

THESIS FOR THE LICENTIATE OF ENGINEERING

**Characterization of cellulose in post-consumer
cotton textiles**

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Forest Products and Chemical Engineering

Department of Chemistry and Chemical Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden, 2015

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Cover: ESEM micrograph, at 5000 times magnification, of a cotton fibre which has been laundered and used many times, causing both surface fibrillation and cracking of the fibre. See Section 3.1.

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Abstract

The overall objective of this thesis is to provide a background to the recycling of cotton. Since cotton consists of pure cellulose, it might be possible to include used cotton, in the already existing viscose industry. In this thesis two aspects important to accomplishing this task have been studied; changes that occur in cotton fibres during service life, and comparison between cotton and dissolving pulp in terms of susceptibility to acid hydrolysis.

During the service life of a cotton textile, it is laundered many times, exposing it to numerous drying and rewetting cycles. From research on paper recycling, it is well known that drying and rewetting induce hornification of cellulosic fibres, making the fibres stiff and less porous. However, no increase in the degree of hornification, during the service life of cotton fibres has been measured, probably due to the high initial hornification of cotton fibres. Laundering, however, decreases the mass average molecular mass of cellulose, down to 151 kDa, after more than 50 laundering cycles, from 1323 kDa in a never-laundered sheet.

The second aspect studied was reactivity of different cellulosic fibres towards acid hydrolysis. It was found that laundering had no effect on the levelling off degree of polymerization (LODP). Despite the initial large difference between new sheets and discarded sheets, the molecular mass distributions were quite similar for the sheet samples, after only 60 min of hydrolysis (0.4 M HCl, 80 °C). With textile recycling in mind, this is promising, since textiles sent for recycling will have been through a different number of laundering cycles.

Keywords: Textile recycling, Laundering, Cotton cellulose, Hornification, Acid hydrolysis, Levelling-off degree of polymerization.

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 fibres: Comparison of bleached kraft pulp, dissolving pulps and cotton textile cellulose**
Anna Palme, Hans Theliander and Harald Brelid
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)

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1 Introduction

Increased awareness of the high environmental production costs of textiles, combined with potentially large values in the textiles discarded in the household waste, calls for action. Improved recycling of textiles could provide more efficient material use. Currently, industrial-scale recycling of textiles is underdeveloped, and thus many basic questions need to be investigated. This thesis sheds light on some questions related to the recycling of cotton textiles and provides a background for developing industrial textile recycling processes.

1.1 Recycling of textiles

Recycling of textiles has to some extent always existed, if the restyling of old garments into new ones is considered. The development of a large-scale chemical recycling industry for textiles is important to cover future needs for textiles. Textiles include a broad variety of materials with different chemical compositions. This thesis only focuses on the recycling of cotton. The overall idea is to use old cotton to produce regenerated cellulosic fibres, such as viscose or lyocell. Since the main raw material used today is cellulose extracted from virgin wood, maybe worn out cotton textiles could be included

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in this already existing industry and be recycled into new textile fibres, Figure 1. To succeed with integrating cotton into this route, it is important to understand the differences between the dissolving pulps used today, and old cotton, as well as how ageing affects cotton.

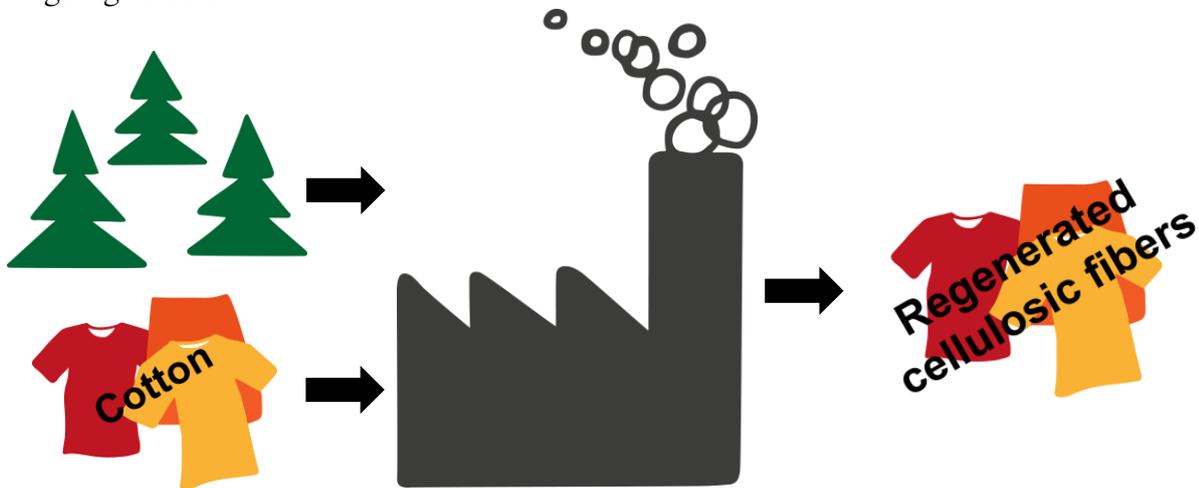


Figure 1 | Recycling of cotton through integration into the viscose industry

Regenerated cellulosic fibres are textile fibres manufactured from wood pulp or cotton linters in an industrial process. The special grade of wood pulp used in this process is referred to as dissolving pulp. The most common regenerated cellulosic fibre, produced from dissolving pulp is the viscose fibre. Lately, much attention has been brought to the lyocell process, claimed to be more environmental beneficial, than the viscose process. The viscose process is by far the largest process for regenerated cellulosic fibres, and the lyocell process only has a very small part of the market share. Both processes require the dissolving pulp to be of very high purity.

1.2 Mistra Future Fashion

This research is a part of Mistra Future Fashion, a cross-disciplinary research programme between several universities and research institutes. The purpose of Mistra Future Fashion programme is to deliver knowledge and solutions that the Swedish fashion industry and its stakeholders can use to significantly improve the fashion sector's environmental performance and strengthen its global competitiveness. The main funding comes from MISTRA the Foundation for Strategic Environmental Research. The sub-project within Mistra Future Fashion that deals with the recycling of cotton

cellulose, which this thesis reports results from, has also received funding from the Swedish Foundation “Södra Skogsägarna Stiftelse för Forskning, Utveckling och Utbildning”.

1.3 Objectives

- 1) How do laundering and use affect the ultrastructural and chemical properties of cotton cellulose?
- 2) What differences are there between cotton and dissolving pulp in terms of susceptibility to acid hydrolysis?

1.4 Outline of thesis

After the introducing words in Chapter 1, the reader will be introduced to earlier literature on the subject, providing a background to the thesis. Understanding material is the basis of this project, and thus the thesis will start by introducing cellulose and cotton structures. Two papers are included in the thesis, and the main focus areas of these are the effect of drying on fibres and the acid hydrolysis of cellulosic fibres, respectively. Thus, a short literature overview of these areas will be given, before a comprehensive overview of the results from the two papers is presented in Chapter 6. Finally, the main conclusions from the papers are presented, as well as a short introduction to future studies.

2 Cellulose

Together with hemicellulose, pectic material and lignin, cellulose forms a biopolymer composite material, which brings strength to the cell walls of plants (Young & Rowell, 1986). Cellulose is also available nearly pure in the seed hair of cotton and may be synthesized by specialized bacteria. The cellulose polymer is a linear polysaccharide, consisting of β -D-glucopyranose units, linked by (1 \rightarrow 4)-glucosidic bonds, see Figure 2. The number of linked glucose units, called the degree of polymerization (DP), has been estimated to be 15000 in cotton and 10000 in wood (Sjöström, 1993).

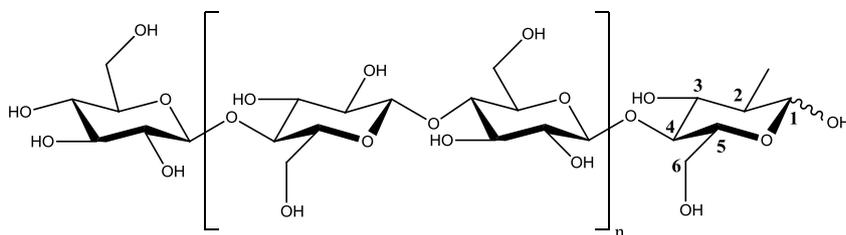


Figure 2 | Cellulose polymer

Cellulose polymers form stable crystals. In total, six different crystalline forms (I_{α} , I_{β} , II, III, IV_I , IV_{II}), also called polymorphs, exist, and they may be interconverted through chemical treatments or heat (O'Sullivan, 1997). In the native cell wall, the cellulose

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chains are synthesized directly to microfibrils by groups of synthesizing units, called “terminal complexes” or “rosettes” (Brown, Saxena, & Kudlicka, 1996). The immediate formation of the microfibrils governs the formation of the cellulose I polymorph. Native cellulose I contains a combination of the two crystalline forms I_{α} and I_{β} , of which I_{α} is less stable and thus more reactive (Atalla & VanderHart, 1984).

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 into cellulose II. Cellulose I and II are the most common polymorphs, and the others will not be discussed in this thesis. One of the main differences between cellulose I and II is the direction of the chains. In Cellulose I, the chains are ordered in a parallel way, whereas in Cellulose II they are anti-parallel. It is still disputed how this change in direction occurs, since no solubilisation is needed to go from I to 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 distribution may be measured using liquid chromatography, after dissolution of the cellulose (Henniges, Kostic, Borgards, Rosenau, & Potthast, 2011). The intrinsic viscosity of a cellulose solution, which may be correlated to the DP, is commonly used to get a simple estimate of the DP. To perform this measurement, a cellulose sample is dissolved, e.g. in Copper(II)ethyldiamine, and run through a thin capillary. The time for the sample to flow through the capillary may be calculated into the intrinsic viscosity of a cellulose solution (E. H. Immergut, Schurz, & Mark, 1953; Krässig, 1993).

The structure of cellulose is characterised by a number of structural levels, each with different arrangement and complexity. Due to intramolecular bonding, a cellulose chain is relatively stiff and rigid. The polymers build up sheets, which lead to the formation of cellulose crystals. The cellulose crystals form elementary fibrils, which are organised into larger microfibrils, and the microfibrils build up the cell walls that form the fibre

(Krässig, 1993). The fibrillar structure of cellulose not only includes crystalline material, but also regions with less order, referred to as amorphous. The term amorphous is somewhat confusing, since the definition, according to the Oxford English Dictionary is “having no determinate shape”. However, the cellulose said to be amorphous, is still 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.

The size and the degree of aggregation of fibrils govern the accessibility of a cellulose sample, and this is an important factor when producing new materials from cellulose. To quantify the degree of crystallinity, there are different tools. One of the earliest methods used was acid hydrolysis, where the amount hydrolysable material was said to be amorphous, and the rest crystalline (Battista, 1950; Immergut & Rånby, 1956; Jørgensen, 1950). Crystallinity can also be measured with non-intrusive methods, such as X-ray diffraction and ^{13}C -NMR. In both methods, different signal peaks, or areas, originating from crystalline parts are compared to ditto from amorphous parts (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998).

Based on the existence of amorphous and crystalline cellulose in cellulosic fibres, 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 through several crystalline and amorphous areas.

In this thesis, cellulosic fibres of high purity, i.e. cotton and dissolving pulp, are mainly discussed, since these may be used in the production of regenerated cellulosic fibres. 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).

2.1 Cotton

The cotton fibres used in textile production are the seed hairs, which the cotton plant uses to protect the seed. The mature cotton lint fibre is a dry and hollow cell wall from one single cell. It has a collapsed and twisted tubular structure, important for the special characteristics of the fibre. The fibre consists of approximately 95% cellulose after chemical and mechanical cleaning. After further treatments, aimed at removing non-cellulosic materials, the cellulose contents in the lint reach over 99%. Out of the thirty-three recognised cotton species, only four are of commercial importance (Lewin, 2007). Cotton fibre is formed through different growth phases, which give rise to the ultrastructural architecture of the fibre. Each cotton fibre is a single cell, and formation starts from an epidermal cell on the seed coat. The first step in the fibres development is elongation of the fibre forming the primary wall on the outside of the cell. When the fibre has reached its full length, cellulose starts depositing on the inside of the fibre, forming the secondary wall. In the last growth step, the cotton boll opens. Before this stage, the fibre has been fully hydrated, and has a cylindrical lumen filled with water. After the boll opens, the fibre dries and collapses to a twisted tubular structure. At frequent intervals along the fibre, these twists change causing “reversals”. These reversals in the twist reflect the change in direction of the microfibrils in the secondary wall (Basra, 1999).

The mature fibres are easily removed from the seed. After removal of the long fibres, shorter fibres remain on the seed. These are called linters or fuzz fibres, not to be confused with the long fibres, called lint. Lint fibres are used in production of cotton textiles. Linters, in contrast, are used in the production of cotton paper, such as filter papers, or as pure cellulose feedstock in the production of cellulose derivatives and man-made cellulosic fibres (Basra, 1999).

Lint and linters can be differentiated by a number of criteria, of which the most important is length. Lint measures an average of 25 mm, whereas linters are only 1.5 - 10 mm. Linters are also darker in colour and adhere stronger to the seed, than the lint. Furthermore, linters lack lumen and are more coarse and stiff than the lint (Lewin,

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2007). Linters, being a pure cellulosic source, are commonly used as a reference in cellulose research, and many times only denoted as cotton fibres. However, as the properties of lint and linters may differ on many levels, it is important to consider which fibre type has been analysed, before comparing results.

The principal organisation of cotton and the wood cells has major similarities, and the development of wood fibre follows, to large extent, the same route as described above for cotton. However, one obvious difference between cotton and wood is the fact that cotton cells are single fibres, whereas wood cells are positioned in a matrix with other cells. A wood fibre is also much shorter, than a virgin cotton fibre (Krässig, 1993).

3 Effect of drying on cellulosic fibres

In order to accomplish cotton recycling, it is important to understand how cellulosic fibres are affected by use and laundering. Paper recycling is a closely connected field from which important knowledge could be transferred. Recycling of papermaking fibres exposes the fibres to numerous drying and rewetting cycles, which may serve as a comparison to laundering.

Cellulosic fibres become more brittle and less swellable after drying, a phenomenon called hornification, first mentioned by Jayme (1944). Chemical pulping removes the lignin and to some extent the hemicelluloses, leaving a porous water-swollen structure (Herbert Sixta, 2006). When the fibres are dried the pores collapse, leaving almost no accessible surface area inside the fibre (Laivins & Scallan, 1993; Stone & Scallan, 1966). When re-wetted, the fibres cannot reach the same degree of porosity due to its denser structure. This less porous structure leads to a more brittle material, just as a stick is more brittle than a rope (Hubbe, Venditti, & Rojas, 2007). The effect is the greatest after the first drying, but also the following steps increase the degree of hornification (Oksanen, Buchert, & Viikari, 1997). Thus, paper recycling will result in less swollen fibres, which are also less flexible. This means that recycled chemical pulp fibres will not have the same ability to form bonds to each other during the formation of paper as

never-dried pulp fibres. Consequently, the tensile strength of paper produced from recycled fibres will be lower than that of paper produced from never-dried fibres.

Hornification is a non-reversible phenomenon, which modifies the fibres both on the microscopic and the macroscopic levels. The exact mechanisms have not been completely clarified, but most agree that both hydrogen bonding and co-crystallisation cause the fibrils to adhere stronger to each other (Idström, Brelid, Nydén, & Nordstierna, 2013; Newman, 2004; Stone & Scallan, 1968).

In the growing native state, all cotton fibres are swollen with water. The fibre walls are thus porous. When the fibre is dried, the walls collapse as the water is removed (Basra, 1999). This causes even virgin cotton to have a high degree of hornification. (Nelson, Rousselle, Ramey, & Barker, 1980)

3.1 Ageing of textiles during laundry and use

Laundering and drying are harsh treatments for cotton fibres. On the molecular level, laundering causes a decrease in the DP, which leads to a loss of strength in the fibre. (Vaeck, 1966) In the alkaline conditions, under which laundering is usually performed, cellulose is degraded by an end-wise degradation, called the peeling reaction, shown in Figure 3. The peeling reaction starts with an isomerization of the glucose unit to a ketose, at the reducing end, and then proceeds through a β -alkoxy elimination. The eliminated anhydroglucose group, continues reacting into different degradation products, of which glucoisosaccharinic acid is the most common (Sjöström, 1993).

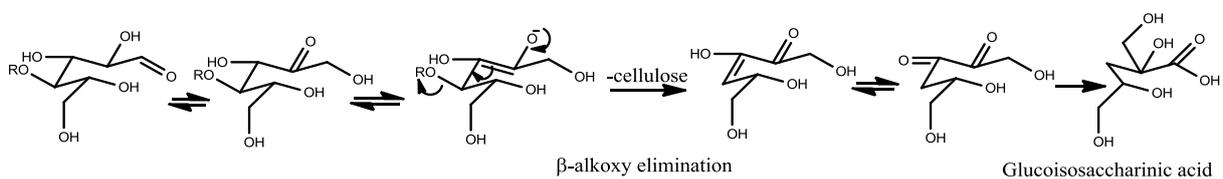


Figure 3 | Alkaline peeling of cellulose

The newly formed end group on the cellulose polymer will continue reacting and peeling off anhydroglucose units, until it is stopped, by either chemical or physical means. (Knill & Kennedy, 2003) The chemical stopping reaction proceeds through a β -hydroxy

elimination, shown in Figure 4, and leads to the formation of the stable glucometasaccharinic acid. The peeling reaction may also stop if a crystalline region, inaccessible to reaction, is approached, and this is referred to as physical stopping. Approximately 65 anhydroglucose units are cut off before stabilization takes place. (Knill & Kennedy, 2003)

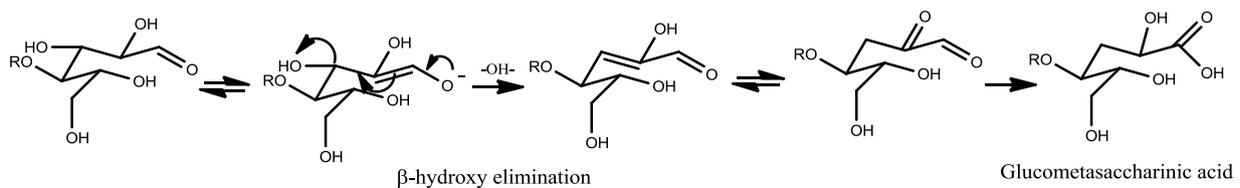


Figure 4 | Mechanism for stopping peeling reaction

In alkaline conditions, cellulose may also be degraded through alkaline hydrolysis and autoxidation. Alkaline hydrolysis requires both higher temperatures and higher alkalinity than what is applied in laundering, and thus does not contribute to degradation during laundering (Loon & Glaus, 1997). Autoxidation, on the other hand, may take place both during aerobic laundering and during tumble drying at elevated temperatures. This leads to the formation of a carbonyl along the cellulose chain. The carbonyl may then react through the same pathway as the peeling reaction; the β-alkoxy elimination, see Figure 3, causing a chain scission. (Knill & Kennedy, 2003) After chain scission, a new reducing end group, susceptible to peeling, is formed, thus decreasing the DP further.

Laundering and tumble drying may also cause fibrillation on the surface of fibres. SEM-studies have shown that surface fibrillation is mainly caused by wet abrasion during laundering, whereas dry abrasion is caused by dry abrasion during tumble drying. (Goynes & Rollins, 1971; Buisson, Rajasekaran, French, Conrad, & Roy, 2000)

4 Acid hydrolysis of cellulosic fibres

Acid hydrolysis of cellulose may take place homogeneously or heterogeneously. In homogeneous hydrolysis, the cellulose is dissolved in the hydrolysing medium. However, when cellulose is present in the solid state in the hydrolysing medium, the reaction will take place heterogeneously. In this thesis, only heterogeneous acid hydrolysis is considered. Industrially, acid hydrolysis is used both in the production of cellulose microcrystals (MCC) and cellulose nanocrystals (NCC) (Siró & Plackett, 2010), in the production of cellulose ethanol and to control the degree of polymerization of cellulose samples (Emsley, Heywood, Ali, & Eley, 1997; Hu & Ragauskas, 2012). Thus, differences in the susceptibility of different cellulosic materials to acid hydrolysis are industrially important. Different levels of susceptibility to acid hydrolysis may be due to differences in swelling ability, the origin of the fibre and the processing history of the fibre.

When cellulosic fibres are subjected to acid, glucosidic bonds are cleaved, leading to a decrease in the DP. For this reason, the degradation of cellulose samples in acid may be monitored by viscosity measurements. This method has a long history due to its simplicity. Independent of acid strength, the degradation almost stops at a certain degree of polymerisation, referred to the “levelling off degree of polymerisation” or the

“limiting degree of polymerisation” (LODP) (Battista, 1950; Håkansson, Ahlgren, & Germgård, 2005). This phenomenon has been explained by differences in susceptibility to acid hydrolysis between amorphous and crystalline cellulose. Davidson (1943) has investigated the loss of hygroscopicity as the acid hydrolysis process proceeds, caused by water being mainly absorbed in the amorphous regions. In crystalline cellulose, the chains are so tightly packed that no water can penetrate between them, whereas the more open structure in the amorphous cellulose, allows more water to interact with the cellulose chains.

The length of the crystalline parts, that remain when the LODP is reached, is in very good agreement with the theoretical length, if the length of an anhydroglucose unit is multiplied by the LODP. (Jørgensen, 1949; Nelson & Tripp, 1953; Battista, Coppick, Howsmon, Morehead, & Sisson, 1956; Scallan, 1971)

Acid hydrolysis may proceed along a number of different reaction pathways. However, the main pathway is via the pyranosyl cation, see Figure 5 (Philipp, Dan, Fink, Kasulke, & Loth, 1981; Sjöström, 1993). The first step in the reaction is the fast addition of a proton to the oxygen. This is followed by the slow formation of a cyclic carbonium ion, which forms a half chair conformation. In the last step water is added and the chain is cleaved.

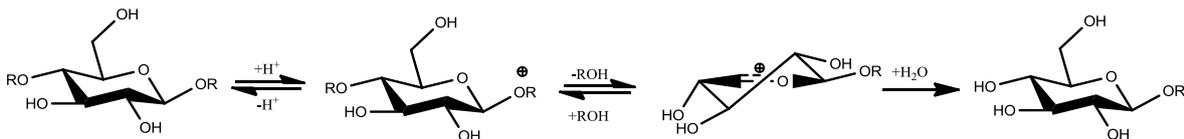


Figure 5 | Acid-catalysed hydrolysis of a glucosidic linkage via pyranosyl cation.

4.1 Impact of drying on acid hydrolysis

The susceptibility to acid hydrolysis of cellulosic fibres is a reflection of the ultrastructure of the material. As described in Chapter 3, drying has a major effect on the ultrastructure of cellulosic fibres, causing a coalescence of fibrils and a decrease in porosity. This makes hornified materials less accessible to chemical reactions, such as acetylation (Chunilall, Bush, Larsson, Iversen, & Kindness, 2010). The same behaviour could be anticipated

when treating dried and never-dried material with acid. However, as early as in the 1950s, the opposite effect was shown (Lindgren & Goliath, 1956; Jørgensen, 1950). Jørgensen (1950) performed acid hydrolysis experiments on dried and never-dried pulp. He also investigated the effect of drying on the accessibility of cellulosic fibres towards chromium trioxide, and he was surprised by the result, which showed that never-dried pulp with higher accessibility towards chromium trioxide was more resistant to an acid attack. However, no clear explanation was presented by Jørgensen. The same observation regarding the effect of drying on acid hydrolysis was made by Lindgren and Goliath (1956), who explained the results by the build-up of strain in the cellulose fibre caused by drying, which made the fibres more susceptible to acid hydrolysis. After this, it would take another 25 years before this behaviour was observed again by Philipp et al. (1981). In that study, the main focus was on enzymatic hydrolysis, and acid hydrolysis was used as a reference. Drying made the samples more susceptible to acid hydrolysis, but less susceptible to enzymatic hydrolysis, due to the size difference between the large enzymes and the small protons. It was speculated that the major effect of drying on acid hydrolysis was due to stress in the fibres. Another 30 years later, Kontturi and Vuorinen (2009), studied the production of NCC from dried and never-dried pulp and strongly asserted the effects on acid hydrolysis to hornification. They found that NCC produced from never-dried pulp had more long NCCs and fewer short NCCs compared to the NCC produced from once-dried pulp, and they argued that this was due to the stress built up during drying.

5 Materials and methods

This section describes the materials and methods used in Papers I and II. In Paper I the main objective was the characterisation of cotton sheets in difference stages of service life, and thus a number of characterisation techniques were used. In Paper II, the material was also characterized thoroughly, but the main objective was to investigate acid hydrolysis. Acid hydrolysis was followed by viscosity measurements at certain time intervals, and the results were modelled to understand the degradation process.

5.1 Materials

Paper I is based on an analysis of four cotton sheets which had been used at hospitals and laundered a different number of times. Two sheets had never been used; one never laundered and one laundered 2-4 times. New sheets are always laundered before being sent out to hospitals. These first launderings remove the weaving additive, applied by the textile manufacturer. The two last sheets had been used and laundered many times. One was moderately worn and laundered approximately 50 times and the other was completely worn out, and ready for incineration. 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, an alkaline detergent which has a pH between 12 and 12.5, in a 1% solution. The detergent did not contain any oxidants. After laundering, water is pressed out of the fabric prior to tumble drying.

The investigated materials in Paper II are listed in Table 1 and comprise two batches of cotton sheets with 5 sheets in each batch (new sheets and sheets discarded after long-time use and frequent laundering), two kinds of once-dried dissolving pulp (Scandinavian softwood Sulphite pulp and a Eucalyptus hardwood pre-hydrolysis Kraft pulp), and bleached Scandinavian softwood Kraft pulp (both never-dried pulp and once-dried pulp).

Table 1 | Degree of polymerisation of original samples

Sample	Original DP
New sheets	2621
Discarded sheets	726
PHK	581
Sulphite	761
BKP	1094

5.2 Characterisation methods

5.2.1 Extraction prior to analysis (Paper I)

In Paper I, the samples were extracted prior to all analysis, except the SEM microscopy; due to a weaving additive that had been added to the sheets. The sheets were cut in to smaller pieces and defibrated using a Wiley mill (<1 mm).

Extraction was performed according to ISO 18:33-1:2010, using light petroleum and water. However, the extraction did not completely succeed in removing the weaving additive and traces were detected using NMR spectroscopy, even after extraction. No further attempts were made to analyse the additive. However, due to this contamination,

measurements of specific surface area, water retention value and carboxylic acid content for the never-laundered sheet were obstructed.

5.2.2 BET (Paper I)

In order to preserve the surface area of the water swollen samples, a solvent exchange procedure was performed. First water was changed into dry acetone, which was then changed into cyclohexane (Köhnke, Lund, Brelid, & Westman, 2010; Wang, Maloney, & Paulapuro, 2003). In each step, the 1 g of sample was first carefully washed with 20 ml solvent, and then dispersed in 20 ml of solvent. The solvent exchange was performed 10 times for each solvent. After the solvent exchange the samples were dried in a nitrogen stream overnight. The nitrogen adsorption was measured with a Micrometrics TriStar 3000 instrument, from which the BET-area was calculated.

5.2.3 SEM microscopy (Paper I)

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

5.2.4 Intrinsic viscosity (Paper I and II)

The samples were dissolved in Cuen (copper(II)ethylenediamine) and analysed according to the SCAN-C 15:99 method to determine intrinsic viscosity. In Paper II the intrinsic viscosity was correlated to the DP according to Immergut (1953), as stated in SCAN-C 15:62.

5.2.5 HPSEC (Paper I and II)

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 the 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 MALS (Down Heleos-II, $\lambda = 658$ 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.

5.2.6 NMR (Paper I)

Solid state ^{13}C NMR experiments were performed on a Varian Inova-600 operating 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-hydrolysed) samples and samples subjected to an acid hydrolysis pretreatment were analysed. The acid hydrolysis was carried out according to Wickholm et al. (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).

5.2.7 WRV (Paper I and II)

The water retention value was measured according to the SCAN-C 62:00 method in which 2 g of a disintegrated and partially dewatered sample were subjected to further dewatering by centrifugation in 3000 g for 15 minutes. The weight after centrifugation was then compared to the weight after drying at 105 °C. All tests were carried out in duplicate.

5.2.8 LODP determination (Paper II)

The LODP was measured as the average degree of polymerisation, measured by intrinsic viscosity, after hydrolysis for 2 and 4 hours. The hydrolysis of 2 g (o.d.) sample was performed in 100 ml 4 M hydrochloric acid in 80°C. After hydrolysis the sample was washed with cold water.

5.3 Acid hydrolysis (Paper II)

Prior to acid hydrolysis, all samples were washed with 0.01 M HCl at R.T. to remove excess alkali. The hydrolysis was performed treating 5 g O.D. of each sample in 100 ml HCl solution (0.4 M) at 80 °C. The samples were preheated in the water bath before the HCl was added. The samples were treated for 15, 30, 60, 120 and 240 min. The hydrolysis was quenched by first cooling the sample and then dewatering followed by washing the samples with deionised water.

5.4 Modelling of data from acid hydrolysis (Paper II)

Hydrolytic degradation of cellulose may be described by a model developed by (Calvini, 2005). The model is based on the general mechanism of hydrolytic degradation:



Cellulose fibres have a complex ultrastructure and it is likely that bonds in different parts of a fibre have different reactivity. For instance, the crystalline parts have very low accessibility compared to amorphous parts. Calvini used 3 components to model this and argue that the different rate constants originate from weak links, amorphous cellulose and crystalline cellulose.

$$S = n_1 (1 - \exp(-k_1 t)) + n_2 (1 - \exp(-k_2 t)) + n_3 (1 - \exp(-k_3 t)) \quad (1)$$

where S is the number of scissions per cellulose chain ($DP_0/DP - 1$), n the initial number of scissile bonds, k the rate constant, and t the time of hydrolysis. The model was fit to minimize the sum of squared errors of prediction (SSE), using the minimization function

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fmincon in Matlab 2013b, for 1, 2 and 3 components. However, a very good fit for the samples analysed in this study was achieved with only one component, as in Eq. 2.

$$S = n (1 - \exp(-kt)), \quad (2)$$

where S is the number of scissions per cellulose chain ($DP_0/DP - 1$), n the initial number of scissile bonds per cellulose chain, k the rate constant, and t the time of hydrolysis.

6 Results and discussion

The main findings of Paper I and II are summarised and discussed in this section. In the first part the results from Paper I will be discussed. This study focus on characterisation of changes during laundering and use of cotton sheets. In the second part the results from Paper II will be discussed. Here, the focus was on understanding differences in susceptibility between different cellulosic materials.

6.1 Changes in cotton fibres during laundering

Cotton is one of the most common textile materials, and thus the properties of virgin cotton have been studied thoroughly. However, the aim of this research is to provide a background for recycling cotton textiles, and in this context, understanding the changes in the material properties, during the service life of the textiles are important. In Paper I, four cotton sheets used at hospitals and laundered industrially were investigated. The sheets had been laundered 0, 2-4, approximately 50 and more than 50 times, respectively. The two first sheets had never been used, and the never laundered sheet had a weaving additive applied to the surface, which made some analyses impossible, since removal of

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the additive would have damaged the sample. In the SEM micrographs in Figure 6, the additive is visible as a coating on the never-laundered sample, whereas it had been removed in the other samples. The fibres are highly aligned in the figure, since they have been photographed in the woven sheet, and not after defibration. When studying the samples up close, it was also possible to detect damage from wet and dry abrasion. Fibrillation on the surface of the fibres was visible as early as in the sheet laundered 2-4 times. However, only the two sheets laundered ~50 and >50 times displayed cracks in the fibres.

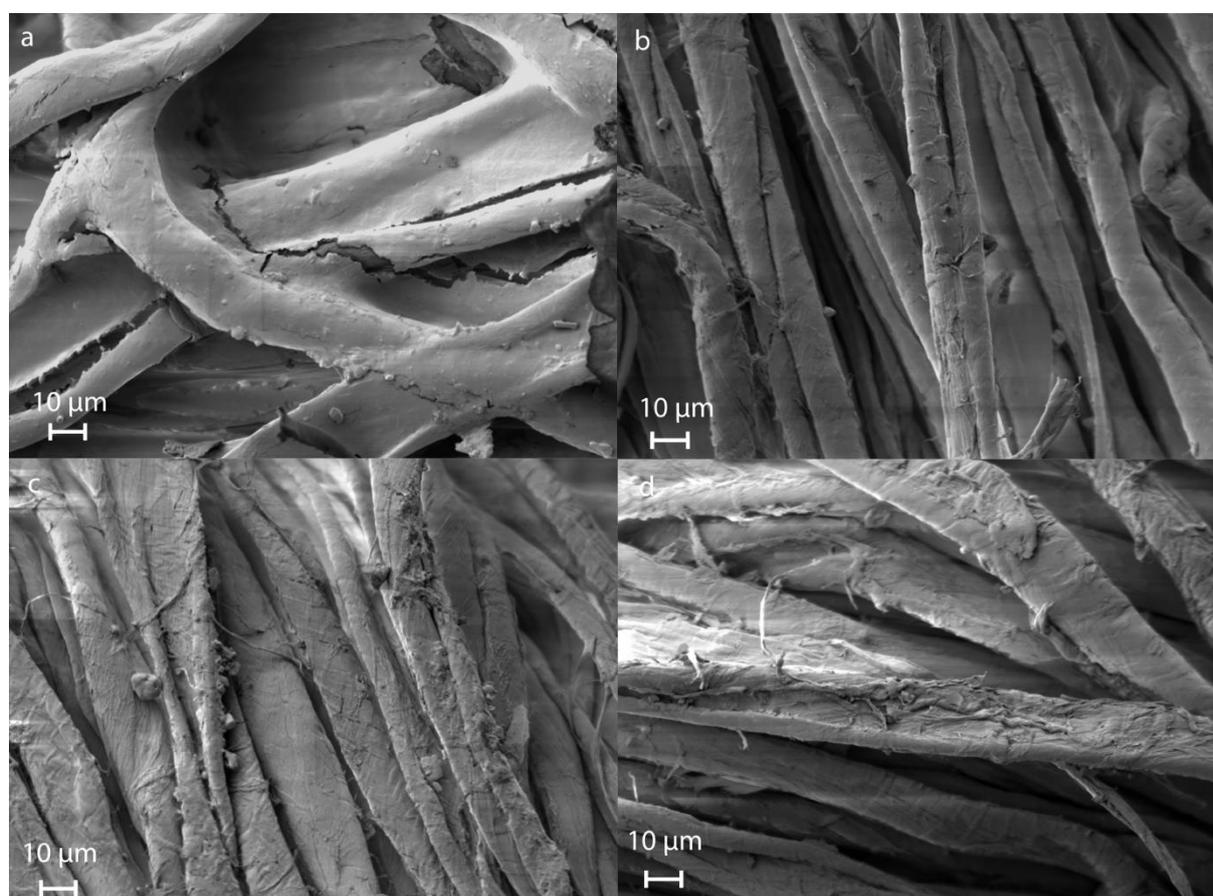


Figure 6 | SEM micrographs of the four sheets, laundered a) 0 times, b) 2-4 times, c) ~50 times and d) >50 times.

Since textiles are dried and rewetted many times during their service life, before reaching the recycling step, changes in hornification were investigated. As described earlier, hornification has mainly been studied in regard to chemical pulp fibres, to describe the irreversible loss of porosity after drying. During pulping, the wood fibre

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becomes extensively porous, due to the removal of lignin and hemicelluloses. As long as the fibre is kept wet, it maintains the highly swollen state, but after drying and rewetting, irreversible changes lead to that the highly swollen state cannot be restored. Porosity and the ability to swell in water have also been positively correlated to accessibility, and may therefore impact the dissolution properties of the cellulosic fibres (Chunilall et al., 2010).

In Table 2, the water retention value of the laundered sheets is listed. During prolonged laundering only a small decrease in the WRV was observed. This is probably due to the high initial hornification of cotton. Since there is no hemicellulose or lignin blocking coalescence, the microfibrils adhere during drying, already on the field before picking. In Paper II, WRVs of once-dried dissolving pulps, with equal purity, i.e. dissolving pulp, were measured, and were found to have 0.72 g/g for a PHK pulp and 0.65 for a Sulphite pulp. The WRVs of cotton sheets are thus much lower than the WRVs of dissolving pulp.

Table 2 | Water retention value of the samples. Values of the WRV and specific surface area could not be measured for the never-laundered sheet due to a weaving additive.

Times laundered	Water retention value (g/g)	Specific surface area (m ² /g)	Elementary fibril (nm)**	Fibril aggregate (nm)**
0	-	-	6.4 ± 0.2***	21.9 ± 2***
2-4	0.40 ± 0.003*	73 ± 4.2*	7.0 ± 0.2***	25.6 ± 2***
~50	0.41 ± 0.005*	66 ± 2.9*	7.2 ± 0.2***	24.2 ± 2***
>50	0.38 ± 0.009*	45 ± 1.4*	7.2 ± 0.2***	24.1 ± 2***

* Standard deviation based on 4 (WRV) and 3-5 (spec. surf. area) replicates. ** Based on acid hydrolysis treated samples.

***Standard deviation estimated from several deconvolutions of different spectra.

The supramolecular structure, with fibrils containing crystalline and amorphous cellulose, gives rise to pores in both the longitudinal and transverse directions. The porosity of the fibres was assessed by nitrogen gas adsorption of dry samples. To maintain as much surface area as possible from the water-swollen state, a solvent exchange was performed, exchanging the solvent from water to acetone and then to cyclohexane, before drying. Such a solvent exchange process had been used earlier to maintain the water-swollen state before BET-measurements (Haselton, 1955; Porter &

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Rollins, 1972; Wang et al., 2003). The resulting specific surface areas are listed in Table 2. In contrast to the WRV, the specific surface area of the fibres, decreases with increasing number of launderings. The WRV measures the water-holding ability of a sample, and thus both water on the fibre surface and in the pores of the fibre walls contribute to this measurement. Thus, changes in a highly hornified sample will only have a small effect on the WRV.

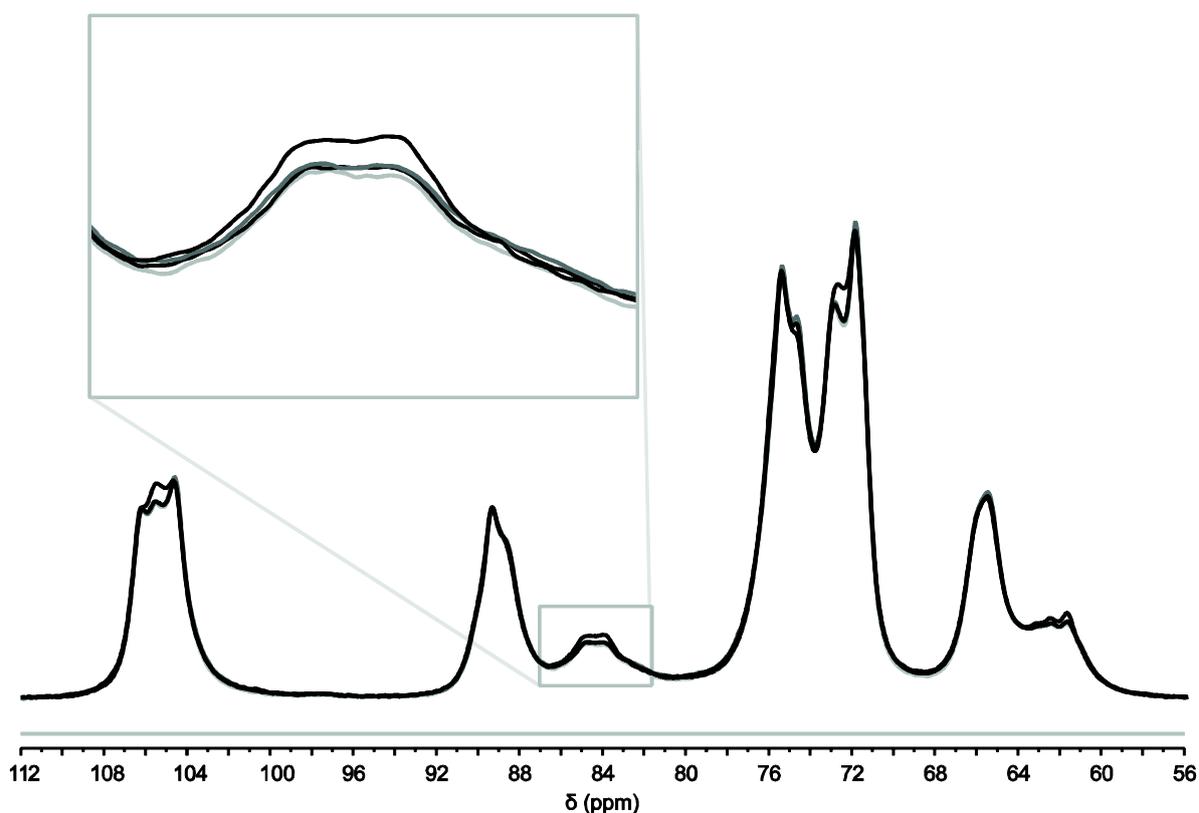


Figure 7 | CP/MAS ¹³C-NMR spectra showing superimposed C4 region of samples laundered 0 (black), 2-4 (dark grey), ~50 (grey) and >50 (light grey) times.

A high specific surface area is positively correlated to a large area accessible for reaction and, thus, a high reactivity of the cellulosic fibre (Chunilall et al., 2010; Nelson & Oliver, 1971). Consequently, the observed decrease in specific surface area may indicate that laundering has a negative impact on the possibility for recycling cotton, in applications where high purity pulps are used today, such as in the production of regenerated

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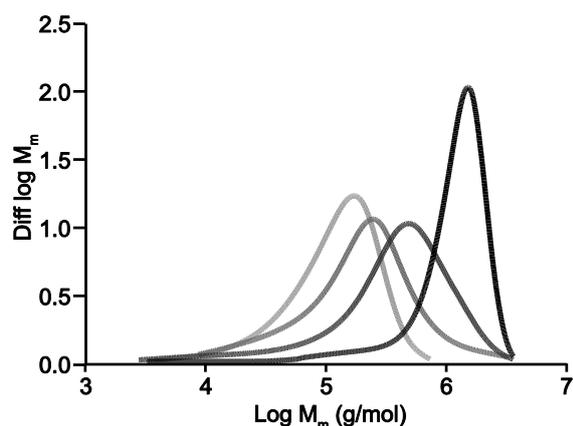


Figure 8 | Molecular mass distributions of cellulose from sheets laundered 0 (black), 2-4 (dark grey), ~50 (grey) and >50 (light grey) times.

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)
0	1323	719	1.84
2-4	567	86	6.62
~ 50	338	93	3.64
> 50	151	64	2.36

aggregate size, were observed. These results are in line with the WRV measurements, which shown that major increase in the degree of hornification occurred after 2-4 launderings.

The changes that occur during laundering discussed so far occur mainly on the supramolecular level. However, laundering also affects cellulose polymers. For this reason, changes in the distribution of the molecular mass were measured with HPSEC, and the results are shown in Figure 8.

cellulosic fibres and cellulose derivatives. In order to investigate the effect of laundering on dissolution, more specific studies must be performed.

Never-laundered and laundered cotton sheets were analysed using solid state NMR spectroscopy. From the deconvolution of the C4 region of CP/MAS ^{13}C -NMR, the dimensions of an elementary fibril and fibril aggregates were calculated and are shown in Table 2. The weaving additive did not affect these measurements and, thus, the change from 0 laundering to 2-4 may be observed. A small size increase, was observed both in the elementary fibril size and in the fibril aggregate size, indicating an initial increase in hornification. From 2-4 to >50 launderings very small changes in both in the elementary fibril size and the fibril

A comparison of the molecular mass distributions of the sheets laundered 0 times and 2-4 times in Figure 8, shows significant differences. The mass distribution of the cellulose polymers in the never-laundered sheet is narrow, in the figure, and the sample contains mainly very long chains. The mass distribution of the cellulose in the sheet laundered 2-4 times, on the other hand, is broader and most of the very long chains in the never laundered sheet have been degraded to shorter fragments. Degradation during laundering is most likely caused by autoxidation followed by chain scission, as discussed earlier, cf. Section 3.1.

Further insights into changes in molecular mass distribution during laundering may be revealed from a survey of Table 3, in which the mass average molecular mass, number average molecular mass and the dispersity are listed. As seen in Table 3, the mass average molecular mass and the number average molecular mass decrease with the number of launderings. The dispersity first increased, due to the chain scission, and then decreased, when the “levelling-off DP” was approached. In Figure 8, it is also interesting to observe that the tail of long cellulose chains had shortened in the sheet laundered more than 50 times compared to the sheet laundered approximately 50 times.

6.2 Acid hydrolysis of cellulosic fibres

Acid hydrolysis was performed both under mild conditions, to study the gradual degradation, and under harsh conditions, to measure the LODP. The purpose was to analyse differences between dissolving pulp and cotton fibres in terms of susceptibility to acid hydrolysis. Drying has a severe impact on cotton fibres, since it is almost pure cellulosic material, and pure cotton is highly hornified compared to dissolving pulp. Thus, the effect of drying on acid hydrolysis was first investigated, through inclusion of never-dried and once-dried paper-grade Kraft pulp.

6.2.1 Levelling off degree of polymerisation

As described in earlier sections, drying induce hornification which leads to a collapse of the porous structure of a fibre, and a coalescence of cellulose fibrils. In this manner, the specific surface area of the fibres decreases. It was expected that this decrease would be

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followed by an increase in the LODP, and to test this, measurements of the LODP of never-dried and once-dried BKP were performed. The WRV of the samples decreased as a result of drying, indicating that hornification had occurred, see Table 6. Against our initial expectations, the LODP also decreased as a result of drying, which indicates that the dried sample had greater susceptibility to acid hydrolysis, even though the swelling ability of that sample had decreased after drying. However, a thorough literature survey showed that this result was in accordance with observations reported in the few (and not widely cited) publications where this phenomenon had been studied, cf. Section 4.1.

The four samples with high purity cellulose, i.e. the dissolving pulps and the cotton sheets, had LODP values in the same range, between 88 and 124, despite the differences in processing history and virgin material. The LODP value of the BKP was higher, than that of the other samples. Hemicellulose content has been shown to affect the LODP, and Håkansson et al. (2005) have suggested, that the hemicelluloses have a protective effect, shielding the amorphous parts of the fibre from acid attack. However, taking into account the protective effect of hemicelluloses against hornification during drying (Köhnke et al., 2010; Oksanen et al., 1997), the observed effect might, at least partly, be a result of decreased hornification, and might not be caused by any direct shielding of cellulose by the hemicellulose.

The LODP of the Sulphite pulp was measured to be somewhat higher, compared to the PHK, a difference which was established earlier in the literature (H Sixta, 2000). The samples in this investigation included one hardwood (PHK) pulp and one softwood (Sulphite) pulp, and it is possible that the LODP had been affected by the raw material. However, the processing method also has an impact. It has been stated that the broad molecular mass distribution of the Sulphite pulp gives rise to a high LODP (H Sixta, 2000). This is possible if the LODP is also considered to be the average of a distribution, and more high molecular mass material may be left in the sample, even after long-time hydrolysis. However, the question remains, why is this part of the cellulose less affected? An explanation in line with the hypothesis for the effect of drying on LODP is based on the difference in fibril aggregation. During drying, fibrils aggregate, or coalesce, building

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up stress in the material and, possibly leading to lower LODP in dried material, than in never-dried material. Hult (2001), showed that lateral fibril aggregation occurs during Kraft pulping, giving larger lateral fibril dimensions in Kraft pulp after pulping, than for a Sulphite pulp. This aggregation may lead to stress, similar to the case in which drying makes some glucosidic bonds in the fibre more susceptible to acid hydrolysis. However, more detailed research is needed to confirm this hypothesis.

Table 6 | Initial DP, LODP, WRV and parameters from modelling of weak acid hydrolysis, n - initial number of scissile bonds, k - rate of acid hydrolysis and LODP values predicted by the model.

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)*

A comparison of the LODP of the two sets of sheets, shows that laundering has no major impact on the LODP, see Table 6. Since cotton fibres dry on the field before picking, they are highly hornified already in the virgin state (Nelson et al., 1980), and this might explain the small difference in WRV between the two batches of sheets. However, some fibril coalescence may be induced during service life, due to the many drying and re-wetting cycles (Fahmy & Mobarak, 1971). A tentative explanation for the observation

that the LODP of New sheets and Discarded sheets was almost the same may be that the linkages broken during ageing are also susceptible to acid hydrolysis. It could additionally be speculated that stresses built up in the cellulose during the drying and rewetting cycles may be released through the oxidative chain cleavage, leaving the LODP unaffected.

6.2.2 Modelling of mild acid hydrolysis

The cellulosic samples were subjected to acid hydrolysis in 0.4 M HCl at 80°C for different lengths of time and the resulting DP was analysed. The obtained data points were then fit to a model, as described in the methods section, 5.4. From the model, the LODP (i.e. $t \rightarrow \infty$) was also calculated. The data points, model and calculated LODP values are shown in Figure 9 and Table 6.

The difference in susceptibility to acid hydrolysis discussed in terms of LODP, for once-dried BKP compared to never-dried BKP, is also valid for the acid hydrolysis in 0.4 M HCl at 80°C, see Figure 9. The hydrolysis of the once-dried pulp was faster, and reached a lower degree of polymerisation, than the never-dried sample. A survey of the modelling parameters in Table 6 shows that the difference depend mainly on the number of scissile bonds per cellulose chain, n , and not the rate constant of the hydrolysis, k . The weak acid hydrolysis of the dissolving pulps shows, as in the case with the LODP measurements, that the hydrolysis of the Sulphite pulp was slower and stopped at a higher level than the PHK sample. An investigation of the parameters from the modelling reveals that the rate constant, k , was about the same for the Sulphite pulp as for the PHK. However, in the case of PHK, n was higher. The amount of scissile bonds per cellulose chain, n , is related to the initial DP, as seen when n for the “New sheets” is compared to the n of the “Discarded sheets”. Nevertheless, regarding the dissolving pulps, the Sulphite pulp had the highest starting DP, but the PHK pulp still had more scissile bonds, n .

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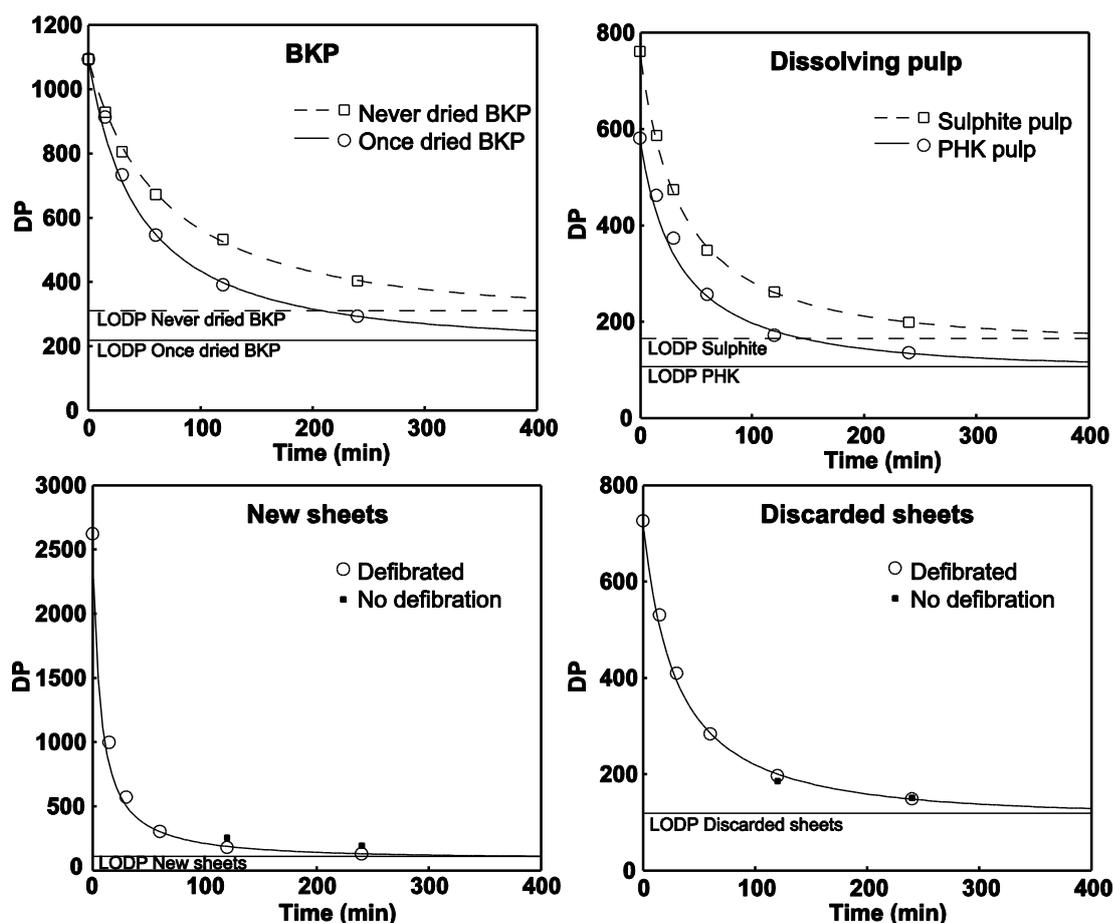


Figure 9 | Weak acid hydrolysis (0.4 M HCl, 80 °C) of cellulosic fibres, lines indicating modelling results. LODP values from modelling shown as straight lines.

6.2.3 Molecular mass distributions

Viscosity measurements provide an estimate of the degree of polymerisation. However, in order to make a more thorough analysis of the changes that occur during degradation, molecular mass distributions were also determined, and the data is presented in Figure 10. Drying of the BKP sample induced significant differences in both LODP and susceptibility to weak acid hydrolysis, as presented above. The BKP samples were not completely dissolved in the sample preparation prior to the chromatographic analysis. Therefore, these results should only be seen as indicative. Nevertheless, the results in Figure 10 suggest that the once-dried BKP was more degraded after hydrolysis than the

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never-dried sample. The molecular mass distribution, in Figure 10 was performed on samples hydrolysed for 60 minutes, corresponding to point number 4 in Figure 9. The

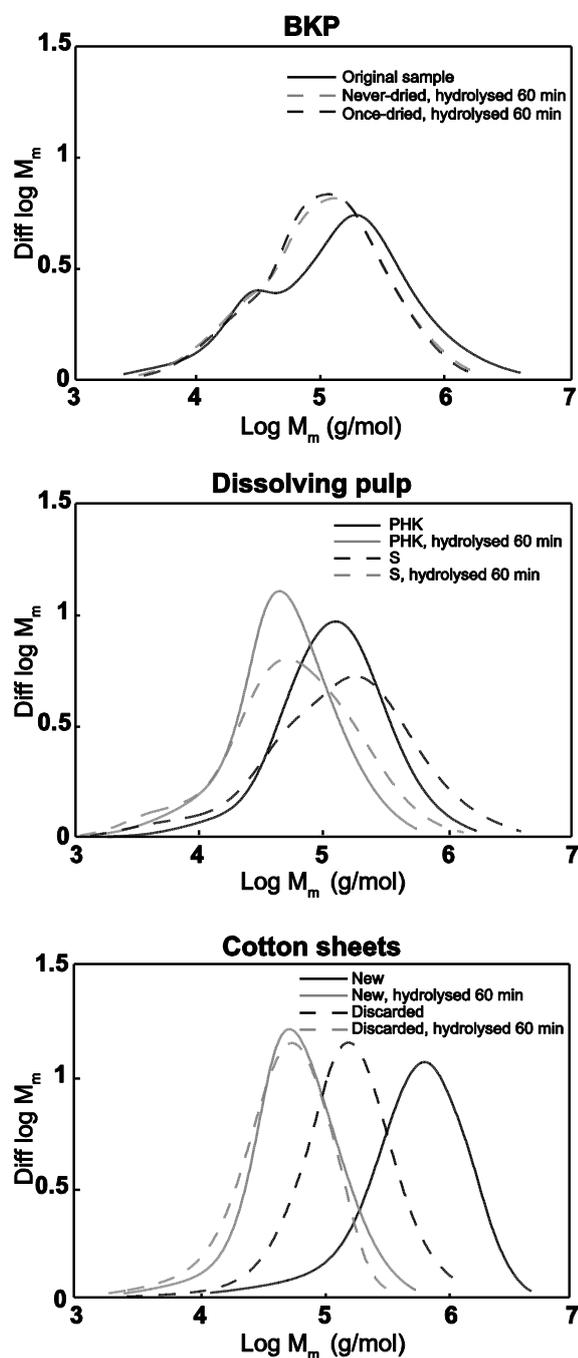


Figure 10 | Molecular mass distributions for the samples.

difference is however, not as visible in the molecular mass distribution.

Sulphite pulping yields a pulp with a broader molecular mass distribution than kraft pulping. It has been claimed that this is because the low degree of swelling of the substrate during Sulphite pulping, which would lead to a higher molecular mass gradient (Krässig, 1993). This difference is clear when the molecular mass distributions are compared in Figure 10. After hydrolysis, the Sulphite pulp still had more high molecular mass material left than the PHK pulp, even though the dispersity of the Sulphite had decreased after hydrolysis.

The initial difference of the sheets decreased, to a large extent, after only 60 min of hydrolysis. However, close inspection of the tails of the distribution, reveals that that the “Discarded” sheets had more low molecular mass material and less high molecular mass material. This minor difference is promising for future textile recycling applications, in which materials with different service lives will be mixed before pretreatment.

7 Conclusions

The experimental work presented in the two papers included in this thesis was executed with the aim of providing a background to industrial recycling through an investigation of cellulosic fibres from cotton textiles. The aim of the study in Paper I was to investigate ultrastructural and chemical changes during laundering.

It was found that laundering had a major impact on the length of cotton cellulose polymers. The mass average molecular mass decreased from 1323 kDa down to 150 kDa after laundered more than 50 times. This was explained mainly through the autoxidation of the samples, leading to chain scissions. In terms of recycling textiles into regenerated cellulosic fibres, such as viscose fibres, this low mass average molecular mass may be a promising feature of heavily used textiles, since the mass average molecular mass is in the same range as that preferred by viscose producers (Woodings, 2001). However, despite the many laundering cycles, which the cotton sheets are exposed to during service life, the WRV remained almost constant throughout the service life of the sheets. The fibril aggregate size may be used to estimate a possible hornification effect, and from CP/MAS C13 NMR measurements, a small increase from 21.9 nm to 25.6 nm in the lateral diameter of fibril aggregates was observed between the never-laundered sheet sample and the sample from the sheet laundered 2-4 times.

CONCLUSIONS

The study in Paper II investigated differences between different cellulosic fibres in terms of susceptibility to acid hydrolysis. It was found that drying decreased the LODP, most likely due to drying-induced stress in the cellulose fibrils. This made the dried fibres more accessible to acid hydrolysis, than never-dried fibres. However, this effect was not observed in cotton cellulose, probably due to initially high degree of hornification.

Acid hydrolysis is a possible pre-treatment of cotton textiles, prior to recycling, which may be used to control the degree of polymerisation of the cellulose. Acid hydrolysis experiments in this study showed that, despite initial large differences between new sheets and sheets ready for incineration, after only 60 min of acid hydrolysis with 0.4 M HCl at 80°C, the molecular mass distribution of New and Discarded sheets was in the same range. This gives a good indication for textile recycling, since materials collected for recycling will have very different degrees of polymerisation, due to different lengths of service life and differences in degradation during service life.

Paper I and II presented in this thesis both focus on materials and processes prior to the recycling of cotton textiles. To further develop the field of textile recycling, understanding of dissolution properties, and differences in reactivity between cotton and dissolving pulp must be developed. In this thesis, only pure cotton materials were used, to avoid impact of other textile materials. However, most textiles are mixed materials, and one of the most common mixtures is cotton/polyester. For this reason, improved techniques for separating of these materials are necessary in order to develop textile recycling on an industrial scale

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