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Differences in Swelling of Chemical Pulp Fibers and Cotton Fibers – Effect of the Supramolecular Structure

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The swelling and dissolution of cellulose are key parameters in the production of regenerated cellulose fibers. Since cotton is almost pure cellulose, it has been proposed that the recycling of cotton textiles may be accomplished through incorporating the cotton textiles into the production of regenerated cellulosic fibers. In this study, the supramolecular structure before and after pretreatment was characterized using solid-state carbon-13 nuclear magnetic resonance (^{13}C NMR), and the findings related to the swelling of dissolving pulp and cotton were quantified with a fiber analyzer. The cotton and dissolving pulp samples were subjected to three different pretreatments: mild acid hydrolysis, acid hydrolysis in ethanol, and a hydrothermal treatment. The results showed that cotton was harder to swell than the dissolving pulp. This indicated that either waste cotton requires another type of activating pretreatment than those included in this study or very good solvents if it is to be included in the production of regenerated fibers.

Keywords: Cotton recycling; Acid hydrolysis; Hydrothermal treatment; CP/MAS ^{13}C NMR; Fiber swelling

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INTRODUCTION

To meet the rising demand for textile fibers caused by population and prosperity growth, it is vital to introduce the recycling of textile fibers (Palm 2011; De Silva *et al.* 2014; Asaadi *et al.* 2016; Elander and Ljungkvist 2016; Haule *et al.* 2016). The chemical recycling of cotton fibers may be accomplished by introducing used cotton as a raw material source into the production of regenerated cellulosic fibers. Currently, regenerated cellulosic fibers are mainly produced from wood-derived dissolving pulp; however, cotton linters are also used as an additional raw material source. Cotton linters are an attractive raw material in different cellulose applications, due to their high cellulose purity. There are two kinds of fibers on a cotton seed, linters and lint fibers. Linters are shorter fibers attached more strongly to the cotton seed than cotton lint fibers that are used in textile production (Wakelyn *et al.* 2006). After the linters have been cut off from the seeds and bleached, they reach a high cellulose purity (Sczostak 2009). Thus, cotton lint fibers from used textiles could possibly also be used as a raw material source in cellulose applications, where high purity is important, such as in the production of regenerated fibers. This is investigated further in the present paper.

Textiles from the service sector, such as hospitals and hotels, should be considered in the first step towards textile recycling, since large volumes of nearly constant quality are available. However, some sheets are discarded after only a few laundering cycles, due to stains or other reasons, while others are laundered many times until the strength is too low and the item is worn out. It has previously been shown that industrial laundering substantially decreases the molecular mass of cotton (Vaeck 1966; Palme *et al.* 2014). Thus, it can be anticipated that the molecular mass distribution of the incoming material to the recycling facility will be broad. To provide an incoming feed of cotton textiles to a recycling facility, with a narrow molecular mass distribution, pretreatment of the material will be important.

Pretreatments of cellulose fibers are performed both to increase the susceptibility of cellulose towards dissolution, and to decrease the cellulose degree of polymerization (DP). Commonly employed methods are acid or enzymatic hydrolysis, thermo-mechanical treatments, and alkaline pretreatments (Yamashiki *et al.* 1990; Wang *et al.* 2008; Struszczyk *et al.* 2009; Le Moigne and Navard 2010). In this study, three acid pretreatments were performed: first, a dilute acid hydrolysis; second, a similar method with ethanol instead of water; and third, a hydrothermal treatment in a weakly acidic buffer solution at elevated temperature.

Mild acid hydrolysis was chosen as the baseline, where the effect on swelling by reducing the DP could be studied. Acid hydrolysis has been used to study cellulose for a long time (Davidson 1943; Battista 1950; Immergut and Rånby 1956) and is also used industrially (Hallac and Ragauskas 2011). As a complement, acid hydrolysis of cellulose in ethanol was included since it has been suggested that it may have a more beneficial effect on cellulose dissolution than acid hydrolysis in water (Trygg and Fardim 2011). In 1923, it was shown that acid hydrolysis in ethanol degrades cellulose faster than acid hydrolysis in water (Coward *et al.* 1923; Reeves *et al.* 1946; Lin *et al.* 2009). Additionally, a hydrothermal pretreatment was included in the current study to test the effect of longer treatment time and elevated temperature (170 °C). A similar method with ascorbic acid has been previously used to promote cellulose dissolution (Struszczyk *et al.* 2009). However, in the current study, the acid used in the referred study (Struszczyk *et al.* 2009) was exchanged for an acetate buffer due to a stability problem of ascorbic acid during the long treatment period at high temperatures.

A key step in the production of regenerated cellulose fibers is the dissolution of cellulose. Different methods have been applied to study cellulose dissolution, in both aqueous and non-aqueous solvent systems. However, there is no consensus regarding how to quantify and compare the dissolution of different fibers in different solvents. Some of the methods that have been suggested are dissolving cellulose at a low concentration and centrifuging off the undissolved parts (Le Moigne and Navard 2010), turbidity measurements (Mazza *et al.* 2008; Olsson *et al.* 2014), light scattering (Röder *et al.* 2000), and analysis with light microscopy (Cuissinat and Navard 2006; Schild and Sixta 2011; Mäkelä *et al.* 2018). The suitability of a certain pulp sample for viscose production may be assessed with either the Fock test (Fock 1959) or the Treiber test (Treiber 1962). Since different properties are measured with all of the above-listed methods, it is important to consider the aim of the study when choosing the evaluation method.

In a recent paper, it has been shown that the swelling of cellulosic fibers in a low concentration of copper ethylene diamine (CED, also referred to as CuEn) solution, measured with a fiber analyzer, is correlated to the Fock reactivity of the fibers (Arnoul-Jarriault *et al.* 2016). This method allows for the quantification of the swelling of a large number of fibers in a dilute solvent with simple equipment. In the present study, this method was used to compare the swelling behavior of dissolving pulp and cotton fibers before and after different pretreatments.

Swelling in water only affects the non-crystalline parts of the fibers, and does not cause any changes in crystallinity. It is thus referred to as intercrystalline swelling. There are, however, some liquids that not only swell the non-crystalline parts, but may also penetrate the crystalline areas of cellulose. This intracrystalline swelling causes irreversible changes in the crystal structure of the cellulosic material (Krässig 1993). Examples of such liquids are NaOH/water, liquid ammonia, and CED. CED is commonly used for determining the intrinsic viscosity of cellulose, but it has also been used to study the swelling and dissolution of cellulose with a light microscope (Schild and Sixta 2011). One of the benefits of CED is that the strength of the solvent can easily be fine-tuned *via* dilution with water.

In this study, the swelling properties of lint fibers from new and discarded cotton sheets were studied. Cotton samples from new and discarded sheets were compared to two dissolving pulp samples, a Scandinavian softwood sulfite pulp and a hardwood pre-hydrolysis kraft (PHK) pulp. The aim was to investigate the swelling behavior of fibers in the different samples before and after acid pretreatment, to relate this behavior to the supramolecular structure. The supramolecular structure was evaluated with solid state Carbon-13 nuclear magnetic resonance (^{13}C NMR), which gave both information on size of the fibrils (lateral fibril dimension, LFD, also referred to as microfibrils) and the fibril aggregates (lateral fibril aggregate dimension, LFAD, also referred to as macrofibrils). Based on this, the crystallinity index (CI) and specific surface area based on the average lateral fibril aggregate dimensions (LFAD SSA) can be calculated (Larsson *et al.* 1997; Wickholm *et al.* 1998; Newman 1999; Chunilall *et al.* 2010).

EXPERIMENTAL

Materials

The starting materials in this study comprised two cotton bed sheets, referred to as New and Discarded. The sheets were provided by a company in the service sector (Textilia, Karlskrona, Sweden) that provides textiles to both hospitals and hotels. The New sheets had been laundered two to four times to remove process additives but were never used. The Discarded sheets had been used and laundered more than 50 times and were ready to be discarded and sent for incineration. Each set of sheet samples comprised of five bed sheets that were cut into smaller pieces and dry milled in a Wiley mill before pretreatment and analysis. For reference, two dissolving pulp samples were included. The dissolving pulps were a Scandinavian softwood sulfite pulp (Sulfite pulp) and a Eucalyptus pre-hydrolysis kraft pulp (PHK-pulp). All chemicals were purchased from VWR International (Spånga, Sweden) and used without further purification.

Pretreatments

Acid hydrolysis in water

Prior to acid hydrolysis (H_2O/HCl), the samples were swelled in water overnight, followed by wet disintegration in 0.01 M HCl. The disintegration was performed in a low acid concentration to remove any alkaline residues in the sheets from the laundering agent. It was performed on all samples to treat them according to the same procedure.

Then the wet sample and additional water to a total water volume of 60 mL was added to a polypropylene container and heated in a water bath to 80 °C. The hydrolysis was started by the addition of 40 mL of 1 M HCl to a total volume of 100 mL, which resulted in 0.4 M HCl solution. The hydrolysis was performed for 60 min. After the hydrolysis was completed, the samples were carefully washed with deionized water at room temperature to remove all acid, and then air-dried before further analysis.

Acid hydrolysis in ethanol

The acid hydrolysis in ethanol (EtOH/HCl) started with swelling of the samples in water, followed by wet disintegration the samples in 0.01 M of 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 of ethanol. The solvent exchange procedure was repeated five times. Next, additional ethanol was added to the sample 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 60 min. The final hydrolysis solvent contained 94 wt% EtOH and 0.46 M HCl. After hydrolysis was completed, the samples were carefully washed with deionized water at room temperature to remove all acid and then air-dried before further analysis.

Hydrothermal pretreatment

Prior to hydrothermal pretreatment (HT), the samples was washed with an acetate buffer (0.02 M, pH 4.75). The sample and the acetate buffer were added to the autoclave at room temperature to a final weight of 300 g with 5 % pulp. The hydrothermal pretreatment was performed in acid-resistant stainless steel autoclaves (1500 mL) placed in a preheated polyethylene glycol bath (170 °C). During the 240 min treatment time, the autoclaves were rotated in the bath. After cooling, the pulp was washed with deionized water and air-dried. According to previous studies on the same system, it takes approximately 25 min to reach 168 °C inside the autoclaves (Bogren 2008).

Analytical Methods

Solid state ^{13}C NMR spectroscopy

The supramolecular properties of cellulose were determined in the water-swollen state (at least 40% water) *via* solid-state cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS ^{13}C NMR), as described in previous papers (Larsson *et al.* 1997; Wickholm *et al.* 1998). The CP/MAS ^{13}C NMR spectra were recorded using a Bruker Avance III AQS 400 SB (Bruker BioSpin Scandinavia AB, Solna, Sweden) instrument operating at 9.4 T. All measurements were conducted at 295 (± 1) K with a magic angle spinning (MAS) rate of 10 kHz. A total of 4096 transients were recorded on each sample depending on the solids content, leading to an acquisition time of 3 h. The software for spectral fitting was developed at RISE (2009-04-07, Stockholm, Sweden) and 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 (Larsson *et al.* 1997; Wickholm *et al.* 1998). Signals intensities of non-crystalline origin (fitted signals in the 82 ppm to 85 ppm C4 spectral range) were used to calculate the degree of crystallinity. The errors given for the parameters obtained from the fitting procedure were the standard error of the mean with respect to the quality of the fit.

Fiber saturation point (FSP)

The measurements were based on the method developed by Stone and Scallan (1968). A water-swollen sample material with a known solids content was mixed with a dextran solution of known concentration (approximately 1%, dextran mass/solution mass)

(CAS No. 9004-54-0, Dextran 2000, from *Leuconostoc* spp., molecular mass approximately 2000 kDa; Sigma-Aldrich, Stockholm, Sweden) in deionized water, approximately 1 mass unit of wet sample mass was mixed with 3 mass units of dextran solution. After mixing, the sample was stored in a sealed vessel at room temperature for 3 days to equilibrate. A liquid sample was subsequently taken and filtered through a Puradisc syringe filter (Whatman, Maidstone, UK) equipped with a 0.45-µm polytetrafluoro-ethylene (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 from the optical rotation of polarized light. The data of the calibration curve were measured through use of a Polartronic NH8 polarimeter (Schmidt+Haensch, Berlin, Germany) operating at 589 nm, with a resolution of 0.005°. Based on the determined hydrodynamic diameter of the dextran, the results obtained for the FSP indicated that the specimens contained in pores were smaller than approximately 100 nm in diameter. The FSP value is expressed as the dimensionless ratio of the mass of pore water to the mass of dry solids (g g^{-1}). When the FSP results were combined with the solid-state NMR measurements of the specific surface area, the average pore size for the water swollen fiber wall could be determined (Larsson *et al.* 2013).

Intrinsic viscosity

The intrinsic viscosity of the cellulose samples was measured after dissolution in CED (copper(II) ethylenediamine) by measuring the time required for each sample to run through a thin capillary, according to the ISO 5351 (2010) standard.

Swelling

The swelling experiments were performed on 0.05 oven-dry g samples that were swollen in water before analysis. During agitation of the fibers in water, CED (1 M) was added to a final liquid weight of 10 g. The final CED concentration was 0.16, 0.18, or 0.20 M, and the pulp consistency was 0.5%. After 2 min, the swelling was quenched by the addition of 0.5 L of acetate buffer (0.01 M, pH 4.5). The fibers were directly analyzed with a fiber analyzer (Kajaani FS300; Metso automation, Kajaani, Finland). This method provides a comparison in the width of fibers swollen in water with fibers swollen in a solvent, which was calculated according to Eq. 1,

$$Width\ variation = ((Width_{\mathrm{CED}} - Width_{\mathrm{H2O}}) \times 100) / Width_{\mathrm{H2O}} \qquad (1)$$

where *Width variation* is the difference in percentage in width of water swollen fibers compared to fibers swollen in CED (%), $Width_{\mathrm{CED}}$ is the width of fibers swollen in CED (µm), $Width_{\mathrm{H2O}}$ is the width of fibers swollen in water (µm).

The determination of the pulp fiber length and width was performed according to the TAPPI T271 (2002) method, and the calculations were based on length average. The length was reported as the centerline length.

Microscopy

The samples were suspended in water to distribute the fibers on the microscope slides and then air-dried on the slides. Before analysis, the fiber concentration on each slide was corrected to reach a similar level for all samples. The swelling was studied by using the time-lapse mode in which images were taken every 2 s for 4.5 min and a total of 136 images were yielded per sequence. The dissolving pulp samples (PHK-pulp and Sulfite pulp) were subjected to 0.16, 0.18, and 0.20 M CED and the cotton sheet samples (New and Discarded) were subjected to 0.16, 0.20, and 0.24 M CED. The solvent was added during the first 10 s, and the delay was accounted for; the microscope used was a Zeiss SteREO Discovery.V12 (Carl Zeiss AG, Oberkochen, Germany) equipped with an Axio Cam ICc1.

Molecular mass distribution (MMD)

In the analyses of MMD with size exclusion chromatography, samples were dissolved in lithium chloride/N,N-dimethylacetamid (Li/DMAc) according to Henniges *et al.* (2011). 20 mg (dry weight) of a sample was suspended in deionized water and then dewatered in a Büchner funnel. This 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. Thereafter, the DMAc was removed and 2 mL of a solution of 9% LiCl (w/v) in DMAc was added. The vials were 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, $\lambda 0$ =658 nm, from Wyatt) were used for the detection process. The value of the d*n*/d*c* used was 0.136 ml/g. Data evaluation was performed with standard Astra and Chromeleon software (6.1.17).

RESULTS AND DISCUSSION

The findings in this study will be presented in four parts. The first part concerns the basic characteristics of the samples before pretreatment. This will be followed by a presentation and discussion of the NMR analysis concerning the effect of the pretreatments on the supramolecular structure, and in the last two sections, this will be put in relation to the swelling experiments that were measured with a fiber analyzer and microscopy.

Basic Characteristics of the Samples

The analysis of carbohydrate content, listed in Table 1, showed that the cotton sheets contained 99.5% cellulose and the dissolving pulps contained approximately 97% cellulose.

The FSP of the samples were analyzed before pretreatment (Table 1). Based on this and the specific surface area that was calculated from the solid state NMR measurements, the average pore size could also be estimated (the NMR results are further discussed in connection to Table 3). One drawback of the FSP method is the rather large sample size needed. Therefore, this analysis could only be performed on the starting material. The findings showed that the wood-derived dissolving pulp samples had higher FSP values than the cotton samples. The PHK-pulp had the highest FSP value, probably due to the swelling action of the alkaline pulping. The noticeable lower FSP values of the cotton samples indicated that the cotton was more hornified. The pore size estimates show similar tendencies as the FSP in the samples. The implications of the differences in FSP and pore size on differences in swelling will be discussed below.

Table 1. FSP, Average Pore Size, and Relative Anhydrosugar Content of the Starting Material in the Study

Sample	FSP (g/g)	Average Pore Size (nm)	Relative Anhydrosugar Content* (%)				
			Glucan	Xylan	Mannan	Galactan	Arabinan
PHK-pulp	0.769 ± 0.031	13 ± 0.7	97.0	2.5	0.2	0.0	0.0
Sulfite pulp	0.611 ± 0.019	10 ± 0.5	97.0	1.3	1.7	< 0.2	0.0
New sheets	0.293 ± 0.015	8 ± 0.5	99.4	< 0.2	< 0.2	< 0.2	< 0.2
Discarded sheets	0.209 ± 0.008	6 ± 0.3	99.6	< 0.2	< 0.2	< 0.2	< 0.2

* Data from a previous study (Palme *et al.* 2016) with the same substrates

Effect of Pretreatments on Molecular and Supramolecular Structure

When cellulosic fibers are subjected to acid hydrolysis, the DP decreases due to cleavage of the (1→4) glycosidic bond between D-anhydroglucopyranose units. This decrease, expressed as intrinsic viscosity, is shown in Table 2 as a result of the pretreatments.

Table 2. Effect of Pretreatments on Intrinsic Viscosity, Fiber Width, Fiber Length, and Fines Content

Sample	Treatment	Intrinsic Viscosity (cm^3/g)	Width (µm)	Length (mm)	Fines (%)
PHK-pulp	Starting material	423	11.5	0.69	5.8
	H_2O/HCl	202	10.7	0.65	6.6
	EtOH/HCl	244	10.8	0.67	6.4
	HT	267	11.4	0.57	12.6
Sulfite pulp	Starting material	540	23.5	1.36	12.8
	H_2O/HCl	267	22.6	1.27	15.6
	EtOH/HCl	289	22.9	1.45	10.7
	HT	295	22.7	1.16	18.4
New sheets	Starting material	1654	18.1	0.86	6.6
	H_2O/HCl	235	18.3	0.89	7.5
	EtOH/HCl	329	18.5	0.81	9.9
	HT	392	18.2	0.70	14.1
Discarded sheets	Starting material	518	18.3	0.69	10.6
	H_2O/HCl	221	17.5	0.76	7.2
	EtOH/HCl	255	17.7	0.62	14.5
	HT	297	17.3	0.56	18.6

The pretreatments were performed to give resulting intrinsic viscosities in the range between approximately 200 and 300 cm^3/g. The treatment time was the same for all of the samples (60 min in H_2O/HCl and EtOH/HCl, and 240 min in hydrothermal treatment, HT), which resulted in intrinsic viscosities somewhat above 300 cm^3/g for the New sheets (see Table 2). This was due to the higher intrinsic viscosity of the New sheet starting material that was 1654 cm^3/g compared to the other starting materials that had intrinsic viscosities in the range of 423 and 518 cm^3/g.

In Table 2, the width, length, and fines content are reported for the starting material and the pretreated samples (H_2O/HCl, EtOH/HCl, and HT). As anticipated, the length of the Scandinavian softwood fibers in the Sulfite pulp were longer than the Eucalyptus fibers in the PHK-pulp. The length of the cotton fibers was affected by the milling in the Wiley mill; however, the hydrothermal treatment further decreased the fiber length. The fines content varied between the different samples; still, there were more fines in all of the samples after hydrothermal pretreatment. High temperature and mechanical agitation have been shown to cause damage to fibers, which may explain this behavior (Fahlén and Salmén 2005b).

Changes in the supramolecular structure were analyzed using NMR analysis, and the findings are reported in Table 3 for the starting material and the pretreated samples. An increase in the fibril aggregate size (LFAD) was found after pretreatment of the Sulfite pulp and the PHK pulp. However, these findings only indicated a minor change in the CI. During the pulping process, when the PHK-pulp is produced, fibers swell due to the alkaline conditions of the process. This swelling, combined with the removal of lignin and remaining hemicellulose, is believed to promote fibril aggregation (Hult *et al.* 2001). However, despite the differences between both the pulping method and wood species, the changes observed in LFAD and CI during acid hydrolysis of the PHK-pulp and the Sulfite pulp were similar, which indicated a co-crystallization and/or coalescence after acid pretreatment. An increase in the degree of coalescence of cellulose fibrils has also been associated with hornification, which increases fibril aggregate size (Hult *et al.* 2001; Kontturi and Vuorinen 2009). Furthermore, partial co-crystallization of adjacent fibrils has been shown to occur during hornification (Newman 2004). In the findings from the NMR analysis of the wood pulp samples (PHK-pulp and Sulfite pulp), shown in Table 3, an increase in fibril aggregate size can be seen, similar to what happened during drying. Based on this observation it is suggested that the decrease in DP is accompanied by a scission of fibrils, which could allow for an increase in the degree of aggregation (coalescence), which could explain the minor increase in the degree of crystallinity/increased LFD.

The findings in Table 3 indicate that the relative increase in LFAD was less for the cotton samples than for the dissolving pulps in acid hydrolysis (H_2O/HCl) and acid hydrolysis in ethanol (EtOH/HCl). The cotton had large fibril aggregates and higher crystallinity from the beginning, and it was possible that this made the cotton less susceptible to acid hydrolysis or a further increase in the LFAD. However, when the cotton samples were subjected to the high temperature in the HT pretreatment, this caused an increase in the fibril aggregate size, both in the New and the Discarded sheets. Furthermore, the largest fibril aggregate size was detected in the Discarded sheets after the HT pretreatment. A tentative explanation for the somewhat lower tendency of fibril aggregation in New sheets could be that the large decrease in the DP of the New cotton sheets may lead to excessive formation of glucan fragments that remain between the fibril, spacers preventing close proximity between neighboring fibrils. It is possible that these can act as a spacer, similar to the effect hemicelluloses have in preventing hornification.

Table 3. Molecular and Supramolecular Properties of the Starting Material and the Pretreated Samples

Sample	Treatment	LFD (nm)	LFAD (nm)	CI (%)	LFAD SSA (m^2/g)
PHK-pulp	Starting material	4.4 ± 0.1	23.2 ± 0.9	55 ± 1	115 ± 4
	H_2O/HCl	4.6 ± 0.1	26.0 ± 1.1	57 ± 1	103 ± 4
	EtOH/HCl	4.6 ± 0.1	28.6 ± 1.1	56 ± 1	93 ± 4
	HT	4.6 ± 0.1	28.2 ± 1.2	57 ± 1	95 ± 4
Sulfite pulp	Starting material	4.3 ± 0.1	22.1 ± 0.7	54 ± 1	121 ± 4
	H_2O/HCl	4.6 ± 0.1	24.6 ± 1.0	57 ± 1	108 ± 4
	EtOH/HCl	4.5 ± 0.1	25.2 ± 1.0	56 ± 1	106 ± 4
	HT	4.6 ± 0.1	29.9 ± 1.4	57 ± 1	89 ± 4
New sheets	Starting material	5.6 ± 0.1	38.9 ± 1.9	64 ± 2	69 ± 2
	H_2O/HCl	6.2 ± 0.2	40.2 ± 2.2	67 ± 2	66 ± 4
	EtOH/HCl	5.9 ± 0.2	33.5 ± 1.9	65 ± 2	80 ± 5
	HT	6.5 ± 0.2	50.2 ± 3.3	68 ± 2	53 ± 3
Discarded sheets	Starting material	6.0 ± 0.2	42.0 ± 2.3	66 ± 2	63 ± 4
	H_2O/HCl	6.3 ± 0.2	37.9 ± 2.2	67 ± 2	70 ± 4
	EtOH/HCl	6.2 ± 0.2	40.7 ± 2.6	67 ± 2	66 ± 4
	HT	6.7 ± 0.2	64.5 ± 4.2	69 ± 2	41 ± 3

The objective of the current study was to investigate the effect of three different pretreatments on cotton fibers and dissolving pulp. The pretreatments are important to provide an incoming feed of cotton textiles to a recycling facility, with a narrow molecular mass distribution. In Table 4, the results from size exclusion chromatography are listed, and this shows that the dispersity of the samples decreased after all pretreatments.

Table 4. Results from Size Exclusion Chromatography Analysis of the Different Cellulosic Fibers Before and After Acid Catalyzed Pretreatment

Sample	Treatment	M_n (kDa)	M_w (kDa)	D (M_w/M_n)
PHK-pulp	Starting material	59	182	3.1
	H_2O/HCl	29	72	2.5
	EtOH/HCl	33	87	2.7
	HT	33	81	2.5
Sulfite pulp	Starting material	40	283	7.0
	H_2O/HCl	34	109	3.2
	EtOH/HCl	33	116	3.5
	HT	33	135	4.1
New sheets	Starting material	193	813	4.2
	H_2O/HCl	36	86	2.4
	EtOH/HCl	55	120	2.2
	HT	60	139	2.3
Discarded sheets	Starting material	87	224	2.6
	H_2O/HCl	32	74	2.3
	EtOH/HCl	39	89	2.3
	HT	46	105	2.3

Effect of Supramolecular Structure on Swelling

After the analysis of the supramolecular structure, presented above, the effect of swelling and dissolution will be presented and discussed. The swelling was studied in dilute CED at three different concentrations (0.16 M, 0.18 M, and 0.20 M), which were chosen to maximize swelling without dissolving the samples. To avoid dissolution, the chosen concentrations were lower than the concentrations used when determining intrinsic viscosity, in which a sample is dissolved in 0.5 M CED. However, the results indicated that partial dissolution did occur. The quantification of the swelling was calculated as width variation (see Eq. 1), in the material and methods section. The width variation is the increase in swelling compared to the water-swollen samples when a sample is subjected to CED.

As expected, the width variation increased with the CED concentration for the two dissolving pulps, PHK-pulp (Fig. 1a) and Sulfite pulp (Fig. 1b), and this was a strong indication that swelling occurred. The decrease in width variation at 0.20 M CED for the Sulfite pulp was probably due to the dissolution of the fibers instead of swelling, as can be seen also in the microscopy section below. To investigate this, the starting material and HT-treated samples of Sulfite pulp fibers were analyzed with solid state ^{13}C NMR after swelling in 0.16 M CED and the subsequent quenching of the swelling by the addition of 0.5 L of acetate buffer. The results showed a small peak from Cellulose II in both samples. This indicated that a small part was highly swollen or dissolved, but at 0.16 M most of the cellulose was only swollen but not dissolved.

None of the pretreatments (H_2O/HCl, EtOH/HCl, or HT) stood out as more effective than any other in terms of fiber swelling. However, the findings indicated that the harsh hydrothermal pretreatment decreased the swellability of the material. This was connected to the increase in the fibril aggregate size that was caused by the long treatment time at high temperature (170 °C). The hydrothermal pretreatment led to the largest increase in fibril aggregate size in both the dissolving pulp samples and in the cotton samples, as presented in the previous section. It has been shown that high temperature treatment may lead to fibril aggregation (Fahlén and Salmén 2005a). It has been proposed that cellulose dissolution must involve two processes: decrystallization and chain disentanglement (Ghasemi *et al.* 2016). Based on this, one can hypothesize that a decrease in the cellulose chain length would mainly impact the disentanglement, but when studying swelling it is mainly the decrystallization that is impacted. This could explain why the pretreatments did not show any large effect in the swelling experiments.

The change in width variation for the two sheet samples, New (Fig. 1c) and Discarded (Fig. 1d), was small for both the pretreated samples and starting material. Thus, the cotton fibers were hard to swell even in the highest concentration of CED. However, one sheet sample stood out as slightly more swellable than the other cotton sheets, the New sheet starting material (Fig. 1c; New starting material). It had a lower LFD than the pretreated samples (see Table 3); however, the difference in LFAD did not indicate large fibril aggregation. Compared to the Discarded sheet samples, it is possible that the slightly higher FSP of the New sheet samples, listed in Table 1, made the New cotton fibers more accessible to the solvent. Due to the high DP of the New starting material, disentanglement of the cellulose chains would still be hard, thus limiting dissolution of the sample (Ghasemi *et al.* 2016).

When comparing the findings from the swelling experiments to the supramolecular structure of the samples, no apparent correlation between the LFAD and width variation was visible. This showed that many factors contributed to swelling. However, the data indicated that cotton, which had much larger fibril aggregates and a lower FSP, was harder to swell than the dissolving pulps. However, the HT, which caused an increase in LFAD and crystallinity, seemed to decrease the swellability of the Sulfite pulp and the PHK pulp samples.

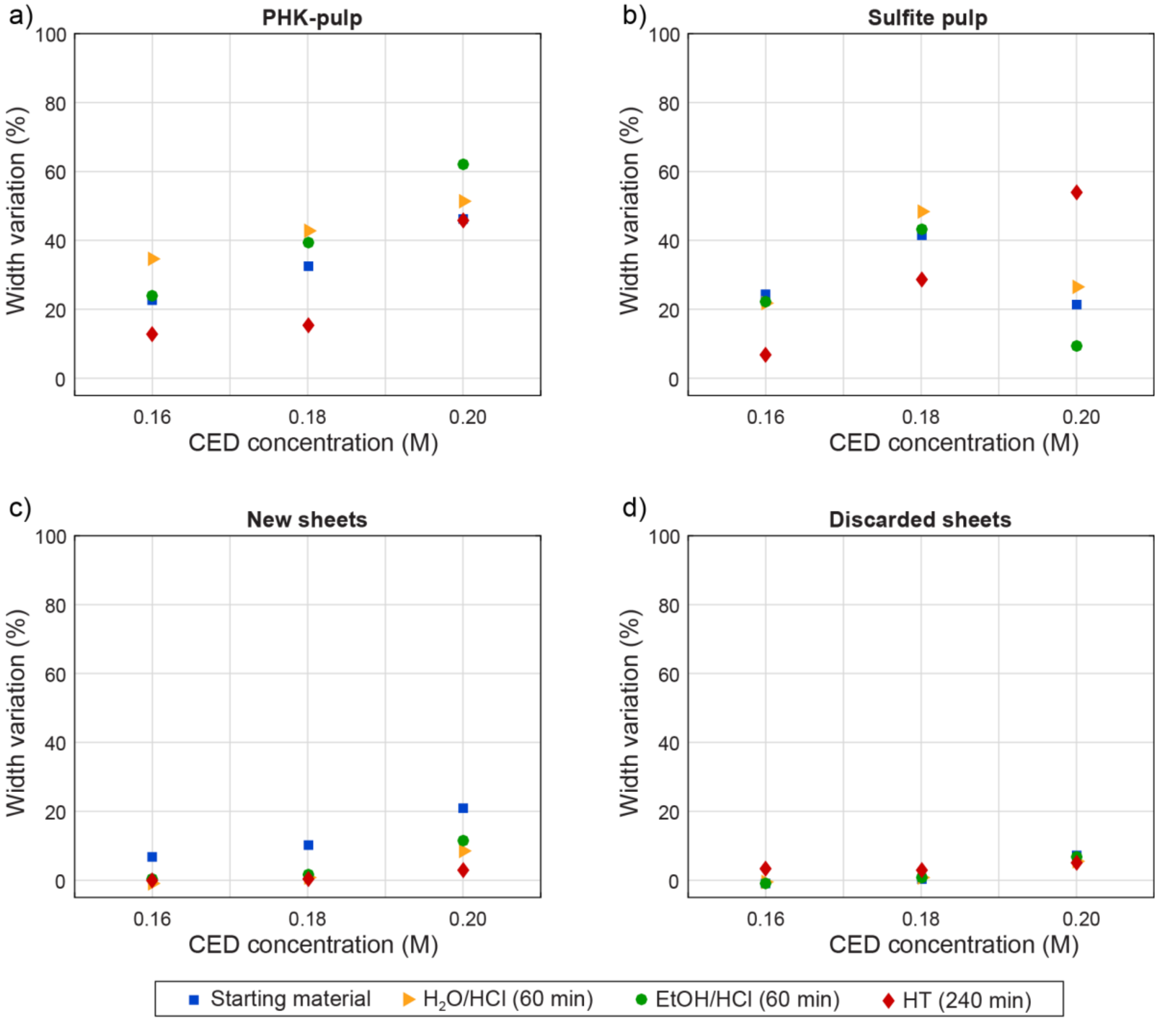

Fig. 1. Width variation at different CED concentrations; sheet samples for which some slightly negative values were obtained are neglected here

Microscopy

In this last part of the Results and Discussion, the swelling measurements by the fiber analyzer are compared to a microscopy analysis. The measurements of swelling presented in the previous section can be considered as an automated microscopy analysis. The benefit of using a fiber analyzer is that the minor differences in width may only be possible to quantify after the measurement of many fibers, which is time consuming using a microscope. During each run in the fiber analyzer, more than 20,000 fibers were analyzed. One drawback, on the other hand, is that details, which may be observed during ocular inspection, are lost with automated equipment. Thus, the swelling measurements analyzed with the fiber analyzer are complemented with ocular inspection using an optical microscope.

The microscopy investigation was performed at the same dilute concentrations of CED as the swelling experiments (0.16 M, 0.18 M, and 0.20 M) for the dissolving pulp samples, and the findings are summarized in Table 5. However, since the cotton was hard to swell, the concentrations were increased when analyzing the cotton samples, and thus 0.16 M, 0.20 M, and 0.24 M CED were used (see Table 5). The images were taken as time-lapse sequences, as described in the methods section, to obtain images evenly spread out over a few minutes. The swelling and dissolution were sensitive to fiber entanglement; therefore, the starting concentration of fibers was carefully controlled to ensure that only a few fibers were present on the microscope slide. The images in Fig. 2 show the dissolution process of the samples pretreated using acid hydrolysis (H_2O/HCl) after being subjected to CED for 1 min.

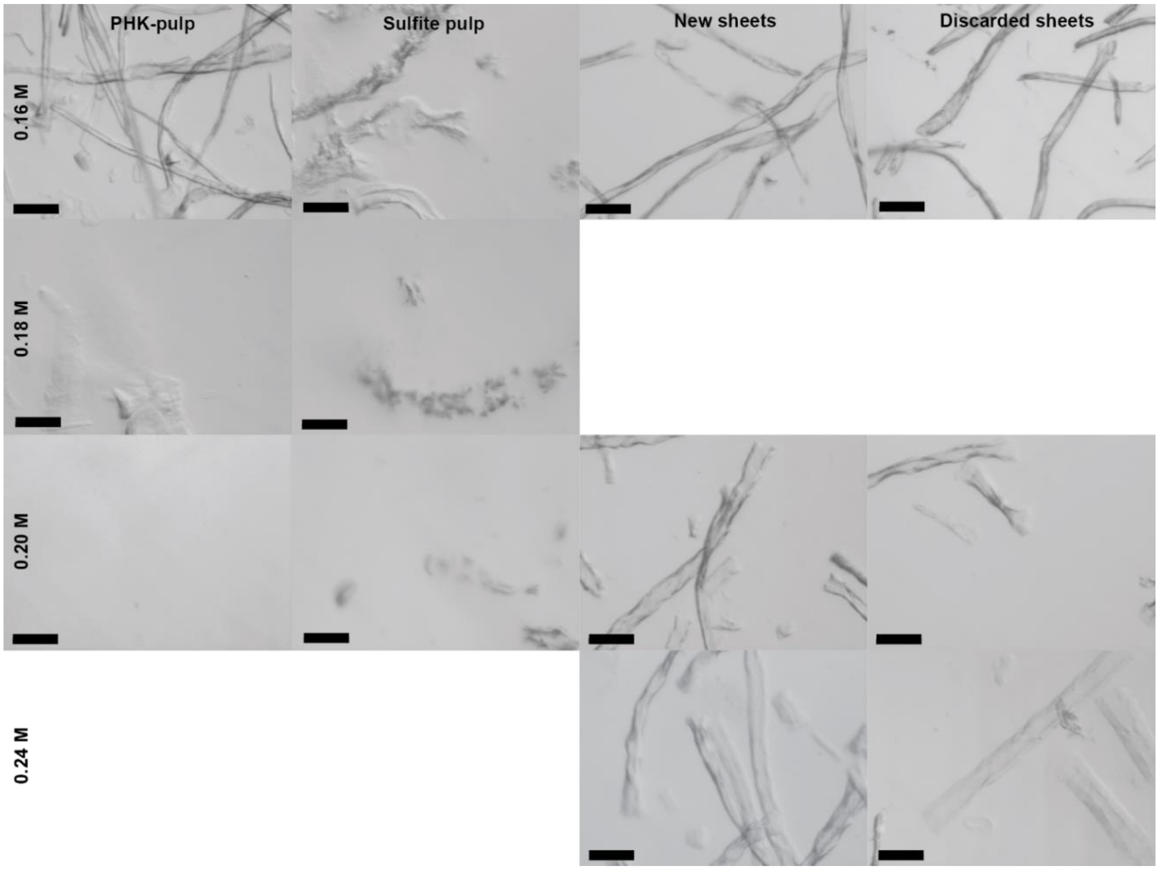

Fig. 2. Microscopy pictures of fiber samples following acid hydrolysis pretreatment after being subjected to different concentrations of CED for 1 min; the scale bar shows 0.1 mm

To compare how far the dissolution process had progressed in different samples, the process was categorized into one of four dissolution modes according to the method developed by Le Moigne *et al.* (2008). In a good solvent, or for a cellulosic material that is easy to dissolve, the dissolution occurs almost instantaneous over a whole fiber, and this is referred to as fragmentation. The second mode is ballooning, in which dissolution still occurs, however, through a different mechanism.

Table 5. Summary of the Findings of Ocular Inspection of the Swelling and Dissolution of PHK-pulp, Sulfite pulp, and New and Discarded Cotton Sheet Samples in the CED Concentrations as Noted

		0.16 M	**0.18 M**	**0.20 M**
PHK-pulp	Starting material	Homogenous swelling; Ballooning	Homogenous swelling; Ballooning	Apparent dissolution; Ballooning
	H_2O/HCl	Homogenous swelling; Ballooning	Apparent dissolution; Ballooning	Apparent dissolution; Ballooning
	EtOH/HCl	Homogenous swelling; Ballooning	Apparent dissolution; Ballooning	Apparent dissolution; Ballooning
	HT	Homogenous swelling; Ballooning	Apparent dissolution; Ballooning	Apparent dissolution; Ballooning
Sulfite pulp	Starting material	Ballooning swelling	Apparent dissolution; Ballooning	Apparent dissolution; Fragmentation
	H_2O/HCl	Apparent dissolution; Fragmentation	Apparent dissolution; Fragmentation	Apparent dissolution; Fragmentation
	EtOH/HCl	Apparent dissolution; Fragmentation	Apparent dissolution; Fragmentation	Apparent dissolution; Fragmentation
	HT	Apparent dissolution; Fragmentation	Apparent dissolution; Fragmentation	Apparent dissolution; Fragmentation
		0.16 M	**0.18 M**	**0.24 M**
New sheets	Starting material	No swelling	Homogenous swelling	Homogenous swelling; Ballooning; Partial dissolution
	H_2O/HCl	No swelling	Homogenous swelling	Homogenous swelling; Ballooning; Partial dissolution
	EtOH/HCl	No swelling	Homogenous swelling	Homogenous swelling; Ballooning; Partial dissolution
	HT	No swelling	Homogenous swelling	Homogenous swelling; Ballooning; Partial dissolution
Discarded sheets	Starting material	No swelling	Homogenous swelling	Homogenous swelling; Partial dissolution
	H_2O/HCl	No swelling	Homogenous swelling	Homogenous swelling; Partial dissolution
	EtOH/HCl	No swelling	Homogenous swelling	Homogenous swelling
	HT	No swelling	Low swelling	Homogenous swelling

In ballooning, the fiber structure is broken at sensitive spots of the fiber, such as dislocations, which allows the dissolution to continue from these points. Both of these modes, fragmentation and ballooning, lead to dissolution. There are also two modes in which dissolution does not occur; ballooning without dissolution and homogenous/low swelling. In Table 5, the samples are categorized according to this system. Since dissolution is a complicated molecular process, the term "apparent dissolution" herein means no cellulose fragments were visible at the resolution of the microscope and at the contrast of the sample materials.

When the PHK-pulp was subjected to CED, there was a clear difference between 0.16 M and 0.18 M. In 0.16 M, homogenous swelling and ballooning occurred, however, no dissolution was detected. In 0.18 M and 0.20 M, apparent dissolution occurred, *i.e.*, after 4.5 min no fiber fragments were detected. The only exception was the starting material, in which 0.20 M was needed to achieve full apparent dissolution. This could have indicated that the concentration of CED used in the swelling experiments was too high, which led to dissolution instead of swelling. However, the microscopy analysis of fibers from the PHK-pulp that had been swelled and quenched using the same procedure as when analyzed in the fiber analyzer previously after quenching, were highly swollen but not disintegrated into fragments. Thus, the apparent dissolution that was observed in some samples, mainly showed highly swollen fibers that can reclaim fiber structure after quenching.

The microscopy images of the Sulfite pulp showed a behavior different from that observed for the PHK-pulp. Fragmentation and dissolution occurred in all of the Sulfite pulp samples except for the starting material at 0.16 M. Analysis of the fibers after quenching showed that these fibers did not regain fiber structure after quenching to the same extent as the PHK-pulp, and this may explain the decrease in the width variation of the Sulfite pulp samples at 0.20 M (see Fig. 1).

The cotton sheet samples (New and Discarded) required a higher concentration of CED to swell, as observed in the swelling experiments (Fig. 1). However, at 0.24 M CED, swelling and apparent dissolution partly occurred. The cotton samples did not exhibit ballooning to the same extent as the PHK and Sulfite pulp samples, although some ballooning was observed in these samples. There was no distinguishable difference between the staring material and pretreated samples, not even in the New starting material, which showed higher swelling in the swelling experiments as measured by the fiber analyzer. Since the difference quantified with the fiber analyzer was small, the difference may be hard to detect *via* ocular inspection of a few fibers.

Overall, findings from the swelling measurements were confirmed with the microscopy analysis. The Sulfite pulp was more swellable than the PHK-pulp, and the cotton sheet samples required higher concentrations of CED to swell than the pulp samples.

CONCLUSIONS

1. There are major differences between the swelling of cotton samples and the swelling of dissolving pulp samples. The pretreatments performed did not substantially increase the swellability of any of the samples. In contrast, the HT pretreatment increased the fibril aggregate size of the samples, which coincided with a decrease in swellability.
2. To swell cotton samples, higher concentrations of CED were needed than for the Sulfite pulp and the PHK pulp. For future recycling of cotton into regenerated fibers, this

indicates that special attention has to be paid to the low susceptibility of heavily used and laundered cotton fibers towards swelling, possibly limiting the dissolution of the fibers.

3. A comparison of the dissolving pulps showed that the softwood Sulfite pulp was easier to swell, and dissolution occurred mainly through fragmentation. The PHK-pulp was also highly swellable, but mainly dissolved through ballooning.
4. The analysis of the effect on the supramolecular structure after the pretreatments showed that these treatments may have an impact similar to drying, which leads to fibril aggregation. This is important to consider when choosing a pretreatment method as it may prove detrimental to dissolution.

ACKNOWLEDGMENTS

This work was performed within the Mistra Future Fashion program. Financial support from Mistra – The Swedish Foundation for Strategic Environmental Research – and from the Swedish foundation “Södra Skogsägarna Stiftelse för Forskning, Utveckling och Utbildning [Södra Skogsägarna Foundation for Research, Development and Education]” is gratefully acknowledged. The authors would also like to thank Textilia for providing the cotton sheets.

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Article submitted: February 26, 2019; Peer review completed: May 3, 2019; Revised version received and accepted: May 24, 2019; Published: June 3, 2019.
DOI: 10.15376/biores.14.3.5698-5715