THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Recycling of cotton textiles: Characterization, pretreatment, and purification

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Cover photo: Micrograph of fibers from pullovers that have been mechanically defibrated, showing a large mix of different fibers, e.g. wool, synthetics and cotton.

Photo of the author: Jonas Wetterling

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Abstract

In many parts of the world, there are well-established systems for material recycling of metal, glass, and paper. However, no large-scale chemical recycling of textiles currently exists. Since the collection of second hand textiles is established on a large-scale, one of the main barriers to obtaining chemical textile recycling is the development of recycling technology. Recently, it has been proposed that recycling cotton may be accomplished using post-consumer cotton to produce regenerated cellulose fibers, such as viscose and lyocell. These fibers are, today, made either from wood-derived dissolving pulp or cotton linters, both of which contain almost pure cellulose. The incorporation of used cotton fibers from textiles is an interesting possibility since cotton also contains almost pure cellulose. The most common textile material on the market contains a mix of polyester, i.e. poly(ethylene terephthalate) (PET), and cotton, referred to as polycotton, and the separation of the two components is necessary before recycling. This thesis investigates some important aspects of the chemical recycling of textiles. The focus is on four areas; property changes during laundering and use of cotton, acid pretreatment of cotton, swelling properties of cotton, and separation of cotton from polycotton textiles.

The first part is based on that during the service life of cotton textiles, laundering is performed many times, and this may change the properties of cotton. When new cotton fibers are compared to cotton fibers from sheets that have been used in hospitals for a long period of time, findings show that laundering and use do not have a large impact on the supramolecular structure of cotton cellulose. However, the cellulose the degree of polymerization decrease greatly after long-term use.

The second and third parts of the thesis investigate the pretreatment of cotton. Pretreatments of cellulose fibers are used to enhance susceptibility to dissolution before the production of regenerated fibers. Three different pretreatments were investigated, acid hydrolysis in water, acid hydrolysis in ethanol and hydrothermal treatment. Findings show that the degradation pattern is similar in cotton and dissolving pulp for all pretreatments.

The last part of the thesis investigates the separation of the components in polycotton. In the process, polyester is hydrolyzed by the action of alkali while cotton is maintained. The process yields three product streams; two containing the two different monomers obtained when hydrolyzing the PET, and one with residual cotton. The yield of the process is high, and the fractions showed high purity.

Keywords: Textile recycling, Cotton, Cellulose, Pretreatment, Polycotton, Hydrolysis

List of publications

This thesis is based on the work presented in the following publications, referred to by Roman numerals in the text.

I.   Chemical and ultrastructural changes in cotton cellulose induced by laundering and textile use
Anna Palme, Alexander Idström, Lars Nordstierna and Harald Brelid
Cellulose, 21(6), 4681-4691, 2014

II.   Acid hydrolysis of cellulosic fibers: Comparison of bleached kraft pulp, dissolving pulps and cotton textile cellulose
Anna Palme, Hans Theliander and Harald Brelid
Carbohydrate polymers, 136, 1281-1287, 2016

III.   Differences in swelling of chemical pulp fibers and cotton fibers – effect of the supramolecular structure
Anna Palme, Fredrik Aldaeus, Per Tomas Larsson, Merima Hasani, Hans Theliander and Harald Brelid
Manuscript

IV.   Acid pretreatment of different cellulosic fibers using HCl in water, HCl in ethanol and hydrothermal treatment
Anna Palme, Merima Hasani, Hans Theliander and Harald Brelid
Manuscript

V.   Development of an efficient route for combined recycling of polyester and cotton from mixed fabrics
Anna Palme, Anna Peterson, Hanna de la Motte, Hans Theliander, Harald Brelid
Submitted manuscript

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

i.   Ageing of cellulose – property changes during long time service of cotton textiles

Anna Palme, Alexander Idström, Lars Nordstierna and Harald Brelid

17th International symposium on wood, fibre and pulping chemistry, Vancouver, Canada, June 12-14, 2013. (Oral presentation)

ii.   Ageing and hornification of cellulose in cotton textiles during long time use

Anna Palme, Alexander Idström, Lars Nordstierna and Harald Brelid

EPNOE 2013 "Polysaccharides and polysaccharide-derived products, from basic science to applications", Nice, France, October 21-24 2013. (Poster)

iii.   Ageing of cellulose – Property changes during long time service of cotton textiles

Anna Palme, Alexander Idström, Lars Nordstierna and Harald Brelid

COST FP1205 Meeting, Gothenburg, Sweden, December 3-4 2013. (Oral presentation)

iv.   Acid hydrolysis of pulp samples with different process histories; effect on hydrolysis rate and LODP

Anna Palme, Hans Theliander and Harald Brelid

5th Avancell conference, Gothenburg, Sweden, October 6-7 2015 (Oral presentation)

Contribution report

The author of this thesis made the following contributions to the papers:

I. Main author. Responsible for the experimental work together with Alexander Idström, who performed the NMR experiments. The HP-SEC analyses were performed at an external laboratory. Planning and evaluation of the results were done with support from Alexander Idström, Lars Nordstierna and Harald Brelid.

II. Main author. Responsible for the experimental work. The X-ray diffraction analyses were performed by Nico Torino at Chalmers. HP-SEC and the carbohydrate content analyses were performed by an external laboratory. Planning and evaluation of the results were done with support from Hans Theliander and Harald Brelid.

III. Main author. Responsible for the experimental work. The NMR and FSP analyses were performed by Fredrik Aldaeus and Tomas Larsson, Innventia. Planning and evaluation of the results were done with support from Fredrik Aldaeus, Tomas Larsson, Merima Hasani, Hans Theliander and Harald Brelid.

IV. Main author. Responsible for the experimental work. The HP-SEC analyses were performed at an external laboratory. Planning and evaluation of the results were done with support from Merima Hasani, Hans Theliander and Harald Brelid.

V. Main author. The small scale experiments and NMR experiments were performed within Anna Petersons Masters thesis, supervised by the author. ATR-IR analyses were performed by Hanna de la Motte. Planning and evaluation of the results were done with support from Hanna de la Motte, Hans Theliander and Harald Brelid.

List of abbreviations

ATR FT-IR – attenuated total reflectance Fourier-transform infrared

BTBAC – benzyltributylammonium chloride

CED – Copper (II) ethylenediamine

CI - crystallinity index

CNC – cellulose nanocrystals

CP/MAS ^{13}C-NMR – cross-Polarization magic angle spinning carbon-13 nuclear magnetic resonance

DMT – dimethyl terephthalate

DP_m – degree of polymerization based on M_m from HP-SEC

DP_v – degree of polymerization based on intrinsic viscosity measurements

EG – ethylene glycol

FSP – fiber saturation point (g/g)

HP-SEC – high pressure size exclusion chromatography

LODP – levelling off degree of polymerization

MCC – microcrystalline cellulose

M_m – mass average molecular mass (kDa)

NMMO - N-methylmorpholine-N-oxide

NMR – nuclear magnetic resonance

o.d. – oven dry

PET – poly(ethylene terephthalate)

PHK – pre-hydrolysis Kraft pulp

TPA – terephthalic acid

WRV – water retention value (g/g)

To Karen, Bitti, and all the others before me

x

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1. Introduction

Material recycling of consumer products such as paper, glass and metal is well developed today in many parts of the world. The reasons for developing material recycling are many, such as reducing the need for landfills as well as contributing to a decrease in the use of virgin materials. When discussing recycling alternatives, the most preferred alternative is always reuse. However, textiles that are not suited for reuse could be recycled into textiles, so called fiber-to-fiber recycling, and this is considered in this thesis.

1.1 Recycling of textiles

Fiber-to-fiber recycling of textiles has not been implemented on a large-scale. Since collection of second-hand textiles is well developed, one of the major barriers to accomplishing the chemical recycling of textiles is development of recycling technology (Elander & Ljungkvist, 2016). The aim of this thesis is to contribute to the development of chemical recycling of textiles.

Fiber-to-fiber recycling of textiles may be performed chemically or mechanically. The mechanical approach has conventionally been used to defibrate textiles into fibers,

which can be spun with or without the addition of virgin fibers into recycled yarn and textiles. Mechanical recycling is possible to achieve with good results for wool and cashmere, however for most other fibers, mechanical recycling lead to recycled fibers of inferior quality. For this reason, mechanical recycling tends to be regarded as down cycling (Morley, Slater, Russell, Tipper, & Ward, 2006). Chemical fiber-to-fiber recycling comprises different processes where changes on the molecular level are made to textile fibers through chemical processing to form recycled fibers, yarn, and textiles. No commercial-scale chemical fiber-to-fiber recycling of textiles exists today, however small-scale projects are ongoing, such as Eco Circle (Teijin), Worn Again, Evrnu, Re:newcell, and Ioncell (Asaadi, Hummel, & Sixta, 2015; Elander & Ljungkvist, 2016).

Textile recycling is complicated since textiles include a broad number of different materials, however, the scope of this thesis is limited to recycling of cotton and polyester. The overall idea is to use old cotton to produce regenerated cellulosic fibers, such as viscose or lyocell. These fibers are made mainly from cellulose extracted from wood today, however, cotton linters are also used as raw material in the production. Since cotton fibers from textiles are an almost pure cellulose source, worn out cotton textiles could possibly be included in this already existing industry and be recycled into new textile fibers, Figure 1. This approach has also been investigated by other researchers (Asaadi et al., 2015; Haule, Carr, & Rigout, 2016; Negulescu, Kwon, Collier, Collier, & Pendse, 1998).
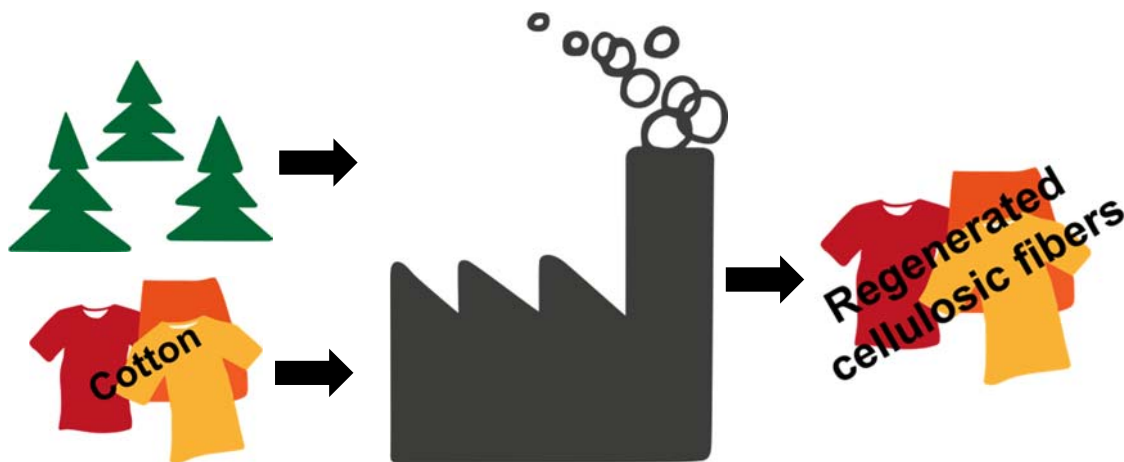

Figure 1: Recycling of cotton through production of regenerated cellulose fibers.

One area of particular interest for textile recycling is the service sector, which handles large amounts of textiles for hotels and hospitals. In a report from 2014, an enquiry was sent out to all Swedish laundering companies, about the amount of textiles they discard each year. Only a few companies responded, but these companies discarded between 379 and 729 tons of textiles per year together (Brismar, 2014). The majority of these textiles are mixed polyester and cotton textiles, so called polycotton.

The focus of this thesis is on the characterization of the starting material, the pretreatment and dissolution of cotton, and the separation of cotton and polyester. Fiber spinning from old cotton has not been included.

1.1.1 Mistra Future Fashion

The Mistra Future Fashion program is a cross-disciplinary research program that holds uniquely a system perspective on the fashion industry. Its vision is to close the loop in fashion and clothing – enabling a systemic change in the Swedish fashion industry, leading to a sustainable development of the industry and society.

The program aims to deliver insights and solutions that will be used by the Swedish fashion industry and by other stakeholders to significantly improve the environmental performance and strengthen the global competitiveness.

This thesis have been performed within Project 5 (Reuse, recycling and end of life issues) in Phase 1 and Theme 4 (Recycling) in Phase 2 of the research program.

1.2 Objectives and overview of papers

The main objective of this thesis was to investigate the preconditions for chemical fiber-to-fiber recycling of cotton textiles. Four main research questions were investigated, and the related papers are indicated in brackets:

1) How do important material properties of cotton fiber change during long-term laundering and use? (Paper I)
2) How are new and used cotton fibers affected by acid pretreatment in comparison to dissolving pulp? (Paper II, IV)
3) How is the susceptibility of cotton fibers and dissolving pulps to swelling changed after acid pretreatment? (Paper III)

4) How can the separation of mixed textiles that contain polyester and cotton be accomplished? (Paper V)

1.3 Outline of thesis

The findings from the research questions posed above will be presented and discussed in this thesis. After a short introduction to the subject, some general background to textile materials will be presented, followed by more specific background on previous literature connected to the four areas; the properties of cotton fibers, acid pretreatment of cellulose fibers, swelling and dissolution of cellulose fibers and separation of cotton and polyester from mixed textiles. Then the materials and methods used in the thesis will be presented, and, in the following sections results, from the four areas will be presented and discussed. The main conclusions will be highlighted, followed by an outline for possible future work within the field of chemical recycling of cotton.

2. Textiles and Fibers

The aim of this thesis is to provide a better understanding of the first process steps in textile recycling. To obtain this, it is important to understand the different size levels in textiles (from the molecular level to the actual fabrics), as well as the main steps in the production processes of the materials. This chapter provides a background to the important terminology of textiles and properties of textile fibers.

Textile fabrics are made from yarns, which are made from textile fibers or filaments. Fabrics may be constructed in many ways, but the most common techniques are weaving and knitting of yarn. All fabrics in this thesis are made from spun yarn, i.e. yarn that has been made through the spinning of staple fibers. Staple fibers are short fibers, either due to their biological origin or because they were cut from longer fibers, so called filaments (Hatch, 1993).

Fibers may either be natural, such as cotton and wool, or man-made. Man-made fibers are mainly petroleum based fibers, such as polyester and nylon. However, a small part of the man-made fibers are made from cellulose, so called regenerated cellulosic fibers. The world production of fibers is increasing, however, cotton production is moving to "peak cotton", and since around 1995 the main increase occurs in the production of man-made fibers (CIRFS European Man-Made Fibres Association, 2016). In 2014, the

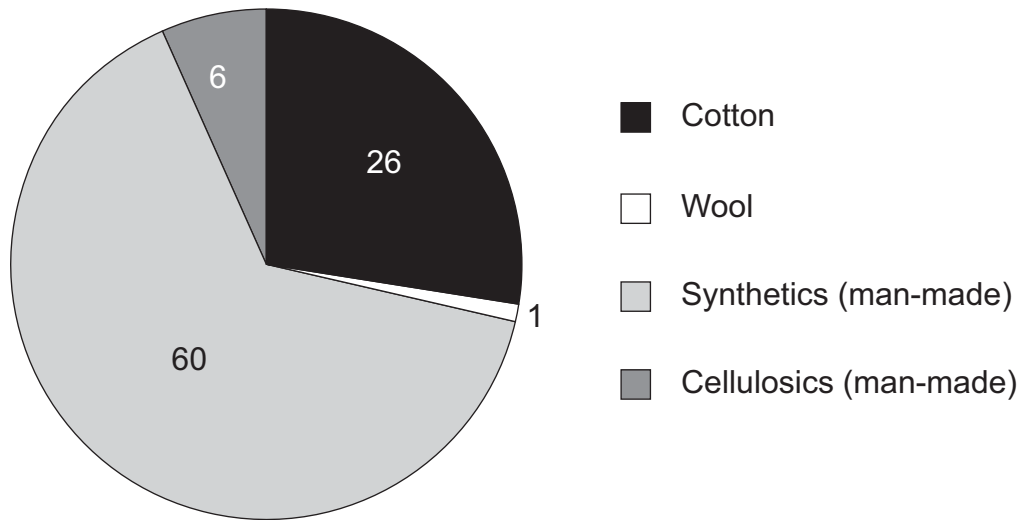production of synthetic fibers was more than twice as large as the production of cotton, see Figure 2.

Figure 2: World production of fibers 2014. The numbers indicate the number of million tons fibers produced (CIRFS European Man-Made Fibres Association, 2016).

The research has been centered on cotton, however, since cotton mainly exists in textile mixes with other materials, and since the most common mix is with polyester, the Paper V investigates mixes of polyester and cotton, so called polycotton.

2.1 Cotton

Cotton fibers are the most common natural textile fiber. Cotton is a staple fiber, and normally the length of the fibers range between 22 and 32 mm, and generally, longer cotton fibers are considered to be of higher quality (Kljun et al., 2014). The fibers are seed hair, similar to the seed hairs of the dandelion, which grow as single cells from the cotton seed. Each cotton seed can produced 5000 to 20000 fibers (Sczostak, 2009). During growth, the lint fibers develops first, as long fibers. Lint fibers are the fibers used in textile production. This is followed by the development of shorter fibers, called fuzz fibers or cotton linters. Linters are shorter fibers only 1.5 - 10 mm long with a thicker fiber wall, and they adhere stronger to the seed (Lewin, 2007). After the harvest of the cotton plants, the lint fibers are removed from the seed and sent for yarn production. The seeds, with the linters on, are treated further. The main purpose is to produce seed oil, however, the first step is to cut the linters from the seeds. The cotton linters are then bleached, to remove non-cellulosic compounds, and reduce the DP. The resulting cotton linters are used both as fibers (in applications such as paper and as reinforcement in

composites) and in chemical conversion (such as regenerated fibers, cellulose acetate, cellulose nitrate and cellulose ethers) (Sczostak, 2009).

Since cotton linters are a pure cellulosic source, they are commonly used as a reference in cellulose research, many times only denoted as cotton fibers. However, as the properties of lint and linters may differ on many levels, it is important to consider which fiber type is being analyzed before comparing results. When referring to cotton fibers in this thesis, cotton lint is intended.

The growth of the fiber starts with the elongation of the primary wall, which is followed by the deposition of cellulose inside the primary wall tube. When the major part of the deposition has taken place, no further elongation occurs. During growth, the lumen of the fiber is filled with water, and the fibers grow inside a closed boll. After about 50 days of growth, the fibers are mature, and the bolls open, which causes the fibers to dry and form the characteristic shape of a flat twisted ribbon fiber structure. Cotton fibers contain 88-97% cellulose, and the non-cellulosic compounds are mainly located on the outer layers and in the lumen of the fibers. The primary wall is composed of less than 30% cellulose and the cellulose chains are relatively short, with a DP (degree of polymerization) between 2000 and 6000. The other 70% of the primary wall is composed of proteins, amino acids, other nitrogen-containing compounds, wax, pectic substances, organic acids, sugars, inorganic salts, and a very small amount of pigments (Phillip J . Wakelyn et al., 2006). The secondary wall on the other hand, is composed of virtually 100% cellulose, and the cellulose in the primary wall has a more narrow molecular mass distribution, with a DP around 14000 (Marx-Figini, 1969).

The sustainability of cotton production has recently been questioned due to major environmental problems, caused by both high water use and the extensive use of pesticide. The production of cotton also requires arable land, which could be used for food production (Chapagain, Hoekstra, Savenije, & Gautam, 2006; Tariq, Afzal, Hussain, & Sultana, 2007).

2.2 Regenerated cellulose fibers

Regenerated cellulose fibers are mainly made from wood pulp, but also other cellulosic fibers may be used, such as cotton linters. The special grade of wood pulp that is used to produce regenerated cellulose fibers is referred to as dissolving pulp (since it is dissolved

in fiber production). Dissolving pulp has a high cellulose content, around 97%. There are two main production methods for dissolving pulp; the acid sulfite process and the pre-hydrolysis Kraft process.

The most well-known regenerated cellulose fibers are viscose (also known as rayon) and lyocell. The main steps in fiber production can be summarized as (pretreatment), dissolution, fiber spinning and regeneration. In viscose production, the cellulose is first pretreated in a pre-ageing process, then reacted to form cellulose xanthate, before dissolution in sodium hydroxide (NaOH), which is followed by a ripening of the spin dope. Viscose fibers are produced through wet spinning, a process in which the spin dope, with the dissolved cellulose xanthate, is extruded into a regeneration bath where xanthate groups are split off. In the production of lyocell fibers, the cellulose is directly dissolved in N-methylmorpholine-N-oxide (NMMO). The fibers are produced through air-gap spinning where the spin dope is extruded at a short distance above the surface of the regeneration bath. The resulting viscose and lyocell fibers are both almost pure cellulose fibers (Woodings, 2001).

2.3 Polyester fibers

Polyester (poly(ethylene terephthalate), PET) is a man-made fiber, which, according to BISFA, the International Bureau for the Standardization of Man-Made Fibres, polyester is defined as:

> *"Fibre composed of linear macromolecules having in the chain at least 85% by mass of an ester of a diol and terephthalic acid. (The international bureau for the standardization of man-made fibres BISFA, 2009)"*

This means that there may be some difference between different polyester fibers, however, the material is most commonly made from the two monomers terephthalic acid (TPA) and ethylene glycol (EG), see Figure 3. In textile applications, PET is also referred to as PES (polyesters). PET was previously produced through the polymerization of dimethyl terephthalate (DMT) and EG, however after polymer-grade TPA was made available on the commercial market in the 1960s, the dominant route has been the TPA route (Gupta, Mukherjee, & Cameotra, 1997; Köpnick, Schmidt, Brügging, Rüter, & Kaminsky, 2000).
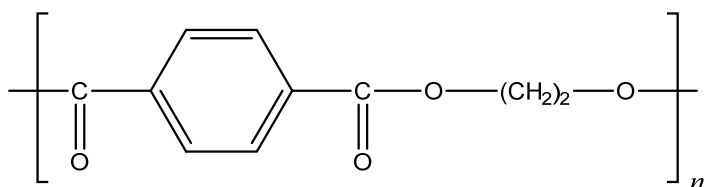
Figure 3: Molecular structure of PET (poly(ethylene terephthalate))

PET polymers are produced through a step-growth polymerization with a 1:1 molar ratio of the monomers followed by fiber formation through melt spinning. In the melt spinning process, the polymers are melted in a screw extruder and then extruded through a spinneret out into cold air, which causes the fibers to solidify. PET may both be produced as staple fibers and as continuous filament fibers (Hatch, 1993). During the production of polyester, different modifications of the polymer chain may be performed, such as crosslinking, to make the fibers more resistant towards wash and wear (Venkatachalam et al., 2012).

PET plastic is also used in many other applications, where the main use is drinking bottles. The PET used in drinking bottles has an intrinsic viscosity around 0.8 dL/g, corresponding to a molecular mass of 48 kDa. PET used to produce fibers, has an intrinsic viscosity around 0.6 dL/g, corresponding to 30 kDa (Upasani, Jain, Save, Agarwal, & Kelkar, 2012; Venkatachalam et al., 2012). Today, there are textiles on the market labelled as "recycled polyester" however, these are currently made by recycling PET bottles into fibers. Due to the difference in intrinsic viscosity, PET fibers cannot be re-melted into bottles, without prior repolymerization.

3. Cellulose

Cellulose is available nearly pure in cotton, as described in Section 2.1, but it is also a major component of wood and other plant materials. Together with hemicellulose, pectic material, and lignin, cellulose forms a biopolymer composite material, which brings strength to the fiber cell walls of plants (Young & Rowell, 1986). Cellulose is also a minor component of mammalian connective tissue, and may be found in the test of ascidians (Endean, 1961). Moreover, cellulose may be synthesized by specialized bacteria, a method that produces very pure cellulose (Iguchi, Yamanaka, & Budhiono, 2000).

The cellulose polymer is a linear polysaccharide, consisting of β-D-glucopyranose units, linked by (1→4)-glucosidic bonds, see Figure 4. The number of linked glucose units is called the degree of polymerization (DP), however the repeating unit consists of a cellobiose unit, with two glucose units, as shown in Figure 4.
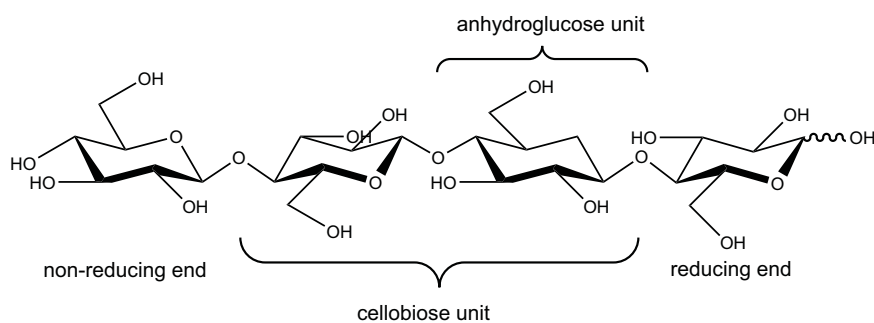
anhydroglucose unit

non-reducing end

cellobiose unit

reducing end

Figure 4: Cellulose polymer

The structure of cellulose is characterized by a number of structural levels, each with a different arrangement and complexity. Due to intramolecular bonding, a cellulose chain is relatively stiff and rigid. The cellulose polymers build up sheets through the formation of hydrogen bonds between the chains. The sheets are stacked into crystals, which are held together by hydrophobic interactions. The cellulose crystals form microfibrils, which are organized into larger fibril aggregates, and the fibril aggregates build up the cell walls that form the cellulose fiber (Krässig, 1993). The fibrillar structure of cellulose not only includes crystalline material, but also regions with less order, referred to as amorphous regions. The term amorphous is somewhat confusing, since the definition of amorphous, according to the Oxford English Dictionary is "having no determinate shape". However, the parts of cellulose that are said to be amorphous, remain in a highly ordered structure, although not in perfect crystals (O'Sullivan, 1997). For instance, the chains on the surface of the crystals are not completely crystalline due to interactions with surrounding non-cellulose material, such as water, hemicelluloses, or lignin.

Based on the existence of amorphous and crystalline cellulose in cellulosic fibers, the fringed fibril model was constructed (Frey-Wyssling, 1954; Hearle, 1958; Scallan, 1971). In this model, the crystalline parts and the amorphous parts are linked without any distinctive boundary, which allows a single polymer to pass though several crystalline and amorphous areas. However, this model is somewhat outdated today. Based on the biosynthesis of cellulose, a model with long periods of order regions, which are interrupted by disordered zones, has been proposed, based on the simultaneous polymerization and crystallization (Stöckmann, 1972).

The size and the degree of aggregation of microfibrils govern the accessibility of a cellulose sample, and this is an important factor when producing new materials from

cellulose. Different methods are available to quantify the degree of crystallinity. The most common methods are X-ray diffraction and solid state ^{13}C-NMR spectroscopy. In both methods, different signal peaks, or areas, originating from crystalline parts are compared to ditto from amorphous parts (Klemm, Philipp, Heinze, Heinze, & Wagenknect, 1998).

In total, six different crystalline forms of cellulose (Iα, Iβ, II, III, IV$_I$, IV$_{II}$), also called polymorphs, have been identified, and they may be interconverted through chemical treatments or heat (O'Sullivan, 1997). Cellulose I and II are the most common polymorphs: The others will not be discussed in this thesis. Cellulose I has been shown to be a composite of two crystalline forms, Cellulose Iα and Cellulose Iβ, which give rise to different chemical shifts in solid-state ^{13}C NMR spectroscopy (Atalla & VanderHart, 1984). The two allomorphs give rise to different hydrogen bonding patterns, and the ratio is dependent on the species (Sugiyama, Persson, & Chanzy, 1991). Cotton predominantly contains the more stable Cellulose Iβ (E.-L. Hult, 2001). In the native cell wall, the cellulose chains are synthesized directly to microfibrils by groups of synthesizing units called "terminal complexes" or "rosettes" (Brown, Saxena, & Kudlicka, 1996).

Cellulose I is said to be meta-stable since it is thermodynamically less stable than the cellulose II polymorph. If the polymers were formed individually, and not simultaneously, it is likely that cellulose II would be formed, instead, due to this difference in stability (O'Sullivan, 1997). After dissolution and regeneration, or swelling in NaOH, cellulose I is transformed to Cellulose II. Thus, the crystalline part of the cellulose in all regenerated cellulosic fibers, such as viscose and lyocell is composed of cellulose II (O'Sullivan, 1997).

As with most polymers, cellulose is polydisperse, i.e. the length of the chains varies, and the DP is only an estimate of the average of the distribution. The full molecular mass distribution may be measured using size exclusion chromatography (SEC) after the dissolution of the cellulose (Henniges, Kostic, Borgards, Rosenau, & Potthast, 2011). The DP can also be estimated from a measurement of cellulose intrinsic viscosity, after the dissolution of cellulose. The standard measurement applied today involves dissolution in cupper ethylene diamine, CED, also referred to as CuEn. In this

measurement, cellulose is dissolved and then the time for the solution to run through a thin capillary is measured. The intrinsic viscosity of the solvent may then be calculated and correlated to the DP of the cellulose.

In this thesis, cellulosic fibers of high purity, i.e. cotton and dissolving pulp, are mainly discussed since these can be used in the production of regenerated cellulosic fibers. However, high purity cellulose is also used in the production of cellulose derivatives, such as nitrocellulose, cellulose acetate, hydroxypropyl methyl cellulose, and carboxymethylated cellulose (Chang & Zhang, 2011).

4. Effect of Laundering on Textile Fibers

Investigation of cotton fibers has previously mainly been conducted on virgin fibers. However, in recycling, fibers are introduced to the process after many laundering cycles, which may alter the fiber properties. One important issue to highlight is the effect of drying and rewetting cellulose fibers, known as hornification. This phenomenon has a major impact on the recycling of paper and, for this reason relevant literature from this area will be presented below.

4.1 Changes during laundering of cotton

Industrial laundering, which service textiles are subjected to, is performed at an elevated temperature (around 80°C, but may vary from one laundering company to another) in an alkaline environment. Laundering is known to decrease the tensile strength of textiles due to chemical and mechanical wear. Chemical wear decreases the DP of cotton, and this decrease may also be correlated to a decrease in the tensile strength of the fabric (Vaeck, 1966). This is a very important factor for industrial laundering companies, which handle large volumes of textiles. If the laundering process is too harsh, the fibers will be degraded too fast, which leads to major economic losses for the laundering companies. For this reason, the decrease in the DP of cotton is used to configure specific laundering processes.

Detergent formulations are often alkaline. This means that laundering is usually performed in an alkaline environment in which, the cellulose may undergo alkali-induced peeling reactions (Sjöström, 1993). In this reaction terminal anhydrosugar units at the reducing end of the cellulose chain are split off, one by one, until stopped by a competing stopping reaction. The first step in the peeling reaction is the rearrangement of the reducing end group, known as the Lobry de Bruyn-Alberda van Ekenstein rearrangement. After further rearrangements, this leads to a β-elimination of terminal monomer from the cellulose chain. The leaving group undergoes further rearrangements, and the main degradation product is isosaccharinic acid. The peeling may be stopped either chemically or physically. In chemical stopping, the reducing end group is most commonly stabilized by conversion into metasaccharinic acid, which stops further peeling reactions. In physical stopping, the peeling ends when an inaccessible part of the cellulose is reached (Sjöström, 1993). The number of glucose units peeled off before stabilization may be approximated to around 65 anhydroglucose units (Franzon & Samuelson, 1957). The decrease in DP during laundering is much larger than this, and, thus, peeling reactions are not the main reason for the decrease in DP during laundering. Furthermore, since laundering is performed at temperatures below 100°C, at moderate alkalinities, there is virtually no risk of alkaline hydrolysis during laundering (Loon & Glaus, 1997). Instead, the dominating factor for the decrease in DP is most likely oxidative peeling, which is related to oxidation reactions that lead to the introduction of carbonyl groups along the cellulose chains, since the presence of such groups is known to induce alkali promoted chain cleavage reactions in cellulose (Lai, 1981; Herbert Sixta, 2006).

4.2   Hornification of cellulose fibers

Another important effect to discuss in relation to the laundering of cotton fibers is hornification. This term is used to define the changes that occur during the drying of cellulose fibers and has been attributed to Jayme (1944), who introduced the measurement of the water retention value, WRV, as a measurement of hornification.

Today, the meaning of hornification has expanded from Jayme's original definition, to describe the effects of drying on cellulose fibers, which leads to a decrease in the water holding capacity of the fibers, in a broader sense (Weise, 1998). Hornification makes the

fibers stiffer and less conformable, and the proposed reason for these changes in the properties is that during drying, the pores in the fiber wall collapse, and if there are no blockers present, such as lignin or hemicellulose, fibril surfaces may come in contact with each other leading to irreversible aggregation (Kontturi & Vuorinen, 2009). When the fibers are rewetted, the pores do not open again since bonds may have formed between adjacent fibrils (Stone & Scallan, 1968). This phenomenon has mainly been studied on chemical pulp fibers in relation to paper recycling. Stiffer fibers lead to a decrease in the ability of the fibers to form fiber-fiber bonds in paper sheets. In this manner, hornification influences the quality of fibers from recycled paper (Hubbe, Venditti, & Rojas, 2007). The decrease in WRV caused by hornification is the greatest in the first drying, from never-dried to once-dried, however the WRV continues to decrease with the number of drying and rewetting cycles. (Yamauchi & Yamamoto, 2008). Hemicellulose (i.e. glucomannan and/or xylan) protect cellulose from hornification, by suppressing the tendency of fibril coalescence during drying. Thus, pulps with higher hemicellulose content are less sensitive to hornification (Köhnke, Lund, Brelid, & Westman, 2010; Oksanen, Buchert, & Viikari, 1997).

Since the secondary wall of cotton consists of pure cellulose, cotton is very sensitive to hornification (Fahmy & Mobarak, 1971; Philip J. Wakelyn et al., 2007). The growth of a cotton fiber ends when the boll opens and the fibers dry. Thus, virgin cotton has already been subjected to initial hornification. The WRV of never-dried cotton from an un-opened ball is 1.4 g/g, which decreases to 0.46 g/g for cotton fibers that have been dried in the field (Nelson, Rousselle, Ramey, & Barker, 1980). This may be compared to the decrease in the WRV of a Kraft pulp sample from 1.5 g/g pulp in the never-dried state, to 1.0g/g after one drying and rewetting cycle (Köhnke et al., 2010).

The mechanism of hornification is largely debated, however some terms are generally used to describe the changes related to hornification. Newman (2004) has used solid-state ^{13}C NMR spectroscopy to study the hornification of pulp fibers and the findings in the paper indicate that the changes cannot be attributed to the transfer of cellulose from non-crystalline domains to crystalline domains. Instead, the findings indicate that the NMR signals change from external surfaces to internal surfaces, thus indicating the coalescence of pairs of surfaces without change in crystallinity. Newman has concluded

that co-crystallization, which increases the lateral dimension of crystallites, is closely connected to hornification. An increase in lateral fibril size has also been observed in Kraft pulp and CNC (cellulose nanocrystals), and a decrease in hemicellulose content has been found to increase fibril aggregate dimensions (E. L. Hult, Larsson, & Iversen, 2001; Idström, Brelid, Nydén, & Nordstierna, 2013).

4.2.1 Measurement of hornification

The original definition of hornification, as formulated by Jayme, is based on the measurement of the WRV, however there are also other methods to quantify the change in cellulosic fibers caused by hornification, such as the measurement of the fiber saturation point (FSP) with solute exclusion. When measuring WRV, a partly dewatered pulp pad is centrifuged for a certain amount of time (in this study, 3000 g for 15 minutes). The weight of the pulp pad after centrifugation is then compared to the weight of the pulp pad after drying, yielding a measure of how much water the pad held during centrifugation. WRV has been used to measure the "fiber saturation point" of chemical pulp fibers, which can be defined as:

> *"The point in drying wood at which all free moisture has been removed from the cell itself while the cell wall remains saturated with absorbed moisture."* *(Merriam-Webster Dictionary)*

However, since WRV does not distinguish between the water inside a fiber wall and on the surfaces of a fiber, the method has been questioned. Instead, it has been proposed that measurement of the FSP may be performed with solute exclusion.

The FSP measurement method based on solute exclusion with dextran was developed by Stone and Scallan (1968), however the method of using solute exclusion to measure the pore size distribution of cellulose fibers had been proposed by Aggebrandt and Samuelson (1964) some years earlier. When measuring FSP with solute exclusion, a solution of dextran polymers, which are too large to penetrate the fiber wall, is added to water-swollen pulp fibers and allowed to equilibrate. Then the difference in concentration between the stock solution and the solution filtered off from the fibers gives a value of how much water that did not dilute the stock. This water was inaccessible to the polymer solution, and, thus, was contained within the fibers.

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4.3   Changes during laundering of polyester

Laundering may also influence the properties of polyester (poly(ethylene terephthalate), PET) fibers, and this is relevant to the last paper included in the thesis, Paper V.

The ester bonds in polyester are sensitive to alkali, and it is, thus, likely that the molecular mass of the polymer decreases during laundering (International Fabricare Institute, 1995). This decrease is important when considering how to recycle polyester fibers, and the implications will be discussed in Section 9.9.5 on the separation of polyester and cotton.

5. Acid Degradation of Cellulosic Fibers

In order to promote the dissolution of cellulose fibers, pretreatments of the fibers may be performed. In this thesis three different acid pretreatments were studied closer; mild acid hydrolysis in water, acid hydrolysis in ethanol and hydrothermal degradation in an acetate buffer solution. This chapter provides some background to acid degradation in general and the specific treatments in particular.

5.1 Acid hydrolysis of cellulose in water

The glucosidic bonds, which link the anhydroglucose units together in cellulose are sensitive to acid. Heterogeneous degradation of cellulosic fibers is dependent on several factors of which the morphology of the fibers is very important. Glucosidic linkages in the amorphous parts of the cellulose fibers are more accessible, and are, thus, more easily degraded than bonds in the crystalline parts (Philipp, 1981). This leads to the specific degradation pattern of cellulose, which consists of two phases. In the beginning the degradation of cellulose is fast, but after prolonged treatment, the degradation reaches the "levelling-off degree of polymerization" (LODP) (Battista, 1950; Battista, Coppick, Howsmon, Morehead, & Sisson, 1956). During this second phase, the rate of degradation is very low, however, the degradation continues even after this point. Bonds in the amorphous regions may also be subjected to strain, which may increase the

hydrolysability of those bonds (Daruwalla & Narsian, 1966). Battista (1950) has compared weight loss and LODP during mild and drastic acid hydrolysis and found that, in both methods, the LODP approached the same level, however, the mild acid hydrolysis resulted in less weight loss. The proposed explanation was that crystallization may occur during mild acid hydrolysis.

As presented in Section 4.2, drying leads to the hornification of cellulose fibers. In enzymatic hydrolysis, hornification has been found to decrease the hydrolysability of chemical pulp fibers (Duan, Long, Li, Ma, & Ni, 2015; Philipp, Dan, Fink, Kasulke, & Loth, 1981), explained by the lower accessibility of dried cellulose fibers. However, in acid hydrolysis, the opposite behavior has been found. Both Jørgensen (1950) and Lindgren & Goliath (1956) reported that that of LODP of never-dried pulp was higher than the LODP of once-dried pulp. Similar results have been presented later and explained with that drying may induce stress, which leads to the higher susceptibility of dried pulp to acid hydrolysis compared to never-dried pulp (Philipp, Dan, & Fink, 1981). In another study on the production of CNC through hydrolysis with sulfuric acid, it was found that the length distribution of the CNCs shifted towards longer CNCs when produced from never-dried pulp, compared to production from once-dried pulp. Those authors concluded that supramolecular changes in the amorphous cellulose occur during drying, which leads to higher susceptibility to acid hydrolysis (Kontturi & Vuorinen, 2009).

5.2   Acid hydrolysis of cellulose in ethanol

If acid catalyzed degradation is performed in ethanol instead of water, the degradation rate increases. This was found as early as in 1923 (Coward, Wood, & Barrett, 1923), however recently, new interest in the method has arisen (Kihlman, Medronho, Romano, Germgard, & Lindman, 2013; Lin, Chang, & Hsu, 2009; Trygg & Fardim, 2011; Trygg, Trivedi, & Fardim, 2016). It must be noted that in all of these experiments there was a low percentage of water in the ethanol, which means that hydrolysis of glucosidic bonds in cellulose may take place, i.e. it is not ethanolysis reactions that lead to depolymerization of cellulose. It has been claimed that acid hydrolysis in ethanol may give pulp samples that are more susceptible towards dissolution than samples treated with acid hydrolysis in water (Trygg & Fardim, 2011; Trygg et al., 2016).

Alcoholysis and acid hydrolysis in alcohols has been investigated previously by Reeves et al. (Reeves, Schwartz, & Giddens, 1946) and Valley (1955)(Valley, 1955). Both found that the same LODP was reached, regardless whether water or alcohol was used as solvent. Valley started the investigations of acid/alcohol system with the aim of investigating alcoholysis of cellulose. However, the studies, performed in methanol, butanol, n-hexanol and n-octanol, with hydrogen chloride, sulfuric acid and p-toluenesulfonic acid, showed that probably no alcoholysis occurred. This was concluded since the same LODP was reached in all the experiments, and the difference in accessibility of the cellulose to degradation was not related to the molecular mass of the alcohols. These findings were explained by the fact that traces of water cannot be completely removed from cellulose fibers, and thus, when acid is added with the alcohol, the polar acid will preferentially be sorbed by the cellulose. This leads to a high acid concentration at the cellulose-liquid interface of the fibers, resulting in a higher degradation rate.

The results of Valley were confirmed by Nevell & Upton (1976), who performed experiments with hydrochloric acid and benzene with increasing additions of water. Those authors also found that the acid added with the benzene was sorbed by the fibers, yielding very concentrated solutions of hydrogen chloride within the fibers.

The combination of these findings in the literature suggests that ethanol may be used to speed up the rate of hydrolysis, but it does not change the degradation mechanism of cellulose if traces of water are present.

In the recent publications, by Trygg et al. (2011; 2016), the higher degradation rate is explained by a higher activity of acid in ethanol than in water. It was also suggested that acid hydrolysis in ethanol may give pulp samples that are more susceptible towards dissolution than samples treated with acid hydrolysis in water.

5.3 Hydrothermal degradation of cellulose

The degradation of cellulose before dissolution in cold NaOH has also been performed at high temperature and with a small addition of acid (Struszczyk, Wawro, Urbanowski, Mikolajczyk, & Starostka, 2009). This pretreatment is included in this thesis to study the effect of temperature on the pretreatment and dissolution of cellulose fibers.

5.4 Modelling of acid degradation of cellulose

Ekenstam (1936a, 1936b) was one of the first to model the degradation kinetics of cellulose and has proposed a linear zero order relationship, Equation 1.

$$\frac{1}{DP} - \frac{1}{DP_0} = kt \hspace{4cm} \text{Equation 1}$$

Ekenstam's experiments were performed in phosphoric acid, which can dissolve cellulose, forming a homogenous system in which all glucosidic bonds are equally accessible for the hydrolytic medium. Sharples (1954a, 1954b) adapted the equation to fit a heterogeneous degradation, by adding an accessibility factor, .

Several attempts have been made to develop new models for cellulose degradation (Calvini, Gorassini, & Merlani, 2008; Dadach & Kaliaguine, 1993; Ding & Wang, 2008; Emsley, Heywood, Ali, & Eley, 1997). Common to all of these models is that they use an exponential relationship. With this kind of relationship, it is possible to obtain a very good fit to experimental data. However, the good fit of a model does not ensure its correctness in terms of physical interpretation. In this thesis, the degradation data from acid hydrolysis were fit to the first-order degradation model developed by (Calvini et al., 2008), see Equation 2.

$$S = \sum_i n_i * (1 - \exp(k_i t)), i = 1, 2, 3 \ldots n \hspace{3cm} \text{Equation 2}$$

Where S is the number of scissions per cellulose chain (DP_0/DP -1), n is the initial number of scissile bonds per cellulose chain, k is the rate constant of the hydrolytic medium, and t is the time of hydrolysis. In the model, it is assumed that each bond may experience a different environment, and, thus, the equations would in the ideal case be expressed as a sum of an infinity of parallel processes. Calvini suggests that the model can be simplified into one, two, or three first-order reactions corresponding to the degradation of weak, amorphous, and crystalline bonds.

6. Swelling and Dissolution of Cellulosic Fibers

This thesis investigates the preconditions for recycling cotton fibers into regenerated cellulosic fibers. When producing regenerated cellulosic fibers, cellulose dissolution is a key step. This chapter discusses some aspects of cellulose dissolution that are relevant to the scope of the thesis.

The dissolution of cellulose fibers has been studied extensively due to its importance in the production of materials and fibers from cellulose, and many books and reviews have been devoted to the subject (Budtova & Navard, 2016; Liebert, Heinze, & Edgar, 2010; Olsson & Westman, 2013). Cellulose fibers are natural fibers with a complicated ultrastructure, as a natural composite, composed of several types of macromolecules, which make dissolution of cellulose fibers complicated. Both intra- and intermolecular hydrogen bonds, and hydrophobic interactions need to be broken in order to the accomplish dissolution of cellulose. In other words, water or common organic solvents cannot dissolve cellulose, and, instead, special solvents are needed to do this (Lindman, Karlström, & Stigsson, 2010). Owing to the effect of entropy, cellulose with a high DP is generally harder to dissolve than cellulose with a low DP. A cellulose chain is also relatively rigid, which decreases entropy gain when the chain is dissolved (Budtova & Navard, 2016).

Depending on the application, different dissolution systems are used. In the production of regenerated fibers, there are two common systems. The most common system is dissolution in NaOH, after derivatization by the introduction of xanthate groups to the cellulose. This is used in the viscose process. The other system is direct dissolution in NMMO, which is used in the Lyocell process (Woodings, 2001). Other systems for the production of regenerated cellulosic fibers have previously been used and new systems are under development. In this thesis, extra focus is on dissolution in cold NaOH.

The direct dissolution of cellulose in cold NaOH has been studied extensively. It has been claimed that cellulose may be dissolved directly in NaOH when the temperature is around -5°C and the NaOH concentration is between 5 and 10% (Budtova & Navard, 2016; Isogai & Atalla, 1998). Much attention has been focused on the production of regenerated cellulosic fibers through dissolution in cold aqueous NaOH. However, dissolution in cold aqueous NaOH is problematic, since it is poor solvent, and the window of dissolution is very narrow. Furthermore, there still remain many questions regarding the conformation of cellulose chains in such a solution (Budtova & Navard, 2016).

The dissolution of cellulose is also important in analytical applications. One of the most basic characterization methods for cellulose is the measurement of intrinsic viscosity, described above. The standard measurement applied today involves dissolution in CED. However, CED has also been used to investigate dissolution of cellulose under a microscope (Schild & Sixta, 2011) and with a fiber analyzer (Arnoul-Jarriault, Passas, Lachenal, & Chirat, 2016). One of the advantages with CED of is that the solvent quality may be controlled with the addition of water.

When analyzing the molecular mass distribution of cellulose, the cellulose must be dissolved first. In this application, a very common analysis method is based on dissolution in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc), either direct or after derivatization, before analysis with size exclusion chromatography (SEC) (Potthast et al., 2015). Differences in dissolution behavior have been discovered from one substrates to another, and, for this reason, the method must be adapted for different materials (Henniges et al., 2011).

In many aqueous solvents cellulose forms colloidal aggregates (Schulz, Seger, & Burchard, 2000), and does not lead to a real solution. This makes the investigation of cellulose dissolution hard. Many different approaches have been used to study cellulose dissolution, such as ocular inspection with light microscopy (Celine Cuissinat & Navard, 2006a; Schild & Sixta, 2011) turbidity measurements (Mazza, Catana, Vaca-Garcia, & Cecutti, 2008; Olsson, Idström, Nordstierna, & Westman, 2014), light scattering (Röder, Morgenstern, Schelosky, & Glatter, 2001) and centrifuging off undissolved fragments (Le Moigne & Navard, 2010).

When studying cellulose dissolution with microscopy, two main dissolution pathways have been identified. If the solvent is very good and/or if the cellulose is very easy to dissolve, the dissolution occurs through fiber fragmentation. Fragmentation leads to fast dissolution, and the fibers look like they have been cut with scissors before dissolving. In a less effective solvent or with a material that is harder to dissolve, first balloons along the fiber are observed, and when these balloons break up, the dissolution continues (Le Moigne, Montes, Pannetier, Höfte, & Navard, 2008). When studying cellulose dissolution with light microscopy, it is consequently, possible to divide dissolution into four modes, fragmentation (dissolution), ballooning (dissolution), ballooning (no, or partial dissolution) and homogenous swelling (no dissolution) (Celine Cuissinat & Navard, 2006a). It must, however, be noted that when dissolution is observed under a microscope, the cellulose may not be completely dissolved on the molecular level.

Le Moigne et al. (2008) have studied dissolution of cotton fibers from different stages in the development of cotton fibers and those authors found large differences in the dissolution capacity of the different layers of the cellulose fibers. Fibers from the elongation stage, which contain only the primary wall, were impossible to dissolve. It was also observed that ballooning only occurred in fibers with a secondary wall. If the primary wall is removed with enzymatic peeling, no balloons are observed, instead homogenous swelling occurs (Céline Cuissinat, Navard, & Heinze, 2008).

In this thesis, a method based on the assessment of swelling, instead of dissolution, has been used to quantify the susceptibility of different cellulose samples to dissolution. When cellulosic fibers are subjected to water, this leads to swelling of the non-crystalline domains of the cellulose without affecting the crystallinity of the cellulose, and this is

referred to as intercrystalline swelling. However, when liquids penetrates the crystalline areas of cellulose, intracrystalline swelling occur, which cause irreversible changes in the crystal structure of the cellulosic material (Krässig, 1993). Examples of such liquids are NaOH/water, liquid ammonia and CED. Arnoul-Jarriault et al. (2016) have developed a method, in which the swelling of fibers in water is compared to the swelling of fibers in dilute CED. The findings of those authors showed that the change in width caused by the swelling could be correlated to Fock reactivity, a method used to quantify the reactivity of different pulp samples toward xanthation, which is the derivatization step in the viscose process (Fock, 1959). The measurement of fiber width was performed with a fiber analyzer, which enables the measurement of a large number of fibers in comparison to microscopy, in which only a few fibers can be analyzed. One advantage of measuring fiber swelling instead of dissolution, is that the problems of determining whether a samples is dissolved or not is avoided. It has been shown previously that the maximum expansion of cellulose fibers is a good indicator of solvent quality (Celine Cuissinat & Navard, 2006b).

7. Separation of Polyester and Cotton Fibers

Most textiles are blends of two or more materials to acquire the properties desired for the final material and to use the benefits of each material optimally. One of the most common textile blends is polycotton. Polycotton are e.g. used in virtually all service textiles, such as sheets and towels at hospitals and hotels. The benefit of polycotton is that it combines the comfort and water absorbency of cotton with the strength, durability, and low price of polyester. The recycling of service textiles may be a possible starting point for textile recycling since, in this sector, there are large volumes of textiles with similar quality. However, in that case, polycotton must be separated into its two components, polyester and cotton. Some background information about this area is provided in this chapter.

7.1 Separation of polycotton

The separation of polycotton may be simplified into four possible main pathways, shown in Figure 5.
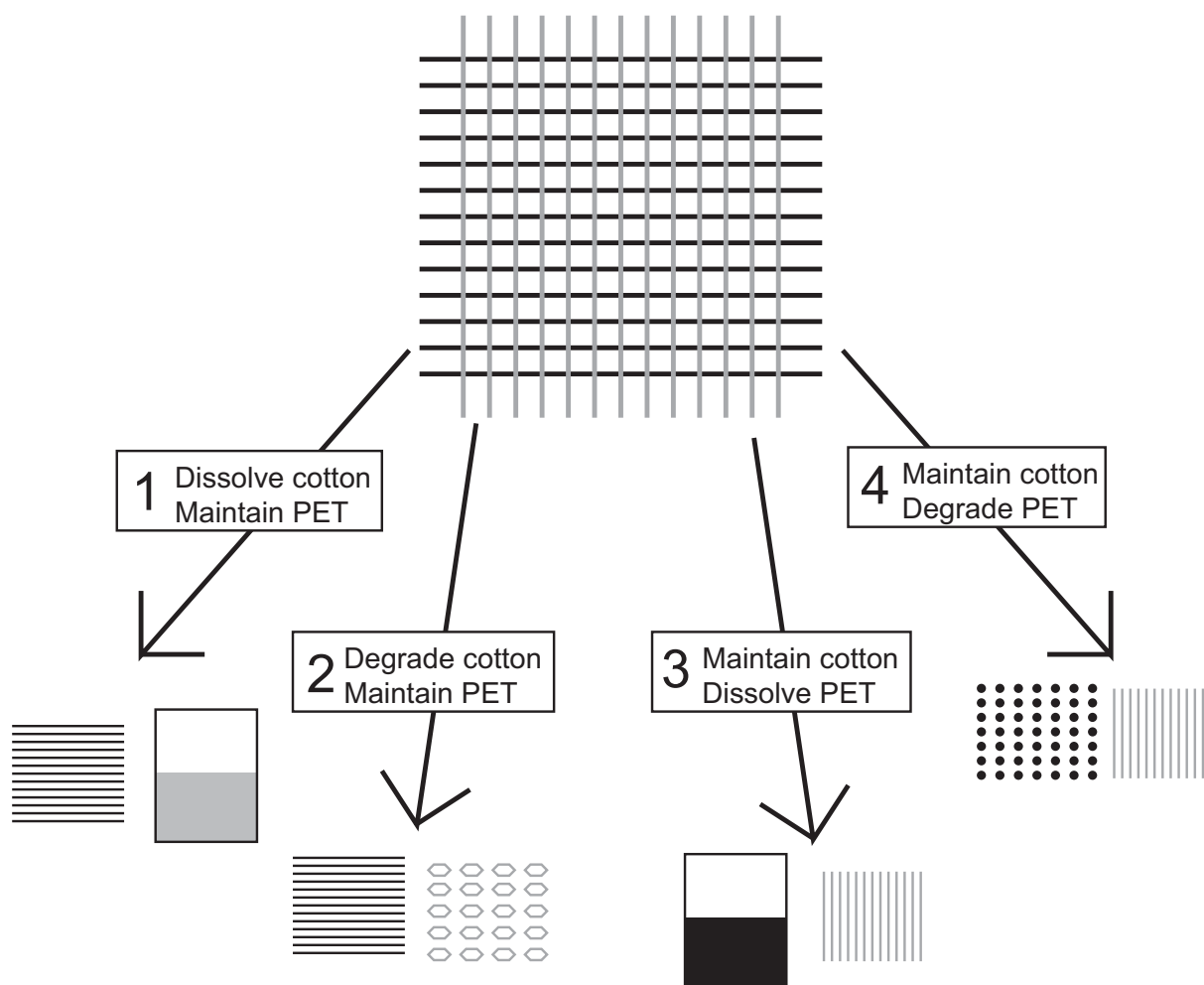
Figure 5: Illustration of the four main pathways for separation of PET and cotton. The grey material symbolizes cotton and the black PET. Please note that this is only an illustration and that fabrics woven of cotton and PET are not constructed in this way.

The first approach is to dissolve the cotton and maintain the PET. This approach was used by Jeihanipour et al. (2010) who dissolved the cotton part in NMMO to separate it from polyester. The cotton was then regenerated, and digested to biogas. De Silva et al. (2014) have shown that cotton and polyester can be separated by dissolving cotton in ionic liquids. Those authors have proposed that the cotton could be used to produce fibers or films and that the recovered PET may be melted into fibers or bottles. It must, however, be pointed out that if the aim is to produce bottles from the recovered polyester, the molecular mass must be increased, through e.g. partial repolymerization, since the polyester that is used in bottles has a much higher molecular mass than the polyester used in textile fibers.

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Instead of dissolving the cotton, separation may also be accomplished through the degradation of the cotton. Cotton is sensitive to acid, which PET is very resistant to. This approach has been proposed by Ouchi et al. (2010). In their article, the separation of cotton and polyester is accomplished by degrading the cotton with 10 M H_2SO_4, which gives a "cotton powder" with a degree of polymerization around 180, probably similar to microcrystalline cellulose, MCC. Other authors have proposed hydrolyzing the cotton with microbes and fermenting the hydrolysate into methane (Bernd & Gerahard, 1996).

Instead of the approaches above, where the polyester is maintained, the opposite, i.e. maintaining the cotton and degrading or dissolving the PET can also be an option. The approach to degrading the polyester while maintaining the cotton has been proposed using hydrolysis (Negulescu et al., 1998) and alcoholysis of the PET (Oakley, Gorman, & Mason, 1993). No examples in the literature could be found in which, the latter approach to dissolving PET and maintaining cotton has been used.

In this thesis, the hydrolysis of PET, with the aim of maintaining cotton has been studied. This approach was chosen since, as described in previous sections, the laundering of both polyester and cotton causes degradation of the polymers. When the molecular mass of polyester decreases, this leads to a lower viscosity of the polyester melt, and, thus, melt spinning may either give fibers of very low quality or may not be possible.

7.2   Polyester degradation

Since PET is used in large volumes to produce PET bottles, different depolymerization processes have been extensively examined, and the findings have been reviewed (Al-Sabagh, Yehia, Eshaq, Rabie, & ElMetwally, 2016; Chen, Wang, Li, & Yang, 2011; Dutt & Soni, 2013; George & Kurian, 2014; Geyer, Lorenz, & Kandelbauer, 2016; Paliwal & Mungray, 2013; Sinha, Patel, & Patel, 2010). There are three main chemical degradation methods for PET; hydrolysis (acid, neutral, or alkaline), alcoholysis (Oakley et al., 1993), and glycolysis (Viana, Riul, Carvalho, Rubira, & Muniz, 2011). However, only hydrolysis degrades PET back to terephthalic acid (TPA) and ethylene glycol (EG) which are the monomers mainly used in PET production today (Gupta et al., 1997).

In this thesis, alkaline hydrolysis with the addition of a phase transfer catalyst is investigated. This method has been proved to be very effective in the hydrolysis of PET

flakes. The hydrolysis is performed at moderate temperatures (70-95°C) and alkalinity in the range 5-15 wt% NaOH (Das, Halgeri, Sahu, & Parikh, 2007; Kosmidis, Achilias, & Karayannidis, 2001; López-Fonseca, González-Marcos, González-Velasco, & Gutiérrez-Ortiz, 2009; Polk et al., 1999). The process starts with hydrolysis for 1-3 hours, which causes the formation of disodium terephthalate salt and ethylene glycol, see Figure 6, which are both soluble in the aqueous phase. When the reaction is finished, the aqueous phase is acidified to a pH around 2.5-3, which causes the formation and precipitation of TPA.
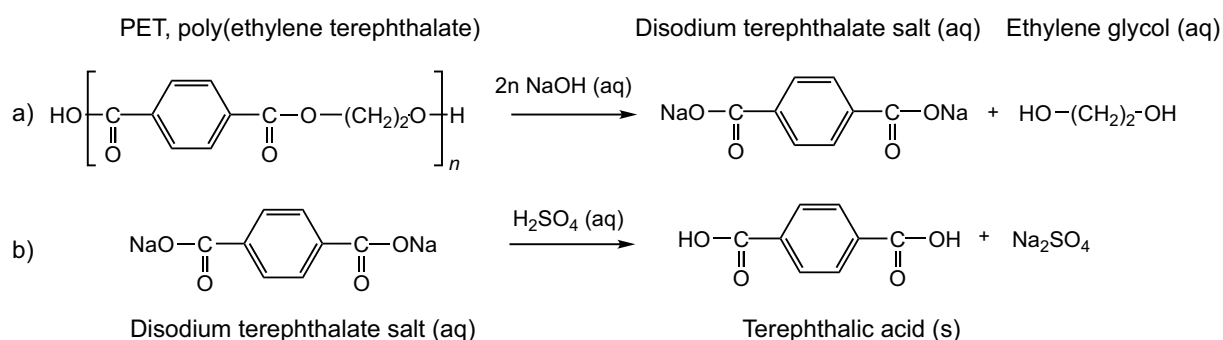

Figure 6: a) Degradation of PET with NaOH, into disodium terephthalate salt and ethylene glycol, b) Formation of precipitated TPA

8. Materials and Methods

8.1 Materials

The present investigation is centered on cotton or polycotton sheets, but wood pulp samples were also included as reference. The materials are presented and divided into three parts below. Part 1 was used in Paper I, Part 2 in Papers II-IV, and Part 3 in Paper V. In Part 1, only cotton sheets were included, however in Part 2 both cotton and wood pulp samples were included.

8.1.1 Background information regarding the cotton sheets used in Part 1 and Part 2

The 100% cotton bed sheets were made from cotton from Pakistan and provided by a major Swedish supplier of service textiles. The sheets indicated as used had been used at Swedish hospitals. The laundering was performed by the service provider using an industrial laundering system with a maximum temperature of 84°C and the washing agent Clax Hellux free 3EP3, from JohnsonDiversey Sverige AB, an alkaline detergent with a pH between 12 and 12.5 in a 1% solution. The washing agent did not contain any oxidants. After laundering, water was pressed out of the fabric prior to tumble drying.

Before all of the analyses, except where noted, the sheets were ripped into approximately 1 cm^2 pieces and defibrated using a Wiley mill (< 1mm).

8.1.2 Part 1 materials

In Part 1, four cotton sheets were used, see Table 1. The defibrated sheet samples were extracted with light petroleum and water, according to ISO 18:33-1:2010.

Table 1: Use and laundering of the cotton sheets included in Part 1.

Laundered number of times	Use
0	
2-4	Never used
~50	
>50	Used

Before weaving, an additive was applied to the yarn to facilitate weaving. All residues of this were removed during laundering, however, on the never-laundered sheet, traces of a non-cellulosic additive were found using ^{13}C solid-state NMR spectroscopy, even after extraction. The presence of the non-cellulosic additive in the never-laundered sheet was also proved in a test in which a water droplet was placed on dried fiber pads containing the extracted fibers. The droplet was immediately absorbed into all of the fiber pads, except for the fiber pad containing fibers from the never-laundered sheet where the contact angle of the droplet was >105°. No further attempts were made to characterize this non-cellulosic material. However, this contamination obstructed the measurements of the specific surface area and WRV for the never-laundered sheet.

8.1.3 Part 2 materials

In Part 2, two fractions with 5 cotton sheets in each batch were investigated, referred to as "New" and "Discarded". The materials in Part 2 materials were the same kind of sheets used in Part 1, however, they had been received at a later date. The New sheets had been laundered 2-4 times but never used, and the Discarded sheets had been

laundered >50 times, used in hospitals and were classified as worn out. The sheets included in this part were not extracted before analysis.

In Part 2, wood pulp samples were also included as references. These comprised two dissolving pulp samples, and a bleached softwood paper grade Kraft pulp. The dissolving pulps were both once-dried and consisted of a Scandinavian softwood sulfite pulp (Sulfite pulp) sample and a pre-hydrolysis eucalyptus Kraft pulp (PHK-pulp) sample. The bleached softwood paper grade Kraft pulp (BKP) sample was split into two parts; a never-dried and a once-dried sample. In the following, the samples are referred to with the names/abbreviations in brackets above.

8.1.4 Part 3 materials

The third group of materials, used in the separation of polycotton, comprised one new polycotton sheet. The sheet was found to contain 52% cotton when analyzed according to European standard "Mixtures of cellulose and polyester fibres (method using sulphuric acid)" (ISO 1833‑11:2006).

In the separation of polycotton, a phase transfer catalyst, benzyltributylammonium chloride (BTBAC, purity >98%), was used. Sodium hydroxide (NaOH, reagent grade) and sulfuric acid (H_2SO_4, reagent grade) were also used in the experiments.

All chemicals were used without any prior purification.

8.2 Cellulosic fiber characterizations

8.2.1 Scanning electron microscopy

Before analysis, the cotton sheet samples (non-extracted) were sputtered with a 30 nm thick layer of gold. The micrographs were collected using a Zeiss EVO HD 15 scanning electron microscopy (SEM) instrument operated at 1.3 kV.

8.2.2 Water retention value

The water retention value (WRV) was measured according to the SCAN-C 62:00 method. A 2 g sample, was centrifuged at 3000 g for 15 min. The sample had been defibrated in water and partially dewatered before analysis. The sample weight after

centrifugation was then compared to the sample weight after drying at 105°C. All tests were carried out in duplicate.

8.2.3 Specific surface area

Before measuring the specific surface area, the samples were subjected to a solvent exchange procedure to avoid pore closure. The exchange was performed by carefully dewatering 1 g o.d. sample swollen in water and displacement washing it with 20 ml dry acetone (>99.8%). The sample was then shaken in 20 ml acetone. The procedure was first performed 10 times with acetone and then 10 times with cyclohexane (Köhnke et al., 2010; X. Wang, 2006). The samples were then dried in a nitrogen stream overnight. Nitrogen adsorption was performed using a Micrometrics TriStar 3000 instrument, and the specific surface area was calculated according to the BET theory (Brunauer–Emmett–Teller). Nitrogen adsorption permits the measurement of all surface area accessible to the nitrogen molecule which is 3.6 Å in diameter (Stone & Scallan, 1966). The measurement of the specific surface area of cellulose fibers using this method requires dry samples, and to evaluate the surface of a water-swollen sample, a solvent exchange may be used, as described above. In this thesis, the samples were dried from cyclohexane. This leads to an underestimated surface area since cyclohexane has been found to cause a slight contraction of pulp fibers (X. S. Wang, Maloney, & Paulapuro, 2003).

8.2.4 Intrinsic viscosity

The intrinsic viscosity of the samples was determined by dissolving the samples in 0.5 M CED (copper(II)ethylenediamine), and measuring the time for the solution to run through a thin capillary. The measured time could then be correlated to intrinsic viscosity, according SCAN-C 15:62. The intrinsic viscosity can be correlated to the degree of polymerization (DP) of a cellulose sample, and when DP_v-values are reported in this thesis, the calculation has been done according to Immergut et al. (1953) (Immergut, Schurz, & Mark, 1953), as stated in SCAN-C 15:62, see Equation 3.

$$DP_v^{0.905} = 0.75[\eta] \hspace{4cm} \text{Equation 3}$$

Measuring intrinsic viscosity is a simple and fast method, however, the correlation to DP is more complicated. The correlation proposed by Immergut et al. in the 1950s may be considered to be outdated, but remains the most commonly used one. This correlation was chosen, despite that it has been criticized, since this would better allow for comparison to data from other papers. Further discussion on the correlation between the intrinsic viscosity and DP of cellulose is presented in Section 9.4.

8.2.5 HP-SEC

Size exclusion chromatography was carried out after the dissolution of the samples in lithium chloride/N,N-dimethylacetamid (Li/DMAc), according to Henniges et al. (2011). 20 mg (dry weight) of sample was suspended in deionized water and then dewatered in a Büchner funnel. The sample was rinsed with ethanol, and then placed in a dry septum-capped glass vial. DMAc (4 ml), was added and the vial was placed on a laboratory shaker overnight for solvent exchange. Following this procedure, DMAc was removed, and 2 ml of a solution of 9% LiCl (w/v) in DMAc was added. The vial was placed on the laboratory shaker for 16 to 40 h at room temperature. After dissolution, 0.9 ml of the solution was diluted with 2.7 ml DMAc. Prior to chromatographic analysis, the dissolved samples were filtered using a 0.45 µm PTFE filter. Chromatographic analysis was performed using a Dionex Ultimate 3000 system with a guard column and four analytical columns (PLgel Mixed-A, 20 µm, 7.5 x 300 mm). DMAc/LiCl (0.9% v/w) was used as the mobile phase. The injection volume was 100 µl. The flow rate was 1.00 ml/min, and the elution was performed at room temperature. RI (Optilab T- rEX from Wyatt) and MALLS (Down Heleos-II, λ_0=658 nm, from Wyatt) were used for the detection process. The value of dn/dc used was 0.136 ml/g. Data evaluation was performed with standard Astra and Chromeleon software (6.1.17). The BKP samples in Paper II were not completely dissolved in the DMAc/LiCl, and no attempts were made to quantify the undissolved fraction.

8.2.6 Solid-state CP/MAS ^{13}C NMR

Part 1 materials

Solid-state ^{13}C NMR experiments were performed on a Varian Inova-600 operated at 14.7 T and equipped with a 3.2 mm solid state probe. Measurements were conducted as

described earlier (Idström et al., 2013). Both untreated (non-hydrolyzed) samples and samples subjected to an acid hydrolysis pretreatment were analyzed. The acid hydrolysis of the samples was performed according to Wickholm et al.(1998) (Wickholm, Larsson, & Iversen, 1998) in 2.5 M HCl at 100°C for 17 hours. The resulting cellulose was washed several times by centrifuging the samples, decanting the supernatant and adding fresh water. Spectral deconvolution was applied to all NMR spectra according to the method described by Wickholm (2001) (Wickholm, 2001).

Part 2 materials

The supramolecular properties of cellulose were determined in the water-swollen state using a method with solid-state cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS ^{13}C-NMR), as described in previous papers (Larsson, Wickholm, & Iversen, 1997; Wickholm et al., 1998). The spectra were recorded in a Bruker Avance III AQS 400 SB instrument operated at 9.4 T. All measurements were carried out at 295 (±1) K with a magic angle spinning (MAS) rate of 10 kHz. A 4-mm double air-bearing probe was used. 4096 transients were recorded for each sample depending on solids content, which led to an acquisition time of 3 h. The software for spectral fitting was developed at Innventia AB and is based on a Levenberg-Marquardt algorithm (Larsson et al., 1997; Wickholm et al., 1998). All computations were based on integrated signal intensities obtained from spectral fitting. Signals intensities of non-crystalline origin (fitted signals in the 82 ppm to 85 ppm C4 spectral range) were used to calculate the crystallinity (CI) of a sample. The errors given for parameters obtained from the fitting procedure are the standard error of the mean with respect to the quality of the fit.

8.2.7 FSP

FSP was measured by following the method developed by Stone and Scallan (Stone and Scallan 1968) (Stone & Scallan, 1968). The samples were swelled in water over-night and partially dewatered. The determination started by mixing a 1% dextran solution (2000 kDA) with the partially dewatered sample, where 1 mass unit of wet sample was mixed with 3 mass units of dextran solution. The samples were then allowed to equilibrate for 3 days in a sealed vessel.

A liquid sample was subsequently taken and filtered through a Puradisc syringe filter (Whatman, Maidstone, UK) equipped with a 0.45 μm polytetrafluoroethylene (PTFE) membrane in a polypropylene housing (VWR International AB, Stockholm, Sweden). The concentration of dextran in the sample was determined using a calibration curve established for the optical rotation of polarized light measured using a Polartronic NH8 polarimeter (Schmidt+Haensch, Berlin, Germany) operated at 589 nm, with a resolution of 0.005 degrees. The FSP value is expressed as the dimensionless ratio of the mass of pore water to the mass of dry solids (g/g).

8.2.8 LODP determination

To determine the LODP, 2 g (o.d.) of sample were hydrolyzed for 2 and 4 hours in 100 ml 4 M hydrochloric acid at 80°C. After hydrolysis the samples were gently rinsed with cold water. The DP of the samples was then estimated though measurement of the intrinsic viscosity, and the average value of the two hydrolysis times were calculated. Each hydrolysis was performed in duplicates.

8.2.9 Fiber analysis

The fibers were analyzed with a Kajaani FS300 according to Tappi standard T271, and the calculations were based on length average. Length is reported as the centerline length. Before analysis, the pulp and the cotton fiber samples were swelled in water over night and gently defibrated.

8.2.10 Swelling experiments

Before the swelling experiments, the samples were swelled in water, and carefully defibrated. During the agitation of 0.05 g (o.d.) sample, CED (1 M) was added to a final liquid weight of 10 g. After 2 min the swelling was quenched by adding the sample to 0.5 L acetate buffer (0.01 M, pH 4.5). The fibers were directly analyzed with a fiber analyzer (Kajaani FS300). During the swelling, the CED concentration was 0.16, 0.18 or 0.20 M.

This method provides a comparison of the difference in the width of fibers swollen in a solvent to fibers swollen in water, which was calculated according to Equation 4.

$$\text{Width variation (\%)} = \frac{(\text{Width}_{CED} - \text{Width}_{H_2O}) * 100}{\text{Width}_{H_2O}} \qquad \text{Equation 4}$$

8.2.11 Optical microscopy of fiber swelling

Microscopy slides were prepared by suspending the fibers in water and distributing them wet on the slides. When the samples were dry, the fiber concentration on each slide was corrected to a similar level for all samples.

The swelling was studied using a Zeiss SteREO Discovery.V12 equipped with an Axio Cam IC1 in time-lapse mode with which images were taken every 2 seconds for 4.5 minutes, yielding 136 images per sequence. Dilute CED was added during the first 10 seconds, and the delay was accounted for. The dissolving pulp samples were treated in 0.16, 0.18 or 0.20 M CED, and the two cotton sheet samples were treated in 0.16, 0.20 and 0.24 M CED.

8.3 Pretreatments

8.3.1 Acid hydrolysis in water

The samples were prepared for acid hydrolysis by swelling the samples in water over night and, subsequently, defibrating them in 0.01 M HCl. The defibration was performed in a low acid concentration to remove any alkaline residues remaining in the sheets from the laundering agent. This was performed on all samples in order to treat them according to the same procedure.

Acid hydrolysis was performed using the following method: water was added to a wet sample to a total water volume of 60 ml, and the sample was heated in a water bath to 80°C in a polypropylene container. After 30 min the sample had reached 80°C, and the hydrolysis was started by adding 40 ml 1M HCl to a total volume of 100 ml and 0.4 M HCl. The hydrolysis was performed for 15, 30, 60, 120, and 240 min. After completed hydrolysis, the sample was carefully rinsed with deionized water at room temperature, in order to remove all acid, and then air-dried before further analysis.

8.3.2 Acid hydrolysis in ethanol

Samples were prepared for acid hydrolysis in ethanol by swelling them in water followed by defibration in 0.01 M HCl. Then a solvent exchange was performed from water to ethanol through displacement washing with 50 ml of ethanol (99.5%) followed by shaking the sample in 50 ml ethanol. The solvent exchange procedure was repeated five

times. After this, additional ethanol was added to the samples to a total ethanol volume of 100 ml and heated to 50°C in a polypropylene container. After 30 min of preheating 4 ml of 37% HCl was added and the hydrolysis was performed for 15, 30, 50, 120 and 240 min. The final hydrolysis solvent contained 94wt% EtOH and 0.46 M HCl. After completed hydrolysis, the samples were carefully rinsed with deionized water at room temperature, to remove all acid, and then they were air-dried before further analysis.

8.3.3 Hydrothermal treatment

Samples were prepared for hydrothermal treatment by swelling them in water followed by defibration in acetate buffer (0.02 M pH 4.75). Then the pulp samples and additional acetate buffer were added to acid resistant stainless steel autoclaves at room temperature to a final weight of 300 g with 5 wt% pulp. The autoclaves were then placed in a preheated polyethylene glycol bath (170°C). The treatment was performed for 30, 60, 120, and 240 min. The time to reach the final temperature 168°C inside the autoclaves was approximately 25 min (Bogren, 2008). Treatment for 360 min was also tested, however, the pH was not maintained by the buffer during long treatment times. The pH was tested before and after all experiments to confirm that it had been maintained. The experiments were stopped by removing the autoclaves from the polyethylene glycol bath and cooling them in cold water. After cooling down, the pulp was carefully rinsed with deionized water and air dried.

8.4 Modelling of acid hydrolysis

The theoretical background to the modelling is described in Section 5.4. The acid hydrolysis was modelled according to the model developed by (Calvini, 2005), with 1, 2 or 3 components, see Equation 5.

$$S = \sum_i n_i * (1 - \exp(k_i t)), i = 1, 2, 3 \dots n \hspace{3cm} \text{Equation 5}$$

Where S is the number of scissions per cellulose chain (DP_0/DP -1), n is the initial number of scissile bonds, k is the rate constant, and t is the time of hydrolysis. The model was fit to minimize the sum of squared errors of prediction (SSE) using the minimization function fmincon in Matlab 2013b. A very good fit for the samples was achieved with only one component, as in Equation 6.

$$S = n \ (1 - exp(-kt)), \hspace{3cm} \text{Equation 6}$$

8.5   Separation of polyester and cotton from mixed textiles

The separation of polyester and cotton was performed in two different systems. One small-scale system (50 ml), where each experiment was run for a certain time period and then analyzed, and a large-scale system (500 g) where samples of the hydrolysis solution were removed out during the experiment.

8.5.1   Small-scale experiments

The small-scale experiments were performed in 50 ml falcon tubes. The NaOH concentration was 10 or 15wt%, and the BTBAC concentration was varied between 0 and 1 mol BTBAC/mol repeating unit in PET, where 1 mol/mol corresponds to 52 mmol BTBAC /kg hydrolysis solution. The hydrolysis started by mixing NaOH and BTBAC to the selected concentrations followed by heating the solution to the selected temperature (80 or 90°C). The reaction was started by adding 1.0 g o.d. polycotton sample to the reaction tube, and the hydrolysis was performed for the selected time period (15 – 240 min). The reaction was quenched by immersing the reaction tube in an ice bath. The remaining solid phase was separated and washed with water on a glass microfiber filter. The liquid phase was acidified to pH 2-3 by the addition of H_2SO_4 (95-97%), which caused the terephthalic acid (TPA) to precipitate. The TPA was separated using a glass microfiber filter and rinsed with water. The weight of the isolated TPA, was determined after drying overnight in an oven at 105°C. The yield of TPA was calculated as the percentage of the theoretical yield of TPA that can be obtained from PET, assuming that the PET is formed by the esterification of equimolar amounts of TPA and EG.

8.5.2   Large-scale experiments

The large-scale experiments were performed in a glass reactor containing 500 g hydrolysis solution. The NaOH concentration in the hydrolysis solution was 5, 7.5, or 10wt%, and the temperature was 70, 80, or 90°C. The BTBAC concentration was 52 mmol/kg in the hydrolysis solution. The hydrolysis started by mixing NaOH and BTBAC to the selected concentrations and heating the solution to the selected temperature. Then 5.0 g o.d. polycotton sample was added, and the hydrolysis started. During the

hydrolysis, samples of the hydrolysis solution, 1.5 g each time, were removed at different times to analyze the course of the reaction.

After the selected reaction period (240 – 420 min) the reaction was stopped by filtering the solid (cotton) residue through a glass microfiber filter. The cotton residue was then rinsed with water, dried and weighed after drying. The liquid phase was acidified and isolated as described in the small-scale experiments.

8.6 Polyester analysis

8.6.1 Optical microscopy

The hydrolysis was followed during 1 hour with the time-lapse mode using a Zeiss SteREO Discovery.V12 equipped with an Axio Cam IC1 and a Linkam PE120 heating stage at 80°C. The fibers were spread out evenly over the microscope slide and then a solution containing 10% NaOH and 0.1M BTBAC, which corresponds to using 2mol BTBAC per mol repeating unit PET, was added.

8.6.2 Solution state NMR

The TPA and the filtrate obtained after separation were analyzed with solution-state NMR spectroscopy, which was performed on a Varian Inova-800 operated at 18.8 T and equipped with a 5 mm TXO cryoprobe. Measurements were performed at 298 K. For ^{1}H spectra 64 acquisitions were recorded. For ^{13}C spectra, 1024 acquisitions were recorded under continuous irradiation of the proton channel.

Before the analyses, water was evaporated from the filtrate, which was then dissolved in DMSO-d6, while the TPA was directly dissolved in DMSO-d6.

8.6.3 UV-vis spectroscopy

The TPA concentration was measured with a UV-vis spectrophotometer (Specord 205, Analytic jena) at 242 nm, using the initial hydrolysis solution as background. The concentration calculations in the large-scale experiments were adjusted to the removal of solvent and TPA.

8.6.4 ATR FT-IR

The IR spectra were recorded at room temperature in air from 4000 to 400 cm^{-1} with 20 scans using a PerkinElmer FT-IR spectrophotometer with the diamond ATR attachment GladiATR from Pike Technologies. The resolution was 2 cm^{-1}, and interval scanning was 0.5 cm^{-1}.

9. Results and Discussion

This thesis is based on five papers, and the findings may be related to four closely connected areas; laundering, pretreatment, swelling, and separation. In this chapter, the results from the papers are combined and discussed to give an overall picture of the findings. The areas will be presented in the order described above. Before the section on separation, the relationship between DP and intrinsic viscosity will be examined and discussed.

9.1   Changes in cotton fibers during laundering

The first step on the road to textile recycling is understanding the material. Chemical recycling should mainly be performed when reuse is not possible anymore, and the textiles have been laundered many times. Thus, a comparison of the characteristics of cotton sheets in different stages on the path to being discarded provides a background to textile recycling. The first paper in this thesis, Paper I, discusses the effect of use and laundering through an investigation using WRV, specific surface area, solid-state ^{13}C-NMR, intrinsic viscosity, and molecular mass distributions. In this section of the thesis, some of these results will be compared to results from Papers II-IV, which also have relevance to the subject.

9.1.1 Observations on fiber level

Paper I is based on the materials referred to as Part 1, and these include four sheets laundered 0, 2-4, ~50, and >50 times. The never-laundered sample was off-white and stiff. The stiffness was probably due to the additive that had been applied during the production process, which made the fibers very hydrophobic. The additive can be seen in the SEM micrograph in Figure 7a as a film covering the fibers.
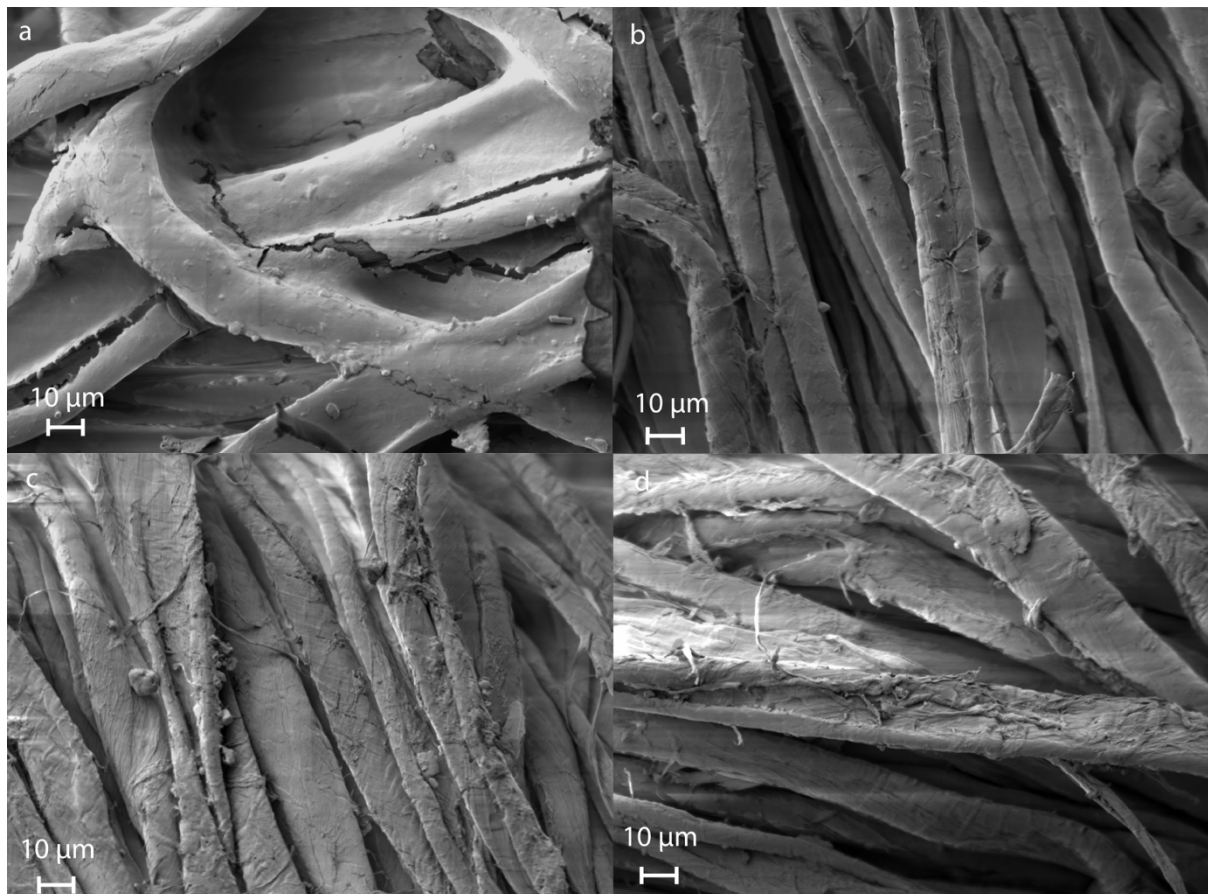

Figure 7: SEM micrographs of the four sheets, laundered a) 0 times, b) 2-4 times, c) ~50 times and d) >50 times.

After being laundered an increased number of times, the sheets became softer and whiter and also easier to tear into smaller pieces. In the SEM micrographs in Figure 7, it is clear that with increasing number of launderings the fiber surface changes. The structure of the outside of the fibers indicates that the primary wall has, at least partly, been removed. This probably mainly occurs in the processing from fiber to fabric.

9.1.2 Ultrastructure of the fibers

Cotton fibers are natural fibers with a number of different structural levels. The supramolecular level influences the accessibility of the fibers and is, therefore, important to study in order to better understand fiber properties. This may be done with a variety of methods, and in this thesis both WRV, FSP, nitrogen adsorption, and solid-state ^{13}C-NMR spectroscopy were used. Here, additional results from Papers II and III will be included to highlight the findings of Paper I. In Papers II and III, analyses were performed on Part 2 materials in which the sample referred to as "New sheet" is comparable to the sheet laundered 2-4 times, and the sample referred to as "Discarded sheets" to the sheet laundered >50 times. The sheets in Part 1 and 2 were the same kind of sheets but from different batches. The analyses results from both Part 1 and 2 are shown in Table 2.

Table 2: Comparison of characterization of Part 1 and Part 2 materials. Values of the WRV and specific surface area could not be measured for the never-laundered sheet due to a weaving additive.

	Sample	WRV (g/g)[*]	Specific surface area (m^2/g)	FSP	Elementary fibril (nm)	Fibril aggregates (nm)
Part 1	0				6.4 ± 0.2**	21.9 ± 2**
	2-4	0.40	73 ± 4.2		7.0 ± 0.2**	25.6 ± 2**
	~50	0.41	66 ± 2.9		7.2 ± 0.2**	24.2 ± 2**
	>50	0.38	45 ± 1.4		7.2 ± 0.2**	24.1 ± 2**
Part 2	New	0.44		0.293	5.6 ± 0.1	38.9 ± 1.9
	New***				6.2 ± 0.2	40.2 ± 2.2
	Discarded	0.43		0.209	6.0 ± 0.2	42.0 ± 2.3
	Discarded***				6.3 ± 0.2	37.9 ± 2.2

*Pooled standard deviation 0.01, **Based on samples treated with strong acid hydrolysis (2.5M HCl, 100°C, 17h) according to (Wickholm et al., 1998), ***Based on samples treated with dilute acid hydrolysis (0.4M HCl, 80°C, 60min)

The findings show that no major increase in WRV or fibril aggregate size occurred during laundering. The WRV from Part 1 and 2 samples was in the same range, and no decreasing trend was observed in Part 2 materials either. This indicates that repeated laundering did not increase the hornification of the cotton sheets. It is important to note

that the solid-state NMR analysis of the two groups of samples was performed by different labs and with different pretreatments of the samples, which partly hinders comparison. However, despite these differences, the elementary fibril size is in the same range in both measurements. The size of the fibril aggregates is, on the other hand, smaller in Part 1 materials, which could possibly be a result of the harsher hydrolysis performed on Part 1 materials.

Investigation of the specific surface area with nitrogen adsorption (BET) showed a decrease with increasing number of launderings. In Paper I the decrease in specific surface area, while the WRV was constant, was found to be confusing. However, when measuring the WRV of highly hornified samples, the water on fiber surfaces will have a major impact, which may disturb the measurement of minor changes.

The water in the fiber wall can also be measured with solute exclusion as the FSP. The FSP measured for Part 2 materials revealed a decrease in FSP with increasing number of launderings. This shows the same trend as the measurement of the specific surface area of Part 1 materials. These two findings indicate that a change in pore structure takes place during laundering. Such a decrease could be due to the coalescence of cellulose elementary fibrils. However, only very minor changes were observed in the fibril aggregate size as a result of laundering. Thus, the decrease in FSP and specific surface area cannot be entirely explained by the increase in the fibril aggregate size. It can, therefore, be suggested that this decrease is due to reorganization on a higher structural level, and it may be hypothesized that if smaller pores are merged into larger ones, these effects would be visible without changing the fibril aggregate size.

9.1.3 Molecular structure of the fibers

The molecular mass distributions of sheets in Part 1 and 2 are shown in Figure 8 and Table 3. It can be seen that the molecular mass decreases with increasing number of

launderings, which is in agreement with earlier findings (Vaeck, 1966). Some differences between Parts 1 and 2 can be observed, which may be because the number of launderings were estimated by the textile provider, and are, thus, not exact. The decrease is probably due to oxidation reactions that occur during laundering (oxygen from the air is likely to give rise to such reactions), which leads to chain scission, as described in more detail in Section 4.1.

The molecular mass distributions of the cotton were narrow before laundering, which can also be seen in the dispersity. With increasing number of launderings, the distribution became somewhat broader, but as the DP approached the LODP, the distribution became narrower again. It has previously been reported that cotton has a second peak at very low molecular mass values (Marx-Figini, 1969), however, this was not observed in the results shown in Figure 8. The second low molecular

Figure 8: Molecular mass distributions of sheets laundered different number of times. The New sheets sample is comparable to the sheet laundered 2-4 times, and the Discarded sheets to Part 1 samples laundered >50 times.

Table 3: Changes in mass average molecular mass, number average molecular mass and dispersity during laundering.

	Times laundered	M_m (kDa)	M_n (kDa)	Dispersity (M_m/M_n)
Part 1	0	1323	719	1.8
	2-4	567	86	6.6
	~ 50	338	93	3.6
	> 50	151	64	2.4
Part 2	New	813	193	4.2
	Discarded	224	86.8	2.6

mass peak has been assigned to the primary wall (Marx-Figini, 1969). In the SEM-micrographs in Figure 7, it can be seen that the primary wall had, at least partly, been

removed, and the results from the molecular mass distributions give further indications of this.

Regarding industrial textile recycling, it is likely that there will be a spread in the number of times the sheets have been laundered before being sent for recycling. Thus, the molecular mass distribution of the incoming material to a recycling facility will be broad. To adjust the molecular mass distribution so that the incoming feed to the dissolution process is homogenous, pretreatment of the material will be important. For this reason, the next section will discuss the pretreatment of cotton fibers.

9.2   Pretreatment of cellulosic fibers

Pretreatment of cellulosic fibers is used prior to dissolution both to adjust the level of the DP and to enhance dissolution. In this section, the effect of the pretreatments on the cotton sheets will be compared to the pretreatment of the two dissolving pulps.

Three different pretreatments were investigated, acid hydrolysis in water (H_2O/HCl), acid hydrolysis in ethanol (EtOH/HCl), and hydrothermal treatment (HT), in order to study the different degradation patterns. First, some similarities and differences among the three pretreatments will be highlighted, and then acid hydrolysis in water will be discussed in more detail.

9.2.1   Comparison of different acid pretreatments

In order to study differences in degradation pattern, three different pretreatments were included in the study. Figure 9 shows the decrease in intrinsic viscosities with time. All pretreatments decrease the intrinsic viscosities of the samples. The intrinsic viscosity approaches the level at which the degradation rate levels off, i.e. the intrinsic viscosity at LODP, shown as a dashed line.

Acid hydrolysis was performed in water and in ethanol, however, the treatment in ethanol was performed at 50°C and the treatment in water at 80°C. The lower temperature was chosen for the acid hydrolysis with ethanol since the aim was to produce samples with a similar DP after similar time periods. Acid hydrolysis in ethanol is faster than acid hydrolysis in water, which has been shown previously (Reeves et al., 1946; Valley, 1955). The reason for this is, however, disputed, as discussed in the

introduction. Despite the lower temperature, the intrinsic viscosity of the samples treated in ethanol reached a lower value at the first measurement point, after 15 min, for all samples except the PHK pulp, see Figure 9. The intrinsic viscosity of the samples treated in ethanol also seems to level off at a higher level than the samples treated in water. This could indicate that hydrolysis in ethanol leads to a higher LODP. However, the inclusion of a few data points from the Discarded sheets treated at 65°C, see Figure 9d, shows that the levelling off is possibly only an effect of the lower temperature. To study this further, longer reaction times would be needed.
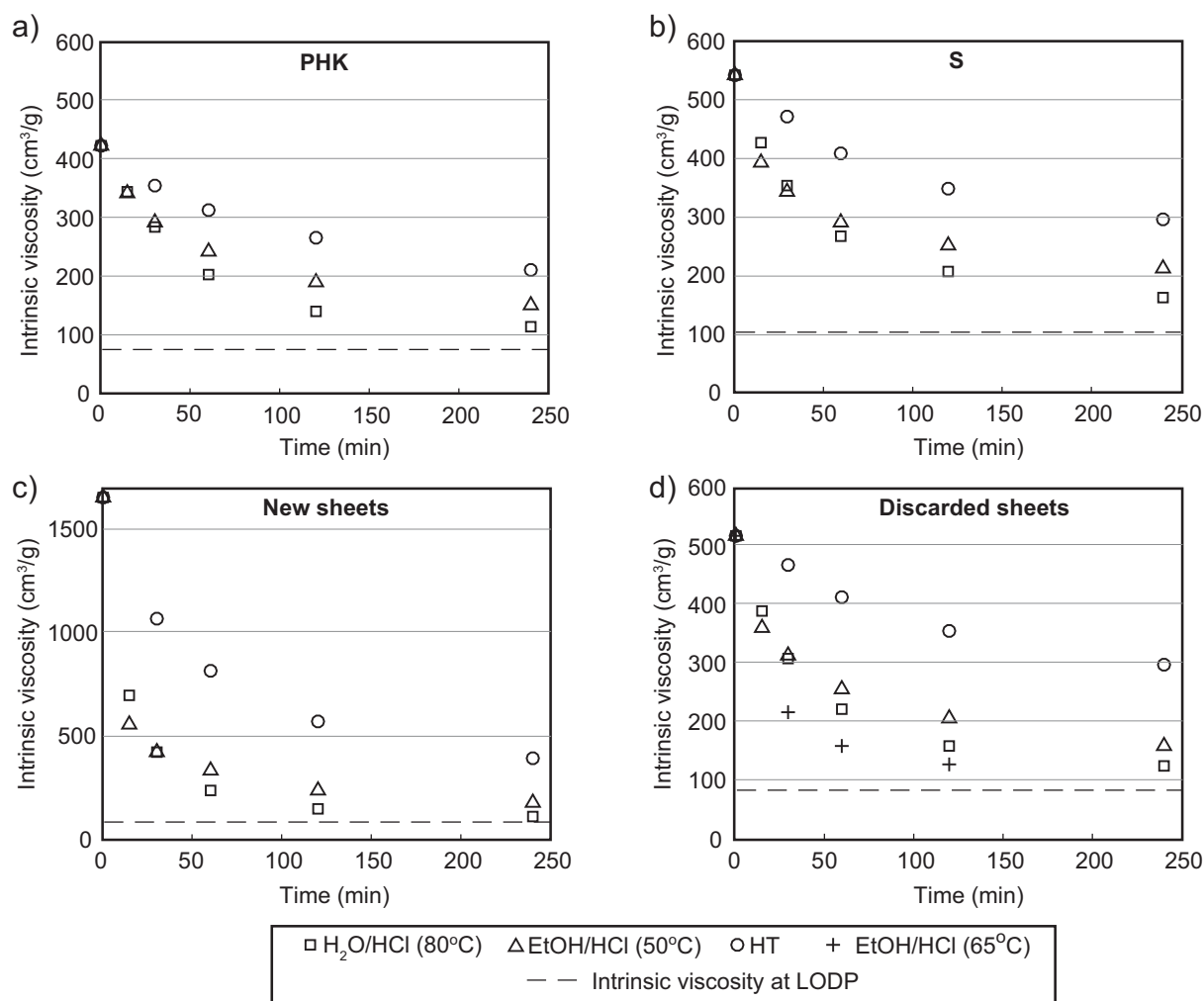
Figure 9: Acid-catalyzed degradation of a) PHK pulp, b) Sulfite pulp, and c) New and d) Discarded cotton sheets.

It has been shown previously that the LODP of samples hydrolyzed in water and in ethanol are very similar (Reeves et al., 1946; Valley, 1955). In Table 4, a small increase in both elementary fibril and fibril aggregate size as well as in CI can be observed as an

effect of acid hydrolysis in water and ethanol. The impact of these mild hydrolysis methods is, however, rather minor.

Table 4: Calculations of the elementary fibril size, the fibril aggregate size, and the crystallinity index from deconvolution of ^{13}C solid-state NMR experiments.

Sample	Treatment	Elementary fibril size (nm)	Fibril aggregate size (nm)	CI (%)
PHK-pulp	Original	4.4 ± 0.1	23.2 ± 0.9	55 ± 1
	H_2O/HCl	4.6 ± 0.1	26.0 ± 1.1	57 ± 1
	EtOH/HCl	4.6 ± 0.1	28.6 ± 1.1	56 ± 1
	HT	4.6 ± 0.1	28.2 ± 1.2	57 ± 1
Sulfite pulp	Original	4.3 ± 0.1	22.1 ± 0.7	54 ± 1
	H_2O/HCl	4.6 ± 0.1	24.6 ± 1.0	57 ± 1
	EtOH/HCl	4.5 ± 0.1	25.2 ± 1.0	56 ± 1
	HT	4.6 ± 0.1	29.9 ± 1.4	57 ± 1
New sheets	Original	5.6 ± 0.1	38.9 ± 1.9	64 ± 2
	H_2O/HCl	6.2 ± 0.2	40.2 ± 2.2	67 ± 2
	EtOH/HCl	5.9 ± 0.2	33.5 ± 1.9	65 ± 2
	HT	6.5 ± 0.2	50.2 ± 3.3	68 ± 2
Discarded sheets	Original	6.0 ± 0.2	42.0 ± 2.3	66 ± 2
	H_2O/HCl	6.3 ± 0.2	37.9 ± 2.2	67 ± 2
	EtOH/HCl	6.2 ± 0.2	40.7 ± 2.6	67 ± 2
	HT	6.7 ± 0.2	64.5 ± 4.2	69 ± 2

The hydrothermal treatment was performed at 170°C, with the addition of acetate buffer (0.02 M, pH 4.75), and the low acidity led to a much slower degradation of the samples than the other pretreatments. The slow degradation at high temperature and in dilute acid, seemed to facilitate recrystallization during hydrolysis. This can been seen in Table 4 as larger fibril aggregates after the HT treatment, and as an increase in the crystallinity index (CI). Slow acid hydrolysis has previously been found to cause crystallization (Battista, 1950).

To investigate the differences between the pretreatments further, the molecular mass distributions of the samples were analyzed, see Figure 10.
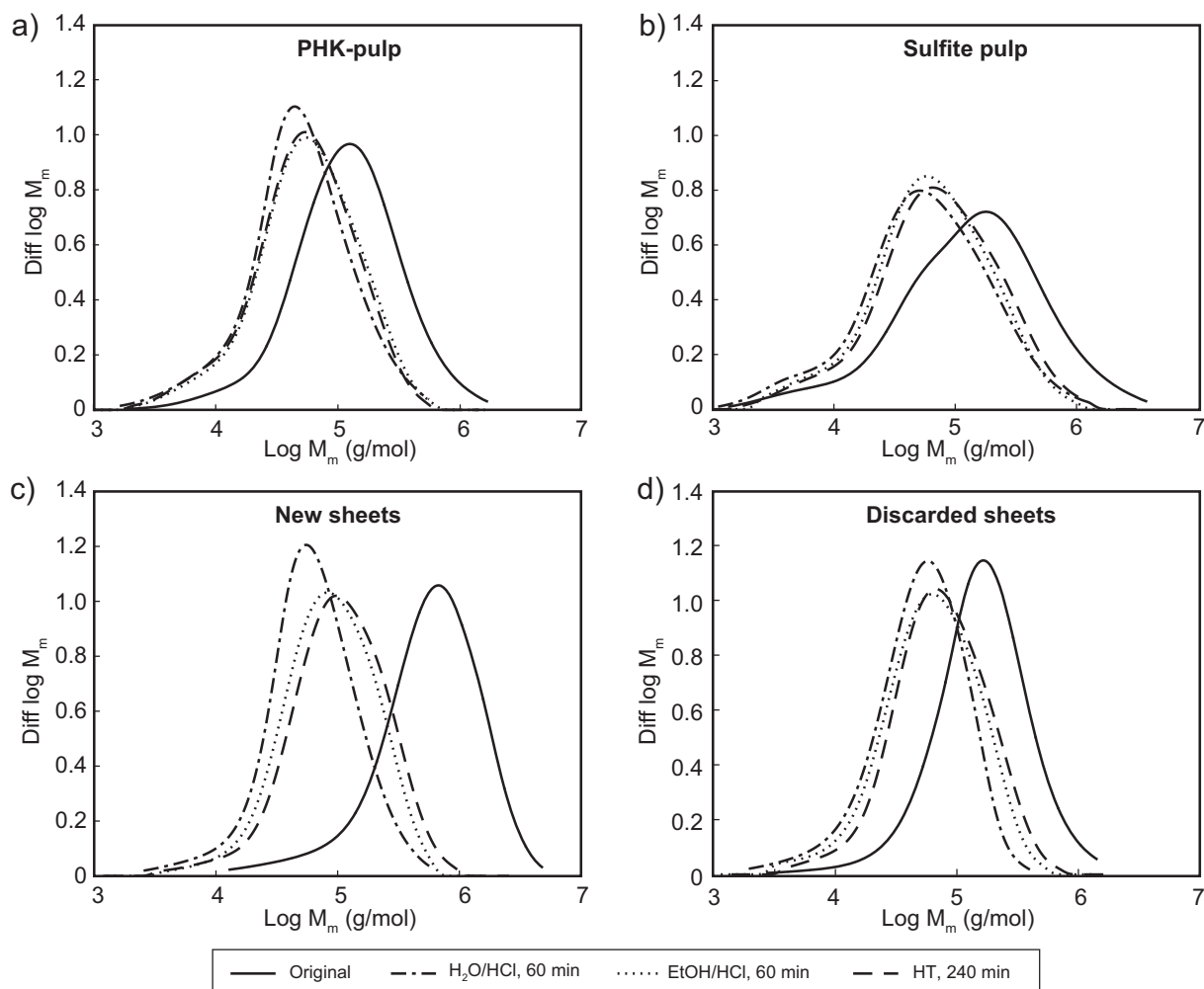

Figure 10: Molecular mass distributions of samples before and after pretreatment.

When the distributions prior to hydrolysis were first analyzed, it was found that the distribution of the Sulfite pulp was much broader than the other distributions, and this is in line with previous research (H Sixta, 2000).

The distributions of the PHK pulp and the two cotton samples (New and Discarded) were similar in shape and narrower than the Sulfite pulp. The molecular mass distribution after the different pretreatments showed that the shape of the distributions was maintained. This indicates that all of the pretreatments had a similar degradation pattern, despite the differences in the pretreatments. It can also be noted that crystallization, which occurred to a greater extent in the hydrothermal pretreatment

than in the other pretreatments, appears not to have given rise to any difference in molecular mass distributions.

9.2.2 Acid hydrolysis

To understand the differences between the different materials better, a deeper analysis of the susceptibility to acid hydrolysis of the cellulose fibers was performed. In this section, findings from modelling the degradation, measuring LODP and CI, will be presented. Since laundering involves many repeated drying and re-wetting cycles, the effect of drying was also studied by including an analysis of the effect of acid hydrolysis of never-dried and once-dried paper pulp samples.

Findings from modelling of the acid hydrolysis of the different samples are presented in Figure 11 and Table 5. When observing the effect of acid hydrolysis on the bleached Kraft pulp, BKP, in Figure 11a, it was found that drying both led to a lower LODP of the dried pulp than the never-dried pulp and that the modelling shows that there were more available bonds n, in the dried pulp. The WRV of the never-dried pulp was higher, and generally, the accessibility of never-dried pulp was higher than that of dried pulp. This finding may seem somewhat surprising. However, as described in Section 5.1, this has been observed before (Jørgensen, 1950; Kontturi & Vuorinen, 2009; Lindgren & Goliath, 1956; Philipp, Dan, & Fink, 1981). The behavior has been explained as that during drying, stresses are built up in the cellulose, and these make the susceptibility of the cellulose to acid hydrolysis higher. The hydrolysis reaction starts with addition of a proton to the oxygen atom of the glucosidic bond, followed by a very slow formation of a carbocation, which adopts a half chair conformation (Edward, 1955). This causes a chain scission and is followed by a rapid addition of water (Philipp, Dan, & Fink, 1981; Sjöström, 1993). The formation of the carbocation is reversible, but when water has added, the reaction is irreversible. A simplistic explanation to the effect of stresses in cellulose on the hydrolysis rate could be that if there is a strain in the chain, the chain scission may lead to the relaxation of the chains and move them apart, thus, making the reaction irreversible. This may contribute to the higher susceptibility of the dried sample to acid hydrolysis.
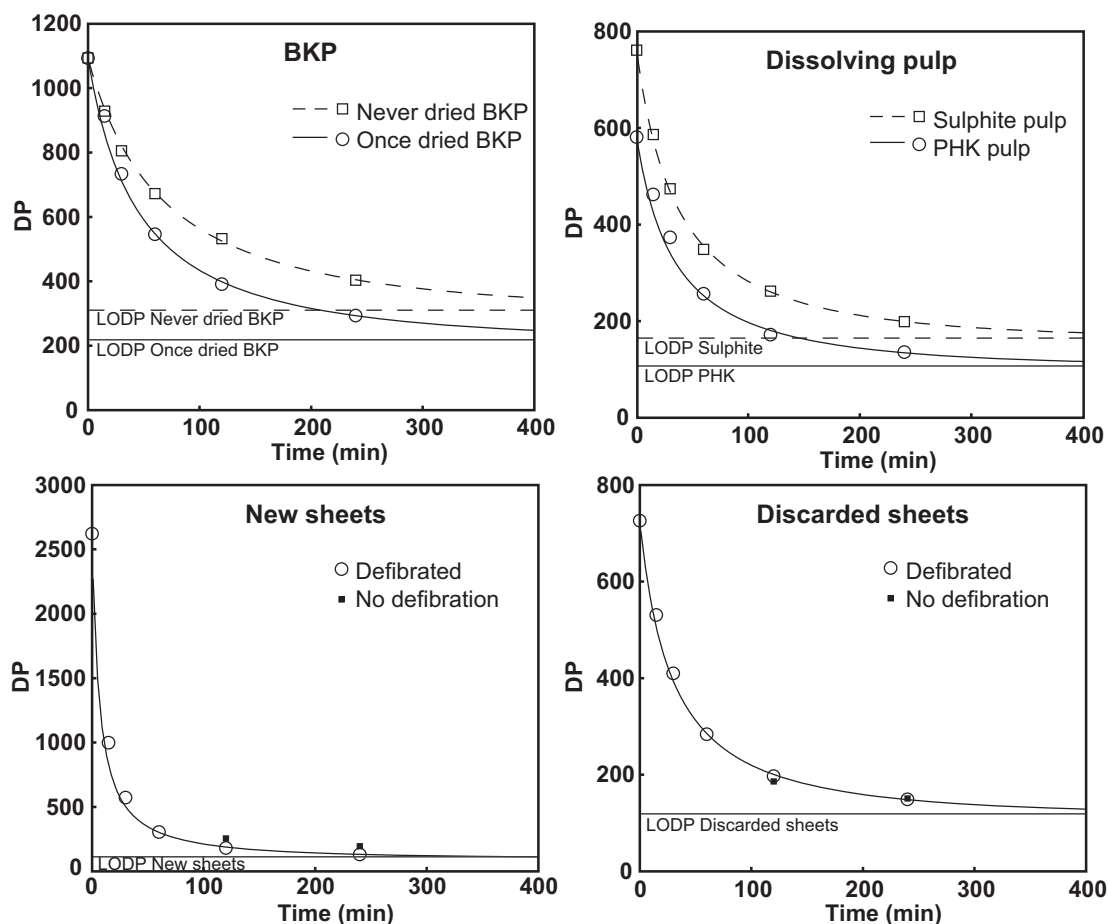
Figure 11: Weak acid hydrolysis (0.4 M HCl, 80 °C) of cellulosic fibers, lines indicate modelling results. LODP values from modelling shown as straight lines.

The comparison of the modelling of acid hydrolysis of the New and the Discarded sheets in Figure 11c and d shows that due to the high starting DP of the New sheets, it is hard to see differences. However, Table 5 lists the rate constant of degradation of the two sheets, and it can be seen that they are very similar. The measured LODP values showed no effect of the drying and rewetting cycles, i.e. no large difference was measured between the New and the Discarded sheets in terms of LODP. This is probably due to the large effect of the initial hornification that occurred before the cotton was harvested.

Table 5: Initial DP, LODP, WRV and parameters from modelling weak acid hydrolysis, n - initial number of scissile bonds, k - the rate constant of the hydrolytic medium and LODP values predicted by the model, see Equation6.

Sample	Measured values			Modelling values		
	Initial DP	LODP	WRV* (g/g)	n	$k*10^2$ (min^{-1})	LODP (calc.)
BKP never-dried	1095	195	1.29	2.53	0.46	310
BKP once-dried	1095	159	0.93	4.02	0.48	218
PHK pulp	581	88	0.72	4.43	0.58	107
Sulphite pulp	761	124	0.65	3.61	0.63	165
New sheets	2621	97	0.44	24.3	0.63	104
Discarded sheets	726	99	0.43	5.11	0.60	119

Pooled standard deviation 0.02 (g/g)

When studying Figure 11, the appearance of the degradation data seems to be similar for the two dissolving pulps. However, an inspection of the parameters from the degradation in Table 5 reveals differences. Inspection of *n*, the number of bonds available to acid hydrolysis, in Table 5, shows that this is higher in the PHK pulp than in the Sulfite pulp, despite that the DP of the Sulfite pulp was higher before hydrolysis. This higher susceptibility to acid hydrolysis of the PHK pulp is also reflected in the lower measured LODP of the PHK pulp. This difference between PHK pulp and Sulfite pulp has been reported earlier (Håkansson & Ahlgren, 2005; H Sixta, 2000). The differences between the two pulps may, at least partly, be understood from differences in the pulping processes. This effect has been discussed by Page (1983), who proposes that the higher susceptibility of Kraft pulp to acid hydrolysis is due to the swelling of the amorphous cellulose that takes place during alkaline pulping, and this may both enhance accessibility and induce stresses. During alkaline pulping, fibril aggregation is also known to occur (Hult, Liitiä, Maunu, Hortling, & Iversen, 2002), and this may also

contribute to building up stresses. Thus, both swelling and fibril aggregation may lead to stress build up, which can lead to higher susceptibility to acid hydrolysis. Parallels can be drawn to the effect of drying on acid hydrolysis where the fibril aggregation caused by drying leads to stress build up and, thus, higher susceptibility to acid hydrolysis.

9.2.3 Effect of hemicellulose on acid hydrolysis of cellulose

If the BKP samples are compared to the other samples (PHK pulp, Sulfite pulp, and cotton sheets), it is clear that the LODP values of these two samples are considerably higher than the other samples, despite the decrease after drying. Furthermore, since these samples are paper-grade pulp, their hemicellulose content is higher than that of the other samples in the study. An investigation by Håkansson et al. (2005) on the effect of hemicelluloses on LODP found that hemicellulose leads to higher LODP, and those authors concluded that hemicellulose protects cellulose from hydrolysis. However, despite the clear relationship between acid hydrolysis and hemicelluloses, the mechanism may be another. Since the samples in that study were dried before hydrolysis, it is possible that the hemicelluloses mainly protected the samples from hornification. Therefore, the stress build up in the hemicellulose-rich samples was lower, and this decreased their susceptibility to acid hydrolysis.

9.3   Swelling of cotton and dissolving pulp in dilute solvent

Pretreatments can be performed before the dissolution of cellulose fibers to make their properties more uniform and to enhance their susceptibility to dissolution. In Section 9.2, the effect on the fibers of three different pretreatment methods (acid hydrolysis in water, acid hydrolysis in ethanol and hydrothermal treatment) was investigated. In this section, the aim is to highlight the susceptibility to dissolution of the different materials both before and after the three pretreatments. However, as presented in the introduction, it is hard to determine if complete dissolution of cellulose has occurred. Thus, instead, the swelling of the cellulose fibers in dilute solvent was assessed with two complementing methods. First, dissolution and swelling were studied in different concentrations of CED using microscopy in order to observe differences in dissolution patterns among the different samples. However, since this method only allows for the investigation of a few fibers, and only qualitative results can be obtained, this was complemented with a quantitative method. In the quantitative method, the samples were subjected to dilute CED for two minutes before the reaction was quenched. The average width of the swollen fibers was then measured with a fiber analyzer, and, based on the change relative to fibers swollen in water, the width variation was calculated, see Equation 4. In each measurement with the fiber analyzer, more than 20 000 fibers were analyzed, making this method less sensitive to fiber-specific effects than microscopy.

Figure 12 shows micrographs of the samples pretreated in acid hydrolysis (0.4 M HCl, 80°C, 60 min) after being subjected to dilute CED for 1 minute. The dissolving pulp samples (PHK and Sulfite) were subjected to the same concentrations of CED as when the width variation was determined, 0.16 M, 0.18 M, and 0.20 M. However, since cotton is very hard to swell, the concentration levels were increased to 0.16 M, 0.20 M, and 0.24 M, when cotton samples were studied. Due to questions regarding the point at which the dissolution of cellulose occurs, the term "apparent dissolution" is used below to describe when no fibers are visible.

Observation of the swelling of the PHK pulp showed that the swelling occurred mainly through ballooning. At 0.18 M CED and higher concentrations, apparent dissolution was observed. When observing the Sulfite pulp, on the other hand, apparent dissolution through fragmentation occurred even at the lowest CED concentration, 0.16 M.

The cotton fibers (New and Discarded sheets) were much less reactive in the CED than the dissolving pulp samples (PHK pulp and Sulfite pulp). In the most dilute CED solution (0.16 M), no visible swelling of the cotton samples occurred, however, at 0.20 M some homogenous swelling did occur. The highest CED concentration 0.24 M led to at least partial apparent dissolution; mainly homogenous swelling was observed, but also some ballooning.

The results from the microscopy study in Figure 12, clearly show that cotton is harder to swell than dissolving pulp. Previous investigations of the dissolution of cotton fibers show that they dissolve through ballooning, similar to wood pulp fibers (Cuissinat & Navard, 2006a; Le Moigne et al., 2008). The cotton fibers in this study mainly showed homogenous swelling, indicating that the primary wall has been removed. This is further supported by the SEM micrographs in Figure 7 and the molecular mass distributions in Figure 8.

The microscopy investigation of the PHK pulp and the Sulfite pulp showed that apparent dissolution was observed in the majority of the samples, even at very dilute CED concentrations. However, it is important that mainly swelling occurred in the quantitative method described above, where the change in fiber width after swelling in CED was measured with a fiber analyzer. The results from the microscopy could, therefore, be worrying, and, thus, the fibers were also investigated with optical microscopy after quenching. This showed that the fibers after quenching were swollen, but their natural fiber structure was maintained. This implies that despite that apparent dissolution occurred in the micrographs, the fibers were not completely dissolved after 2 min. This shows that analysis of dissolution with microscopy should be accompanied with other analyses to obtain a more complete picture of the dissolution process.
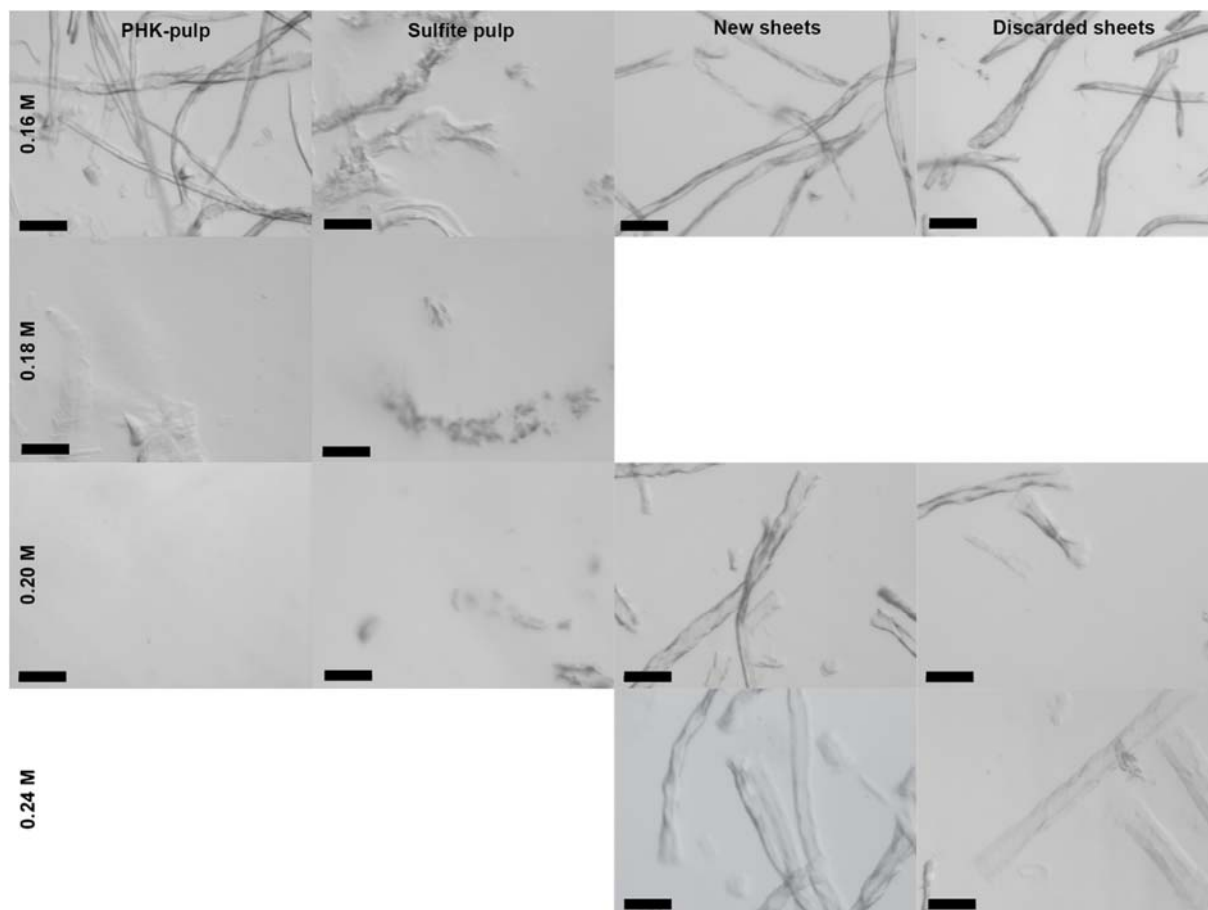
Figure 12: Micrographs of fiber samples treated with acid hydrolysis for 60 min and subjected to different concentrations of CED for 1 min. The black scale bar indicates 0.1 mm.

The results from the quantitative swelling experiments performed to complement the analysis of the fiber swelling in light microscopy are shown in Figure 13. The results from the swelling of the PHK pulp and the Sulfite pulp clearly show that with increasing CED concentration, the width variation, i.e. the fiber width after swelling, increases. The three Sulfite pulp samples, original, H_2O/HCl, and EtOH/HCl, are the only exception where the width variation decreased at the highest CED concentration, 0.20 M. This is probably because the Sulfite pulp samples started to dissolve. In the microscopy analysis, it was found that the Sulfite pulp dissolved through fragmentation. Fragmentation is a more efficient dissolution pathway than ballooning and causes fibers to break up in smaller parts during dissolution (Cuissinat & Navard, 2006a). The dissolution of the PHK pulp, on the other hand, proceeded through ballooning, and high swelling through ballooning may not break up the fibers to the same extent as fragmentation.
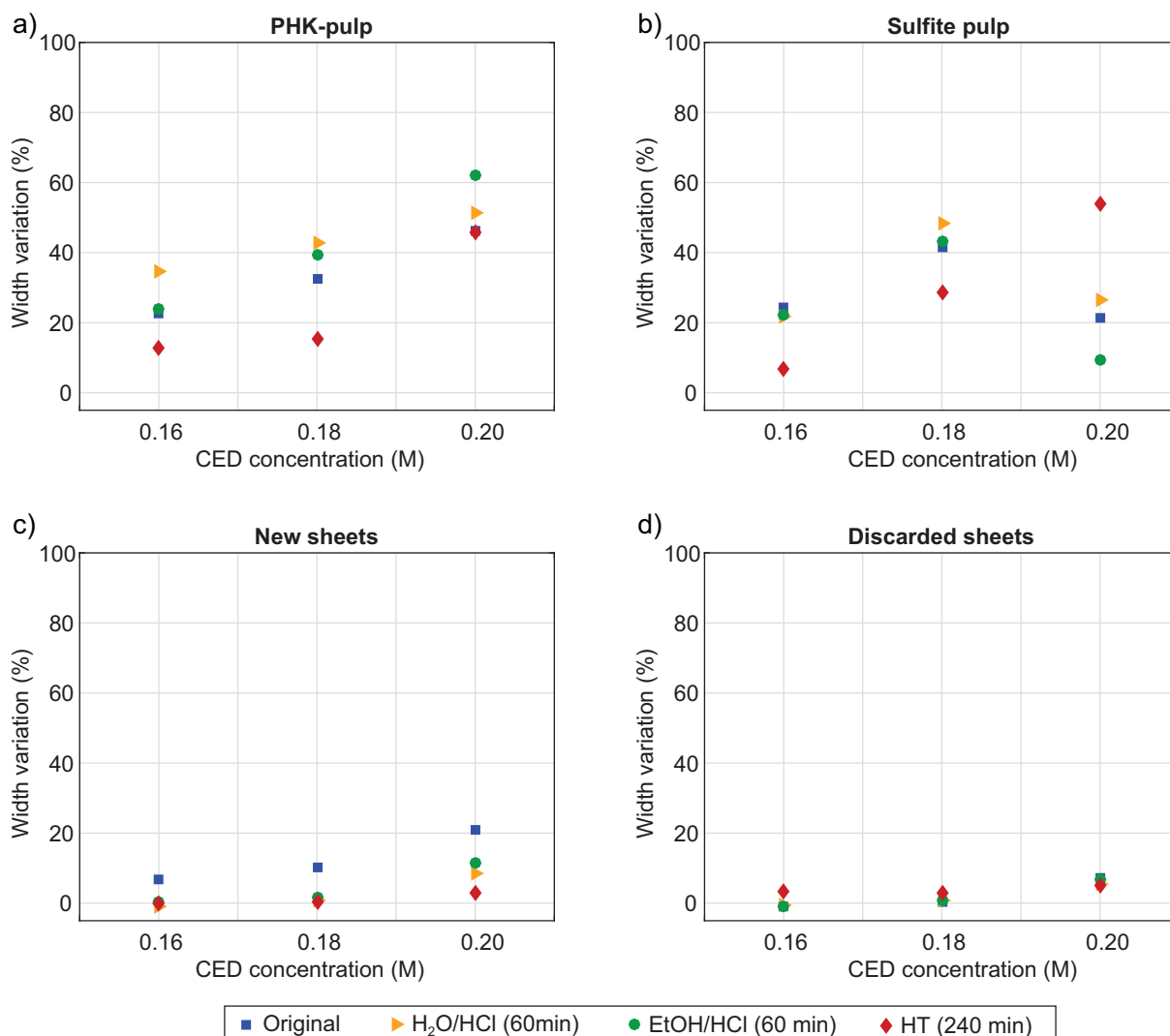
Figure 13: Width variation, calculated according to Equation 4 at different CED concentrations, of dissolving pulp (PHK and Sulfite) and cotton sheets (New and Discarded) subjected to three different pretreatments (H₂O/HCl, EtOH/HCl, and HT).

The results in Figure 13 show that none of the pretreatments (H$_2$O/HCl, EtOH/HCl, or HT) led to a significant increase in width variation, and, thus, the swellability of the fibers, compared to the original samples. On the contrary, the samples pretreated with the HT pretreatment show a decrease in swellability in both the PHK pulp and the Sulfite pulp. This may be related to the changes in the supramolecular structure caused by the HT pretreatment: the HT pretreatment increases the size of fibril aggregates and also leads to a small increase in the CI, see Table 4.

The change in width variation with increasing CED concentration was very much lower in the sheet samples (New sheets, Figure 13c, and Discarded sheets, Figure 13d). This

confirms the trend observed in the micrographs that cotton samples are much harder to swell. This indicates that the dissolution of cotton samples would require stronger solvents than the dissolving pulp samples. This could be due to the larger fibril aggregates in cotton than in the dissolving pulp samples (see Table 4). Large fibril aggregates decrease the accessibility of cellulose to solvent, and may, in this manner, contribute to hindering dissolution. The CI of cotton is also higher than that of dissolving pulp, and since crystalline cellulose is harder to dissolve than amorphous cellulose, this would also decrease the susceptibility of cotton to dissolution.

The CED had barely no swelling effect on the cotton samples, except the New sheets sample which had not been pretreated (New sheets, original). The width variation of the original New sheets sample was much lower, at all three concentrations, compared to the dissolving pulp samples. However, the width variation increased with increasing CED concentrations. The M_m of this sample was the highest among all samples, 813 kDa, corresponding to a DP of around 5000. Despite the large decrease, caused by the pretreatments, the swellability of the New sheets decreased after pretreatment. Investigation of the fibril and the fibril aggregate size showed a slight increase in fibril size, but only minor changes in the fibril aggregate size. The reasons for the higher swelling are, therefore, not completely understood from these analyses.

The method for evaluating the dissolution properties of different pulp samples by measuring width variation in a fiber analyzer is based on a few assumptions. The first assumption is that the swelling of fibers may be used to evaluate the susceptibility of pulp fibers to dissolution. The authors who first presented the method showed that the increase in swelling could be correlated to an increase in Fock reactivity (Arnoul-Jarriault et al., 2016). Fock reactivity is a simplified method for evaluating the reactivity of pulp fibers to the viscose process (Fock, 1959). This shows that swelling in dilute CED is clearly connected to susceptibility to dissolution.

The second assumption is that, in the dilute solvent, the sample only swells. However, the question may be asked whether the samples mainly swell or if both dissolution and swelling occur. The amount of dissolved material has not been quantified in the current study, but the evaluation of the results may give some answers. Observation of fibers after quenching in water in light microscopy in the current study showed that they

resembled natural fibers, and no fragments of regenerated cellulose were visible. Furthermore, the clear decrease observed at the highest concentration of CED in the Sulfite pulp samples, indicates that when a considerable amount of cellulose is dissolved, the width variation decreases. Since the width variation in the other samples increased with increasing CED concentration, this strengthens the hypothesis that swelling can be studied by measuring width variation.

9.4 Correlation between intrinsic viscosity and DP

In the research performed herein, a number of molecular mass distributions of cellulose were analyzed to complement the measurements of intrinsic viscosities. The intrinsic viscosity of cellulose dissolved in CED is related to the mass-average DP of the cellulose. Many different correlations have been proposed to give a correlation between the intrinsic viscosity and the DP of cellulose. In this section, the measured data of the molecular mass will be combined with the measured data from the intrinsic viscosity measurements, and the most common correlations will be investigated.

The Mark–Houwink–Sakurada (MHS) equation relates the intrinsic viscosity of a polymer solution to the molecular mass of the polymer, see Equation 7 (Kamide, Saito, & Miyazaki, 1993).

$$[\eta] = K M^a \qquad\qquad \text{Equation 7}$$

This equation may be rewritten in the form of Equation 8

$$DP_v^a = b[\eta] \qquad\qquad \text{Equation 8}$$

This thesis uses the correlation proposed by Immergut et al. (1953) (Immergut et al., 1953), as stated in SCAN-C 15:62, see Equation 3.

$$DP_v^{0.905} = 0.75[\eta] \qquad\qquad \text{Equation 9}$$

Other correlations have been proposed, however, this correlation was chosen despite critique since this would better allow for a comparison with data from other papers. Today, one of the most cited works on the correlation between intrinsic viscosity and DP is that by Evans & Wallis (Evans & Wallis, 1989), see Equation 4.

$$DP_v^{0.90} = 1.65[\eta] \qquad\qquad \text{Equation 10}$$

It needs to be pointed out that the range of DP in the correlation proposed by Evan & Wallis is 700 to 7000, and, consequently, many of the data points are below this range.

The measurements of DP_m from molecular mass distributions and the intrinsic viscosity of 20 different dissolving pulp and cotton samples were combined, and the parameters a and b were estimated by fitting Equation 8 to the experimental data, yielding Equation 11.

$$DP_v^{0.85} = 0.85[\eta] \qquad\qquad \text{Equation 11}$$

In Figure 14, the data from intrinsic viscosity measurements are plotted against the DP_m values, measured with HP-SEC. The three correlations in Equations 9-11 are also included for comparison. This shows that the correlation proposed by Evan & Wallis (1989) overestimates the DP obtained from these samples, while the correlation ascribed to Immergut et al. (1953) underestimates it. The deviations can be explained by the measurement methods used to determine DP_m.

The kinetic modelling presented in Section 8.2.2 was performed with both correlations, and both the trend and the fit of the data were similar.
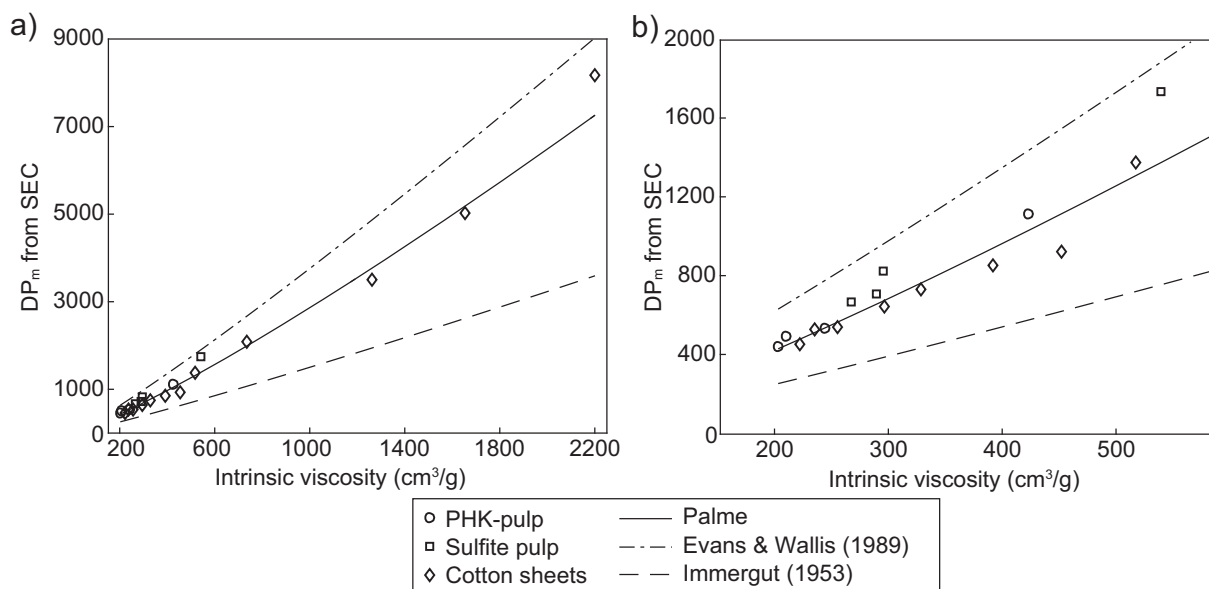
Figure 14: DP_m values from SEC plotted against the intrinsic viscosity of cellulose in CED with the correlations in Equation 9-11 shown, a) showing all data points and b) data in the range 200 < Intrinsic viscosity < 600.

Molecular mass distribution may also influence the intrinsic viscosity, for example, Figure 14b shows the difference between the different pulp samples. The DP_m from the Sulfite pulp samples are all located above the correlation based on the experimental data. This is an effect of the broad molecular mass distribution of the Sulfite pulp, as can be seen in Figure 10. If the correlation presented in this thesis would have been used to calculate the DP_m of the Sulfite, the DP_m would have been underestimated.

Furthermore, the samples investigated in Figure 14 contained very low levels of hemicellulose, and, consequently, the effect of hemicellulose has not been taken into consideration. A discussion of this in more detail can be found in Van Heiningen et al. (2004).

The findings presented in this section show the importance of investigating the background to a correlation before using it.

9.5   Separation of polyester and cotton

The main objective of this thesis was to investigate chemical fiber-to-fiber recycling of cotton. To accomplish this on an industrial-scale, a pure fraction of cotton must be made available. Service textiles, such as hospital sheets and towels, are available in large quantities and could serve as a first step in textile recycling. However, most of these textiles contain mixes of PET and cotton, referred to as polycotton. Thus, separating the components in polycotton is important for the overall objective.

The separation process, studied in this section, is illustrated in Figure 15. It starts with the degradation of the PET in the polycotton mix and the degradation products, which are dissolved, are then separated from the solid cotton phase through filtration. The filtrate is then acidified, lead to precipitation of TPA. The solid TPA is then separated from the liquid phase through filtration. The liquid phase then contains the EG, the phase transfer catalyst (if used) and process chemicals. Some of the parameters governing this separation as well as the purity of the products will be discussed below.
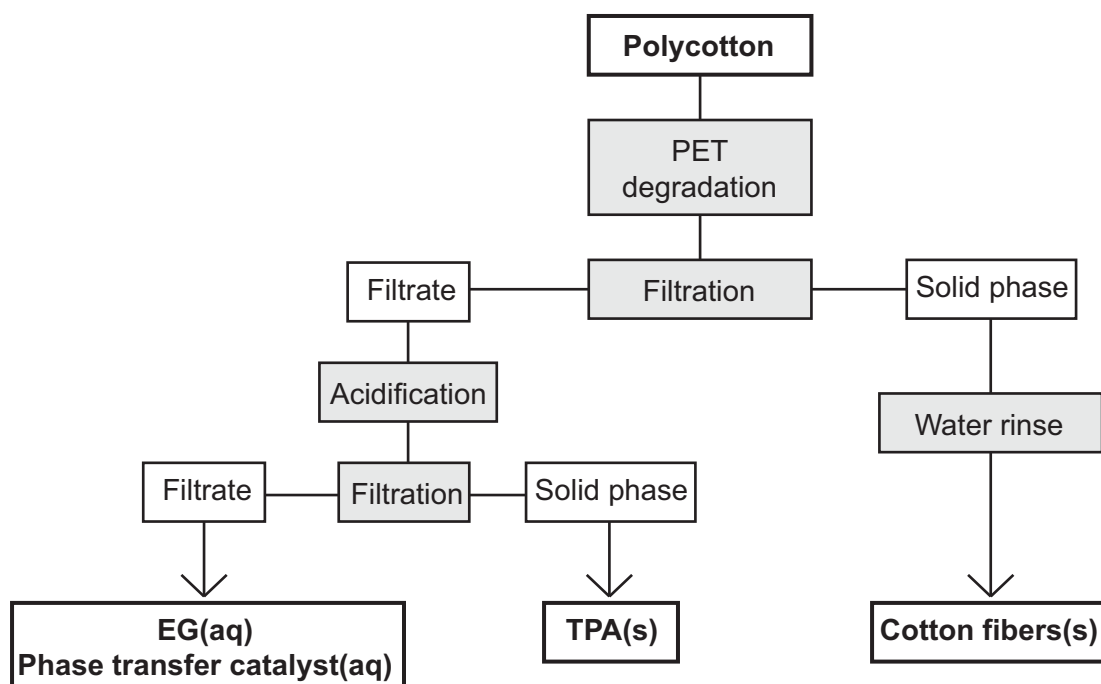
Figure 15: Illustration of the main steps in the separation of polycotton into cotton fibers and the two PET monomers, ethylene glycol (EG) and terephthalic acid (TPA), for detailed method description, see the Methods section.

The gradual degradation and dissolution of PET can be observed with optical microscopy, and an example of this is shown in Figure 16. At the start of the experiment, shown in Figure 16a, both PET and cotton fibers are visible. After 37 min, the PET fibers have partly been degraded, and only small fragments are visible. At the end of the experiment, after 1 hour, no solid PET fibers are visible anymore, and the cotton remains solid but swollen in the alkaline solution. The bubbles in Figure 16b and c are the degraded and dissolved components from the PET.
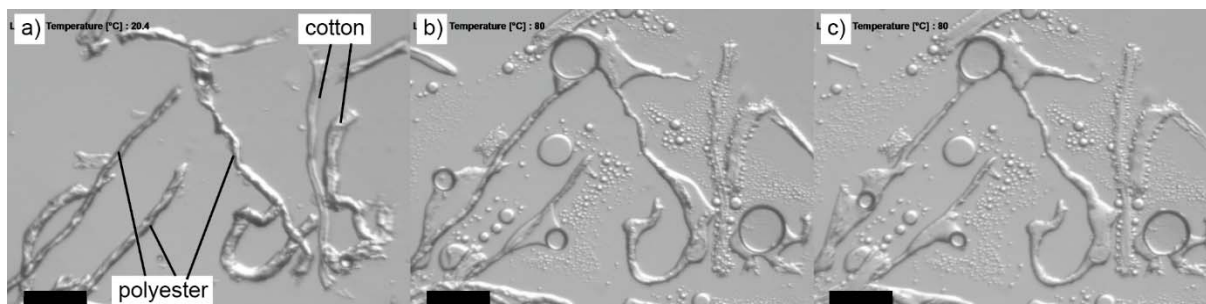
Figure 16: Micrographs of PET and cotton fibers subjected to selective hydrolysis of PET in 10wt% NaOH, 0.1 M BTBAC, a) at start, 23°C, b) after 37 min, 80°C, and c) after 1 hour, 80°C. The black scale bar indicates 0.1 mm.

There are several parameters that affect the degradation of PET in an alkaline solution, such as the concentration of NaOH and phase transfer catalyst (BTBAC), time, and temperature. In the small scale system, used herein, the effect of the NaOH-concentration was investigated with and without the addition of a phase transfer catalyst for a 100-min reaction, see Figure 17a. Without the addition of BTBAC, 15% NaOH was required to reach full yield, whereas, very low, or no yield was reached with 1.5% NaOH and 5% NaOH. A yield higher than 50% was reached even with as little as 5% NaOH, when 0.1 mol BTBAC/mol repeating unit in PET, corresponding to 52 mmol/kg solution, was added to the solution, which shows the major impact of the phase transfer catalyst.

Figure 17b shows the effect of increasing the BTBAC concentration at two temperature levels, 80°C and 90°C, for a 100-min reaction. The findings show that less BTBAC is needed to reach the same yield when a higher reaction temperature is used. At 90°C, only 0.1 mol BTBAC/mol repeating unit in PET was needed to reach full yield, however, at 80°C 0.7 mol BTBAC/mol repeating unit in PET was needed.
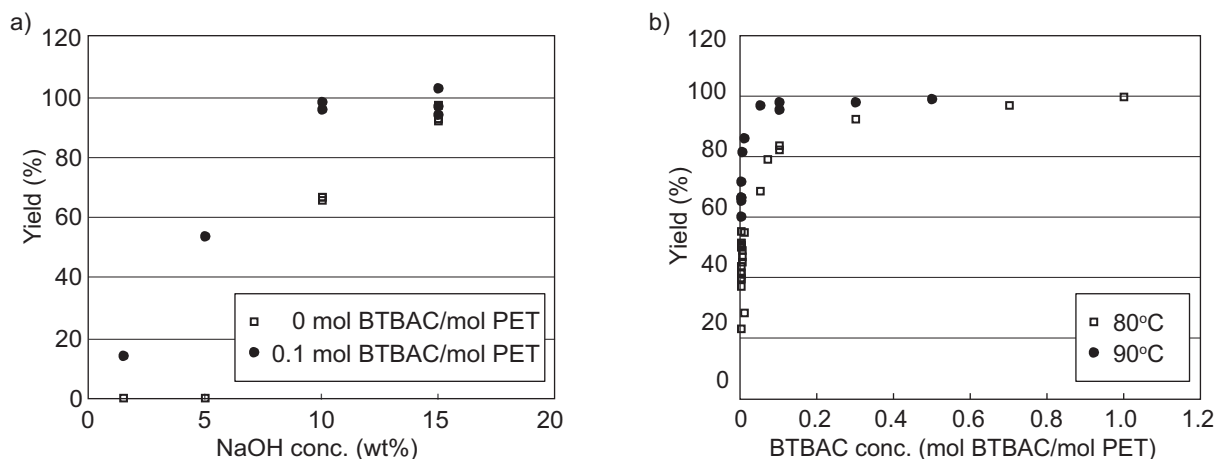
Figure 17: a) Yield of TPA against the NaOH concentration, with and without the addition of BTBAC at 90°C, b) Yield of TPA against different BTBAC concentrations at 80°C and 90°C using 10% NaOH concentration. Both figures are from the small-scale experiments, and the reaction time was 100 min.

To investigate the degradation of PET during the experiment, a large-scale set-up was used. In these experiments, a small amount of polycotton sample was added to a large volume of reaction solution, and then samples of the solution were removed at different times. The TPA content of the solution was then analyzed with UV-vis spectroscopy. Figure 18a shows that the hydrolysis rate of the PET sample increased when the NaOH concentration increased. The experiment with 5% NaOH at 70°C was stopped after 120 min and, thus, only yielded around 66% TPA.

The effect of the phase transfer catalyst can be seen in Figure 18b where the results from experiments with 10% NaOH and BTBAC (52 mmol/kg solution) at 70°C, 80°C, and 90°C are compared to the results from an experiment at 10% NaOH and 90°C without the addition of BTBAC. Without BTBAC, it took about 160 min to reach full depolymerization of the PET sample, however, at the same conditions (10% NaOH and 90°C) with BTBAC, full depolymerization was reached after less than 40 min. This shows that BTBAC acts as a catalyst since it increases the rate of degradation, however, complete degradation can also be obtained without a catalyst.
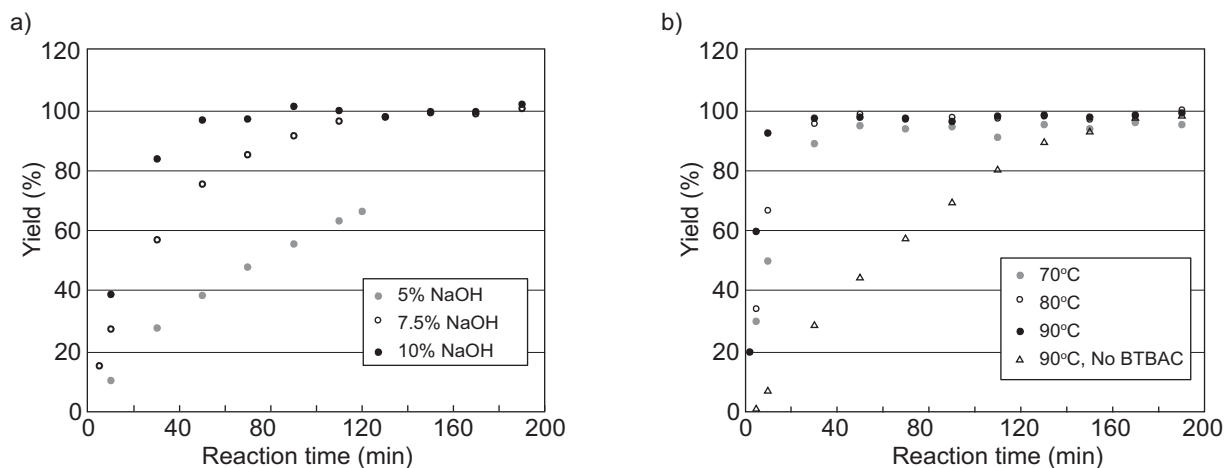
Figure 18: Time dependence of degradation with a) increasing NaOH concentrations (5%,7.5% and 10% NaOH at 70°C), and b) increasing temperature (70°C, 80°C, and 90°C at 10% NaOH), with BTBAC (52 mmol/kg solution) and one trial at 90°C with 10% NaOH without any addition of BTBAC).

The results presented above show that the yield was influenced by temperature, NaOH-concentration, BTBAC addition and residence time. These findings are a good framework within which to further optimize the process.

The aim of the separation is to degrade PET into TPA and EG while leaving the cotton as unaffected as possible, thus, generating three product streams. To be able to use the products in the production of new fibers, the purity of the product streams is important. For this reason, the purity of the degradation products from PET, EG and TPA, was analyzed with solution-state NMR spectroscopy. The analyses showed that no other components could be found in the crystallized TPA, and the only components in the filtrate were EG and BTBAC (when added). This is discussed further in Paper V, where the NMR spectra also are shown.

The process aims to leave the cotton as unaffected as possible, however, cotton is not completely chemically resistant to NaOH at these conditions. Therefore, it was expected that at least signs of some cellulose degradation products, i.e. hydroxy acids, would be present, since cellulose is known to generate such degradation products when treated under alkaline conditions (Sjöström, 1993). However, more thorough analyses with focus on cellulose degradation products would certainly show the presence of some cellulose degradation products.

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The degradation of the cotton cellulose decreases both the yield and the DP of cotton. In Figure 19, the yield of cotton is plotted versus the intrinsic viscosity of cotton cellulose. The results show that the highest yields and DP values are from experiments with the lowest temperature (70°C).
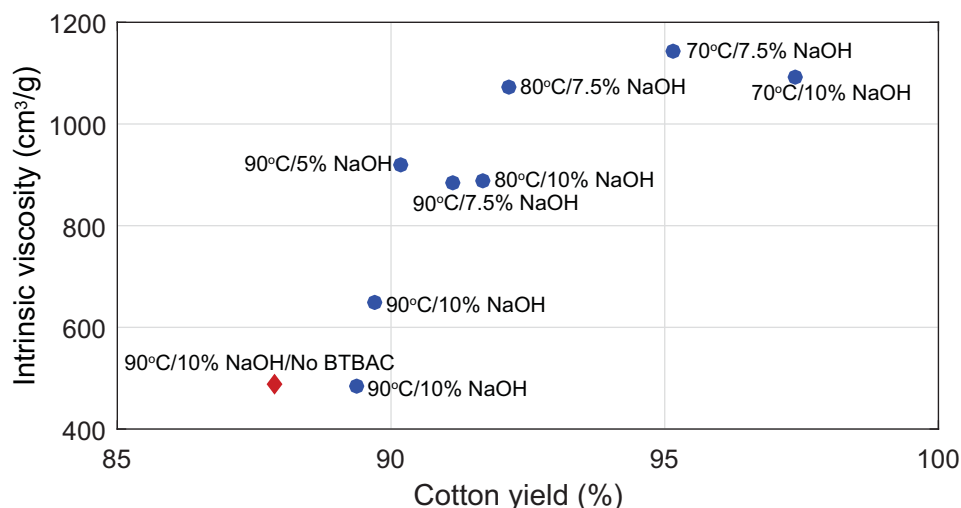

Figure 19: Yield of cotton plotted vs intrinsic viscosity of cotton cellulose recovered after separation from polycotton textiles. All separation experiments were performed in the large-scale set-up for 240 min, except the two with the lowest DP, which were performed for 360 min.

The degradation of cellulose in alkaline solutions follows three main paths, alkaline hydrolysis, peeling, and chain scission after oxidation (oxidative peeling), as introduced in Section 3.3.1. The decrease in intrinsic viscosity that takes place during the separation experiments is probably both caused by alkaline hydrolysis and oxidative peeling (chain cleavage due to β-elimination), while primary and secondary peeling decrease the cotton yield. Alkaline hydrolysis is generally described to occur mainly at higher temperatures than what is used in these experiments, however, it cannot be excluded that some alkaline hydrolysis occurs even at these low temperatures (Nieminen, Testova, Paananen, & Sixta, 2015).

The purity of the cotton fraction was investigated with ATR FT-IR. IR spectra from two experiments are compared in Figure 20. The hydrolysis performed at 70°C and 5% NaOH had only reached a yield of 66% TPA when stopped, as shown in Figure 18.

The residual PET in this sample can be seen in two absorption bands in the range between 1150 and 1250 cm^{-1}, and 1715-1740 cm^{-1}, enlarged in Figure 20. The first band

was assigned to the C-O stretch, and the second to the C=O stretch, both from the ester bonds in the PET. The IR spectra from the hydrolysis performed at 90°C and 10% NaOH, which had reached full yield according to Figure 18, showed no peaks in these two absorption bands, which implies that the PET has been removed from this sample.
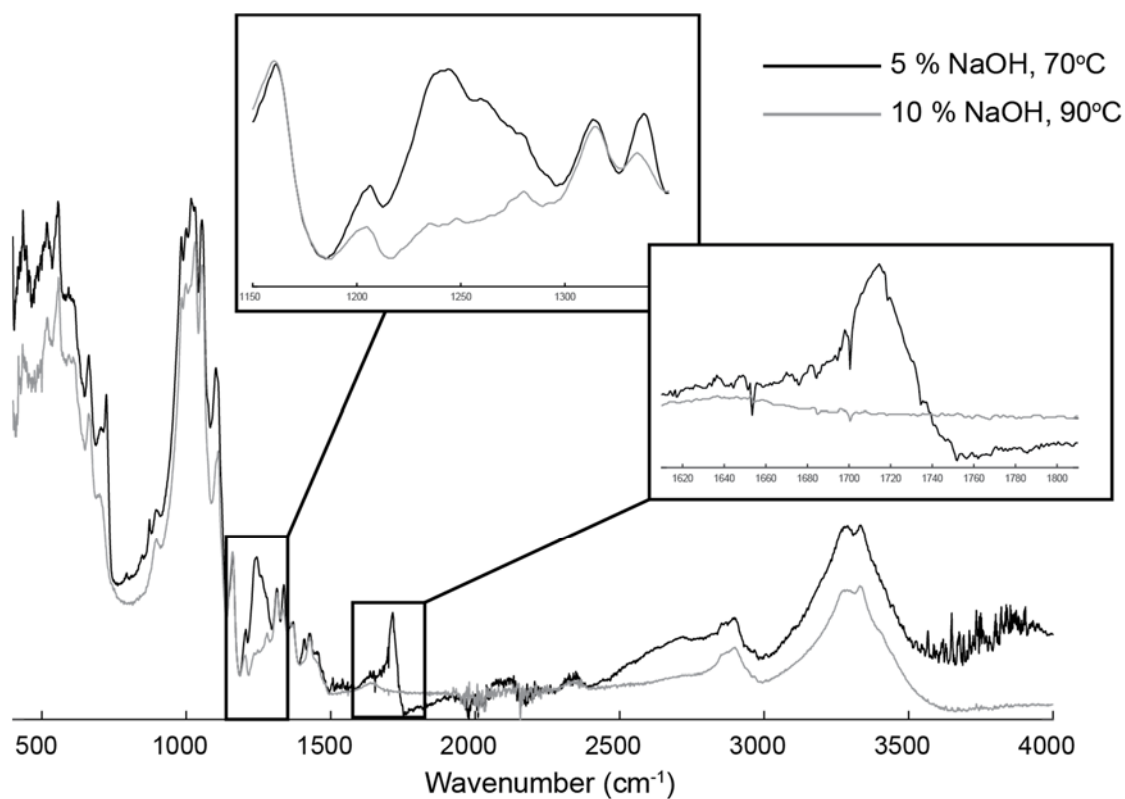

Figure 20: ATR FT-IR spectra of the solid (cotton) residue after PET hydrolysis. The experiments were performed in the large-scale set-up with 52 mmol BTBAC/kg solution.

10. Concluding remarks

The main objective of this thesis was to investigate the preconditions for chemical fiber-to-fiber recycling of cotton textiles. This was investigated through the evaluation of four research questions. The main results from each question are summarized below.

1) *How does important material properties of cotton fiber change during long-term laundering and use? (Paper I)*

   An investigation of sheets used in hospitals, and laundered different number of times showed that during service life there was initially a small decrease in WRV and fibril aggregate size. This indicates a minor initial hornification, however, long-term use did not increase the hornification. In contrast, long-term use induced a decrease in FSP and specific surface area, which indicates that the pore structure of the cotton cellulose changed over long-term use.

   Long-term use and extensive laundering were also found to decrease the mass-average molecular mass of cotton cellulose from 1323 kDa, in a new, never laundered sheet, down to 151 kDa of a sheet ready to be discarded after more than 50 use and laundering cycles.

2) How are new and used cotton fibers affected by acid pretreatment, in comparison to dissolving pulp? (Paper II, IV)

Acid-catalyzed pretreatment of cellulose was investigated using three different methods: acid hydrolysis in water, acid hydrolysis in ethanol, and hydrothermal treatment in a dilute acidic buffer. In the case of acid hydrolysis in ethanol, the pretreatment solution contained 6 wt% water. The degradation was investigated both for cotton cellulose and dissolving pulps. A comparison of the effect of the different pretreatment methods on cellulose degradation showed that degradation caused by acid in water and acid in ethanol was similar, however, the degradation with acid in ethanol was faster. The higher degradation rate of cellulose fibers during treatment in acid hydrolysis in ethanol can possibly be explained an elevated acid concentration in the fibers due to sorption of acid from the bulk phase by the cellulose, making the actual acidity at the cellulose-liquid interface to be higher than in the bulk phase. Degradation in the hydrothermal treatment was slower, i.e. higher temperature and longer pretreatment times were required to reach the same degree of degradation, and the high temperature and low acidity induced fibril aggregation.

The degradation pattern of cotton was similar, to that of PHK pulp. However, the Sulfite pulp showed a slower degradation rate, and higher LODP. It was found that both drying and PHK pulping increase the susceptibility to acid hydrolysis of cellulose fibers, probably due to the build-up of stress in the cellulose during fibril aggregation.

3) How is the susceptibility of cotton fibers and dissolving pulp to swelling changed after acid pretreatment? (Paper III)

An investigation of the swelling of cotton fibers and dissolving pulps in dilute CED showed that the susceptibility of these materials to swelling was much lower for the cotton fibers than for the dissolving pulps. It was found that the fibril aggregate size in the cotton samples was higher than in the dissolving pulp samples, and this probably contributed to the difference in swelling.

The swelling of dissolving pulp fibers after pretreatments involving acid hydrolysis in water, acid hydrolysis in ethanol, or hydrothermal treatment in dilute acidic buffer did not increase, compared to the original samples. In contrast, the hydrothermal treatment tended to decrease the swelling. Since the hydrothermal treatment increased the size of the fibril aggregates, it is possible that this change in properties decreased the swellability of the fibers.

4) *How can separation of mixed textiles containing polyester and cotton be accomplished? (Paper V)*

In the last paper alkaline hydrolysis of PET was used on polycotton textiles, with the aim of separating the components. It was found that PET could be completely degraded after 40 min hydrolysis in 10% NaOH at 90°C, with the addition of 52 mmol BTBAC/ kg solution. Complete hydrolysis without BTBAC also yielded pure streams, however, longer reaction times were required, and, thus, the cotton yield decreased.

After the process, three product streams were recovered; the residual cotton, solid TPA, and an aqueous stream containing EG. The isolation of cotton and TPA as pure streams implies that recycling may be accomplished through the repolymerization of the TPA with EG (recycled or virgin), and that the cotton fibers could possibly be used in the production of regenerated cellulosic fibers. However, before the process is ready to be implemented industrially, optimization, scaling-up experiments, as well as a techno-economical assessment of the process must be performed.

Based on the findings presented under each research question, some general conclusions about textile recycling can be drawn.

- The cotton fibers investigated in this thesis are harder to swell, than conventional dissolving pulp, and thus recycling of cotton fibers into regenerated cellulosic fibers require very good solvents.
- The pretreatment of cotton and dissolving pulp may possibly be performed simultaneously since the degradation patterns are similar.

- One possibility to separate the components in a polycotton mix is through alkaline hydrolysis of the polyester.

Some general conclusions about the susceptibility of cellulose fibers to acid hydrolysis and dissolution can also be drawn. It is commonly stated that the ultrastructure of cellulose governs much of its reactivity. However, the findings presented in this thesis indicate an opposite susceptibility. The Sulfite pulp had a higher susceptibility to swelling, but a lower susceptibility to acid hydrolysis. In contrast, the PHK pulp and the cotton sheets were more reactive to acid but showed less susceptibility to swelling. This shows that despite that ultrastructure is important in both processes, different aspects of the ultrastructure are important in the two processes. More specifically, stress in the cellulose proved to be important for the rate of acid degradation. Drying cellulose fibers leads to greater susceptibility of the cellulose fibers to acid hydrolysis, however, drying may also decrease susceptibility to swelling/dissolution.

11. Future work

Chemical recycling of textiles is a relatively new research field, and thus there are many questions waiting to be investigated. Development in this field is closely connected to increased regulations by authorities aimed at increasing textile recycling, as well as an increased awareness in society and industry of the large volumes of waste from textiles. A key issue will be to build up knowledge of end-of-life issues throughout the value chain. This means that to be able to recycle textiles in large volumes, the companies in every part of the value chain must take responsibility for end-of-life issues.

The work presented in this thesis is only the very first step towards chemical recycling of textiles, and it opens up many further research questions. In this section, some future aspects of each of the four parts of the thesis, will be outlined.

In the first part, cotton sheets were characterized after use and laundering. Since pure cotton textiles are rare in service textiles, understanding how laundering and use affects polycotton sheets, would provide further understanding of these materials. The characterization in this thesis was based on cotton sheets used in hospitals and laundered industrially. To get a more complete picture, comparisons between different sheet qualities and laundering companies in Sweden and other parts of the world, would need

to be studied. All sheets included in the study were white, as are most service textiles, however, the effect of dyes on the properties of textile fibers is important to know to achieve large-scale textile recycling.

Acid degradation of cellulose was investigated in this thesis, and, despite the long history of this research field, many more aspects remain interesting to study. The findings in this thesis show that strain may be an important component for the susceptibility of cellulose fibers to acid hydrolysis. Thus, more focus on how strain is built up in different ways in cellulose fibers would possibly provide more understanding of differences in susceptibility to acid.

Swelling of cotton cellulose was investigated to get an idea of differences in susceptibility to dissolution. The low swellability of cotton fibers indicates that cotton lint fibers have a lower susceptibility to dissolution than dissolving pulp fibers. To further investigate this, future investigations may include both different cotton fibers, additional solvent systems and complementing investigation methods. The connection between swelling in dilute solvent and dissolution could be examined by analyzing the amount of dissolved material after swelling in dilute solvent. This would complement the very convenient method of assessing swelling in a dilute solvent with a fiber analyzer. Furthermore, the behavior of cotton cellulose from different types of discarded textiles should be evaluated in commercial processes for production of regenerated cellulose fibers i.e. viscose and lyocell.

In the last part, a separation process for polycotton textiles was presented. Currently, many different processes for this are being investigated, and the future will reveal which is the most efficient. To develop the process presented in this thesis, both fundamental and applied questions remain. The separation of cotton and polyester was performed using new white sheets, however, to be more industrially relevant, sheets laundered and used many times should be studied, and the effect of different dyes need to be included. Many process aspects need to be investigated, such as the effect of higher concentrations of solid material, the reactor design, recycling the phase transfer catalyst, and the mechanical pretreatment of polycotton material. The three process streams does also need to be further evaluated. The susceptibility of cotton to dissolution, after the separation process also needs to be assessed.

To evaluate the industrial potential of the process, a techno-economical assessment of the process and an LCA analysis of possible environmental benefits call for careful investigation.

12. Acknowledgements

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