

CHALMERS



Absorbent cellulose based fibers Investigation of carboxylation and sulfonation of cellulose

**Master of Science Thesis in the International Master's program
Chemical Engineering**

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Division of Materials Science
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2011

MASTER'S THESIS

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Abstract

In wound dressings the absorption and retention properties are important. Absorption due to the ability to absorb all wound fluids that can exude from wounds. This amount can be quite abundant. Retention properties is important especially for wounds that are situated to pressure, e.g. wounds on the back for bed-bound patients.

These properties can be increased for cellulose products by modifications. In this thesis two different modifications on cellulose fibers have been studied. Carboxylation by reacting the cellulose with sodium chloroacetate in a Williamson ether synthesis and sulfonation by reacting the cellulose with sodium vinylsulfonate in an Oxa-Michael addition has been studied. One method that can be easily repeated for each modification has been derived.

The most important parameters for the studied interval in each modification were determined. For the carboxylation reaction the concentration of the sodium chloroacetate was the most important and for the sulfonation reaction the temperature closely followed by the concentration of sodium hydroxide was the most important. The absorption and retention properties were most increased for the carboxylated cellulose fibers due to the more stable products of the Williamson ether synthesis compared to the Oxa-Michael addition. By investigating the modified fibers with Raman spectroscopy it was concluded that the most substituted cellulose showed greatest absorption and retention properties.

Key words: cellulose fibers, absorption, retention, carboxylation, sulfonation.

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1 Introduction

1.1 Background

The use of good absorbent materials is important in wound care products. Two important properties of a wound dressing are the ability to absorb and retain wound fluids. Absorption is the ability of a material to soak up liquids and retention is the ability to retain the liquid in the material during pressure. [12] Some wounds exude high amount of liquids, so called wound exudates, which have varying pH [14] and protein composition etc. During the making of wound dressing the property of the different wound fluids has to be taken into account. [11] Good absorbing is important so that all wound fluids can be soaked up. Retention is an important property for wounds that are situated where it might be subject to pressure, i.e. by lie on them. The dressing is then washed away with saline, a procedure that might be unpleasant and even painful for the patient. [2]

Polysaccharide materials, such as dressings comprising alginate fibers, have been and are still today used in absorbent wound care products. Alginate fibers are made from sodium alginate and are a natural polymer that can be extracted from brown seaweeds. [1] In the presence of multivalent metal ions alginate fibers can when situated to water form a hydrogel. The most common multivalent metal ion for gelling sodium alginate is the calcium ion. Together with the alginate fibers calcium ions form a crosslinked network. The density of the crosslinks will influence the absorption capability. With increasing density of crosslinks, i.e. calcium ions, the absorption capability will decrease. [31] There are today alginate based products that have good absorption properties, the major drawback with this kind of products is the retention properties. In some cases the dressing is not possible to remove from the wound in one piece.

Cellulose in its natural form show quite low absorbency and retention but can after modification show good values for both absorption and retention. Products based on cellulose with introduced carboxymethyl groups are gaining market shares. The most important advantage of these products is the retention capability which is better compared to competitor products. However when these modified cellulose fiber absorb fluids they form a gel. This gel doesn't have the same physical properties as the dry fiber. What is lost in physical properties is gained in retention property. The formation of the gel, i.e. the absorption is almost instant which makes the time for absorption a non-issue. [3]

One drawback with wound dressing which consist of this carboxymethyl cellulose is that the absorption capacity is reduced quite heavily when pH is reduced to acidic environment. This is a major drawback since wound fluids usually are in the pH range of 4-8 depending on in what curing stage it is. It has also been shown that wound heal faster if the atmosphere around the wound is artificially turned more acidic. Due to founding like this the need for wound dressings is that they should perform well over a wide range of pH and especially acidic pH. As previously stated the carboxymethyl cellulose based dressing lack the property of performing well at low pH. [14] Another aspect that is important regarding the absorption and retention is the salinity of the fluid that is supposed to be absorbed. A liquid that contains high concentrations of salt will be less

absorbed compared to liquids without salt or ions, e.g. distilled water. The ions of the salt block the acidic group in the carboxymethyl cellulose and hinder the absorption of the water. [32]

Cellulose is used in personal care products together with other materials such as acrylic acid polymers (SAP). The main reason for adding SAP materials is that absorbed liquid is not retained to sufficient amount when just cellulose is used.

In order to make the cellulose fiber more tolerant to acidic pH it can be modified by sulfonation. One of the most common sulfonated cellulose included the cellulose alkyl sulfonates where one or more of the hydroxyl groups of the cellulose backbone are substituted with an alkyl sulfonate. One large disadvantage of the previous cellulose alkyl sulfonate is that it requires substitution of two different groups, compared to single substitution this requires additional reactants and more processing steps which will lead to higher costs. Also properties like biodegradability may be impaired when modifying the cellulose too much. [14]

1.2 Aim

The aim of this master thesis is to investigate how known reactions and modifications can be carried out in laboratory scale at Mölnlycke Health Care facilities. With gathered information about reaction media, temperature and other parameters the aim is to compile a handbook with methods that can be followed for future research in this field. Also the theory of the reactions involved is to be investigated to increase the knowledge on what other chemicals that can be used in similar modifications. The master thesis can also be used to gain deeper understanding about competitor products. Competitors that today have products on the market based on the investigated modifications.

2 Theory

2.1 Cellulose

To be able to understand the complex nature of the cellulose molecule it is common to divide the structure of the molecule into three levels, a) the molecular level of the single molecule; b) the supramolecular level of packing and mutual ordering of the macromolecules; c) the morphological level concerning the architecture of already rather complex structural entities, as well as the corresponding pore system. [5]

After a general description of cellulose each of above mentioned aspect will be investigated.

2.1.1 General aspects

Cellulose is a renewable resource and one of the most abundant organic materials on the planet. It exists for example in cotton where the cellulose content can be up to 94 % and in other plant sources. In wood from trees it exists in lower content due to the presence of lignin however the cellulose content is over 50 %. Cellulose can also be made by bacteria and are then called microbial or bacterial cellulose. Compared to cellulose from cotton and wood this is not produced by photosynthesis and pure cellulose is produced. [13]

Cellulose in its form as a polymer raw material have been used mainly in two general areas: one being the use in constructing materials based on wood and cotton and also paper and board. Also cellulose has been widely used as a starting material for chemical reactions in attempt of create cellulose based artifacts that can be used in a wide area of applications. Examples of reactions that can be performed on cellulose are etherification, esterification and oxidation. [5]

Cellulose fibers are insoluble in natural environments. The fibers are also relatively strong and showing specific breaking stress values of $0.59 \text{ Pa mm}^3/\text{g}$. This can be compared to steel wire with a value of $0.26 \text{ Pa mm}^3/\text{g}$. When taking the densities into consideration the values can be converted to 0.9 GPa for cellulose and 2.0 GPa for steel wire. [4]

2.1.2 Molecular structure

The molecular structure of cellulose is a linear syndiotactic homopolymer which consist of D-anhydroglucopyranose units, called AGU. These units are linked together by β -(1 \rightarrow 4) - glycosidic bonds. One molecule can consist of up to 20000 units but shorter chains also occur. The number of units is called the degree of polymerization (DP) of the molecule.

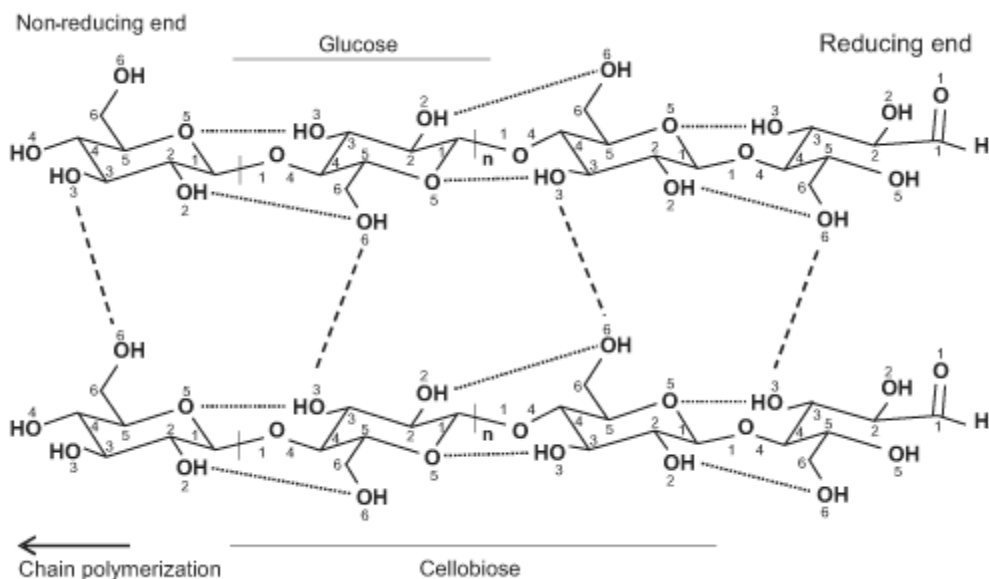


Figure 1. Structure of cellulose with inter- and intramolecular hydrogen bonds. [34]

On every AGU there are hydroxyl groups on the C-2, C-3 and C-6 carbon. These hydroxyl groups are capable of being involved in known typical reactions concerning primary and secondary alcohols. The C-1 tends to have reducing properties and the C-4 end is non-reducing.

The cellulose has a high regularity of the molecules. Despite that cellulose shows properties, i.e. flexibility, that doesn't cohere with the crystalline criterion the regularity is sufficient to meet the criteria for crystallinity. Cellulose can form dense crystals that have strong van der Waals forces and hydrogen bonds. One major difference between the cellulose crystals and crystals of molecules that not form fibers is that the cellulose crystals are very small crosswise but also relatively long.

2.1.3 Supramolecular structure

Cellulose is a polymorph which means that it can crystallize in different kinds of crystalline structures. The different structures are named with Roman numerals I to IV and each form depends on the source and treatment of the cellulose. The two most important structures are cellulose I and cellulose II. Cellulose I have subclasses I α and I β where I α is shown to be most abundant in algae and bacteria while I β is present to a higher degree in higher order plant such as cotton. That is to say both are usually formed in the biosynthesis of cellulose. Cellulose II occurs when cellulose is formed by regeneration from solution or when cellulose I is treated with NaOH and then dried. In industry dilute solutions are used at elevated temperature while in laboratory scale it is more common to use concentrated solutions at low temperature. Cellulose I have a parallel chain structure and cellulose II have an anti parallel structure. There are also cellulose III and IV, cellulose III is formed when cellulose is exposed to amines or liquid ammonia and cellulose IV is formed when cellulose is treated with glycerol at high temperatures. [4]

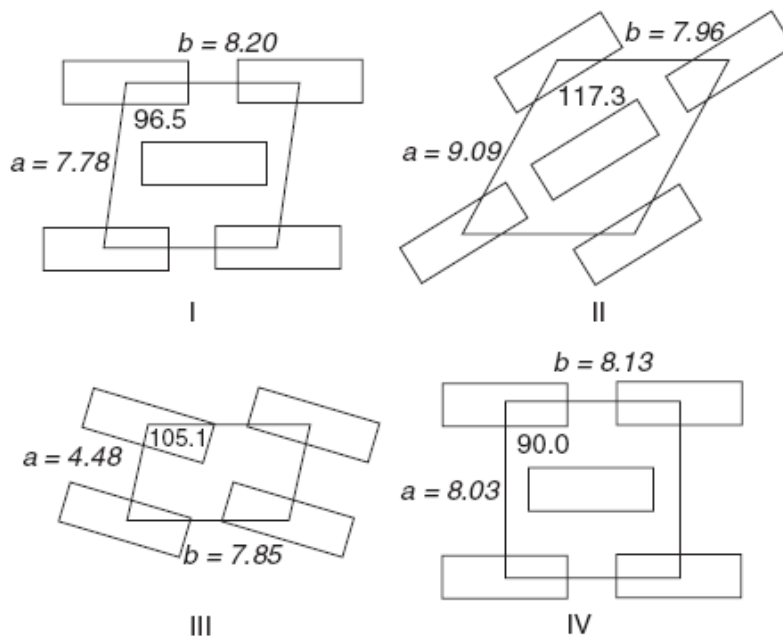


Figure 2. Unit cells for cellulose I-IV. The c dimension (perpendicular to the plane) in all cells is 10.31-10.38 Å.

The packing of the cellulose chains can result in micro crystals or micro fibrils. These are 3-30 nm across and around 7 μm in length. Micro crystals or micro fibrils can organize into macro fibrils which are 60-300 nm wide and they organize in their turn into fibers.[6] One important aspect for the polymer chains to pack together efficiently is that the long axes of the chains are parallel to each other. A distinguished difference between the cellulose forms is the orientation of the rotatable hydroxyl and primary alcohol groups. The ability orient creates a variety of hydrogen bonding and crystal packing arrangements and makes the hydroxyl groups more or less available for chemical reactions.

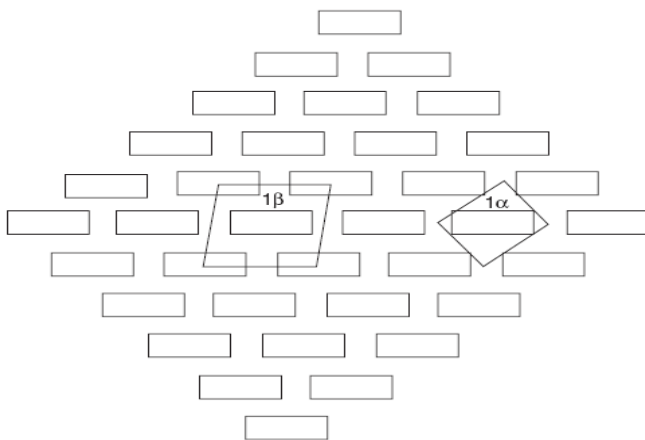


Figure 3. Cross section of a cellulose micro fibril, the individual molecular chains shown as rectangles. Also the unit cells for cellulose 1α and 1β are shown.

The cellulose chains have a large affinity to aggregate into highly ordered structures due to the chemical constitution and spatial conformation. The reason behind the tendency for cellulose to aggregate into this supramolecular structure is the combination of intramolecular and intermolecular hydrogen bonds. The most important factor for the cohesion between the cellulose chains are the intermolecular hydrogen bonds. The good cohesion is also favored due to high spatial regularity of the hydroxyl groups and also the fact that all hydroxyl groups are involved in the network. The latter reason is important to have in mind when heterogeneous reactions of cellulose are carried out since it is at the hydroxyl groups the cellulose is susceptible to chemical modifications.

The order of the macromolecules in a cellulose fiber is not constant but consists of both amorphous as well as highly crystalline regions. This behavior is most often represented by a two phase model assuming amorphous and highly crystalline regions and where the parts with properties between these two are neglected (fringed fibril model). The degree of crystallinity varies a lot between different cellulose samples and depends on the cellulose source and pretreatment of the polymer.

Analyses of the hydrogen network show that cellulose II has a more complicated network than cellulose I and that these leads to a higher density of cross linking. According to Kolpack and Blackwell the hydrogen bonds in cellulose I is linked together by adjacent chains through the O-6···H-O-3 which leads to sheets of chains parallel to the a-axis. In cellulose II Blackwell and Kolpack suggest that -CH₂OH groups are in the trans-gauche position and the center chains form sheets similar those in cellulose I.

2.1.4 Morphological structure

The morphological structure of cellulose is important regarding modification of cellulose. The morphology can be represented by a well organized architecture of fibril elements. For native cellulose the fibrils organize in layers where the different layers have different texture. Regenerated cellulose fibers are generally thought to be built up by fibrillar network. [5]

Besides the fibril architecture of the cellulose the morphology is also dependent on the pores and voids that exist in the cellulose structure. The pores are not uniform in its structure and size and the understanding is of interest when heterogeneous reactions on cellulose are carried out since the reactants must be able to penetrate into these voids to be able to react. [4, 5]

2.2 Swelling of cellulose

In order to be able to control the functionalization of cellulose a prerequisite is the swelling of the cellulose fibers. Without swelling the desired reactions will only occur on the surface layer of the cellulose. When cellulose in form of fibers is situated to a limited swelling the gross structure is maintained despite an increase in volume of the sample due to uptake of swelling agent and the physical properties have changed significantly. During swelling of cellulose the system remains a two phase system in comparison to

dissolution where the system becomes one phase. Despite this difference there are also features that are similar. One such thing is the loosening or even elimination of the supramolecular structure caused by the intermolecular forces overcome by a stronger interaction. The purpose is also the same for both processes which is to enhance the accessibility of the hydroxyl groups on the cellulose molecule for following reactions. One specific system can act as both a swelling agent and as solvent of the cellulose depending on degree of polymerization and the structure of the cellulose. [5]

Limited swelling of cellulose can affect the easily accessible regions, called intercrystalline swelling, of the cellulose or it can also affect the crystalline regions, intracrystalline swelling. The intermolecular cohesion is maintained in both cases but the intermolecular bonds between the polymer chains are broken to different extent. When intercrystalline swelling occur the swelling and increase in weight is due to that the pore system of the cellulose is filled with swelling medium. During intracrystalline swelling an increase in the lattice dimensions of the crystalline regions occur which results in swelling of the sample.

Cellulose is highly hygroscopic due to its hydroxyl groups and their interactions with the water molecule, it is however not soluble in water due to the highly ordered supramolecular structure. The cellulose-water interaction can be depicted as a competition of hydrogen bond formation between one hydroxyl group of the polymer chain and a water molecule. This implies that the interaction is highly depended on the supramolecular structure of the cellulose specimen, the amount of water already present and temperature which affect the structure of the water.

Swelling of cellulose in sodium hydroxide (NaOH) is a very important phenomenon in the complex process of cellulose-alkali interaction. It is important since it influence the cellulose in all three levels of structure. On the molecular level the ion dipoles of the NaOH and the hydroxyl groups of the cellulose creates a strong interaction. This strong interactions results in a cleavage of both inter- and intramolecular hydrogen bonds. The supramolecular level is altered in the lattice dimensions and chain conformation. The inter- and intracrystalline swelling of the fiber structure in NaOH gives a different composition of the amorphous and crystalline parts of the alkali cellulose. Also the fibril architecture is changed which give a different structure on the morphological level.

When the lye concentration is increased the amount of hydrates of the NaOH ion dipoles decreases. The water cluster structure is disturbed already at low lye concentrations by the hydrated alkali ions, which results in the formation of monomolecular water in the system. This monomolecular water penetrates into the cellulose structure and enables further swelling by breaking intermolecular hydrogen bonds and makes it possible for hydrated ion dipoles to enter the structure. The degree of swelling is dependent on two factors. First the amount of water molecules transported into the cellulose structure by the alkali ions or ion dipoles and secondly the depth of this penetration. The first factor decreases with increased lye concentration while the second factor increase with increased lye concentration until even the crystalline regions are transformed into alkali

cellulose. Since these two factors counteract the swelling of cellulose in sodium hydroxide will have a maximum. [5]

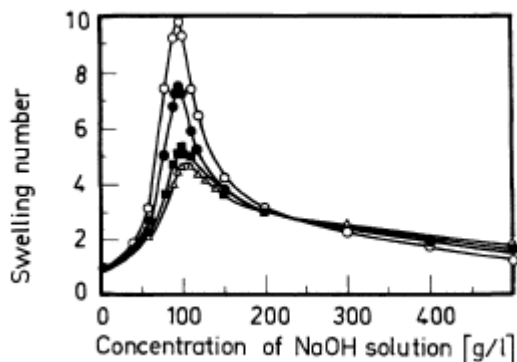


Figure 4. Swelling of cellulose (rayon). ○ 14 °C, ● 20 °C, ■ 25 °C, △ 31 °C.

The height of the swelling maximum curve, i.e. the relative swelling, and the position of the swelling maximum on the concentration axis is dependent on the structure of the cellulose sample. As the structure gets more and more fiber like the maximum is shifted to higher lye concentrations. Also the height of the swelling maximum is dependent on the temperature of the sodium hydroxide solution, as can be seen in figure 4. [5]

2.3 Absorption mechanism

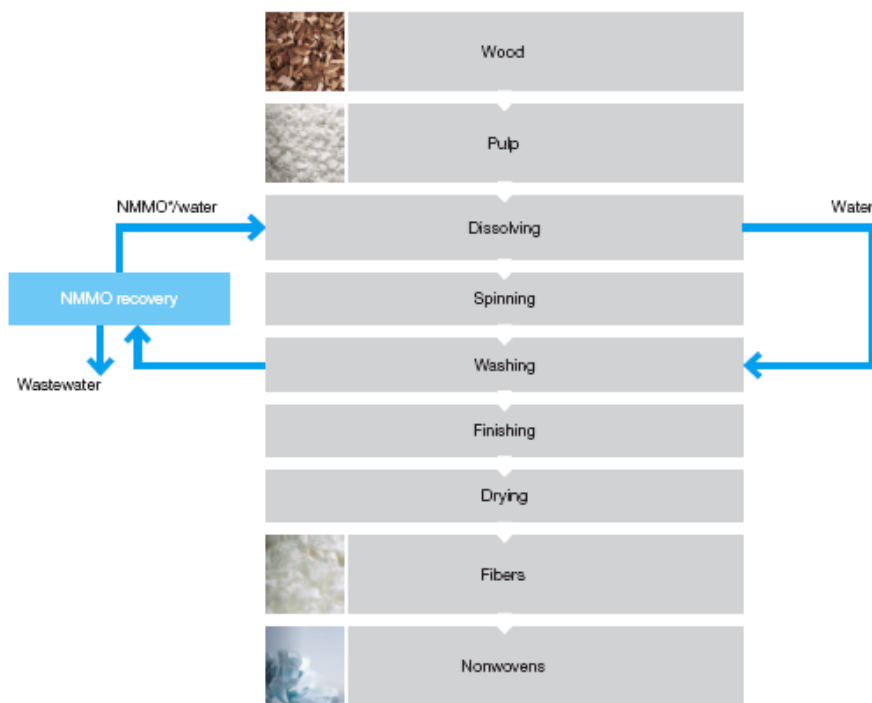
After the modification of the cellulose fibers they will show the same behavior as super absorbent polymers (SAP) and the absorption mechanism of fluids are the same. Ionic polymers such as those made by the modification of the cellulose are electrically neutral due to that the negative carboxylate and sulfonate groups are neutralized by the positive sodium ions. When the polymer come in contact with water the sodium ions becomes hydrated and lose their attraction to the carboxylate/sulfonate groups, this makes it possible for the sodium ions to move around in the polymer network. This movement gives rise to an osmotic pressure within the gel. However the sodium ions still have an affinity to the negatively charged ions which hinders them from get out from the network. The driving force for the swelling is due to the osmotic pressure difference over the gel. The maximum swelling will occur for deionised water, if the fluid contains high concentration of salt there will be no or little swelling since the osmotic effect will be small. [33]

2.4 Preparation of fibers

2.4.1 Tencel process

The manufacture process of the Tencel fibers is started with wood pulp being shredded and mixed with NMMO (N-methylmorpholine-N-oxide) and water. The water is being evaporated by stirring in a vacuum vessel at elevated temperature. When the amount of water has reached a certain level the cellulose is dissolved. This solution is then filtered and extruded through a spinneret, tiny holes on a plate, with high pressure and high

viscosity into a spinning bath which contains an aqueous solution of NMMO. The filaments that are formed when extruded through the spinneret are gathered to form a tow, a rope of parallel filaments. After this step the tow is either further treated as a tow and goes through cleaning and finishing steps or the tow can be cut into staple fibers which in their turn are cleaned and finished. [7]



Scheme 1. Schematic representation of Tencel process. [7]

2.5 Chemical reactions

Chemical reactions that can be carried out involving the structural units of a polymer can in general also be carried out by the macromolecule of the polymer. There are however some aspects that will have to be taken under consideration. First there is a limitation in the completeness of the reaction. This is due to the covalent bonds that exist between the polymer chains to create the macromolecule and the fact that they occupy sites that in low molecular chemistry could act as reactive sites. This will also affect the purity of the product. Second the relevance of intramolecular interactions in the polymer reactions compared with chemical transformations in low molecular chemistry. [5]

In chemical reactions with solid polymers that are swollen the supramolecular and morphological structure are determining the rate and extent of the chemical reaction. Side reactions are difficult to avoid and they can lead to complex structures of the desired reaction product. The products of these side reactions cannot be purified by the same methods as in low molecular chemistry due to the covalent bonds between the repeating units.

Cellulose macromolecule is due to its three hydroxyl groups a polyfunctional molecule. This polyfunctionality is both advantages and disadvantages. When carrying out a chemical reaction there is more likely that the reaction is complete due to an increase in the degree of freedom. On the other hand when having several sites where the reaction can take place it is difficult to control the uniformity of the reaction. Another aspect regarding the cellulose structure is derived from the glycosidic bond between the AGU units. This bond is susceptible to hydrolytic cleavage which will result in chain degradation and a limit in some reactions, especially those who are carried out in acid conditions.

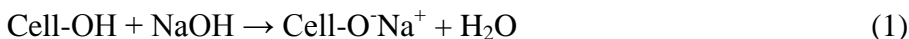
Reactions sites of the cellulose molecule for functionalization are limited to the three alcoholic hydroxyl groups on every AGU unit. Changes in C-1 and C-4 regions are more important regarding degradation of the cellulose macromolecule and also the oxygen atom within the ring have some role in intermolecular interactions but not regarding covalent derivatization. At C-6 the hydroxyl group is a primary alcoholic hydroxyl group while the C-2 and C-3 are secondary alcoholic hydroxyl groups. They can all precipitate in classic, well known reactions involving alcoholic hydroxyl groups such as esterification, etherification and oxidation. All cellulose derivatives that are available commercially today are done by complete or partial esterification or etherification and the products will have covalently bound substituents.

In general cellulose ethers are very stable and resistant to hydrolytic removal of substituent groups. This is held true both for acid as well as alkaline conditions. Reactions based on condensation such as the Williamson ether synthesis is regarded to derive derivatives that are somewhat more stable than derivatives that are made with addition reaction such as the Michael addition. This difference in stability is due to the equilibrium nature of the addition reaction. [6]

2.5.1 Williamson ether synthesis (carboxylation)

In a Williamson ether synthesis an alkoxide ion, RO^- reacts with an alkyl halide, RX , in a nucleophilic substitution. R is an alkyl group and X is the halide F, I, Cl or Br. It is a method that is suitable for a wide range of reactions. The alkoxide is the conjugate base of an alcohol. The halide should be primary since this gives as little steric hindrance as possible. [15, 22] The alkoxide ions are strong bases and therefore the risk for elimination reactions to occur is always needed to be accounted for. In order for the reaction to be carried out to a sufficient extent the substrate of the reaction needs to be unhindered and contain a good leaving group. [9] The solvent, isopropanol, have less polarity than water and therefore the polarity of the aqueous solution will decrease and this lead to an increase of the efficiency of the wanted reaction. [16]

In the specific case of carboxymethylation of cellulose a first step is to make alkali cellulose which is then further reacted by a Williamson etherification with sodium chloroacetate in an aqueous/alcoholic system. The reaction scheme where alkali cellulose is made is represented in reaction 1.



The aqueous solution of NaOH also precipitates in a side reaction with the etherifying agent, i.e. the sodium chloroacetate. Sodium glycolate is formed by hydrolysis of the chloroacetate. The reaction is shown in reaction 2. This can continue to an extent where 30 % of the sodium chloroacetate is consumed. [18]



There are several reasons to use an alcohol in the system. The cellulose gets more dispersed, it provide heat transfer, reduce reaction kinetics and to assist the recovery of the product. [17] However the use of alcohol means a competition with the hydroxyl groups of the cellulose molecule. In order to minimize the hydroxyl groups of the alcohol to react with sodium chloroacetate isopropanol is chosen due to its lower hydroxyl group reactivity. When sodium chloroacetate reacts with the hydroxyl groups of the alcohol low molecular ethers are formed with the structure $\text{ROCH}_2\text{COO}^-\text{Na}^+$. [18]

The alkoxide ion of the alkali cellulose formed in reaction 1 reacts with the sodium chloroacetate in an $\text{S}_{\text{N}}2$ reaction and results in the ether carboxymethyl cellulose, reaction 3.



Reaction 1 is an endothermic reaction and the $\text{S}_{\text{N}}2$ reaction in the Williamson ether synthesis, reaction 3, is exothermic which release 41.3 kcal/mol. [16]

2.5.2 Michael addition (sulfonation)

The Michael addition reaction is a conjugate addition between a carbon nucleophile and an electron deficient alkene. In the case when the carbon nucleophile is an alcohol the reaction is called oxa-Michael addition. [19] The nucleophile Nu^- is formed by deprotonation of the precursor NuH and is added at the β -position in the α - β -unsaturated acceptor. [20]

Due to the electron withdrawing sulfuric acid group in the sodium vinyl sulfonate the π -double bond system becomes α - β -unsaturated. This activation of the π -double bond system makes the double bond susceptible to nucleophile attacks compared to the π -double bond system which is not. [21]

Sulfonation of cellulose by Michael addition results in a sulfoalkyl ether of cellulose. The reaction is carried out in presence of alkali cellulose at elevated temperature. The reaction of cellulose and sodium hydroxide to create alkali cellulose is the same as in the carboxylation, reaction 1. The reaction formula for the sulfoalkyl ether is represented in reaction 4. [18]



The oxa-Michael addition reaction is reported to proceed inefficiently due to low reactivity and reversibility. Several catalysts have been used such as strong acids and bases, red mercury oxide, boron trifluoride etherate and a couple of transition metals such as lead and copper. However there are some drawbacks with these catalysts such as violent reaction condition and environmental factors. [23]

2.6 Evaluation methods

2.6.1 Free swell and retention

When determining the absorption and retention of the modified cellulose fibers a method used internally at Mölnlycke Health Care is used. The method has been developed to determine the capacity of fibers to absorb and retain polar liquids. The polar liquid used in this method is a liquid called Solution A. Solution A is made by weighing 8.298 grams NaCl and 0.368 grams CaCl₂ in a 1 liter metering flask and filling it with distilled water. This liquid is supposed to mimic the properties of body fluids. Testing is carried out in a conditioned room with a temperature of 23 °C±2 and a relative humidity of 50 % ±2.

The procedure of the method to determine the absorption capacity is as follows:

1. Weigh 0.5 grams of fibers in a 100 ml beaker. Weigh 30 grams of Solution A and pour it over the fibers. Shake the beaker for about 5 seconds to get a good distribution of the liquid into the fibers.
2. Let the fibers swell in Solution A for 5 minutes (±10s)
3. Filter out the excess liquid with a Buchner funnel Ø 70 mm with a Quantitative filter paper Grade 00R Ø in it. Before adding the solution containing the test fibers the filter paper needs to be saturated by adding 10 ml of Solution A through the funnel.
4. Put a weighed beaker, W1, under the funnel. Pour the fiber containing solution through the funnel and let it filtrate for 10 minutes (±10s).
5. Shake the funnel carefully to detain all liquid. Weigh the beaker W1 again and obtain the value W2. The free swell absorbency is calculated by following formula:
$$2 \times (30 - (W2 - W1)) = \text{grams absorbed Solution A} / \text{gram fiber} = \text{FSA}$$
6. Repeat the procedure 3 times and calculate the average for the 3 measuring points.

The retention capacity of the fibers can be determined directly after the free swell test. After the free swell test the tested fibers are fully absorbed. These fibers are subjected to a static pressure of 20 mm Hg. The retention capacity is defined as the difference between the amount of absorbed liquid and the amount liquid squeezed out. The following procedure was followed:

1. Put a weighed beaker, W3, under the funnel.

2. Put a Ø 70 mm plate onto the test material in the funnel and weights on top. The total weight creates a pressure of 20 mm Hg. Leave the pressure for 5 minutes (± 10 s) and then shake the funnel carefully.
3. Weigh the beaker again, this time with the test liquid and obtain the value W4. The retention capacity is calculated as grams of liquid left in the test fiber after added pressure per gram of dry fiber with the formula:
$$\text{FSA} - (2 \times (W4 - W3)) = \text{grams of Solution A left in fiber after pressure of 20 mm Hg} / \text{gram fiber} = R$$
4. Repeat the procedure 3 times and calculate the average for the 3 measuring points.

2.6.2 Raman spectroscopy

Raman spectroscopy is a spectral measurement that is based on scattered monochromatic radiation. Energy is exchanged between the photons of the incoming monochromatic light from a laser and the molecule that is subjected for testing. The energy of the scattered photon is either higher or lower than the incoming photons. This difference is due to rotational and vibrational energy of the subject molecule and gives information about its energy levels. [24] Raman spectroscopy requires a change in the frequency of the vibrations and polarizability of the subjected molecule. The most appropriate source for the monochromatic light is a laser. [25] The development of effective Raman spectrometers for cellulose materials is to a large extent due to the NIR (Near Infrared) lasers that avoid fluorescence of the samples that normally blank the Raman signals. [26] Advantages with the Raman spectroscopy is that no sample preparations are required, it can be used for gases, solids and aqueous solutions where the latter is a huge advantage compared to the similar IR spectroscopy. It is also a relatively fast technique. [27]

3 Materials and Methods

3.1 Materials

3.1.1 Tencel fibers

The Tencel fibers are obtained from the company Lenzing. The process for making these fibers are previously described and is claimed to be more environmentally friendly than previous similar processes. The fibers are close to circular in cross section and are delivered as staple fibers with a length of 50 mm and 2.2 decitex (grams / 10000 m).

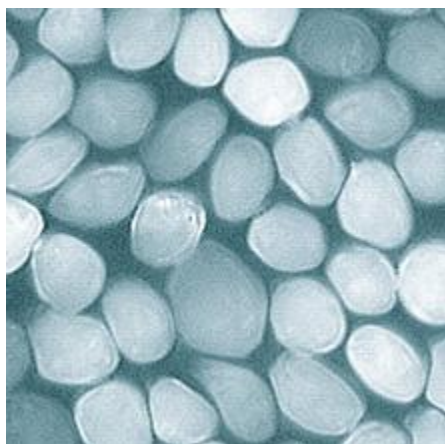


Figure 5. Cross section of Tencel fibers. [7]

3.1.2 Chemicals

The sodium hydroxide, sodium chloroacetate and sodium vinyl sulfonate were all bought from Sigma Aldrich. The sodium chloroacetate is in powder form, the sodium hydroxide in pellets and the sodium vinyl sulfonate in 25 % aqueous solution.

3.2 Methods

The starting point of the experimental part of this master thesis has been a number of patents present in the field of wound dressings. According to these patents there are several methods that can be used to carboxylate and sulfonate cellulose fibers. These methods have been tested and evaluated and in some cases also modified so they are suitable to use at Mölnlycke Health Cares facilities. After several test runs where equipment, drying procedure and reaction parameters were tested two methods that were the most appropriate for carboxylation and sulfonation was derived. A more detailed description of the screening tests is represented in Appendix A.

3.2.1 Carboxylation

The method for carboxylation starts with making of aqueous solution of the two reactants involved in the reaction. Sodium hydroxide pellets are dissolved in water to its desired concentration. Sodium monochloroacetate powder is also dissolved in water. The two reactants should not be mixed until instantly before the reaction is about to start. This in

order to as far as possible avoid the side reaction where sodium glycolate are formed between sodium hydroxide and sodium monochloroacetate. The reaction media also contains an alcohol. The most appropriate one used, due to its low reactivity to the reactants, is isopropanol. The relation water/isopropanol in the system is 2:1 by weight. Next the sample, in this case cellulose fibers, are weighed and put in the reaction beaker. For the type of fibers used, about 70 ml reaction solution / gram fiber is used in order to get a good dispersion of the fibers and also to keep the viscosity of the slurry sufficiently low so that it can be stirred. However since the fibers used are quite long (50mm) they have a tendency to wind up on the propeller stirrer used. Depending on how much the fibers are dissolved in the reaction mixture more or less fibers are winded up on the propeller. More dissolved fibers result in less winding.

The temperature of the reaction is controlled by an oil bath on a magnetic heating plate with controlled temperature. The stirring equipment is an electrical stirrer with a propeller mounted to it.



Picture 1. The setup for the carboxylation.

After the reaction the fibers are washed in two steps. First step is to wash the fibers in 70 % denaturated ethanol with 1-2 % acetic acid followed by washing in pure 70 % denaturated ethanol. The acetic acid is added to neutralize the alkaline conditions of the reaction media. The fibers are then air dried at room temperature to constant weight before analyses are carried out on them.

Below an example of the carboxylation is represented:
12 g NaOH is dissolved in 30 ml water

27 g $\text{ClCH}_2\text{COO}^-\text{Na}^+$ is dissolved in 70 ml water

The two solution are mixed with 64 ml isopropanol which gives a reaction solution containing 6,3% NaOH and 14,3% $\text{ClCH}_2\text{COO}^-\text{Na}^+$. The solution is then poured over 2,52 Tencel fibers in the reaction beaker and is lowered into the heated oil bath. The oil bath holds a temperature of 50°C and the fibers are reacted for 5 hours. After the reaction the fibers are washed in two steps. First step is in ethanol with acetic acid and then in only ethanol. The fibers are dried at room temperature until constant weight.

3.2.2 Sulfonation

The sulfonation method is a two step method. In the first step cellulose fibers are swelled in a sodium hydroxide solution for thirty minutes. The solution is made from sodium hydroxide pellets that are dissolved in water. This is an exothermic reaction and the solution is cooled to 20°C before the fibers are added. The fibers sample just barely needs to wet in order for the sodium hydroxide to swell the fibers to a sufficient degree. When the fibers have swelled the sodium hydroxide is squeezed out of the fiber sample. The second step is started when the sodium vinyl sulfonate solution is poured over the swelled fiber sample in a small e-flask. The reaction takes place in an oil bath holding the wanted temperature. The e-flask is sealed with parafilm so that the amount of solution stays the same throughout the entire reaction time.



Picture 2. The setup for the sulfonation.

The washing procedure is the same as in the carboxylation method, i.e. a two step method in 70 % denaturated ethanol where in the first step 1-2 % acetic acid is added in order to

neutralize the alkaline condition. The modified fiber sample is then air dried at room temperature.

Below an example of the sulfonation reaction is represented:

20 g NaOH is dissolved in 20 ml water

20 ml 25% $\text{CH}_2\text{CHSO}_3\text{Na}$

The NaOH solution is cooled to 20° C and poured over 2,49 g Tencel fibers and the fiber are swelled for 30 minutes. After 30 minutes excess solution is squeezed out of the fibers and the fibers are put in an e-flask. 20 ml of the reaction solution is added to the fibers and the fibers and solution is lowered into a heated oil bath (100°C). The fibers are reacted for 1 hour. After the reaction the fibers are washed in two steps, first with acetic acid in ethanol and then in only ethanol. The fibers are dried at room temperature until constant weight.

3.2.3 Disregarded methods

At an early stage of the laboratory work a couple of similar but different from the above mentioned methods were tested. These methods together with some comments on why they were disregarded are presented below.

In one carboxylation method ethanol was used as a solvent instead of isopropanol. However the use of ethanol gave poorer results and this is thought to be due to that ethanol is more reactive and their hydroxyl groups compete with the sodium hydroxide and if hydroxyl groups of ethanol is reacted the cellulose hydroxyl groups becomes activated to lesser extent. The reaction was also tested with only water, i.e. no organic solvent at all. This however gave poor results.

At an early stage of the carboxylation the stirring equipment consisted of just a magnetic stirrer. This didn't give enough torsion to disperse the fibers so that the reaction solution could disperse and react with all fibers in the sample.

Tests were also made where the cellulose fibers were only padded with the reaction mixture for a short period of time and then dried at elevated temperature in an oven. The reaction is supposed to be carried out at the same time as the drying is achieved at quite high temperatures (100-150°C). However the drying at such high temperatures results in fibers that are very hard and depending on temperature in some cases almost burned. This padding method is more likely to be useful if the fiber sample is in the form of a tow since then the individual fibers are less exposed to the high temperatures.

As an alternative to the sulfonation method a similar method where tested. The difference from the one finally used is that both the swelling of the cellulose with the sodium hydroxide and the reaction with the sodium vinyl sulfonate are done simultaneously in a one pot reaction. The gelling properties of these fibers were about the same, but somewhat lower, as for the used two step methods but according to literature and also the

feel of the fibers suggest that the tensile strength is noticeable lower. A property that is unwanted in further processing of the fiber.

The method that is used in the sulfonation process was also evaluated for carboxylation. The reaction is carried out but according to the degree of gelling, not to the same extent as for the method used.

4 Results and Discussion

In order to get an estimation on what parameters that affect the involved reactions a screening test is done. From this screening test it is suggested that important parameters for the sulfonation reaction is the concentration of sodium hydroxide, amount of sodium vinylsulfonate, time and temperature. For the carboxylation reaction the sodium hydroxide concentration, monochloroacetate concentration, time and temperature are suggested as important parameters. The screening test for the sulfonation and the carboxylation is represented in detail in Appendix A.

The reacted fibers are first tested for absorption in a simple and non quantitative way by just adding, drop wise, regular tap water on the almost dried and dried fiber samples. The absorption is instant and this simple test gives a first approximation if the reaction is carried out or not. The increased absorption compared to untreated cellulose fibers is a first evidence of a successful modification. One observation that applies for almost all samples is that it seems that the fibers can absorb more water when they are a little damp compared to when they are dried to constant weight, i.e. completely dry. The screening test gives an indication on that the carboxylated fibers show greater absorption and retention properties compared to the sulfonated ones.

Based on the results from the screening test a more systematic test run is setup with the computer software program Modde. The reaction parameters determined in the screening test is evaluated and based on the results from absorption and retention tests the most important parameters are derived.

The Modde program also gives information about how reliable the system is and how good predictions that can be done by comparing observed values with predicted ones.

4.1 Results from Modde

The complete result from the Modde program for the carboxylation is represented in Appendix B and for the sulfonation in Appendix C. In this part the most important diagrams and figures are explained and discussed. The same model is used for both the carboxylation and the sulfonation but with different parameters. The amount of test done is made accordingly to the chosen model. When feeding data to the model some values doesn't follow the model, these are called outliers. The retrieved data for free swell and retention shows one outlier for every reaction. These outliers are removed from the model in order to get a better estimation. Apart from these outliers the data follows the model. Therefore the outliers can be neglected when analyzing the model. The outliers are more likely due to errors in the reaction carried out rather than error in the model.

4.1.1 Carboxylation

When determining how good the applied model is figure 6 is a powerful tool. It includes predictions on four parameters that give information about significance, prediction, validity and reproducibility of the model.

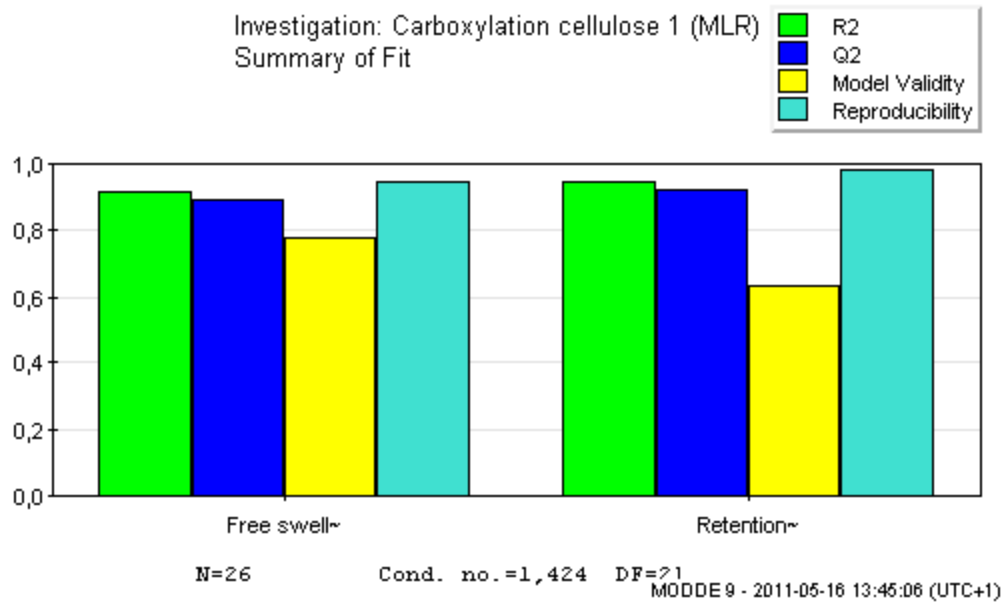


Figure 6. Model statistics for carboxylation.

The value R2 shows the model fit and the significance. Values below 0,5 represent a model with low significance. The value for the carboxylation model is over 0,9 and can be considered to have high significance both for free swell and retention. Q2 estimates the precision of future predictions, for the model to be significant the value should be over 0,1 and for a good model the value should be higher than 0,5. For both free swell and retention Q2 is above 0,9 which indicates that the model can be used to predict future testing with good results. The model validity tests the model for diverse problems. A value below 0,25 indicate statistically significant model problems, such as the presence of outliers, an incorrect model or transformation problems. From figure 6 it can be said that the model is better for free swell. But there are no severe deviations in either model. Reproducibility is the variation of the replicates compared to overall variability. Both free swell and retention have very good reproducibility, i.e. close to 1. The reproducibility is derived from the center points in the model.

Investigation: Carboxylation cellulose 1 (MLR)

Scaled & Centered Coefficients for Free swel Scaled & Centered Coefficients for Retentior

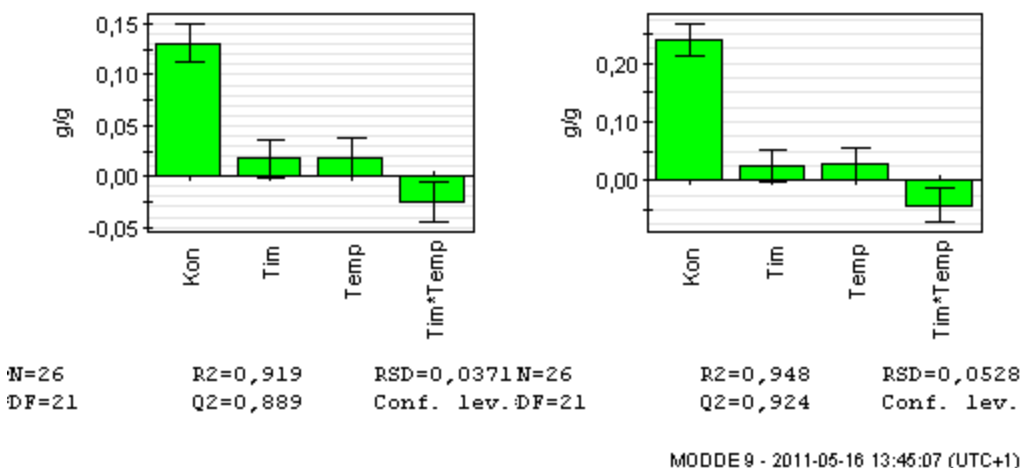
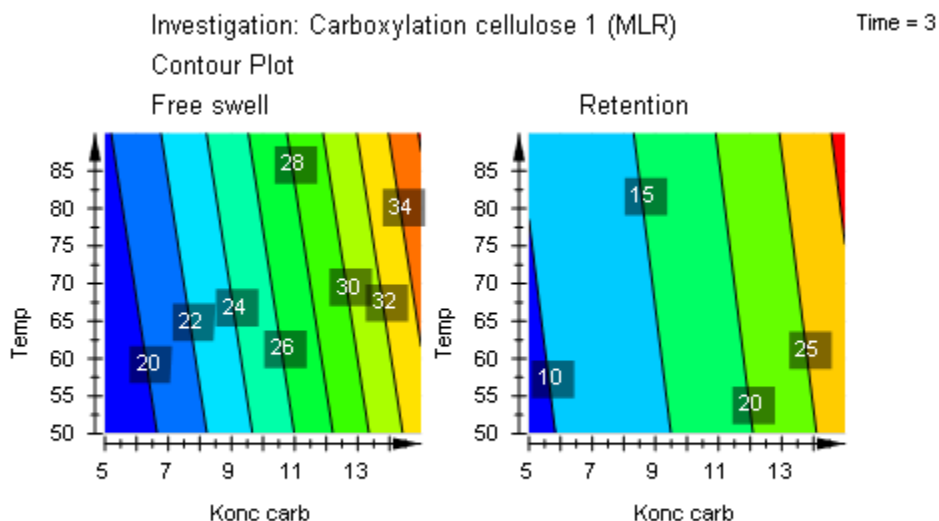


Figure 7. Scaled and centered coefficients for carboxylation.

From figure 7, the importance of the different parameters is shown. It is clear that for both free swell and retention the concentration of monochloroacetate is the most important parameter. The higher the bar in the bar diagram is relative the confidence interval the more relevance the parameter have for the investigated property. The temperature has a small influence on the free swell and retention. The confidence interval for the time parameter is just crossing the zero value which indicates that it is not significant for the outcome of the reaction. One interesting observation is that when the time and temperature is changed and the others parameters are held constant the effect on both free swell and retention is negative, i.e. a decrease in the free swell and retention is to expect. This might be due to degradation of the cellulose molecule that can occur when it is situated to harsh environments. The value on the y-axis differs between the free swell and retention. Free swell maximum is about 0,125 g/g with confidence interval between 0,11-0,15 g/g and for the retention the analogous values are maximum 0,24 g/g and interval 0,22-0,27 g/g. This difference indicates that the concentration of monochloroacetate have a larger impact on the retention than that is has on the free swell. Similar trend is also seen for the other parameters but to a much smaller extent. A reason for this trend might be that the samples that have been reacted with the highest concentration of monochloroacetate are the ones that create the most gelled fibers when wet. Samples that are reacted with less concentration might show value of the free swell close to the ones with high concentration but due to the high degree of gel in the high concentration sample they will retain more.

In the model that has been used in this case the concentration of the sodium hydroxide has no influence on either the free swell or the retention. However it is important to have in mind that the concentration interval is rather small and that it is only in this interval that the concentration of sodium hydroxide has no influence. The interval was defined by the screening test and by literature studies of previously performed reactions. In future

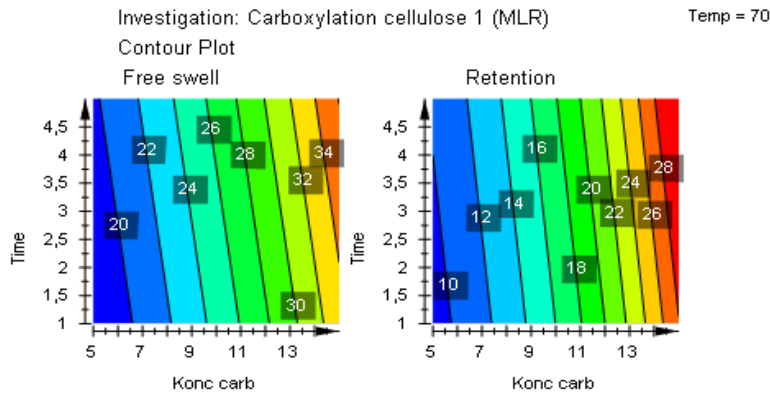
research it would be interesting to investigate what the lower concentration limit is for the sodium hydroxide.



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Figure 8. Free swell and retention plot, carboxylation.

In figure 8 the free swell and retention values are plotted depending on the temperature and the concentration of monochloroacetate. According to these plots it would be of interest to increase the concentration of the monochloroacetate. In the screening test such reaction was carried out (sample 30). However it did not result in fibers with increased free swell and retention capabilities. The fiber became more dissolved in the reaction solution than for lower concentration. In this case to such degree that when dried they had lost their fiber properties completely and what is left is just a lump of cellulose and monochloroacetate. This lump doesn't show any ability to absorb water. Instead of adding all the monochloroacetate in the beginning of the reaction it could be gradually added during the reaction, by doing this the concentration of the monochloroacetate would be lower during the reaction as the reaction proceeds and more can be added without dissolving the fibers. Such tests have not been done during this work but are interesting for future work. Increasing the temperature could marginally affect the free swell and retention properties. This is also suggested in figure 7 where the time parameter shows small significance.



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Figure 9. Free swell and retention plot, carboxylation.

Figure 9 shows the free swell and retention depending on concentration of monochloroacetate and time. The same reasoning is true for the increase of monochloroacetate concentration as stated according to figure 8. The time parameter in figure 7 argues that it has low significance for the reaction. An increase of the time is therefore not likely to give better free swell and retention properties. The fact that the free swell and retention values decrease when increasing both time and temperature might also be a reason to be careful when elaborate with the time parameter.

4.1.2 Sulfonation

The same model has been when evaluating the sulfonation as the carboxylation and the equivalent diagrams and figures are used to determine which parameters have the most impact on the reaction and how good the model is. The parameters are almost the same with the difference that instead of concentration of monochloroacetate the amount of sodium vinylsulfonate is investigated. The intervals within in the parameters are also different between the two reactions.

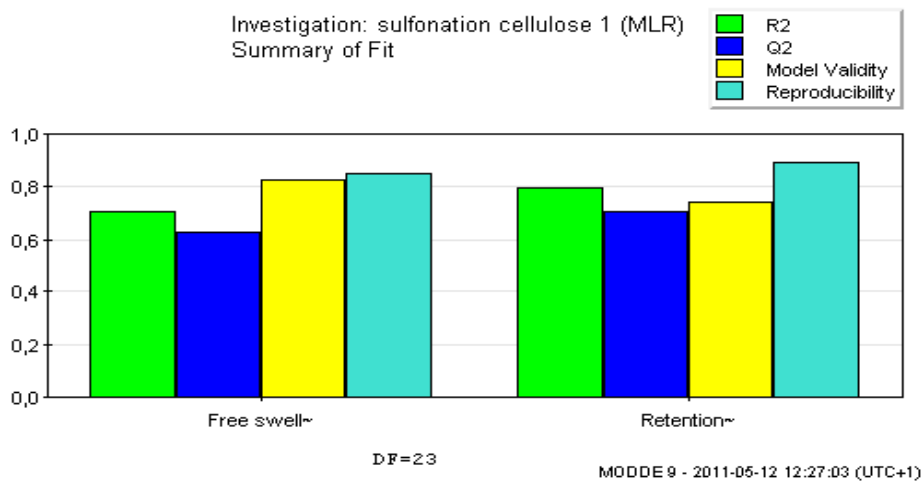


Figure 10. Model statistics for sulfonation.

The value for R2 should be higher than 0,5 in order for the model to have good significance. The retention have somewhat higher value then free swell 0,8 and 0,7 respectively which indicates that the model is slightly more significant for the retention. If the Q2 value is higher than 0,5 the model is considered good and this can be stated for both free swell and retention, 0,6 and 0,7. If the value for model validity is below 0,25 there is some significant model problems such as outliers or an incorrect model. The values for both free swell and retention are well above this and the model can be regarded as a model without any significant problems. The reproducibility is good for both free swell and retention, 0,8 and 0,9.

The values for the sulfonation model are consistently lower than that for the carboxylation, except the values for model validity. This indicates that the model is better for the carboxylation reaction than for the sulfonation reaction. Another observation that can be done is that the retention values are higher than the free swell values for both reactions, however once again the model validity shows opposite behavior.

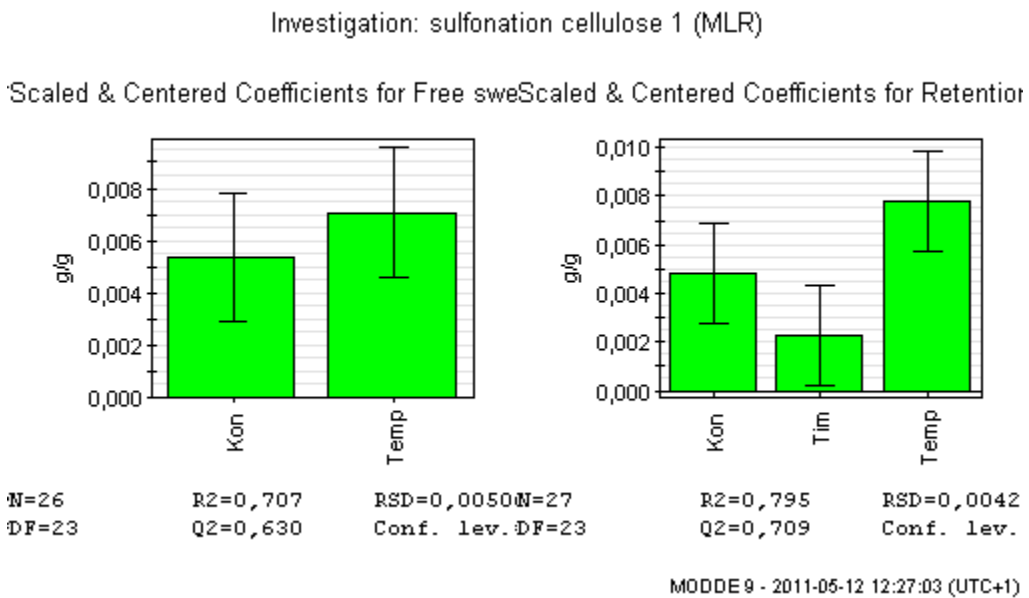


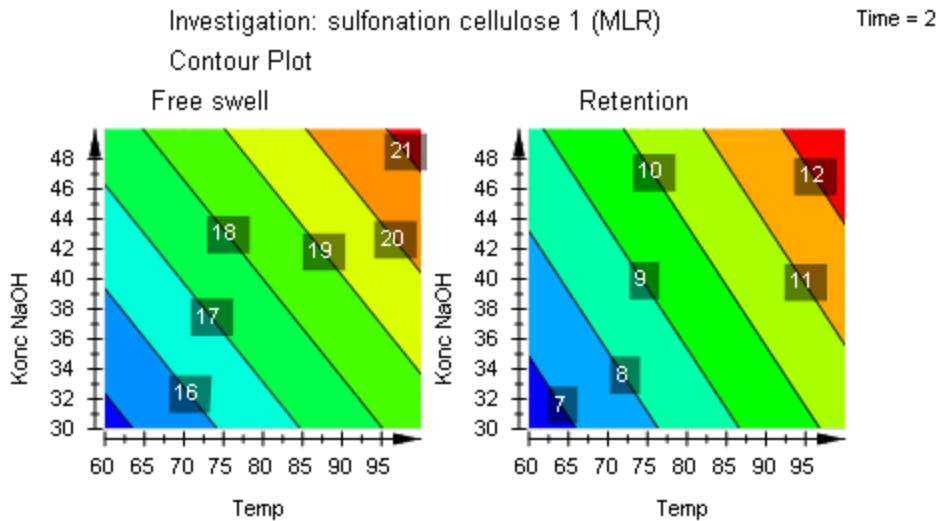
Figure 11. Scaled and centered coefficients for sulfonation.

In figure 11 the most important parameters for the sulfonation reaction is represented. For the free swell the concentration of the sodium hydroxide and the temperature are the two most important parameters and where the temperature shows the most effect. For the retention again the concentration of sodium hydroxide and the temperature is the most important but time is also a factor. The value is about the same for the free swell and retention regarding the sodium hydroxide concentration and the temperature. This indicates that the parameters influence the free swell and retention to the same degree. Compared to the carboxylation model the values of the bars are much smaller. Also the confidence intervals are smaller compared to the carboxylation. This indicates that the carboxylation model is better than the sulfonation model.

The fact that the concentration of sodium hydroxide is an important parameter indicates that the swelling of the cellulose is a crucial aspect regarding the outcome of the sulfonation reaction. This suggests that during the sulfonation reaction the hydroxyl groups on the cellulose needs to be easily accessible in order for the reaction to occur. This preference doesn't seem as important for the carboxylation reaction. The Michael addition reaction which is the reaction involved in the sulfonation is reported to have low reactivity and hence the accessibility might be more crucial for this type of reaction compared to the substitution reaction in the Williamson etherification that is the major reaction in the carboxylation.

Another reason for the importance of the concentration of sodium hydroxide is that with an increase more hydroxyl groups of the cellulose becomes susceptible to reaction, i.e. more alkoxide ions are formed.

In the same way as the concentration of sodium hydroxide in the investigated interval doesn't influence the carboxylation the amount of sodium vinylsulfonate doesn't influence the sulfonation. Again this is only in the investigated interval and it might be of interest to evaluate which amount that is the lower limit. This can reduce the amount of chemicals needed which is favorable.



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Figure 12. Free swell and retention plot, sulfonation.

Figure 12 shows the predictions for the free swell and retention parameters based on the temperature and the sodium hydroxide concentration. As seen in figure 11 these are the two parameters that influence the outcome of the reaction the most. In future work an increase of both these parameters would be of interest to investigate. Since an increase of the temperature will lead to exceeding the boiling point it would be appropriate to carry out the reaction in an autoclave.

Throughout the processes there are some error sources that can affect the reactions and the model. The temperature of the reaction is difficult to control and it fluctuates before leveling off to the desired temperature. This might affect the outcome of the reaction especially for the sulfonation where the importance of the temperature is large. Error may also occur during the reaction when handling the chemicals by e.g. weighing. During the Free Swell and Retention test it might be some errors due to liquid that isn't filtrated due to it is hindered by for example the fibers themselves. This might give false results since the liquid is not really absorbed by the fiber.

4.2 Free swell and retention method

The free swell values or the absorption capacity is given in the unit of grams absorbed Solution A / gram fiber. The retention value has the unit grams of Solution A left in fiber after pressure of 20 mm Hg / gram fiber. After the fibers have absorbed the liquid they show different behavior depending on how much liquid they can absorb. It ranges from fibers that are quite similar to untreated fibers and maintain their fiber structure to fibers that completely lose their fiber structure and form a transparent gel. In the free swell and retention method these transparent gels are difficult to measure and to obtain a representative value due to that the gel might hinder free liquid to pass through the system. This leads to a large variation in the measuring points and the average value might be misleading.

The free swell absorption and the retention properties vary a lot between the modified fibers. The fibers with the lowest absorption and retention show about the same values as for the pure cellulose samples which indicate that no reaction has taken place or only to small degree. The carboxylated fibers are able to absorb and retain more liquid than the sulfonated fibers. The maximum value for the free swell for carboxylation is 39,4 g absorbed Solution A / g fiber and for sulfonation the maximum value is 23,7 g absorbed Solution A / g fiber. The maximum values for retention is 34,2 grams of Solution A left in fiber after pressure of 20 mm Hg / gram fiber for carboxylation and 14,6 grams of Solution A left in fiber after pressure of 20 mm Hg / gram fiber for sulfonation. The values for untreated fibers are 15,43 g Solution A / g fiber for the free swell and 8,77 g Solution A left in fiber after pressure of 20 mm Hg / g fiber. These results are schematic presented in figure 13.

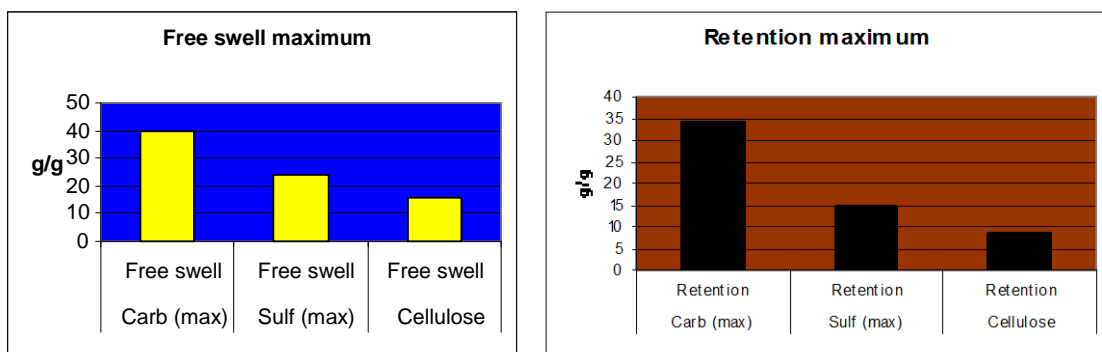


Figure 13. Free swell and retention maxima.

One other correlation that can be done to the amount of absorbed and retained liquids is the relationship between the hardness of the reacted fibers and the absorption capacity. After the fibers have been treated they tend to glue together and the clusters that are formed are hard and difficult to separate. The clusters are also brittle and may quite easily be fractionated into smaller parts. Due to this aggregation of the fibers it is harder for the liquid to penetrate to the fibers in the center of these clusters. This can be seen in the free swell and retention test as unaffected fibers inside the formed gel.



Picture 3. Different degree of gelling.

This phenomenon is most prominent in the carboxylation but the tendency is also true for the sulfonation. A reason for this might be that the carboxylation reaction is carried out to a higher degree and more hydroxyl groups are substituted by the reactant compared to the sulfonation reaction. This is reasonable also when taking into consideration that with an increase of the reactant concentration in the carboxylation reaction the more clustered the resulting fibers are and the fact that the absorption is higher for the clustered fibers compared to more dispersed fibers.

In the Free Swell and Retention test when the treated fibers are swelled and in some cases dissolved to some extent it is apparent that in a couple of the reactions the fibers have lost some of their physical properties that they had before the treatment. The length of the fibers is one property that is visualized when the fibers are situated to the test liquid. It is difficult to see how the length is affected when the fibers are dry. During the free swell and retention test it becomes obvious that some fibers have been shortened. This observation is more significant for samples that show average to high degree of absorption and retention.

4.3 Raman spectroscopy

According to literature the ability of modified cellulose fibers to absorb and retain fluid increase with an increase degree of substitution. In order to verify this trend and also validate that the desired reactions take place Raman spectroscopy was used to analyze some selected modified samples. Three samples from each modification, carboxylation

and sulfonation, were chosen. One sample from each modification with good absorption and retention abilities, one with poor absorption and retention and one sample that have properties between these two for each modification were investigated with the Raman spectroscopy. Also non treated cellulose was analyzed with Raman spectroscopy in order to have a reference to compare the modified samples with. A Bruker MultiRam spectrometer with a liquid-nitrogen cooled Ge diode as detector was used for the Raman experiments. A cw-Nd:YAG-laser (wavelength 1064 nm) was applied as excitation source. The spectra were recorded over the range of -100-3600 cm^{-1} , with a spectral resolution of 2 cm^{-1} , a laser power of 400 mW, and averaged over 500 scans. Analyzing the peaks of the resulting spectra estimation with eye measure is the main tool.

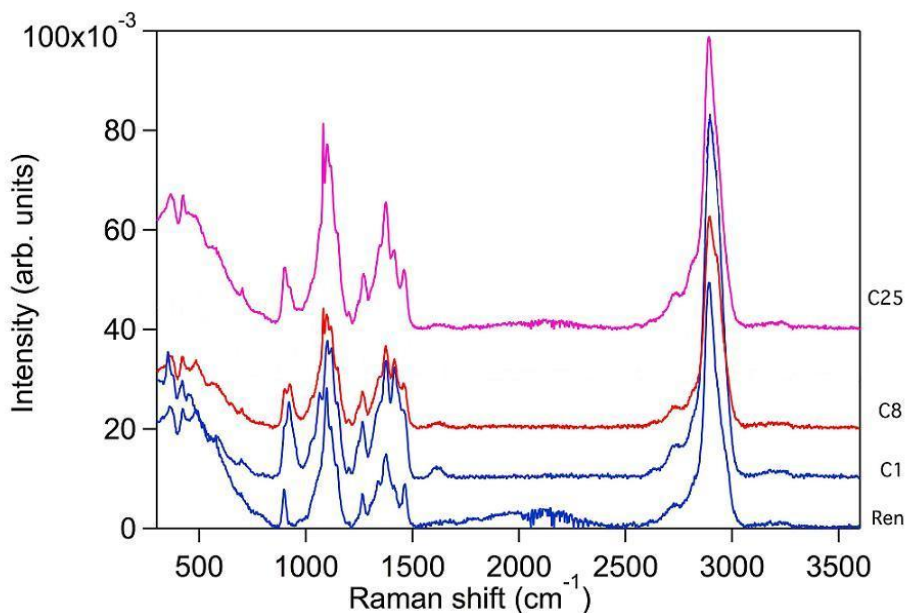


Figure 14. The entire spectra for the carboxylation.

In figure 14 the full spectra of the carboxylation is represented. The peak at 2900 cm^{-1} is derived to CH_2 vibrations. The intensity of the peaks does show a small increase due to the introduction of CH_2 . The peaks below 700 cm^{-1} is according to Yuen et al. due to vibrations from the backbone of the cellulose structure and is difficult to interpret. At about $3200\text{-}3300 \text{ cm}^{-1}$ there is beginning of a peak. This peak is due to OH vibrations but the machine used doesn't have enough energy at this area and therefore the peaks can be used for interpretation.

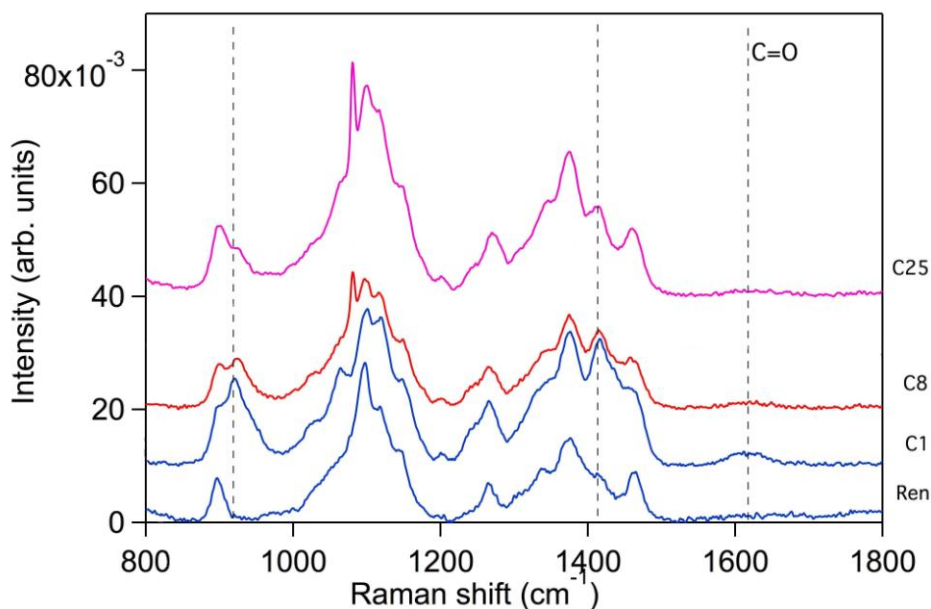


Figure 15. Zoomed in area of the Raman spectra for carboxylation.

In figure 15 the Raman spectra of the carboxylated samples are zoomed in on the interval $800 - 1800 \text{ cm}^{-1}$ in order to analyze the peaks better. The peak at approximately 1605 cm^{-1} is the peak corresponding to the vibrations from the C=O bond according to Yuen et al. [28] There is no C=O bonds present in the pure cellulose sample while all of the three modified sample indicate an introduction of the C=O bond. This indicates that the desired reaction is successful to some extent in all samples. The peaks at 900 cm^{-1} and 1400 cm^{-1} is also depending on the carboxymethyl groups they are not appropriate to use as indicators since they also depend on other vibrations such as C-H and C-O-H while the peak at 1605 cm^{-1} is only due to the substituted carboxymethyl groups. According to literature the peaks are broad due to that sodium chloroacetate was used as a reactant instead of the chloroacetic acid. However the C1 peak is determined to have the largest intensity, followed by C8 and last C25. Following the reasoning that the 1605 cm^{-1} peak is only due to the carboxymethyl groups leads to the conclusion that higher intensity corresponds to more carboxymethyl groups, i.e. higher degree of substitution. This ends up in the conclusion that C1 have the highest degree of substitution followed by C8 and C25 the lowest. This correspond with the free swell and retention values for the samples where C1 have best free swell and retention properties while C25 show the lowest values with C8 in between.

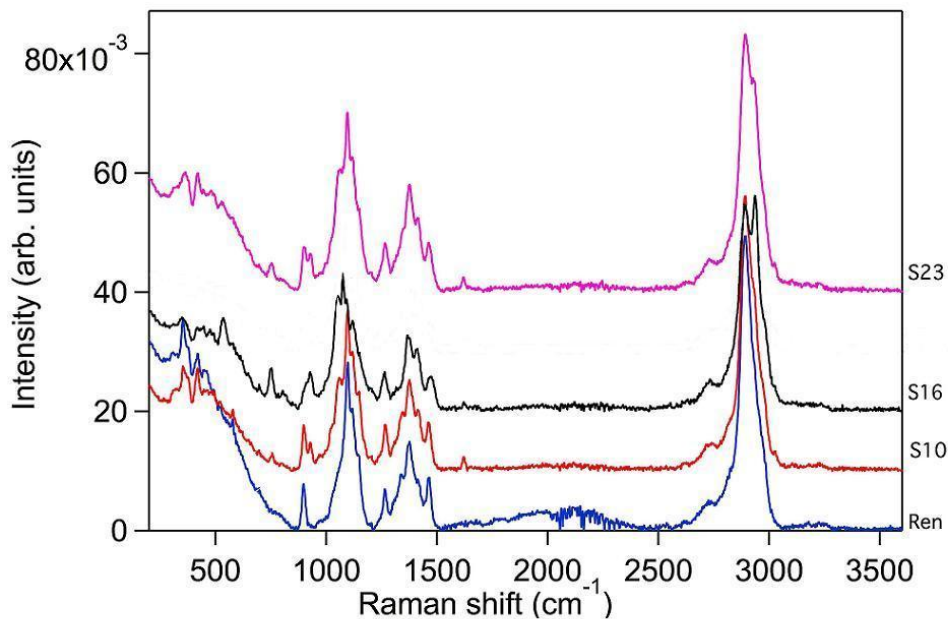


Figure 16. The entire spectra for the sulfonation samples.

In figure 16 the spectra from the sulfonation samples are represented. The peaks around 3000 cm^{-1} are due to the CH and CH_2 vibrations. For the pure cellulose sample there is only one peak at this area. For the sulfonated sample the peak will gradually split into a double peak. This new peak is due to the introduction of the CH groups from the sulfoalkyl according to Zhang et al. [29] The higher the intensity of these peaks, the more sulfoalkyl groups and higher degree of substitution. This implies that S16 is the sample with highest degree of substitution followed by S23 and last S10. To validate this first assumption the spectra was further analyzed in the region between 600 cm^{-1} and 1700 cm^{-1} .

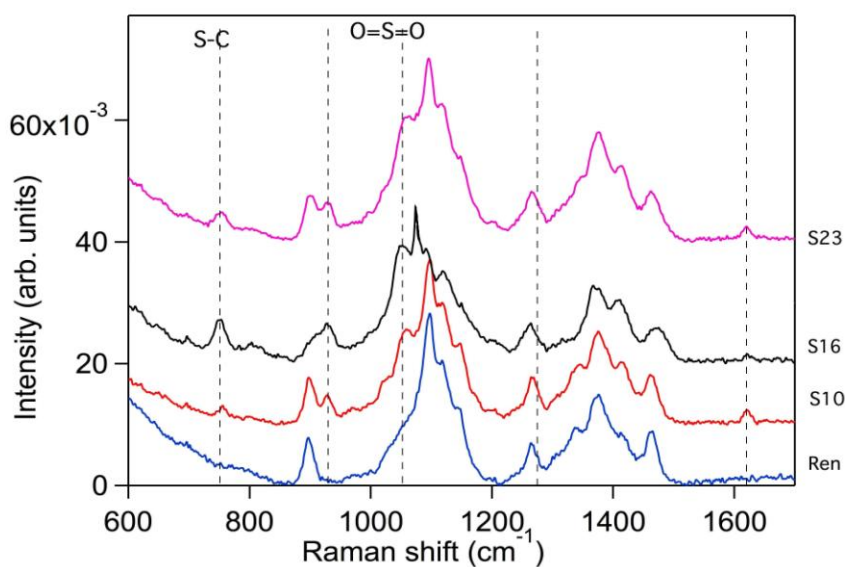


Figure 17. Enhancement of the region $600\text{-}1700\text{ cm}^{-1}$ for the sulfonation.

In figure 17 the sulfonation spectra have been enhanced in order to analyze the specific area better. Several peaks emerge for the sulfonated samples. At roughly 750 cm^{-1} a new peak appears, according to Zhang et al. this is due to stretching vibrations from S-C groups. At 1050 cm^{-1} a shoulder on the peaks appears which is due to the O=S=O vibrations in the sulfate groups and further indicates the introduction of the sulfoalkyl groups. The peak at 750 cm^{-1} is most reliable regarding quantification for the sulfonation. Based on this and the observation in the full spectra the conclusion is that the sample with highest degree of substitution is S16 followed by S23 and last S10.

From the Raman spectroscopy results an internal quantification between the analyzed samples can be derived. Combining the Raman results with the results from the Free Swell and Retention method implies that the higher degree of substitution of the modified cellulose the better absorption and retention properties. It is desirable to achieve a total quantification for the degree of substitution similar those in previous literature. However it turned out the Raman spectra for the analyzed samples differ slightly from those in literature. It is difficult finding a peak that remains constant for all samples which is needed as a reference. It should also be mentioned that it is only a small sample of the modified fibers that have been analyzed with the Raman spectroscopy and the results is based on that the reaction is homogenous throughout the fibers. This is however an unlikely scenario since the substitution of the hydroxyl group is random and the degree of substitution is an average value.

According to literature an absorption capability of 20-40 times its own weight is achieved when reaching a degree of substitution of 0,30 for the carboxylation. A degree of substitution of 0,5 and over would lead to fibers that are more water-soluble than water-swellaable [30]. Based on this data the conclusion is that the degree of substitution of the modified fibers is about of 0,5 for the most substituted sample. For the most gelling fibers it looks like some fiber are dissolved in the test liquid but most of the fibers form a clear gel and this indicates that the degree of substitution is near the critical value of 0,5.

Similar upper limits exist for the sulfonation process. The upper limit for water-swellaable fibers is 0,4 according to literature. [14] Since there is no problem with fibers being to water-soluble it can be assumed that the maximum degree of substitution of the modified fibers are less than 0,4. Given that the absorption and retention properties aren't as good as for the carboxylation it is more likely that the maximum degree of substitution is somewhat lower than this upper limit. An approximated value based on this data and observations is about 0,3 for the degree of substitution for the sulfonation.

5 Conclusion

In this study two modifications of cellulose fibers were analyzed in attempt to gain deeper knowledge of what challenges each modification holds, important reaction parameters, different methods used and the absorption and retention capacity.

It is clear that both carboxylation and sulfonation of cellulose fibers can be done in a rather straight forward modification. Both reactions can be controlled by some important parameters. The Williamson synthesis in the carboxylation is most affected by the concentration of the sodium monochloroacetate and the Michael addition of the sulfonation is almost equally affected by the concentration of sodium hydroxide and the reaction temperature.

Absorption and retention properties for the modified fibers were determined with the Free swell and Retention test and the results varied from fiber with low degree of gelling to fibers that totally lost their fiber structure and became hydrogels. The fibers with highest absorption capabilities were carboxylated fiber and they could absorb almost 40 g/g. The equivalent value for the sulfonation was almost 24 g/g. The retention is perhaps the most interesting property and for the most absorbed fibers carboxylated fibers the retention is 34 g/g and 15 g/g for sulfonated fibers.

Raman analysis was used to determine that the fibers that formed hydrogels were the fibers that had the highest degree of substitution. The Raman results are based on a comparison between the tested sample and from this it can be determined which sample that has the highest degree of substitution but it doesn't give quantification information. However based on some literature references a quite good approximation of the degree of substitution can be made. Comparing the properties of the formed gels with literature renders in an approximated value for the degree of substitution for carboxylation of about 0,5 for the most substituted and about 0,3 for the most substituted sulfonation.

The fact that the carboxylated fibers can absorb and retain more fluid compared to the sulfonated indicates that the nucleophilic substitution in the carboxylation is a more effective reaction than the addition reaction in the sulfonation since the absorption and retention capacity can be derived to the amount of functionalized hydroxyl groups of the cellulose.

6 Future work

During the work with modification of the cellulose fibers a variety of challenges have been encountered. Some of them have been successfully handled, however there are still a couple of factors that can be subjects for future investigations and research.

One challenge is to be able to make the current reactions in such way that the fibers keep their physical properties to a higher extent. When the fibers become hard and clustered as in the cases for the most carboxylated reactions they lose their abilities for following treatments. This will make it difficult to use them in a future product such as non-wovens. It is suggested that it is during the washing and drying processed this problem can be affected the most. By for example tumble-drying the fibers should be dried more individually and more separated, this will give them less opportunity to dry together into hard clusters. By washing the fibers in acetone or ethanol with higher percentage might remove more water and hence reduce the cluster formation.

The sulfonation reaction might be improved by introduction of a catalyst. However this introduction will lead to a harsher environment and violent reactions. Examples of catalysts are transition metals as lead and copper and boron trifluoride etherate.

In the future it would be interesting to analyze how other molecules, containing similar acid groups as those used in this thesis, can be functionalized onto cellulose structure. For the wound care market molecules that are gentle against the skin and body are of extra interest.

Regarding the Raman analysis it could be more thoroughly investigated how to quantify the degree of substitution.

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Appendix A

Sample 1

9,17 g NaOH in 25 ml water.

9,9 g ClCH₂COONa in 25 ml water.

The two solutions were mixed with 126 ml ethanol (IMS) to give a solution containing 5,4% NaOH and 5,9% ClCH₂COONa. The solution was pored over 3,127 g Tencel fibers in an e-flask. It reacted for 3 hours at 60 °C with reflux and magnetic stirrer. The fibers were washed after reaction in a solution of 56% ethanol, 43% water, 0,7% acetic acid, 0,3% citric acid. The fibers were than air dried at room temperature.

Observations: The fibers were not totally covered with the reaction solution the whole time. The reacted fibers showed some, but quite poor gelling properties.

Sample 2

8,85 g NaOH in 25 ml water.

24,98 g ClCH₂COONa in 65 ml water.

The two solutions were mixed with 64 ml ethanol and gave a solution with 5,1 % NaOH and 14,3% ClCH₂COONa. 2,42 g Tencel fibers were reacted for 3 hours at 60 °C with magnetic stirrer and reflux.

Observations: The fibers were wetted throughout the whole reaction, compared to sample 1. By a simple test where some water only was dripped on the fibers these fibers seems to have better gelling properties than fibers in sample 1.

Sample 3

8,44 g NaOH in 25 ml water.

22,11 g ClCH₂COONa in 75 ml water.

The two solutions were mixed and formed one solution with 6,5% NaOH and 17,0% ClCH₂COONa. 2,0 g of Tencel fibers were then padded with the mixed solution for 2 minutes. The excess of the solution were then squeezed out of the fibers using a press driven by compressed air. The weight after press was 4,7g. Then the fibers were dried in oven at 180 °C for 4 minutes and then washed in 50% ethanol, 40% water and 10% acetic acid.

Observations: After drying the fibers became hard and turned golden brown in color. It was hard to separate the fibers and the sample almost turned into a cluster. However some fibers showed some gelling properties.

Sample 4

4,19 g NaOH in 12,5 ml water.

11,0 g ClCH₂COONa in 37,5 g water.

The two solutions were mixed into one solution containing 6,4% NaOH and 16,9% ClCH₂COONa. 2,1 g Tencel fibers were padded with the mixed solution for 2 minutes and then squeezed by manual force into a weight of 8,9 g. The fibers were dried in oven at 150 °C for 6 minutes followed by washing in 56% ethanol, 43% water, 0,7% acetic acid and 0,3% citric acid. After the washing step the fibers were dried in a fume cupboard, at room temperature.

Observations: The fibers became hard and difficult to separate. An attempt of mixing them with HMDS (Hexamethyldisilazane) and run in speed mixer was done in order to try to soften the fibers and make them more dispersed, without any results.

Sample 5

5,1 g NaOH in 9 ml water.

11,0 g ClCH₂COONa in 25 ml water.

The two solutions were mixed to create a solution consisting of 10,2% NaOH and 22,0% ClCH₂COONa and the solution was used to pad 2,0 g of Tencel fibers for 2 minutes. The fibers were dried at 100 °C in an oven for 10 minutes followed by washing in a solution of 56% ethanol, 43% water, 0,7% acetic acid, 0,3% citric acid. Then dried in oven again at 60 °C to a constant weight was achieved.

Observations: The fibers were still hard and stiff and difficult to separate, but with the lower temperature in the oven the fibers don't turn brownish in color. The fibers however show some gelling properties.

Sample 6

4,34 g NaOH in 51 ml water, gave a solution of 7,8% NaOH.

11,03 g ClCH₂COONa in 39 ml water, gave a solution of 22,0% ClCH₂COONa.

3,04 g Tencel fibers were padded with the NaOH solution for 2 minutes and then dried in oven at 170 °C for 3 minutes. Thereafter the fibers were padded with the ClCH₂COONa solution for another 2 minutes, followed by drying in oven at 170 °C for 4 minutes. The sample was washed in a solution of 50% ethanol, 40% water and 10% acetic acid and then dried at room temperature to constant weight.

Observations: The fibers showed some gelling properties but they were quite hard and difficult to separate.

Sample 7

4,29 g NaOH in 46 ml water, gave a solution of 8,5% NaOH.

33,15 g ClCH₂COONa in 117 ml water, gave a solution of 22,1% ClCH₂COONa.

1,94 g Tencel fibers were padded with the NaOH solution for 2 minutes. Excess solution was squeezed out and the sample was dried in oven at 170 °C for 8 minutes. Then the

fibers were added to the $\text{ClCH}_2\text{COONa}$ solution, holding a temperature of $80\text{ }^\circ\text{C}$, for 30 minutes. The sample was washed in the same washing solution as in sample 6.

Observations: The fibers became very hard and stiff. The gelling properties were quite poor compared to the other samples.

Sample 8

11,97 g NaOH in 40 ml water.

15,1 g $\text{ClCH}_2\text{COONa}$ in 50 ml water.

The two solutions was mixed into one solution with 10,2% NaOH and 12,9% $\text{ClCH}_2\text{COONa}$. 1,99 g Tencel fibers was added to the solution and a more rigorous stirring equipment was mounted to the reaction beaker and the beaker was sealed but no reflux was used. The reaction temperature was $70\text{ }^\circ\text{C}$ and the reaction was allowed to run for 2 hours. The washing was carried out in 70 % ethanol with 1% acetic acid and the sample was dried at room temperature.

Observations: The fibers were winded up on the stirrer and were not completely wetted the entire time. The fibers were rather soft while they still were a bit wet after drying but when they were let dry to a constant weight they became hard and stiff. However the gelling properties were rather good.

Sample 9

4,23 g NaOH in 16 ml water.

10,98 g $\text{ClCH}_2\text{COONa}$ in 30 ml water.

The two solutions were mixed into one containing 6,9% NaOH and 17,9% $\text{ClCH}_2\text{COONa}$ and 3,05 g Tencel fibers were padded with the solution. Then the fibers were dried in oven at $180\text{ }^\circ\text{C}$ for 4 min. Washed in 70% ethanol with 10% acetic acid and dried to constant weight in room temperature.

Observations: Quite bad gelling properties and hard and stiff fibers.

Sample 10

14,98 g NaOH in 40 ml water.

25,0 g $\text{ClCH}_2\text{COONa}$ in 60 ml water

The two solution were mixed together with 64 ml (50g) isopropanol to create a solution containing 7,9% NaOH and 13,2% $\text{ClCH}_2\text{COONa}$. 1,98 g of Tencel fibers were added to the solution and it was reacted at $70\text{ }^\circ\text{C}$ for 2 hours with vigorous stirring and without reflux. Washing was done in 70% ethanol with 1-2% acetic acid and the sample was dried to constant weight at room temperature.

Observations: After the reaction the fibers were almost dissolved in the reaction solution and it was very difficult to get them out of the solution due to this. When washed in ethanol with acetic acid the fibers become less dissolved and more fiber like again. The

fibers showed good gelling properties but there were still problem with the fibers being hard and stiff.

Sample 11

9,97 g NaOH in 30 ml water.

15,0 g ClCH₂COONa in 40 ml water.

The two solutions were mixed together with 102 ml (80 g) isopropanol into one solution containing 5,7% NaOH and 8,6% ClCH₂COONa. The solution was poured over 2,95 g Tencel fibers and was reacted with stirring at 70 °C for 1 hour.

Observations: The fibers were wetted throughout the whole time. The fibers became almost gel like during the reaction and the excess reaction solution was hard to squeeze out of the fibers. After washing, in the same washing liquid as in previous sample, and drying the fibers were quite hard but show rather good gelling properties.

Sample 12

15,04 g NaOH in 40 ml water.

25,0 g ClCH₂COONa in 60 ml water.

50 g = 64 ml isopropanol.

The two solutions were mixed into one solution containing 7,9% NaOH and 13,1% ClCH₂COONa. 2,04 g Tencel fibers were reacted with stirring in the prepared solution for 3 hours at 70 °C. The fibers were washed in similar washing fluid as the previous samples and dried at room temperature.

Observations: The fibers showed great gelling properties while they still were a little damp and when dried to constant weight they still had very good gelling properties. However the problem with the fibers being hard and stiff when dry still remains.

Sample 13

7,95 g NaOH in 10 ml water (44% NaOH).

13 ml CH₂CHSO₃Na as 25% aqueous solution.

The NaOH solution and the CH₂CHSO₃Na solution were poured over 2,86 g fibers. The quite small amount of solution wasn't enough to wet all the fibers. The fibers were heated on a heating plate at 83 °C for 70 minutes. After washing in 70% ethanol with 1-2% acetic acid followed by just ethanol the fibers were dried in oven at 60 °C.

Observations: The fibers turned a bit yellow in color. They showed some gelling properties but not very much. The problem with the fibers turning hard and stiff after the reaction seems less than for the carboxylated fibers. The fibers were however not as dispersed as before the reaction.

Sample 14

4,95 g NaOH in 15 ml water.
10,05 g ClCH₂COONa in 30 ml water.
50 g = 64 ml isopropanol.

Mixing into one solution gave a solution containing 4,5% NaOH and 9,1% ClCH₂COONa. 2,05 g Tencel fibers were reacted during stirring at 70 °C for 2 hours. Then they were washed and dried.

Observations: The fibers became significantly dissolved and it was difficult to get all of them out of the reaction beaker. After washing the fibers and when they were still wet it felt like they had swelled and when they were dry they were quite hard and were difficult to distinguish individual fibers.

Sample 15

15,07 g NaOH in 20 ml water (43% NaOH).
22 ml 25% CH₂CHSO₃Na solution.

The NaOH solution was cooled to room temperature (22 °C). 2,41 g fibers were added to the solution. The fibers were just about wetted with the solution. The fibers were left in the solution for swelling for 30 minutes. After 30 minutes the NaOH solution that could be squeezed out of the fibers was removed. The sodium vinyl sulfonate solution was poured over the swelled fibers and the beaker with the fibers and the solution was put on a heating plate holding 83 °C. The fibers were reacted for 2 hours and a lid of parafilm was used to prevent the fibers to dry out. The fibers were washed in the ethanol/acetic acid mixture and then ethanol. The drying was carried out in oven at 60 °C for 20 minutes then in room temperature until constant weight.

Observations: The fibers turned bright yellow. They showed rather decent gelling properties and are relatively soft and separated. The temperature became higher at some local spots compared to the rest of the sample which results in that the fibers tend to dry out at these spots and the fibers risk to get hard and burned.

Sample 16

15,07 g NaOH in 20 ml water (43% NaOH).
4,89 g ClCH₂COONa in 25 ml water (16,4% ClCH₂COONa)

2,43 g Tencel fibers were added to NaOH solution at room temperature and swelled for 30 minutes. Excess liquid were squeezed out. The fibers were put in an e-flask and the ClCH₂COONa solution was poured over them. The fibers were heated at 83 °C for 2 hours on a heating plate. The reaction solution was then squeezed out and the fibers were washed in 70 % ethanol with 1% acetic acid and the only ethanol. They were dried in oven at 60 °C for 10 minutes and then at room temperature until constant weight.

Observations: The temperature of the reaction solution went up to 95 °C before it went down again and stabilized on the wanted temperature. The fibers showed some gelling properties and were soft when still wet but became harder during drying.

Sample 17

15,12 g NaOH in 20 ml water (43 % NaOH)
25 ml 25% CH₂CHSO₃Na solution

2,58 g fibers were put in the NaOH solution holding 22 °C for 25 minutes. The excess NaOH solution was then squeezed out by hand. The CH₂CHSO₃Na solution were then poured over the swelled fibers and put on a heating plate holding 91 °C. Parafilm were used as a lid and the fibers were reacted for 90 minutes. The fibers were washed in 70 ethanol with 1 % acetic acid and then in only ethanol and dried in oven at 60 °C for 5 minutes and then at room temperature until constant weight.

Observations: The temperature went up to 96 °C before is adjusted to the correct temperature. The fibers became rather soft and showed quite good gelling properties.

Sample 18

14,98 g NaOH in 20 ml water (43% NaOH)
4,90 g ClCH₂COONa in 25 ml water (16,4% ClCH₂COONa)

2,50 g Tencel fibers were put in the NaOH solution holding a temperature of 25 °C for 25 minutes. The excess of the solution was squeezed out of the sample. The fibers were then put in the ClCH₂COONa solution and heated to 91 °C on a heating plate. The fibers were reacted for 90 minutes. Then the fibers were washed in 70 % ethanol with 1% acetic acid followed by washing in only ethanol. The fibers were dried at room temperature.

Observations: The temperature went up to 99 °C before it leveled off to the desired reaction temperature. The fibers were harder compared to the sulfonation process and showed some gelling properties when wet but almost none when dry.

Sample 19

15,08 g NaOH in 23 ml water (39,6% NaOH)
25 ml 25% CH₂CHSO₃Na solution

2,53 g Tencel fibers were swelled in the NaOH holding 20 °C for 30 minutes. The excess was squeezed out and CH₂CHSO₃Na solution was added. The fibers were heated up to 82 °C on a heating plate and reacted for 3 hours. The washing procedure was the same as in the previous sample. Drying was first in oven at 60 °C until a weight of 5,9 g and then dried at room temperature.

Observations: The temperature rose to 98 °C before it leveled off. The fibers became quite soft but show bad gelling properties.

Sample 20

15,03 g NaOH in 20 ml water (43% NaOH)

8,02 g ClCH₂COONa in 25 ml water (24,3% ClCH₂COONa)

2,58 g Tencel fibers were swelled in the NaOH solution holding 25 °C for 30 minutes. Excess solution was squeezed out of the fibers and they were then put in the ClCH₂COONa solution. Reacted on a heating plate at 92 °C for 2,5 hours. The excess reaction solution was squeezed out and the fibers were washed as previously stated. Drying in oven at 60 °C for 3 minutes and then in room temperature.

Observations: The fibers became more dissolved then previous with similar reaction conditions. The temperature rose to 104 °C before leveling off. Good gelling properties when fibers were wet but lost these properties when dried.

Sample 21

15,05 g NaOH in 20 ml water (43% NaOH)

25 ml 25% CH₂CHSO₃Na solution

2,58 g Tencel fibers in NaOH solution, 22 °C, for 30 minutes. Excess solution was squeezed out and the CH₂CHSO₃Na solution was poured over the fibers. The fibers were reacted on a heating plate, 91 °C, for 2 hours. Excess was squeezed out and the previous washing procedure was used. Dried at room temperature.

Observations: Quite soft and separated fibers with rather bad gelling properties. Temperature rose to 100 °C before it leveled off.

Sample 22

15,05g NaOH in 20 water (43% NaOH)

25 ml 25% CH₂CHSO₃Na solution

2,50 g Tencel fibers were put in the NaOH solution, 20 °C, for 30 minutes. Excess solution was squeezed out and the CH₂CHSO₃Na solution was added to the fibers. The fibers and the CH₂CHSO₃Na solution were heated on a heating plate to 91 °C. Parafilm was used as a lid to prevent the solution from evaporating.

Observations: The temperature rose to 100 °C before it leveled off. The parafilm was not properly mounted so the reaction solution was evaporated which lead to dry fibers that were burnt.

Sample 23

14,92 g NaOH in 20 ml water (43% NaOH)

25 ml 25% ClCH₂COONa solution

The NaOH solution holding a temperature of 24 °C was poured over 2,51 g Tencel fibers on an glass plate. The fibers were then allowed to swell for 30 minutes and then the excess was squeezed out. The fibers were put in a beaker and the CH₂CHSO₃Na solution

was poured over them. The beaker was placed on a heating plate, 91 °C, with a parafilm lid. The fibers were reacted for 1,5 hours. During the reaction there was some shock boiling and some of the fibers were burnt to the bottom of the beaker. After the reaction the fibers were washed with the previous washing procedure and dried in room temperature.

Observations: The fibers that were not burnt to the beaker were quite soft after washing and drying and the gelling properties were good.

Sample 24

14,95 g NaOH in 40 ml water (10,7% NaOH)

25,01 g ClCH₂COONa in 60 ml water (17,9% ClCH₂COONa)

80g = 102 ml isopropanol

The NaOH and ClCH₂COONa solutions were mixed with the isopropanol and gave a reaction mixture with 6,7% NaOH and 11,4% ClCH₂COONa. To the reaction mixture 2,71 g of Tencel fibers were added and the reaction was carried out for 2 hours at 70 °C. The same washing liquid as previous was used and the fibers were dried at room temperature.

Observations: The fibers became very hard and were hard to separate. However when water was poured on them they gelled.

Sample 25

8,07 g NaOH in 25 ml water (24% NaOH)

10,05 g ClCH₂COONa in 50 ml water (17% ClCH₂COONa)

Another 45 ml water was added to the solutions creating a reaction solution containing 5,8 % NaOH and 7,3 % ClCH₂COONa. This solution was poured over 2,59 g of Tencel fibers and was reacted for 2,5 hours at 65 °C. Washing procedure was the same as previously and the fibers were dried at room temperature.

Observations: The fibers became soft and separated. The gelling properties however were bad.

Sample 26

6,97 g NaOH in 10 ml water (41% NaOH)

25 ml 25% ClCH₂COONa solution

The NaOH and ClCH₂COONa solutions were mixed and poured over 3,01 g Tencel fibers in a beaker. The fibers were reacted for 75 minutes at 82 °C on a heating plate. Parafilm was used as a lid to prevent the mixture from evaporate. Washing was done as previously and the fibers were first dried in oven at 60 °C for 2 minutes and then in room temperature.

Observations: No gelling properties were shown and the fibers were poorly separated. The parafilm lid was not entirely sealed which led to some dry spots of the fibers that became hard and dry. The temperature was hard to control and went up to 106 °C before it leveled off.

Sample 27

7,05 g NaOH in 10 ml water (41% NaOH)
25 ml 25 % CH₂CHSO₃Na solution

The NaOH and CH₂CHSO₃Na solutions were mixed into one solution. 3,01 g Tencel fibers were put in a small e-flask and the mixed solution was poured over them. The e-flask with the fibers and the solution was lowered into an oil bath holding 83 °C. This was done in an attempt to create an even heat distribution and prevent the fibers from burning onto the beaker. The reaction was done for 70 minutes then the fibers were washed with mentioned washing procedure. Drying was done in oven at 60 °C for 2 minutes followed by room temperature.

Observations: The fibers were tested for gelling properties directly after the oven, and then the fibers showed good gelling properties. However when the fibers were allowed to dry further the gelling properties were reduced.

Sample 28

7,06 g NaOH in 10 ml water (41%)
25 ml 25 % CH₂CHSO₃Na solution

The two solutions were mixed into one and that solution was poured over 3,0 Tencel fibers in a small e-flask. The e-flask was lowered into an oil bath holding 93 °C for 80 minutes. The washing procedure was the same as previous and drying was first carried out in oven at 60 °C for 3 minutes and then in room temperature.

Observations: The fibers were tested for gelling directly after oven and then they showed quite good gelling properties. The gelling properties became worse when the fibers were dried further.

Sample 29

14,96 g NaOH in 20 ml water (43 % NaOH)
22 ml 25 % CH₂CHSO₃Na solution

The NaOH solution holding a temperature of 22 °C was poured over 2,46 g Tencel fiber and they were left to swell for 30 minutes. Excess solution was squeezed out by hand. Next the CH₂CHSO₃Na solution was added and the fibers were reacted in an oil bath, 83 °C, for 2 hours. Same washing and drying procedure as previous sample was used.

Observations: Same tendency as previous sample where the gelling properties were good for moist fibers but became worse when dried. However this sample showed better gelling properties in general.

Sample 30

14,95 g NaOH in 30 ml water (33 % NaOH)

38,5 g ClCH₂COONa in 70 ml water (35% ClCH₂COONa)

40 g = 51 ml isopropanol

The two solutions were mixed together with the isopropanol into one reaction solution containing 7,7% NaOH and 20% ClCH₂COONa. 2,47 g Tencel fibers were added to the solution and were reacted for 3 hours at 70 °C. The fibers were then washed with the same procedure as previously and dried at room temperature.

Observations: The fibers became almost totally dissolved and it was difficult to retrieve all fibers from the reaction solution. The fibers almost became like a gel during the reaction and washing steps. After drying the fiber structure was gone and there were only a lump left. The lump didn't show any gelling properties and didn't absorb any water.

Appendix B

In Appendix B all the results from the Modde program regarding the carboxylation is represented.

Table 1 represents how the model is chosen and designed for the carboxylation investigation.

Maximum Runs	2048
Objective	RSM
Process Model	Quadratic
Mixture Model	--
Design	CCF
Runs in Design	24
Center points	3
Replicates	0
N = Actual Runs	27

Table 1. Selected model and design.

In table 2, the parameters and settings for the carboxylation are represented. Based on table 2, a worksheet is created to test and evaluate the parameters. The values for the settings are derived from the screening test. Konc carb is the concentration of monochloroacetate and konc NaOH the concentration of sodium hydroxide.

Name	Abbr.	Units	Type	Use	Settings	Transform	Prec.	MLR Scale	PLS Scale
Konc carb	Kon	Weight%	Quantitative	Controlled	5 to 15	None	Free	Orthogonal	Unit Variance
Konc NaOH	Ko2	Weight%	Quantitative	Controlled	6 to 10	None	Free	Orthogonal	Unit Variance
Time	Tim	h	Quantitative	Controlled	1 to 5	None	Free	Orthogonal	Unit Variance
Temp	Temp	C	Quantitative	Controlled	50 to 90	None	Free	Orthogonal	Unit Variance

Table 2. Parameters and settings for the carboxylation.

In table 3 the worksheet for carboxylation is represented. The values for the free swell and retention are determined by the Free Swell and Retention method. Free swell is the value for the absorption of the fibers. The run order is determined by the Modde program. The values for experiment number 2 have been removed from the model in order to get a better response. The values for the free swell and retention are average numbers and there are quite large differences between the three measuring points for each reaction.

Exp No	Exp Name	Run Order	Incl/Excl	Konc carb	Konc NaOH	Time	Temp	Free swell	Retention
6	N6	1	Incl	15	6	5	50	39,4133	34,22
19	N19	2	Incl	10	6	3	70	31,5	21,5067
21	N21	3	Incl	10	8	1	70	25,1133	15,62

4	N4	4	Incl	15	10	1	50	31,1333	22,2067
27	N27	5	Incl	10	8	3	70	25,1	16,1133
3	N3	6	Incl	5	10	1	50	15,3067	8,42
25	N25	7	Incl	10	8	3	70	27,4867	17,7333
24	N24	8	Incl	10	8	3	90	25,4	16,3867
15	N15	9	Incl	5	10	5	90	17,82	7,73333
9	N9	10	Incl	5	6	1	90	20,34	10,2133
5	N5	11	Incl	5	6	5	50	20,6133	11,0067
14	N14	12	Incl	15	6	5	90	34,76	31,7333
17	N17	13	Incl	5	8	3	70	18,86	10,12
12	N12	14	Incl	15	10	1	90	34,8733	32,2467
26	N26	15	Incl	10	8	3	70	28,4467	18,2533
23	N23	16	Incl	10	8	3	50	19,86	12,0067
8	N8	17	Incl	15	10	5	50	36,78	31,9133
16	N16	18	Incl	15	10	5	90	36,1867	32,18
2	N2	19	Incl	15	6	1	50	17,1	10,0867
22	N22	20	Incl	10	8	5	70	25,72	16,2533
1	N1	21	Incl	5	6	1	50	17,34	8,34
20	N20	22	Incl	10	10	3	70	24,18	15,1733
18	N18	23	Incl	15	8	3	70	34,3	32,2533
13	N13	24	Incl	5	6	5	90	20,7267	11,6533
7	N7	25	Incl	5	10	5	50	18,7	10,76
10	N10	26	Incl	15	6	1	90	34,5267	32,0267
11	N11	27	Incl	5	10	1	90	21,0267	11,6867

Table 3. Worksheet for the carboxylation.

Figure 1 shows the spreading of the replicates. The spreading is a bit larger for the free swell than for retention. The replicates are the experiment number 25-27 and are plotted on the same bar in the diagrams.

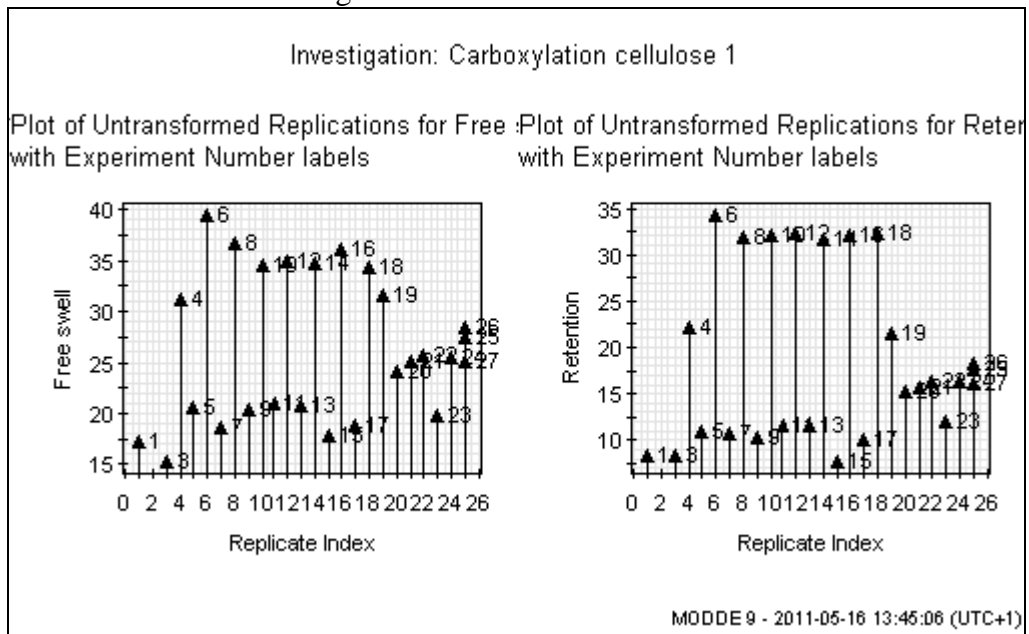


Figure 1. Spreading of the replicates.

Figure 2 show the response distribution for the model and are used to determine if any transformations is needed. The desired form of the distribution is a normal distribution, a so called bell shaped distribution and the more bell shaped the distribution is the better the model statistics is in general.

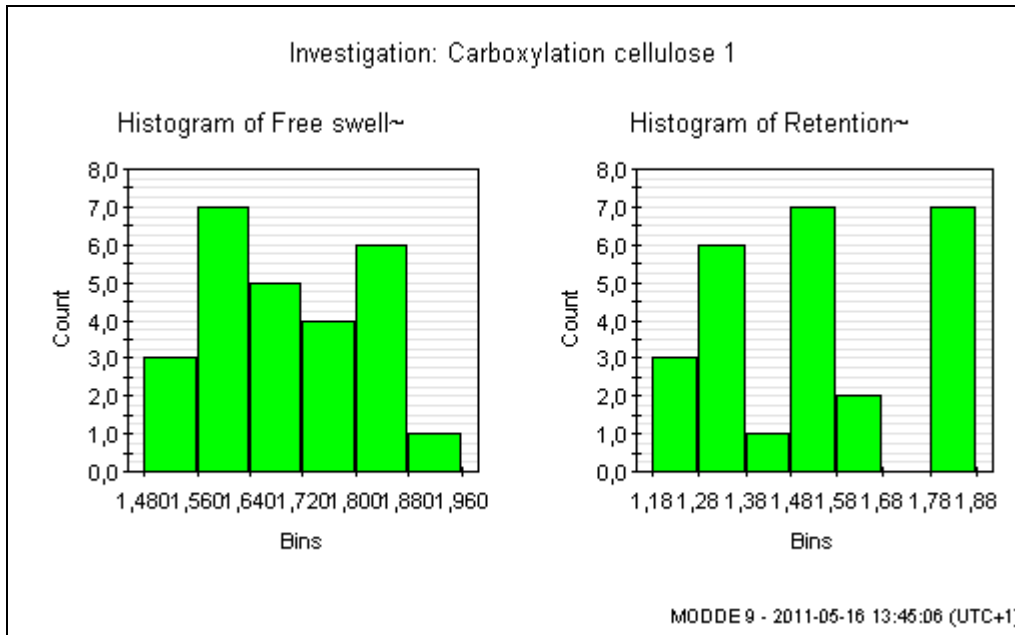


Figure 2. Response distribution.

The model statistics for the carboxylation is represented in figure 3. The meaning of the picture is further evaluated in the report under results and discussion. However it can be basically summarized by that the higher the value of the bars the better the model is where 1 is equal to 100% and a perfect model.

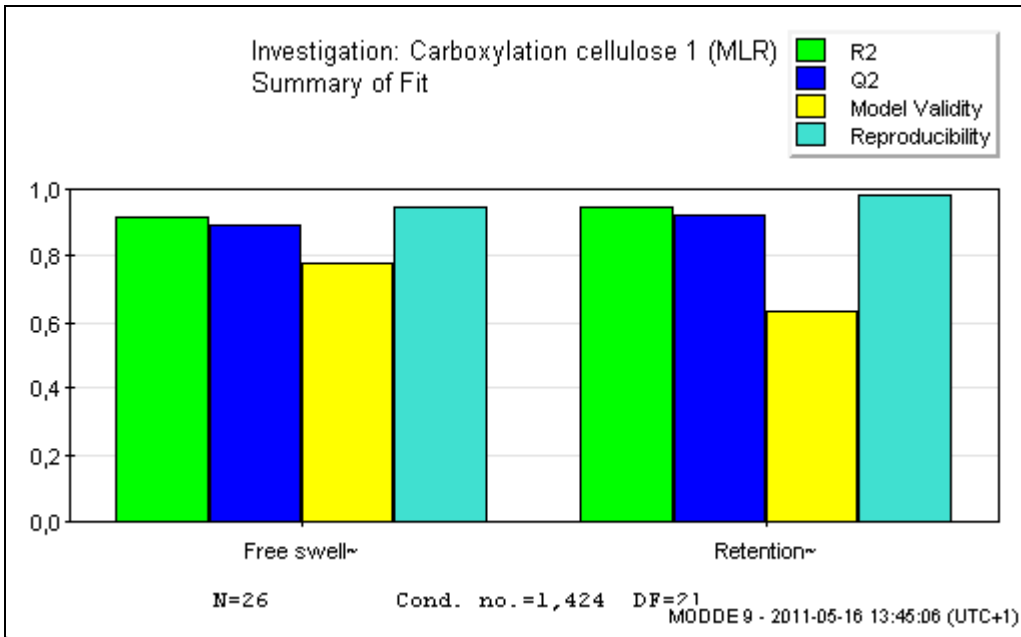


Figure 3. Model statistics.

Figure 4 gives information on which parameter that influence the reaction most and how much these parameters influence in relation to each others. The bar named “kon” is the concentration of monochloroacetate.

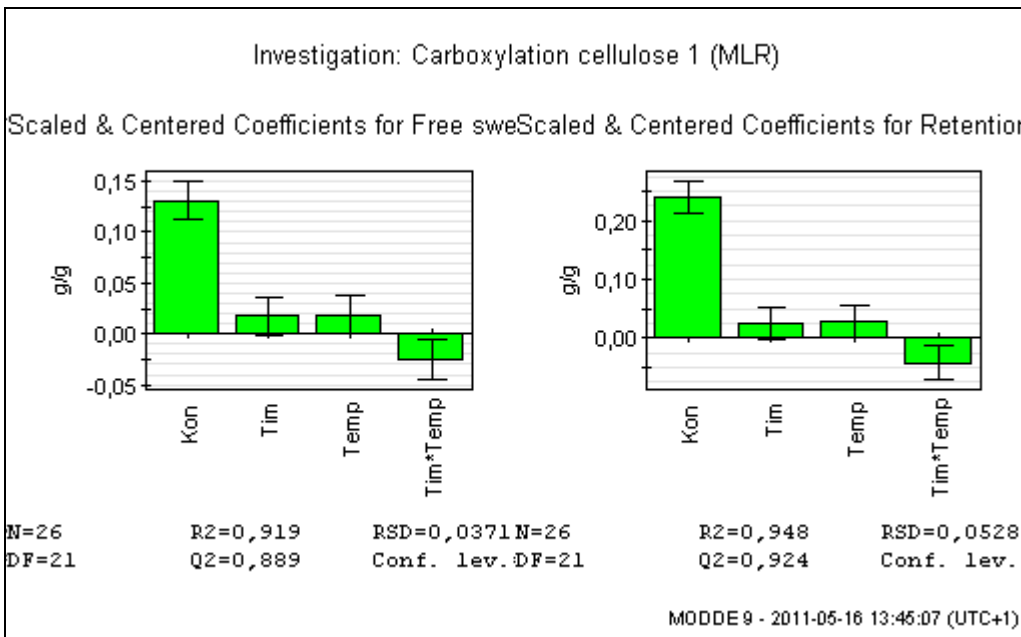


Figure 4. Important parameters for carboxylation.

If any points occur outside the red lines in figure 5 this is an indication for present outliers which should be investigated. The ideal plot is a straight line on the diagonal.

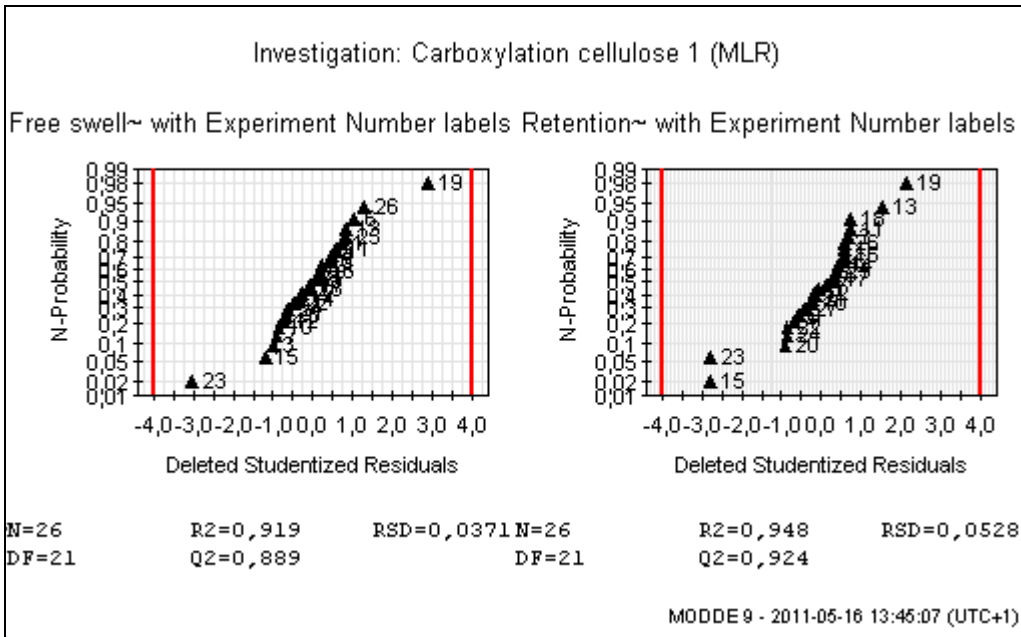


Figure 5. Normal probability plot of residuals.

In figure 6 the observed values are plotted against predicted ones. A good model will result in points that are on a straight line and with an angle of 45°.

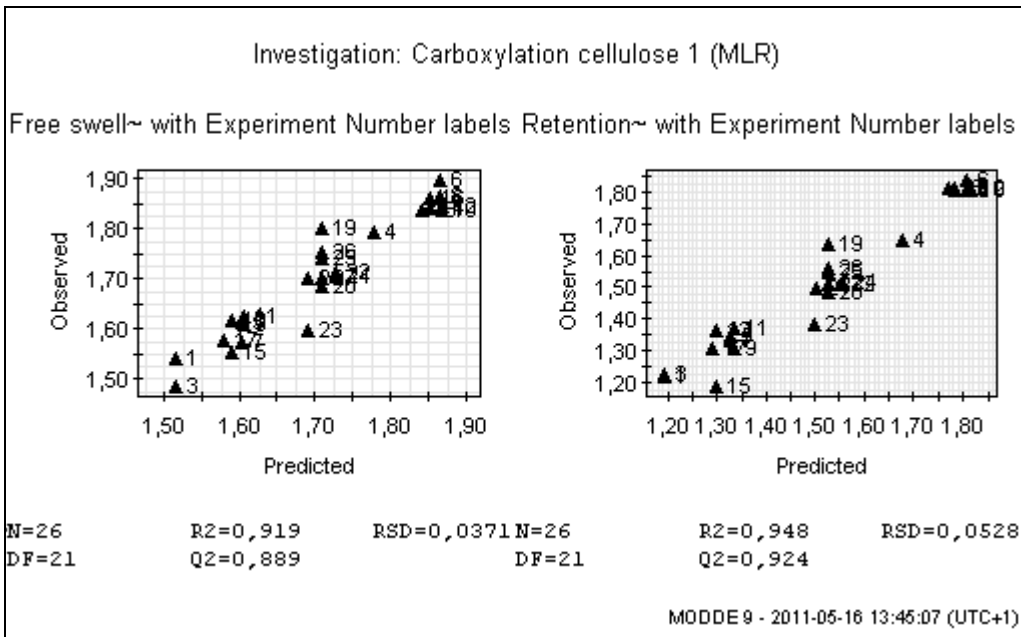


Figure 6. Plot over observed against predicted values.

Figure 7 and 8 are similar plots that show how the free swell and retention depends on different parameters.

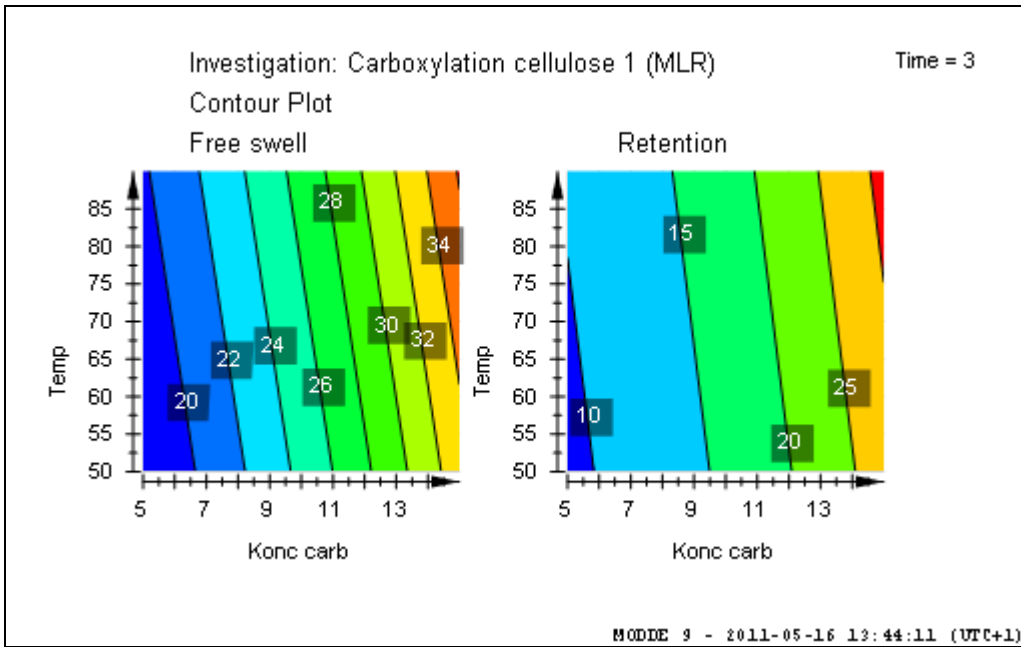


Figure 7. Temperature against concentration of monochloroacetate plot.

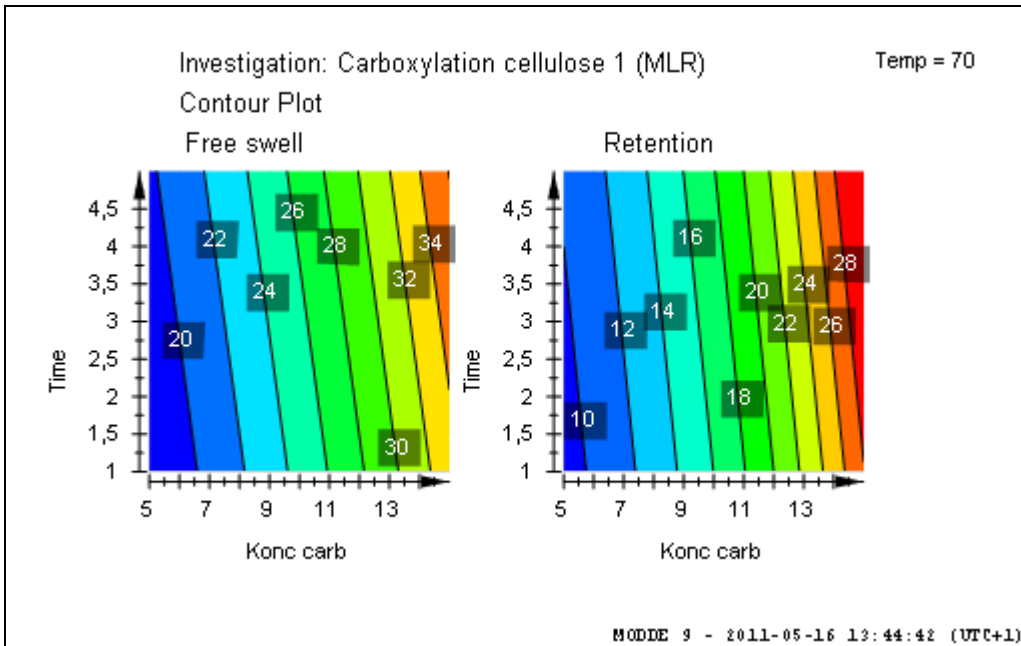


Figure 8. Time against concentration of monochloroacetate plot.

Appendix C

In Appendix C all the results from the Modde program for the sulfonation is represented.

Table 1 represents how the model is chosen and designed for the sulfonation investigation.

Maximum Runs	2048
Objective	RSM
Process Model	Quadratic
Mixture Model	--
Design	CCF
Runs in Design	24
Center points	3
Replicates	0
N = Actual Runs	27

Table 1. Selected model and design.

Table 2 includes the parameters and settings for the sulfonation reaction. The worksheet in table 3 is based on these parameters and settings. The settings are the results from the screening test.

Name	Abbr.	Units	Type	Use	Settings	Transform	Prec.	MLR Scale	PLS Scale
Sulf	Sul	ml	Quantitative	Controlled	20 to 30	None	Free	Orthogonal	Unit Variance
Konc NaOH	Kon	Weight%	Quantitative	Controlled	30 to 50	None	Free	Orthogonal	Unit Variance
Time	Tim	h	Quantitative	Controlled	1 to 3	None	Free	Orthogonal	Unit Variance
Temp	Temp	C	Quantitative	Controlled	60 to 100	None	Free	Orthogonal	Unit Variance

Table 2. Parameters and settings for the sulfonation.

In table 3 the worksheet for the sulfonation is represented. The run order is determined by the Modde program and is designed so that is minimum risk for errors. The free swell value for experiment number 25 has been removed to fit the model better. Free swell and retention value are average values from the Free Swell and Retention method.

Exp No	Exp Name	Run Order	Incl/Excl	Sulf	Konc NaOH	Time	Temp	Free swell	Retention
1	N6	1	Incl	20	30	1	60	16,1067	6,30667
4	N4	2	Incl	30	50	1	60	16,64	8,4
9	N15	3	Incl	20	30	1	100	17,5467	8,44667
13	N17	4	Incl	20	30	3	100	17,7067	10,8733
25	N7	5	Incl	25	40	2	80	14,9067	8,86667
16	N23	6	Incl	30	50	3	100	20,3733	11,5
8	N24	7	Incl	30	50	3	60	18,12	8,66
5	N27	8	Incl	20	30	3	60	14,78	7,22667
19	N2	9	Incl	25	30	2	80	16,48	7,08

6	N3	10	Incl	30	30	3	60	14,48	7,19333
24	N13	11	Incl	25	40	2	100	20,56	12,68
26	N10	12	Incl	25	40	2	80	18,1	9,84
21	N1	13	Incl	25	40	1	80	17,1533	9,52
22	N20	14	Incl	25	40	3	80	21,5133	11,86
10	N9	15	Incl	30	30	1	100	17,42	9,72667
11	N5	16	Incl	20	50	1	100	23,7333	14,5933
7	N25	17	Incl	20	50	3	60	17,8	9,97333
15	N26	18	Incl	20	50	3	100	22,3533	14
3	N21	19	Incl	20	50	1	60	15,2	6,94667
14	N12	20	Incl	30	30	3	100	18,1	10,98
12	N14	21	Incl	30	50	1	100	19,0067	11,1333
27	N11	22	Incl	25	40	2	80	19,44	10,31
18	N16	23	Incl	30	40	2	80	18,5333	8,46
2	N19	24	Incl	30	30	1	60	14,6333	6,94
17	N8	25	Incl	20	40	2	80	17,9933	8,82
23	N18	26	Incl	25	40	2	60	14,4133	6,83333
20	N22	27	Incl	25	50	2	80	20,4533	11,64

Table 3. Worksheet for the sulfonation.

In figure 1 the spreading of the replicates are demonstrated. For the free swell plot there are only two replicates and this is due to that one of the replicate values have been removed to fit the model better.

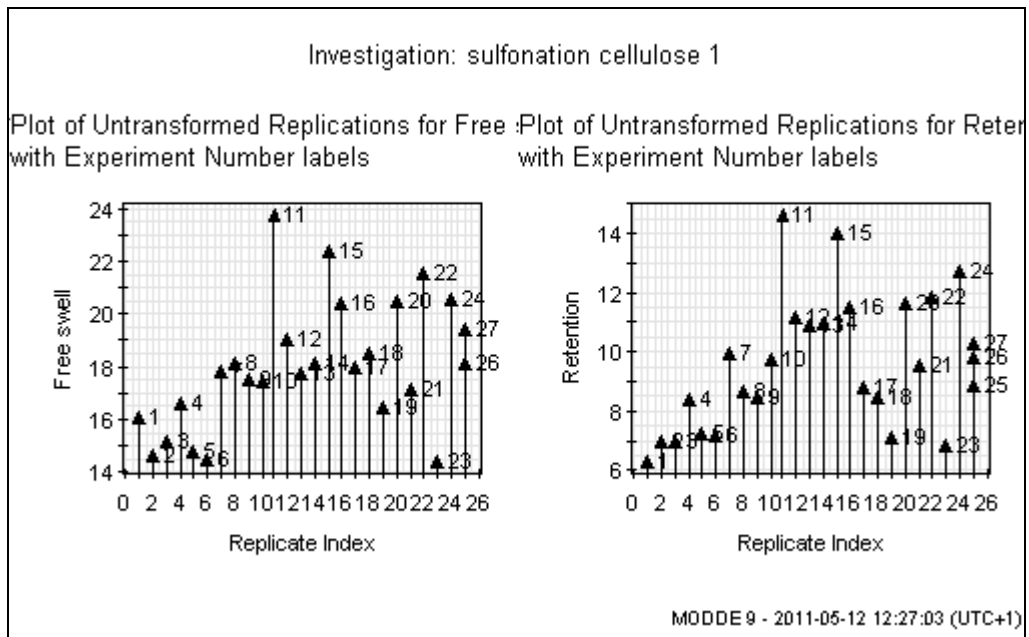


Figure 1. Spreading of the replicates.

The response distribution is represented in figure 2. The distribution should look like a normal distribution curve for the perfect model.

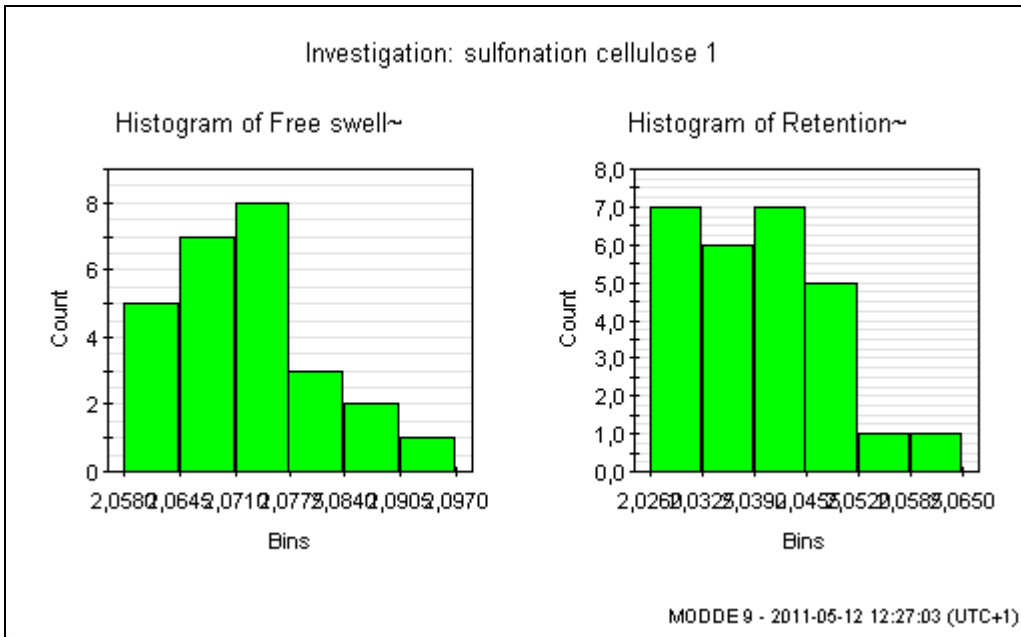


Figure 2. Response distribution.

From figure 3 an good estimation on how well the models work can be drawn. The four bars show four important parameters when evaluating the model. The closer the bars are to 1 the better the model is and 1 is a perfect model.

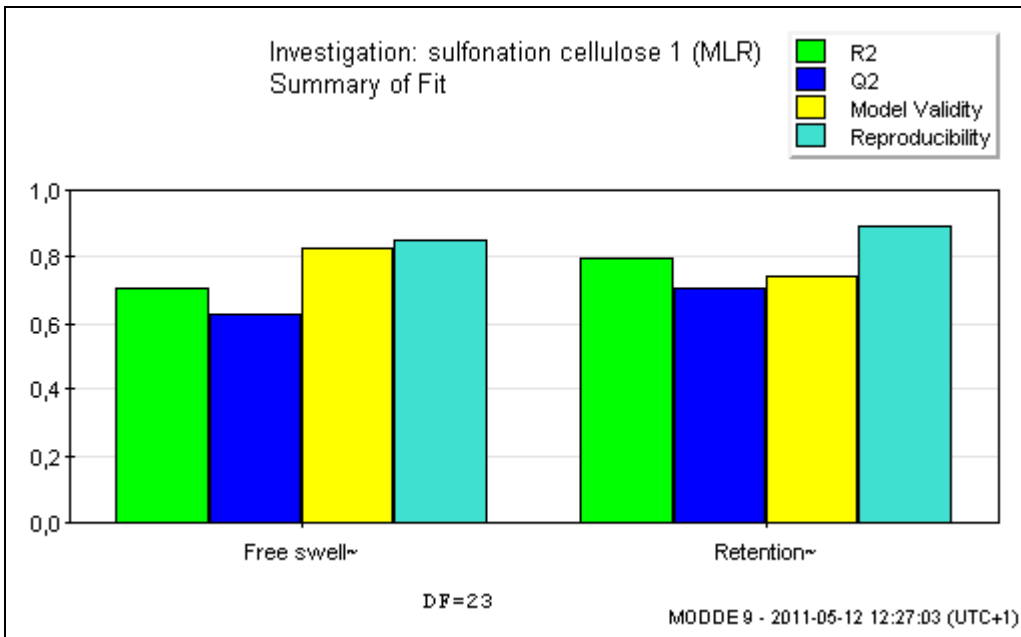


Figure 3. Model statistics.

From figure 4 the most important parameters for the sulfonation is derived. For the free swell concentration of sodium hydroxide and temperature is the most important while for retention time also show a small effect.

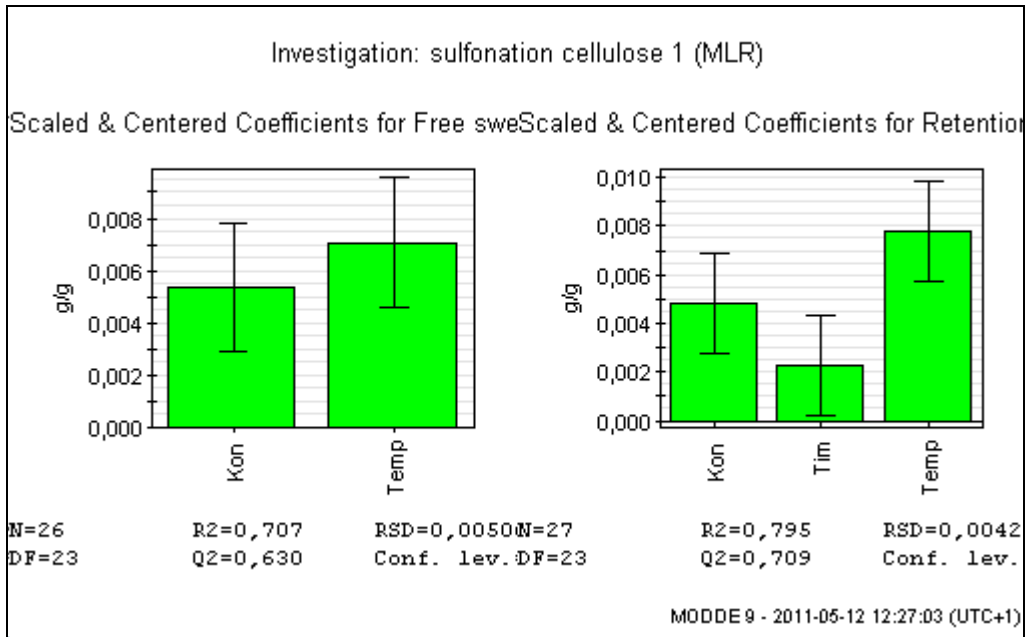


Figure 4. Important parameters for the sulfonation.

From figure 5 it can be seen if points are so called outliers. If there are outliers present they will be outside the red lines. The ideal plot is a straight line on the diagonal.

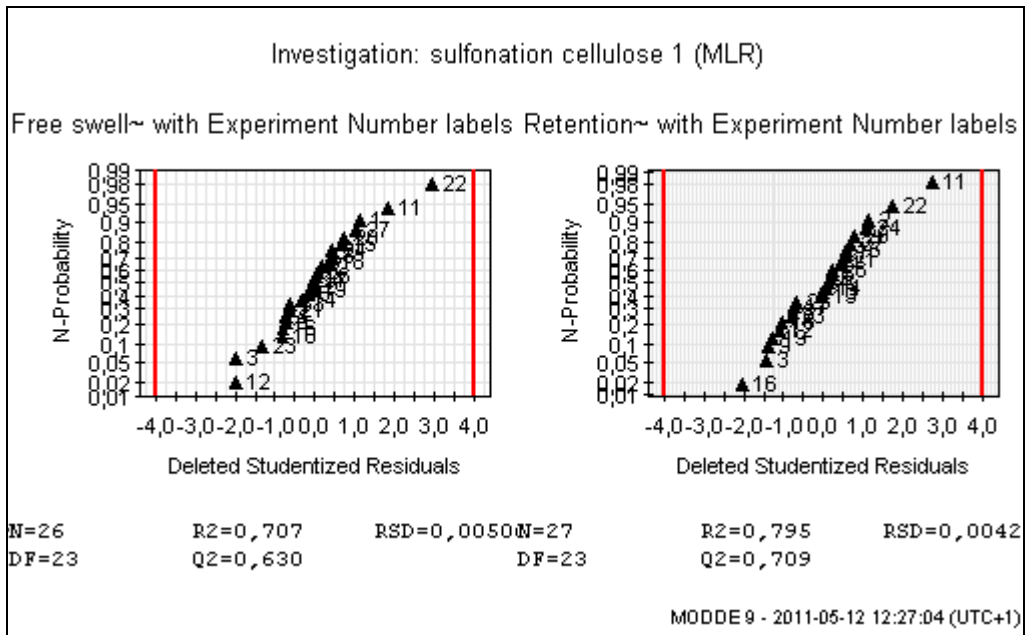


Figure 5. Normal probability plot of residuals.

In figure 6 observed values are plotted against predicted values. The better the model is the straighter the line made up by the points is.

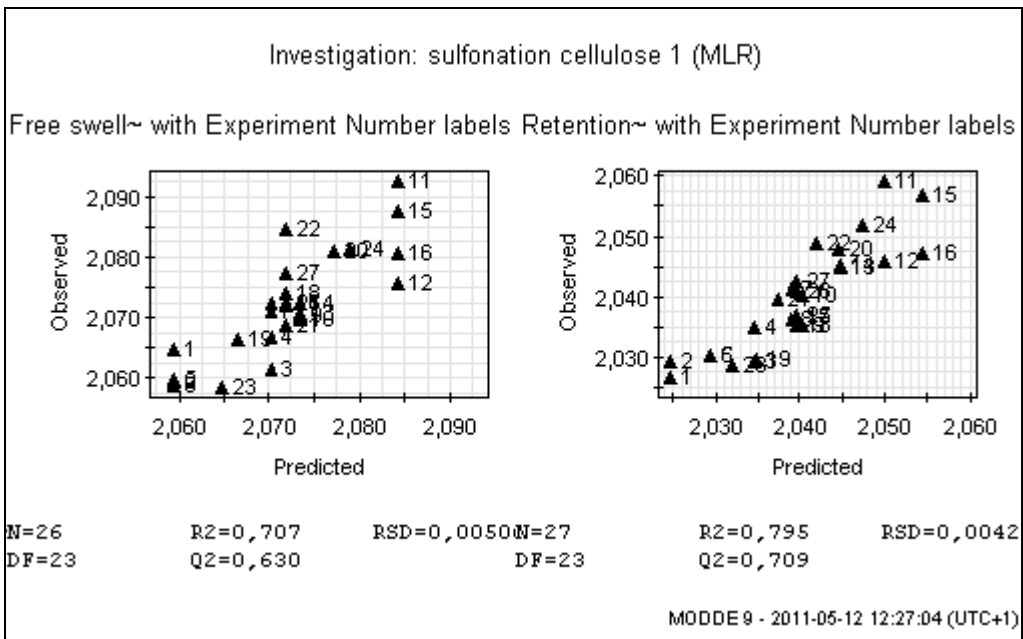


Figure 6. Observed against predicted values.

Figure 7 shows a plot for the concentration of sodium hydroxide against temperature. The acquired data from the free swell and retention method are source. From these plots predictions on future change in parameters can be estimated.

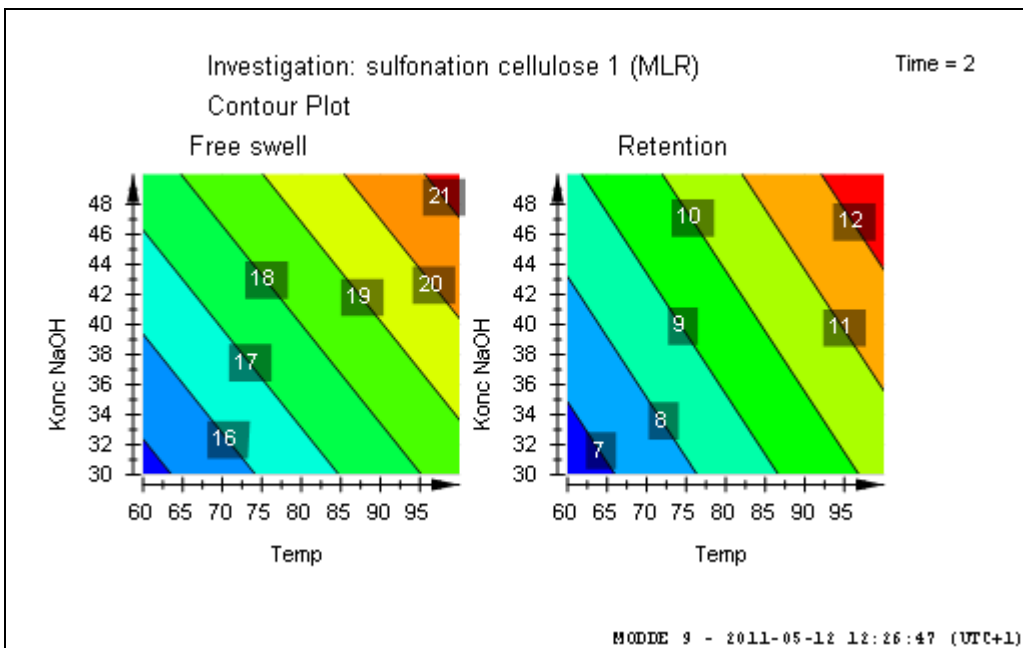


Figure 7. Concentration of sodium hydroxide against temperature plot.