THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Radiation crosslinking of cellulose fibers to obtain rigid lightweight paperboard

MIKAELA BÖRJESSON

Department of Chemical and Biological Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2013

Radiation crosslinking of cellulose fibers to obtain rigid lightweight paperboard
MIKAELA BÖRJESSON

Technical report no. 2013:22
ISSN 1652-943X

Department of Chemical and Biological Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone + 46 (0)31-772 1000

Printed by Chalmers Reproservice
Gothenburg, Sweden 2013

Radiation crosslinking of cellulose fibers to obtain rigid lightweight paperboard

Mikaela Börjesson

Department of Chemical and Biological Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY

ABSTRACT

Cellulosic materials are used in a wide range of areas of application, and one of these is paperboard for packaging solutions. Paper or paperboard as a packaging material has benefits like low density, low costs, high stiffness, good printability, and paper is environmentally friendly. Compared to other packaging materials, such as plastics, paper has some weaknesses By improving some of its weaknesses, paper as a packaging material, can become more competitive on the market, and knowing how to utilize this resource in a more effective and sustainable way will become increasingly important in the future.

One way to decrease the amount of fibers needed in paper and paperboard is by improving the strength properties of cellulose fibers. Greater fiber strength can be achieved by, for example crosslinking the fibers, and crosslinking can be achieved with only a small amount of chemicals. By using electromagnetic radiation, like ultraviolet (UV) radiation, the fibers can be crosslinked with the aid of a UV curing solution. Pretreatment of the fibers through an acrylic esterification reaction may enhance UV curing since polyester and acrylate groups are prone to be more reactive for UV radiation.

In this thesis, UV curing of paper sheets with the aid of a UV curing solution is evaluated with tensile tests, microscopy and water retention measurements. Both acrylic esterified paper sheets and non-treated paper sheets are evaluated. Due to acid hydrolysis on the acrylic esterified paper sheets, the non-treated paper sheets showed the highest value in strength properties with a doubled increase in tensile index. Acrylic-acid-modified (AA-modified) sheets showed an increase in tensile index that was four times higher than non-radiated AA-modified sheets, but were weaker overall than the non-treated paper sheets due to the acrylic acid pre-treatment.

Keywords: Cellulose, Ester, Acrylates, Modification, Paper, Packaging, Crosslinking, UV radiation

LIST OF PUBLICATIONS

The thesis is a summary of the following papers:

I. **Thermal esterification of cellulose fibers for improved functionality and reactivity**
Mikaela Börjesson, Gisela Richardson and Gunnar Westman
Manuscript

II. **UV crosslinking of cellulose fibers for improved stiffness in paper sheets**
Mikaela Börjesson, Gisela Richardson and Gunnar Westman
Manuscript

Work related to the thesis has been presented at the following conferences:

1st Avancell conference
Gothenburg, Sweden 2011 (poster presentation)

243rd ACS meeting
San Diego, USA 2012 (poster presentation)

2nd Avancell conference
Gothenburg, Sweden 2012 (poster presentation)

LIST OF ABBREVIATIONS

AGU	Anhydroglucose unit
^{13}C-NMR	Carbon-13 NMR
CD	Cross direction
CMC	Carboxymethyl cellulose
CTMP	Chemithermomechanical pulp
$CuSO_4$	Copper sulfate
D_2O	Deuterium oxide
DP	Degree of polymerization
DS	Degree of substitution
E-beam	Electron beam
FAO	Food and Agriculture Organization
FBB	Folding box board
FDA	Food and Drug Administration
FTIR	Fourier-Transform Infrared spectroscopy
H_2SO_4	Sulfuric acid
HCHPK	1-hydroxycyclohexyl phenyl ketone
HDODA	1,6-hexanediol diacrylate

HMAA	*N*-(hydroxymethyl) acrylamide
HW	Hardwood
KBr	Potassium bromide
KCL	Company name (Oy Keskuslaboratorio - Centrallaboratorium Ab)
KrCl*	Krypton-Chloride excimer lamp
LPB	Liquid packaging board
MD	Machine direction
NMR	Nuclear magnetic resonance
OsO_4	Osmium tetroxide
PI	Photoinitiator
PMMA	Poly(methyl methacrylate)
SEM	Scanning electron microscopy
SW	Softwood
TAAB	Company name (TAAB Laboratories Equipment Ltd)
TEM	Transmission electron microscope
TGA	Thermo gravimetric analysis
TLV	TAAB low viscosity resin
TMPTA	Trimethylolpropane triacrylate
UV	Ultraviolet
WHO	World Health Organization
VOC	Volatile organic compound
WRV	Water retention value
ZD	Thickness direction

TABLE OF CONTENT

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The paper and pulp used in packaging materials originates in biomass, an important base and raw material used in a wide range of applications. Tons of biomass are produced every year by nature itself and are used in various materials and products in our daily lives. One important source of biomass comes from trees; wood. The main constituent of wood is cellulose, a biopolymer consisting of glucose monomers linked together in linear chains. The cellulose molecule can be changed through various methods or processes (for example chemical or mechanical treatment) and different properties can be achieved depending on the structure and composition of the cellulose polymer.

Some beneficial properties of wood pulp are its low density, low cost, high stiffness, good printability, and it is environmentally friendly. Products and materials made from cellulose pulp can be both reused and recycled and as a consequence, landfill can be avoided. When the properties of cellulose fibers are modified, new materials and application areas can be found which makes cellulose-based materials more competitive on the market. A more competitive material with many areas of application requires more raw material, and awareness of how to utilize the resource in a more effective and sustainable way becomes increasingly important.

Less cellulose needed for a required stiffness can be achieved by increased strength properties. A common way to modify the strength and stiffness properties of polymeric materials is to enhance the interaction between the polymer chains of the material either by creating hydrophobic or ionic interactions or by crosslinking the polymer chains. There are different ways to crosslink materials, and the ability to control the crosslinking effect in a material is important in many respects. There are some different methods available for crosslinking like heating (Hasani and Westman 2011), radition exposure (Kumar et al. 2006) and alkali-catalyzed wet crosslinking (Reddy et al. 2009), and there is an interest in finding new routes for crosslinking cellulose fibers, which are important for environmental reasons.

The ability to crosslink cellulose fibers by electromagnetic radiation, which is classified as a green technology, could reduce the amount of volatile organic substances (VOC), or the need for VOCs can be fully excluded (Clough 2001; Davidson 2001; Glöckner et al. 2008). Radiation treatment is also energy saving compared to crosslinking materials through heat where the cost for heating up a material is much higher than for exposure to radiation. The radiation treatment is faster in many cases, and some seconds to minutes is often enough time to fully crosslink a material.

For the paperboard used in liquid packaging, strength and stiffness properties are important for the packaging to be able to hold the content (Robertson 2009). Crosslinking cellulose fibers provides improved strength and stiffness properties to paper material (Horvath et al. 2010), and radiation crosslinking might therefore be used on the top ply of the paperboard structure to increase the stiffness of the paperboard, thus requiring less material.

1.2 AIM

The aim of this licentiate thesis is to find a reaction route that produces a cellulosic material with new properties suitable for further reactions with electromagnetic radiation. The first part is to produce a cellulose acrylate ester, since acrylate esters are one of the most reactive groups compared to other functional groups when exposed to UV radiation. The second part is to control the crosslinking effect. The cellulosic ester material is to crosslink when exposed to UV radiation and no crosslinking is to occur until exposure.

By crosslinking the material, the expected results are an increase in fiber stiffness and, in turn, a decrease in the amount of cellulose fibers needed in a paper material. This could subsequently decrease the amount for pulp as a raw material in paper packaging.

Paper structures in liquid packaging boards are multi-ply structures (Figure 2.2). This study will focus on the top ply structure of the paperboard since electromagnetic radiation has a short depth of penetration.

One important issue that has to be kept in mind is that an increase in stiffness often gives a less flexible material, and flexibility is important for the ability to convert paperboard to packaging. Another important issue to address is that the reaction methods and chemicals used should be able to be implemented in pulp- and paper-mill processes. If possible, organic solvents should be avoided.

CHAPTER 2

PAPERBOARD AND PACKAGING

Paperboard packaging offers some great advantages compared to many other packaging materials, but at the same time it has some drawbacks. This chapter will discuss the function of paper packaging, its properties and what affects the properties of paperboard and paper packaging.

2.1 FOOD AND LIQUID PAPER PACKAGING

The idea of using paper for food packaging solutions came about around the year 1665 and a patent by Charles Hildeyerd with the title, “*The way and art of making blew paper used by sugar-bakers and others*”. This is the oldest reference that can be found in that area (Kirwan 2003). Other common food packaging materials used today are plastics, glass and aluminum which all offer good packaging for food products but with varying properties.

The Codex Alimentarius Commission[1] defined in 1985 the functions of a food packaging as ”*Food is packaged to preserve its quality and freshness, add appeal to consumers and to facilitate storage and distribution”.* Packaging products used for food and liquids therefore require high standards since the packaging comes in contact with food products. There are at least four primary functions needed to

---

[1] The Codex Alimentarius Commission is a collection of international food standards, guidelines and recommendations related to food and food safety. The commission was established in 1963 by FAO and WHO with the purpose of protecting the health of the consumers and ensuring fair practices in the food trade.

fulfill the definition of the functions of food packaging; containment, protection, convenience and communication (Robertson 2009).

Different food products have different demands on the packaging material. Some food products are sensitive to moisture, oxygen, light or microbial growth, and therefore there is no general packaging solution. The packaging has to act as a barrier to protect the food product and preserve its color, flavor and aroma, and the packaging plays an important role in the preservation of the shelf life of the food product (Stöllman et al. 1994).

The main functions of food packaging are to store the food product and protect the content from external damage. Through protection, the food will be preserved for a longer time and, subsequently, food waste will be prevented. Depending on the food product, the protection of the packaging can vary from protecting the content from physical damage to creating oxygen, light or liquid barriers. In order to keep the food fresh the packaging needs to fulfill requirements for cleanliness throughout the whole packaging process.

The packaging should also bring convenience to the customer. Distribution and handling is important and geometrical shape and weight are of great importance, especially for transportation. Stability and stiffness are needed to fulfill logistic requirements and avoid damage. The last requirement for a food and liquid packaging is communication. The customer needs to be informed about the content in the package, and it is of great interest for the producing company to market themselves and profile their brand. This requires good printability on the packaging which is where paper packaging has a better foundation than other packaging materials (Robertson 2009).

Apart from these primary functions of food packaging, there are also some other aspects that need to be taken into account when designing packaging, for example consumer trends and environmental aspects.

2.2 PAPERBOARD AND PACKAGING

Paper and paperboard are pliable materials formed as sheets made up from a three-dimensional network of cellulose fibers normally derived from wood or other vegetable fibers. A fiber is a tubular or cylindrical component containing cellulose as the main constituent, and the properties of the pulp fibers determine many of the properties of the final paper product (Biermann 1996). The structure and properties of cellulose fibers are described in Appendix A. Cellulose fibers can form hydrogen bonds within the fiber network and thus form a paper sheet (Figure 2.1).

Figure 2.1. *A SEM picture of the cellulose fiber network in a paper sheet.*

There is no clear definition between the differences of paper and paperboard, but normally the basis weight for a paperboard is over 150 g/m^2 and lower for a paper sheet. Paperboard is often constructed in multi-ply structures where the different plies can have different types of fibers and different basis weights. One or several plies can have a lower basis weight than 150 g/m^2 but still be designated as paperboard. Paperboard is classified into different categories and the most common type of paperboard for consumer product packaging, like food, liquids and pharmaceuticals products, is cartonboard. Depending on the product, there are different subgrades for cartonboard; folding boxboard (FBB) or liquid packaging board (LPB). The different subgrades are used for different products and it is mainly the fiber raw material used in the paperboard that differs (Kiviranta 2000). The paperboard in focus for this thesis is liquid packaging board which will be discussed later in this chapter.

Paper and paperboard can be used for writing, packaging or other specialized purposes due to printability and other beneficial physical properties. The strength of paper and paperboard sheets depends on different factors like the strength of the fibers and fiber bonds, the processing method, basis weight and the formation of the fiber network. The different properties of the paper sheets enable them to be made into flexible and rigid packaging (Didwania 1968; Kirwan 2003).

A paperboard needs to resist mechanical damage and sometimes there are high requirements on purity, cleanliness and visual properties. The mechanical demands on paper packaging include having certain levels of mechanical strength and stiffness, compression strength for facilitating stacking and bending stiffness. Bending stiffness is affected by the thickness of the board and the fiber raw material. The optimal structure of paperboard consists of several plies, where the middle plies have a bulky structure while the top and back plies have high stiffness (Figure 2.2). If the packaging is to be used for food products, there are high demands on purity and cleanliness. Microbiological particles in the paperboard can cause problems with odor and tainting of the food product. These microbiological particles are often found in recycled fibers due to the variety of fibers and fiber sources. To avoid this problem in food packaging, virgin-fiber-based paperboard is used in the food industry (Kiviranta 2000).

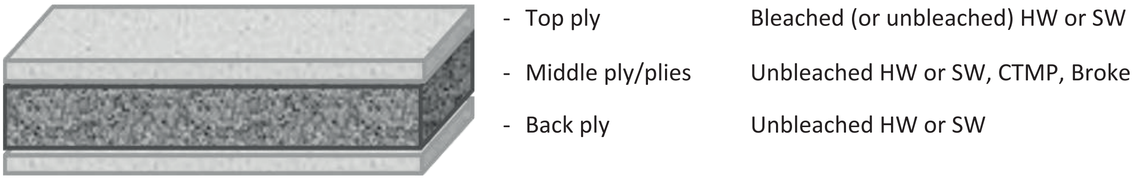


Figure 2.2.*The different plies in a multi-ply structure LPB and the pulps that are normally used for the different plies. Hardwood (HW), softwood (SW), chemithermomechanical pulp (CTMP) or broke pulp (pulp reused in the paper mill).*

Paper packaging has some advantages compared to other material-based packaging like plastics, glass or aluminum. Paper-based packaging is lightweight, has low cost, high stiffness, good printability and is more environmentally friendly since it is easily biodegradable and recyclable. Some weaknesses with paper-based packaging are opacity, the low ability for deformation and mouldability. Paper-based packaging is not heat sealable and barriers are needed to protect the content from gases, liquids, fats or light. By improving some of these weaknesses paper-based packaging can become much more competitive against the other materials used for packaging applications.

2.3 LIQUID PACKAGING BOARD (LPB)

Liquid packaging board is a type of carton board and often consists of several layers of paperboard, called a multi-ply structure. To protect the paperboard from the liquid food content and to protect the food product from the outer environment, different plastics or alumina barriers are necessary (Figure 2.3).

For LPB, purity and cleanliness are of the utmost importance and therefore only virgin fibers are used. High paperboard stiffness is needed to protect the content and this can be achieved by using a multi-ply structure with two-, three-, or even more plies. By choosing a bulky middle layer consisting of, for example CTMP (chemithermomechanical pulp), and the top and back ply of a paperboard with a high modulus of elasticity, a lower basis weight at a given stiffness can be achieved (Kiviranta 2000). CTMP consists of long fibers, which are strong, flexible and have high stiffness but give a rougher surface. By choosing CTMP as the middle layer a lower basis weight can be obtained for a given stiffness.

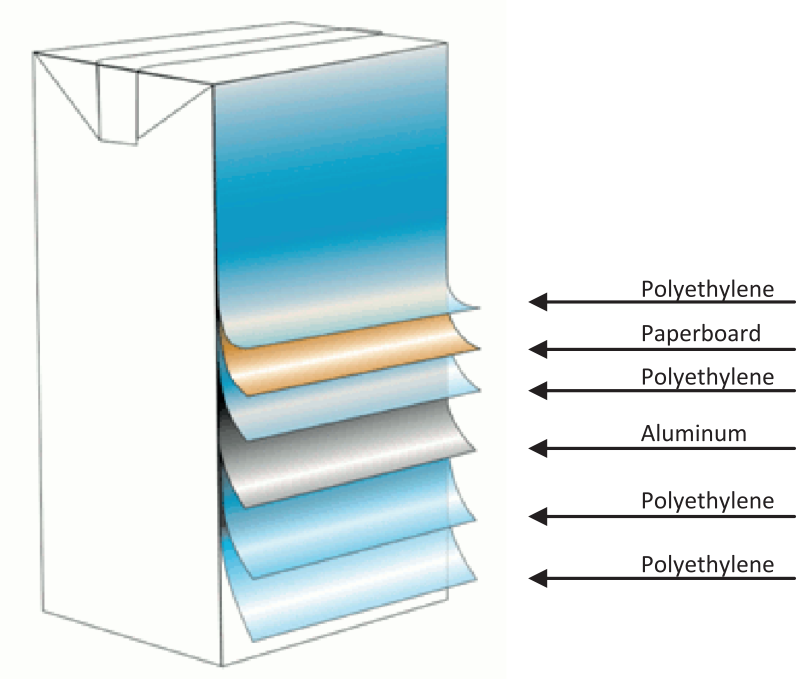


Figure 2.3. *The different material layers in liquid packaging. The number of plastic barriers can vary as well the aluminum foil layer depending on the food product and how it needs to be protected.*

2.4 IMPORTANT PROPERTIES OF PAPERBOARD

The properties of a liquid packaging are affected by many parameters, for example the type of fibers used in the paperboard, the processing of the fibers and the bleaching processes. By choosing the fibers, the processing methods and the structure of the multi-ply paperboard, the desired properties can be achieved for the paperboard packaging. The main properties of the paperboard can be divided into four different categories; optical, surface, strength and absorption properties.

Optical properties

The optical properties of the paperboard do not affect the physical properties of the packaging but they might affect the printing results. Colors printed on paperboard with different whiteness will give different impressions on the printed board. Paperboard that needs to be printed requires a good printing surface.

Surface properties

The surface properties of the paper or paperboard are important for the visual impression, the feeling of the paperboard, the printing technique that can be used and the application of the paperboard. The surface roughness depends on the fibers used in the board. Hardwood (HW) fibers are often shorter than softwood (SW) fibers and shorter fibers can pack more densely and give a smoother surface than longer fibers. In addition, the pulping process affects the fibers and, subsequently, affects the surface properties of the paperboard. Mechanical pulping causes more fibrils than chemical pulping and the fibrils can fill out space in between the longer fibers, which produces a smoother surface (Höglund 2004).

Strength properties

The strength properties of the paperboard are of major importance for the physical properties of the final packaging. To be able to form a paper at all, the paper must have a certain strength and depending on how the fibers align in the wire in the papermaking process the paper can have different strengths in the cross direction (CD) and in the machine direction (MD) of the paperboard.

The strength properties affect the runability properties of the printing process and also the requirements for converting the paperboard to packaging. One crucial strength property is the rigidity or stiffness of the paper. The stiffer the paper, the less flexible it is and the paperboard needs a certain flexibility throughout the whole papermaking process, and also for the possibility to fold the paperboard into packaging. Stiffness is influenced by factors such as basis weight, thickness, raw material, pulp processes and moisture content.

In this study the strength properties were measured with tensile tests. Elongation, stiffness and tensile index are some of the properties that can be evaluated using this test. The tensile test is described in section 4.3.7.

Absorption properties

Absorption properties are important for the printing process since ink has to penetrate the surface and have good adhesion to the paper. There are different methods for measuring the absorption properties of a cellulosic material, for example the water retention value (WRV) and the Cobb index. Both of these methods are evaluated in this study; the WRV method is described more in section 4.3.5 and the Cobb test is described in section 4.3.6.

The properties of the different fiber raw materials and pulping processes are discussed more in Appendix A.

CHAPTER 3

THE CROSSLINKING OF CELLULOSE

A stronger and stiffer paper material might decrease the amount of raw material in the packagine paperboard. Crosslinking the fiber network in paper has been proven to increase strength and stiffness properties. A green technology for creating crosslinks is electromagnetic radiation, for example UV radiation, which will be discussed in this chapter.

3.1 CROSSLINKING

Many linear polymers are too flexible to be used in various applications due to lack of strength, rigidity or elasticity. By forming new bonds between the linear polymers, it is possible to create a difference in their physical properties, and an increase in stiffness and strength can be achieved in the polymer material. Crosslinking is a chemical process in which two or more molecules are joined through a covalent or ionic bond. When polymeric chains are linked together they lose some of their ability to move as individual chains and the structure becomes more locked. The change in molecular structure changes the properties of the polymer chains.

Crosslinks can be formed chemically under different conditions like heat, pressure, changes in pH or by radiation treatment. Crosslinks can also be formed through oxidation when polymeric materials are exposed to atmospheric oxygen, or enzyme-catalyzed crosslinks that take place in the proteins of our body to form mechanically stable structures like hair and skin. Crosslinks that are covalently bonded between the polymer chains are more mechanically and thermally stable than non-crosslinked polymers. Due to the improved strength properties of crosslinked materials, they may be harder to recycle depending on the degree of crosslinking.

3.2 CROSSLINKING CELLULOSE FIBERS

The introduction of covalent crosslinks between cellulose chains is commercially one of the most important tools in controlling the performance of cellulose materials, ranging from textile wrinkle resistance to fluid retention and the dimensional stability of paper. Several methods for chemically crosslinking cellulose fibers already exist. The crosslinking can be between different cellulose polymers or within the same cellulose polymer. Crosslinking can also occur between different cellulose fibrils or between different cellulose fibers.

The different degrees of crosslinking will give different properties in the final product; for instance a low degree of crosslinking is favorable for stiffness and strength while a high degree of crosslinking gives a more brittle product with lower strain at break. The location of the crosslinking on the fibers affects the mechanical properties of the final product and the crosslinking can be located on the fiber surface or in the fiber cell wall (Horvath et al. 2010).

Covalent crosslinks can be formed from different conditions like heat or radiation treatment. Crosslinking cellulose by radiation treatment has been done by modifying carboxymethyl cellulose (CMC) and cellulose acetate by the addition of acrylic groups. The modified cellulose fibers are polymerized using UV radiation, both through purely radical (Kumar et al. 2006) and metal-catalyzed (Chen and Wang 2006) reaction schemes. Böhm et al. (2013) introduced an approach for preparing functional paper in which functional acrylic groups are attached to cellulose microfibers first by absorbing poly(methyl methacrylate) (PMMA) copolymers to the paper substrate and then covalently bonding the substrate through UV radiation.

By modifying the cellulosic fibers prior to crosslinking, the crosslinking effect can be controlled and the crosslinking will not start until treatment with heat or radiation occurs on the cellulosic fibers. By having reactive groups that are activated by heat or radiation, crosslinking can be achieved within the process line. Controlled crosslinking of cellulose fibers by thermal treatment has been obtained by using the good leaving group character of the N-methyl morpholinium substituent on modified cellulose fibers (Hasani and Westman 2011).

Modified cellulose fiber systems that are polymerisable by UV radiation have been patented and suggested for possible use in several fields, including hydrogels for contact lenses (Menashe 1986) and general coating uses (Cook 1988; Cook and Simm 1998).

3.3 CROSSLINKING BY RADIATION

The ability to crosslink or cure materials by exposure to ultraviolet (UV) radiation has been known since the beginning of the 20th century, and electron beam (E-beam) radiation has been used in industrial applications since the early 1970s. In the beginning of the radiation curing process, there was a strong focus on the E-beam curing technology and not until the 80s and 90s did the UV curing technology become more attractive and the first choice for radiation curing. Both E-beam and UV radiation have been proven to work successfully for curing applications on flat substrates (Glöckner et al. 2008).

Today there is a strong focus on environmental issues and crosslinking by radiation treatment can offer a lot of advantages compared to conventional crosslinking with chemical additives. Some general advantages of electromagnetic radiation are listed below;

1. The cure speed is faster for radiation curing than using chemical additives to crosslink a material. Faster curing also gives a fast line speed, saving both time and costs which is necessary if the method is to be implemented in existing processes. It is possible to cure preformed parts at room temperature and heating is not necessary. A reduction in energy consumption leads to cost savings and a lower impact on the environment.

2. The need for volatile organic compounds (VOC) decreases and there may be no need at all for using VOCs. This reduces the emitted level of VOC into the atmosphere and subsequently has a lower environmental impact. The radiation curing technology is so far classified as a green technology.

3. Radiation crosslinked materials have generally better strength and better resistance to impact and stress cracking (Clough 2001), compared to a crosslinked material from a conventional curing process. The improved properties of the cured object could be in terms of mechanical properties or glossiness (Davidson 2001).

There also some drawbacks with the radiation curing technology and the main drawbacks are;

1. Shadow areas could cause problems in the ability to cure three-dimensional objects.

2. Some raw materials used for radiation crosslinking can cause skin irritations or allergy. The raw material might cause yellowing of the product.

3. The curing depends on the thickness of the object and pigmentation levels. High pigmentation levels cause problems due to the pigment particles hindering the crosslinking. The penetration depth of UV radiation is just a few μm to mm, so thick materials are not fully crosslinked (Glöckner et al. 2008).

Many radiation curing formulations for production are solid systems and the curing process does not lead to a loss of solvents to the atmosphere (Figure 3.1). Normally there are no volatile solvents present at all in the system. The substances present in the film consist of polymers and monomers (crosslinking agents) that carry reactive groups that can crosslink to each other (Glöckner et al. 2008). The polymer in this study is a cellulose polymer, modified with an acrylate-functional group that might increase the reactivity of the cellulose polymer.

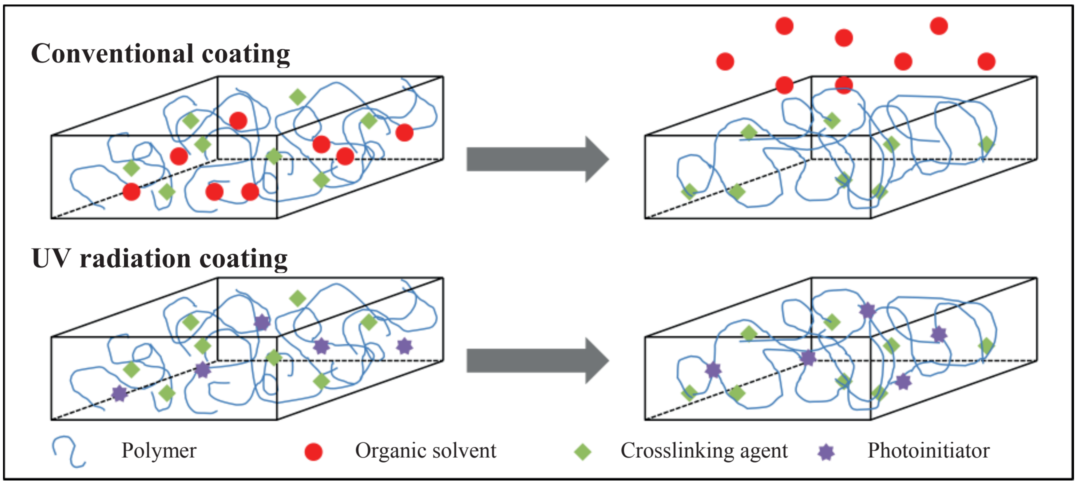


Figure 3.1. *Differences between conventional coating compositions and a UV curing coating composition. In the case of conventional coating, organic compounds leave the film during drying and crosslinking, while the UV curing coating does not emit any solvents during crosslinking.*

3.4 THE CHEMISTRY BEHIND RADIATION CURING

In this study, the focus is on the UV radiation curing technique. In general there are two different polymerization routes for radiation curing; radical polymerization and cationic polymerization.

Radical polymerization

Radical polymerization is normally initiated by the photoinitiators in the reactive mixture. The basic principle of the photoinitiators consists of two main steps; absorption of the incident photons and the generation of the initiating species that are formed (Scherzer 2004), see figure 3.2. The photoinitiator is activated with light of a specific wavelength and radicals are formed (photolysis). A free radical will attach to the carbon-carbon double bond, in the functional group of the polymer chain, and form a carbon-centred radical.

The radicals derived from the initiating step react with the polymerizable species by a free radical mechanism which leads to the generation of a substrate-derived radical. The propagation process continues until all the polymerizable substrates have been used up (Glöckner et al. 2008).

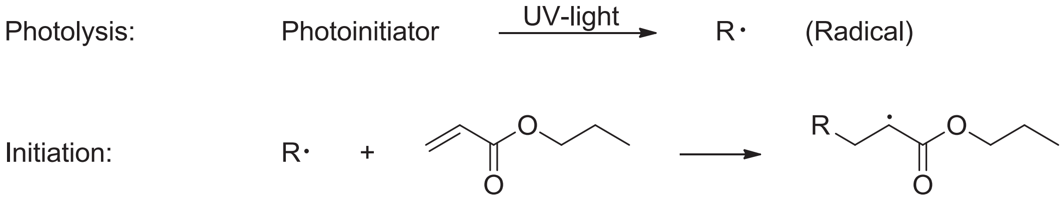


Figure 3.2. The photolysis and initiation step of a free radical polymerization. The product formed after the initiation is a carbon centred radical.

Cationic polymerization

As in radical polymerization, cationic polymerization consists of a photolysis that activates the photoinitiator followed by initiation and propagation steps. In a light-induced system, a cationic photoinitiator is used. The photoinitiator absorbs light of a specific wavelength and yields a protonated acid (Davidson 2001; Glöckner et al. 2008).

The photoinitiators used in cationic polymerization form charged ions that initiate polymerization. The charged ions react with either the double bond in the vinyl ether group or the epoxy ring, and the charge is transferred to the next molecule. The charged groups react further with new molecules and the crosslinking reaction has started (Figure 3.3).

Cationic polymerization is affected by water, which inhibits the reaction. Water is a nucleophile and is involved in ring-opening polymerization. If cationic polymerization is used on cellulose, water need to be removed from the cellulose sample before reaction.

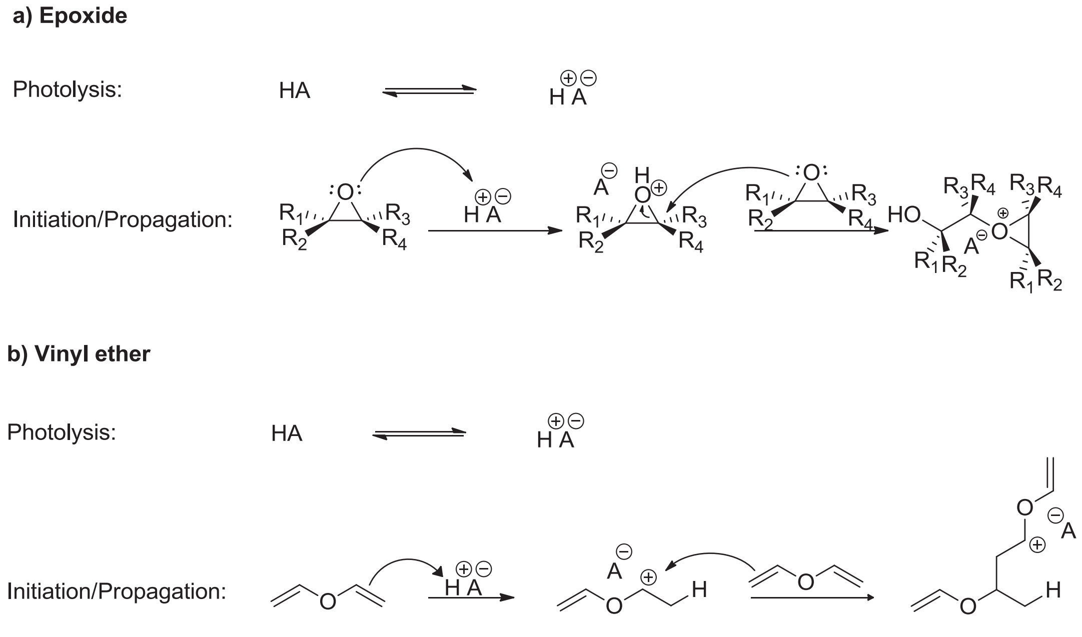


Figure 3.3. *Cationic polymerization for a) epoxides and b) vinyl ethers.*

3.4.1 UV-RADIATION CURING

Ultraviolet (UV) radiation is used in many industrial applications including electronics, chemicals and water, food and medical treatment. UV radiation can initiate a polymerization with low activation energy. This allows high polymerization rates at room temperature.

UV curing is a fast and efficient way to transform a liquid resin into a solid polymer that is totally insoluble in organic solvents and resistant to both heat and mechanical treatments (Decker 2001). The principle with UV curing is to crosslink polymer chains into a three-dimensional network by irradiating UV light of a specific wavelength. The UV radiation is absorbed by photoreactive groups which form reactive species, and subsequently react further with a multifunctional monomer and cause a crosslinking of the polymer chains.

A UV curing mixture generally consists of different ingredients like stabilizers, additives or chain-transfer agents and the three most important ingredients that are found in almost all formulations are (Decker 2003; Shukla et al. 2004):

1. A (multi-)functionalized polymer.
2. Monomeric diluents that will crosslink with the polymer.
3. A photoinitiator that can provide the necessary activation.

The UV-curing mixture typically consists of 50-80 wt% polymer, 0-50 wt% monomeric diluents and 0.5-8 wt% of photoinitiators, additives and pigments (Glöckner et al. 2008; Kim and Seo 2004).

The multifunctional polymer creates the backbone during crosslinking and confers the final mechanical properties to the material. The backbone in this study is the modified cellulose fibers. The most widely used functional groups are various types of acrylates for radical polymerization and epoxy or vinyl ether for cationic polymerization. Acrylated structures are most widely used since they demonstrate the highest reactivity. The following order of reactivity has been recognized (Allen 1996).

Acrylic groups > Methacrylic groups > Alkyl groups > Vinyl groups

The monomeric diluents copolymerize with the functional groups on the polymeric backbone and incorporate into the polymer matrix during the curing process (Glöckner et al. 2008). If a multifunctional monomer is used it can polymerize with itself, forming a polymer that can act as a crosslinker between the polymeric backbone. The monomeric diluents will impact on the physical properties of the cured material. Many monomeric diluents are excellent solvents and can help the dissolution of additives in the UV curing mixture, for example aid the dissolution of the photoinitiator (Davidson 2001; Shukla et al. 2004). As little monomeric diluents as possible should be used to retain good reactivity in the mixture. A small amount of monomers is preferable for toxicological reasons and to avoid skin irritations that might be caused by a high amount of monomers (Durgavale 2002).

There are different photoinitiators used in the UV-curing mixture depending on if a radical or cationic polymerization is sought. A large amount of photoinitiators are necessary to achieve fast and efficient UV curing, but levels that are too high can cause problems with mixing or dissolving in the resin system. An optimum content of photoinitiators depends on the wavelength of radiation, the absorption spectrum of the photoinitiators and the reflection characteristics of the material (Kim and Seo 2004).

It is possible to cure a material without using photoinitiators if the multifunctional polymer absorbs wavelengths by itself, for example acrylates that absorb wavelengths within the UV range area. Scherzer (2004) studied the photo polymerization of acrylates by using short wavelengths of UV light from a KrCl* excimer lamp, which emits at 222 nm. One drawback with not using a photoinitiator is that the penetration depth into the material decreases compared to a mixture in which a photoinitiator is used.

3.5 PROPERTIES OF CROSSLINKED FIBERS

Monomeric diluents act as crosslinkers between cellulose fibers (Figure 3.4) and in this way bring about property changes to the cellulosic material. Depending on the type of property desired, different monomeric diluents can be chosen. Xu and Yang (1999) have found that the size of monomeric diluents affects the crosslinking and the properties of the crosslinked material. High-molecular weight molecules favor the formation of interfiber crosslinking, which improves the dry strength and the toughness of the material, while low-molecular weight molecules gives intrafiber crosslinking which causes embrittlement of fibers and decreases the flexibility of the crosslinked material.

Other properties that are affected by crosslinking are hydrophobicity and absorption. A crosslinked material is more locked in its network structure and may hinder liquids from penetrating the paper. Absorption properties are important if the paper is to be printed. In this thesis, the hydrophobicity of paper sheets is evaluated with a Cobb test (described in section 4.3.6).

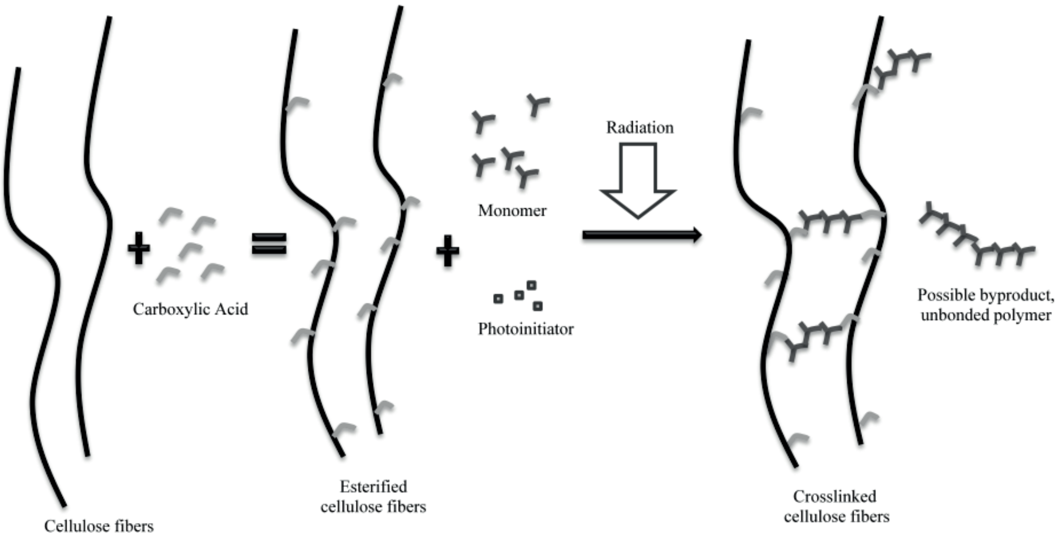


Figure 3.4. *The crosslinking process. Monomeric diluents act as crosslinking agents between the cellulose polymers.*

3.6 CHEMICAL MODIFICATION OF CELLULOSE

The ability to chemically modify cellulose fibers has given many new possibilities for applications of cellulose and wood fibers. There are several ways to chemically modify cellulose fibers and some of these are esterification (Gardea-Hernández et al. 2008; Heinze and Liebert 2004), etherification (Baiardo et al. 2002; Barba et al. 2002), crosslinking (Yang and Xu 1998; Zhou et al. 1995) and grafting (Carlmark and Malmström 2003; Paquet et al. 2010).

There are generally three different ways in which cellulose can react. One way is through hydrolysis of the glycosidic bond, on the anhydroglucose unit (AGU). This is what happens during degradation reactions. Another way in which cellulose can react is through the hydroxyl groups which can be oxidized or substituted in different ways. The last way in which cellulose can react is on the C-H bond or other low energy bonds, which can be broken by energy radiation (Didwania 1968).

The degree of substitution (DS) is a measure of how many hydroxyl groups per AGU that have been substituted. On every AGU there are three hydroxyl groups which means that the highest number of DS for a cellulose molecule is three. A low DS for a cellulose molecule indicates that the reaction takes place at the fiber surface while a high DS indicates that the reaction is extended to the inner part of the cell wall.

In this study, the focus on cellulose modification is on esterification reactions. Since radiation crosslinking is favorable for acrylate groups, the focus is on producing a cellulose acrylate ester that creates the potential for further reactions with electromagnetic radiation.

3.6.1 ESTERIFICATION OF CELLULOSE

The esterification of cellulose is normally based on the reaction of the hydroxyl groups on the cellulose molecule with acids and derivatives. Most common on the lab scale is esterification through carboxylic acid chlorides or anhydrides with the aid of a catalyst (Heinze 2005). One problem with esterification methods is that the reaction is reversible and to avoid a reversible reaction, one of the reactants needs to be in excess, or one of the products needs to be removed. The catalyst used could be either a base or acid, depending on the reaction conditions, but a catalyst-free reaction would be the most desirable. Cellulose esters can be produced in different ways either in a homogenous system in which the cellulose is dissolved in an appropriate medium, for example ionic liquids (Heinze et al. 2005; Hussain et al. 2004) or a heterogeneous system performed in organic solvents (Freire et al. 2006), a vapor-phase system (Yuan et al. 2005) or solvent-free systems (Gardea-Hernández et al. 2008). The esterification of cellulose affords access to a range of properties that make cellulose esters workhorse materials in many applications.

A cellulose acrylate ester is the desirable product for the crosslinking process in this study. Acrylated esters or esters from acrylic acid and various alcohols are commercially important, and polymers from these esters are used for application areas like paints, adhesives, fibers, rubbers, electronic materials and optical materials. These esters are produced through a condensation between acrylic acid and alcohol. In the case of a cellulose acrylate ester, the hydroxyl groups on the cellulose chain act as an alcohol.

CHAPTER 4

MATERIALS AND EXPERIMENTAL TECHNIQUES

This chapter describes the materials and experimental techniques used in the study that was presented in Paper I (Thermal esterification of cellulose fibers for improved functionality and reactivity) and Paper II (UV crosslinking of cellulose fibers for improved stiffness in paper sheets). All characterization techniques used in the study are described last in this chapter.

4.1 ESTERIFICATION OF CELLULOSE

Two different esterification routes were studied to obtain a cellulose acrylate ester. The functional acrylate group contained an alkene group, making the cellulose chain more reactive for further reactions.

4.1.1 MATERIALS

A dried, industrially produced Scandinavian softwood Kraft pulp bleached in a totally chlorine-free, peroxide-based sequence was obtained from Södra Cell AB and used for the study. The dried pulp was disintegrated at 30 000 revolutions before use, according to the standard EN ISO 25264-2. Copper sulfate, used as a catalyst in the production of acrylamide sulfate, was purchased from Fluka and used as received. All other chemicals (acrylonitrile, fumic sulfuric acid, acrylic acid, acetic acid, propionic acid, hexanoic acid, dodecanoic acid and cinnamic acid) were purchased from Sigma-Aldrich without further preparation.

4.1.2 PREPARATION OF ACRYLAMIDE SULFATE

The preparation of acrylamide sulfate was based on a patent for acrylamide production in which acrylamide sulfate was the intermediate to acrylamide (McNae 1964). A suggested reaction scheme for forming the acrylamide sulfate can be seen in Figure 4.1.

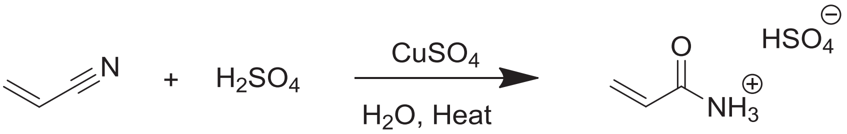


Figure 4.1. Reaction scheme for acrylamide sulfate, which was formed from acrylonitrile and sulfuric acid where copper sulfate was used as catalyst and water as a solvent.

In a round bottom flask, 0.05 g copper sulfate, 1.8 ml distilled water and 10.8 g fumic sulfuric acid were mixed before 5.3 g acrylonitrile was added dropwise over a period of 10 minutes. The mixture was magnetically stirred and kept at 95 °C for 60 minutes. The acrylamide sulfate mixture was cooled down to room temperature and used in the reaction with cellulose without further purification. The acrylamide sulfate product was a gold-brown highly viscous solution, see Figure 4.2.

Figure 4.2. *The acrylamide sulfate, a gold-brown, highly viscous solution.*

4.1.3 ESTERIFICATION WITH ACRYLAMIDE SULFATE AND CELLULOSE

The esterification reaction between cellulose and acrylamide sulfate was performed in water, and the reaction was investigated at different temperatures (30 to 70 °C), reaction times (2 to 6 hours) and mole concentrations of reagent (1.9 to 7.7 moles of reagent/AGU). Before the addition of acrylamide sulfate, distilled water was added to the pulp, which caused the fibers to swell. The amount of distilled water was adjusted to give the pulp a dry content of 6.25 %, to enhance the magnetic stirring. After reaction, the samples were diluted and washed with large quantities of distilled water and, for some samples, also tap water.

Additional thermal treatment at high temperatures was needed to form the cellulose acrylate ester. The absorbed acrylamide sulfate pulp, prepared with 5.8 moles of acrylamide sulfate/AGU at 40 °C for 3 hours, was heated in an oven at 150 °C for 30 minutes (Figure 4.3).

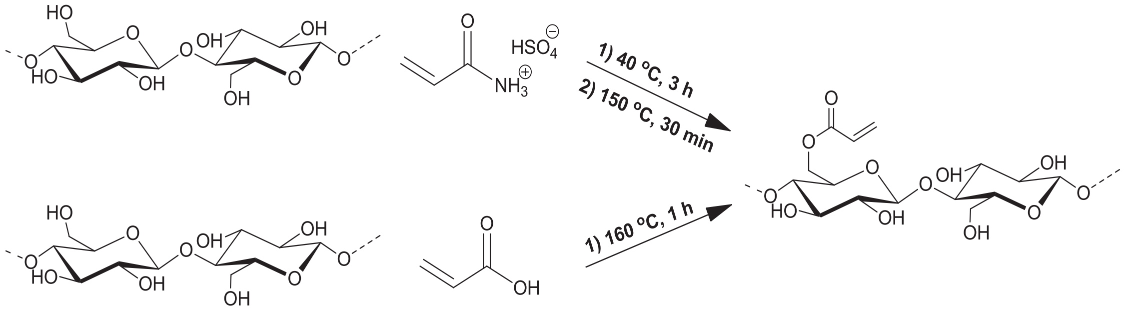


Figure 4.3. *Reaction schemes for the formation of the cellulose acrylic ester. Route 1 (top), acrylamide sulfate was added to the cellulose chain. Route 2 (bottom), acrylic acid was added to the cellulose chain.*

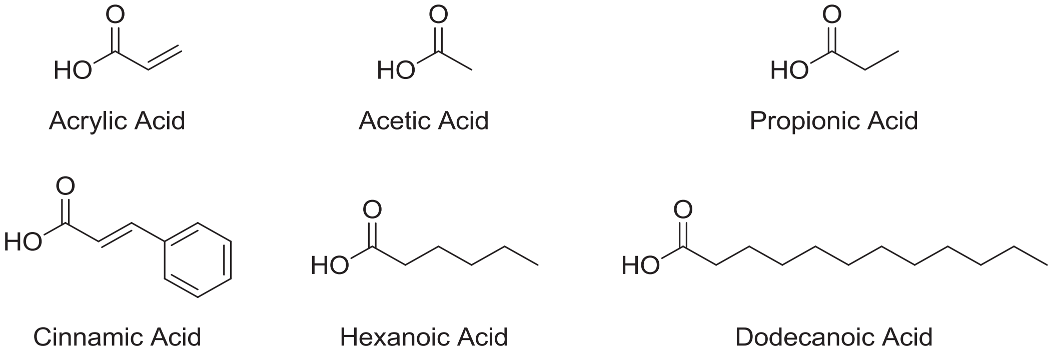
4.1.4 MODIFICATION WITH CARBOXYLIC ACIDS

Acrylic acid was used in the esterification reaction to obtain the same unsaturated cellulose ester as for acrylamide sulfate, but through a different reaction process. The esterification reaction was studied for six different carboxylic acids; acrylic acid, acetic acid, propionic acid, cinnamic acid, hexanoic acid and dodecanoic acid. The molecular structures for the carboxylic acids used are shown in Figure 4.4.

Acrylic acid (2 to 3 moles of reagent/AGU) and distilled water were mixed together, poured over the cellulose samples and kneaded for approximately two minutes. The amount of water was adjusted to give the pulp a dry content of 10 % to 40 % of the cellulose pulp. The samples were allowed to absorb the carboxylic acid/water solution for 30-60 minutes prior to heating in an oven (120-180 °C) at different reaction times (5 to 120 minutes). After heating, the samples were cooled down to room temperature, diluted with distilled water, and washed with acetone, ethanol and distilled water. The esterification reaction was performed both on pulp and on handmade paper sheets. For the reaction on handmade paper sheets an acrylic acid/water solution was poured over one side of the sheets and allowed to absorb for 30-60 minutes prior heating. The reaction route for the esterification process with cellulose and acrylic acid is shown in Figure 4.3 (Route 2).

The same procedure as for acrylic acid was used for all the carboxylic acids with the exception of cinnamic acid and dodecanoic acids, which were only weak water-soluble solids and dissolved in ethanol. The reaction parameters for the carboxylic acids were; heating in oven at 160 °C for 60 minutes with a dry pulp content of 20 % and the addition of 3 moles of carboxylic acid/AGU.

For dodecanoic acid and cinnamic acid, the solid crystals (3 moles/AGU) were dissolved in ethanol and then poured onto the cellulose pulp. After absorption for 30-60 minutes the samples were heated in an oven at 160 °C for 60 minutes, cooled down to room temperature and then washed with acetone, ethanol and distilled water.



Acrylic Acid

Acetic Acid

Propionic Acid

Cinnamic Acid

Hexanoic Acid

Dodecanoic Acid

Figure 4.4. *The molecular structure for the six different carboxylic acids tested for the high temperature heating esterification method.*

4.2 CROSSLINKING OF PAPER SHEETS

The esterification reaction with acrylic acid (AA) was performed on handmade paper sheets in the same way as cellulose pulp. The AA-modified paper sheets were then crosslinked as described in this section.

4.2.1 PREPARATION OF SHEETS

A semi-automatic Rapid Köthen sheet former designed for paper making was used to prepare handmade sheets with a basis weight of approximately 80 g/m^2. All sheets were made from Scandinavian dried softwood pulp disintegrated at 30 000 revolutions before use.

4.2.2 CROSSLINKING WITH UV RADIATION

For crosslinking with UV radiation, the cellulose acrylate ester prepared from acrylic acid (see section 4.1.4) was used together with a UV curing solution. The UV curing solution consisted of a monomeric diluent, a photoinitiator (PI) and ethanol. Three different monomeric diluents were evaluated; *N*-(hydroxymethyl) acrylamide solution (HMAA), 1,6-hexanediol diacrylate (HDODA) and trimethylolpropane triacrylate (TMPTA). The photoinitiator used was 1-hydroxycyclohexyl phenyl ketone (HCHPK). The structures of the monomers and photoinitiator can be seen in Figure 4.5.

The esterification reaction was conducted on handmade sheets. A water/acrylic acid solution with 3 moles of acrylic acid/AGU and a pH of 1.5 was added to the sheets and heated in an oven at 160 °C for 60 minutes.

For the crosslinking samples, a solution of PI (0-5 wt% of the paper sheet), monomer (0-20 wt% of the paper sheet) and ethanol was mixed, and the amount of ethanol was set to give a dry content of 20 % of the paper sheets. The solution was shaken until all the PI was dissolved, and then poured over one side of the paper sheets. The ethanol was allowed to evaporate at room temperature before the paper sheets were exposed to UV light for 30 minutes.

The UV lamp used was a Black-Ray XX-15M UV Bench Lamp (15 W), that emitted UV radiation of 302 nm. The distance between the UV source and the samples was 13.5 cm.

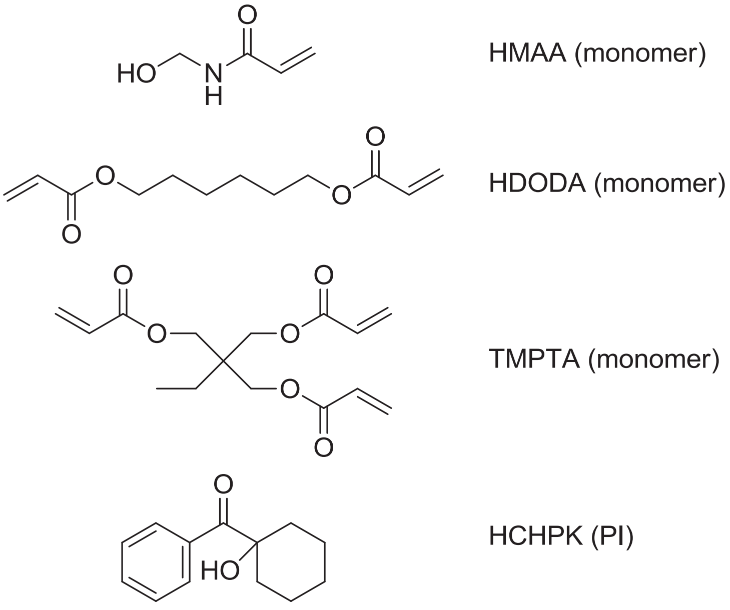


Figure 4.5. *The molecule structure of the three different monomeric diluents tested and the photoinitiator (PI).*

4.3 CHARACTERIZATION

Different microscopy techniques and analyzing methods were used to evaluate the products formed and the structure of the cellulosic fibers and paper network. The different characterization techniques used are described in the following section.

4.3.1 NUCLEAR MAGNETIC RESONANCE (NMR)

The Nuclear Magnetic Resonance (NMR) analyses were conducted on the acrylamide sulfate solution, diluted with deuterium oxide (D_2O), to determine if the desired product was formed. The NMR spectrum was recorded at 25 °C on a Varian 400-MR 400MHz spectrometer operated at 399.95 MHz for proton detection and at 100.58 MHz for carbon detection.

4.3.2 FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fourier-Transform Infrared (FTIR) spectroscopy was used to evaluate carbonyl groups (C=O) in the modified cellulose samples. This method was mainly used to study the presence of an ester which gave an absorption peak around 1750-1735 cm^{-1} if saturated or 1725-1715 cm^{-1} if unsaturated. The FTIR was recorded on a Perkin Elmer Spectrum One instrument using the potassium bromide (KBr) pellet technique.

Brodin (2013) found a relationship between the wavenumber of the absorption ester band and the degree of substitution (DS). The more substituted sample, the higher the absorption band wavenumber. To estimate the results from the esterification and to indicate a DS, the ratio between the intensity of the carbonyl absorption band and the absorption band at 1330-1320 cm^{-1}, corresponding to the CH vibration in the cellulose ring, was compared for the different samples (Nada et al. 2000).

4.3.3 TENSILE TEST

The tensile tests were performed on paper strips using an Instron 5565A. The dimensions of the paper strips in the measured area were 50 x 8.6 x 0.2 mm. Each paper strip was first incubated at 23 °C and 50 % RH for at least 24 hours before being attached between two clamps. One of the clamps in the testing device was still and the other one was moved away from the still clamp, and the paper was stretched until it broke. The strips were pulled at a strain rate of about $17 \cdot 10^{-3}$ s^{-1}, following the ISO standard 1924:3. The tensile curve was analyzed with Bluehill 2.0 and parameters such as tensile strain at max load (elongation), tensile stress at max load (tensile strength) and Young's modulus (stiffness) could be measured. The addition of a UV curing solution to the paper changed the basis weight of the sheets and the tensile index was used as a measure of the inherent strength of the paper. The tensile index (σ_T^w) is the tensile strength (N/m) divided by the basis weight (Equation 4.1).

$$\sigma_T^w = \frac{F_T}{b \cdot w} \qquad \left[\frac{Nm}{g}\right] \qquad \text{(Equation 4.1)}$$

Where F_T was the maximum force (N), b was the width (m) of the tested paper strip and w was the basis weight (g/m^2) of the tested paper strip.

4.3.4 THERMO GRAVIMETRIC ANALYSIS (TGA)

Different substances decompose at different temperatures, and these were measured with a thermogravimetric analys (TGA). TGA was performed with a PerkinElmer TGA 7. Samples (two replicates) were heated at 5 °C/min under a nitrogen flow from 25 to 550 °C. The TGA of a reference and of AA-modified sheets was measured, both UV-radiated and non-radiated. The UV-radiated sheets had an addition of 20 wt% TMPTA and 5 wt% PI. Weight losses were calculated from the TGA measurements and the actual amount of TMPTA could be compared to the added amount of TMPTA.

4.3.5 WATER RETENTION VALUE (WRV)

The Water Retention Value (WRV) measures how much water a cellulose sample can retain after controlled centrifugation. 200 mg cellulose pulp was soaked in distilled water for 3 hours before centrifuging in vivaspin tubes at 4000 rpm for 10 minutes. The samples (three replicates) were weighed before and after oven drying (approximately 100 °C for at least 24 hours) in order to estimate how much water was retained in the sample after centrifugation. The WRV is the ratio between the weight of the water and the weight of the dry sample, and the value reflects structural changes in the sample due to the ability of the cellulose pulp to hold water. The WRV was calculated using Equation 4.2.

$$WRV = \frac{m_{wet\,sample} - m_{dry\,sample}}{m_{dry\,sample}} = \frac{m_{water}}{m_{dry\,sample}} \qquad \text{(Equation 4.2)}$$

Where $m_{wet\,sample}$ was the weight of the sample after centrifugation and $m_{dry\,sample}$ was the weight of the sample after oven drying. The difference between the wet and dry sample was assumed to be the loss of water during drying, m_{water}.

The WRV method was used on cellulose pulp (unmodified and AA-modified, non-radiated and radiated) to indicate structural changes in terms of the esterification of cellulose fibers and the crosslinking effect due to UV radiation.

4.3.6 COBB INDEX

The Cobb index defines how much water a piece of paper can absorb during a certain time period. The method is based on changes in weight before and after water absorption. The procedure for the Cobb index measurements followed the standard, SCAN-P 12:64 ($Cobb_{60}$). A weighted paper sheet larger than 100 cm^2 was attached to the Cobb testing device and 100 ml distilled water was poured over the paper sheet. For $Cobb_{60}$ measurements, the paper sheets were in contact with the water for 45 seconds before the excess water was poured off and after an additional 15 seconds, the remaining water was removed with blotter paper. The paper sheet was weighed immediately afterwards. The weight difference was multiplied by 100 to get the Cobb index (g/m^2).

4.3.7 TRANSMISSION ELECTRON MICROSCOPE (TEM)

Transmission Electron Microscope (TEM) samples were prepared by fixing paper samples in osmium tetroxide (OsO_4) vapor for 2 hours. Dehydration in 99.5 % ethanol was followed by embedding in a TAAB low viscosity resin (TLV). Thin sections of 70 nm were cut with an ultramicrotome and stained according to the thiosemicarbazide-silver-proteinate method described by Thiéry (1967). Images were taken with a LEO 906 E TEM at an accelerating voltage of 80 kV.

The transition metal, OsO_4, adds to the alkenes to give diolates which hydrolyze to *cis*-diols. These diol groups provide the contrast for the TEM image. The transition metal does not add to the cellulose polymer but it adds to the functional acrylate groups and to the unsaturated monomeric diluents. TEM images were taken of the reference and the AA-modified sheets, both UVradiated and non-radiated. The UV-radiated sheets had an addition of 20 wt% TMPTA and 5 wt% PI.

4.3.8 SCANNING ELECTRON MICROSCOPE (SEM)

The Scanning Electron Microscope (SEM) technique was used for imaging the fiber network structure. A high energy focused beam of electrons scanned the fibers and an image was obtained caused by the backscattered electrons after interaction between the electrons and the sample. To avoid the accumulation of electrostatic charge on the surface, the samples needed to be electrically conductive. By sputtering the samples with an electrically conductive material, like gold, accumulation was prevented.

The gold sputtering was performed in vacuum for 80 seconds at 10 mA, and yielded approximately a 10 nm thick gold coating. A LEO Ultra 55 FEG SEM, operated at an accelerating voltage of 1.5 kV, was used for the analyses.

CHAPTER 5

SUMMARY OF RESULTS

A summary of the results presented in Paper I (Thermal esterification of cellulose fibers for improved functionality and reactivity) and Paper II (UV crosslinking of cellulose fibers for improved stiffness in paper sheets) will be described in this chapter. A short discussion of the results obtained is also given.

5.1 ESTERIFICATION REACTIONS

The first part of this study, the esterification reactions described in Paper I, dealt with two different reaction routes for preparing a cellulose acrylate ester. The results are presented below.

5.1.1 FORMATION OF ACRYLAMIDE SULFATE

To verify that the formed product was acrylamide sulfate, an NMR spectrum was performed with D_2O as solvent. The ^{13}C-NMR spectra (Figure 5.1) showed a peak at 170.72 ppm, which corresponded to the carbonyl group, and two peaks at 129.05 ppm and 128.45 ppm, which corresponded to the C=C double bond. An FTIR spectrum for the formed acrylamide sulfate was analyzed, and an absorption peak around 1692 cm^{-1} showed the carbonyl group, and a peak at around 1644 cm^{-1} showed the alkene group. Peaks between 1120-1340 cm^{-1} showed the sulfuric compounds, and the absorption band around 2500 cm^{-1} showed the OH groups from the sulfate compound. Since no absorption bands were detected between 2440-2215 cm^{-1} in the FTIR spectrum, it was assumed that all acrylonitrile had been consumed.

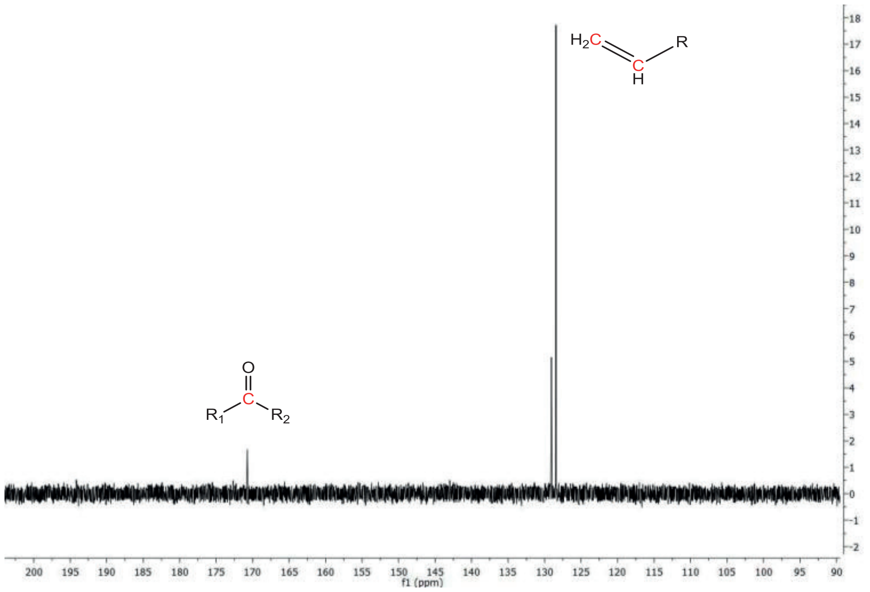


Figure 5.1. *The ^{13}C-NMR spectra for acrylamide sulfate.*

5.1.2 MODIFICATION WITH ACRYLAMIDE SULFATE

For the esterification reaction between cellulose and the formed acrylamide sulfate, FTIR analyses were conducted to examine the carbonyl bond. The reaction of acrylamide sulfate and cellulose, washed with distilled water, showed a small absorption band at 1719 cm^{-1} corresponding to a carbonyl group in the FTIR spectra. The samples washed with tap water showed no absorption band in the carbonyl group frequency area. This showed that the acrylamide sulfate had only been absorbed into the cellulose, not covalently bonded. The KBr pellets were oven-dried at approximately 100 °C for one week before FTIR analyses (Robin and Rouxhet 1976).

No clear relationship was seen when the ratio of the carbonyl absorption band and the absorption band at 1320 cm^{-1} were examined (see Table 5.1). The reaction temperatures were evaluated and almost no cellulose pulp could be collected after washing and filtration at a temperature of 70 °C, and the samples were assumed to be acid hydrolyzed. The highest possible reaction temperature without too much hydrolysis of the cellulose pulp was 50 °C.

Table 5.1. *The absorption band ratio between the carbonyl absorption band and the absorption band at 1320 cm^{-1} were calculated for different reaction temperatures and reaction times. All values are from heat-dried KBr pellets.*

Time / Temperature	Ratio 2 h	3 h	6 h
30 °C	1.007	0.686	1.076
40 °C	1.907	1.654	2.230
50 °C	0.411	0.370	0.975
60 °C	0.855	0.830	1.515
70 °C	1.143	---	---

The concentration of the acrylamide sulfate added to the cellulose was evaluated at the reaction parameters 40 °C for 3 hours. Four different concentrations of acrylamide sulfate were added. Table 5.2 shows the results and no clear relationship was found for the ratio between the carbonyl absorption band and the absorption band at 1320 cm^{-1}. Heat drying of the KBr pellets favored the carbonyl group formation.

Table 5.2. *Different mole concentrations of acrylamide sulfate added to the cellulose pulp. The absorption band ratio between the carbonyl absorption band and the absorption band at 1320 cm^{-1} were calculated.*

Mole reagent/AGU	Ratio Heat drying	No heat drying
1.9	1.598	0.499
3.9	1.525	0.309
5.8	1.838	0.571
7.7	1.654	0.460

Washing the acrylamide sulfate modified pulp with tap water and analyzing it with FTIR showed no carbonyl group at all. This indicated that the acrylamide sulfate had been absorbed onto the cellulose and not covalently bonded. Since the heat drying of KBr pellets favored the carbonyl group formation, the absorbed acrylamide sulfate cellulose samples were heated at 150 °C for 30 minutes. The formed cellulose ester turned brown during high temperature heat treatment, due to the formation of sulfuric acid (Figure 5.2.).

After washing the brown pulp samples with tap water, an FTIR analysis indicated that the absorption band at 1718 cm^{-1} was the cellulose acrylate ester (Figure 5.3). The formation of sulfuric acid during heating hydrolyzed the cellulose fibers. The brown-colored cellulose pulp was not desirable for further crosslinking applications and was not additionally evaluated.

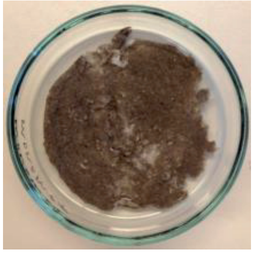


Figure 5.2. *The cellulose acrylate ester from acrylamide sulfate turned brown when heated at high temperatures.*

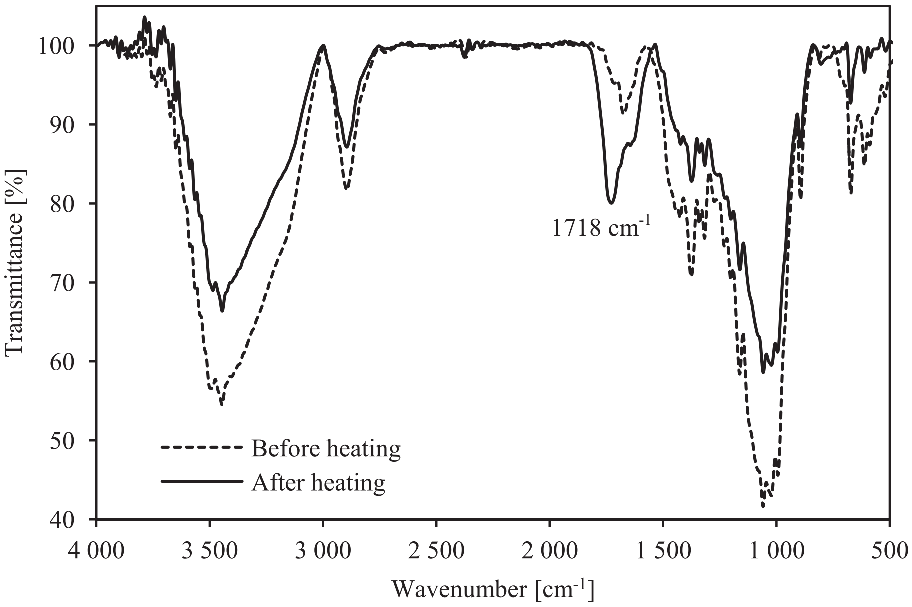


Figure 5.3. *FTIR spectrum of acrylamide sulfate absorbed cellulose pulp (- - -) and the same pulp heated at 150 °C for 30 minutes (—).*

5.1.3 MODIFICATION WITH ACRYLIC ACID

Because the pulp became hydrolyzed and discolored with acrylamide sulfate as the reagent, acrylic acid was used instead. For the esterification reaction with acrylic acid and cellulose, absorption bands around 1718 cm^{-1} to 1725 cm^{-1} were detected with the FTIR method. An optimization study for the acrylic acid modification reaction was conducted in which the mole concentration of the acrylic acid, the reaction temperature and the reaction time were in focus. Table 5.3 shows the different reaction parameters tested and their wave number for the carbonyl absorption band in FTIR.

Table 5.3. *Reaction parameters, FTIR absorption band frequency and absorption band ratio between the carbonyl group and the absorption band at 1320 cm^{-1}.*

Sample	**Reaction temperature** [°C]	**Reaction time** [min]	**Acrylic acid concentration** [mole/AGU]	**Absorption band** [cm^{-1}]	**Ratio**
120-01	120	30	2	---	(0.199)
120-02	120	30	3	---	(0.388)
120-03	120	60	2	---	(0.299)
120-04	120	60	2.5	---	(0.327)
120-05	120	60	3	---	(0.291)
120-06	120	120	2	---	(0.499)
140-01	140	15	2	---	(0.166)
140-02	140	15	2.5	---	(0.193)
140-03	140	15	3	---	(0.186)
140-04	140	30	2	---	(0.322)
140-05	140	30	3	---	(0.433)
140-06	140	60	2	---	(0.461)
140-07	140	60	2.5	---	(0.536)
140-08	140	60	3	1722	0.677
140-09	140	120	2	1719	0.677
140-10	140	120	3	1725	1.020
160-01	160	15	2	---	(0.184)
160-02	160	15	2.5	---	(0.285)
160-03	160	15	3	---	(0.254)
160-04	160	30	2	1722	0.590
160-05	160	30	3	1718	0.770
160-06	160	60	2	1723	0.769
160-07	160	60	2.5	1725	0.889
160-08	160	60	3	1725	1.067
180-01	180	5	2	---	(0.129)
180-02	180	5	3	---	(0.175)
180-03	180	15	2	1719	0.647
180-04	180	15	2.5	1722	0.620
180-05	180	15	3	1722	0.642
180-06	180	30	2	1723	0.938
180-07	180	30	3	1725	1.007
180-08	180	60	2	1725	1.020
180-09	180	60	2.5	1725	1.219
180-10	180	60	3	1725	1.147

The higher the absorption band ratio, the more acrylic acid has bonded to the cellulose. According to Brodin et al. (2013) the FTIR carbonyl absorption band increased with an increase in the DS, which correlates with the results in Table 5.3. The results indicate that a higher reaction temperature requires a shorter reaction time and vice versa.

Other parameters tested were the dry content of the pulp at the start of the reaction, the time for absorption of the solution before heating in an oven and the time between the end of heating and the washing of the samples. From the FTIR studies it was found that the dry content at the start of the reaction and the time between the heating and washing had a larger influence on the absorption band ratio than the time for absorption before heating. A higher dry content gave a higher absorption band ratio and a waiting time of 48 hours between reaction and washing gave a lower ratio than after a waiting time of 1 hour. The heating reaction used was similar to the etherification method described by Motte and Westman (2012), which found that a reduction in temperature or consistency had a negative impact on the rate of reaction, which correlates with the results presented in Table 5.3

5.1.4 OTHER CARBOXYLIC ACIDS

The esterification reaction, in which the cellulose samples were heated with a carboxylic acid reagent, was evaluated for carboxylic acids other than acrylic acid. Table 5.4 shows the results from the different carboxylic acids tested. The reaction parameters were; heating in oven at 160 °C for 60 minutes with a dry pulp content of 20 %, and 3 moles of carboxylic acid/AGU were added to the different samples. Only the water-soluble carboxylic acids gave an absorption band in the area of an ester when analyzed with the FTIR method. Both the water-soluble carboxylic acids; acetic acid and propionic acid, gave a weaker absorption ester band than acrylic acid; probably due to the higher reactivity of acrylic acid.

Table 5.4. *FTIR absorption band frequency and absorption band ratio between the carbonyl group and the absorption band at 1320 cm^{-1}.*

Sample	**Absorption band** [cm^{-1}]	**Ratio**
Acrylic Acid	1725	1.254
Acetic Acid	1731	0.477
Propionic Acid	1719	0.433
Hexanoic Acid	(1718)*	(0.636)
Dodecanoic Acid	(1718)*	(0.874)
Cinnamic Acid	(1705)*	(0.329)

** The absorption band at these wavelengths comes from unreacted carboxylic acid.*

5.2 CROSSLINKING OF HANDMADE SHEETS

The UV-radiated paper sheets were characterized with tensile tests, TGA, water absorption properties and microscopy analysis. The crosslinking reaction was performed on sheets modified with acrylic acid and on non-modified sheets (reference sheets). The reference sheets were treated in the same way as the modified sheets since the heating and washing steps affected the fibers in the sheets.

5.2.1 TENSILE TESTS

Tensile tests were performed on reference sheets, AA-modified sheets and sheets (both modified and non-modified) treated with a UV curing solution and UV radiated. There was a big difference in strength properties between the reference sheets heat treated in the oven and then washed (Table 5.5, no. 2), compared to the sheet without any treatment at all (Table 5.5, no. 1). Therefore the reference sheets were treated in the same way as the AA-modified sheets but without any reagents.

Tensile tests of the acrylic acid modified sheets (Table 5.5, no. 3) showed lower strength properties than the unmodified reference sheets (Table 5.5, no. 1 and 2). This was probably due to the acrylic acid that hydrolyzed the cellulose fibers and made them weaker.

Three different monomeric diluents were tested for UV curing and analyzed with the tensile test. Table 5.5 (no. 4-6) shows the results from the tensile test for the three different monomeric diluents added to an AA-modified sheet. The monomeric diluents tested were *N*-(hydroxymethyl) acrylamide solution (HMAA), 1,6-hexanediol diacrylate (HDODA) and trimethylolpropane triacrylate (TMPTA). The amount of PI in the UV curing solutions with HDODA and TMPTA was 3 wt% and 5 wt% for HMAA.

Table 5.5 shows that the three-functional monomeric diluent, TMPTA, gave the highest increase in strength properties (Table 5.5, no. 6). This also corresponds well with literature since high-molecular weight molecules improve the dry strength and toughness of a material (Xu and Yang 1999). Figure 5.4 illustrates the tensile test curves where tensile strength is on the y-axis and elongation is on the x-axis. The slope of the linear part of the curve is the modulus (stiffness) of the material. A high slope means a stiffer material. TMPTA showed the highest increase in the modulus of the tested monomers, and therefore only TMPTA was selected for further tests.

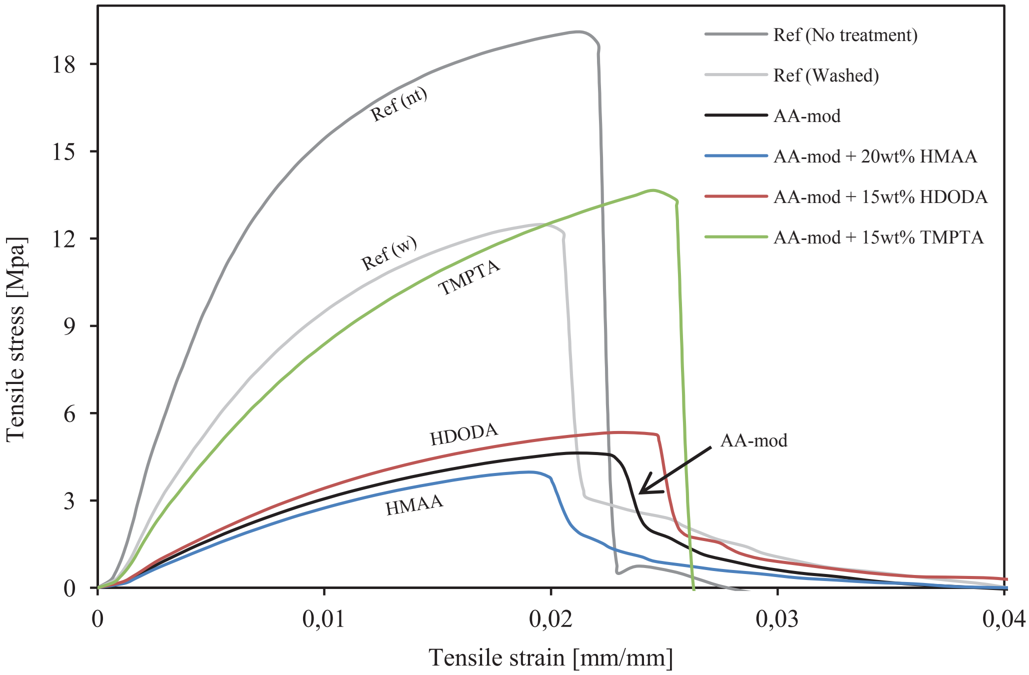
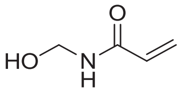
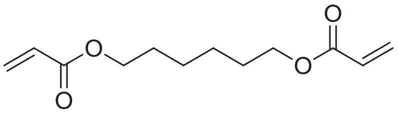
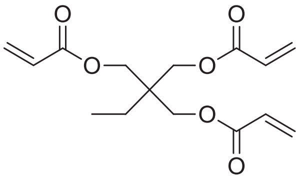


Figure 5.4. *Tensile test for three different monomeric diluents. The two grey lines show the differences in the reference paper before and after heating and washing.*

Table 5.5. *Tensile test measurements for different paper sheets. 3-5 replicates were made of each sample and standard deviations are shown in the brackets.*

No.	**Sample**	**Tensile strain at max load** [mm/mm]	**Tensile stress at max load** [MPa]	**Young's Modulus** [MPa]	**Tensile Index** [Nm/g]
1	Non-treated reference sheet	0.021 (0.001)	18.84 (0.82)	1842 (109)	27.54 (0.81)
2	Washed reference sheet	0.017 (0.020)	11.78 (1.17)	1055 (90)	18.49 (0.88)
3	Acrylic acid (AA) modified sheet	0.014 (0.010)	3.95 (0.10)	395 (5)	6.29 (0.07)
4	AA-mod sheet + 20 wt% HMAA 	0.023 (0.010)	4.72 (0.29)	339 (17)	10.46 (0.35)
5	AA-mod sheet + 15 wt% HDODA 	0.022 (0.002)	5.04 (0.28)	373 (10)	9.88 (0.80)
6	AA-mod sheet + 15 wt% TMPTA 	0.032 (0.002)	14.81 (0.87)	890 (28)	22.02 (0.46)

The acrylic acid modification made the sheets weaker but the heat and washing processes also affected the strength properties of the sheets (see Figure 5.4). To avoid losses in strength properties, different concentrations of TMPTA were added to handmade sheets, without any pretreatment (dark grey line in Figure 5.4). Tensile tests of UV-radiated paper strips with different TMPTA concentrations and 3 wt% PI added showed an increase in strength properties. Table 5.6 shows the results from the tensile test measurements. Figures 5.5 and 5.6 show the stress-strain curves for non-treated reference sheets (Figure 5.5) and AA-modified sheets (Figure 5.6).

Table 5.6. *Tensile test measurements for handmade sheets with different amounts of TMPTA added. 3-5 replicates were made for each sample and standard deviations are shown in the brackets. nt= non-treated reference sheet.*

No.	**Sample**	**Tensile strain at max load** [mm/mm]	**Tensile stress at max load** [MPa]	**Young's modulus** [MPa]	**Tensile index** Nm/g]
1	Ref (nt) + 0 wt% TMPTA	0,021 (0,001)	18,84 (0,82)	1842 (109)	27.54 (0.81)
2	Ref (nt) + 5 wt% TMPTA	0,045 (0,007)	32,96 (1,46)	1983 (55)	49.44 (1.58)
3	Ref (nt) + 10 wt% TMPTA	0,055 (0,004)	38,84 (1,18)	2109 (45)	58.92 (1.37)
4	Ref (nt) + 15 wt% TMPTA	0,054 (0,005)	39,72 (2,93)	2106 (118)	57.36 (3.05)
5	Ref (nt) + 20 wt% TMPTA	0,044 (0,004)	33,45 (1,73)	1928 (138)	47.27 (0.70)
6	AA-mod + 0 wt% TMPTA	0.014 (0.001)	3.95 (0.10)	395 (5)	6.29 (0.07)
7	AA-mod + 5 wt% TMPTA	0.028 (0.003)	15.97 (0.19)	1014 (48)	25.17 (1.28)
8	AA-mod + 10 wt% TMPTA	0.027 (0.002)	15.09 (1.42)	871 (33)	23.43 (3.06)
9	AA-mod + 15 wt% TMPTA	0.032 (0.002)	14.81 (0.87)	890 (28)	22.02 (0.46)
10	AA-mod + 20 wt% TMPTA	0.018 (0.002)	10.79 (0.45)	858 (128)	15.87 (0.35)

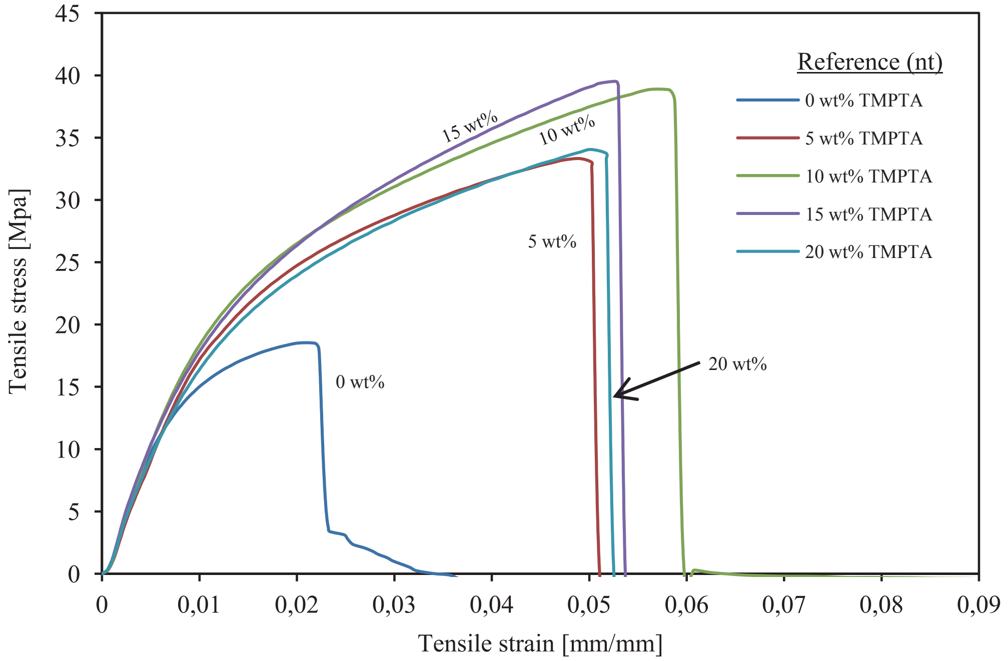


Figure 5.5. *Tensile test curves for different amounts of TMPTA added to non-treated reference sheets.*

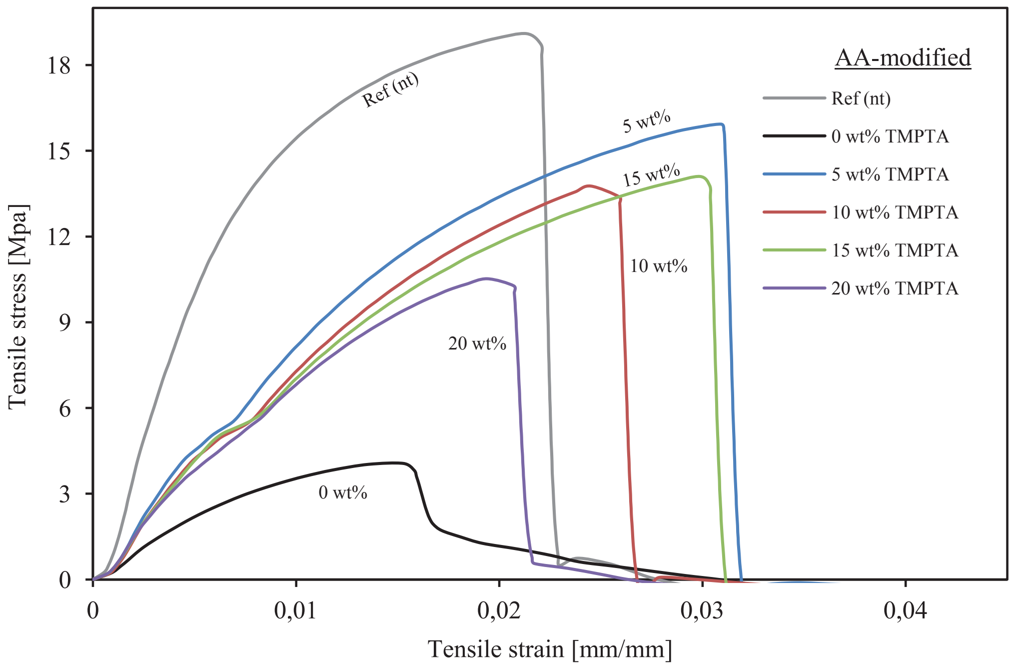


Figure 5.6. *Tensile test curves for different amounts of TMPTA added onto AA-modified paper sheets. The dark grey line is the non treated paper sheet.*

Table 5.6 (no. 1-5) and Figure 5.5 show that the optimum amount of TMPTA added to the reference sheets for the maximum increase in tensile index and Young's modulus, was 10 wt% (Table 5.6, no. 3), which gave a tensile index value that was twice as high as the non-radiated reference sheet (Table 5.6, no. 1). The results were consistent with the literature; a low degree of crosslinking favors stiffness and strength while a high degree of crosslinking gives a more brittle product with lower strain at break (Horvath et al. 2010).

For the AA-modified sheets with different amounts of TMPTA and 3 wt% PI added (Figure 5.6), the optimal amount of TMPTA for the highest increase in tensile index and Young's modulus was 5 wt% (Table 5.6, no. 7). The greatest increase in tensile index of a radiated, AA-modified paper sheet compared to a non-radiated, AA-modified paper sheet was four times higher (Table 5.6, no. 7 compare to no. 6). Despite the high increase in the strength of the UV-radiated AA-modified paper sheets, the strength properties were not higher than those of the non-treated reference sheets (Table 5.6, no. 1), which means that acrylic acid modification may enhance the crosslinking of the cellulose fibers but the modification cannot compensate for the weakness caused by acidic hydrolysis.

5.2.2 TGA MEASUREMENTS

TGA was measured for the reference and the AA-modified sheets, both radiated and non-radiated. The UV curing solution used consisted of 20 wt% TMPTA, 5 wt% PI and ethanol. A TGA sample with the radiated UV curing solution was also analyzed (Figure 5.7c).

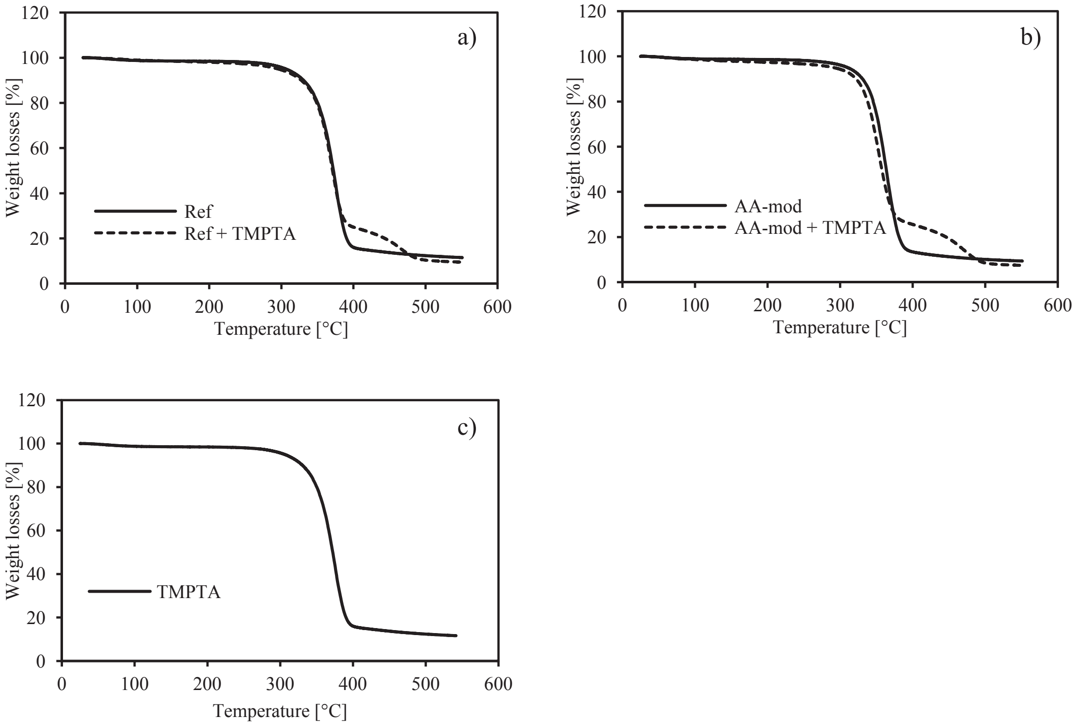


Figure 5.7. *TGA curves for a) reference paper sheets, b) AA-modified paper sheets and c) the radiated UV curing solution (TMPTA).*

TGA analyses of sheets (references and AA-modified) were compared for both non-radiated and UV-radiated samples (Figure 5.7a+b). Differences between a UV-radiated paper and a non-radiated paper were seen and a new decomposition region was found at approximately 400-500 °C for the UV-radiated paper samples. The sample with the radiated UV curing solution (Figure 5.7c) decomposes at the same temperature as cellulose (approximately 300-400 °C) which means that the new region that was found in the UV radiated paper samples is due to the crosslinking between cellulose and TMPTA. The weight loss for the new region caused by crosslinking could be evaluated to approximately 20 % which corresponded well to the added amount of TMPTA. Since the decomposition of the cellulose was similar in both non-radiated and radiated samples, the crosslinking was located to the surface of the fibers.

5.2.3 ABSORPTION PROPERTIES

Water retention value (WRV)

The WRV was measured for the different pulp samples (reference samples and AA-modified samples) treated with different amounts of the three-functional monomeric diluent, TMPTA. The UV curing mixture consisted of TMPTA (0-20 wt%), 3 wt % PI and ethanol. Three replicates were made of each sample.

Table 5.7 indicates that there was a reduction in the WRV for an AA-modified pulp (Table 5.7, no. 7) compared to its reference pulp (Table 5.7, no. 2). A reduction in WRV indicates structural changes due to the esterification reaction.

Table 5.7. *The WRV values for samples treated with different amounts of TMPTA and UV-radiated (3 wt % PI was used for the samples with UV radiation).*

No.	Sample	WRV	% water in sample
1	Reference (nt)	1.11 (0.01)	52.5 (0.2)
2	Reference (washed)	0.67 (0.05)	40.2 (1.7)
3	Reference + 5 wt% TMPTA	0.64 (0.06)	39.0 (2.3)
4	Reference +10 wt% TMPTA	0.62 (0.03)	38.2 (1.2)
5	Reference + 15 wt% TMPTA	0.59 (0.01)	37.1 (0.4)
6	Reference + 20 wt% TMPTA	0.52 (0.01)	34.2 (0.4)
7	AA-sample	0.54 (0.02)	35.0 (0.8)
8	AA-sample + 5 wt% TMPTA	0.53 (0.02)	34.6 (0.8)
9	AA-sample + 10 wt% TMPTA	0.50 (0.02)	33.4 (0.9)
10	AA-sample + 15 wt% TMPTA	0.49 (0.01)	33.0 (0.5)
11	AA-sample + 20 wt% TMPTA	0.50 (0.04)	33.2 (1.9)

For the UV-radiated samples with different amounts of TMPTA added, all samples had a lower WRV than the non-radiated samples without a UV curing solution. The AA-samples showed a lower WRV than the reference samples due to the lower

WRV from start, but lowering in the WRV may also indicate a better crosslinking effect.

Cobb-index

The UV-radiated pulp samples with different amounts of TMPTA added were more hydrophobic than cellulose pulp without TMPTA (Figure 5.8). The hydrophobicity was therefore measured with a Cobb test: The lower the Cobb index value, the more hydrophobic the paper sheet. The $Cobb_{60}$ method was used and the Cobb index for the tested paper sheets can be seen in Table 5.8.

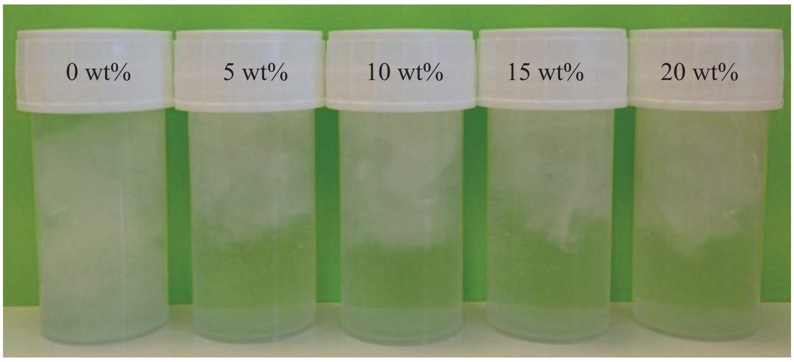


Figure 5.8. *Cellulose pulp samples in water. The samples were UV radiated with different amount of TMPTA added.*

There was a difference in hydrophobicity for UV-radiated sheet with the addition of TMPTA and 3 wt% PI, compared to non-radiated sheets (0 wt% TMPTA). As expected, the more TMPTA added to the paper sheets before UV radiation, the lower the Cobb index (Table 5.8). A lower Cobb index means a more hydrophobic paper and the results in Table 5.8 correspond with the WRV results in Table 5.7.

Table 5.8. *The Cobb index for UV-cured paper sheets.*

Sample	Cobb-index
0 wt% TMPTA	222.8
5 wt% TMPTA	151.8
10 wt% TMPTA	86.5
15 wt% TMPTA	97.8
20 wt% TMPTA	33.5

5.2.4 MICROSCOPY ANALYSIS

Transmission electron microscope (TEM)

TEM analyses of AA-modified sheets and the reference sheets showed that the surface of the fibers had changed. By OsO_4 fixation, the unsaturated ester bonds as well as the TMPTA were stained, which can be seen on the surface of the fibers as darkened areas. AA-modified fiber (Figure 5.9b) shows a dark area located on the surface of the fibers which cannot be seen in the reference sample (Figure 5.9a). The darkening was due to the esterification reaction with acrylic acid. Figures 5.9c and 5.9d show a UV-radiated reference fiber and an AA-modified fiber both with 20 wt% TMPTA and 5 wt% PI added. In both figures, a darkened area on the fiber surface was seen caused by TMPTA, which encapsulated the fibers like a thin film and smoothed out the roughness of the fibers.

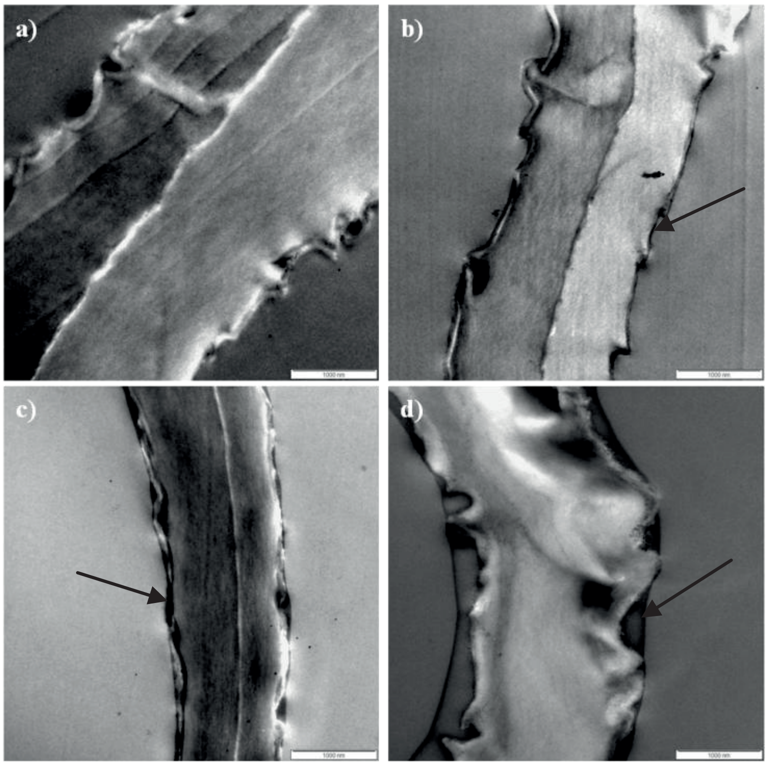


Figure 5.9. *TEM images of cellulose fibers stained with OsO_4: a) reference, b) AA-modified, c) reference UV-radiated with TMPTA and d) AA-modified sheet UV-radiated with TMPTA.*

Scanning electron microscope (SEM)

The fiber network surface of the handmade paper sheets was examined with SEM. Figure 5.10 shows the fiber network for non-radiated AA-modified paper sheets (Figure 5.10a), UV-radiated AA-modified sheets with 10 wt% TMPTA and 3 wt% PI (Figure 5.10b), non-radiated reference sheets (Figure 5.10c) and UV-radiated reference sheets with 10 wt% TMPTA and 3 wt% PI added (Figure 5.10d)

SEM images of the fiber surface network showed no significant differences between a non-radiated and a UV-radiated, AA-modified paper sample (Figures 5.10a and 5.10b). Differences could, however, be seen in the AA-modified sample compared to a non-treated reference sample (Figure 5.10c). The non-treated reference sample consisted of small fiber fragments in between the long fibers, which caused more fiber joints in the network and increased strength properties (Horvath et al. 2010).

Differences in fiber structure were seen between a non-treated reference sample and a UV-radiated sample with 10 wt% TMPTA and 3 wt% PI added. There was a decrease in small fiber fragments in the radiated sample (Figure 5.10d) probably caused by the addition of the UV curing solution. At higher magnification, the fiber joints of the UV-radiated reference sample (Figure 5.10f) seem to be more melded together than in the non-treated reference sample (Figure 5.10e).

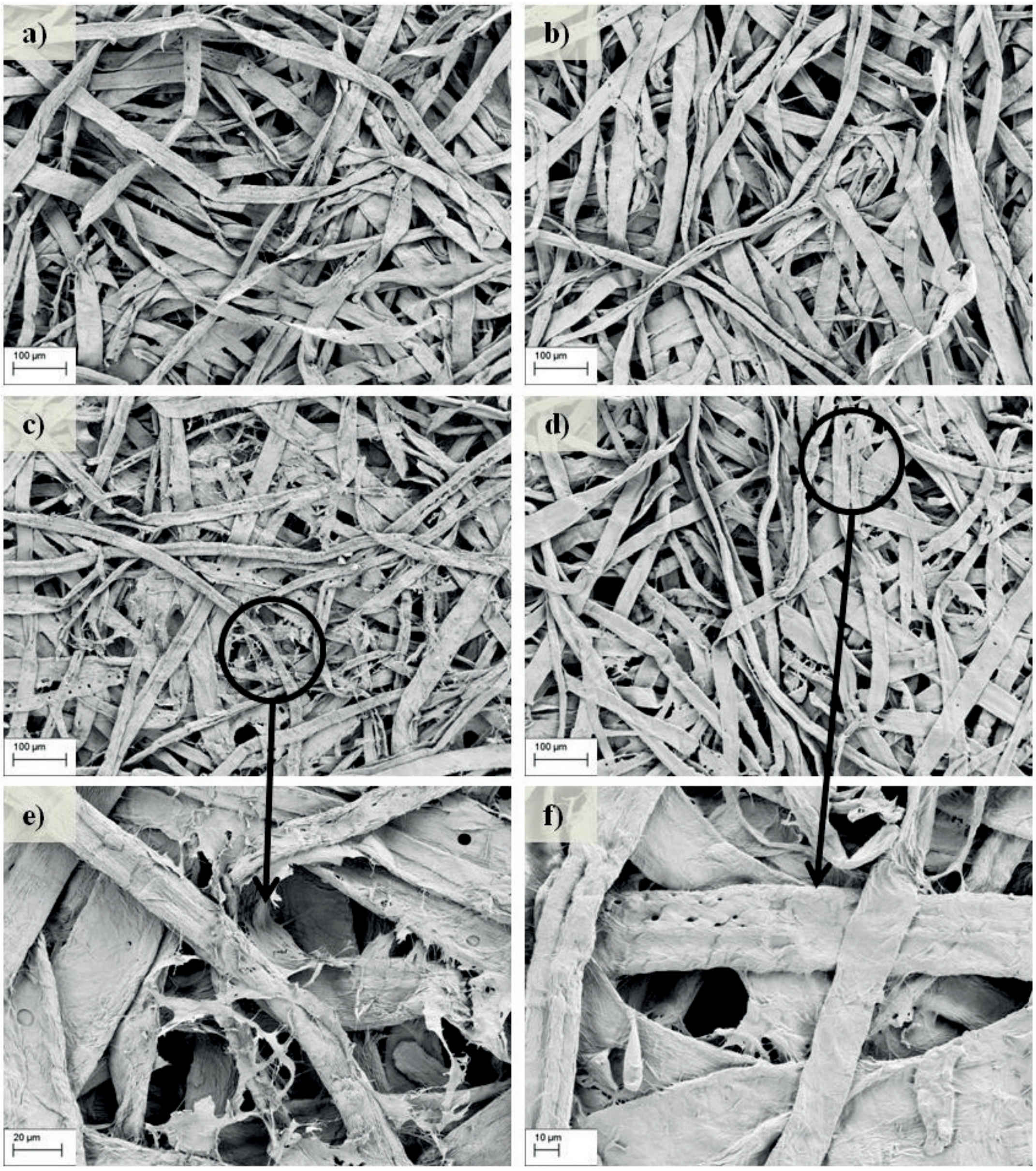


Figure 5.10. *SEM images of paper sheets a) AA-modified, b) AA-modified + TMPTA and UV-radiated, c) reference (nt), d) reference (nt) + TMPTA UV-radiated, e) reference (nt) (higher magnification) and f) reference (nt) + TMPTA UV-radiated (higher magnification).*

CHAPTER 6

CONCLUDING REMARKS

The thesis consisted of two sections in which the first part dealt with the esterification of cellulose fibers with both acrylamide sulfate and six different carboxylic acids. The second part of the thesis dealt with the radiation crosslinking of cellulose fibers; both acrylic acid esterified paper sheets and non-treated paper sheets were evaluated. This chapter will deal with some concluding remarks and suggestions for future research in the area.

6.1 CONCLUSIONS

Acrylic acid was a better reagent than acrylamide sulfate in terms of forming an unsaturated cellulose ester. The sulfuric acid formed in the acrylamide sulfate esterification reaction hydrolyzed the cellulose pulp and the pulp turned brown. The heating technique in which acrylic acid was used as the reagent worked well at high temperatures and a clear correlation between reaction time and reaction temperature was found. The heating technique worked for water-soluble carboxylic acids but not for weak or non-water-soluble carboxylic acids. The acrylic acid cellulose ester could be useful in applications for further reactions due to the unsaturated double bond, for example in crosslinking reactions.

The crosslinking reactions were mainly performed on sheets and a UV curing solution consisting of a monomer, a photoinitiator (PI) and a solvent (ethanol) were poured onto one side of the paper sheets. Only the different concentrations of the three-functional monomer, TMPTA, were analyzed, and not the amounts of the PI or the radiation time. For further research it is of interest to fully optimize the crosslinking reaction. Of the three tested monomeric diluents, TMPTA was the most suitable and the strength properties of crosslinked paper increased with several percent compared to the reference paper.

The acrylic acid esterification of the fibers and the washing steps affected the strength properties of the paper and made it weaker. The crosslinking of the acrylic acid esterified paper did not have the ability required to compensate for the loss in strength. Therefore radiation of non-treated paper sheets was performed instead. The non-treated paper sheets showed the highest value in strength properties with a doubled increase in tensile index (10 wt% TMPTA added). AA-modified sheets showed an increase in tensile index that was four times higher than the non-radiated AA-modified sheets (5 wt% TMPTA added). Despite the high increase in tensile index, the UV-radiated, AA-modified sheets were weaker than the non-treated paper sheets.

6.2 FUTURE RESEARCH

Some suggestions for further research within this area;

- To optimize the UV curing reaction. This thesis only dealt with the optimization of the three-functional monomer, TMPTA, but a lot of other parameters need to be understood, for example the UV source, the UV curing time, and the amount and type of photoinitiator used.
- A study of the disintegration of a UV-cured material. UV curing increases the strength and stiffness of paper but it is important that the paper material is recyclable.
- TMPTA is an FDA-approved monomeric diluent and is used for the UV curing of ink in food packaging today. Even if TMPTA is FDA-approved, the migration of unreacted monomers into the packaging needs to be controlled, which was not done in this thesis.
- The potential to use other types of electromagnetic radiation on paper material in the process line, for example the E-beam.
- To study the esterification reaction with water-soluble carboxylic acids in the presence of a catalyst. The catalyst might improve the reaction in several ways and prevent or hinder the hydrolyzation of the fibers.

ACKNOWLEDGEMENTS

This research has been carried out within Formulosa – a research collaboration between Södra Cell AB, Tetra Pak, BillerudKorsnäs and Chalmers. The companies involved in the project together with VINNOVA are gratefully acknowledged for financing this study.

Some special persons I would like to thank for making this thesis possible;

First of all, my supervisor Gunnar Westman for his great support, encouragement and never ending enthusiasm!

My co-supervisor at Tetra Pak, Andrew Horvath, for all the guidance and helpful discussions.

Gisela Richardson, my colleague and co-author, are acknowledged for her unbelievable help with both microscopy analyses and lab work.

Everyone involved in the Formulosa project for support, inspiration and good collaboration.

All my present and former colleagues at floor 9 and especially everyone involved in our research group. A special thanks to Johannes Thunberg for all the help with SEM and for forcing me to learn new things.

Finally, my lovely family and friends are all gratefully acknowledged for their incredible support. Thank you!

REFERENCES

Allen, N. S. (1996). "Photoinitiators for UV and visible curing of coatings: Mechanisms and properties." *Journal of Photochemistry and Photobiology A: Chemistry*, 100 (1-3), 101-107.

Baiardo, M., Frisoni, G., Scandola, M., and Licciardello, A. (2002). "Surface chemical modification of natural cellulose fibers." *Journal of Applied Polymer Science*, 83 (1), 38-45.

Barba, C., Montané, D., Farriol, X., Desbrières, J., and Rinaudo, M. (2002). "Synthesis and characterization of carboxymethylcelluloses from non-wood pulps II. Rheological behavior of CMC in aqueous solution." *Cellulose*, 9, 327-335.

Biermann, C. J. (1996). "Paper and Its Properties", *Handbook of Pulping and Papermaking*. pp. 158-189.

Brodin, M. (2013). *Shapeable cellulosic materials*, Licentiate Thesis, Chalmers University of Technology, Gothenburg.

Brännvall, E. (2006). "Overview of Pulp and Paper Processes", *Ljungberg textbook. Pulping Chemistry and Technology*. Stockholm: Fiber and Polymer Technology, KTH.

Böhm, A., Gattermayer, M., Trieb, C., Schabel, S., Fiedler, D., Miletzky, F., and Biesalski, M. (2013). "Photo-attaching functional polymers to cellulose fibers for the design of chemically modified paper." *Cellulose*, 20, 467-483.

Carlmark, A., and Malmström, E. E. (2003). "ATRP Grafting from Cellulose Fibers to Create Block-Copolymer Grafts." *Biomacromolecules*, 4, 1740-1745.

Chen, C.-C., and Wang, C.-C. (2006). "Crosslinking of cotton cellulose with succinic acid in the presence of titanium dioxide nano-catalyst under UV irradiation." *Journal of Sol-Gel Science and Technology*, 40 (1), 31-38.

Clough, R. L. (2001). "High-energy radiation and polymers: A review of commercial processes and emerging application." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 185 (1-4), 8-33.

Cook, P. M. (1988). *Radiation-Polymerizable Cellulose Esters*. U.S patent application 147,474.

Cook, P. M., and Simm, R. A. (1998). *UV Curable Cellulose Esters*. U.S. patent application 558 995.

Davidson, R. S. (2001). *Radiation Curing (Rapra Review Reports)* Smithers Rapra.

Decker, C. (2001). "UV-radiation curing chemistry." *Pigment & Resin Technology;*, 30 (5), 278-286.

Decker, C. (2003). "Kinetic Study and New Applications of UV Radiation Curing." *Macromolecular Rapid Communications*, 23 (18), 1067-1093.

Didwania, H. (1968). *A study of the effects of hydroxyethylation on bonding of paper*, Doctoral Disseration, Institute of Paper Chemistry, Wisconsin.

Durgavale, S. V. (2002). "Unsaturated polyester resins for UV curable coatings." *Paintindia*, 52, 35-42.

Freire, C. S. R., Silvestre, A. J. D., Neto, C. P., Belgacem, M. N., and Gandini, A. (2006). "Controlled Heterogeneous Modification of Cellulose Fibers with Fatty Acids: Effect of Reaction Conditions on the Extent of Esterification and Fiber Properties." *Journal of Applied Polymer Science*, 100, 1093-1102.

Gardea-Hernández, G., Ibarra-Gómez, R., Flores-Gallardo, S. G., Hernández-Escobar, C. A., Pérez-Romo, P., and Zaragoza-Contreras, E. A. (2008). "Fast wood fiber esterification. I. Reaction with oxalic acid and cetyl alcohol." *Carbohydrate Polymers*, 71, 1-8.

Glöckner, P., Jung, T., Struck, S., and Studer, K. (2008). *Radiation Curing for Coatings and Printing Inks: Technical Basics and Application*, Vincentz Network.

Hasani, M. (2010). *Chemical modification of cellulose. New possibilities of some classical routes*, PhD-thesis, Chalmers University of Technology, Gothenburg.

Hasani, M., and Westman, G. (2011). "Self-crosslinking of 2-hydroxypropyl-N-methylmorpholinium chloride cellulose fibres." *Cellulose*, 18 (3), 575-583.

Heinze, T. (2005). "Chemical Functionalization of Cellulose", in S. Dumitriu, (ed.), *Polysaccharides. Structural Diversity and Functional Versatility*. Marcel Dekker, pp. 551-590.

Heinze, T., and Liebert, T. (2004). "Chemical characteristics of cellulose acetate." *Macromolecular Symposia*, 208 (1), 167-238.

Heinze, T., Schwikal, K., and Barthel, S. (2005). "Ionic Liquids as Reaction Medium in Cellulose Functionalization." *Macromolecular Bioscience*, 5, 520-525.

Henriksson, G., Brännvall, E., and Lennholm, H. (2006). "The Trees", *Ljungberg Textbook. Wood Chemistry and Wood Biotechnology*. Stockholm: Fiber and Polymer Technology, KTH.

Horvath, A. T., Pelton, R., Larsson, P. T., and Wågberg, L. (2010). "Effect of Cross-Linking Fiber Joints on the Tensile and Fracture Behavior of Paper." *Industrial & Engineering Chemistry Research*, 49 (14), 6422-6431.

Hussain, M. A., Liebert, T., and Heinze, T. (2004). "Acylation of Cellulose with N,N′-Carbonyldiimidazole-Activated Acids in the Novel Solvent Dimethyl Sulfoxide/Tetrabutylammonium Fluoride." *Macromolecular Rapid Communications*, 25, 916-920.

Höglund, H. (2004). "Mechanical pulping", *The Ljungberg Textbook, Cellulose Technology*. Stockholm: Fiber and Polymer Technology, KTH.

Kim, D. S., and Seo, W. H. (2004). "Ultraviolet-Curing Behavior and Mechanical Properties of a Polyester Acrylate Resin." *Journal of Applied Polymer Science*, 92 (6), 3921-3928.

Kirwan, M. J. (2003). "Paper and paperboard packaging", *Food Packaging Technology*. Blackwell Publishing.

Kiviranta, A. (2000). "Paperboard Grades", in H. Paulapuro, (ed.), *Paper and Board Grades*. The Finnish Paper Engineers' Association and TAPPI.

Klemm, D., Heublein, B., Fink, H.-P., and Bohn, A. (2005). "Cellulose: Fascinating Biopolymer and Sustainable Raw Material." *Angewandte Chemie International Edition*, 44 (22), 3358-3393.

Kumar, R. N., Po, P. L., and Rozman, H. D. (2006). "Studies on the synthesis of acrylamidomethyl cellulose ester and its application in UV curable surface coatings induced by free radical photoinitiator. Part 1: Acrylamidomethyl cellulose acetate." *Carbohydrate Polymers*, 64 (1), 112-126.

McNae, C. (1964). *Production of Acrylamide*. U.K. patent application GB19640005603.

Menashe, T. (1986). *Hydrogel-forming polymers*. European patent application EP19850309168.

Motte, H. d. l., and Westman, G. (2012). "Regioselective cationization of cellulosic materials using an efficient solvent-minimizing spray-technique." *Cellulose*, 19, 1677-1688.

Nada, A.-A. M. A., Kamel, S., and El-Sakhawy, M. (2000). "Thermal behaviour and infrared spectroscopy of cellulose carbamates." *Polymer Degradation and Stability*, 70 (3), 347-355.

Paquet, O., Krouit, M., Bras, J., Thielemans, W., and Belgacem, M. N. (2010). "Surface modification of cellulose by PCL grafts." *Acta Materialia*, 58, 792-801.

Reddy, N., Li, Y., and Yang, Y. (2009). "Alkali-Catalyzed Low Temperature Wet Crosslinking of Plant Proteins Using Carboxylic Acids." *Biotechnology Progress*, 25 (1), 139-146.

Robertson, G. L. (2009). "Food Packaging and Shelf Life", *Food Packaging and Shelf Life*. CRC Press, pp. 1-16.

Robin, P. L., and Rouxhet, P. G. (1976). "Contribution of molecular water in the infrared spectra of kerogens and coals." *Fuel*, 55 (3), 177-183.

Roy, D., Semsarilar, M., Guthrie, J. T., and Perrier, S. (2009). "Cellulose modification by polymer grafting: a review." *Chemical Society Reviews*, 38 (7), 1825-2148.

Scherzer, T. (2004). "Photopolymerization of Acrylates without Photoinitiators with Short-Wavelength UV Radiation: A Study with Real-Time Fourier Transform Infrared Spectroscopy." *Journal of Polymer Science: Part A: Polymer Chemistry*, 42 (4), 894-901.

Shukla, V., Bajpai, M., Singh, D. K., Singh, M., and Shukla, R. (2004). "Review of basic chemistry of UV-curing technology." *Pigment & Resin Technology;*, 33 (5), 272-279.

Stöllman, U., Johansson, F., and Leufvén, A. (1994). "Packaging and food quality", in C. M. D. Man and A. A. Jones, (eds.), *Shelf Life Evaluation of Foods*. Chapman & Hall, pp. 52-71.

Thiéry, J. P. (1967). "Mise en evidence des polysaccharides sur coupes fines en microscopie électronique." *Journal de Microscopie*, 6, 987-1018.

Xu, G. G., and Yang, C. Q.-X. (1999). "Comparison of the kraft paper crosslinked by polymeric carboxylic acids of large and small molecular sizes: Dry and wet performance." *Journal of Applied Polymer Science*, 74, 907–912.

Yang, C. Q., and Xu, Y. (1998). "Paper wet performance and ester crosslinking of wood pulp cellulose by poly(carboxylic acid)s." *Journal of Applied Polymer Science*, 67 (4), 649-658.

Yuan, H., Nishiyama, Y., and Kuga, S. (2005). "Surface esterification of cellulose by vapor-phase treatment with trifluoroacetic anhydride." *Cellulose*, 12, 543-549.

Zhou, Y. J., Luner, P., and Caluwe, P. (1995). "Mechanism of Crosslinking of Papers with Polyfunctional Carboxylic Acids." *Journal of Applied Polymer Science*, 58, 1523-1534.

APPENDIX A

CELLULOSE

Appendix A describes the cellulose structure at different levels and should be seen as a support for a better understanding of the thesis. The main focus in the thesis was the packaging product and paperboard properties.

CELLULOSE STRUCTURE

Cellulose (Latin: *Rich in small cells*) is a biopolymer found naturally in plant cells like wood, algae and cotton. It is a linear homo-polysaccharide consisting of D-anhydroglucopyranose units (AGU) joined by β-1,4-glycosidic bonds (Figure A.1). Each AGU has tree hydroxyl groups. The hydroxyl group at the 6th carbon position acts as a primary alcohol, while the hydroxyl groups at the 2nd and 3rd carbon positions behave as secondary alcohols. These hydroxyl groups are all possible sites for the chemical modification of cellulose where the hydroxyl group at the 6th carbon is the most reactive (Roy et al. 2009). The smallest repeating unit in cellulose consists of two AGUs and is called a cellobiose unit. The degree of polymerization (DP) of the linear cellulose molecule can be as high as 300-1700 in wood and even higher in, for example cotton plant fibers (Klemm et al. 2005). After degradation reactions and purification processes the DP is reduced.

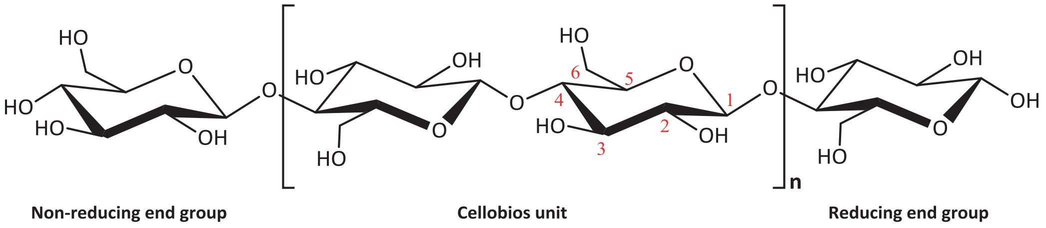


Figure A.1. *Partial chemical structure of a cellulose molecule. The three hydroxyl groups in one AGU are located on the* 2^{nd}*,* 3^{rd} *and* 6^{th} *carbon positions.*

Due to the linear and quite regular structure of cellulose and the many hydroxyl groups in the molecule, cellulose polymers can form ordered crystalline structures held together with hydrogen bonds and van der Waals forces. These crystalline regions give important mechanical properties to the cellulose fiber. The hydroxyl groups in the cellulose polymer can form hydrogen bonds between different cellulose polymers (intermolecular hydrogen bonds) or within the polymer itself (intramolecular hydrogen bonds). The different types of bonding give different properties to the cellulose fiber. The crystallinity and the many hydrogen bonds in the cellulose fibers make cellulose insoluble in water or in most conventional organic solvents.

The structure of a cellulose fiber can be divided into three different levels; the molecular level, the supramolecular level and the morphological level. The molecular level was described in the beginning of this section (Figure A.1). The supramolecular level is the polymer chains ordered in crystalline and amorphous regions with hydrogen bonds and van der Waals forces (Figure A.2). The last level is the morphological level and consists of the cellulose fiber and its cell walls.

Figure A.2 shows the different levels of the cellulose structure where the cellulose molecule chains are ordered in crystalline and amorphous regions in a microfibril. Several microfibrils are assembled together to a macrofibril. The macrofibrils are oriented in different layers in the cell wall and the different layers differ in fibril direction, densities and textures. Wood cells are glued together by the lignin rich middle lamella.

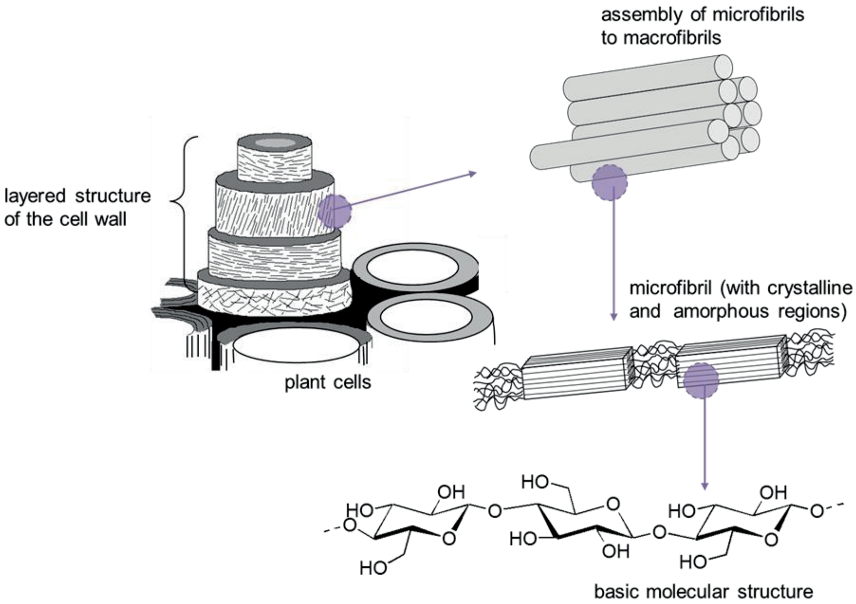


Figure A.2. *Formation of cellulose biopolymers in plant cell walls. Picture:(Hasani 2010).*

FIBER PROPERTIES AND TREATMENT

The properties of the natural fibers depend on different factors like the source of the fibers and pulp treatment. Wood fibers, which are the most common cellulose source for packaging products, can be either hardwood (HW) pulp or softwood (SW) pulp.

Wood fibers mainly consist of 40-45 % cellulose, around 30 % hemicelluloses and around 25 % lignin. Depending on wood type the amount of hemicelluloses and lignin differ but generally HW consists of more hemicelluloses and less lignin than SW (Henriksson et al. 2006).

Hardwood fibers are found in trees like birch or aspen, and have a typical fiber length of 0.7-1.6 mm. HW fibers are shorter than SW fibers and shorter fibers can pack more closely in the structure of paper and therefore HW fibers are suitable for use in fine papers.

Softwood fibers are found in trees like spruce or pine and the fibers are longer, approximately 2.5-4.5 mm. SW pulp is very abundant and used in both mechanical and chemical pulping. SW pulp is very common in the Kraft pulp process. Due to the long fibers in SW, the fibers are suitable for paper and paperboard where certain strength is required. Long and short fibers can be mixed in order to get suitable properties (Henriksson et al. 2006).

Pulping processes liberate the fibers from the wood matrix and there are generally two different methods; mechanical pulping or chemical pulping.

Mechanical treatment

Wood or wood chips are ground until the fibers in the wood are released. The pulp yield for mechanically treated pulp is 90-100 %. The fibers obtained from mechanical pulping are stiff and most of them are uncollapsed. During mechanical pulping lots of fiber fragments and fines are formed; these are small parts from the fiber wall. Due to these smaller fragments in combination with longer fibers, a very smooth paper surface and excellent optical properties can be formed. On the other hand, a lot of fines and fiber fragments give weaker materials since long fibers have higher strength properties than short fibers (Brännvall 2006).

Chemical treatment

The idea of chemical pulping is to remove the lignin that glues the fibers together and thereafter release the fibers. This is done by degrading the lignin molecules and introducing charged groups. The yield with this method is much lower for chemical pulping than for mechanical pulping but less energy demanding. The yield is around 50 % and the other half of the fibers are dissolved. There are no pulping chemicals that can remove all lignin without damaging the fibers too much. Chemical pulped fibers are much more flexible than mechanical pulped fibers due to their longer fiber length. The fibers adapt well to each other when forming a paper structure and this creates good strength properties (Brännvall 2006).

Kraft cooking is the dominant chemical pulping method, and the cooking chemicals used are sodium hydroxide and sodium sulfide. The pulp used in this thesis is a Scandinavian Kraft pulp from softwood fibers. The Kraft pulp obtained from the Kraft process consists of cellulose wood fibers, containing around 85 % cellulose and some residual hemicelluloses and lignin. The small amount of lignin can give a brownish color to the fibers, therefore the manufacture of white fibers requires further delignification and bleaching. This is done through a series of alternating oxidation and extraction treatments. Removal of lignin through bleaching processes makes the fibers resist ageing and yellowing (Brännvall 2006).