Cross-linking and hydrophobization of chemically modified cellulose fibers

by

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Abstract

Owing to its unique structure, along with the inexhaustible renewability, cellulose has been a subject of scientific and commercial interest for over 150 years. However, given attractive structural properties, such as stiffness, hydrophilicity, stereoregularity, potential for chemical modifications and ability to form superstructures, utilization of this biopolymer is far below its potential. Over the past few years the number of research projects to modify cellulose fibers to make them more suitable for numerous applications has increased. Transforming hydrophilic cellulose fibers into hydrophobic, non-hygroscopic fibers could potentially lead to a variety of new products, such as flexible packaging, self-cleaning films and strength-enhancing agents in polymer composites. To achieve this, we choose two different routes to chemically modify the cellulose fibers.

In first method, cellulose fibers were oxidized with peridoate oxidation to different extent to prepare reactive dialdehyde cellulose (DAC) derivatives. Because introducing too many charge groups leads to fiber disintegration, we decided to cross-link the fibers to prevent this. These DAC fibers were in turn successfully cross-linked with 1,12-diaminododecane using methanol as solvent. Next, the cross-linked fibers were amidated in another Schiff-base reaction with n-butylamine to introduce the hydrophobic non-polar aliphatic chains. The cross-linked fibers exhibited stronger structural stability and the fibers did not disintegrate upon further alkylation with butylamine. The fibers were characterized with FTIR, ^{13}C-NMR, SEM, TGA, X-ray, contact angle and water sorption measurements. This procedure yielded very hydrophobic fibers with contact angles as high as 145^{o}. Moreover, they had very low moisture uptake and high thermal strength, which makes them suitable for many potential products specially to be used in composites.

The second method was based on intermediate carboxymethylation of cellulose with monochloroacetic acid, followed by subsequent substitution with an amine. The carboxylmethylated cellulose fibers (CCF) were cross-linked in an EDC assisted bioconjugation reaction with adipic acid anhydride (ADH). In order to alkylate the fibers and introduce aliphatic amine chains to the cross-linked fibers, a second carboxymethylation reaction was performed to introduce more charge groups to the cross-linked fibers to act as reactive sites for further alkylation reaction with butylamine. The resulting carboxymethylated cross-linked fibers were then reacted with n-butylamine to introduce non-polar aliphatic amine chains. The modified fibers were characterized by a variety of techniques, such as conductometric titration, infrared spectroscopy (FTIR), scanning electron microscopy (SEM), mechanical properties such as tensile strength and Young's modulus, water contact angle and water vapor transition rate (WVTR) measurements.

Abstrait

Grace à sa structure unique et son renouvellement quasi-inépuisable, la cellulose a été un sujet d'intérêt scientifique et commercial depuis plus de 150 ans. Toutefois, avec ses propriétés structurelles fascinantes, telles la rigidité, l'hydrophilie, la stéréorégularité, le potentiel de modifications chimiques et la capacité à former des superstructures, l'utilisation de ce biopolymère est bien en deçà de son potentiel. Au cours des dernières années, la recherche visant à modifier les fibres de cellulose pour les adapter à de nombreuses applications a augmenté. La transformation de fibres cellulosiques hydrophiles en fibres hydrophobes et non-hygroscopiques pourrait potentiellement mener à une variété de nouveaux produits, tels que des emballages flexibles, des films autonettoyants et des agents qui augmentent la résistance des composites polymériques. Pour atteindre ce but, nous avons choisi deux voies différentes pour modifier chimiquement les fibres de cellulose.

Dans la première méthode, les fibres de cellulose sont oxydées à divers degrés par du periodate pour obtenir un dérivé réactif, le dialdéhyde de cellulose (DAC). Parce que l'introduction de beaucoup de groupements chargés mène à la désintégration des fibres, nous avons décidé, pour éviter cela, de réticuler les fibres. Les fibres de DAC ont donc été réticulées avec succès avec du 1,12-diaminododécane en utilisant du méthanol comme solvant. Ensuite, ces fibres réticulées ont été transformées en amides par une autre réaction de base de Schiff avec du n-butylamine qui a pour effet de greffer des chaînes hydrophobes aliphatiques non polaires. Les fibres réticulées se sont avérées avoir une stabilité structurel accrue et ne se sont pas désintégrées lors d’une alkylation plus poussée avec du butylamine. Les fibres ont été caractérisées par FTIR, 13 C-RMN, MEB, TGA, diffractométrie par rayons X, mesures de l'angle de contact et de sorption d'eau. Cette procédure a donné des fibres très hydrophobes avec des angles de contact plus élevés que 145°. De plus, elles ont une absorption d'humidité très faible et une résistance thermique élevée, ce qui les rend potentiellement adaptables à des usages dans de nombreux produits et tout spécialement dans les produits composites.

La seconde méthode est basée sur la carboxyméthylation intermédiaire de la cellulose avec de l'acide chloroacétique, suivie d'une substitution ultérieure avec une amine. Les fibres de cellulose carboxyméthylées (CCF) ont été réticulées par une réaction de bioconjugaison classique utilisant l'EDC et l'anhydride d'acide adipique (ADH). Une seconde réaction de carboxyméthylation est alors effectuée sur les fibres réticulées pour y introduire plus de groupements chargés qui pourrons ensuite servir de sites réactifs pour une réaction d'alkylation. Cette réaction est accomplie avec du n-butylamine et a pour résultat la greffe de chaînes non polaires aliphatiques. Les fibres modifiées ont été caractérisées par une variété de techniques, telles le titrage conductimétrique, la spectroscopie infrarouge (FTIR), la microscopie électronique à balayage (MEB), les mesures de propriétés mécaniques telles la résistance à la traction et le module de Young, la mesure de l'angle de contact avec l'eau et la mesure du taux de transmission de la vapeur d'eau.

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Chapter 1. Introduction

Finding original and efficient methods to prepare highly hydrophobic and non-hygroscopic cellulose-based materials has stimulated a large number of studies, and the topic is still hot, because of their potential applications in such important areas as papermaking, textile and packaging. This is further motivated by the exploitation of an environmental friendly renewable resource, as opposed to fossil-based counterparts.

This thesis reports some interesting results on new hydrophobically modified cellulose derivatives prepared under different conditions.

The aim of this project is to study the preparation of non-hygroscopic and hydrophobic cellulose fibers by means of chemical reactions. In the present study our main objectives are to determine the least degradative method for substituting the cellulose with long chain hydrophobic aliphatic amino groups and a preliminary study of the effect of these modification on fibers properties and their interaction with water.

In the following literature review, we address different chemical modifications of cellulose fibers, as well as explain their effect on their characteristics, especially their hydrophobicity and moisture uptake. At first, the significance of each of these reactions in chemical modification of cellulose is described, followed by a review on more important or relevant examples of chemically modified cellulose. In the end, few relevant cellulose characteristics and the effect of modifications are investigated.

1. Literature Review

Cellulose as part of plants has been used as reinforcing materials since the beginning of our civilization [1]. However, new synthetic materials gradually replaced cellulose and its use has become more limited ever since. Over the past decade or so, the use of cellulose has witnessed a renewed interest mostly due to environmental related concerns; more and more researchers are looking for a new way to substitute non-renewable polymeric materials from petrochemical resources by naturally occurring and abundant polymers like cellulose [2].

Cellulose is the most abundant naturally occurring biopolymer and compared to their fossil-based counterpart, cellulose fibers have many advantages, which makes them effective and suitable candidates for many applications. Moreover, they are cost effective because they come from abundant and renewable resources at very low costs [3]. They are also biodegradable [4,5], non-toxic [6], and economical, they require low processing energy and offer a high ability for surface modification [7].

Despite these advantages, however, these fibers have certain limitations, which consequently hinder their potential applications. For example, they have limited thermal stability during composite processing [4,7], limited matrix compatibility due to their highly hydrophilic character [3], and high moisture absorption of the fibers that can affect the dimensional and mechanical stability of the final products [7]. (see section 1.7)

Attempts to rectify these shortcomings and make cellulose more conducive for different application means there is thus a great need to modify the cellulose and incorporate different functionality in it to make innovative materials. In the field of cellulose chemistry, numerous studies have been conducted within the last decades that have been aimed at searching for an appropriate application of cellulose for a variety of novel derivatives, or modification of the fibers themselves to provide them with specific properties like compatibility with composite material, hydrophobicity, and decrease in moisture absorption [8, 9, 10]. This ongoing research concerning the development of novel original materials has already produced many significant contributions through controlled physical and/or chemical modification.

1.1. Structural properties and reactivity of cellulose

The chemical and physical properties of cellulose depend on its specific structure, likewise making the comprehension of its structural character very important for the control of its modification. The polymeric structure of cellulose was first demonstrated by Staudinger in 1920 [11]. Cellulose is a naturally occurring biopolymer, which consists of long chains of anhydro-D-glucopyranose units with three hydroxyl groups per unit. The chemical reactivity and physical properties of cellulose are affected by both its chemical composition and its supramolecular structure [12]. It is furthermore known that cellulose structure has both amorphous (low order) and crystalline (high order) domains with a crystallinity degree ranging between 40%-60% in cellulose from plants and trees. The morphology of cellulose affects its reactivity: the hydroxyl groups in the amorphous region are more accessible and reactive compared to those in the crystalline region [11], while hydroxyl groups found on the surface of cellulose fibers are also highly reactive regardless of crystallinity levels.

Cellulose has a high cohesive energy due to these hydroxyl groups forming complex and strong hydrogen bond networks between and within the chains, and it is insoluble in water and in most common solvents because of this phenomenon [11]. As a result, and owing to the fact that solid cellulose usually is suspended in a liquid medium, the reactions of cellulose typically occur under heterogeneous conditions.

Under such conditions, the reactivity of the three hydroxyl groups are affected by steric effects of the supramolecular structure of cellulose. The relative reactivity of the hydroxyl groups of the cellulose are found to be as OH-C6>> OH-C2 > OH-C3 [13,14]. In general, cellulose is very reactive because of the presence of hydroxyl groups that are responsible for the reaction that cellulose undergoes. The degree of substitution (DS) is the average number of hydroxyl groups per glucose units that have been substituted. If all three hydroxyl groups of each glucose units are substituted, this equates to a DS of 3.0 [13].

1.2. Physical treatment

Fibers can be modified by physical and chemical methods. The composition of the fibers is not affected by physical treatments. Physical treatments are often applied to cellulose to impart a certain characteristic to its surface. They change the structural and surface properties of the fiber and influence the mechanical and bonding properties of its character and configuration [15].

Several methods have been used over the years. Thermo-treatment of the surface, corona discharge [16], cold-plasma [17, 18, 19] or laser treatment [20], or coating the surface of the fibers without covalent attachments [21] are few examples of this type of approach.

Physical treatment can also lead to chemical modification. Corona treatment is a technique for surface oxidation activation and it changes the surface energy of the cellulose fibers [16]. Similarly, in cold plasma treatment (depending on the type of the gas that is used) different surface modification and surface crosslinking could be introduced in the fibers [18].

Nanoscale roughness was also achieved by domain-selective oxygen plasma etching of the amorphous regions of the cellulose, followed by coating the etched surface with a thin fluorocarbon film using pentafluoroethane by plasma-enhanced chemical vapor deposition [17]. Two types of "roll of" and " sticky" superhydrophobicity were obtained by a variation of plasma treatment (Figure 1.1).

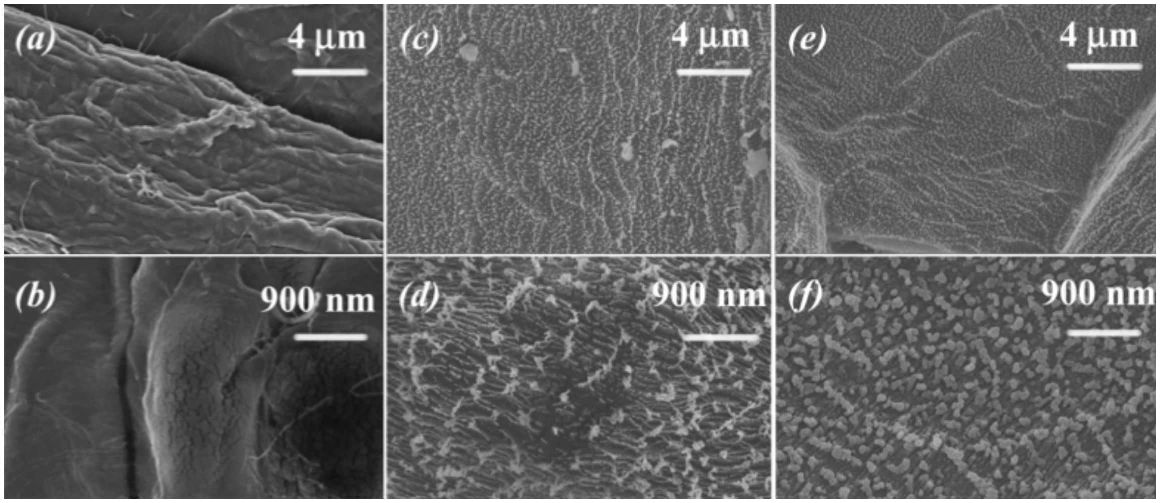


Figure 1.1. SEM images of (a,b) untreated hand-sheet fiber, (c,d) oxygen-etched hand-sheet fiber, (e,f) oxygen-etched and PFE-coated hand-sheet fiber. (Adapted from ref. [17])

In a recent study by Sarkar *et al.* [22], differential superhydrophobicity and hydrophlicity on each side of a thin cellulose fabrics was achieved by two-step coating with electro-spraying cotton fibers with polyvinylidene fluoride and fluorinated silane molecules.

1.3. Chemical modification

As described earlier, to improve cellulose processability and to make new cellulose derivatives for specific industrial application, chemical modification of cellulose is a necessity. Cellulose can be derivatized in various ways by modifying its abundant hydroxyl groups. New functional groups can be introduced into cellulose through chemical modification; these functional groups can accordingly introduce new properties to the cellulose without destroying its many desirable intrinsic properties. This derivatization of cellulose has opened windows of opportunities and has, as a result, broadened its use.

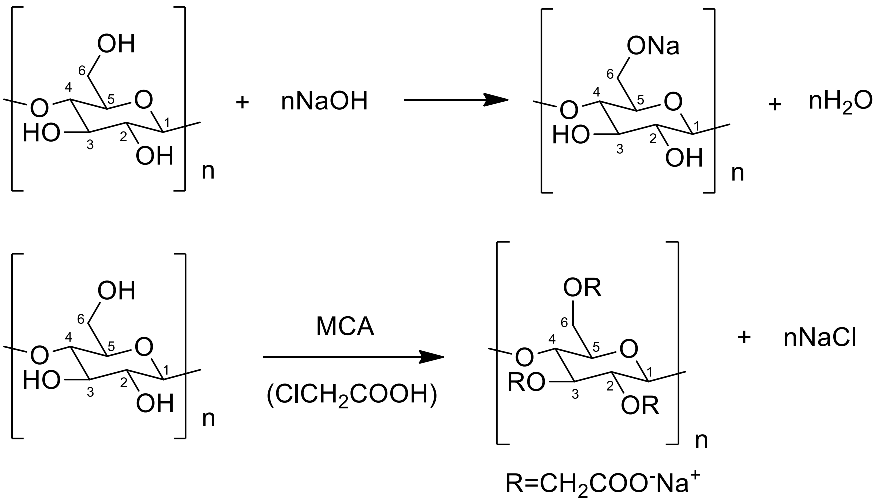
The first chemical modification of cellulose to introduce new properties dates back to 1870 when the first thermoplastic polymeric material, ‘‘celluloid’’, was produced with the etherification of cellulose with nitric acid [23]. Many chemical modifications of cellulose have additionally been reported in the literature. Esterifications and etherifications at the hydroxyl groups of cellulose are two of the most typical modifications. Most water-soluble and organic solvent-soluble cellulose derivatives are prepared by these substitution reactions. Other modifications are ionic and radical grafting, acetylation, deoxyhalogenation, and oxidation [24]. Some of the original properties of cellulose can be altered by these chemical modifications.

1.3.1. Etherification

Cellulose ethers are an important class of cellulose derivatives. Methylcellulose (MC) was first produced in early 1900, followed by other nonionic alkyl ethers of cellulose and carboxymethyl cellulose (CMC), and hydroxyethyl cellulose (HEC) shortly thereafter. Cellulose ethers have many important properties, such as high solubility, high chemical stability and non-toxicity. Their water solubility can be controlled by the degree of substitution, the nature, and the distribution of the substituents. Cellulose ethers are used either in a dissolved or highly swollen state [25]. The vast majority of cellulose derivatives are prepared by chemical modification of these dissolved celluloses in what is referred to as “homogenous derivatization” [26]. They are the dominant polymers in numerous industrial applications and are widely used in the manufacture of detergents, textile, paint-and-varnish, food, cosmetic, and fragrance industries [27].

1.3.1.1. Principle of carboxymethylation

Among the ionic derivatives of cellulose, carboxymethyl cellulose sodium salt (NaCMC) is most widely used. Carboxymethyl cellulose is a typical polyelectrolyte and is formed when the hydroxyl groups of anhydrous glucose are replaced by the carboxymethyl group of monochloroacetic acid (MCA). For the production of CMC to be possible, two consecutive steps of reactions are required [28] which are known as basification and etherification. The principle of this reaction is shown in scheme 1.1 below.



Scheme 1.1. Two-step reaction conversion of cellulose to carboxymethyl cellulose

During the initial basification stage, the crystalline structure of cellulose is modified and the alkaline treatment leads to an increase in amorphous content of cellulose at the expense of the crystalline region [29]. Cellulose fibers are swollen in concentrated NaOH, which increases the accessibility of fibers to chemicals and the hydroxyl group of cellulose shows higher activity under alkaline conditions [28].

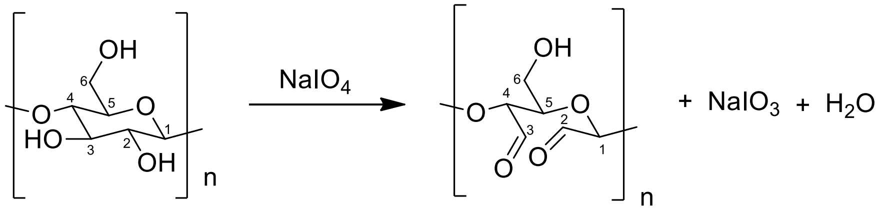
Moreover, the CMC obtained after reacting hydroxyl groups at the 2-, 3-, or 6-positions of the anyhdroglucose unit generally display a non-uniform distribution of the substituent [30] and it has been found the effect of temperature and shear on CMC's viscosity is reversible [31]. The application field of this ionic derivative of cellulose can be further extended by chemical modification since the produced carboxylic functionalities are very reactive and may serve as a strong intermediate for further reactions.

1.4. Oxidation

Another class of cellulose derivatives are oxycelluloses (or oxidized celluloses). They usually are water insoluble materials that are produced by oxidizing cellulose with an oxidant such as hydrogen peroxide, gaseous chlorine, peracetic acid, chlorine dioxide, nitrogen dioxide, persulfates, permanganate, hypochlorous acid, hypohalites or periodates. Depending on the nature of the oxidant and the reaction condition used, these oxidized celluloses may contain carboxylic, aldehyde, and/or ketone functionalities, in addition to the hydroxyl groups [32].

1.4.1. Periodate oxidation

One method for derivatization of cellulose is the use of partial oxidation with periodate. Periodate oxidation of cellulose was first investigated by Jackson and Hudson [33, 34]. Periodate oxidation can cleave C2-3 bonds and selectively oxidize C-2 and C-3 vicinal hydroxyl groups to form 2, 3-dialdehyde units along the cellulose chains [35, 36]. The principle of this reaction is shown in Scheme 1.2.



Scheme 1.2. Reaction for periodate oxidation of cellulose

Despite the relatively simple chemical structure of cellulose, oxidation of cellulose is a complex process because of its insolubility and partial crystallinity. Generally, amorphous regions are preferred by most chemical oxidations of cellulose in heterogeneous systems. In instances of periodate oxidation, however, crystalline domains are also affected and upon the introduction of aldehyde groups, crystallinity decreases with increasing level of oxidation [37]. Varma *et al.* reported that oxidized cellulose is thermally more stable than unmodified cellulose at higher temperature but less stable at lower temperatures below 250° C [38]. Moreover, upon the study of the morphology of the oxidized fibers it was found that the oxidized derivatives of cellulose showed a decreased aspect ratio when the cellulose samples were oxidized at a level of 30% [39].

The aldehyde groups serve as reactive chemical anchors for further reactions, and DAC can then be a useful intermediate for other products. For instance, dialdehyde can be further converted to carboxylic groups [40], primary alcohols [41], or Schiff bases [42]. In one study, further oxidation to the corresponding acids introduces new functionality as anionic ion exchange material [43]. The reactivity of the dialdehyde functions allows for novel cellulose-based material with enhanced degradability and green characteristics. Consequently, this serves as a good vehicle for chemical derivatisation.

1.5. Principle of Amidation

In order to further modify the partially substituted cellulose, two methods can be employed. The first is to introduce new functional groups at the unreacted remaining hydroxyl groups in the anhydroglucose units, or to selectively modify the already present substituents.

Reactions that build up carbon-carbon bonds and at the same time introduce nitrogen-containing functionalities into the structural framework are especially appealing for the rapid construction of organic molecules. Consistently, the majority of multicomponent reactions developed to date relate to the -aminoalkylation of carbonyl compounds [44], which is a powerful synthetic tool that uses the paired electrophilic and/or nucleophilic reactivity of imines for the synthesis of amine-bearing compounds. The Strecker reaction (1850) (figure 1.2), a one-pot reaction of three-component coupling of an amine and an aldehyde with hydrogen cyanide, is the earliest known multicomponent reaction [45, 46].

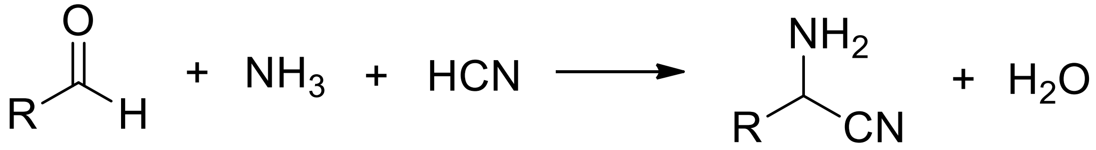


Figure 1.2. Schematic representation of Strecker reaction. (Adapted from ref. [46])

Over the years, a variety of reaction conditions have been developed and inspired new interest in this reaction. Nucleophilic attack onto an intermediate imine or iminium ion is essential to all of these reactions. When a carbonyl group is introduced adjacent to the nitrogen atom, the electrophilic reactivity of an imine (or iminium ion) is greatly improved. This increased reactivity of iminium ions significantly increases the range of nucleophiles that can be used in carbon-carbon bond forming reactions [46]. There have been a number of studies on ways of amidation of cellulose or cellulose derivatives. Different methods, based on the nature of the functional group to be reacted with amine, have been used in the past.

1.5.1. Schiff-base reaction

Due to their numerous properties, there has always been an interest in introducing aliphatic alkyl chains to cellulose via versatile modifications. The dialdehyde cellulose can be used as a reactive intermediate for various derivatives from cellulose. The Schiff base forming reaction between aldehyde and primary alkyl amine is a useful procedure to introduce these substituents. Cellulose can be coupled with amine derivatives and give rise to various nitrogen-containing derivatives in good yield by reaction at ambient temperature in a variety of solvents [42]. The nucelophilic addition reaction between a carbonyl group of dialdehyde cellulose and a primary amine results in a condensation product of amide. The reaction scheme can be seen below in figure 1.3 a. The proposed mechanism of the reaction (figure 1.3 b) shows that the nucleophilic addition of the amine to the carbonyl compound of the molecule gives rise to a hemiaminal intermediate, followed by transfer of a proton from nitrogen to oxygen. In the case of alkyl or aryl amines, water is lost in an elimination reaction to give yield to a stable Schiff base product [47].

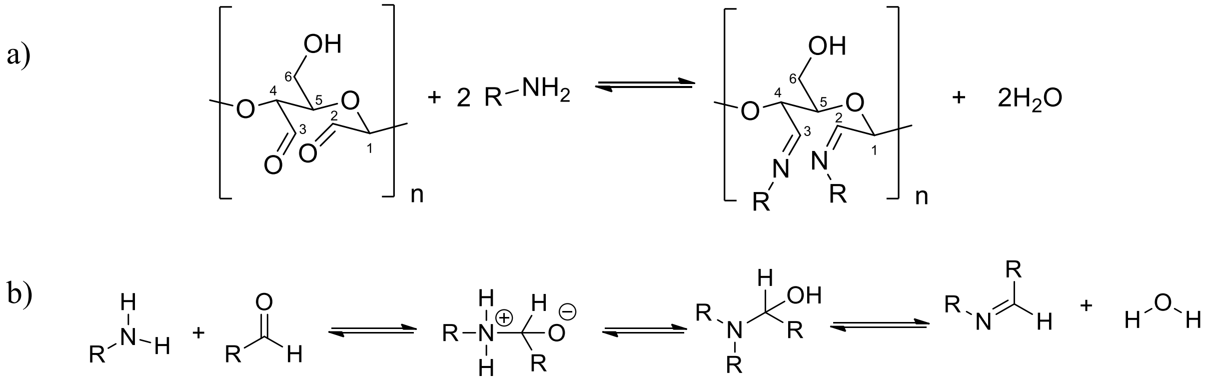


Figure 1.3. (a) Schematic representation of Schiff base reaction, (b) proposed mechanism for the coupling of aldehyde and amine

However, there haven't been many reports regarding the fabrication and characterization of these derivatives for specific applications. Recently, Kim *et al.* [48] studied the thermal decomposition of the resulting oxime and hydrazine derivatives of dialdehyde cellulose. These nitrogen-containing derivatives showed lower initial decomposition temperature and samples with higher degree of oxidations showed some explosive decomposition. They relate this phenomenon to the C=N-N or C=N-O groups in the chemical structure.

1.5.2. CMC Amides

It is of significant scientific and practical interest to synthesize CMC amides (CMCAs) and study the effect of newly introduced substituents on different properties of the product. The chemical modification of amine or carboxyl functionalized polysaccharides has been accomplished through amidation reactions with carboxylic acids and amines respectively. These reactions have been performed both homogeneously and heterogeneously on polysaccharides such as hyaluronic acid [49], chitosan [50], and carboxyl functionalized celluloses including derivatized products from TEMPO-mediated oxidation [51].

CMC amides can be synthesized by the reaction of amines with CMC acid chloride [52] or CMC in the H form. Most of the available work published on this topic involves the use of carbodiimides as coupling agents. EDC (1-ethyl-3-[3-(dimethyl-aminopropyl)] carbodiimide) is known to promote cross-linking of different polysaccharide molecules through both ester formation between COOH and OH [53] and amide bridges if primary amines are present [54]. During these reactions, EDC is converted into a stable urea derivative and is released into the reaction medium as a non-toxic by-product, without EDC itself participating in the bond forming process.

Bulpitt and Aeschlimann [49] were the first who used this approach to functionalize hyaluronic acid with several bi-functional amines towards the development of cross-linked biocompatible hydrogels. The method has consequently been used for the coupling of carboxycelluloses (homogeneous phase reactions)[51] and carboxyl-functionalized nanocelluloses (heterogeneous phase reactions) [55].

One of the important properties that are affected here with this modification is the thermodynamic affinity of the resulting product with water. It has been found that the degree of CMC amidation changes the solubility of the final products. The Zabivalova *et al.* studies [52] show that at high degree of amidation the solubility in water is very low, but the products become soluble in aqueous-organic solvents. Conversely, the team also found that a lower degree of amidation has no considerable effect on the solubility of carboxymethyl cellulose in water. Moreover, the degree of amidation of carboxymethyl cellulose is affected by the amount of the amine added and the liquor ratio [52]. Hence, by varying the molecular weight, the degree of substitution in CMC and the nature of an amine and degree of amidation, new cellulose derivatives soluble in water and organic solvents are able to be synthesized. The resulting products can behave as polyacids, weak polybases, nonionic materials, or polyampholytes. They have numerous applications such as drug delivery [51], biocompatible hydrogels [49], cross-linked biodegradable coatings/materials [50], and stabilization of colloidal suspensions [55].

1.6. Principles of crosslinking

The term "crosslinking" refers to the association of polymers through the chemical bond [56]. In most cases, the phenomenon of crosslinking is irreversible and it may be intra- and intermolecular. Crosslinking is achieved by using suitable crosslinking agents. In most cases, some form of pretreatment is required to make the cellulose chains capable of the crosslinking reaction. Some di-functional or poly-functional compounds are moreover used to covalently bind the cellulose or its derivatives functional groups and bring stability to the structure of cellulose [57].

Based on the cellulose functionalities, different methods may accordingly be used to cross-link the fibers. Different crosslinkers have been used to prepare hydrogels by crosslinking via hydroxyl groups under alkali conditions [58, 59]. Crosslinking of cellulose using adipic dihydrazide produced gels with various physicochemical properties [60]. There are many reports of EDC assisted crosslinking of the water-soluble cellulose derivatives [57-60], but few reports exist regarding the crosslinking of the solid cellulose especially between the micro-fibrils inside the fiber wall.

Chemical crosslinking not only increases the structural stability of cellulose, it moreover leads to the improvement of the wet state properties and moisture sorption of cellulose materials [61], because the covalent bridges between cellulose chains limit the swelling of cellulose and thus protects the hydrogen bonds against the disrupting action of the water molecules [62].

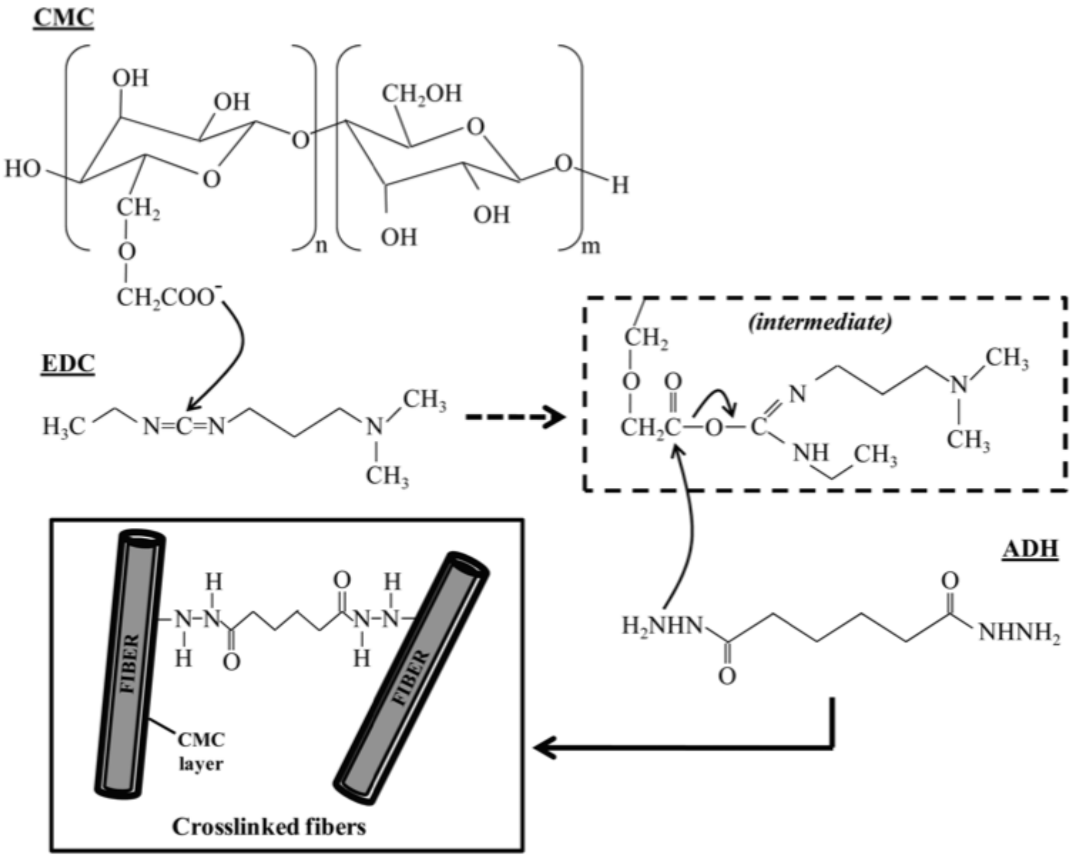


Figure 1.4. Schematic representation of the EDC assisted cross-linking reaction mechanism. (Adapted from ref. [63])

In a very recent study done in our group, the EDC-assisted reaction of carboxyl and amine groups is shown to increase the wet-web strength (WWS) of papers made from hardwood kraft pulp, after pretreating the fibers with carboxymethyl cellulose and using adipic dihydrazide as the cross-linker [63]. By using such chemistry increases as high as 500% and 100% in the wet-web strength (WWS) of paper was reported. The schematic representation of the reaction mechanism is shown in figure 1.4.

1.7. Fiber characteristics

1.7.1. Hydrophobicity

The hydrophobicity of a material may be assessed by the contact angle of a water droplet deposited onto its surface. In general, hydrophobicity is achieved either by lowering the surface energy - and more specifically, the polar contribution to it- or by creating suitable surface micro- and/or nano-morphologies that hinder water spreading. When the water contact angle is higher than 90°, the corresponding material is conventionally defined as hydrophobic [64]. When the contact angle is higher than 150^o, the surface is defined as super-hydrophobic [65].

The hydrophobization of non-hydrophobic materials by appropriate modifications involving either physical treatment or chemical reactions applied to the surface or the bulk of the concerned substrate has been a topic of chemical research for at least 60 years [66]. As for cellulose, there has always been an interest in hydrophobizing this hydrophilic biopolymer to increase its suitability for numerous applications such as the reduction in the wettability of paper, to increase its mechanical strength in humid environments, and to augment its compatibility with polymer composites used for different applications [67].

The hydrophobization of cellulose fibers not associated with paper properties was first investigated by Butler and Dixon using cellulose esters, of both alkyl and aryl carboxylic acids [68]. Over the years, several methods such as: surface derivatization [69-71], grafting with polyethylene glycol [55], and surfactant adsorption [72] have been reported.

Stable hydrophobic perfluorinated cellulose derivatives were reported by Gandini *et al*. [73] via the surface esterification of cellulose fibers with pentafluorobenzoyl chloride PFBz under controlled heterogeneous conditions.

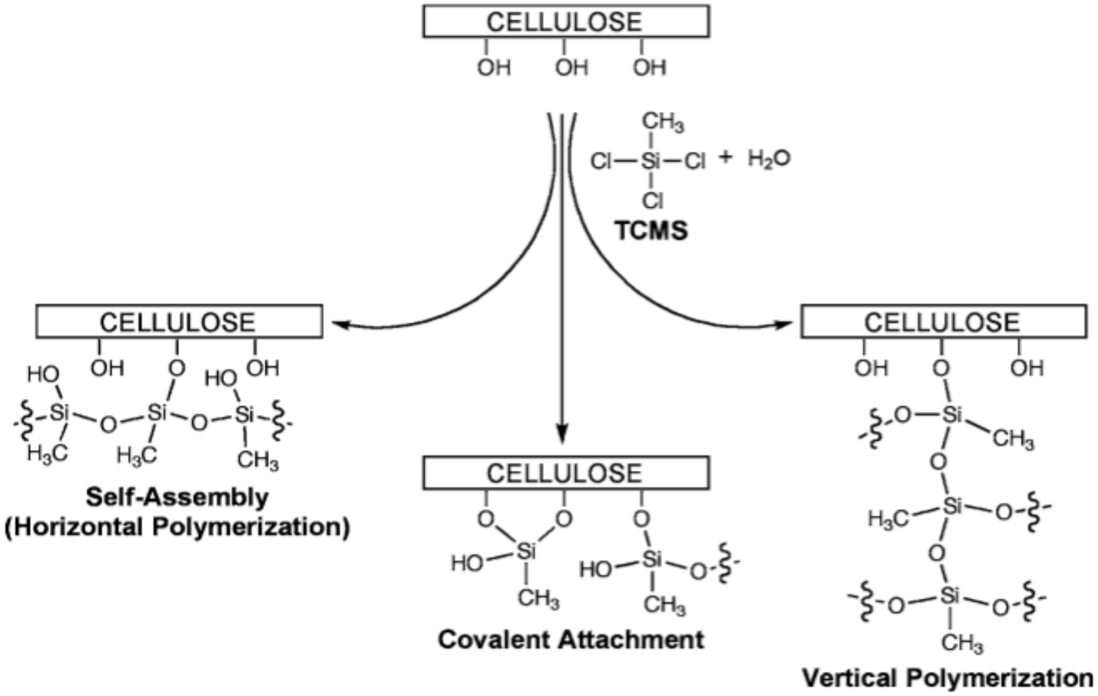


Figure 1.5. Schematic representation of the possible products of the reaction of TCMS with a cellulose substrate in the presence of controlled humidity (Adapted from Ref. [75])

In another instant, Cunha *et al*. [74] recently developed a simple method to attain a high hydrophobic cellulose structure with the gas-phase coupling of trichloromethylsilane (TCMS) onto the surface of cellulose fibers, in the presence of small amounts of moisture. TCMS reacts with both the surface OH groups of cellulose and with the water present and generates a surface coverage whose chemical features, shown schematically in Figure. 1.5 for the different possible constructs and depends on the actual experimental conditions. These structures were accompanied by a surface morphology that displayed micro-asperties and nano-asperities, which create the required roughness for hydrophobic contact angle. After the extraction of cellulose-unbound species, water contact angles higher than 130° were measured together with correspondingly high contact angles with non-polar liquids, showing that highly bi-phobic cellulose surfaces had been generated by the concomitant action of nano-roughness and chemical inertness.

1.7.2. Moisture sorption

Paper is a hygroscopic material, i.e. the fibers spontaneously lower their free energy by adsorbing water [76]. When fibers sorb water within the fiber wall, hydrogen bonds are broken and the fibrils within the fiber wall are separated from each other [77], resulting in a swelling of the whole fiber and hence a change in the dimensions of the entire network.

Cellulose-based materials are broadly used in everyday life. Water and humid environments are challenging for these materials and can cause a loss of dimensional stability, poor wet stiffness, and the tendency to creep under load, for instance. The extent to which the properties of fibers are modified by the sorption of water vapor combined with finding ways to introduce water-repelling moieties to the cellulose has been a pervasive pursuit in this subject [78].

It has been moreover demonstrated from different independent methods that the adsorption properties of fiber forming polymers are primarily determined by the amorphous regions and the interaction properties of the surface. The influence of the crystalline regions, their size and orientation on the adsorption character is less important [78].

The amount of moisture absorption in the cellulose fibers can be considerably reduced through chemical modification, such as the acetylation of some of the hydroxyl groups present in the fibers [76-78]. Other feasible methods include graft polymerization with vinyl monomers like acrylonitrile; to enhance the fiber properties acrylonitrile was grafted on cellulose. The moisture regain was found to decline dramatically as the degree of grafting increased for both systems. As for mechanical properties, these increased with degree of grafting [79].

1.7.3. Thermal stability

One of the drawbacks of cellulose fibers is their limited thermal stability with obvious degradation occurring as the melt processing temperature approaches 200^{o}C [79]. This limits their application for thermoplastic composites. Higher processing temperatures that reduce melt viscosity and enable good mixing are possible, but only for short periods of time. To correct for this many chemical modification of fibers have been reported. One simple method that can be used to overcome this problem involves acetylation. This procedure was first applied by Stamm in 1947 [33] Rana *et al.* (1997) [80] who studied the effect of acetylation on fibers at different reaction times and reaction temperatures. The modified fibers were characterized by FTIR, DSC, TGA and SEM studies. The extent of moisture regain and thermal stability was subsequently reported and it was concluded that the thermal stability of acetylated fibers improved [80].

As this review clearly reveals, the search for original and effective methods to modify cellulose fibers and render them more compatible for different industrial applications has attracted very considerable attention. However, this topic still has so much room for further improvements and hence further research involving both novel strategies and the optimization of the previous ones is necessary. Moreover, efforts should concentrate to have systems with green character and an economically viable application potential.

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Chapter 2. Fabrication and Characterization of Cross-linked and Hydrophobically Modified Cellulose Fibers

2.1. Abstract

Attempts to chemically modify oxidized cellulose fibers were made using amine terminated molecules. Softwood cellulose pulp was chemically modified with successive chemical treatments; including (1) periodate oxidation selectively oxidizing C2 and C3 hydroxyl groups to reactive dialdehyde units on the cellulose chain; (2) Oxidized celluloses with a degree of substitution as high as 2 were obtained and coupled with butylamine by a Schiff base reaction; and (3) to prevent fibers disintegration during the previous amidation step, dialdehyde cellulose (DAC) fibers were cross-linked via a Schiff base reaction using 1,12-diaminododecane as cross-linker. This procedure yielded highly hydrophobic and low-hygroscopic cellulose materials with various extent of surface and bulk modification. The modified cellulose fibers obtained with these methods were investigated by a variety of techniques, including infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), field-emission scanning electron microscopy (FE-SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD), moisture sorption and water contact angle (CA) studies. On the basis of scanning electron microscopy (SEM) images of the fibers, the incorporation of nano- and micro-sized roughness on the surface of the fibers is evident which, combined with lower surface energy of the hydrophobic aliphatic chains, is responsible for the high water contact angle (143^{o}) obtained for the final products. From TGA and moisture sorption studies, the cross-linked fibers showed higher thermal stability and lower water absorption. All of the final products maintained

their cellulose I crystalline structure based on angle X-ray diffraction results, and crystallinity indices approximately in the range of 50%-70% were observed for all final samples. The unique characteristics of these fibers are very promising for potential application in composites, packaging and other technologies. A general overview of preparation, characterization and properties of these novel materials will be presented here.

2.2. Introduction

There is a growing interest in replacing non-renewable polymeric materials obtained from petrochemical resources by naturally occurring and abundant polymers such as cellulose [1]. To make cellulose more suitable for different applications, there is a need to modify the cellulose and incorporate different functionalities in it.

The preparation of highly hydrophobic cellulose-based materials has stimulated a large number of studies and the association of water with cellulose is of significant technological importance because of their potential applications in such important areas as papermaking, textile and packaging [2]. Therefore, the development of new methods to make novel cellulose materials that are hydrophobic and have low hygroscopicity, is of utmost importance.

Many different cellulose derivatives have been produced by a variety of chemical modifications. Periodate can oxidize vicinal hydroxyl groups of cellulose at C2 and C3 positions to aldehyde groups, and at the same time cleave the corresponding carbon-carbon bond of the anhydro D-glucopyranose ring to form 2,3-dialdehyde cellulose (DAC) [3,4]. The reaction proceeds under mild conditions and hence the amount of introduced aldehyde can be easily controlled [5]. DAC is a very reactive intermediate and the resulting dialdehyde cellulose can be potentially useful for further modifications to carboxylic acids [6-8], primary alcohols [9], or imines [10-11] from its intrinsic reactivity with primary amines.

In addition to regioselectivity, periodate oxidation differs from most other oxidizing methods as it has the property to penetrate and react with the crystalline as well as the amorphous parts of cellulose without causing much degradation. Moreover, with periodate oxidation the reaction is more uniformly distributed throughout the cellulose fibers and hence more suitable as an anchor for further modifications [12].

Grafting and coupling of amine on to the modified fibers has been the topic of research for the past decade [5, 10, 11]. The Schiff base forming reaction between aldehyde and primary alkyl amine is a useful procedure to introduce these substituents. Cellulose can be coupled with amine derivatives and give rise to various nitrogen-containing derivatives in good yield by reaction at ambient temperature in different solvents [11]. The nucelophilic addition reaction between a carbonyl group of dialdehyde cellulose and a primary amine followed by transfer of a proton from nitrogen to oxygen results in a stable Schiff base. When a carbonyl group is introduced adjacent to the nitrogen atom, the electrophilic reactivity of an imine (or iminium ion) is greatly enhanced [13]. Moreover, the same principle and mechanism is applied when a bi-functional amine such as 1,12-diaminododecane is used in the Schiff base reaction with dialdehyde cellulose. As shown in figure 2.1, using a sufficiently long diaminoalkane, the aldehyde groups in adjacent cellulose chains and hence the micro-fibrils within the fiber can be cross-linked.

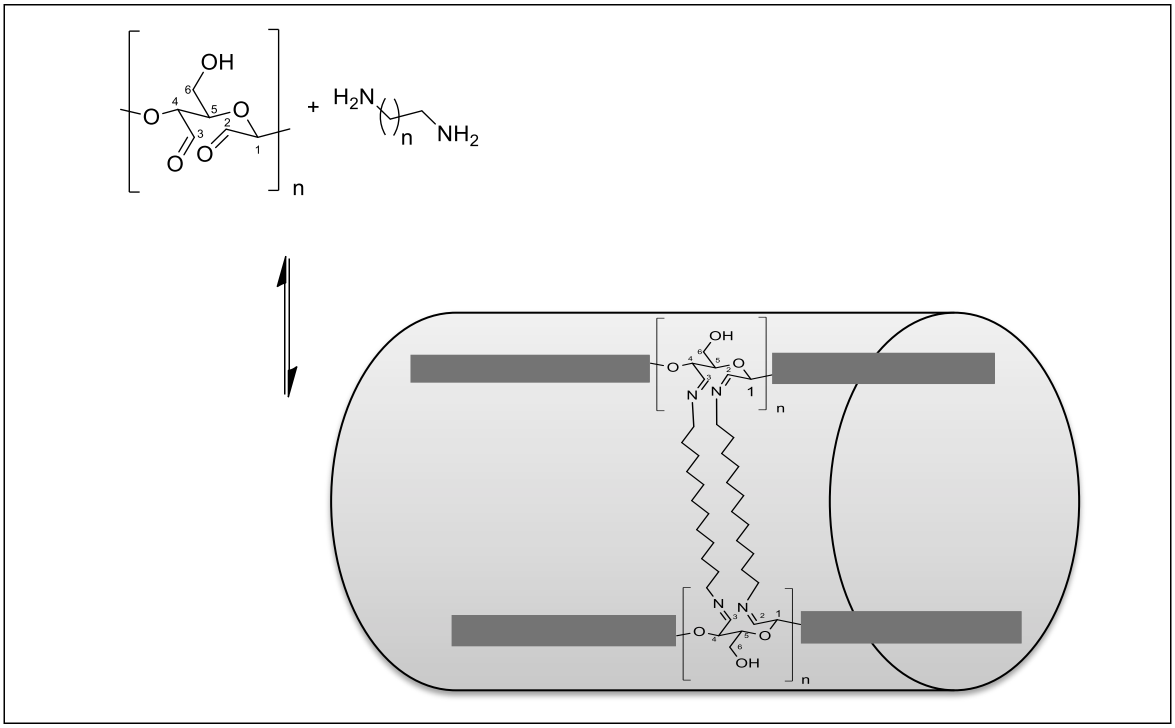


Figure 2.1. Schematic representation of the Schiff base cross-linking reaction within the micro-fibrils in a fiber.

In this work we show that water contact angle and moisture sorption properties of fibers can be substantially improved by first cross-linking the oxidized dialdehyde cellulose fibers with 1,12-diaminododecane, followed by n-butylamine coupling of the cross-linked fibers. The butylamine coupling reaction is tested with both non cross-linked and cross-linked fibers to study the effect of cross-linking in preventing the disintegration of the fibers after introducing butylamine to dialdehyde cellulose. Results prove the ability of the proposed method to cross-link the fibers and promote higher water contact angles and structural strength.

2.3. Experimental

2.3.1. Materials

Q-90 softwood pulp sheets supplied by Domtar Inc. Canada were used as raw material for chemical treatments. Chemicals for oxidation and titration: sodium meta-periodate ($NaIO_4$), ethylene glycol, hydroxylamine hydrochloride ($NH_2OH.HC$), sodium hydroxide (NaOH) standard solution (0.5N), and hydrogen chloride (HCl) standard solutions (0.1M and 0.5M) were all purchased from Sigma-Aldrich, and sodium chloride (NaCl) from ACP chemicals Inc. Chemicals for cross-linking and amidation: 1,12-diaminododecane, and n-butylamine were purchased from Sigma-Aldrich, and methanol, dioxane, and toluene from ACP chemicals Inc. All chemicals were used as received. Milli-Q water was used in all experiments.

2.3.2. Methods

Chemical treatments

Cellulose fibers in the form of pulp suspensions were subjected to successive chemical treatments, carried out to various extents in order to achieve various degrees of modification.

2.3.2.1. Periodate oxidation of cellulose pulp

Initially, three gram of Q-90 softwood pulp sheets were made into small pieces and placed in distilled water for 24 hours. The wet pulp was thoroughly dispersed by a disintegrator, and then filtered a few times to remove the fines and extra water from the pulp. Next, NaCl (11.7 g; 1 M based on overall solution) and NaIO4 (3.96g; 21.50 mmol; 100mol% based on moles of anhydroglucose in pulp) were dissolved in water in a glass beaker with overhead stirrer, and the wet pulp was dispersed in this solution. Including the moisture in the wet pulp, the total volume of water was 200 mL. The beaker was then completely covered with aluminum foil during the reaction in order to prevent light from activating side reactions [14], and the mixture was stirred at 105 rpm at room temperature. After the desired reaction time (16 h, 48 h, 96 h and 144 h) ethylene glycol was added to the beaker to quench the reaction by removing the residual unreacted periodate. The modified pulp (dialdehyde cellulose) was thoroughly washed with deionized water repeatedly and filtered out.

2.3.2.3 Schiff base reaction with alkylamine

The aldehyde groups of DAC were coupled with an amine derivative by a Schiff base reaction. Two grams of periodate oxidized pulp was solvent exchanged from water to dioxane and then toluene. The reason for this is that the final product is non-polar and hence it is better dispersed in a non-polar solvent such as toluene. To do this, the oxidized pulp was first filtered from water, and added to dioxane and stirred for 10 minutes, this process was performed twice with dioxane and then the pulp was filtered from dioxane and added to toluene and the same procedure was performed twice. N-butylamine (2.14 g; 29.26 mmol; 1.3 eq. based on mols of aldehyde groups per gram of DAC) was added into this suspension (1.5 w/w%) and the mixture was stirred at a speed of 150 rpm at room temperature. The experimental conditions were varied with different times and different DS of aldehyde groups. Where possible, the final product was thoroughly washed with toluene and then ethanol to get rid of the physically adsorbed butylamines. The final product was filtered and dried in air.

2.3.2.5. Cross-linking the fibers; Schiff base reaction with diamine

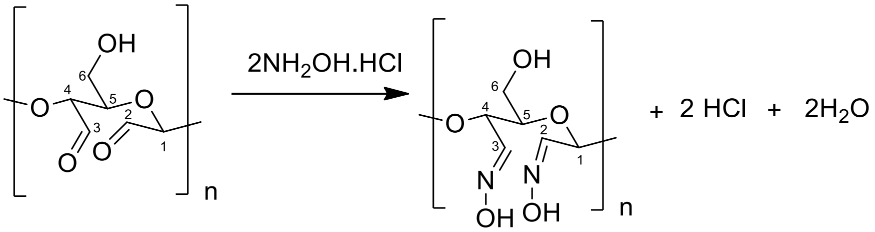
To prevent the fibers from disintegration, the chains within the microfibrils of DAC were cross-linked with bi-functional amine by a Schiff base reaction. Different lengths of diamines were used and the optimum length was found to be a twelve carbons chain of 1,12- diaminododecane. Using the same procedure mentioned in the previous section (2.3.2.4) for Schiff base reaction, one gram of oxidized cellulose fibers were solvent exchanged to methanol since 1,12- diaminododecane is most soluble in methanol. Next, 1,12-diaminododecane (0.22 g; 1 mmol; 0.1 eq. based on mols of aldehyde group per gram of DAC cellulose) was added to the suspension (1.5 w/w%) and the mixture was stirred at a speed of 150 rpm at room temperature for 72 h. The amount of the cross-linking agent was varied to find the optimum condition for cross-linking and to investigate the effect of cross-linking on fiber disintergration. The final product was thoroughly washed with methanol, and then ethanol to get rid of the physically adsorbed diamines. The final product was filtered and dried in air.

2.3.3. Characterization

2.3.3.1. Determination of aldehyde content

The aldehyde content of the dialdehyde cellulose produced by the periodate oxidation reaction was determined using the hydroxylamine-hydrochloride ($NH_2OH \cdot HCl$)

titration method [4]. In this method, the aldehyde is converted to oximes by a Schiff base reaction with hydroxylamine-hydrochloride (Scheme 2.1). The HCl released from this reaction is back-titrated with a NaOH solution of known concentration. A known weight of DAC sample was mixed with 40 mL of isopropanol, making a final proportion of isopropanol/water of 2/1 v/v, and the mixture was sufficiently stirred to prepare a well-dispersed slurry. The pH of the mixture was then adjusted to 3.5 with HCl. The pH of the hydroxylamine hydrochloride solution (5 wt.%) was also adjusted to 3.5 before it was added to the suspension. Finally, the HCl released from the reaction was titrated with 0.5 N NaOH solution and the pH of this suspension was always kept at 3.5 by adding NaOH until no decrease of pH was observed.



Scheme 2.1. Schematic representation of the hydroxylamine-hydrochloride ($NH_2OH\cdot HCl$) titration reaction

The aldehyde content was then calculated using the following equation:

$$[A_{ald}] = V_{NaOH} \cdot N/W$$

Here $[A_{ald}]$ is the aldehyde content in mmol per gram of cellulose, V_{NaOH} is the volume of NaOH (mL) used in the titration, N is the normality of the NaOH (eq/L) and W the dry weight of cellulose (g) used in titration [15]. The aldehyde titration was used to confirm the amine coupling and further cross-linking of cellulose fibers by determining the decrease of aldehyde groups caused by these processes.

2.3.3.2. Surface chemical properties

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR measurements of the samples were performed on a FTIR spectrometer from Perkin Elmer with single bounce diamond ATR (Attenuated Total Reflectance) accessory. Solid samples were placed directly on the ATR crystal and maximum pressure was applied by lowering the tip of the pressure clamp using a rachet-type clutch mechanism. All the spectra of measured samples were averaged from 32 scans from 550 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Solid-state ^{13}C NMR

Solid-state ^{13}C NMR spectra were obtained on a Varian/Agilent VNMRS-400 instrument operating at 100.5 MHz. Samples were packed uniformly in 7.5 mm zirconium rotor and spun at 5500 Hz. Spinning sidebands were suppressed using the TOSS sequence. Spectra were acquired using a contact time of 2 ms and a recycle delay of 2 s. Typically 6000 transients were acquired.

2.3.3.3. Morphological properties - Scanning electron microscopy

The surface morphology of fibers was examined by field emission high resolution scanning electron microscopy FE-SEM (S-4700 Hitachi, Tokyo, Japan). The fibers were dried under ambient conditions and pressed onto a double-sided tape adhered to the sample holder surface and sputtered with gold and palladium for 2 min. The applied accelerating voltage and current were 5,10,15 kV and 10 μA, respectively.

2.3.3.4. Crystallinity properties - X-ray Diffraction analysis

Samples were studied by X-ray Diffraction (XRD) to determine the effect of oxidation and Schiff base reactions on the crystalline properties of the cellulose. The XRD measurements were performed on a Bruker Discover D8 Discover two dimensional diffractometer with VANTEC 2D detector and CuKα radiation (λ=1.54 Å). The X-ray diffractograms were obtained with a 2θ range of 10-30° at a scan rate of 0.005° s^{-1}.

2.3.3.5. Thermal properties - thermogravimetric analysis (TGA)

To study the thermal stability of the samples, thermogravimetric analysis was performed on a Q500 TG analyzer. Samples were heated in a pure nitrogen atmosphere between room temperature to 550^{o} C at a rate of 20^{o} C/min with a flow rate of 60 mL/min. The weight loss (TG curve) and its first derivative (DTG curve) were recorded simultaneously as a function of time and temperature.

2.3.3.6. Water hydrophobic properties - Contact angle measurements

Contact angle measurements were performed on a contact angle system OCA20 (Dataphysics, Germany) at room temperature. A 2 μL water droplet from a micro-syringe (Hamilton-Bonaduz) was placed on the surface of the fibers and pictures were taken by a CCD camera. Each measurement was performed on a different new spot of the sheet and the results were based on the average of at least three measurements. Contact angles were calculated on the basis of the Young-Laplace equation by the software provided by the instrument.

2.3.3.7. Moisture sorption measurements

Moisture sorption measurements were performed in a constant humidity standard room with a relative 50% constant humidity at room temperature. The fibers were dried in an oven at 60^{o} C for 24 h followed by 30 minutes at 100^{o}C. The fibers were then weighed on a microbalance (W_0). The changes in the weights of the fibers were recorded as a function of time (W_t). Moisture uptake% was measured based on the following equation:

Moisture content % = $100\ (W_t - W_0/W_0)$

2.4. Results and discussion

2.4.1. Effect of periodate oxidation and degree of substitution

The periodate oxidation reaction was performed to different extents. Figure 2.2 shows that the aldehyde content and degree of substitution (DS) of oxidized fibers increases as a function of reaction time. In the presence of salt and higher reaction times, a DS up to 2 can be achieved. The recovered yield of fibers decreases with increasing level of periodate oxidation and ranges from 92 to 98%. These values are in good agreement with previous results reported by Maekawa and Koshijima [16]. It is found that the decreased yield during periodate oxidation is likely primarily due to the dissolution of hemicelluloses. Therefore, the recovered yield can likely be further improved by using cellulose pulp with a lower hemicellulose content (e.g., dissolving pulp) instead of Q-90 pulp [17].

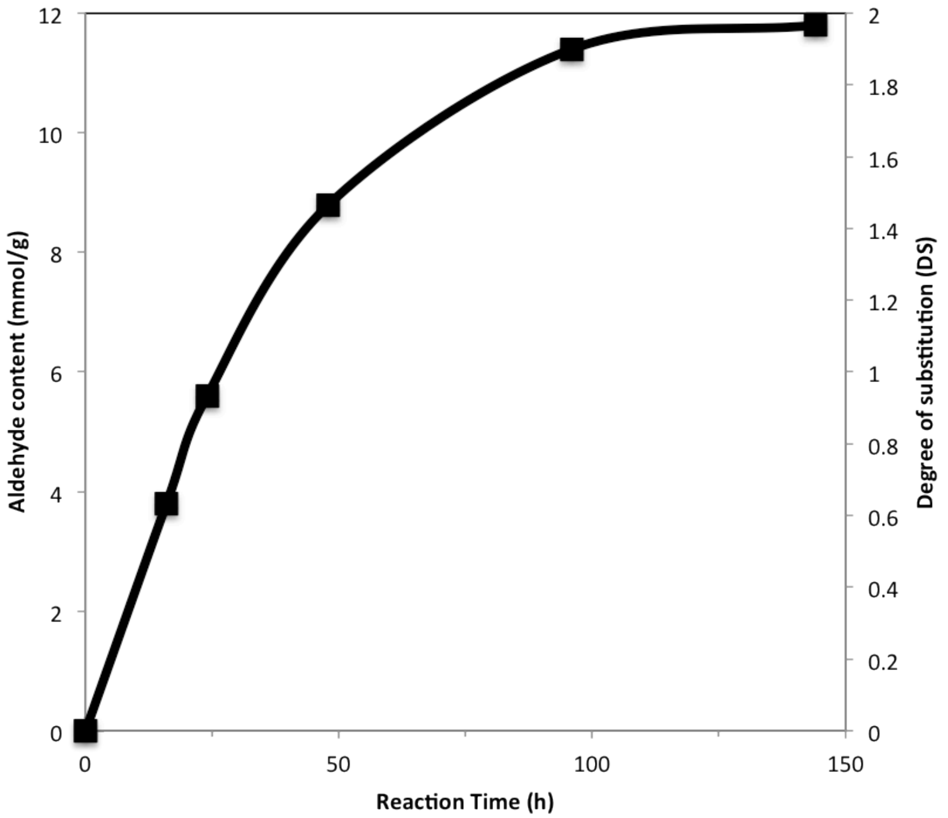


Figure 2.2. Aldehyde content and degree of substitution of periodate oxidized cellulose fibers as a function of reaction time.

2.4.2. Nitrogen-containing derivatives

The aldehyde groups in oxidized cellulose were undergone the Schiff base reaction with n-butylamine to produce the alkylated cellulose. However, at higher reaction times, the fibers decomposed completely and the reaction medium turned to a yellow-brown clear solution with some brown sticky product, which was hard to collect and purify. Purifying this gooey substance and getting rid off excess unreacted chemicals is a cumbersome practice. Longer reaction times resulted in a complete clear yellow-brown liquid with almost all the fibers gone. At lower initial aldehyde content or at lower reaction times, however, some of the fibers were still intact and collectable but at very low yields. The yield of the recovered fibers with their charge content can be seen in table 2.1.

Table 2.1. The experimental conditions, charge content and yield of different Schiff base reactions of DAC with primary amines.

Sample	Initial aldehyde content (mmol/g)	Aldehyde content after crosslinking (mmol/g)	Schiff Base reaction			Final aldehyde content (mmol/g)	Yield (%)
			Amine	Amount (mmol)	Time (h)		
DAC1-Ba1	3.8	-	Butylamine	4.9	24	0.9	73.1
DAC2-Ba2	8.5	-	Butylamine	11.0	24	2.5	60.4
DAC3-Ba3	11.8	-	Butylamine	15.3	24	6.0	36.8
DAC3-Cr1	11.8	-	1,12-diaminododecane	1	72	9.9	96.7
DAC3-Cr2	11.8	-	1,12-diaminododecane	2	72	8.0	97.2
DAC3-Cr3	11.8	-	1,12-diaminododecane	3	72	6.1	96.8
Cr1-Ba1	-	9.9	Butylamine	12.9	72	2.4	86.0
Cr2-Ba2	-	8.0	Butylamine	10.4	72	1.9	90.6
Cr3-Ba3	-	6.1	Butylamine	7.9	72	1.3	92.8

The reason for fiber disintergration is not very clear, but could be attributed to the possibility that as the number of aliphatic groups within the cellulose interior wall increases with reaction time, there are less aldehyde groups available for forming bridging hemiacetal bonds between the cellulose chains. Also the steric effect due to the crowding of the long aliphatic groups causes repellence between the cellulose chains and the decrease of the hemiacetal bonds between the chains within the fibers can contribute to breaking of the fibers or the dissolution of the cellulose chain in the non-polar organic solvent. Therefore, if any of the fibers remain intact, this is mostly due to lower charge content and amount of aldehyde groups reacting with alkylamine. If there is enough conversion then the fibers will disintegrate. As it can be seen that the recovered intact fibers still have a significant amount of aldehyde groups left.

The disintegration can also be explained by the fact that the oxidation reactions occur to a large extent in the amorphous domains of cellulose, and with the introduction of long aliphatic chains these domains become soluble in organic solvents. The amidated product is a mixture of different forms of cellulose particles and nano-crystalline cellulose (NCC) stabilized with dissolved butylated cellulose (DBC).

As a result, to increase the structural stability of the fibers and prevent them from disintegration, cellulose chains within the fibers were cross-linked with a 1,12-diaminedodecane as cross-linker agent in a Schiff base reaction. With this procedure the fibers stayed intact after long reaction times, and the yield of the recovered fibers was as high as 97.2%. These cross-linked fibers now reinforced with amide bonds within the chains were further alkylated using n-butylamine in another Schiff base reaction. Charge content measurements prove that the butyl groups were indeed introduced in the place of the unreacted aldehyde groups remaining after the crosslinking. These new fibers showed strong stability and did not disintegrate upon longer reaction times. The yield and charge content of the fibers at different stage of the experiment can be seen in table 2.1.

2.4.3. Surface chemical properties

The changes in chemical structures were examined by FTIR and solid state ^{13}C NMR. The FTIR spectra of the unmodified and modified cellulose pulp with different chemical modification are shown in figure 2.3. The broad peak at 3310 cm^{-1} is due to the stretching of –OH groups, the peak at 1300 cm^{-1} is for the –OH bending vibration [18];

the peaks at 1050 cm-1, 1430 cm^{-1} and 2900 cm^{-1} are assigned to CH_2-O-CH_2 stretching, -CH_2 scissoring and C-H vibration respectively [19].

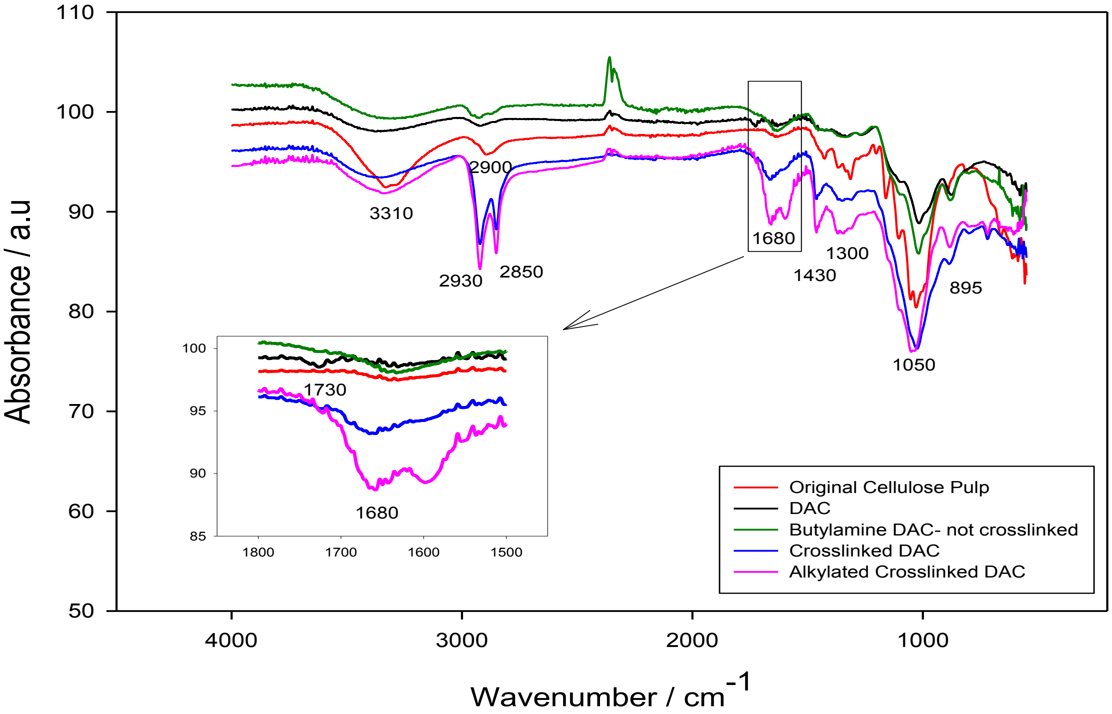


Figure 2.3. FTIR spectra of unmodified and modified cellulose

The spectrum for DAC shows characteristic bands at 1730 and 895 cm^{-1} regions. The diffuse band at 895 cm^{-1} is assigned to hemiacetal and hydrated forms of aldehyde groups and the band at 1730 cm^{-1} is due to the aldehyde carbonyl groups [20]. The characteristic aldehyde peak at 1730 cm^{-1} it's not very sharp and direct spectroscopic detection of this peak is often hampered by the presence of hydrates and hemiacetals, which are formed depending on the moisture content of the sample material [21].

Looking at the spectra of cross-linked fibers, the introduction of long twelve member chains is further confirmed by the strong peak at 2850 and 2930 cm^{-1} which are assigned to asymmetric and symmetric –CH2- stretching and shows that high a amount of carbon groups were introduced, which in turn indicates that relatively long aliphatic chains were introduced to the cellulose.

In the spectra of alkylated fibers, the functionality of the alkylated cellulose is confirmed by the disappearance of the aldehyde C=O stretch band at 1730 cm^{-1} and the appearance of amide C=O stretch bands at 1680 cm^{-1}. The not cross-linked alkylated DAC spectrum has a small peak at 1680 cm^{-1} compared to the peak at 1015 cm^{-1}; the alkylated cross-linked DAC has, however, a much stronger peak at 1680 cm^{-1}. This shows that after cross-linking, the fibers can undergo a Schiff base reaction with butylamine to a higher extent and higher amounts of alkyl groups can be introduced to the fibers. These results show that the multifunctional amines were successfully introduced into the modified fibers.

Solid ^{13}C NMR

Spectra of periodate oxidized, cross-linked, alkylated and cross-linked alkylated cellulose are shown in fig 2.4. In the spectrum for DAC, a characteristic feature is the lack of aldehyde carbonyl signal expected at 175-180 ppm even at high oxidation degrees. This indicates that the aldehyde groups of solid DAC are hydrated or forming hemiacetals with remaining hydroxyl groups [4].

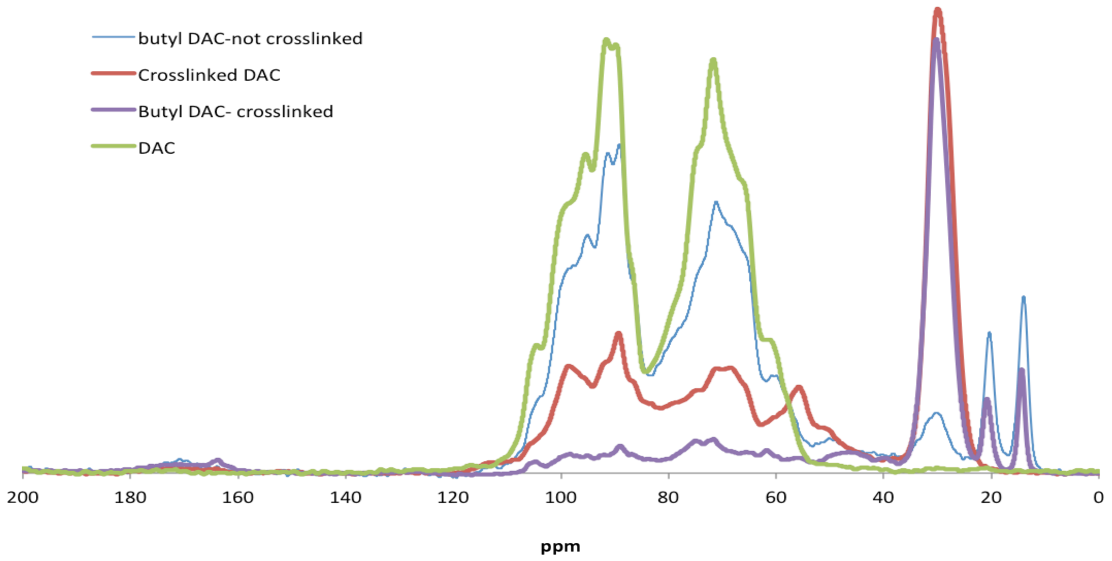


Figure 2.4. Solid ^{13}C-NMR of chemically modified celluloses

The broad signal at 165-175 ppm is due to the amide carbonyl signal. It is more pronounced in both not cross-linked and cross-linked alkylated forms of cellulose.

The peaks at 15 and 20 ppm belong to aliphatic carbons. The relative intensity of these peaks compared to the intensity of the carbohydrate region, 60-110 ppm, is more pronounced in the butylated DAC that has been already cross-linked compared to the not cross-linked butylated one. This is another proof that when cross-linked, fibers are more capable of reacting with butylamine and not disintegrating at high alkyl group concentrations.

Almost all the chemical shifts of the 1,12-diaminododecane fall between 26 and 34 ppm. The characteristic broad peak at 28 ppm possibly encompassing all the shifts of the amino compound in cross-linked cellulose belonging to the twelve carbon of the diamine seen in the spectra for the cross-linked DAC. The relative intensity of the carbohydrate region, 60-110 ppm, compared to the intensity of the peak at 28 ppm decreases with increasing extent of crosslinking. (Figure 2.5.)

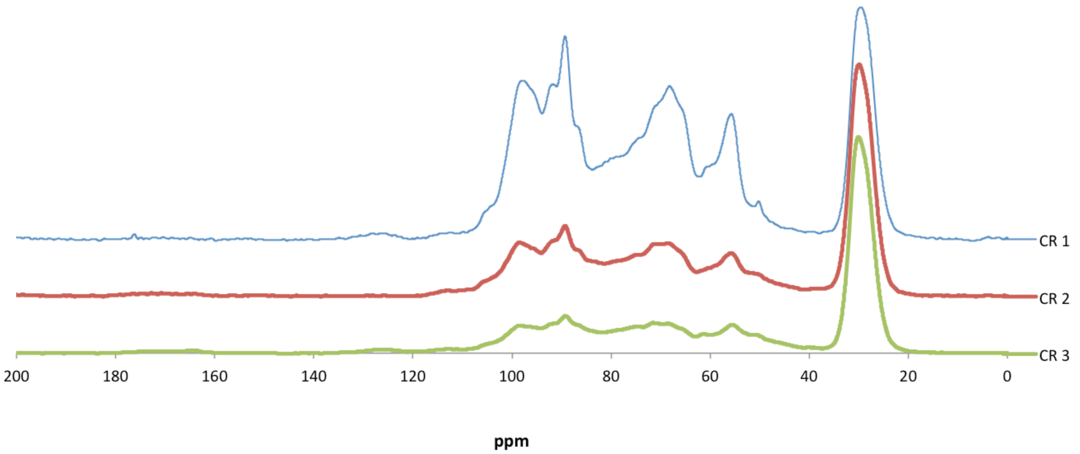


Figure 2.5. Comparison of Solid ^{13}C-NMR spectra of different cross-linked DAC.

2.4.4. Crystallinity of modified fibers

The products of each of the steps of the chemical modification on cellulose were examined by X-ray diffraction. The X-ray diffractograms of starting cellulose, DAC, alkylated and cross-linked products are shown in Figures 2.6 and 2.7. The typical crystalline and amorphous peaks of cellulose were assigned according to the literature [22]. The peak at the 2θ angle at 22.6° is the reflection at the 200 plane, which represents the main crystalline region of cellulose [5] and 2θ angles at 15.3° and 16.5° are the 101, $1\bar{1}0$ peaks respectively.

The crystallinity index (CI) of cellulose has been used for more than five decades to interpret changes in cellulose structure after physicochemical and biological treatment and it is calculated empirically according to an equation below by Segal et al. [23],

$C.I. = 100(I_{200}-I_{AM})/I_{200}$

where I_{200} is the intensity of the 200 planes reflection; I_{AM} is the intensity of the amorphous content reflection corresponding to the minimum in a diffractogram between the I_{101} and I_{200} peaks, where amorphous cellulose is maximum [24].

Typical X-ray diffraction pattern of native softwoods and oxidized native softwood can be observed in all the XRD curves of figure 2.6. It is seen that the intensity of the crystalline peaks of cellulose diminished with progressive periodate oxidation and the loss of crystallinity and lower CI values are consistent with previous observations [25, 4, 26]. It also indicates that no rearrangement of the cellulose structure into another crystalline form occurred. The calculated crystallinity indices (CI) obtained from these curves (79.3, 54.7, 28.7, 25.9 and 20.4%, respectively for original cellulose, 16h, 48h, 96h, and 144h DAC) decreased almost linearly as a function of the aldehyde content of cellulose. The loss of crystallinity apparently results from opening of the glucopyranose ring and destruction of ordered packing of cellulose molecules [27].

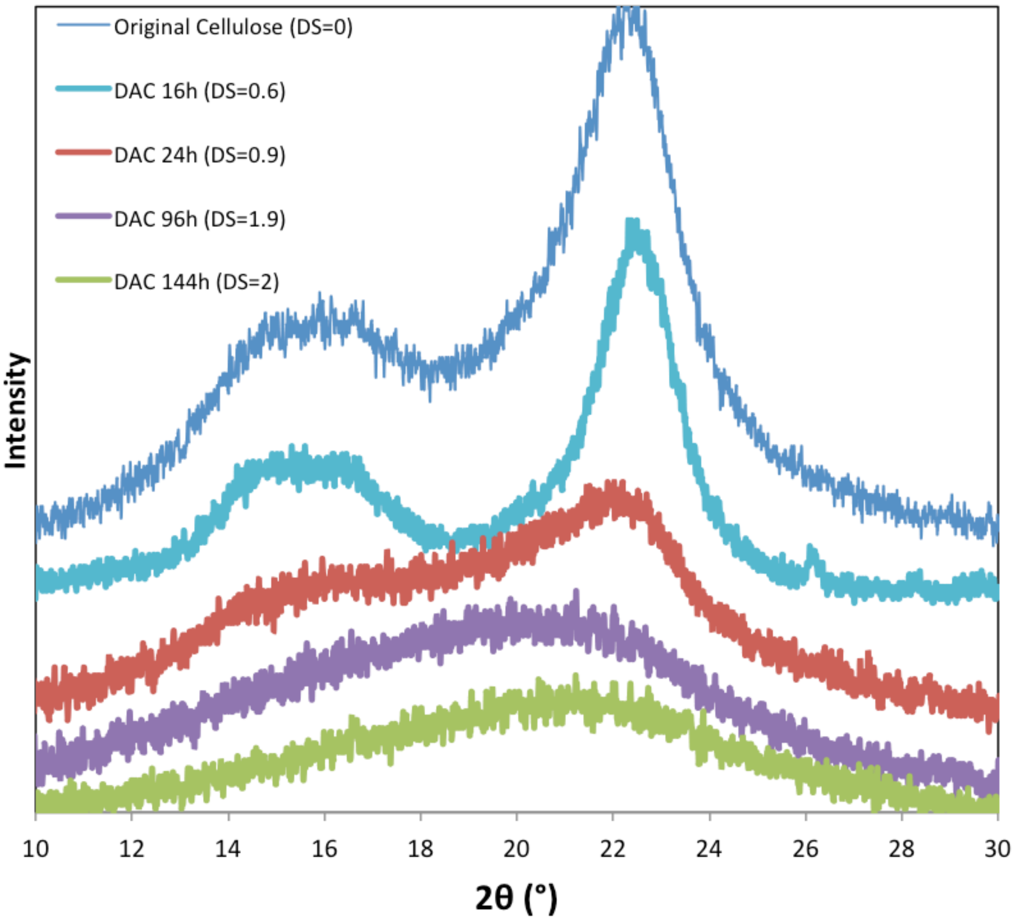


Figure 2.6. X-ray diffraction profiles of original and dialdehyde cellulose.

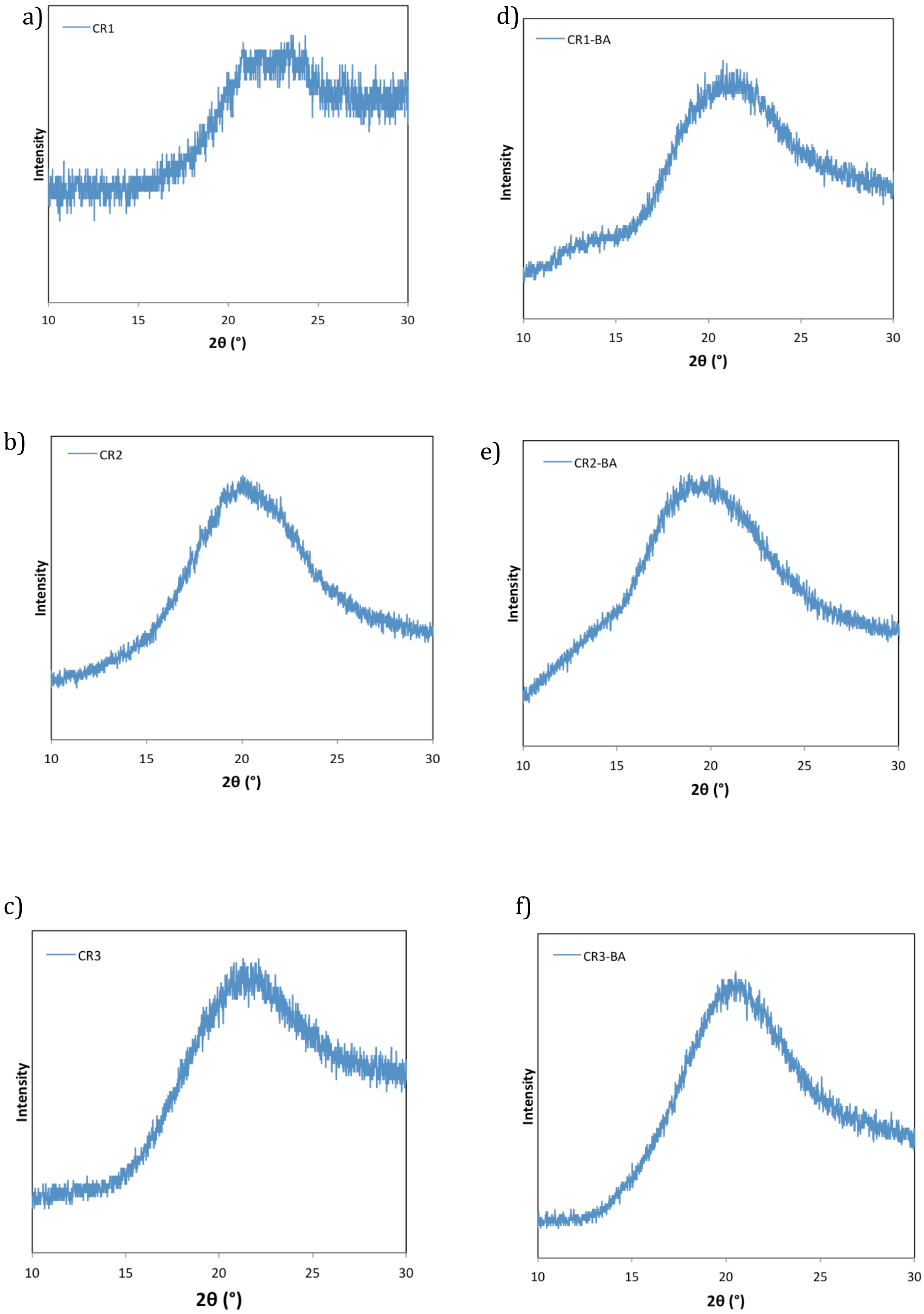

a)
CR1
Intensity
10
15
20
25
30
2θ (°)
d)
CR1-BA
Intensity
10
15
20
25
30
2θ (°)
b)
CR2
Intensity
10
15
20
25
30
2θ (°)
e)
CR2-BA
Intensity
10
15
20
25
30
2θ (°)
c)
CR3
Intensity
10
15
20
25
30
2θ (°)
f)
CR3-BA
Intensity
10
15
20
25
30
2θ (°)

Figure 2.7. X-ray diffraction profiles of (a) Cr1, (b) Cr2, (c) Cr3, (d) Butylated CR1, (e) Butylated CR2, (f) Butylated CR3 (see table 2.1 for charge content).

Figure 2.7 shows the effect of chemical modification on cellulose crystallinity for cross-linked and alkylated samples. Figure 2.7 (a, b, and c) are X-ray diffractorgrams of the cross-link product of the DAC sample with DS of 2 (DAC 144h) and figure 2.7 (d, e, and f) belong to the alkylated product of the cross-linked DAC. The crystallinity of the starting material (DAC 144h with DS=2) before cross-linking and alkylation is very low. We see very small changes in crystallinity after further modification and all of the samples have a large content of amorphous region. It can be seen that cross-linking and alkylation does not change the structure of DAC very much.

2.4.5. Vapor sorption of chemically modified cellulose

In general, water vapor sorption can occur either at the surface or in the bulk of a material. For fibers, it is mostly related to the total sites of water absorption in the fiber internal surface [28] and moisture uptake by cellulose is thought to occur mainly in the bulk of disordered region. So fibers with higher crystallinity should show lower moisture uptake at lower humidity's below 75% [29]. Even though the aldehyde groups are less prone to absorb water molecules than hydroxyl groups, the results of the moisture sorption of fibers seen in figure 2.8 show that the water take-up increases after periodate oxidation reaction, which is likely a result of the decrease in the crystallinity of the cellulose due to peridoate oxidation (as seen in section 2.4.4.). The resulting fibers are less ordered and therefore the moisture can penetrate more readily.

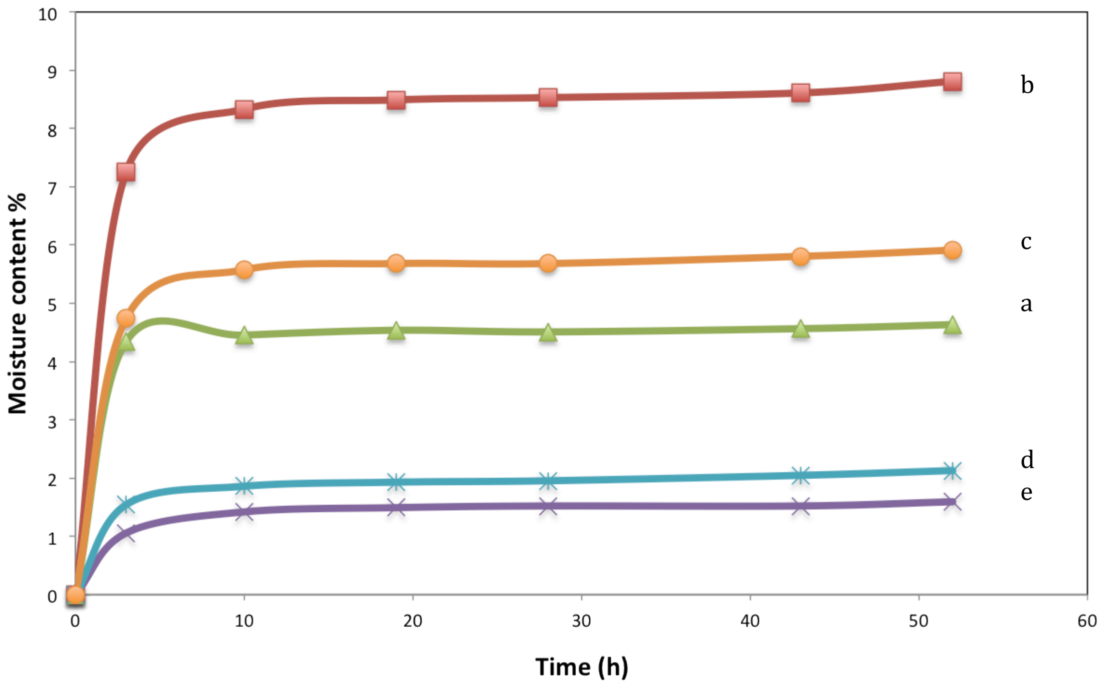


Figure 2.8. Moisture sorption profiles of (a) original cellulose, (b) dialdehyde cellulose (DAC), (c) alkylated DAC cellulose, (d) cross-linked DAC cellulose, (e) alkylated cross-linked DAC cellulose (DS of different samples can be seen in table 2.2).

In alkylated or cross-linked cellulose, moisture sorption decrease due to the decrease in available absorption sites for water molecules due to introducing long hydrophobic aliphatic groups. The introduction of amine linkage between the DAC and diamine causes the fibers to have less available aldehyde groups to absorb water molecules. Moisture sorption as low as 1.1% is obtained for the alkylated cross-linked fibers, which have a high amount of chemically bound alkyl groups. Moisture sorption decreases as the hydrophobicity increases [30]. The reason for this low moisture content can be attributed to the increase of the hydrophobic alkyl groups and the cross-linked groups within the chains, which prevent the fibers from binding with water molecules. Crosslinking the fibers can reduce the hygroscopicity and swelling of the cellulose because the sites where usually water take-up occurs, are now occupied with cross-linker [28, 30].

2.4.6. Thermal stability and decomposition properties

Weight loss and derivative weight loss (DWL) curves for all measured samples are shown in Figure 2.9 and 2.10. According to the literature, chemically modified cellulose, such as 2,3-dialdehydecellulose (DAC) has less thermal stability compared to unmodified cellulose [31]. This is mostly due to the fact that oxidation increases the amorphous region and hence lowers the thermal stability. In figure 2.9 (b), the DWL curve of the unmodified cellulose shows a big sharp peak, which has the highest initial decomposition temperature (300^{o} C) of all the samples. The DWL curves of oxidized cellulose all have two smaller peaks, with the intensity of the first peak increasing and the intensity of the second peak decreasing with increasing aldehyde content. First transition peak of all the oxidized samples are at the same place with the initial decomposition temperature of 220^{o} C. According to figure 2.9 (a), the first step weight loss between 150 and 400^{o} C decreases with the oxidation levels, which is in agreement with the previously reported results by Kim *et al*. [5].

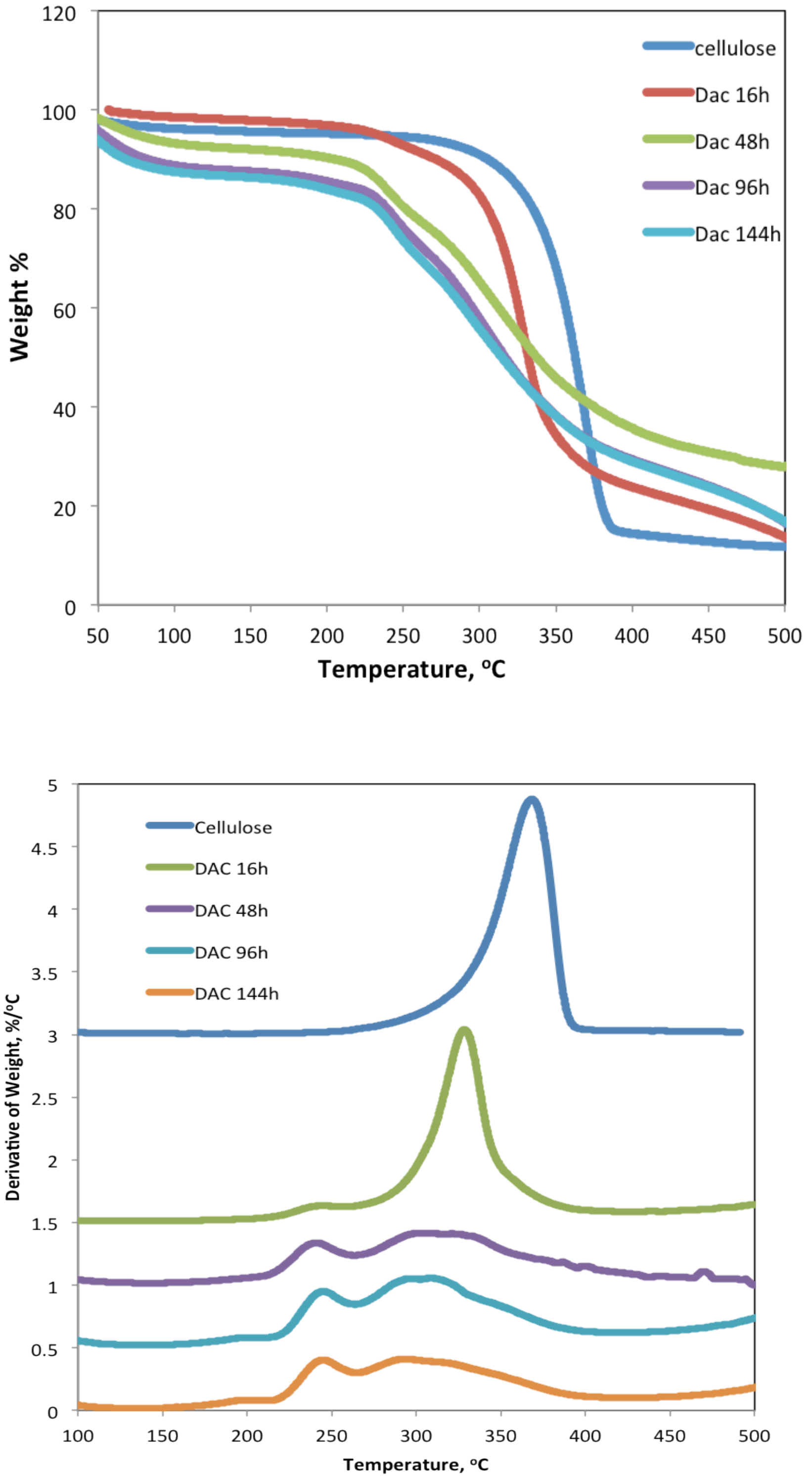


Figure 2.9. Thermogravimetric and derivative weight loss curve of original and dialdehyde cellulose.

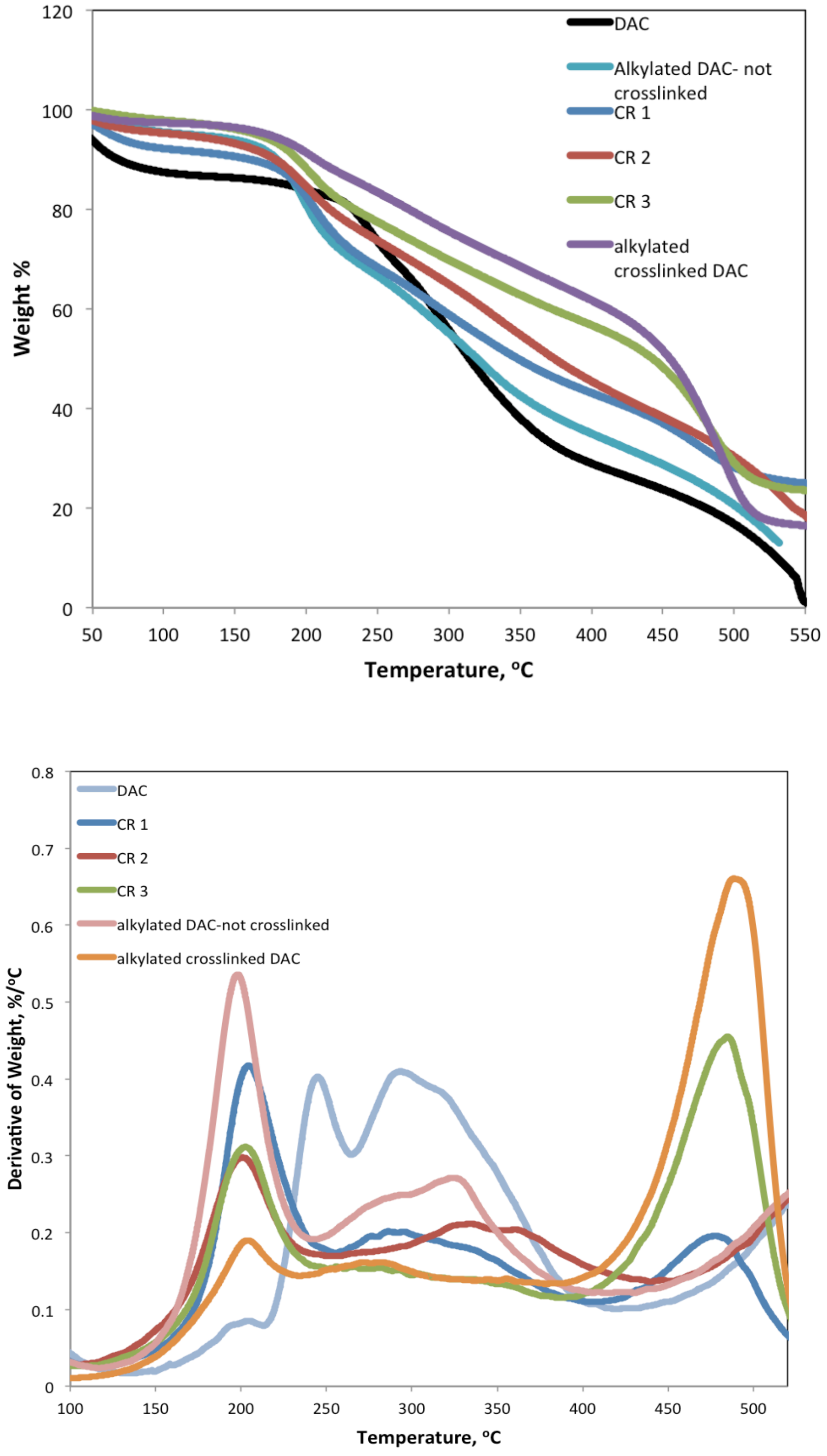
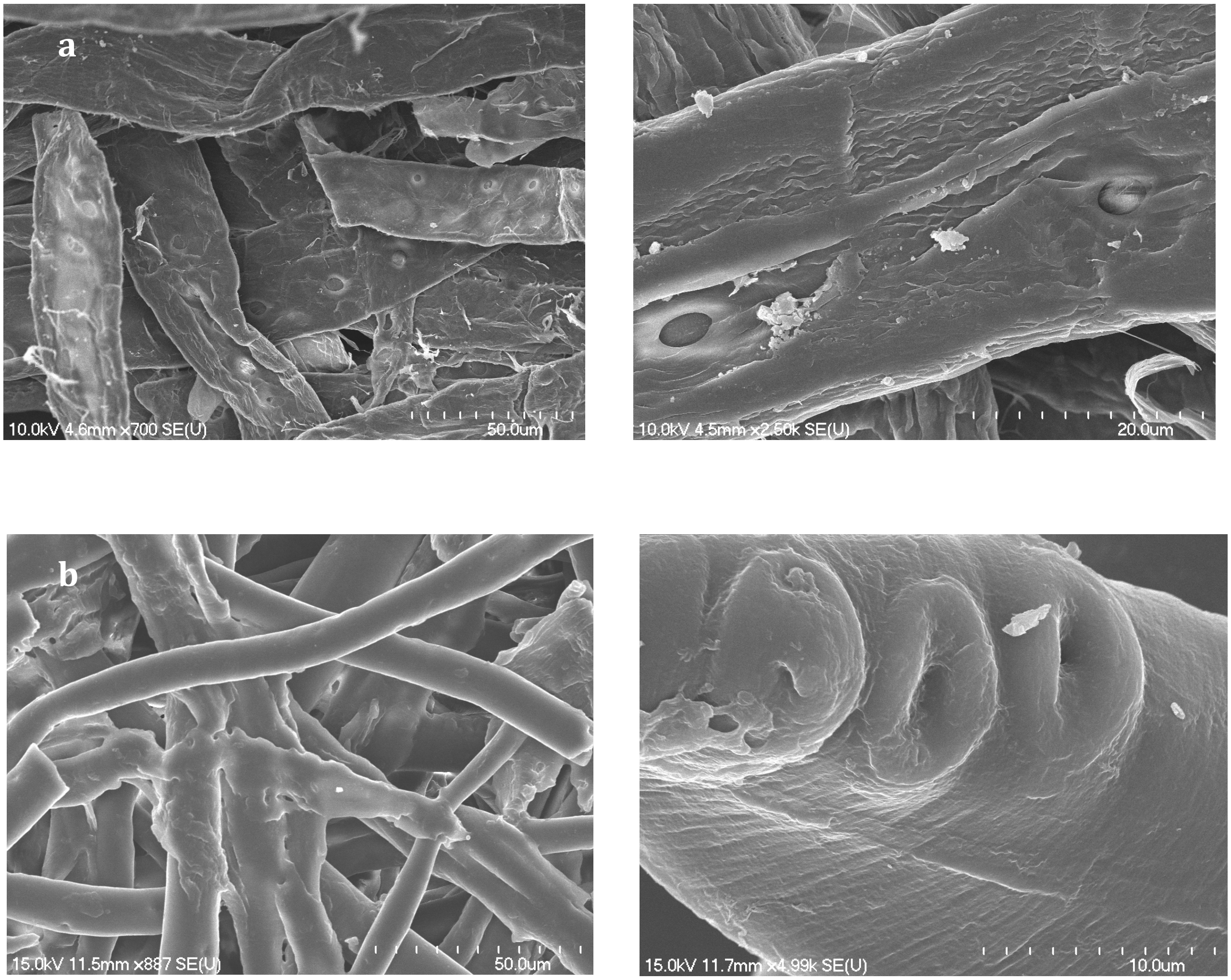


Figure 2.10. Thermogravimetric and derivative weight loss curve of dialdehyde, cross-linked and alkylated cellulose.

According to fig 2.10 (b), the initial decomposition temperature of all the modified samples (Shiff base amines) are at the same temperature (175° C) and are lower than the unmodified cellulose and oxidized fibers. It can be seen that after the reaction between the DAC and amines, the first step weight loss occurring between 150 and 400°C is more pronounced. The second step weight loss at 450°C, however, increased and fibers were found to have higher thermal stability. In the case of cross-linked fibers, this can be attributed to the possibility that the molecular chain mobility is somewhat restricted by chain crosslinking, so the thermal stability increased. The TGA results also indicated an increase in fiber hydrophobicity after modification, as shown by the absence of the typical moisture loss around 100° C, suggesting negligible water adsorption, compared with that of the original and oxidized fibers [32], which is also in agreement with the result obtained with moisture content measurements in section 2.4.4.

2.4.7. Morphological properties

The surface morphology of the fibers was studied by SEM imaging before and after the modifications. The effect on fiber ultrastructure can be seen in SEM analysis of cellulose fibers in figure 2.11. The surface of the original cellulose with visible pittholes is seen in figure 2.11a at two different magnifications. In figure 2.11b alkylated fibers seem more swollen compared to the collapsed structure of the original fibers. Figure 2.11c shows the hierarchical surface morphology of the fibers created after cross-linking. Lastly, in figure 2.11d, the same kind of hierarchy can be seen for alkylated cross-linked fibers. Moreover, from looking at the images of the unmodified and modified fibers it can be seen that the alkylated and cross-linked fibers are not collapsed and the width of the fibers is smaller than the width of the collapsed unmodified fibers seen in figure 2.11a. This can be explained by the many hydrophobic chains inside the fiber, which prevent the lumen from collapsing.



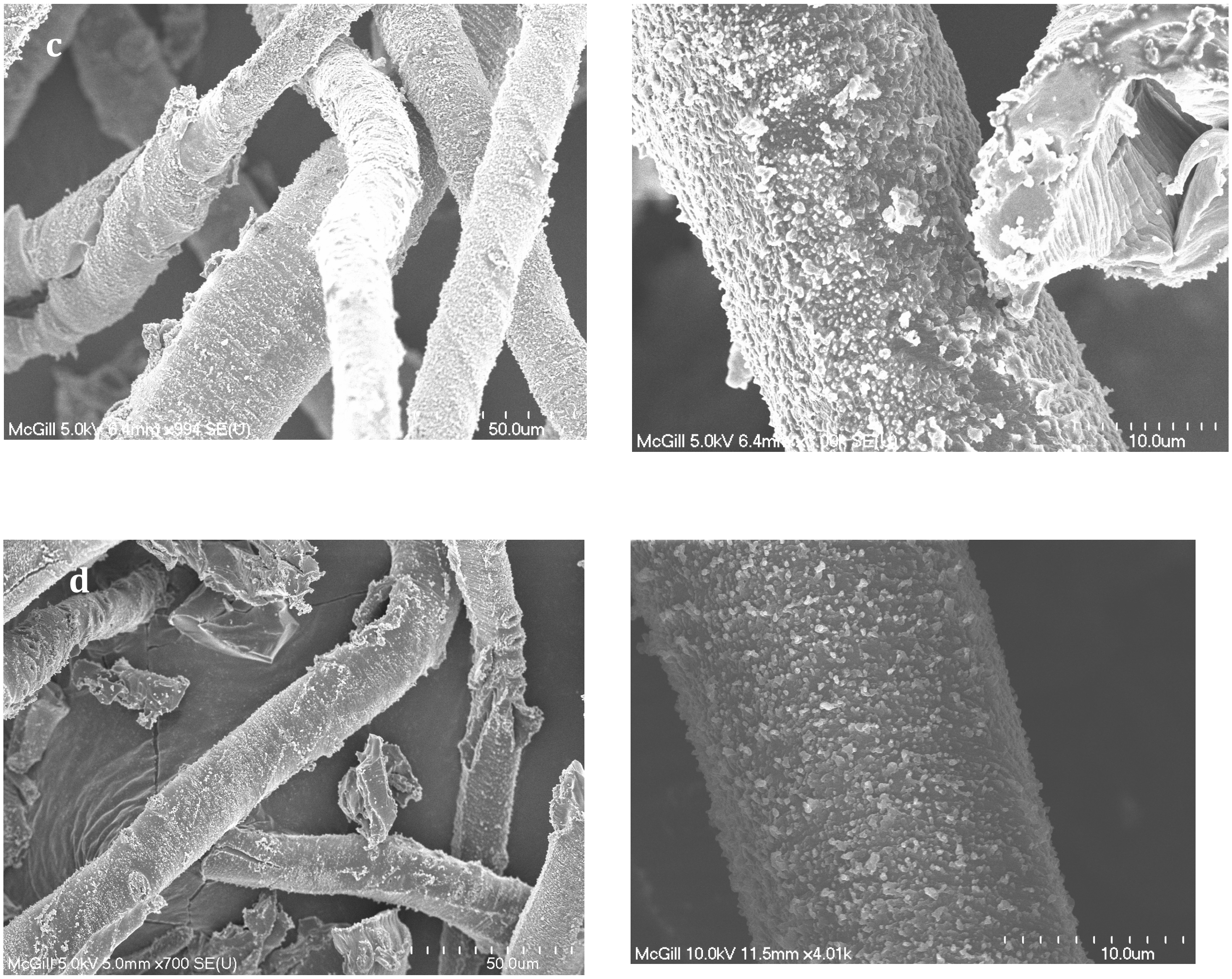


Figure 2.11. SEM images of (a) unmodified cellulose fiber (DS=0), (b) alkylated DAC fibers (DS=0.92), (c) cross-linked DAC fibers (DS=0.95) and (d) cross-linked alkylated DAC fibers (DS=1.75).

The cross-linked fibers, whether alkylated or not, show increased surface roughness, with submicron-sized dimensions. The reason for this phenomenon is not very clear, but it can be attributed to the fibrils cross-linked back on the surface of the fibers by diamine cross-linker. The decline observed in the structure of the fibers indicates that the reaction went deeper in the structure of the fibers. The surface roughness of these modified fibers is shown with higher magnification in figure 2.12. The size of the features varies from 20 nm to 1μm.

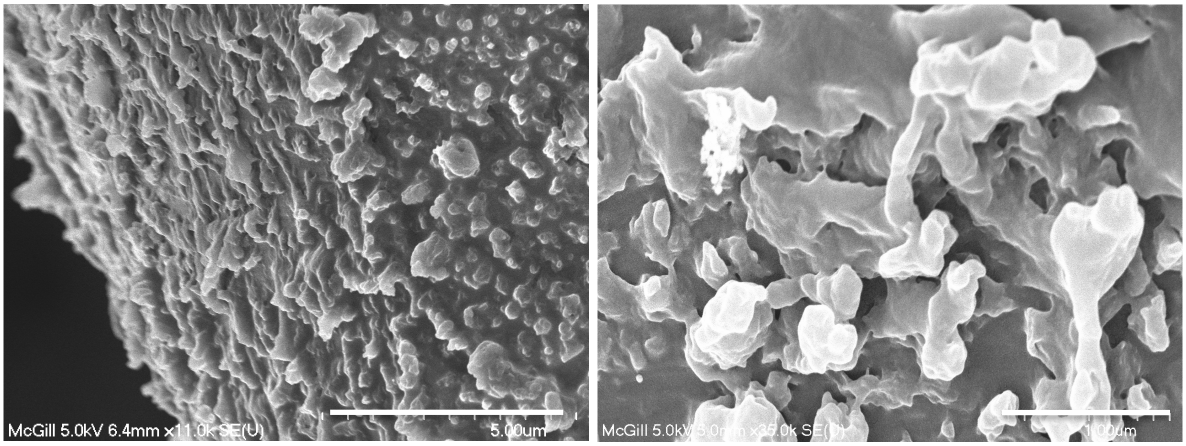


Figure 2.12. Higher magnification SEM images of cross-linked fibers with 5 μm (Left image) and 1μm (Right image) scale bars.

2.4.8. Contact angle measurements

As mentioned earlier, cellulose is hydrophilic in nature, which is mostly due to their abundant hydroxyl groups and the hydrogen bonding with water molecules. The considerable increase in the hydrophobicity of the modified fibers is demonstrated by the corresponding increase in their contact angle with water (table 2.2.). Due to the replacement of the hydroxyl groups by the non-polar aliphatic chains, the surface energy of the modified cellulose fibers decreased substantially after chemical modification with butylamine and 1,12-diaminododecane essentially due to the reduction in its polar component.

Table 2.2. Water contact angles of different samples prepared with Schiff base reaction with their respective degree of substitution (DS).

Sample	Initial Aldehyde (DS)	Aldehyde content after cross-linking (DS)	Final degree of substitution of product (DS)			Contact angle (θ)
			Final Aldehyde (DS)	Butylamine (DS)	Diamine (DS)	
DAC1-Ba1	0.63	-	0.15	0.38	-	105±2
DAC2-Ba2	1.42	-	0.42	1.00	-	113±3
DAC3-Ba3	1.97	-	1.00	0.97	-	126±2
DAC3-CR1	1.97	-	1.65	-	0.32	129±1
DAC3-CR2	1.97	-	1.33	-	0.64	139±1
DAC3-CR3	1.97	-	1.02	-	0.95	140±1
CR1-Ba1	-	1.65	0.41	1.24	-	137±1
CR2-Ba2	-	1.33	0.32	1.01	-	143±1
CR3-Ba3	-	1.02	0.22	0.80	-	141±2

The hierarchical structures seen in the previous section including nanostructures obtained after cross-linking the fibers and micrometer scale roughness inherent to the cellulose fiber surface, give a novel approach to constructing very hydrophobic surfaces, similar as occurring in the natural world, and provide an alternative method to roughened structures created by traditional polymer grafting, nanoparticle deposition, or other artificial means [33].

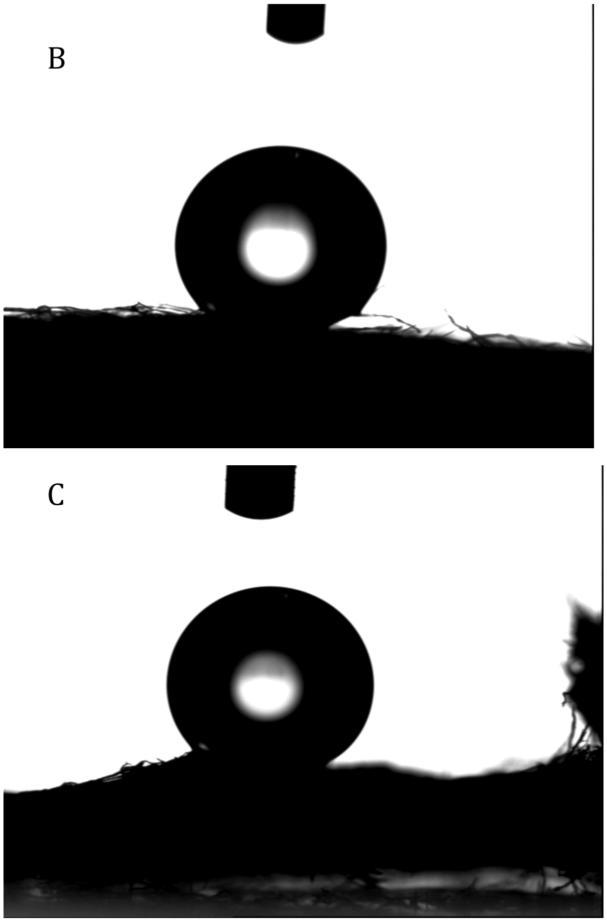


Figure 2.13. Profiles of water contact angle on (A) butyl cellulose (not cross-linked) (B) cross-linked cellulose (C) butyl cellulose (cross-linked).

2.5. Conclusion

Cellulose fibers were chemically modified with sequential regioselective periodate oxidation and Schiff base reactions with amine terminated molecules. The oxidized celluloses with degree of substitution as high as 2 were obtained and coupled with butylamine via a Schiff base reaction; Fibers were successfully cross-linked by 1,12-diaminododecane to prevent the fibers from disintegration during the butylamine reaction. This procedure yielded highly hydrophobic and low-hygroscopic cellulose materials with various extents of surface and bulk modification. These amidated cross-linked fibers showed improved thermal stability and moisture sorption. They had contact angles as high as 143^{o}C possibly due to their hierarchical surface morphology and lower polar contribution due to the introduction of hydrophobic aliphatic groups. From TGA and moisture sorption studies, the cross-linked fibers showed higher thermal stability and lower water absorption compared to the non-cross-linked fibers. All of the final products maintained their cellulose I crystalline structure based on angle X-ray diffraction results, and crystallinity indices of approximately 50%-70% were observed for all final samples. The unique characteristics of these fibers are very promising for their potential applications in composites, packaging and other technologies.

2.6. References

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Chapter 3. Cross-linking and Amidation of Carboxymethylated Cellulose

3.1. Abstract

Cellulose is a hydrophilic biopolymer that can be transformed into hydrophobic, non-hygroscopic polymer to enhance its potential applications in fields such as packaging, self-cleaning films and strength enhancing agent in polymer composites. To achieve this goal, here we introduce carboxyl groups into the cellulose fibers, to which long chain aliphatic amine groups can be grafted. Because introducing too many carboxyl groups leads to fibers disintegration, we decided to also cross-link a fraction of the carboxyl groups by a bioconjugation reaction. First, carboxymethylated cellulose fibers (CCF) were synthesized under alkaline condition using monochloroacetic acid (MCA) as carboxymethylating agent. Next, the modified cellulose fibers were cross-linked with an EDC assisted biocojugation reaction of carboxyl groups with adipic acid dihydrazide (ADH) to prevent fiber disintegration. The optimum pH for this reaction was found to be around 6.6. Most of the available carboxylic groups on the fibers were substituted during the cross-linking reaction and therefore more carboxylic groups were introduced to the cross-linked fibers with a subsequent alkaline reaction with MCA. The resulting carboxymethylated cross-linked fibers were then reacted with n-butylamine to introduce non-polar aliphatic amine chains. The modified fibers were characterized by a variety of techniques, such as conductimetric titration, infrared spectroscopy (FTIR), scanning electron microscopy (SEM), mechanical properties such as tensile strength and young modulus, water contact angle and water vapor transition rate (WVTR) measurements.

The modified fibers had higher tensile strength and lower WVTR values. Values as low as 75 g m^{-2} day^{-1} were obtained for butylated cross-linked cellulose films. The highest tensile strength and Young modulus obtained were 91 MPa and 4.80 GPa, respectively.

3.2. Introduction

Cellulose, an inexhaustible raw material, is a natural carbohydrate polymer consisting of repeating β-D-glucose monomer units. A large amount of research has been focused on natural cellulose fibers, and the interest in associated polymer systems based on this natural polymer, which is biodegradable and environmentally friendly, is growing [1]. The ether and ester derivative of cellulose such as methyl cellulose (MC), hydroxypropyl cellulose (HPC), and the ionic carboxymethyl cellulose sodium salt (NaCMC) have many applications in manufacturing detergents, oil production, and textile, paint, food, and cosmetic industries [2]. Hydroxyl groups at the 2-, 3-, or 6-positions of the anhydro-glucose units are reacted with monochloroacetic acid (MCA) to form the carboxymethyl cellulose (CMC) derivative [3]. Carboxyl groups are reactive entities and carboxymethylation of the fibers makes them more reactive toward further chemical modification, which can extend their applications [4]. There has been two approaches to chemically modify these partially substituted cellulose ethers. One is to introduce new functional groups at free un-substituted hydroxyl groups in the anhydroglucose units, and the second method is the selective modification of the already present carboxyl substituents [1]. This was first introduced by Landoll [5] and studied by several other groups [6, 7]. These modified cellulose derivatives have many enhanced properties and applications [8].

The EDC-assisted cross-linking of water-soluble cellulose derivatives has been quite extensively studied in the past [9-11]. EDC is known to promote cross-linking of different polysaccharide molecules through both ester formation between COOH and OH [10] and amide bridges if there are primary amines present [13]. Such reactions occur at very precise conditions, without EDC participating itself in the bond. Instead EDC gets converted into a stable urea derivative and is released into the reaction medium as a nontoxic byproduct [10, 12].

However, in the case of porous solid cellulose fibers the efficiency of heterogeneous reactions is not comparable to homogenous reactions. Therefore, if there are a sufficient number of carboxymethyl charge groups introduced to and within the cellulose fibers, there is the possibility to cross-link the microfibrils within the fibers and improve the strength of the fibers and keep their structure intact [14].

In a recent study proteins were cross-linked through their COOH-containing residues using the EDC/dihydrazide approach [15]. Different dihydrazide molecules were studied and it was found that the minimum length of these molecules required to cross-link the proteins was 5.8 Å. Therefore adipic acid dihydrazide (ADH) can act as a suitable spacer within the fibers and moreover, due to its water-soluble characteristic has the required mobility for a good cross-linker in water.

Studies to make new substituted CMCs that have less thermodynamic affinity for water have gained interest recently [1, 16, 17]. By varying the nature of amine and degree of amidation, one can achieve new cellulose derivatives with new characteristic and soluble in a variety of solvents.

In this study, we prepare and examine new cellulose derivatives by first introducing carboxyl groups to the anhydro-glucose ring followed by cross-linking the carboxymethylated fibers with EDC assisted bioconjugation reaction of ADH and the substituted carboxyl groups. To introduce more functional groups after cross-linking, more carboxymtheylation is required since most of the carboxyl charge groups react with ADH. Following the second cabroxymethylation, fibers then undergo another bioconjugation reaction with n-butyamine to introduce non-polar aliphatic amine groups to the available carboxyl groups. In order to find out the most efficient reaction conditions several parameters are varied such as, monochloroacetic acid (MCA) concentration, carboxymethylation temperature, and EDC assisted reaction pH. The resulting modified fibers were characterized with a variety of techniques such as FTIR spectroscopy, SEM imaging, water contact angle and WVTR measurements.

3.3. Experimental

3.3.1. Materials

Pretreated never-dried softwood kraft pulp supplied by FPInnovations was used as starting cellulose material. Chemicals used for carboxymthylation and titration include: monochloroacetic acid (MCA), sodium hydroxide (NaOH) and hydrogen chloride (HCl) standard solution (0.1 M, 0.5 M), all purchased from Sigma-Aldrich, and sodium chloride (NaCl) from ACP chemistry. Chemicals for cross-linking and amidation: 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) with ≥97% purity and adipic acid dihydrazide (ADH) ≥98% pure were obtained from Fluka and Sigma, respectively. 1,12-

diaminododecane, and n-butylamine were purchased from Sigma-Aldrich. All chemicals were used as received. Milli-Q water was used throughout the experiments.

3.3.2. Methods

3.3.2.1. Preparation of carboxymethylated cellulose fibers (CCF)

Sequential experiments were conducted as follows: a modified carboxymethylation method was used. In this method fibers are first impregnated with MCA. By letting MCA molecules penetrate the fibers before activation with sodium hydroxide, more uniform modification of the interior and exterior of the fibers is possible. Based on the reaction scheme seen in figure 3.1, the dried pulp is first impregnated with sodium monochloroacetate (MCA). A desired amount of MCA (15, 30 or 40 g) is initially dissolved in water and added to the pulp (2 g effective weight) together with 30 mL of a NaCl solution in water (0.2N) in a 1-L, covered round-bottomed reactor flask equipped with a stirrer. The mixture was then stirred at 200 rpm for 5 hours to allow the chemicals to penetrate the fibers. Next, the estimated amount of aqueous NaOH ranging from 10-30% was added into the reactor flask and the reaction was stirred at 300 rpm at the desired temperature (55^{o}, 65^{o}, or 75^{o}C) for 5 hours. After 5 hours the reaction mixture was left to cool down to room temperature with continuous stirring overnight. The reaction pH was then adjusted to 4-5 by adding 0.5 N HCl to get rid of excess NaOH. Then the products were purified by dialysis for 24 hours. The effect of temperature and MCA and NaOH concentration was studied and the optimum condition for the carboxymethylation reaction in water was evaluated.

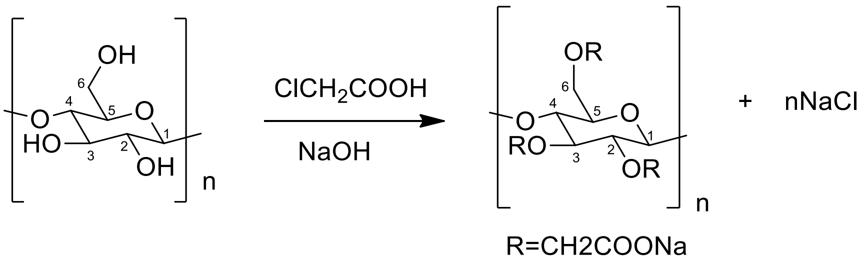

Figure 3.1. Reaction scheme for carboxymethylation of cellulose

3.3.2.2. Cross-linking CCF

After the first carboxymethylation step, excess amount of EDC and ADH were added to carboxymethylated cellulose under various pH conditions. The reaction was performed at different pHs in order to evaluate the effect of pH on the cross-linking and amidation steps. Based on the numbers seen in table 3.2 (section 3.4.1.), pH 6.6 was found to be the most effective. Therefore, unless otherwise stated, the pH during this reaction was typically adjusted to 6.6 with 0.5 N HCl after adding EDC and ADH to get optimum conversion. This mixture was allowed to react overnight at room temperature under magnetic stirring. To get rid of unreacted or physically absorbed reactants, fibers were then washed with a water and ethanol mixture twice and filtered and redispersed in distilled water.

The introduced carboxyl charge groups are consumed in the cross-linking step. Therefore to introduce more carboxyl charge groups on the cross-linked fiber, a second carboxymthylation reaction with identical conditions as section 3.3.2.1. was performed immediately after cross-linking the fibers.

3.3.2.3. CCF amidation

In order to hydrophobize the cross-linked carboxymethylated cellulose fibers (CCF) obtained, butylamine groups were introduced to the substituted carboxyl groups. First, two gram of pulp was added to the water (2% consistency). Excess amount of EDC and butylamine were added to react with CCF pulp dispersed in distilled water at room temperature overnight with magnetic stirring. The reaction of CCF with n-butylamine was performed under different pH conditions to find an optimum pH for the reaction. The same pH of 6.6 as before was found to be the most effective as seen in table 3.2. The reaction product was then washed with a water and ethanol mixture twice followed by a wash with 100% ethanol. The precise recipe used for each experiment is shown in table 3.1 and 3.2 in Section 3.4.1.

3.3.2.4. Film preparation

The films were prepared by dispersing the fibers in Milli-Q water to obtain a 0.5% (W/W) suspension. Next, 20 mL of this suspension was poured into a Millipore vacuum filtration glass holder with a polyester membrane filter (Sterlitech, pore size 0.2 μm, diameter 47 mm) and was filtrated until complete dryness under vacuum created by a water aspirator. Using this method, films with approximate 30 to 40 μm thickness and diameter of 25 mm were formed on the membrane. The films were then peeled from the membrane and were dried in an oven at 50 °C for 24 h and then at 105 °C for 2 h. The films were stored in a standard conditioned room (50% humility, 22 °C) for further measurements.

3.3.3. Characterization

3.3.3.1. Charge group content of carboxymethylated cellulose - Conductometric titration

The degree of substitution (DS), i.e. the average number of functional groups introduced per anhydro-glucose unit (AGU), mainly determines the properties of polysaccharide derivatives including carboxymethylated products. In addition, the exact determination of DS and functionalization pattern is important for the optimization of reaction conditions as well as for understanding of structure property relationships [18, 19]. Here, conductometric titration (Figure 3.2.) was used to measure the increase and decrease of carboxyl groups caused by the carboxymethylation reaction and crosslinking and amidation reactions respectively [14].

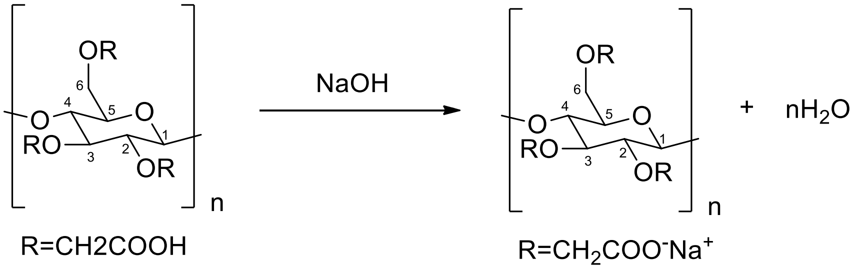

Figure 3.2. Reaction scheme for conductometric titration.

Conductometic titration was performed on a Metrohm 836 Titrando instrument. Samples were first purified by dialysis (Spectra/Pro; MWCO 1000) for 24 hours. The content of carboxyl groups was determined according to Robertson *et al.* [20]. A certain amount of sample (with a solid content of around 0.02 g depending on its concentration) and 2 mL (20 mM) NaCl solution were added to 140 mL milli-Q water, then this mixture was stirred to obtain a very well dispersed suspension. 0.1 M HCl was added to adjust the pH of this mixture to around 3.5. Then a 10 mM NaOH solution was added at a rate of 0.1 mL/min into the mixture up to a pH around 11. The part of the curve as seen in figure 3.3, which represents weak acid on the titration graph gives the carboxyl content based on the following equation:

Carboxyl content (mmol/g)= volume of NaOH (ml) x molarity of NaOH /dry cellulose (g)

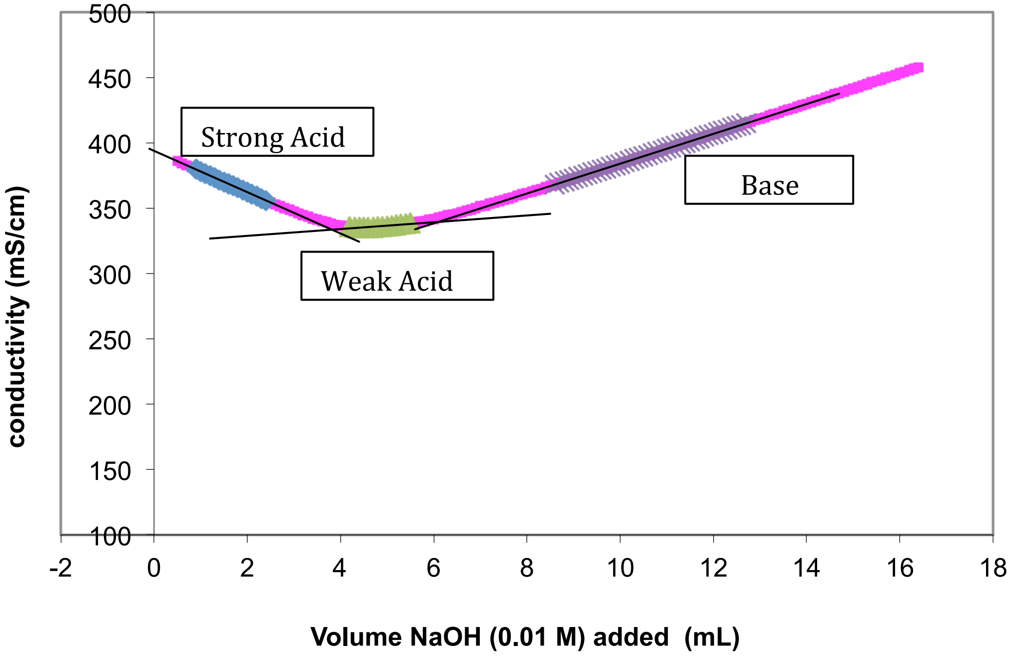

Figure 3.3. Acid-base titration curve to determine the carboxyl content.

3.3.3.2. Fourier Transform Infrared Spectroscopy (FTIR)

Samples were characterized with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), using a spectrometer from Perkin Elmer with single bounce diamond ATR accessory. Solid samples were placed directly on the ATR crystal and maximum pressure was applied by lowering the tip of the pressure clamp using a rachet-type clutch mechanism. All the spectra of measured samples were averaged from 32 scans from 550 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

3.3.3.3. Mechanical properties - tensile test and Young modulus

The tensile strength and Young's modulus of the papers and films were measured on an Instron Mini 44 tensile tester with 500 N load cell. The average thickness values were used in calculating tensile strength. Films were cut into strips 5 mm in width and 20 mm in length. Strips were stretched at a crosshead speed of 1 mm/min with a specimen gauge length of 10 mm.

3.3.3.4. Morphological properties - Scanning electron microscopy

The surface morphology of fibers was examined by field emission high resolution scanning electron microscopy FE-SEM (S-4700 Hitachi, Tokyo, Japan). The fibers were made into films by vacuum filtering as described in detail in section 3.3.2.4. and placed onto a double-sided tape adhered to sample holder surface and sputtered with gold and palladium for 2 min. The applied accelerating voltage and current were 5,10,15 kV and 10 μA, respectively.

3.3.3.5. Water hydrophobic properties - Contact angle measurements

Contact angle measurements were performed on a contact angle system OCA20 (Dataphysics, Germany) at room temperature. A 2 mL water droplet from a micro-syringe (Hamilton-Bonaduz) was put on the surface of a flat film and then pictures were taken every minute up to six minutes with a CCD camera. The results of at least three measurements were averaged for each film. Contact angles were calculated on the basis of the Young-Laplace equation by the software provided by the instrument.

3.3.3.6. Water permeability properties- water vapor transmission rates (WVTR)

The water permeability of the films and papers produced with this method are of importance for their applications. Hence, The rates of water vapor transmission through the prepared films were measured in a standard conditioned room (temperature: 22.2 ± 0.6 °C and relative humidity: 50 ± 3%).

Figure 3.4. The assembled glass vials used for WVTR determination.

The technique used here was a modification of the dry cup method described by ASTM, E 96-93 [21]. Thickness of the films was measured with a digit gauge at a minimum of three positions on a test specimen. The standard deviation of the thickness for each specimen was typically less than 4%. In this technique, a 15 mm diameter film was placed between two ring-shaped rubber washers with inner diameter of around 10 mm and outer diameter around 15 mm and then placed on the mouth of a specially made glass vial with a threaded neck, which was filled with anhydrous calcium chloride (Sigma-Aldrich) as desiccant to maintain 0% relative humidity (RH) inside the glass [22]. A plastic cap was tightly screwed on top of this vial to acquire a good seal between the film and the mouth of the vial, ensuring that water vapor can only travel though the film (Figure 3.4.). To ensure air circulations around this vial during the experiments an electric fan was placed before the vial. Water vapor absorbed by the desiccant through the film, leads to an increasing weight of the whole vial. The vials were re-weighed hourly (except at night) for 72 hours to calculate the WVTR.

The WVTR of films with units of g d^{-1} m^{-2} was measured from the following equation:

$$\text{WVTR} = \text{slope/film area} = \text{flux/ area}$$

where slope is the slope of the linear equation of weight gain (x-axis) as a function of time (y-axis).

3.4. Results and discussion

3.4.1. Effect of modification on cellulose

Both the irreversible carboxymethylation of the fibers and the actual EDC assisted cross-linking and amidation reactions on pulp fibers were further confirmed through the conductometric titration of samples before any modification, after carboxymethylation, after CCF/EDC/ADH treatment, after second carboxymethylation and after CCF/EDC/ butylamine. The measured carboxyl group concentrations for these reactions can be seen in table 3.1 and 3.2.

The maximum content of carboxyl groups obtained for the CMC reaction was 1.78 mmol/g (DS ~ 0.3). However, a further increase in NaOH concentration resulted in lower DS values. This observation and the low obtainable DS can be explained by the possibility that two competitive reactions are taking place simultaneously. The first reaction is the etherification between the cellulose and NaMCA in the presence of NaOH and the second reaction is between NaOH and NaMCA, which yields sodium glycolate (OH-CHCOONa) as seen in equation below [23]:

NaOH +ClCH2COONa → OH −CHCOONa + NaCl

Table 3.1. Experimental conditions used for carboxymethylation step

Sample	NaOH (g)	MCA (g)	Rxn time (h)	Temperature (^{o}C)	COOH (mmol/g)
Original	-	-	-	-	0.39
CMF-1	20	15	5	75	0.95
CMF-2	20	30	5	75	1.22
CMF-3	20	40	5	75	1.78
CMF-4	20	40	5	65	1.45
CMF-5	20	40	5	55	1.37
CMF-6	30	40	5	75	1.29

After the treatment with EDC/ADH the concentration of COOH returns close to the original value, confirming that the reaction takes place, since the reaction product holds no charge. The optimum pH for the bioconjugation EDC assisted reaction of amines with carboxyl groups is found to be at 6.6.

Table 3.2. Experimental condition of EDC assisted CCF cross-linking and amidation

Sample	Original COOH (mmol/g)	EDC[1] (mmol)	ADH[1] (mmol)	Butylamine[1] (mmol)	pH	Final COOH (mmol/g)
CMF-3	1.78	-	-	-	-	1.78
CMF-CR1	1.78	2.0	0.8	-	4.35	1.28
CMF-CR2	1.78	2.0	0.8	-	5.25	0.70
CMF-CR3	1.78	2.0	0.8	-	6.60	0.45
CMF-BU1	1.72[2]	2.0	-	1.8	4.45	1.16
CMF-BU2	1.72[2]	2.0	-	1.8	5.50	0.78
CMF-BU3	1.72[2]	2.0	-	1.8	6.65	0.50

Notes: [1]Dosages of reactant (EDC, ADH, butylamine) are expressed in mmol per gram of dried CMF pulp; [2]The charge content of the pulp after cross-linking and second carboxymethylation

3.4.2. Surface chemical properties - Fourier Transform spectroscopy (FTIR)

The FTIR spectra presented in figure 3.5. show typical absorption bands of a cellulose backbone. The absorption bands at 3300 cm^{-1} and 2900 cm^{-1} are due to O-H stretching vibration and C-H stretching respectively. The C-O stretching is found in the broad band at 1000-1100 cm^{-1} range. The band at 1300 cm^{-1} is characteristic of the –CH$_2$ symmetrical band [24].

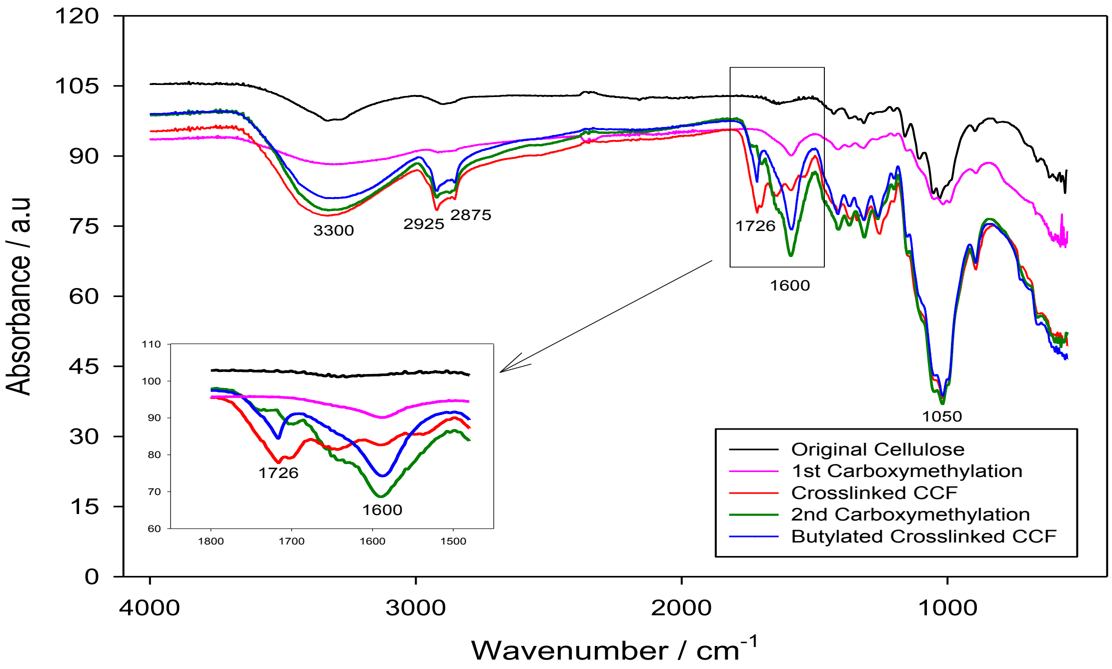

Figure 3.5. FTIR spectra of unmodified and modified cellulose fibers.

As expected, the characteristic carboxylate bands of CCF (mainly 1415 cm^{-1} and 1600 cm^{-1} due to symmetrical and asymmetrical stretching vibrations of C=O in carboxylate groups, stretching of O−C at 1320 cm^{-1} and broadening of the stretching vibration of OH centered at 3250 cm^{-1} [24]) were transformed into amide bands (1726

cm^{-1} for N–H amide I band, 1560 cm^{-1} for bending vibration of N-H groups) [25], while those characteristic for cellulose remain unaltered [26].

After substitution of even a small amount of the carboxyl groups with amide groups, we observed splitting of the band at 2900 cm^{-1}, which should be assigned to additional CH_2 groups of the primary amine used in amidation. The absorption bands at 2875 and 2925 cm^{-1} are assigned to symmetrical and asymmetrical vibrations of the CH_2 groups of the substituent, respectively [1].

3.4.3. Mechanical properties - tensile strength and Young modulus

Tensile strength and Young modulus are important properties of a material. After introducing carboxyl groups, the tensile strength of the modified cellulose films increases and is in the range of 60-75 MPa with a Young modulus as high as 3.46 GPa. This is due to the fact that the carboxyl groups can form ester bonds with hydroxyl groups and these bonds are stronger than the hydrogen bonds of the unmodified cellulose fibers. After cross-linking, the tensile strength of the films does not increase much. This increase can be attributed to the amide bonds between the fibers. However, the lack of ester bonds due to decreasing the number of carboxyl groups can be responsible for a smaller increase in the tensile strength upon cross-linking. Moreover, there is an increase in the Young modulus of the films after butylation.

Table 3.3. Tensile strength and Young modulus of the modified fibers (each result is based on three measurements)

Films	Tensile strength (MPa)	Young modulus (GPa)
CCF2	60±5	3.19±0.35
CCF3	75±2	3.46±0.20
Cross-linked CCF	82±4	3.60±0.32
2nd CCF	86±2	3.60±0.20
Butyl cross-linked CCF	91±2	4.80±0.15

3.4.4. Surface morphology - SEM

The carboxymethylated cellulose with higher DS showed a slimy appearance but still maintained some of their fibrous composition. Carboxymethylated fibers in their Na form are more swollen than the starting fiber material. The degree of swelling increases with increasing degree of carboxymethylation. The structure of the fibers remains intact after cross-linking and butylation reactions.

The morphological properties of modified cellulose films were studied with SEM imaging and the surface morphology of the films after carboxymethylation, cross-linking and butylation can be seen in SEM images in figure 3.6. The individual fibers can be seen in SEM images. Flat images also show that films have condensed structure but still show the presence of porous structures.

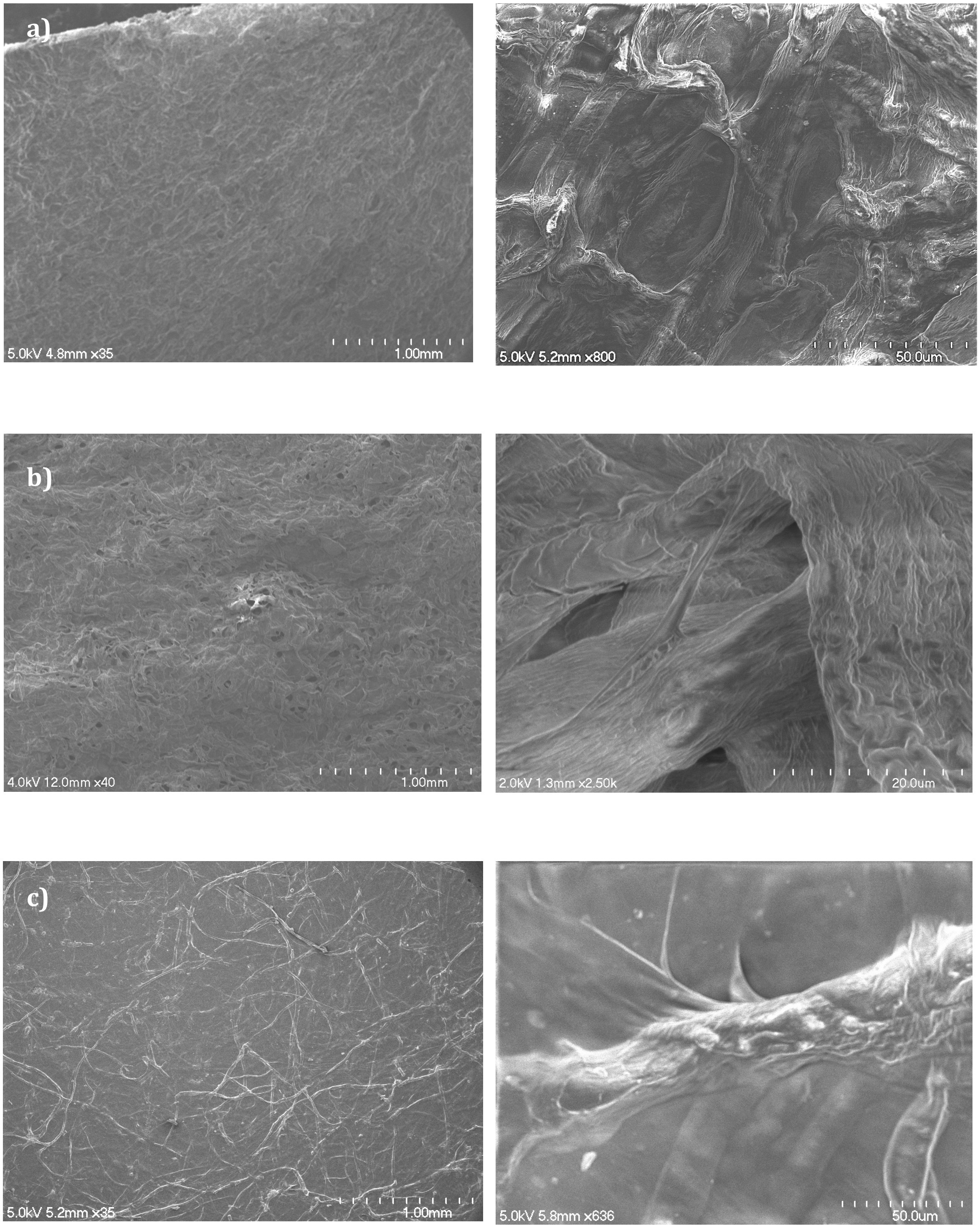

Figure 3.6. SEM images of (a) CCF fibers, (b) Cross-linked fibers, (c) Butylated CCF fibers

3.4.5. Water vapor transmission rate - WVTR

Water vapor transmission rates were determined using a method mentioned in section 3.3.3.6. WVTR of different samples including office paper, unmodified cellulose (as control), and modified cellulose films were determined and the results can be seen in Figure 3.7. Without any barriers, copy paper gave a WVTR of 1000 g m^{-2} day^{-1} [22]. Due to high affinity of cellulose fibers for water, unmodified microfibrillated cellulose film gives a WVTR of 800 g m^{-2} day^{-1}. WVTR value decreases to around 160 g m^{-2} day^{-1} with introduction of carboxyl groups to the anhydroglucose units. Even though the carboxyl groups are hydrophilic and have high affinity for water, this decrease can be attributed to the ester bonds between the carboxyl groups and the hydroxyl groups, therefore decreasing the number of available sites for hydrogen bonding. Moreover close packing of the films and smaller pores makes it more difficult for water vapor to travel through the films (figure 3.6). After introducing amide groups, the WVTR was decreased substantially to 135.6 g m^{-2} day^{-1} for cross-linked CCF films and 75.7 g m^{-2} day^{-1} for butylated cross-linked CCF films. This more than 50% reduction in WVTR after amidation can be attributed to the non-polar nature of the introduced aliphatic amide bonds. The lower water permeability of these films makes them better candidates for packaging and composites applications.

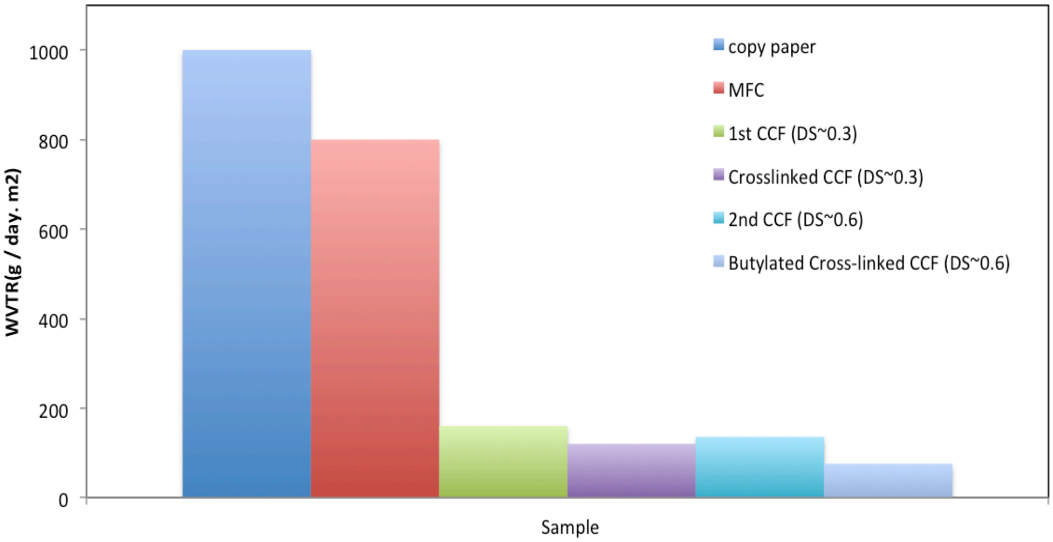

Figure 3.7. Comparison of WVTR measurements for different fiber samples

3.4.6. Water contact angle measurements

One intrinsic property of cellulose is its hydrophilic character. However, even after modifying cellulose fibers, they did not become hydrophobic and only minor hydrophobic characteristics were observed. Likely this is due to the low degree of substitution (DS~ 0.6), leaving a large number of hydroxyl groups unreacted. The initial water contact angle on the CCF film was around 65°. But this contact angle was not stable and dropped to around 50° at the end of the measurements (5 minutes later) which is due to the hydrophilic character of the carboxyl groups substituents. Even after amidation the contact angle was only increased to 95° and the fibers remained hydrophobic for only about 30 s. As it is illustrated in figures 3.7 and 3.8, the WVTR values decrease while the water contact angle increases after cross-linking and further Butylation.

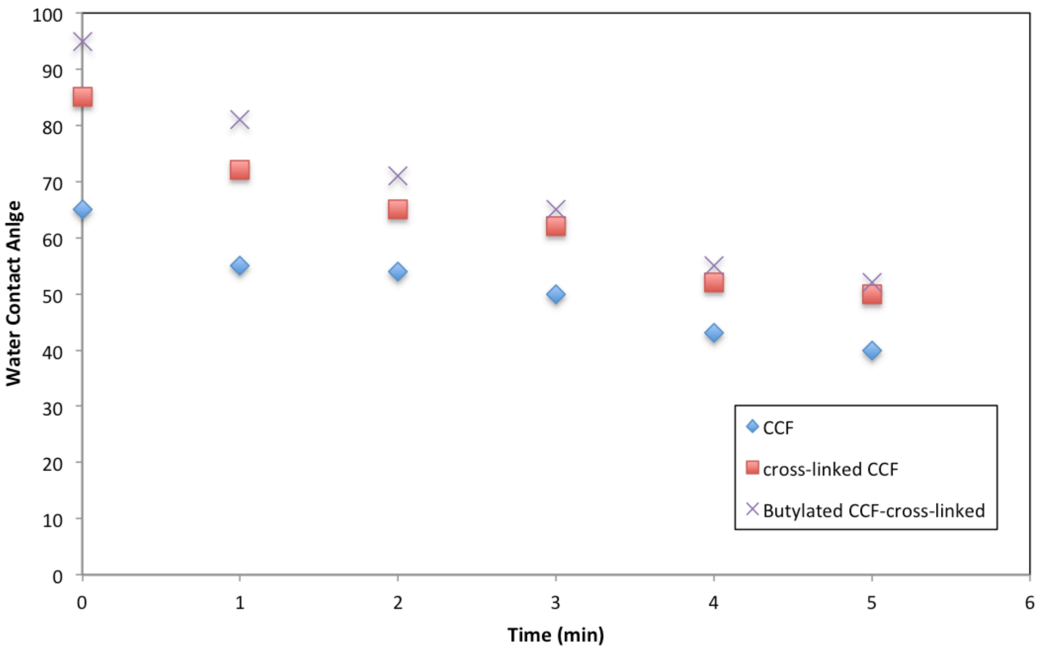

Figure 3.8. Change in water contact angle on the modified films with time

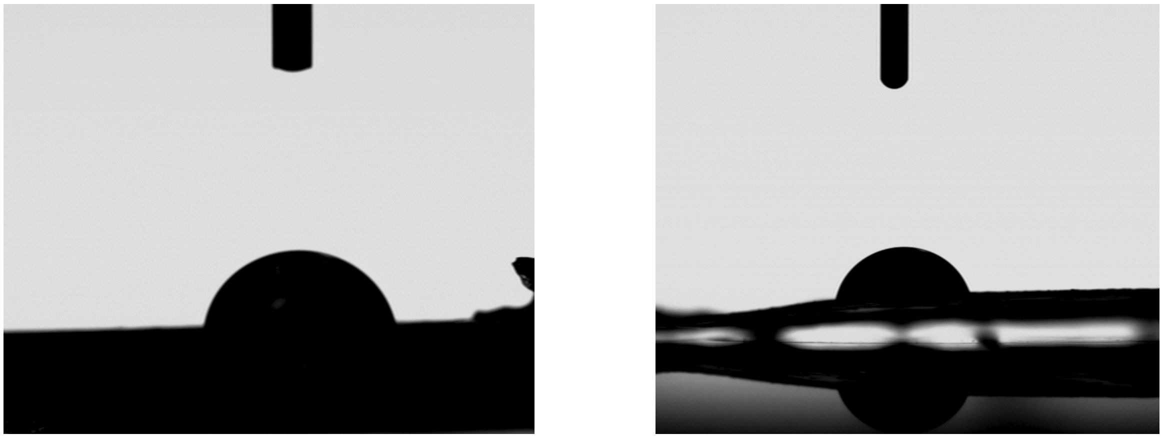

Figure 3.9. Images of water droplets on the surface of the modified films.

3.5. Conclusion

Novel cellulose derivatives were made with sequential chemical modifications. Carboxymethyl cellulose fibers (CCF) were produced under alkaline condition using monochloroacetic acid (MCA) as carboxymethylating agent. The modified cellulose fibers were cross-linked with EDC assisted biocojugation reaction of carboxyl groups with adipic acid dihydrazide (ADH) to prevent fiber disintegration. Cross-linked fibers were carboxymethylated for the second time to introduce more carboxyl groups. This cross-linked CCF was coupled with butylamine to introduce non-polar aliphatic long chain amine to the structure of the fibers. The new material showed higher tensile strength and Young modulus values. WVTR values as low as 75.7 g m^{-2} day^{-1} for butylated cross-linked CCF films were obtained, which makes these films suitable for many applications. The reaction conditions can further be optimized to introduce more alkyl groups to the cellulose backbone and hence improve the final properties of the films.

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Chapter 4. Conclusion, Contributions to Original Knowledge, and Suggestions for Future Work

The main objective of this thesis was to prepare chemically modified hydrophobic and non-hygroscopic cellulose fibers, to find a way to prevent the fibers from disintegration during the hydrophobization, and to study the effect of these modifications on fibers properties. The main findings and original studies are summarized here.

In chapter 2 of this thesis we focused on preparing new hydrophobically modified cellulose fibers with sequential chemical reactions. Cellulose fibers were chemically modified with sequential regioselective periodate oxidation and Schiff base reaction with amine terminated molecules. The oxidized celluloses with degree of substitution as high as 2 were obtained and coupled with butylamine via Schiff base reaction; However, fibers disintegrated upon longer reaction times in what is most likely attributed to the solubilizing the butyl chains in organic solvent and causing the modified cellulose to go in solution. To prevent this, fibers were successfully cross-linked by 1,12-diaminododecane to prevent fiber disintegration during the butylamine reaction. The cross-linking reaction was effective in strengthening the fibers and keeping their structure intact.

This procedure yielded highly hydrophobic and low-hygroscopic cellulose materials with various extent of surface and bulk modification. These amidated cross-linked fibers showed improved thermal stability and moisture sorption. They had contact angles as high as 143^{o}C possibly due to their hierarchical surface morphology and lower polar contribution due to the introduction of hydrophobic aliphatic groups. From TGA and moisture sorption studies, the cross-linked fibers showed higher thermal stability and lower water absorption compare to the non-cross-linked fibers. All of the final products maintained their cellulose I crystalline structure based on angle X-ray diffraction results, and crystallinity indices of approximately 50%-70% were observed for all final samples.

In chapter 3, novel cellulose derivatives were made with sequential chemical modifications. Carboxymethyl cellulose fibers (CCF) were produced under alkaline condition using monochloroacetic acid (MCA) as carboxymethylating agent. The modified cellulose fibers were cross-linked with EDC assisted biocojugation reaction of carboxyl groups with adipic acid dihydrazide (ADH) to prevent fiber disintegration. Cross-linked fibers were carboxymethylated for the second time to introduce more carboxyl groups. This cross-linked CCF were coupled with butylamine to introduce non-polar aliphatic long chain amine to the structure of the fibers. The new material showed higher tensile strength and Young modulus values. WVTR values as low as 75.7 g m^{-2} day^{-1} for butylated cross-linked CCF films were obtained, which makes these films suitable for many applications.

4.1. Suggestions for further research

As we have seen in chapter 2, the unique characteristics of these fibers are very promising for potential application in composites, and packaging and other technologies. Due to their higher thermal stability and low moisture sorption these fibers are very good candidates as strength-enhancing additive in polymer composites. Their very high hydrophobicity makes them very compatible with other hydrophobic polymers to make strong and long lasting polymer composites. Therefore more investigation in studying different polymer composites containing these fibers and different composites ratios can give great insight into the potential future applications.

It was seen in chapter 2 that fibers disintegrate when the DAC fibers are amidated without cross-linking. This was assumed to be due to the solubilization of the highly hydrophobic aliphatic chains in the organic solvent resulting in what is most likely NCC (nanocrystalline cellulose) stabilized with highly charged DBC (dibutyl cellulose). However, to further prove this hypothesis more investigation of the dissolved portion of the samples with techniques such as TEM and AFM will help us understand the mechanism of the reactions better.

As discussed in chapter 3, in order to introduce more carboxyl charge groups to the fibers after cross-linking, fibers were carboxymethylated for the second time and higher charge groups were introduced to the fibers. Therefore, it would be possible to introduce more carboxyl groups after amidation reaction and do these sequential cabroxymethylation until all the hydroxyl groups are converted. Using this method it might be possible to make highly hydrophobic cross-linked fibers. The reaction conditions can further be optimized to introduce more alkyl groups to the cellulose backbone and hence improve the final properties of the films.