrils with crystalline and amorphous regions. These microfibrils form packed aggregates called fibrils which constitutes parts of the cell wall structure. (Lennholm, H. Blomqvist, K. 2008)

2.2 Esterification of cellulose

Cellulose is often modified to organic esters to change its physical properties, like its poor solubility in many solvents and that it cannot be melted without decomposing. These properties makes it hard to process together with other materials, but by converting it into cellulose esters new properties are gained which makes it easier to process and opens for a greater application area for the parent cellulose polymer. Some areas where these derivatives are used today are in coatings, membranes, optical films and composites. (Edgar, K, J. Buchanan et al. 2001)

Esters can be the product from many different derivatives but a general method to produce an ester is by reacting carboxylic acid and alcohol in the presence of a strong acid at about 100°C (Atkins, P., & Jones, L. 2013). From Figure 3 showing a general esterification reaction, the ester formation is controlled by the equilibrium position. To tilt the equilibrium towards increased ester formation, additional acid or alcohol can be added to the mixture. Removing water during the reaction has the same effect.

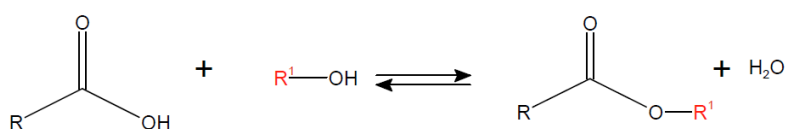


Figure 3. A general esterification reaction between carboxylic acid and alcohol. Adapted from Atkins, P., & Jones, L. (2013)

This general concept of esterification can be applied on cellulose modification. By the same manner as described above it is possible to produce a cellulose ester as the one seen in Figure 4, showing the product of cellulose that has reacted with acetic acid. Cellulose derivatives like cellulose acetate are formed by nucleophilic substitution reaction of the hydroxyl groups with a reagent e.g. carboxylic acid.

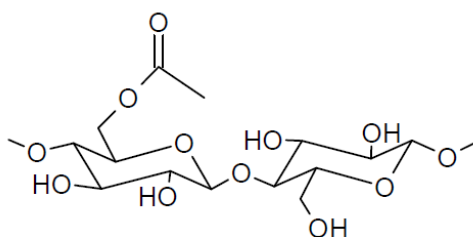


Figure 4. Cellulose acetate. Esterified AGU to an acetate molecule.

The amount of reacted hydroxyl groups on average per AGU is defined as degree of substitution (DS). This number ranges from 1-3 since three is the amount of hydroxyl groups per AGU. The hydroxyl groups in the AGUs have different susceptibility to react depending on their situation in fibre since cellulose do not fully dissolve in reaction mediums with heterogenous conditions. Some AGUs are not laid bare for those reasons and thereby are not available for any reagents. AGUs situated on the surface of a fibre are more accessible for reactions than those inside. This means that under the named conditions the DS cannot get to three. It also means that the amount of substitution will be unevenly distributed on the fibre. (Brodin, M. 2013).

2.3 Polyethylene Cellulose Composites

Polyethylene is one of the most common plastic polymers used today and is mostly produced from a fossil feedstock. Polyethylene is a thermoplastic meaning that it has the property of a lower melting temperature than its decomposition temperature and thereby can repeatedly be reshaped while above melting temperature (*Pritchard, G 1999*). Depending on the polymers application area, the properties of polyethylene can be tailored by varying production parameters or conditions resulting in polymers with different degree of crystallinity, density, molecular weight and amount of branching. LDPE, that was used during this thesis, is a linear polymer whose backbone has a high amount of long-chain branching. The branching chains prevents alignment and tightly packing with other polymer chains, leading to low crystallinity and thereby low density (*Sastri, V. R. 2013*). LDPE has good dielectric, chemical resistance and flexibility properties and is commonly used for electric cables, plastic bags and sterile packaging.

Composites are materials consisting of at least two different raw materials that are bound together in such a way that stress can transfer through the boundary of the two phases (*Hench, L., & Jones, J. (Eds.). 2005*). By combining two materials with different physical or chemical properties one can obtain a material that has a combination of the two. Polymer composites can be mixes of glass fibre, carbon fibre or cellulose fibre, where one wants to obtain the strength properties from the fibre and flexibility and toughness from the plastic polymer. In the case of a thermoplastic like LDPE it will mean that the composite mixture of LDPE and a fibre is stronger and stiffer, yet still mouldable when above melting temperature. When reinforcing a hydrophobic material such as LDPE with cellulose fibres however, there are some properties that needs to be altered before they make a good composite (*Brodin, M. 2013*). The hydrophilic areas of the cellulose polymer have a negative effect to the interfacial adhesion when preparing

a composite with a hydrophobic matrix. The poor adhesion affects the stress transfer between the boundary surfaces leading to weak composite. Cellulose also have a strong affinity for other cellulose molecules which make them tend to agglomerate into aggregates. Cellulose aggregates further reduce the stress transfer due to decreased amount of surface area that can interact in the matrix. These compatibility obstacles can be counteracted by modifying the cellulose fibre. (Herrera-Franco, P, J. & Valadez-Gonzalez, A 2005)

2.4 Cellulose modification reagents

In this section a short reaction theory description is done for the different cellulose modification reagents that were used during this thesis.

2.4.1 Amide salt reagents

Preparation of amide salts reagents in this thesis were based on methods done by (Börjesson, M. 2013) where she produced acrylamide sulphate from acrylonitrile, water and sulfuric acid. In her work she managed to derivatise the AGUs by substituting hydroxides with acrylic molecules on the AGU. However, the cellulose ester did not form without acidic hydrolysis degrading the cellulose chain and turning it black. It is thought that it is the sulphate ion who reacts to form sulfuric acid when the hydroxide group is derivatised. The general desired esterification reaction of amide salts with cellulose at elevated temperatures is seen in Figure 5 below.

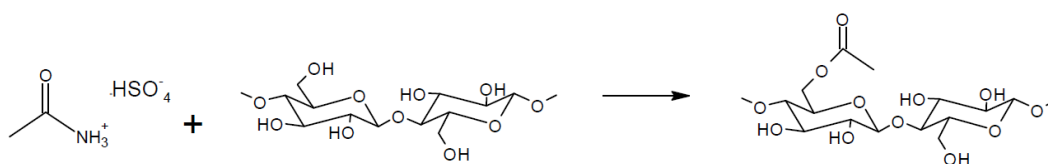


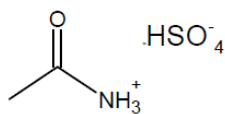
Figure 5. Reaction of cellulose monomer with acetamide sulphate giving an acetate substituted AGU product without cellulose degradation.

In this thesis it was explored if this undesired reaction could be counteracted by trying out different types of amide salts and by using additives. Since this type of substance is relatively unexplored in this field the following text in this section is hypothesis and theories regarding its esterification mechanism with cellulose. They were applied to get a better understanding of the mechanism and to see what conclusions that can be drawn, facilitating further future research.

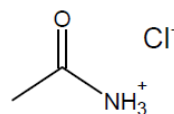
To study the reaction mechanism, three different approaches were conducted. The first being how the effect of using nitrile substrates producing amides with different electrophilic properties could influence the reaction. Secondly, if it was possible to produce amides using acids other than sulfuric acid and thereby obtaining a salt with a different anion. Thirdly, if additives could be used to inhibit the cellulose degradation by precipitation of the sulphate anion.

Amide salts in this thesis were prepared from acetonitrile and allyl cyanide substrates with respective desired product, acetamide and 3-butenamide, seen in Figure 6. It was proposed that the electrophilic properties of the 3-butenamid salt would be better than the acetamide salt making it more prone to form an amide with other acids. A reaction which demands a strong acid, and as an amide more prone to react with AGUs. Using hydrochloric acid to form amide has been proven to work however the effect of substituting sulfuric acid and having a chloride anion in the salt was unexplored in this field. It was hypothesised that the acetamide chloride would change the reaction characteristics while still having strong nucleophilic properties. The significant size difference between the sulphate and chloride anion was thought to possibly effect the reaction. The chloride anion by having less sterically hindrance. The sulphate anion by being bigger with oxygen atoms possibly being able to coordinate in such a way that it might interact more significantly in the esterification reaction. To test the theory of coordination significance it was hypothesised that by using amide salt with phosphate anion possibly could provide this information because of the sulphate structural similarities, though being slightly bigger and less nucleophilic (Figure 6. 3-butenamide phosphate). The phosphate ion also being less nucleophilic should also in theory reduce the chance of cellulose degradation (*Noè, M., Perosa, A., & Selva, M. 2013*).

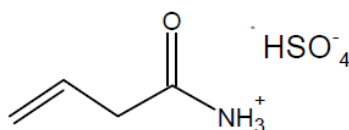
Additives hypothesised to inhibit the acid hydrolysis of the cellulose was $\text{Ba}(\text{OH})_2$ respectively $\text{Ca}(\text{OH})_2$ together with carbonated water. The hydroxide ions provide a basic environment neutralising the acid and the Barium ions would precipitate as barium sulphate as it has a notably low K_{sp} in water, thereby possibly prevent degradation. Excessive barium would precipitate as Barium carbonate. Same theory applies for $\text{Ca}(\text{OH})_2$ though calcium sulphate not having as low K_{sp} as barium sulphate in water, it was chosen since it is more environmentally friendly.



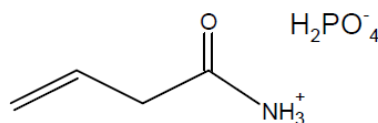
Acetamide sulphate



Acetamide chloride



3-Butenamide sulphate



3-Butenamide phosphate

Figure 5. Amide salt reagents used in esterification of cellulose.

2.4.2 Alkyl ketene dimer

Alkyl ketene dimer, AKD, is a reagent substance commonly used in paper making processes to improve the papers ability to resist wetting, improving the papers e.g. printability properties. AKD is kept in a dispersion of cationic starch that acts as a stabiliser preventing AKD particles from agglomerating. AKD hydrolyses at neutral to basic conditions and is therefore also kept in an acidic environment of around pH 3 (*Hubbe, M. A. 2007*) (*Lindström, T. 2004*). Figure 7 shows some different reaction paths that AKD can take where one is hydrolysis into a ketone in the addition of water which then is unable to react with cellulose. The other is an esterification reaction with the hydroxyl groups, acting as a nucleophile, of the AGU in a heated environment forming a β -keto cellulose ester. Both reactions occur in the presence of cellulose although the esterification reaction being the more favourable of the two.

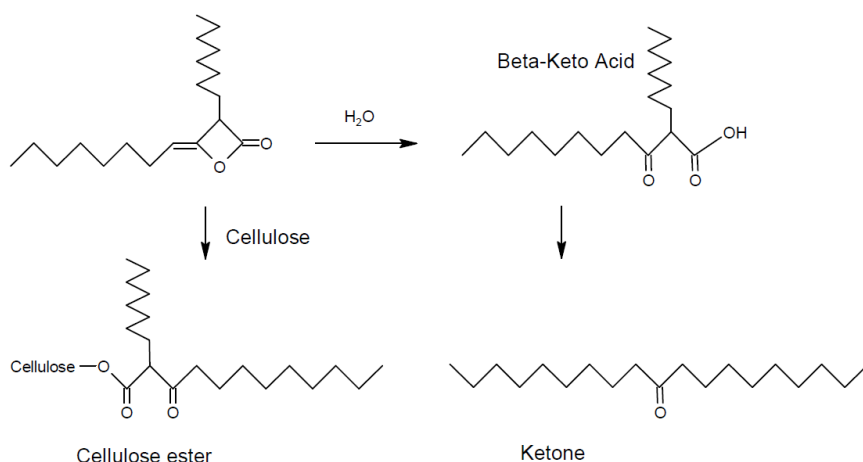


Figure 7. AKD reaction paths with cellulose and water. Adapted from Hubbe, M. (2000)

The reaction between the AGUs and AKD can be further accelerated by using HCO_3^- as a catalyst. The general practice in papermaking processes using AKD as an agent is to use NaHCO_3 , to add a reaction catalyst and to increase the stock alkalinity. For the covalent bonds to form the molecules needs to be in close contact, which do not occur much in cellulose suspension with low dry content due to waters high surface tension. For sufficient reaction, the dry content needs to be above 60% (Lindström, T. 2004).

2.4.3 Diketene-Acetone Adduct

DAA, 2,2,6-trimethyl-4H-1,3-dioxin-4-one, is a substance that can be used for acetoacetylation of aromatic and aliphatic alcohols, amines, and thiols. Reactions are rapid, effective and do not require a catalyst. It is stable in room temperature but starts to decompose in temperatures above 100°C to acetyl ketene and acetone. The acetoacetylation reaction then occurs when the acetyl ketene is in the presence of a nucleophile. (Pawlowski, W. P. et al. 1968) In this thesis DAA is used to acetoacetylate i.e. esterify cellulose to make the AGUs more hydrophobic (Figure 8). This reaction happens when decomposing DAA form acetyl ketene and acetone under heated conditions. The hydroxyl groups of the AGUs then acts as a nucleophile and reacts with acetyl ketene forming a β -ketobutyric acid cellulose ester.

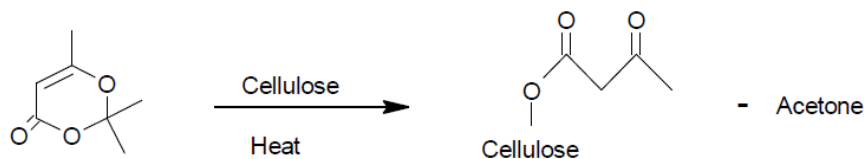


Figure 8. DAA reaction with cellulose forming the products β -ketobutyric acid cellulose ester and Acetone. (Clemens, R. J., & Hyatt, J. A. 1985).

2.5 Spectroscopy

Following spectroscopy instruments were used during the thesis to validate the reaction results.

2.5.1 Nuclear Magnetic Resonance spectroscopy

Nuclear Magnetic Resonance; NMR, is a spectroscopy method that measures a nucleus absorption of electromagnetic radiation in a constant strong magnetic field. It uses the property of nuclides with odd numbered protons or neutrons having a non-zero spin unlike even number nuclides that have a spin of zero. When exposed to electromagnetic field, the non-zero spin nucleus can either align in or against the direction of the field. The two positions have different energy levels and the one aligning in the magnetic field being the lower of the two. When the nucleus then absorbs electromagnetic radiation, it will make the spin to either flip or realign to the higher energy level and then fall back while reemitting electromagnetic radiation. The absorption frequency of an atom is dependant of the environment around the atom. Meaning that a non-zero spin isotope will absorb a frequency that is specific for that isotope in that molecular structure. This property makes NMR a useful tool for identification of molecular structures (*Brian M. Tissue 1996*).

2.5.2 Fourier Transform Infrared spectroscopy

Fourier Transform Infrared spectrometer is a widely used instrument for identifying molecules using the infrared absorption characteristics of molecules. The instrument is commonly set to measure in the mid infrared region $4000\sim400\text{ cm}^{-1}$ because most organic and inorganic ions absorb infrared radiation in this region. The infrared radiation causes molecules to selectively absorb different wavelengths. This changes the dipole moment of the molecules which causes them to vibrate between the energy levels of ground and elevated state. Frequency of absorption is the level of energy gap and is represented on the X-axis in the spectrum in cm^{-1} , telling us what type of molecules, functional groups and linkages there are in the sample. The intensity of absorption is represented on the Y-axis as transmittance and is related to the amount of a certain molecule or functional group etc. there is in the sample. (*Chemistry Libre Texts. 2015 (1)*)

Carbonyl groups absorb infrared radiation in the region of $1800 - 1600\text{ cm}^{-1}$ depending on if it is a ketone, aldehyde, ester or carboxylic acid. Carbonyl groups on esters absorb infrared radiation in the region $1750 - 1715\text{ cm}^{-1}$ and is one of the most relevant absorption bands in this thesis. (*Chemistry Libre Texts. 2015(2)*)

2.6 Extrusion

Extrusion is a common processing method when converting one or a combination of polymeric materials, often in the form of granulates, into a new desired shape or form. This is often either done through a single or a twin-screw extruder. (Kochhar, A. K., & Parnaby, J. 1977).

The process starts by feeding the desired material into the barrel of the extruder. Along the barrel there are heaters that help melt the material in combination by the mechanical energy that is transferred from the turning screws. The screws force the molten polymer to move along the barrel into a die where it is reshaped and then cooled.

3 EXPERIMENTAL

Introduction to some of the more general techniques and experimental parts that have been used during this thesis work are explained in this chapter. Production of substrate, reagents the techniques and performance are explained. For further experimental observations see Appendix V.

3.1 Cellulose Substrate

Three different cellulose substrates were used in different episodes of the thesis work. Explanations on how much of the substrates were used in the experiments are presented as well as the manufacturers.

3.1.1 Microcrystalline Cellulose

The substrate used in the first experiments was microcrystalline cellulose, Sigma-Aldrich, Avicel PH-101 ~50um particle size, with an average DP of 200.

The microcrystalline cellulose was mixed with distilled water to absorb and swell, the reagent will then penetrate the cellulose molecule easier.

3.1.2 Dissolving Pulp sheets

The dissolving pulp used in the experiments were sheets of bleached pre-hydrolysis Kraft eucalyptus pulp with an average DP of 1340, produced by Bahia pulp S.A., Camaçari in Brazil. The sheets were cut in small pieces of 9g. Distilled water was added to penetrate the pulp with the reagent easier.

3.1.3 Mashed up Dissolving Pulp

A sheet of dissolved pulp of 74g were mashed together with 2 litres of water. It was mixed for 30 minutes and a solid weight of 25% was generated. The weight was controlled by drying it with infrared heating for 1 hour at a temperature of 100°C.

3.2 Reagents

The preparation of the reagents will be explained during this section. Six reagents were tested to start the desired chemical reaction. Four of the reagents were prepared during the thesis work. In this section the preparation part will be explained. The other two reagents are chemical substances that did not need any preparation before the reaction.

3.2.1 Acetamide Sulphate

10,8g of fuming sulphuric acid was added to a mixture of 1,8ml distilled water and 0,05g copper(II)sulphate. 4,1g of acetonitrile were then dropped in the beaker for a time of 10 minutes. When the acetonitrile was added, the sample were heated to 95°C and stirred magnetically for 60 minutes. After heated in 60 minutes the result was a highly viscous and yellow, sticky mass (Figure 9). Because of the highly viscous mass only 50% of the produced acetamide sulphate could be extracted from the round bottom flask.

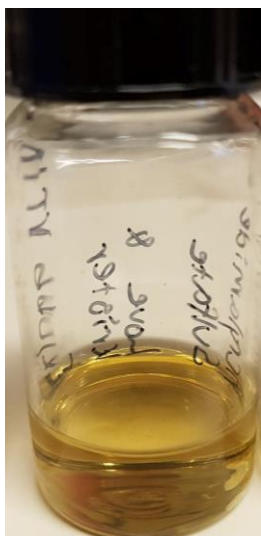


Figure 9: Acetamide sulphate produced from actonitrile, water and sulphuric acid.

3.2.2 Acetamide Chloride

Acetamide chloride was produced through the setup you can see in the picture (Figure 10). The big round bottom flask was connected to another flask through a pipe with a glass pipette in the



end to reach the bottom of the smaller flask. It is necessary that the system is tight, so the hydrogen chloride gas does not leak. 14,75ml of sulphuric acid dripped onto 14,8g ammonium chloride for 10 minutes. A mixture of distilled water and acetonitrile was placed in the smaller flask. The hydrogen chloride gas that was produced from the sulphuric acid and the ammonium chloride, was transported through the pipe to the mixture containing 2,5ml distilled water and 2,45ml acetonitrile. This setup created small transparent salt crystals. The crystals were filtered and washed through vacuum filtration and afterwards the crystals were dried for 17h.

Figure 10. The setup used for the acetamide chloride preparation.

3.2.3 3-Butenamide Sulphate

3-butenamide sulphate (Figure 11) was made from allyl cyanide, distilled water and sulphuric acid.



Allyl cyanide with molar mass 67,09g/mole, water 18,015g/mole and sulphuric acid (98%) 98,079g/mole. Copper(II)sulphate (0,05g) acted catalyst and were added to a round bottom flask with 0,0998 mole distilled water. Sulphuric acid was added with ratio (1:1). Allyl cyanide was added dropwise during 10 minutes with a ratio (1:1). The reaction took place during 60 minutes of magnetic stirring at 95°C.

Figure 11. 3-butenamide sulphate produced from sulphuric acid, water and allyl cyanide.

3.2.4 3-Butenamide Phosphate

3-butenamide phosphate was made of allyl cyanide, distilled water and poly phosphoric acid. Allyl cyanide has a molar mass of 67,09g/mole, water 18,015g/mole and phosphoric acid 97,99g/mole. Dipotassium phosphate (0,05g) acted catalyst and were added to a round bottom flask with 0,0998mole distilled water. Phosphoric acid was added with ratio (1:1). Allyl cyanide was added dropwise during 10 minutes with a ratio (1:1). The reaction took place during 60 minutes of magnetic stirring at 95°C.

3.2.5 Alkyl Ketene Dimer

AKD was used as a reagent with microcrystalline cellulose. The AKD-stock solution from BillerudKorsnäs was added directly to the substrate without any preparations or modifications.

3.2.6 Diketene-Acetone Adduct

Diketene-Acetone Adduct, 2,2,6-Trimethyl-4-H-1,3-Dioxine-4-one, manufactured by Sigma Aldrich with CAS-5394-63-8. It has a density of 1,07g/mL and a Molar mass of 142,15g/mole and was added directly to the cellulose substrate without any preparations or modifications.

3.3 Production of esters

To increase the cellulose molecules adhesion to the polyethylene molecules it must be more hydrophobic. By creating an ester on the cellulose hydroxide group the cellulose can acquire a sidechain that is more willing to bind into polyethylene. In the following part of the thesis the production of the earlier mentioned esters will be explained in an experimental way.

3.3.1 Production of esters using Acetamide Sulphate

110mg of MCC was added to a round bottom flask with magnetic stirring in 15ml of distilled water for 15 minutes to let the MCC swell and be more available for the reagent. After the swelling of the MCC, it was added to the reagent with a molar ratio (1:1) and stirred on a heating plate at a temperature of 50°C for 3 hours. The product was then filtered and washed with ample amount of distilled water. After the filtration the sample was put in the oven for 5 minutes in 105°C for reaction (Appendix III, Figure AIII.3).

The reaction was added two different types of additives. The first additive that was used was barium hydroxide, $\text{Ba}(\text{OH})_2$ and CO_3 .

Excess of $\text{Ba}(\text{OH})_2$, ratio (2:1) were added to the sample after the filtering to ensure that the reaction did not create any sulphuric acid that breaks down the cellulose molecule. The heating in the oven was extended because of the added moisture from $\text{Ba}(\text{OH})_2$. The reaction occurred in the oven for 40 minutes at 110°C (Appendix III, Figure AIII.2).

The second additive that was used was calcium hydroxide, Ca(OH)_2 and CO_3 .

Excess of Ca(OH)_2 , ratio (2:1) were added to the sample after the filtering to ensure that the reaction did not create any sulphuric acid that breaks down the cellulose molecule. The heating in the oven was extended because of the added moisture from Ba(OH)_2 . The reaction occurred in the oven for 20 minutes at 140°C (Appendix III, Figure AIII.1).

3.3.2 Production of esters using Acetamide Chloride

70mg of MCC were added to a round bottom flask with magnetic stirring in 15ml of distilled water for 15ml so the MCC should swell and be more available to the reagent. The MCC absorbed with water were added to the acetamide chloride and was stirred at 50°C for 3 hours. The sample was filtered through vacuum filtration and washed with ample amount of distilled water. After the filtration, four samples were placed in the oven for 20 minutes in 105, 140, 180°C and the last one in room temperature for reaction (Appendix III, Figure AIII.6.).

Two different types of additives were added to the reaction. The first additive that was used was barium hydroxide, Ba(OH)_2 and CO_3 .

Excess of Ba(OH)_2 , ratio (2:1) was added to the sample after the filtering to ensure that the reaction did not create any sulphuric acid that breaks down the cellulose molecule. The heating in the oven was extended because of the added moisture from Ba(OH)_2 . The reaction occurred in the oven for 40 minutes at 110°C (Appendix III, Figure AIII.4).

The second additive that was used was calcium hydroxide, Ca(OH)_2 and CO_3 .

Excess of Ca(OH)_2 , ratio (2:1) was added to the sample after the filtering to ensure that the reaction did not create any sulphuric acid that breaks down the cellulose molecule. The heating in the oven was extended because of the added moisture from Ba(OH)_2 . The reaction occurred in the oven for 20 minutes at 140°C (Appendix III, Figure AIII.5).

3.3.3 Production of esters using 3-Butenamide Sulphate

110mg of MCC were added to a beaker with magnetic stirring in 15ml of distilled water for 15 minutes. After absorbing the water, the MCC was added to the round bottom flask containing 3-butenamide sulphate with a 3:1 molar ratio (3-butenamide sulphate: MCC). The sample was mixed during magnetic stirring for 3 hours at a temperature of 50°C . The product was filtered and flushed with ample amount of distilled water. The reaction took place in oven for 5 minutes at 105°C .

The 3-butenamide sulphate was also added directly onto Dissolving Pulp that were cut into pieces of 9g. They were put in glass slips in access of water and then placed in the oven until dry and blackened, to obtain the esterification.

A new piece 9g of dissolving pulp was added 3-butenamide sulphate in access of water with additive of barium hydroxide, $\text{Ba}(\text{OH})_2$ in carbonated water CO_3 . And followed the same procedure as mentioned above for the dissolving pulp. (Figure AIII.8, Figure AIII.9).

3.3.4 Production of esters using Alkyl Ketene Dimer

During production of esters 110mg of MCC was placed in 15ml of distilled water with magnetic stirring for 15 minutes and applied heating of 50°C . The AKD was calculated to have a Molar mass of 308,488g/mole. 1,5ml of AKD-solution was added to the MCC in three different concentrations and one with an additive (Sodium Bicarbonate) to catalyse the reaction. Three samples with AKD was prepared. One diluted 100 times, one 50 times and one time with concentrated AKD (100 times higher concentration than what is recommended for good dispersion). The one with concentrated AKD was also prepared with an additive which consisted of sodium bicarbonate (2:1). The samples reacted in the oven for 5 minutes at 120°C (Appendix III, Figure AIII.7).

3.3.5 Production of esters using Diketene-Acetone Adduct

7,7g of the mashed-up dissolving pulp were added to three different beakers and 2g MCC were added to three different beakers. First one with a reference, second one with molar ratio (1:1) and a third with molar ratio (3:1). 5,7g Distilled water were added to the beakers containing MCC to obtain the same amount of weight percent, dry weight as the dissolving pulp. 6ml of distilled water were added as a swelling agent to all samples. 10 ml of Propan-2-ol were added for the sample as a transport medium for the DAA. After 2-3 minutes, 4,9ml of DAA were dripped over the samples and pressed until a homogenous colour occurred. The samples were placed in the oven for 60 minutes at a temperature of 160°C . After the reaction in the oven, the samples were rested in room temperature for 4 days. The samples were then washed with acetone, ethanol, distilled water and ethanol again to easier dry the samples. The samples were then dried in oven for 20 minutes at a temperature of 105°C . (Appendix III, Figure AIII.10)

DAA were used during an extra experiment with a higher temperature and with tap-water. Three beakers of 7g, dissolving mass (25 wt%) were added to three different beakers. 10 ml of propan-2-ol were added to the samples. Two of the samples were added 4,9ml of DAA (3:1) and the other one was added 1,6 ml of DAA (1:1). One of the (3:1) samples were added 6ml of tap-

water and the other one was added 6ml of distilled water. The sample with (1:1) ratio were added 9,3ml Distilled water to gain the same amount of dry content in all samples. The reaction occurred in the oven at 180°C for 60 minutes. After the samples were dried, half the amount of the samples was washed in ample amount of acetone, ethanol, distilled water and ethanol again to clean the samples and then placed in the oven to dry for 5 minutes in 105C (Appendix III, Figure AIII.11-13).

3.3.6 Production of esters using Diketene-Acetone Adduct scale-up

20g mashed-up dissolving pulp were added to three big glass beakers. 25ml propan-2-ol were added to each beaker as a transport medium for the DAA. The reference sample was added 27,25ml of distilled water to gain the same amount of fluids as the other samples. Sample 2 (1:1) was added 4,1ml of DAA and 23,15ml of distilled water to replace the amount of fluids from the reagent in sample 3. To sample 3 (3:1) was 12,25ml of DAA added and 15ml distilled water. After absorbing the reagent, the reaction took place in an oven for 60 minutes in 180°C. The samples were then washed with acetone, ethanol, distilled water and ethanol again to wash away all left-overs from the reagent. The samples dried in oven for 3 hours in 105°C and were then left in room temperature for 16 hours (Figure AIII.14, Figure AIII.15).

The same procedure was performed with 5g of MCC with 15ml of distilled water as cellulose substrate.

3.4 Analysis

Different types of analysis methods were used during the thesis work. Three different types of spectroscopy were analysed during the thesis and one type of water retention value test.

3.4.1 Spectroscopy

NMR-spectroscopy was made on the reagents and FTIR-spectroscopy was made on the reacted cellulose.

3.4.1.1 Nuclear Magnetic Resonance Spectroscopy



The NMR-machine that was used during this thesis was a Varian instrument in the chemistry building shown in Figure 12. It was used during the thesis to analyse the reagents and understand the different amides that were created (explained in section 3.2). The NMR provided the thesis work with diagrams and spectra that are presented in Appendix I for H-NMR and Appendix II for C-NMR. H-NMR provides the information about the proton placements in the molecules. C-NMR reveals where the carbons can be found in the molecules. The samples were prepared in NMR-tubes placed in a flask. A glass-pipette was used to gather the small number of samples. The samples were then flushed down in the NMR tubes with 0,7ml of a suitable solvent. The NMR-tubes were carefully shaken and turned upside down a couple of times until the sample was dissolved and ready to be analysed.

Figure 12. The NMR-machine used during the thesis.

3.4.1.2 Fourier Transform Infrared spectroscopy

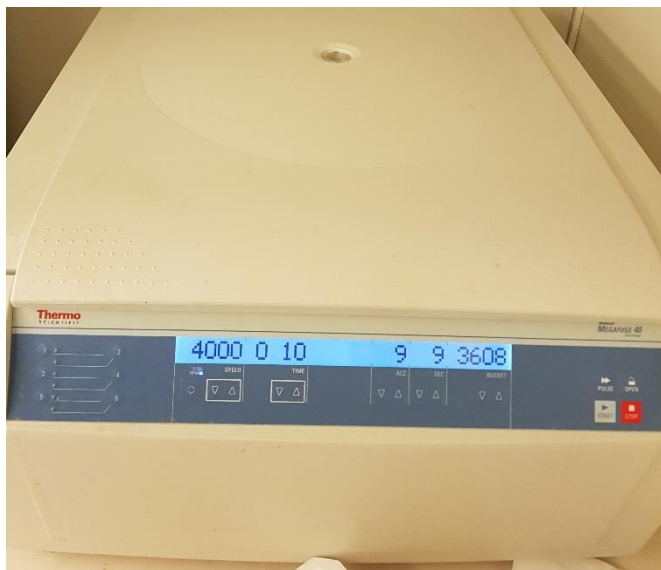
FTIR was made by mixing a small amount of our sample with 300mg of potassium bromide and was grinded in a mortar until the mixture was a homogeneous powder. The pastille was pressed during vacuum for a total time of three minutes at a pressure of 8 ton. The FTIR-machine that was used was a Perkin Elmer Spectrum One (Figure 13). The results and graphs from FTIR are presented in Appendix III.



Figure 13. The Perker Elmer Spectrum One FTIR-spectrometer used during the thesis.

3.4.1.3 Water Retention Value method

Water retention value test were conducted on a reference samples as well as DAA reacted samples for both microcrystalline cellulose and dissolving pulp. 400mg of each sample were put in access of water for 3h with magnetic stirring. The access of water were filtered through a Büchner funnel. The samples were then placed in a filter fabric in VIVASPIN-tubes and were centrifuged for 10min at 4000rpm. The samples were then weighed to obtain the mass of wet cellulose. After being weighed, the samples were dried in the oven at 105 °C overnight. After



17h in the oven the samples were weighed to obtain mass of dry cellulose. The centrifuge machine that was used during the thesis work was a Thermo Scientific Megafuge 40 (Figure 14).

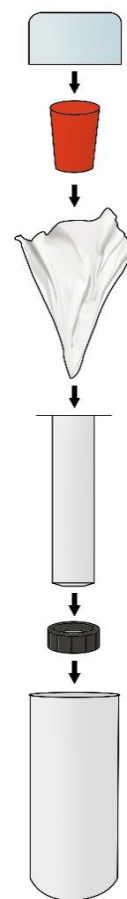


Figure 14. Thermo Scientific Megafuge 40 centrifuge used for WRV-test.

The setup used in the centrifuge is shown in Figure 15. The cellulose could not release water if it did not have a free space in the centrifuge-tubes. The setup from bottom and up; Centrifuge-tube, vacuum cork, the barrel from a plastic syringe without the tip, a fabric filter containing the samples, a rubber cork to hold the filter in the barrel and lastly the centrifuge lid. This needed to be done to free the space between the syringe barrel and the centrifuge tube to make water release easier.

Figure 15.
The setup used for achieving satisfying separation of aqueous phase during centrifugation.

3.5 Extrusion

Before the extrusion could take place, the dissolving mass needed to contain less agglomerated cellulose since the extruder will not be able to extrude dissolving mass with big fibre lumps. Therefore, the dissolving was milled in a mixer. The mixer was an IKA-WERKE from Yellow Line (Figure 16).

Plastic tubes were prepared with a total mass of 5g. In each tube reacted dissolving respectively MCC combined with low-density-polyethylene, with mass ratio 5%, 10% and 30%, was combined for easier feeding into the extruder. Another sample as a reference for low density polyethylene was prepared with 10g in a plastic tube.



Figure 16. Mixer used to mill the dissolving mass before extrusion.

Extrusion was made with Haake MiniLab Twin-screw extruder (Figure 17). The machine was heated 30 minutes before extrusion could begin, where initial extrusion attempts were done on three different temperatures (190, 180 and 170°C). The best result without getting a low viscous filament was given at a temperature of 170°C. The extruder was fed with 2,5g of the given mixtures at the start. Then another 2,5g was added. When flushed the product weighed ~2g. The loss of material during extrusion was approximately 3g per sample, which gave an estimated material loss of 30% for each new sample. The extrusion machine was fed four times on each sample to get filaments of total 6g.



Figure 17. Haake MiniLab Twinscrew extruder used for extrusion during the thesis work.

3.6 Hot-Pressing

The Hot-Pressing was needed to melt the filament produced by the extrusion process in section 3.5. The pressing machine was heated and pressed the samples to a thin film for the following punching of the dog bone composites samples. Four pieces of 0,5mm thick aluminium was the frame for the filament. Two pieces on 9,9cm and two pieces on 7,5cm was placed in a rectangle and 4,5g of the filament was cut in pieces and placed inside the frame. The pressing machine was heated to 180°C and when the desired temperature was obtained the plates with the frame



and filament was placed in the pressing machine for 2 minutes until melted. It was then pressed slowly up to 8 ton and was under pressure for 30 seconds. The plates were then placed on the desk with metal weights until the temperature of the metal plates slowly approached room temperature (approximately 15 minutes). The higher amount of cellulose in the filament the lower pressure and lower temperature was added in the press. Several errors with bubbles occurred with a high temperature and a high pressure in the filaments with a higher amount of cellulose. The hot-pressing machine that was used during the thesis work is shown in Figure 18.

Figure 18. Picture of the hot-pressing machine used during the thesis work.

3.7 Tensile Stress Test



Figure 19. The tensile stress machine used during the thesis work.

The Tensile Stress Tests were performed in the machine technology building at Chalmers University of Technology with guidance from Lilian Forsgren. The dog bone shaped composites were 0,47 mm thick. The machine was working at a speed of 6mm per minute. When the composite broke the graph showed the stretch at breaking point and the force that was needed to brake it. The machine that was used was a Zwick material testing machine type BZ2.5/TN1S Figure 19.

Diagrams and graphs are presented in Appendix IV.

4 RESULTS AND DISCUSSION

The main results from the reactions were made by analysing the FTIR-spectrums, presented in Appendix III. If the reagent did not manage to create esters or if it did at the expense of breaking down the cellulose structure, the reagent was rejected and another reagent with similar functionalities were tested.

4.1 Analysis of the results with Acetamide Sulphate

The reaction results when using Acetamide Sulphate was not as good as desired.

The NMR-spectra proved that the result from the acetamide sulphate preparation worked according to (Börjesson, M. 2013) research though with another nitrile substrate. First attempt, to create the esterification, the cellulose molecule turned grey in a couple of minutes which indicated that we got a reaction similar to the research mentioned above.

The esterification and degradation did not take place in the first attempt to recreate this reaction. A new NMR test was made to verify if the reagent had changed in structure, possibly

decomposing over time. It showed that nothing had happened in the structure and that it was the same substance. One conclusion that has been made in hindsight is that the reagent possibly got washed away when filtrating the sample leaving little to no reagent left to react in the oven. But attempts with additives was still made to see if they might have effects on the reaction mechanism.

The purpose of adding Barium- and Calcium Hydroxide in combination with carbonated water was to counter act the side reaction. The result however when using them together with the reagent that did not manage to esterify the cellulose on its own, showed absorption peaks in the same frequency as esters. Initially this made us believe that the additive had a significant effect of the reaction mechanism, but later reference testing of the additive showed that it was Barium- and Calcium carbonate. (Appendix III, Figure AIII.1-2)).

4.2 Analysis of the results with Acetamide Chloride

Like the result from Acetamide Sulphate, the Acetamide Chloride was not successful in esterification reactions.

The NMR-spectra proved that the result from the Acetamide Chloride preparation worked according to scientific publications (Appendix II, Figure AI.2).

Samples were running parallel to the Acetamide Sulphate and showed no esterification's at all regardless of temperature in the oven. When using additives, just like Acetamide Sulphate, peaks appeared in the same intervals as esters which again initially made us believe that the additive had a significant effect of the reaction mechanism. (Appendix III, FigureAIII.4-6).

NOTICE! When the experimental part of the thesis was done, discussions and analysing of the results made us assume that the reagent might have been washed away during filtration. A new attempt for making an esterification was made on a dissolving sheet in access of water. The sheet turned brown in the oven at 150°C, and at a reaction time of 60 minutes (Figure 20). The FTIR diagram below shows a small but significant peak at 1725cm^{-1} which indicates esters (Figure 21).



Figure 20. Picture of the dissolving sheet reacted with Acetamide Chloride, additional attempt post bachelor thesis experiments.

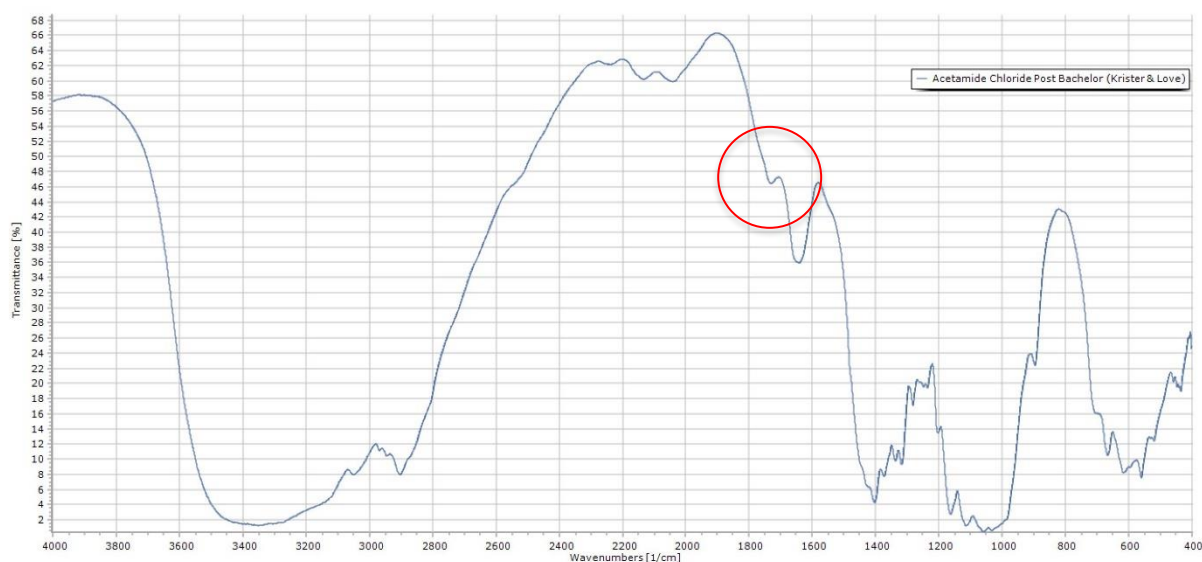


Figure 21. FTIR-spectra for dissolving sheet reacted with acetamide chloride additional attempt post bachelor thesis experiments.

4.3 Analysis of the results with 3-Butenamide Sulphate

Using 3-Butenamide Sulphate as a reagent proved to be successful in forming esters, however just as acrylamide sulphate in (Börjesson, M. 2013) research it did not form without degrading the cellulose and turning it black.

The NMR-spectra proved that the result from the 3-butenamide sulphate preparation in fact formed the desired product (Appendix II, Figure AII.1). Various attempts were conducted where temperature, reaction time and additives varied. All results showed that the further the reaction went, regardless of temperature alterations, the more esters were formed and with that a black degraded cellulose backbone. The additives used did not seem to have any influence on the reaction. The results from the FTIR (Appendix III, Figure AIII.8) where a sample was taken out of the oven at the first sight of discolouration, shows that only the area on the dissolving pulp with discolouration had ester absorption peaks in the spectrum. This happened despite being in presence of the Barium additive.

4.4 Analysis of the results with 3-Butenamide Phosphate

The attempt to create an amide with poly phosphoric acid was not successful. No salt formation could be observed, leaving just a transparent liquid left as a product. This was probably because the poly phosphoric acid is a too weak of an acid to be used in this type of reaction, something that was feared before the attempt.

4.5 Analysis of the results with Alkyl Ketene Dimer

The results from adding the AKD to the cellulose showed no visible alterations and the FTIR showed no indications of a reaction either. Analysing with FTIR (Appendix Figure AIII.7) one could see that the AKD reference showed absorption peaks at 1840cm^{-1} and 1730cm^{-1} , which also were seen in our sample with MCC and H_2O . These peaks correspond to carbonyl groups found in a four-ringed lactone and a saturated ketone, indicating that in the AKD dispersion there was a mixture of AKD and hydrolysed AKD that had formed a ketone. If a reaction had occurred there should have been dual absorption indication in the band of $1750\text{--}1710\text{cm}^{-1}$, which is the characteristics of the desired β -keto ester. These were not seen when the catalyst HCO_3^- was added either.

4.6 Analysis of the results with Diketene-Acetone Adduct

The NMR results from running a verification sample of diketene-acetone adduct indicated the characteristics of the desired molecule, proving that nothing had happened to the reagent over time in storage (Appendix II, Figure AII.4.).

The DAA, that is a dark brown-coloured reagent, was easily absorbed by the cellulose when applied and coloured it with the same dark brown colour, something that got even more profound after reacting in the oven. The FTIR spectrums showed strong indicative absorption peaks in the area of β -keto esters in all samples, where increased reagent load had significant influence of the absorption strength (Appendix III, Figure AIII.10-13) as did temperature (not showed in appendix spectrums). The test to see reaction medium influence, if ions and other impurities in tap water would affect the outcome of the reaction, showed that it did (Appendix III, Figure AIII.10-13). This is seen through the difference in height between the hard-coupled water, about 1645cm^{-1} , and the ester peaks which is greater for samples with distilled water compared with tap water. The difference is not that profound, and its significance would likely not be economically defendable on industrial level. The strong reaction results from the cellulose surface modification with DAA proved good enough to proceed to scale-up trials for subsequent composite compounding.

4.7 Analysis of scale-up results

4.7.1 Analysis of reaction

The FTIR results from the scale-up reactions did not show as strong absorption peaks as in the small-scale (Appendix III, Figure AIII.14-15). This is thought to be the reason of having the extra volumes of liquid in the glass container. When placed in the oven, this extra volume possibly kept the reaction temperature down for a large portion of the cellulose mass which consequently then needed more reaction time to obtain similar results to the small-scale samples. The scale-up MCC samples added an extra difficulty and a possibility for result deviations. When MCC samples were placed in the oven to react, the reaction caused the samples to have small explosions. Something that did not happen to the dissolving samples. This is believed to be acetone forming during DAA decomposition, which instantly vaporises. The MCC acted as a thick cake sheet constraining the gas from escaping and thereby building up pressure causing the sample to have small explosions. To decrease the explosions, the oven door was opened several times in order to stir the samples which in turn cooled the reaction temperature from the desired 180°C to about 160°C.

Results of the water retention value tests for MCC and dissolving, Table 2 and 3, show that the value for samples containing the highest reagent load contains the least amount of water after the test. Which is in accordance with the physiology of increasing the hydrophobicity of cellulose surface. Noteworthy however is that the samples with (1:1) reagent load holds water better than the reference. This is presumed to be that it has not become more hydrophilic, but that the esterification reactions have opened up crystalline parts of the cellulose aggregates when substituting the hydroxyl groups. The surface area is then increased which initially can constrain more water before enough substitution has made it too hydrophobic.

Table 2. Result of WRV for MCC with DAA.

	Wet MCC <i>m(g)</i>	Dry MCC <i>m(g)</i>	WRV-value <i>m(water)/m(dry)</i>
<i>Reference</i>	0,462	0,301	0,53488
<i>(1:1)</i>	0,45	0,287	0,56794
<i>(3:1)</i>	0,4145	0,303	0,36798

Table 3. Result of WRV for dissolving with DAA

	Wet Dissolving $m(g)$	Dry Dissolving $m(g)$	WRV-value $m(water)/m(dry)$
<i>Reference</i>	0,629	0,397	0,58438
<i>(1:1)</i>	0,523	0,315	0,66031
<i>(3:1)</i>	0,532	0,376	0,41489

4.7.2 Analysis of composites

The dissolving pulp seem to get altered mechanical properties when subjected to the reagent based on how it acted when processed in the mixer. The milled reference dissolving cellulose look like cotton with fines in and the 1:1 sample as well, although with slightly more fines in. The 3:1 sample however looked more like MCC, a brown powder which it turned into within a second.

A problem for the compounded samples with high reagent load was that they contained a lot of bubbles which consequently meant that they needed to be pressed several times before they produced a sufficiently good film for the subsequent tensile tests. An observation that also was made in the research by (*Brodin, M. 2013*) when compounding cellulose samples modified with DAA.

The results from the tensile tests, displayed in Table 4, show that the composites notably have a higher value of young's Modulus, indicating that they have a greater material stiffness than the LDPE reference. The composite containing 30% dissolving reference has the highest value of Young's Modulus. This follows the trend of increased cellulose content in the composite increases the material stiffness. The 30% dissolving reference also contains the most unmodified cellulose fibres meaning that they are the longest cellulose polymer chains with the least degree of freedom of rotation making them a stiff and strong reinforcement material. They also have the greatest tendency to agglomerate and not easily be well mixed in the extruder due to hydrophilic interactions, producing a non-homogenous mixed composite material. Regarding maximum tensile strain at max tensile stress, LDPE reference is the most elastic material which also follows the trend of composites with less amount of cellulose seem more elastic. The tensile stress, tensile strength, seem to follow the trend, although not fully consistent, that increased cellulose amount in respective category increases max tensile stress.

Table 4. Table with bio-composite tensile test values based on 4-5 samples per sample category. * Orange row had defects in the dog bone structures.

Sample Description	Maximum Tensile Strain (mm/mm)	Max Value Tensile Stress (MPa)	Young's Modulus (MPa)
LDPE Reference	0,354	7,69	21,74
5% MCC Reference	0,253	8,80	34,82
10% MCC Reference	0,082	8,60	105,09
30% MCC Reference	0,063	5,01	80,08
5% MCC (1:1)	0,083	8,83	106,05
10% MCC (1:1)	0,103	9,26	90,20
30% MCC (1:1)	0,043	9,81	226,69
5% MCC (3:1)	0,270	8,58	31,80
10% MCC (3:1)	0,082	8,82	107,14
30% MCC (3:1)	0,109	10,23	93,78
5% Dissolving Reference	0,123	6,86	55,87
10% Dissolving Reference	0,143	7,26	50,70
30% Dissolving Reference	0,040	10,05	250,56
5% Dissolving (1:1)	0,163	7,95	48,68
10% Dissolving (1:1)	0,110	7,07	64,17
30% Dissolving (1:1)	0,063	11,44	181,80
5% Dissolving (3:1)	0,283	7,82	27,66
10% Dissolving (3:1)	0,127	6,99	54,86
30% Dissolving (3:1)	0,061	8,54	140,77

5 SUMMARY OF RESULTS

The results from the acetamide salts were non-successful. Neither of the attempts to counteract the cellulose degradation worked and the fact that the additives did not seem to have any influence on the reaction tells us that there is more complexity to the reaction mechanism than we initially thought.

The attempts of using AKD as a reagent proved also to be non-successful under the conditions that were tried. No indications of ester formation could be seen in the FTIR spectrums and for that reason AKD was discarded.

The DAA managed to modify the cellulose surface in all attempts, where strong correlations could be drawn between reagent load and temperature which notably increased the absorption peaks in the FTIR spectrums. The successful surface modifications made us proceed on to scale-up trials and composite compounding.

The WRV shows that higher amount of water is bound to the cellulose compared to the reference when using (1:1) reagent load, believed to be due to increased surface area being able to constrain water.

Tensile test show that all composites have a higher Young's Modulus, indicating that they have a greater material stiffness than the LDPE reference. In general, it is seen that maximum tensile stress is increased for samples with reagent load (1:1) and then slightly decreased again for samples with reagent load (3:1). This contradicts the theory of increased hydrophobicity should increase the interfacial adhesion and thereby the composites mechanical properties. However, clearly the additional amount of DAA added influenced the cellulose mechanical properties. This is thought to be the consequence of substituting degree of the hydroxide groups, making the molecule less able to form hydrogen bonds and thereby making it less rigid and stiff. Something that was seen when the dissolving (3:1) sample was milled. A consequence of this might be that the higher maximum tensile stress trend seen in MCC compared to dissolving is due to dissolving having less accessible hydroxide groups and thus have less well distributed DS, generating mechanical weak spots.

6 CONCLUSIONS

In this thesis, three different types of reagents were investigated to see which formed the most successful esters. The amide salts, initially investigated, proved to have too complex reaction mechanisms and was discarded due to time limitations and of the scope of this thesis.

Only a few attempts were done before ruling out AKD as modifying agent. Since it is a commonly used agent in the industry it clearly works under right conditions but there are also many reports of it not working accordingly. In our case we suspect that the reaction time might have been too short for the reaction to take place, though small indications of absorption in the desired interval would have been likely.

DAA proved successful forming esters and samples were made for composite compounding using two different cellulose substrates with three degrees of surface modification respectively. Results show that using cellulose as a reinforcement for composite material increases the mechanical properties. However, increasing the cellulose surface hydrophobicity does not necessarily seem to improve this property. The surface modification seems to be too tough and weaken the cellulose polymer chain. Suspected un-dispersed substitution creates mechanical weak spots when less hydrogen bonding can be formed. For that reason, it looks like there is a trade of when high hydrophobicity is obtained regarding strength properties. Therefore, a balance must be found between hydrophobicity and the cellulose polymers mechanical strength to obtain the best composite material. In conclusion, improving the cellulose surface hydrophobicity to increase the interfacial adhesion to the matrix, is just one variable among many that one needs to consider when creating bio-composite materials.

7 FUTURE WORK

In future research, amide salts like acetamide sulphate or acetamide chloride might work as a good esterification agent in another reaction environment where the cellulose degradation is inhibited. Further research may be done to see if there are any substances that could be added to facilitate this. One way to see if 3-butenamide phosphate would work is if an ion exchange is performed instead with an already formed amide salt, e.g. with the sulphate anion of 3-butenamide sulphate. To facilitate this reaction more energy might be needed as heat during the reaction in the oven because phosphate is a weaker nucleophile.

AKD works commercially but not for us? There is a possibility that it was discarded too quickly due to limited time. This because results might have been misleading since reactions could have occurred without appearing in the FTIR spectrums. The reaction results from AKD could be tested with a water retention value instead of FTIR. More tests with new prepared AKD dispersion batches could be conducted. It might be suitable for composites and in addition, it does not discolour the cellulose and it also gets a slippery surface which might be interesting for the mixture of LDPE regarding extrusion.

Optimizing the reaction with DAA. Try to make a Design of Experiment (DoE) at the scale-up and get better results from the scale-up process at lower temperatures for application in industry.

Try to find another suitable substance that easily reacts with cellulose in a water reaction medium and where the temperature is beneath 100°C for optimization, which would be an ideal case

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APPENDIX I, H-NMR

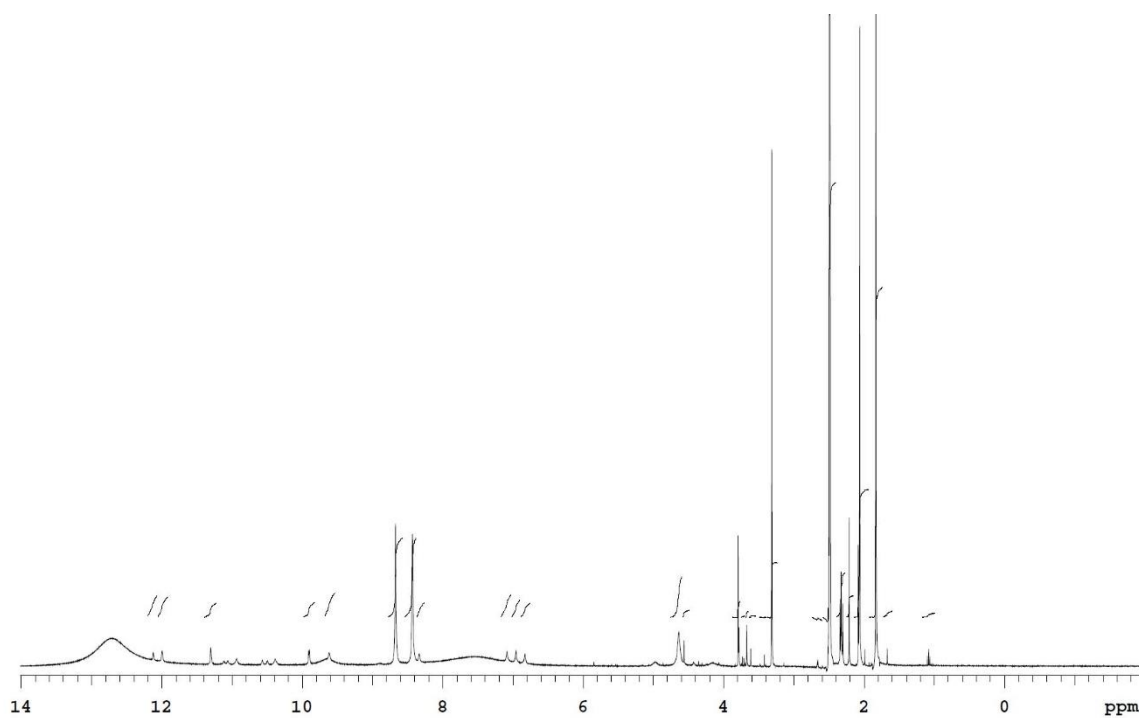


Figure AI.1. H-NMR for 3-butenamide sulphate in DMSO.

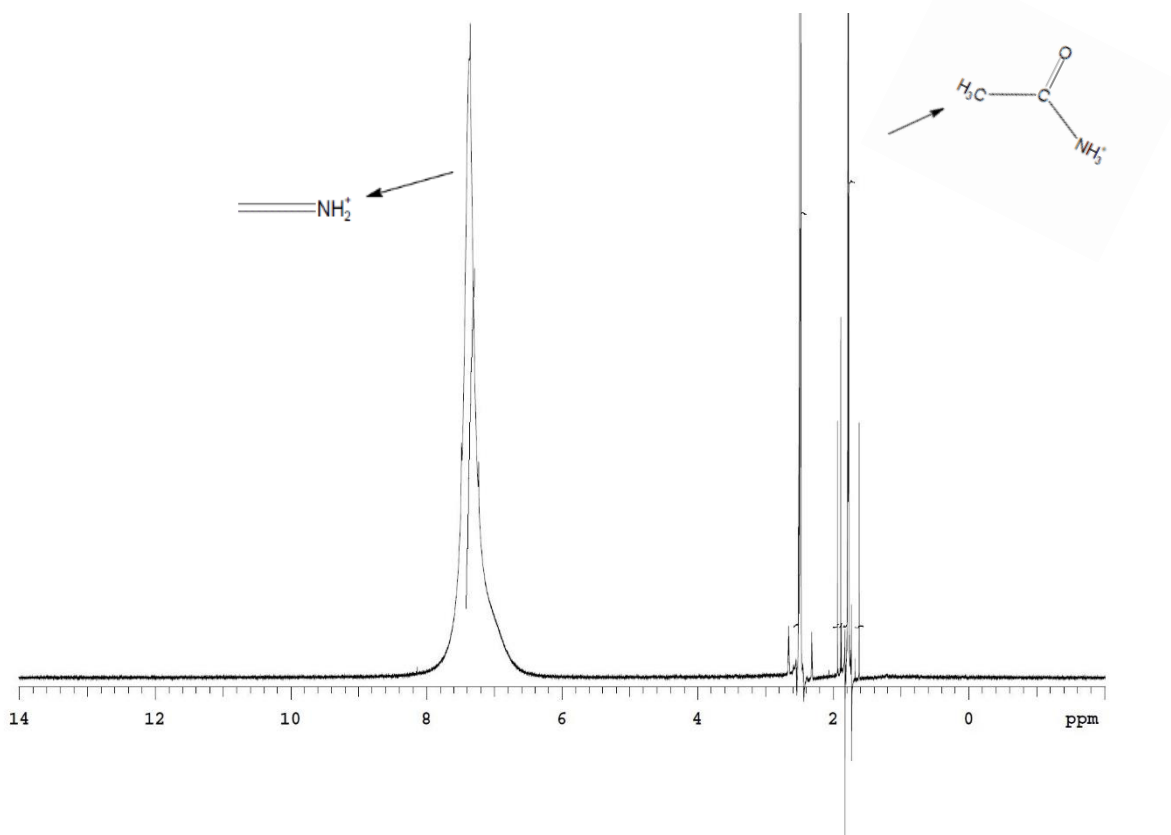


Figure AI.2. H-NMR for acetamide chloride in D₂O.

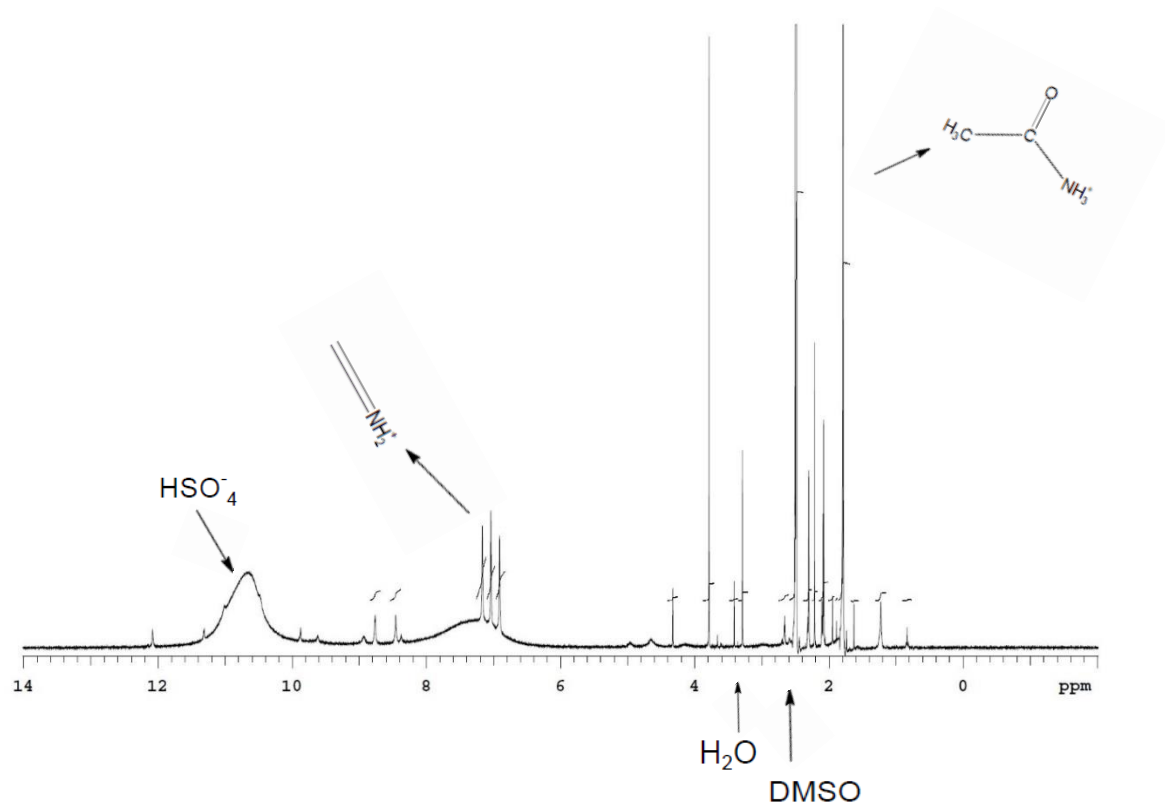


Figure AI.3. ^1H -NMR for acetamide sulphate in DMSO.

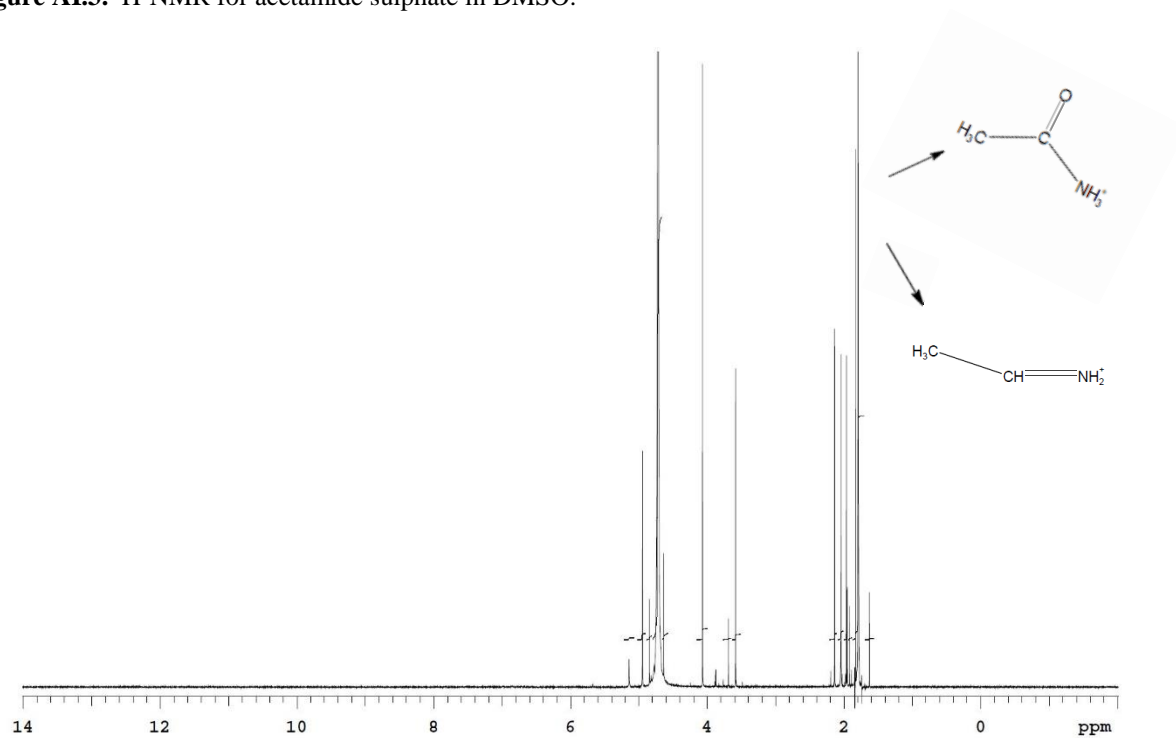


Figure AI.4. ^1H -NMR for acetamide sulphate in D_2O .

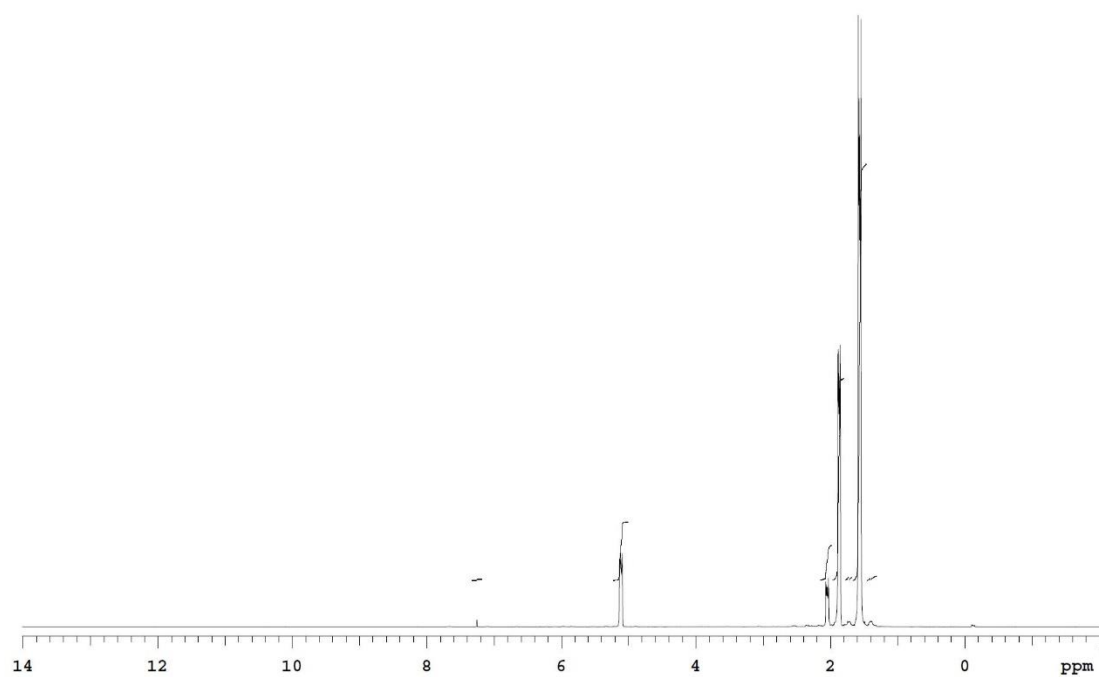


Figure A1.5. ^1H -NMR for DAA in CDCl_3 .

APPENDIX II, C-NMR

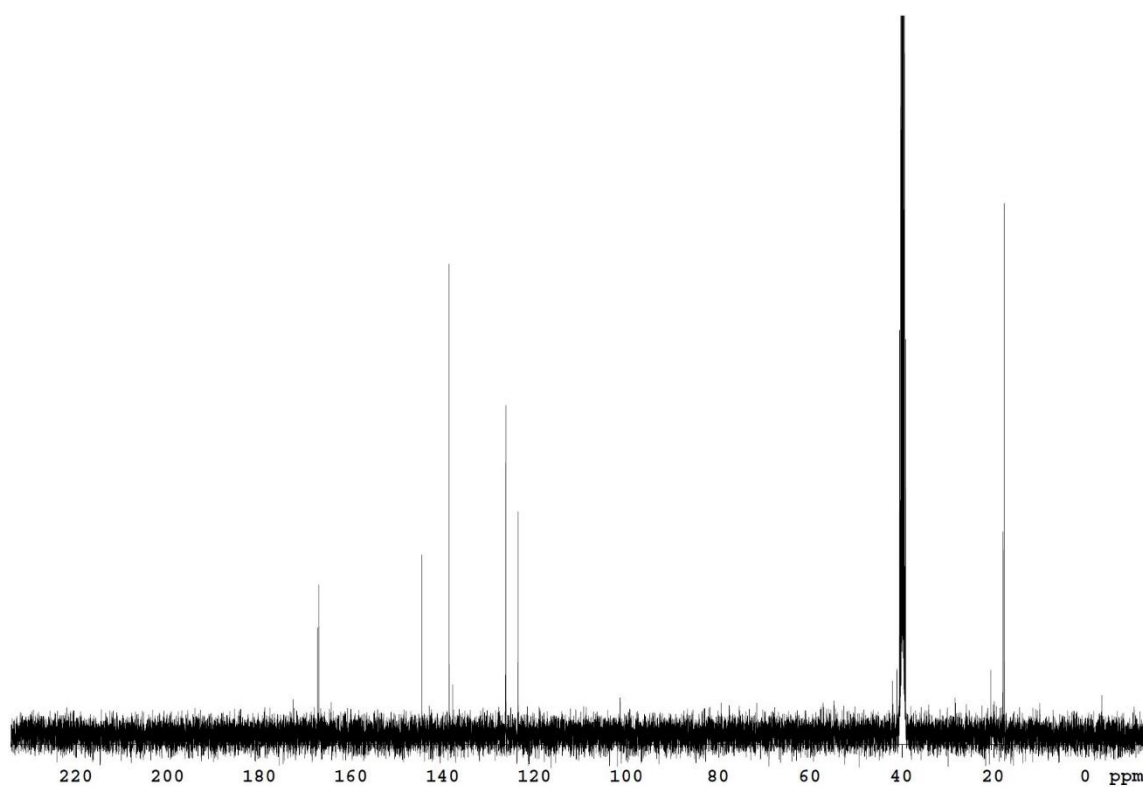


Figure AII.1. C-NMR for 3-butenamide sulphate in DMSO.

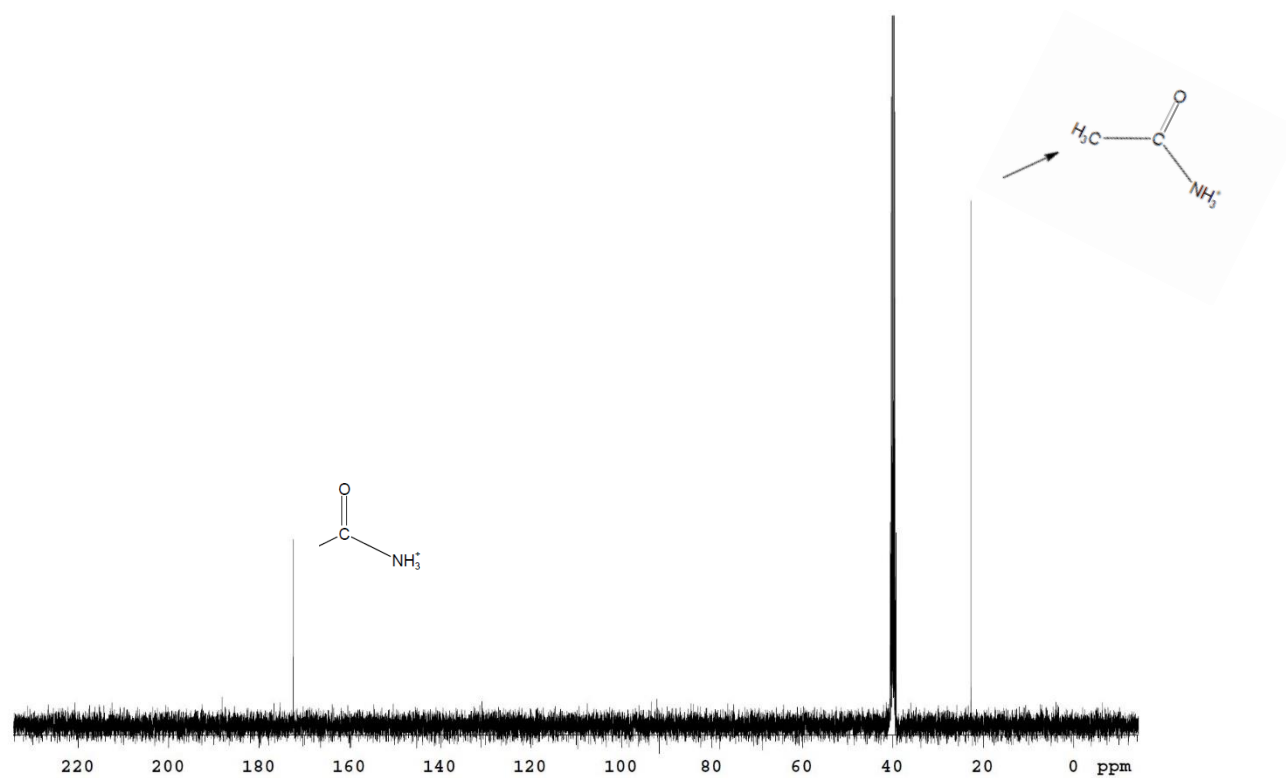


Figure AII.2. C-NMR for acetamide chloride in DMSO.

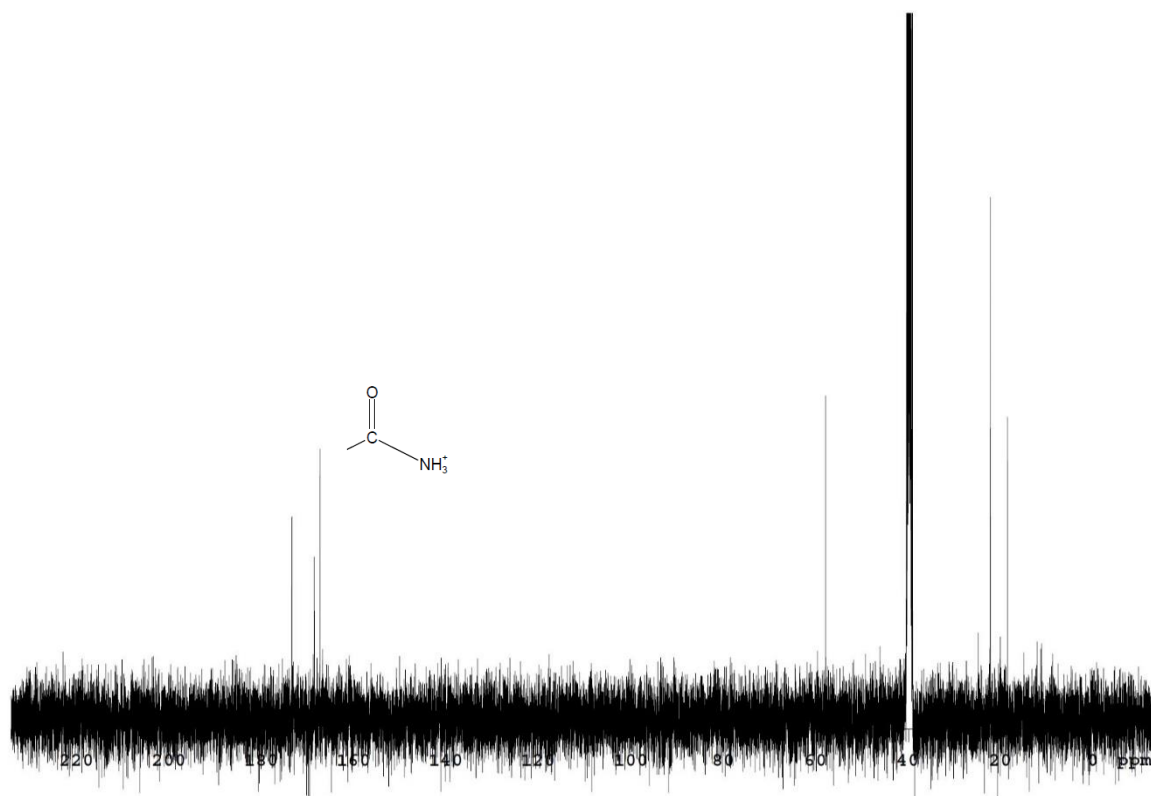
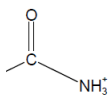


Figure AII.3. C-NMR for acetamide sulphate DMSO.

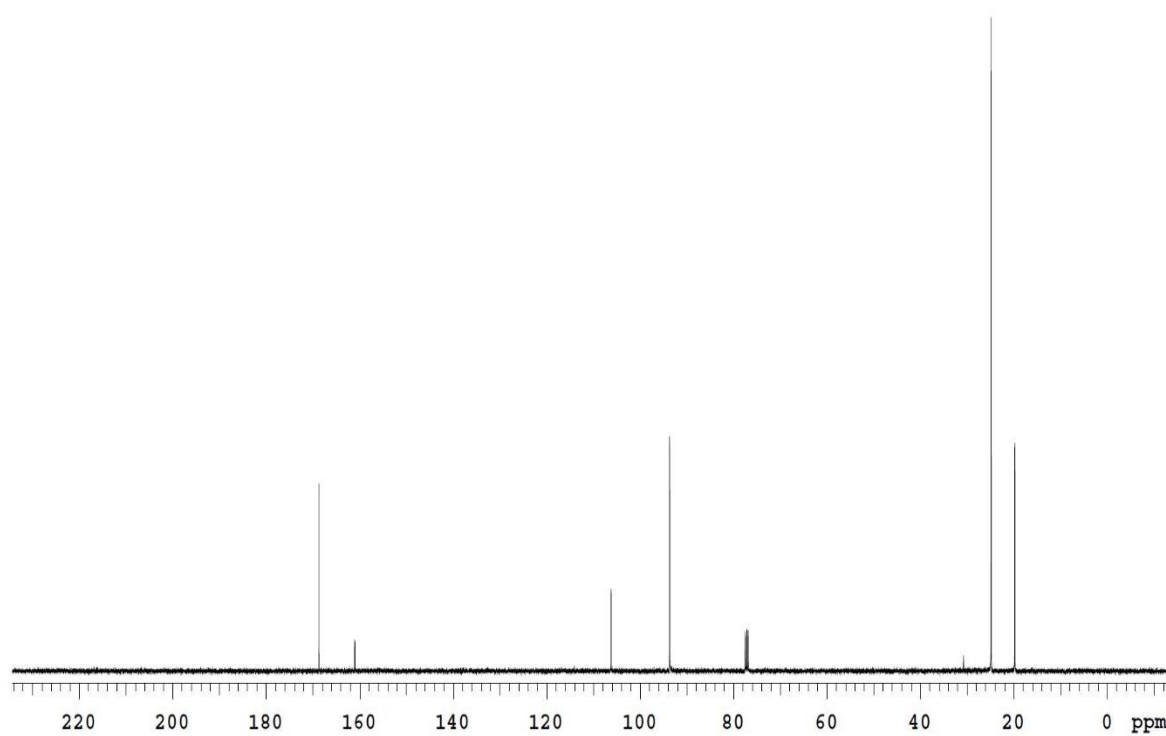


Figure AII.4. C-NMR for DAA in CDCl_3 .

APPENDIX III, FTIR-graphs



Figure AIII.1. FTIR-spectra for MCC with acetamide sulphate, trial and error with Ca(OH)_2 as additive.

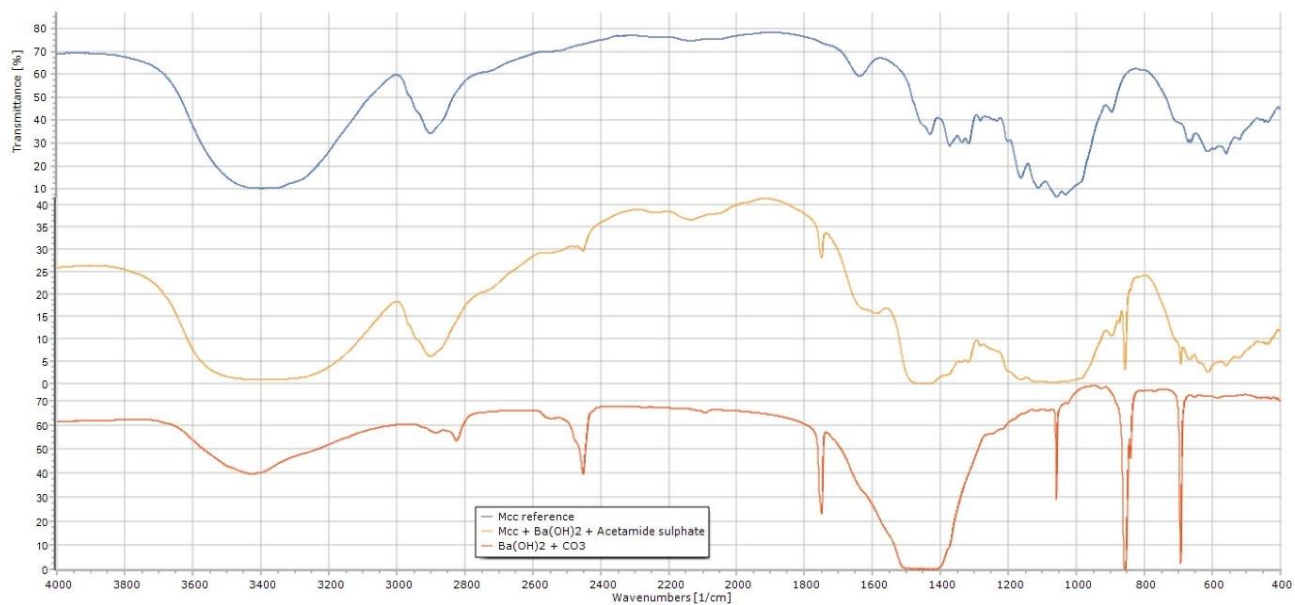


Figure AIII.2. FTIR-spectra for MCC with acetamide sulphate, trial and error with Ba(OH)_2 as additive.

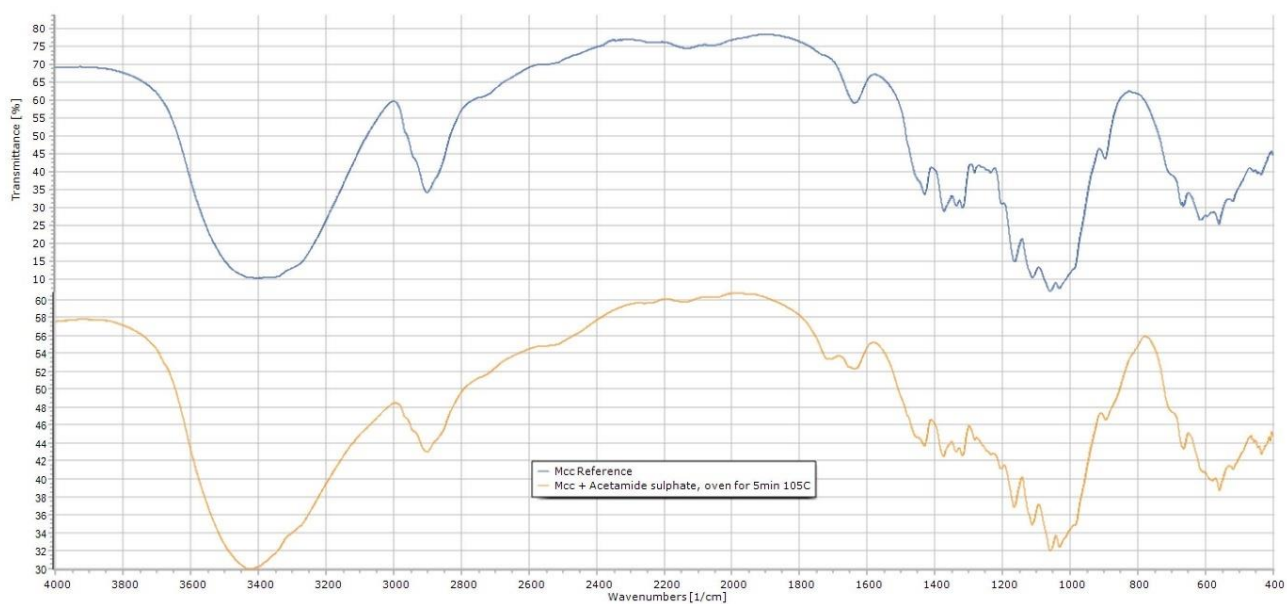


Figure AIII.3. FTIR-spectra for MCC with acetamide sulphate

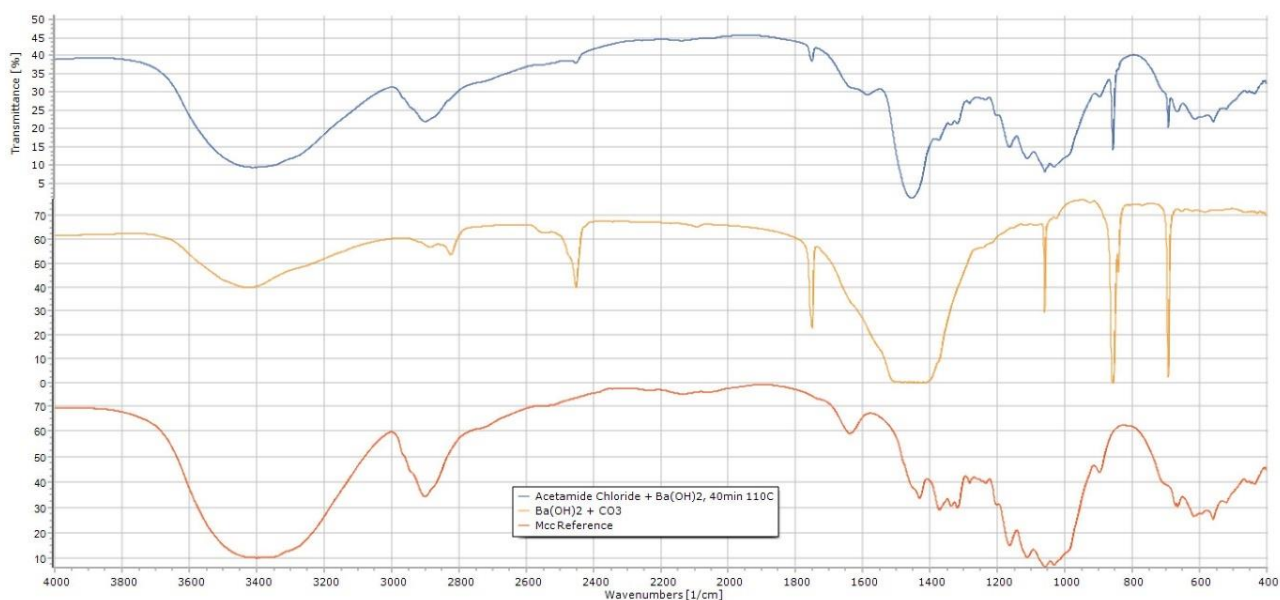


Figure AIII.4. FTIR-spectra for MCC with acetamide chloride, trial and error with $\text{Ba}(\text{OH})_2$ as additive



Figure AIII.5. FTIR- spectra for MCC with acetamide chloride, trial and error with Ca(OH)_2 as additive

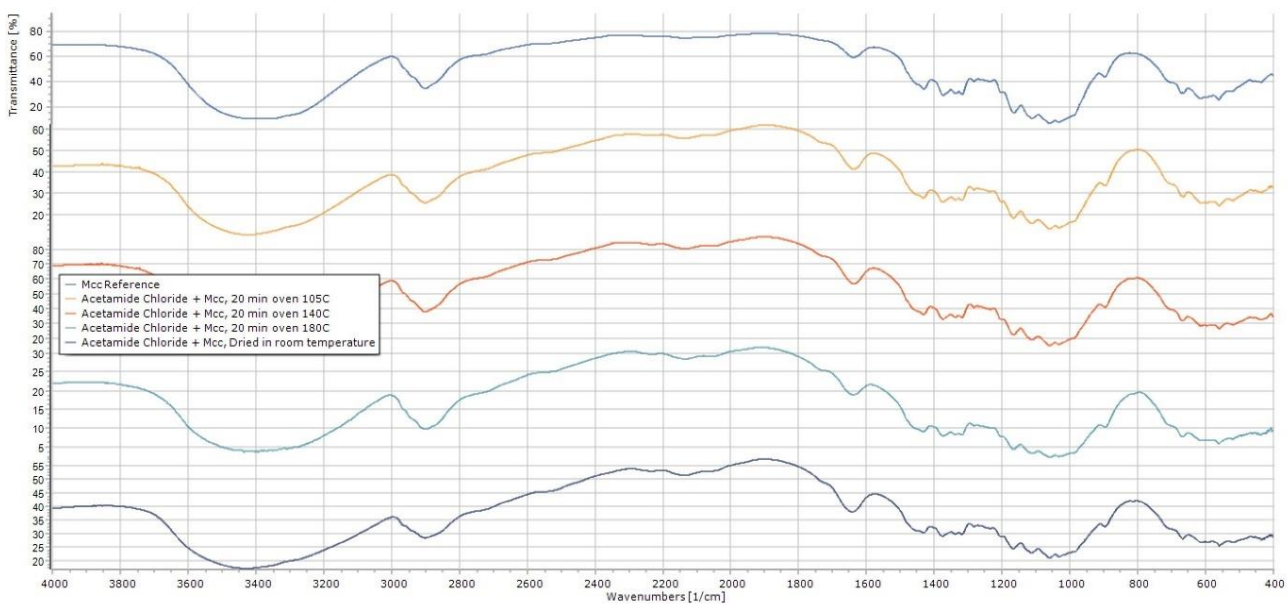


Figure AIII.6. FTIR-spectra for MCC with acetamide chloride, temperature dependence

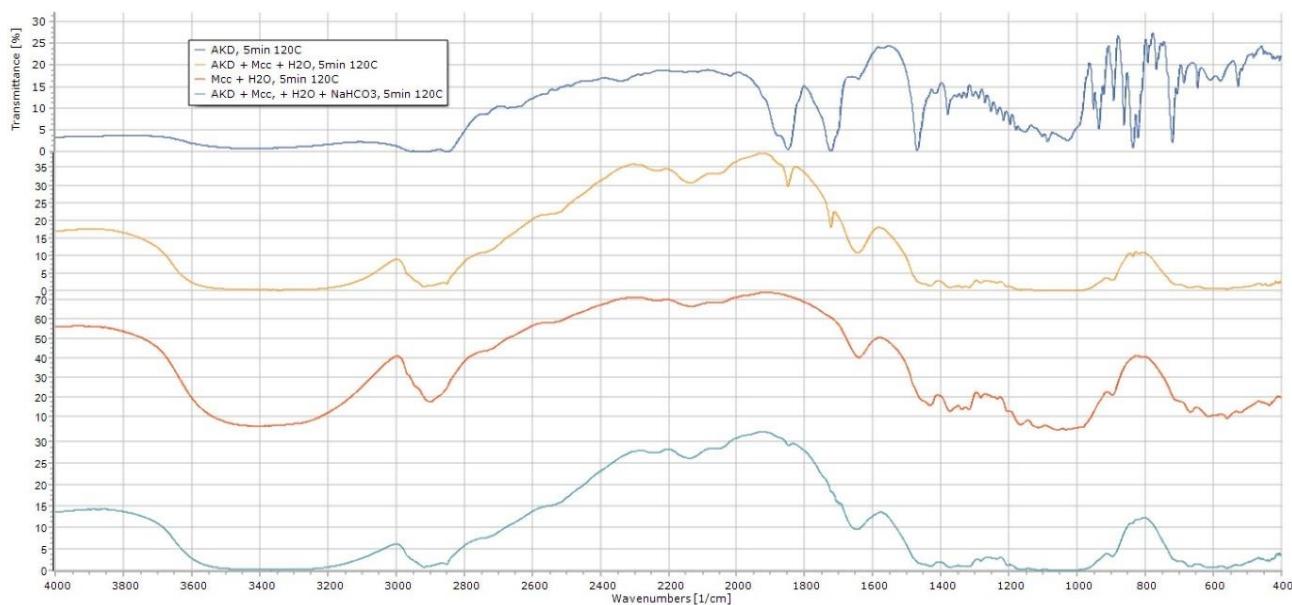


Figure AIII.7. FTIR-spectra for MCC with AKD. From the top: AKD reference, MCC with 50 times diluted AKD, MCC with 100 times diluted AKD and last MCC with AKD and additive NaHCO_3 .

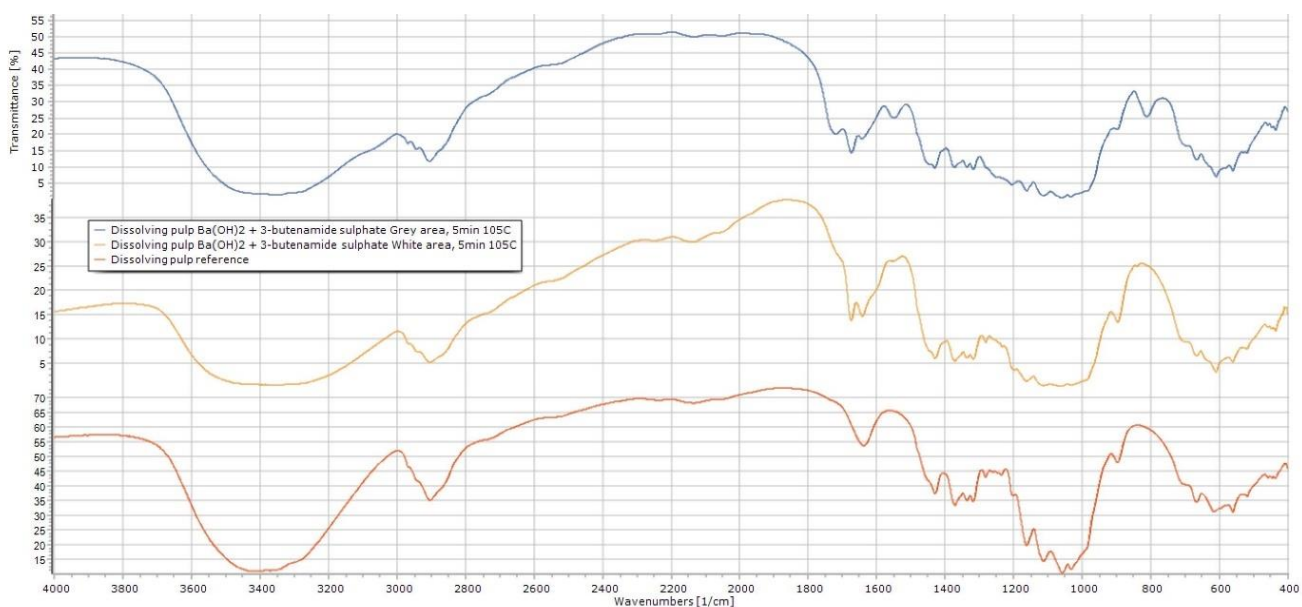


Figure AIII.8. FTIR-spectra for dissolving pulp with 3-butenamide sulphate with Ba(OH)_2 diffusion from middle to edges. Grey area shows absorption peak of an ester and the white does not, telling us that esterification reactions does not seem to occur without degradation of the cellulose.

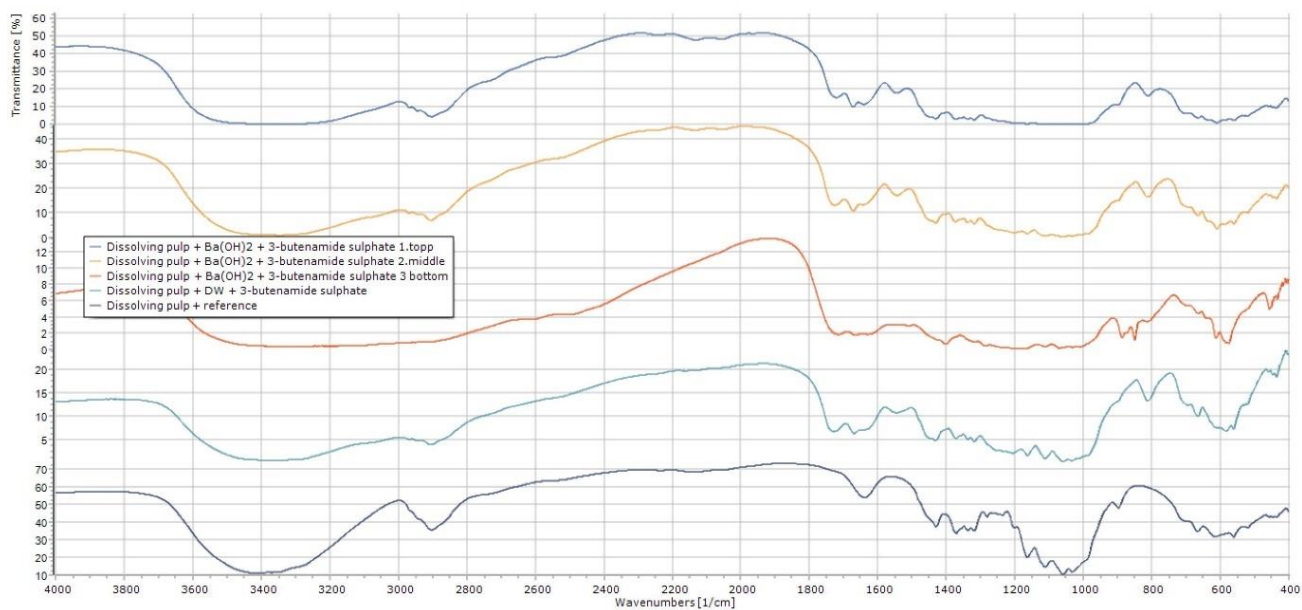


Figure AIII.9. FTIR-spectra for dissolving pulp with 3-butenamide sulphate with $\text{Ba}(\text{OH})_2$ diffusion from top to bottom

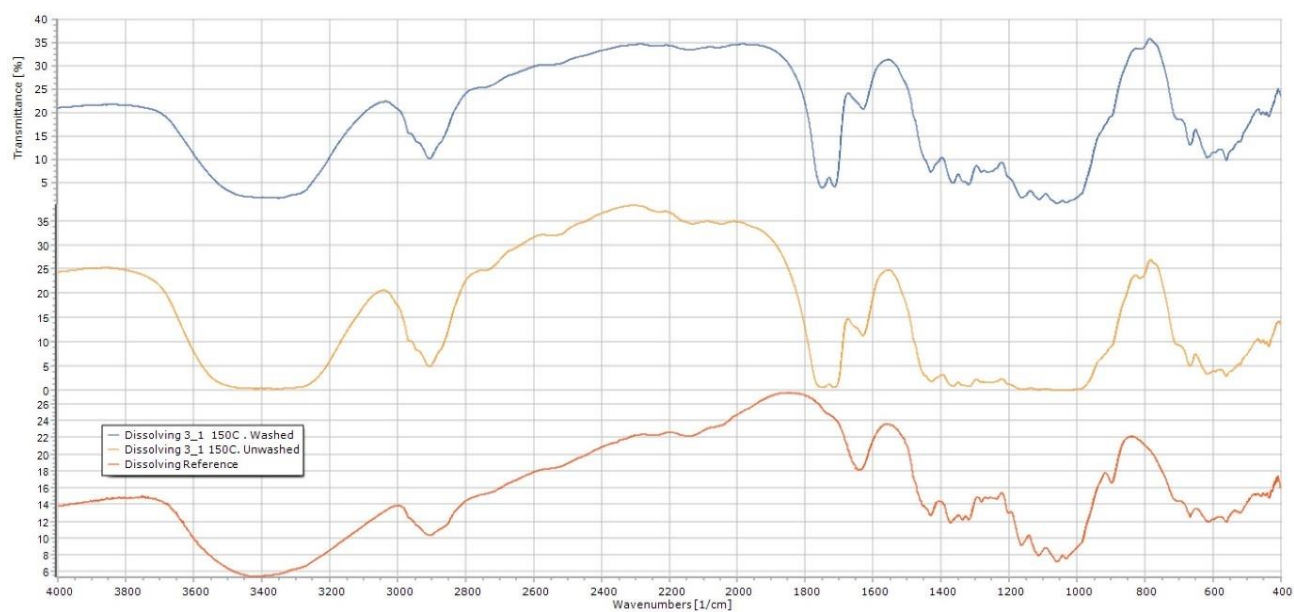


Figure AIII.10. FTIR-spectra for dissolving pulp (3:1) with DAA, washed and unwashed.

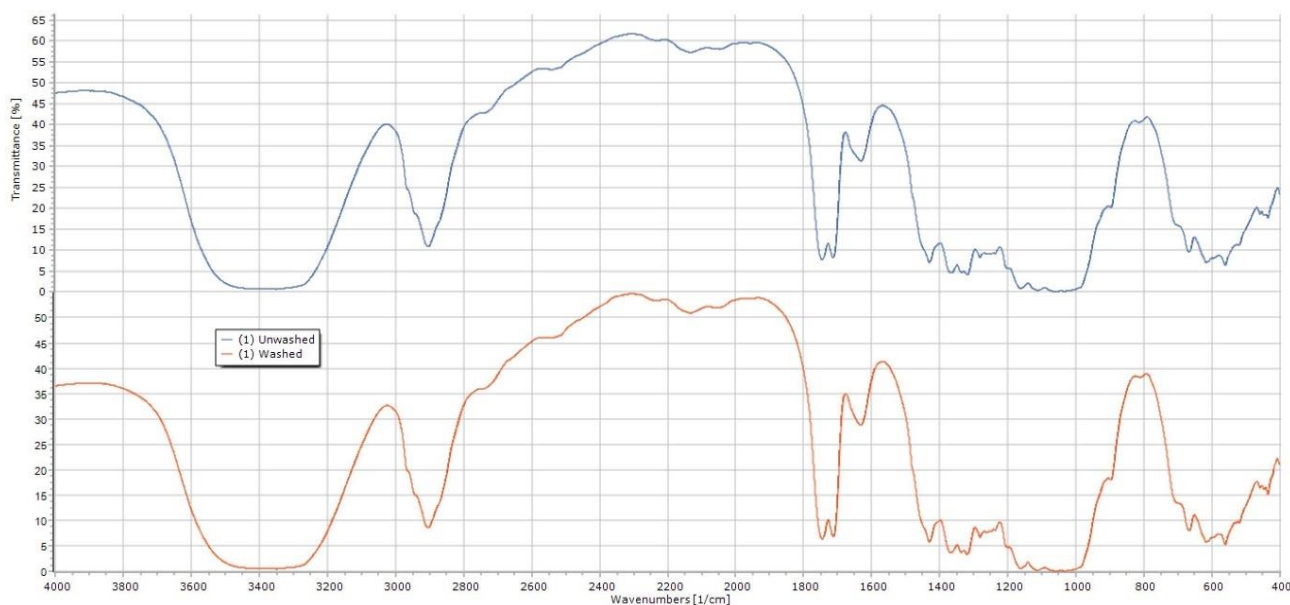


Figure AIII.11. FTIR-spectra for dissolving pulp (3:1) with DAA, propan-2-ol, distilled water and reaction in oven at 180°C for 60min.

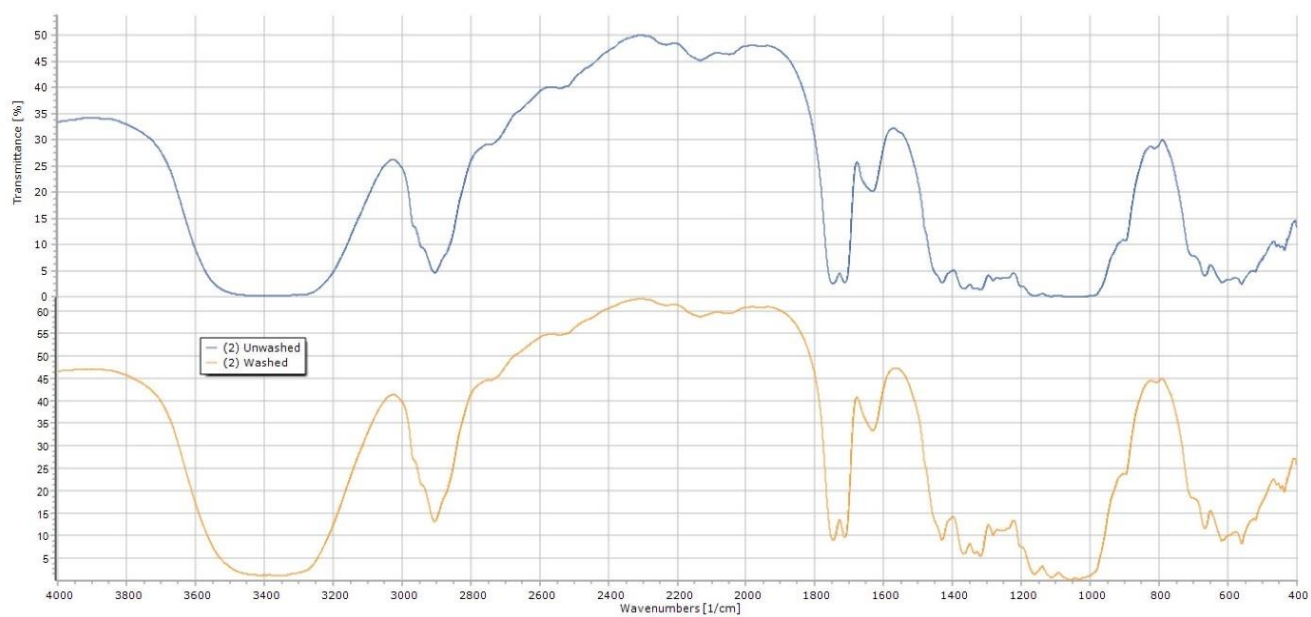


Figure AIII.12. FTIR-spectra for dissolving pulp (3:1) with DAA, propan-2-ol, tap-water and reaction in oven at 180°C for 60min.

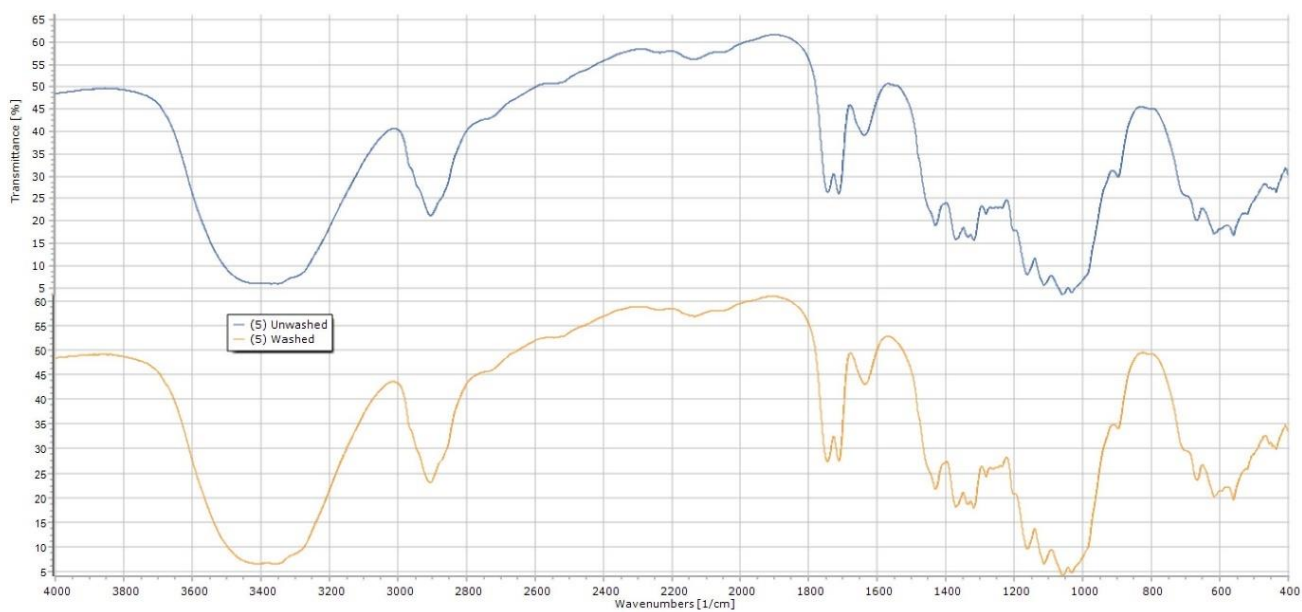


Figure AIII.13. FTIR-spectra for dissolving pulp (1:1) with DAA, propan-2-ol, distilled water and reaction in oven at 180°C for 60min.

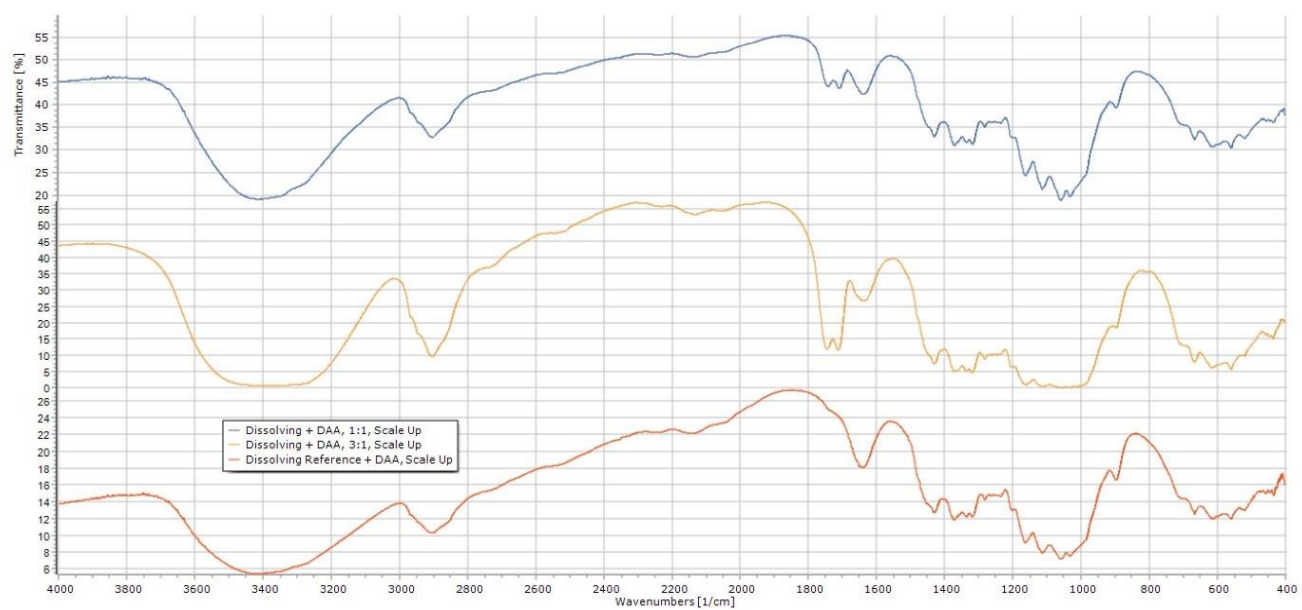


Figure AIII.14. FTIR-spectra for dissolving pulp with DAA, scale-up.

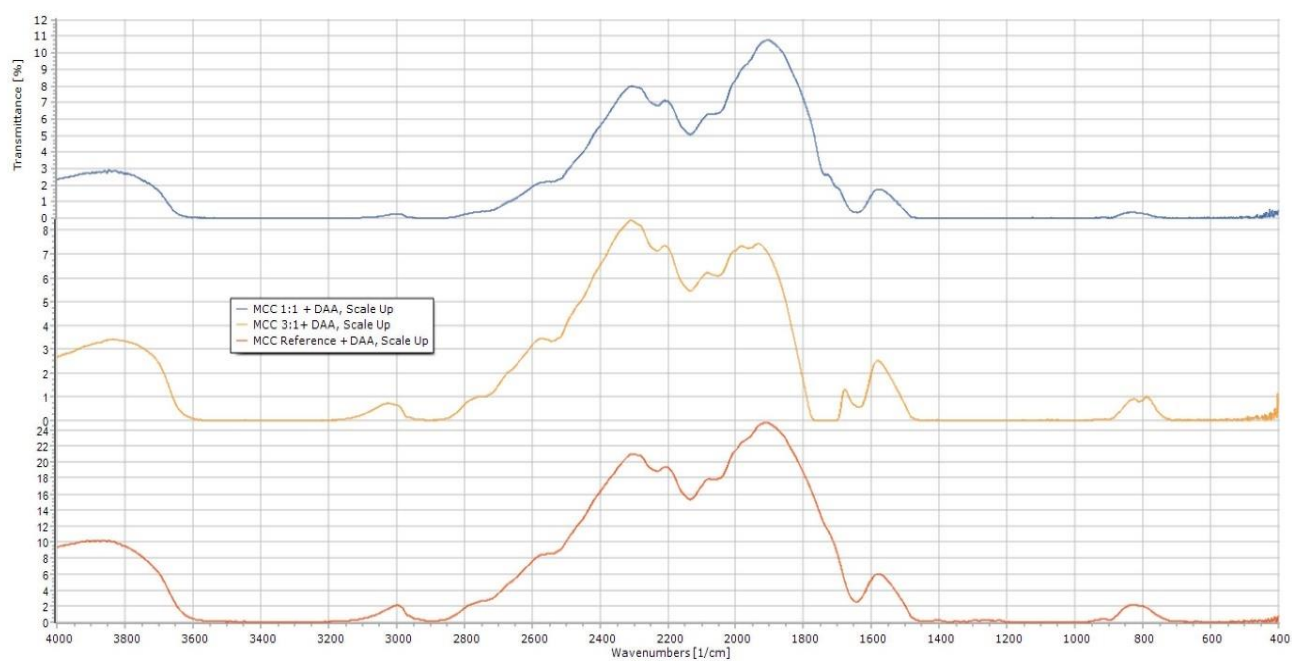


Figure AIII.15. FTIR-spectra for MCC and DAA, scale-up.

APPENDIX IV, Tensile stress test

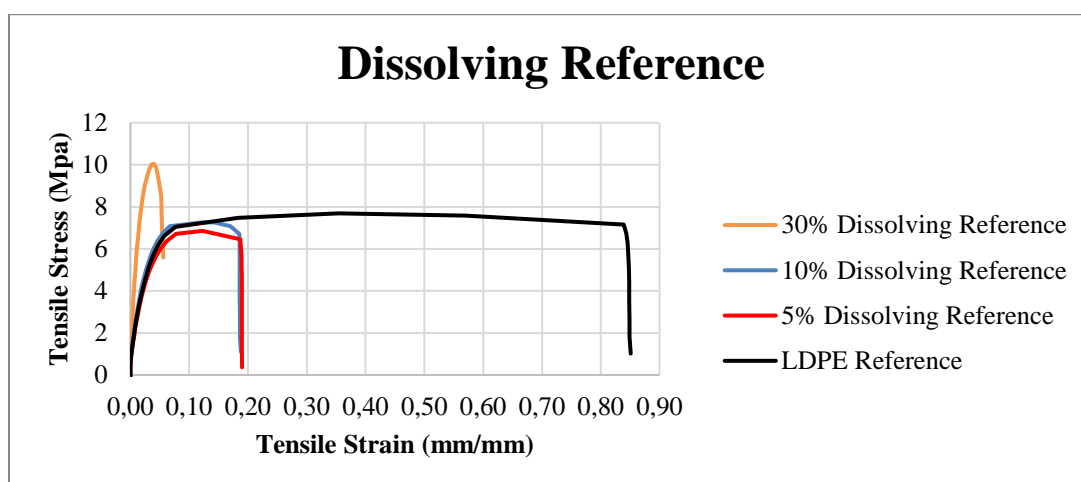


Figure AIV.1. Tensile stress curve for dissolving reference samples.

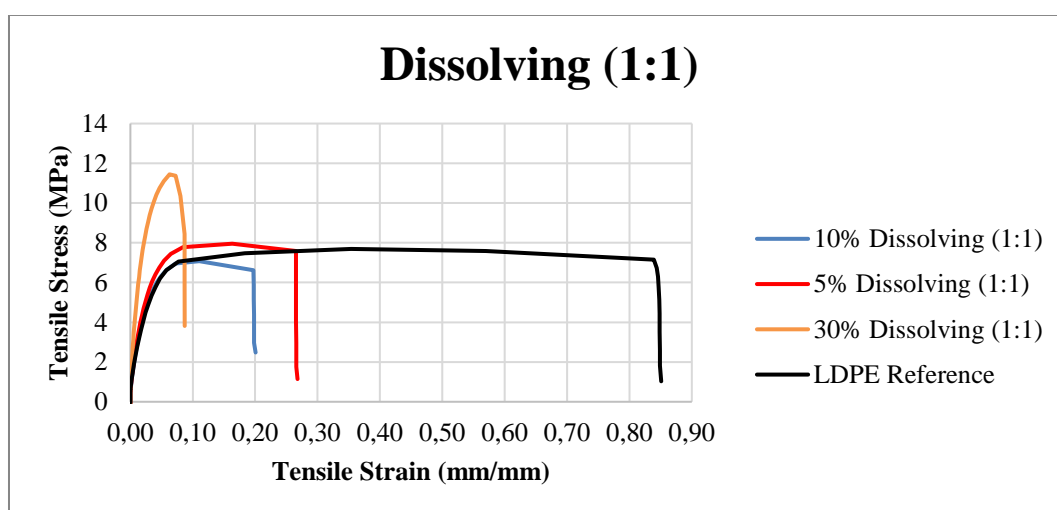


Figure AIV.2. Tensile stress curve for dissolving with molar ratio (1:1).

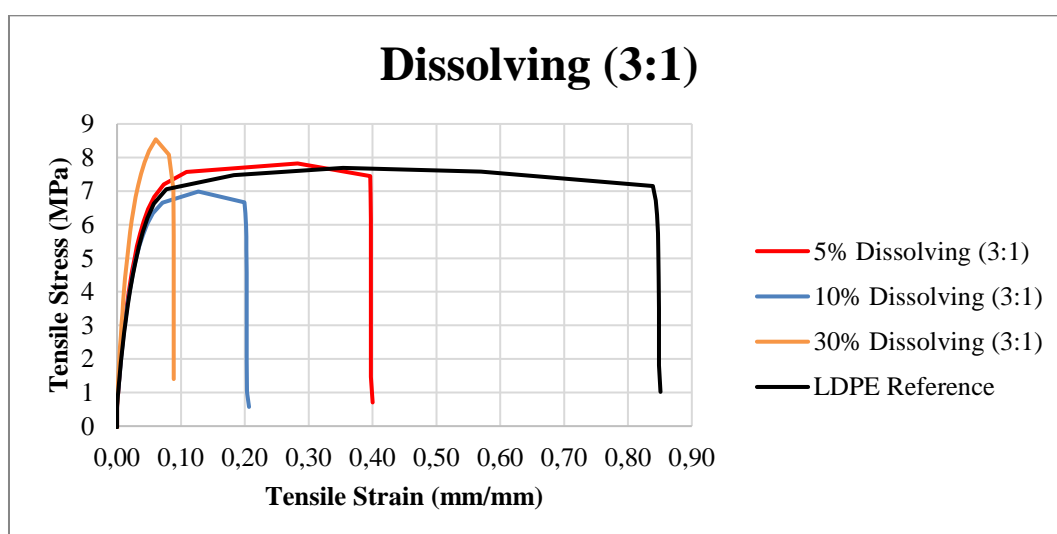


Figure AIV.3. Tensile stress curve for dissolving with molar ratio (3:1).

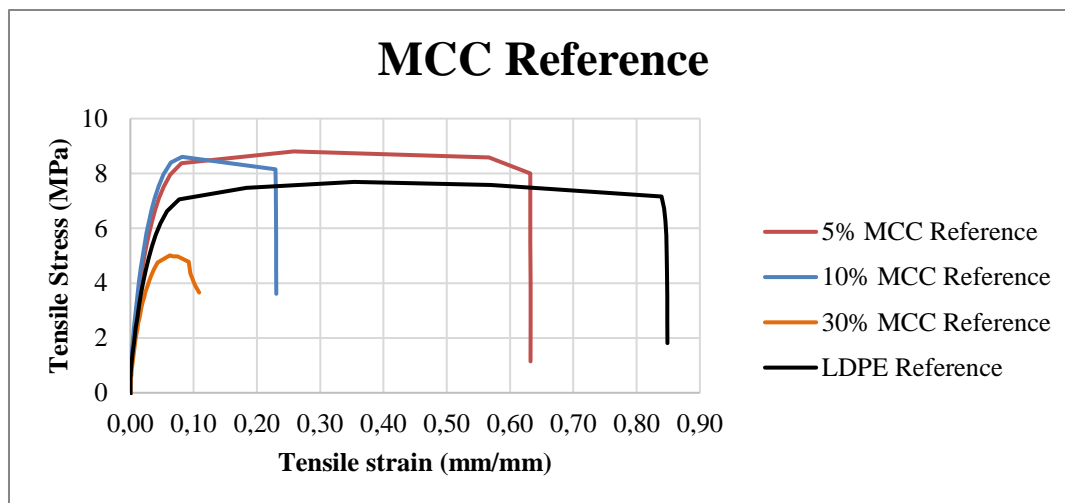


Figure AIV.4. Tensile stress curve for MCC reference samples.

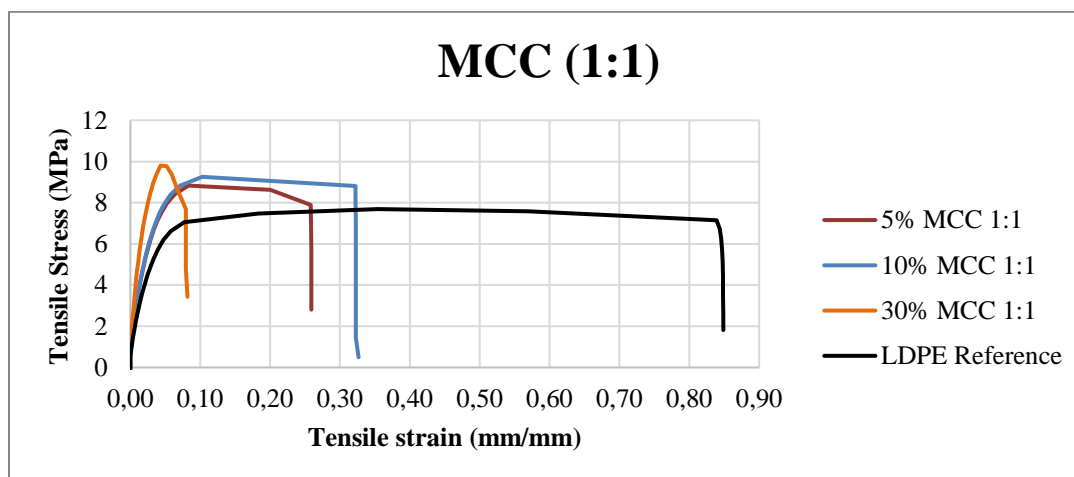


Figure AIV.5. Tensile stress curve for MCC with molar ratio (1:1).

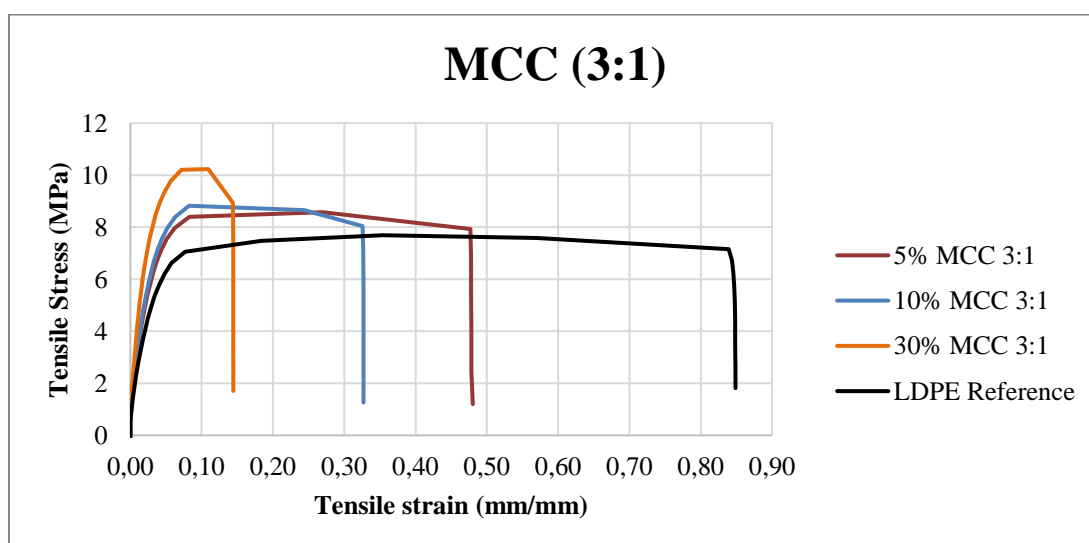


Figure AIV.6. Tensile stress curve for MCC with molar ratio (3:1).

APPENDIX V, EXPERIMENTAL OBSERVATIONS

Acetamide sulphate

The prepared amide salt product was an extremely high viscous brown honey like substance. Needed high temperatures to get a low fluid like viscosity. It was easy to dissolve in water but hard to dissolve in acetamide. The very high viscosity made it hard to work with and is therefore not recommended for usage in that aspect.

Acetamide Chloride

The acetamide chloride product was a white flake salt substance that was rather easy to work with and to produce.

3-butenamide sulphate

This product was a brown wax like substance much easier to work with than acetamide sulphate. Easy to produce and managed to produce esters and degrade the cellulose.

3-Butenamide phosphate

Did not manage to produce this substance. Ended up with a transparent liquid. The poly phosphoric acid was likely to be too weak of an acid to form the amide.

Alkyl Keten Dimer

Applying this on MCC made it very slippery after it had been dried in the oven. The slippery characteristic made the cellulose hard to mortar before doing FTIR. A property that might be interesting for other purposes.

Diketene-Acetone Adduct

When DAA was applied on dissolving sheets, we first used water to swell the pulp and then added DAA with isopropanol as a transporting agent since DAA is not miscible in water. When the isopropanol was added we could see that the pulp sheet absorbed the solvent quickly and that it seemed to push out air from fibre sheet, signs of it having good molecular interactions of some kind.

When the same procedure was done on the mashed-up dissolving pulp in a beaker, we could observe that isopropanol made the pulp swell fast, such that it got sticky in the beaker.

These observations were not seen on MCC samples.

When MCC samples were placed in the oven to react, the reaction caused the samples to have small explosions. Something that did not happen to the dissolving samples. This is believed to be from DAA decomposing and forming Acetone that instantly vaporises and the MCC being like a thick cake sheet, constraining it from escaping and thereby building up pressure causing the sample to have small explosions.

Mixing of dissolving fibres prior to extrusion

Mixing of dissolving fibres was done prior to extrusion to make the mixing of LDPE granulates better. The results from this made the unreacted fibres, the reference, look like cotton with fines in and the 1:1 sample as well, although with slightly more fines in. The 3:1 sample however looked more like MCC, a brown powder. Clearly the additional amount of DAA added influenced the cellulose properties. This is thought to be the consequence of substituting degree of the hydroxide groups, making the molecule less able to form hydrogen bonds and thereby making it less rigid and stiff.

Extrusion

Reference and 1:1 samples of dissolving fibres did not mix optimally with LDPE in the extruder, consequently making the filaments to contain aggregates of cellulose. More aggregates in the reference compared to 1:1 samples and more the higher cellulose proportion to LDPE. The filaments produced with 3:1 samples contained a lot of air bubbles, more the higher cellulose content.

Pressing of filaments into films

The filaments containing a lot of bubbles produced films that also had many bubbles. To reduce the amount of bubbles the films were cut into pieces and repressed several times, were colder temperature, about 160°C, seemed to be more favourable than for others.