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Chemical and ultrastructural changes in cotton cellulose induced by laundering and textile use

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Abstract The textile industry is currently under pressure to decrease environmental load related to both the manufacture and the use of textiles. Material recycling may be one of many ways to accomplish such a decrease. Age-induced property changes in cotton textiles are important to understand in order to facilitate the recycling of cotton textiles. Consequently, this study investigates ultrastructural and chemical changes that take place in the cellulose of cotton sheets over a long time period of use and laundering. Ultrastructural changes were studied using water retention value (WRV), specific surface area measurement, scanning electron microscopy and solid state NMR spectroscopy. Chemical changes through measurement of intrinsic viscosity with and without reductive treatment, molecular mass distribution and carboxylate group content. A substantial decrease in mass average molecular mass from 1,320 to 151 kDa was observed when subjecting the sheets to more than 50 launderings. In contrast, only small differences in WRV, in fibril dimensions and crystallinity estimated using solid state NMR spectra, were observed between sheets laundered 2–4 times and more than 50 times. On one hand, the combination of minor laundering effects of WRV and solid state NMR spectra, together with the large decrease in molecular mass are positive indications for the possibility of recycling cotton into regenerated cellulosic fibres. On the other hand, results show that the specific surface area decreased, which implies that the reactivity of cotton cellulose may decrease during long-term use and laundering.

Keywords Cotton · Cellulose · Hornification · Laundering · Solid state NMR · Molecular mass distribution

Introduction

Systems for collection and recycling of common consumer goods, such as paper, plastics and glass are well developed in many parts of the world today. One product category which is still underdeveloped in terms of recycling is clothing and textiles. The lifecycle of a garment may be expanded through reuse, but only if the garment still has good quality without damages or stains. Garments and textiles that are not suitable for reuse may be mechanically shredded and

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used for products such as carpet underlays and upholstery (Morley et al. 2006; Palm 2011). In order to gain both economic and environmental benefits, more efficient recycling of textiles is needed. Using old cotton textiles as a raw material to produce regenerated cellulosic fibres, such as viscose or lyocell, is an attractive alternative end-of life scenario in comparison to incineration or landfilling (Negulescu et al. 1998). To enable this development, more knowledge of changes induced by use and laundering in post-consumer cotton textiles is needed.

The focus of this study is on ageing cotton textiles, and the motivation, apart from the applied perspective, is that understanding of this process will contribute to more basic understanding of how cellulosic materials age. The ageing of cellulose in paper has been extensively investigated in applications such as archiving of books (Wilson and Parks 1979) and the recycling of paper (Hubbe et al. 2007). Books or other archived paper, produced under acid conditions, may deteriorate rapidly through the acid hydrolysis of the cellulose (Kato and Cameron 1999). In paper recycling, the repeated drying and rewetting cycles lead to a decrease in the swelling ability of chemical pulp fibres. This change in swelling behaviour has been defined as hornification by Jayme (1944; Weise 1998). Today, the term hornification is used in a broader sense to describe changes in chemical pulp fibres attributed to drying, such as stiffer and less conformable fibres (Hubbe et al. 2007). These changes are associated with the non-reversible closing of nano-sized pores in the fibres during drying, due to coalescence of cellulose fibril aggregates (Pönni et al. 2012). The coalescence is often explained by the formation of hydrogen bonds between the cellulose fibril aggregates in the fibre walls, but cross-linking reactions that lead to the formation of covalent bonds have also been suggested (Hubbe et al. 2007; Laivins and Scallan 1993). In addition, solid state NMR studies have shown that co-crystallization between cellulose fibrils is another possible reason for the formation of bonds between fibril aggregates (Idström et al. 2013; Newman 1999). Furthermore, the closing of small pores and the increase in fibril aggregate size will lead to a decrease in accessible surface area.

A textile is subjected to numerous laundering cycles during its life time, and, consequently, many drying and rewetting cycles. It is, therefore, reasonable to believe that used cotton fibres, ready for recycling, have different properties compared to virgin cotton. Detergent formulations are often alkaline and may contain oxidants, such as peroxides and hypochlorite. This means that laundering may lead to the chemical degradation of cellulose through cellulose oxidation and alkali-promoted reactions. Laundering is known to cause a decrease in the degree of polymerization (DP) of cellulose in cotton. Such a decrease is well correlated with a reduction in the tensile strength of fabrics, and consequently, chemical wear during washing is important to control in industrial laundering (Vaeck 1966). This correlation between laundering, the decrease in the DP and strength loss is also one of the reasons to why mechanical recycling of cotton fibres from textiles gives a product of low strength, even if long fibres are maintained.

In the present study, ultrastructural changes and chemical degradation during the use phase of cotton textiles are examined, since these are important factors to consider when evaluating possibilities for recycling cotton cellulose. To gain comprehensive knowledge about the development of changes in the cotton fibre during the use phase, cellulose in cotton sheets used at hospitals for different length of times has been characterized.

Experimental

Material

Four cotton sheets, made from cotton from Pakistan, were provided by a large Swedish supplier of service textiles. Before weaving, an additive had been applied on the yarn to facilitate weaving. One sheet had never been laundered, one had never been used, but laundered 2–4 times, since it is a general procedure of the textile provider to launder these sheets before use. The other two sheets had been in use in hospitals, one was laundered approximately 50 times and the other one was laundered more than 50 times. This sheet was from the fraction laundered maximum 150 times and classified as worn out and ready for incineration. The never-laundered sheets are off white, and the first 2–4 launderings remove most of the colour and the sheets are perceived as white, when used the first time.

The laundering was performed by the service provider using an industrial laundering system with a maximum temperature of 84 °C and the washing agent Clax Hellux free 3EP3, from JohnsonDiversey Sverige AB, an alkaline detergent with a pH between 12 and 12.5, in 1 % solution. The washing agent does not contain any oxidants. After laundering, water is pressed out of the fabric prior to tumble drying.

Before all of the analyses, with the exception of scanning electron microscopy (SEM) imaging, the sheets were ripped into approximately 1 cm^2 pieces and ground using a Wiley mill (<1 mm). The ground textiles samples were extracted with light petroleum and water, according to ISO 18:33-1:2010. In the case of the never-laundered sheet, traces of a non-cellulosic weaving additive on the fibres were found using NMR spectroscopy, even after the extraction. The presence of the non-cellulosic additive in extracted fibres from the never-laundered sheet was also proved in a test in which a water droplet was placed on dried fibre pads from the extracted fibres. The droplet was immediately absorbed into all of the fibre pads, except for the fibre pad containing fibres from the never-laundered sheet where the contact angle of the droplet was >105°. No further attempts were made to characterize this non-cellulosic material. However, this contamination obstructed the measurements of specific surface area, water retention value (WRV) and carboxylic acid content for the never-laundered sheet.

Methods

The WRV was measured according to the SCAN-C 62:00 method. The ground and extracted samples were maintained in the wet state before the analysis to avoid further hornification.

The specific surface area was calculated according to the BET theory (Brunauer–Emmett–Teller) from measurement of nitrogen adsorption using a Micromeritics TriStar 3000 instrument. In order to avoid hornification during the drying of the samples, a solvent exchange was performed to replace water with cyclohexane. This was done through a solvent exchange procedure in which the water was initially replaced with dry acetone, and then the dry acetone was replaced with cyclohexane (Köhnke et al. 2010; Wang et al. 2003). After the solvent exchange, the samples were dried in a nitrogen stream overnight.

Micrographs of non-extracted samples were collected by 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.

The intrinsic viscosity of the cellulose samples was measured after dissolution in Cuen [copper(II)ethylenediamine] according to the SCAN-C 15:99 method. Before the analysis, the samples were ground, extracted and dried. The analysis was also performed on samples after reductive treatment with sodium borohydride ($NaBH_4$) essentially according to Lindholm (1992). The samples were reacted with 5 % $NaBH_4$ relative to the pulp at 4 % consistency for 24 h at room temperature. After this reaction, the samples were carefully washed with water.

Size exclusion chromatography was carried out after dissolution of the samples in lithium chloride/N,N-dimethylacetamid (Li/DMAc) according to Henniges et al. (2011). 20 mg (dry weight) of the sample was suspended in deionized water and then dewatered on 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 vials were placed on the laboratory shaker for 16–40 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 was 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 × 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 dn/dc used was 0.136 ml/g. Data evaluation was performed with standard Astra and Chromeleon software (6.1.17).

The content of carboxylate groups was analysed using the adsorption of methylene blue on the ground and extracted samples (Davidson 1948; Fardim et al. 2002). In the analysis, approximately 1 g of sample was suspended in a 100 ml phosphate buffer solution (pH 7.8, 0.1 mM Na^+) containing methylene blue (0.16 g/l). After 1 h of stirring in the dark the sample was filtered off and a sample of the filtrate was taken out and analysed using UV–Vis spectroscopy. The adsorbed amount of methylene blue was measured using an UV–Vis spectrophotometer (Specord PC 205, Analytikjena) at 664 nm through comparison of the absorption of the filtrate and a calibration curve, prepared from solutions of known amounts of methylene blue. The molar concentration of carboxylate groups was estimated as equivalent to the molar concentration of adsorbed methylene blue.

All 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 of was carried out according to Wickholm et al. (1998) in 2.5 M HCl at 100 °C for 17 h. The resulting cellulose was washed several times by centrifuging the samples, decanting the supernatant and adding fresh water.

NMR data analysis

Spectral deconvolution was applied to all NMR spectra according to the method described by Wickholm (2001). The well-resolved C4 region, between 80 and 91 ppm, consisting of one crystalline and one amorphous region respectively, can be deconvoluted as a sum of seven signals, as illustrated by the CP/MAS spectrum in Fig. 1a. The crystalline region was deconvoluted as a sum of four signals where the three narrow signals originate from crystalline parts of the cellulose, and the broader, underlying signal, originates from paracrystalline parts (Atalla and VanderHart 1999). The amorphous region was deconvoluted as a sum of three signals where two sharper signals, at 85 and 84 ppm, originate from accessible surface nuclei (Park et al. 2010) and the broad signal at 84.5 ppm corresponds to inaccessible surface nuclei (Wickholm et al. 1998). Based on this deconvolution pattern, Wickholm (2001) has proposed a cross-sectional model of the fibril aggregate, seen in Fig. 1b. By using this model, all deconvoluted signals can be attributed to cellulose chains in different parts of the cellulose fibril (Wickholm 2001).

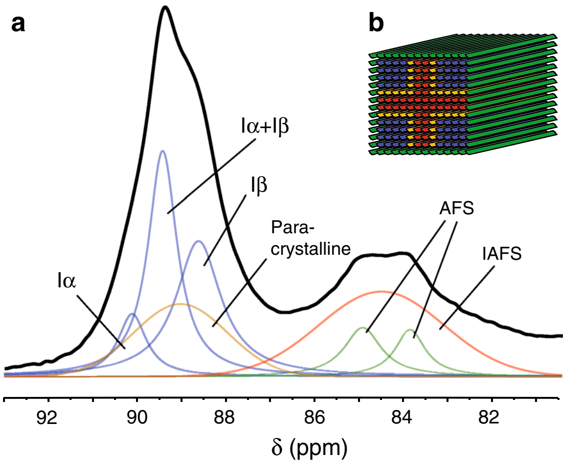

Fig. 1 CP/MAS ^{13}C-NMR spectrum with **a** deconvolution of the C4 region of a cellulose I sample and **b** the cellulose fibril model, as described by Wickholm (2001). Deconvoluted signals in the spectrum can be attributed to cellulose chains in different parts of the cellulose fibril model. Crystalline chains (Iα and Iβ) are shown in *blue*, paracrystalline chains in *yellow*, accessible fibril surface (AFS) in *green* and inaccessible fibril surface (IAFS) in *red*. (Color figure online)

The lateral size of the elementary fibril and the fibril aggregate of cellulose could be determined using the model proposed by Wickholm. However, in order to determine accurate dimensions of elementary fibril and fibril aggregates in cellulosic fibres with solid state NMR, the internal amorphous signals must be distinguished from those of external amorphous signals. This has previously been accomplished by either using acid hydrolysis (Virtanen et al. 2008; Hult et al. 2001) to remove the unwanted signals, or using spin-relaxation editing (Newman 1999). In this investigation, the amorphous cellulose that did not originate from the elementary fibril and fibril aggregate surfaces was removed with an acid hydrolysis pretreatment. The lateral dimensions of the elementary fibril were calculated based on the assumption that the crystalline signals originate from the inner part of the elementary fibril, whereas both the signals from the accessible and inaccessible surfaces originate from the surface of the elementary fibril, Fig. 2a. In the calculations of the lateral dimensions of the entire fibril aggregate, the surface is assumed to be accounted for in the accessible surface, and both the inaccessible surfaces and the crystalline signals are counted as internal signals, Fig. 2b.

Assuming a square cross-section, the average number of cellulose chains, n, in the lateral dimension can be calculated, using the equation derived from (Newman 1999),

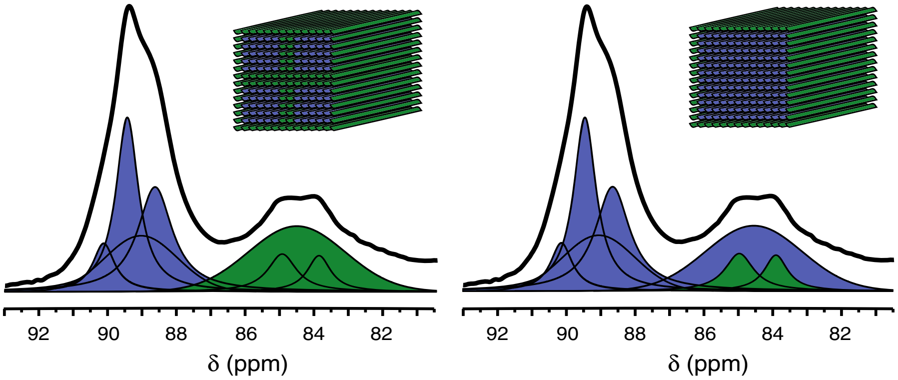

Fig. 2 CP/MAS ^{13}C-NMR spectra shows the deconvolution of internal and surface signals used for determining the dimensions of fibril and fibril aggregates. Models as described by Wickholm (2001) are shown as *insets*

$$n = 2/(1 - \sqrt{q})$$

where q is the fraction of the total signal originating from internal cellulose chains. The number of chains can then be multiplied by the thickness of the cellulose chains, to give the dimensions. A value of 0.57 nm per cellulose chain (Sugiyama et al. 1991) was used to calculate the elementary fibril and fibril aggregate dimensions.

The crystallinity index (CI) of non-hydrolysed material was calculated from the CP/MAS ^{13}C-NMR spectra using two different methods. In the first method, the NMR signals of the C4 carbon in cellulose were separated into two spectral regions, one at 87–93, originating from crystalline cellulose, and one at 80–87 ppm, originating from amorphous cellulose. The CI was calculated by dividing the intensity of the signal at 87–93 ppm by the total C4 area (Newman 1999). The second method accounted for the deconvolution of the C4 signals. The CI was calculated by dividing the integral of deconvoluted signals that originate from crystalline chains with the total integral of all deconvoluted C4 signals (Hult et al. 2001).

Results and discussion

The analysed material comprised samples prepared from cotton sheets used at hospitals and laundered a different number of times. The estimated number of launderings of the sheets was 0, 2–4, approx. 50, and more than 50 times. During textile production, an additive had been applied to facilitate the weaving. Comparison of the SEM-micrograph of the never-laundered sample, Fig. 3a, with the sample laundered 2–4 times, Fig. 3b, shows that the weaving additive had been removed in the first launderings. Inspection of the micrographs also revealed damage from wet and dry abrasion that occurred during laundering and drying. Fibrillation of fibres is mainly caused by wet abrasion in the laundering, whereas cracking is caused by dry abrasion in the tumble drying (Goynes and Rollins 1971; Buisson et al. 2000). Only two of the sheets displayed cracks. These were the sheet laundered 50 times, Fig. 3c, and the sheet laundered more than 50 times, Fig. 3d. However, some fibrillation was observed as early as after 2–4 launderings.

The ability of the cotton fibres to swell in water was determined by analysing the WRV of the samples in order to investigate how the use of the sheets affects the extent of hornification. When cotton fibres mature in the field, the cotton bolls open and dry. Measurements on never-dried cotton fibres are rare, since the cotton bolls must be picked before opening. However, Nelson et al. (1980) have measured the WRV of never-dried and air-dried cotton fibres. The measurements have shown that the WRV of an un-opened cotton boll (never-dried) was 1.4 g/g, whereas the WRV of field-dried cotton was 0.46 g/g. For comparison, the WRV of never-dried Kraft pulp has been reported to drop from 1.5 to 1.0 g/g when subjected to one drying and rewetting cycle (Köhnke et al. 2010). The decrease in the WRV of cotton during the initial drying is, thus, much larger in cotton compared to pulp. Furthermore, if the relative decrease in WRV is used as the definition of hornification (cf. Jayme 1944), then

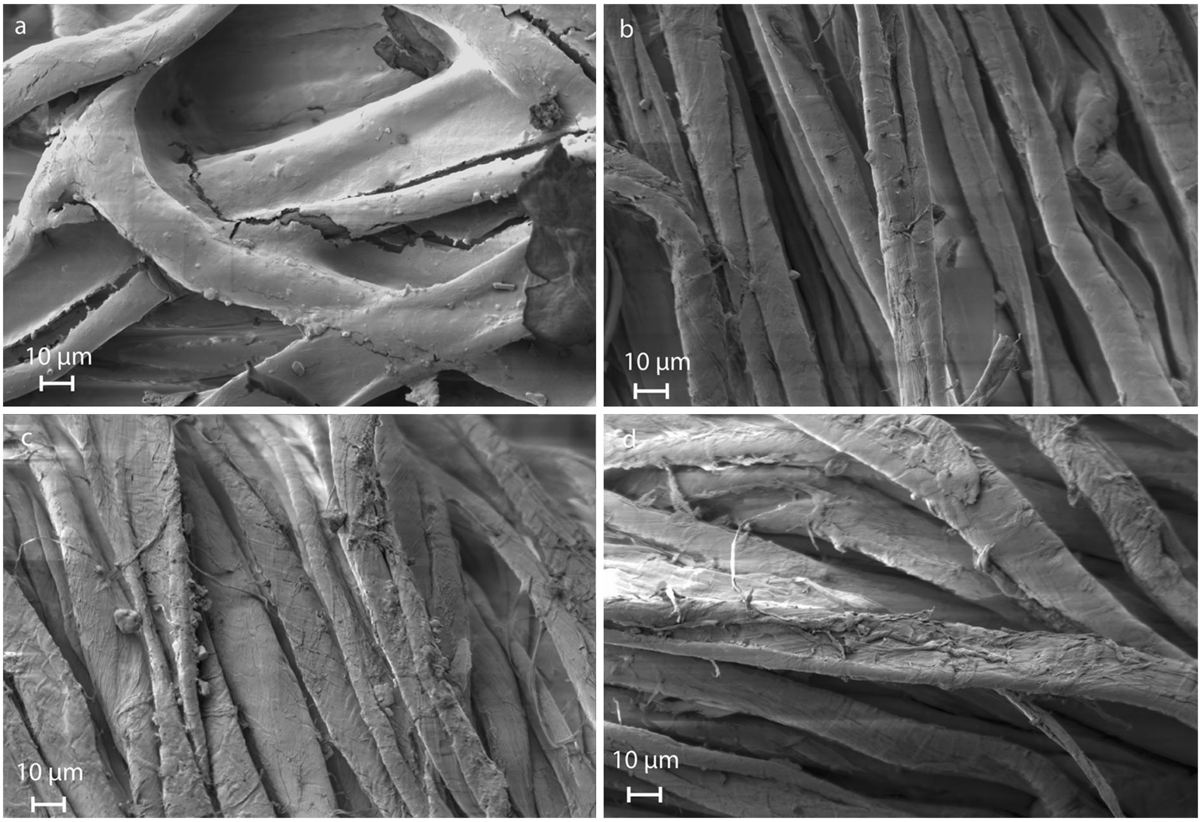

Fig. 3 Micrographs of the four sheets prior to extraction, laundered **a** 0 times, **b** 2–4 times, **c** ~50 times and **d** >50 times

Table 1 Water retention value (WRV) and specific surface area of the samples

Times laundered	WRV (g/g)	Specific surface area (g/m^2)
2–4	0.40 ± 0.003[a]	73 ± 4.2[a]
~50	0.41 ± 0.005	66 ± 2.9
>50	0.38 ± 0.009	45 ± 1.4

[a] Standard deviation based on 4 (WRV) and 3–5 (spec. surf. area) replicates

virgin cotton textiles already have a high degree of hornification before the first laundering.

The results from measurements of the WRV, presented in Table 1, show a minor decrease in the WRV between the never-used sheet, laundered 2–4 times, and the heavily-used sheet, laundered >50 times, from 0.40 to 0.38 g/g. Never-used and heavily-used cotton are, thus, comparable in terms of hornification.

The specific surface area was measured using nitrogen adsorption, a method that requires dry samples. To maintain the same structure in the dry state as in the water swollen state, a solvent exchange, involving a change from a polar to a non-polar solvent, was applied. This has been reported earlier using a number of different solvent systems (Haselton 1955; Porter and Rollins 1972; Wang et al. 2003). In this study, the water was first replaced with dry acetone, and subsequently, the acetone was replaced by cyclohexane. The level of the specific surface area values obtained in the present study, Table 1, is in line with what others have found for cotton fibres (Porter and Rollins 1972).

The results in Table 1 show a decreasing trend in the specific surface area when the number of launderings was increased from 2 to 4 times to >50 times. This trend implies an increase in the extent of coalescence of cellulose fibrils. Consequently, the results suggest that laundering yields an increase in the lateral dimension of cellulose fibril aggregates. The decrease

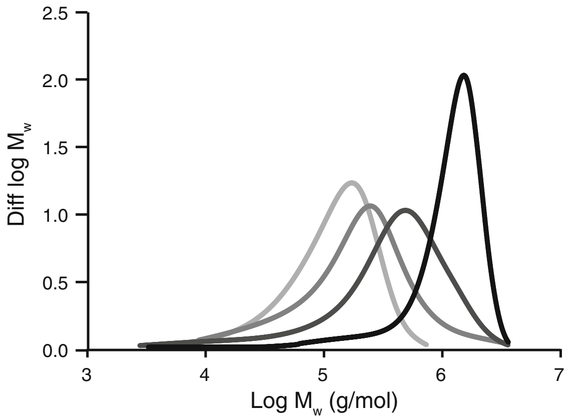

Fig. 4 Molecular mass distributions of cellulose from sheets laundered 0 times (*black*), 2–4 times (*dark grey*), ~50 times (*grey*) and >50 times (*light grey*)

Table 2 Changes in mass-average molecular mass, number-average molecular mass, dispersity and carboxylate group content during laundering

Times laundered	M_m (kDa)	M_n (kDa)	Dispersity (M_m/M_n)	Carboxylate groups (μmol/g)
0	1.323	719	1.84	–
2–4	567	86	6.62	13 ± 0.4[a]
~50	338	93	3.64	12 ± 0.4
>50	151	64	2.36	9 ± 0.4

[a] Pooled standard deviation based on six sets of duplicates

in the specific surface area does not match the relatively small changes observed in the WRV. However, the WRV measures the ability of a pad of fibres to retain water during centrifugation and the water contributing to the WRV will also be present on fibre surfaces, not only in the pores of the fibre walls. This means that the WRV of a sample is rather insensitive to differences in swelling ability of fibres with a high degree of hornification.

A high specific surface area suggests that a large cellulose surface is available for reaction and thus measurements of the specific surface area may indicate the level of reactivity of cellulosic fibres (Nelson and Oliver 1971; Chunilall et al. 2010). The decrease observed here may signal that laundering has a negative impact on the possibility of recycling cotton into cellulose derivatives or regenerated cellulose. More specific studies must be performed in order to predict the effect of laundering on the reactivity and accessibility of cotton cellulose.

The molecular mass distributions in Fig. 4, show a narrow distribution for the never-laundered cotton, and this is in accordance with what others have found for native cotton fibres (Kleman-Leyer et al. 1992; Timpa and Ramey 1989). The molecular mass distribution of native cotton may contain a second smaller peak at around 10^4 g/mol (Wakelyn et al. 2007), but no such peak is observed in the data presented here. The absence of this second peak could, at least partly, be a consequence of the processes applied in the manufacturing of the sheets. The difference between the never-laundered sheet and the sheet laundered 2–4 times includes both a broadening of the peak, as well as a large decrease in molecular mass, Table 2. The molecular mass distributions show that most of the long chains, predominant in the never-laundered sheet, were degraded after a couple of launderings, Fig. 4. After long time use, >50 launderings, the dispersity decreased, as an effect of levelling of the DP.

Under alkaline conditions, cellulose undergoes alkali-induced peeling reactions, in which rearrangements of the reducing end-groups result in the elimination of the terminal glucose residues (Knill and Kennedy 2003). A peeling reaction shortens the cellulose chain by approximately 65 anhydroglucose units before a stabilization takes place (Franzon and Samuelson 1957). The stabilization could be due to rearrangements that lead to the formation of a metasaccharinic acid end-group, which prevents further peeling reactions, or due to physical stopping when the reducing end of the peeled cellulose chain approaches a crystalline region (Knill and Kennedy 2003). Such a peeling reaction has only a minor effect on the DP of native cotton cellulose, since the frequency of end-groups will be low at a high DP of cellulose. Therefore, the decrease in DP is mainly caused by chain scission reactions. In highly alkaline environments, alkaline hydrolysis of cellulose may cause a drop in DP, but since alkaline hydrolysis requires both high temperature and high alkali concentration to be significant (Loon and Glaus 1997), it is probably not the main mechanism causing degradation during laundering. However, it is reasonable to believe that an autoxidation process takes place both during the aerobe alkaline laundering process and during tumble drying at elevated temperatures. Autoxidation leads to formation of carbonyl groups along the cellulose chain, which readily react through β-alkoxy elimination reactions under alkaline conditions and result in scissions of the cellulose chain (Knill and Kennedy 2003). After a chain scission, a new reducing end-group is formed, which means that the peeling reaction can cause an end-wise degradation of the cellulose chain until the end-group becomes stabilised. The carboxylic acid content of the cotton cellulose shows a slight decreasing trend, Table 2, and is thus, not correlated with the increase in number of chain ends. This implies that after long time use, the peeling reactions mainly stop owing to a physical cessation of the reaction at a point where no carboxylic acid containing end-group is formed.

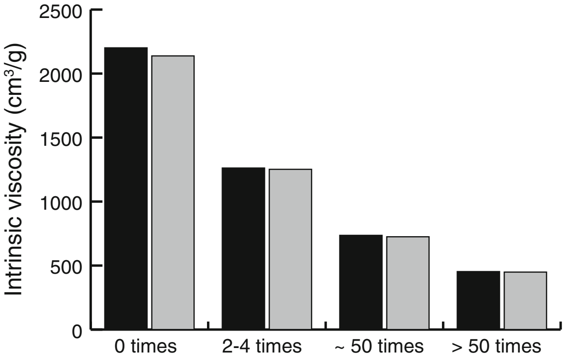

Fig. 5 Intrinsic viscosity of samples without reductive sodium borohydride treatment (*black*) and with this treatment (*grey*) prior to analysis. The pooled standard deviation based on ten sets of duplicates was 8 cm^3/g

Measurements of the intrinsic viscosity of the samples were performed both with and without a preceding sodium borohydride reduction treatment. The sodium borohydride treatment was performed in order to reduce the carbonyls in the cellulose to alcohol groups. Results in Fig. 5 show that the reduction did not give any significant impact on the intrinsic viscosity. This insignificant difference between the measurements implies that there were no carbonyls along the cellulose chains in the samples prior to the sodium borohydride treatment, since, during dissolution in the alkaline Cuen-solution such carbonyl groups would have led to a chain scissions and thus a reduction in intrinsic viscosity (Ahn et al. 2013). Accordingly, results imply that when autoxidation occurs, the β-alkoxy elimination reaction proceeds relatively quickly through chain scission, leaving no carbonyls along the chain.

The amorphous part of the C4 region of CP/MAS ^{13}C-NMR of the cotton cellulose samples can be seen superimposed in Fig. 6. There is a visible decrease in the signal in this region between the never-laundered sheet and the sheet laundered 2–4 times. The deconvolution of the C4 region,

Fig. 6 CP/MAS 13C-NMR spectra showing superimposed C4 region of non-hydrolysed sheets washed 0 (*black*), 2–4 (*dark grey*), ~50 (*grey*) and >50 (*light grey*) times. A clear decrease in the amorphous region, compared to the crystalline region, can be seen between never-washed and washed sheets

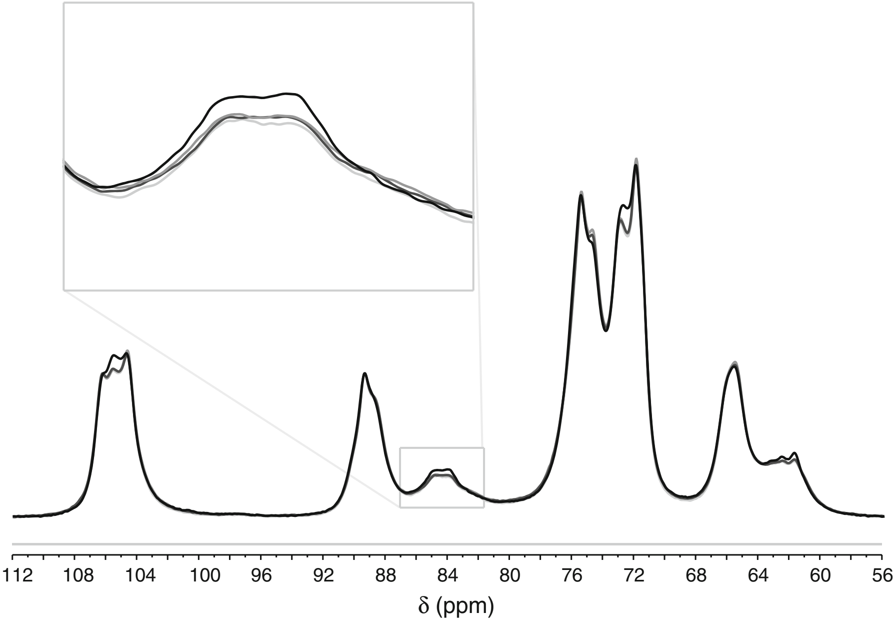

Table 3 Determination of crystallinity index (CI), elementary fibril and fibril aggregate size from solid state NMR

Times laundered	CI average[a] (CI deconv./CI int.) (%)	Elementary fibril[b] (nm)	Fibril aggregate[b] (nm)
0	62.4 (60.9/63.8)	6.4 ± 0.2[c]	21.9 ± 2[c]
2–4	63.6 (61.7/65.4)	7.0 ± 0.2	25.6 ± 2
~50	64.1 (62.8/65.4)	7.2 ± 0.2	24.2 ± 2
>50	63.7 (61.9/65.6)	7.2 ± 0.2	24.1 ± 2

[a] Based on non-hydrolysed samples

[b] Based on acid hydrolysis pretreated samples

[c] Standard deviation estimated from several deconvolutions of the different spectra

performed as in Fig. 1a, suggests that the decrease originates from the accessible surface signals. This decrease has, in previous studies, been assigned as an NMR fingerprint of hornification (Idström et al. 2013; Newman 2004). However, loss of material, due to e.g. leaching of shorter amorphous cellulose chains, would also give a similar decrease in this area of the spectrum. Nevertheless, since the decrease in the amorphous part could be observed also after acid hydrolysis pretreatment of the samples (spectra not shown) for sheets laundered 0 and 2–4 times, it was concluded that the decrease was not due to any loss of material. The sheets laundered more than 2–4 times showed only a minor decrease in amorphous signals compared to crystalline signals.

The measurements of the CI in Table 3 indicate no large changes during use and laundering. The average elementary fibril size of the never-laundered sheet, in Table 3, was determined to be around 6 nm, and this is in line with what has been reported in the literature (Wickholm et al. 1998; Newman 1999). The elementary fibril size of the samples increases initially, but no major differences could be found between the samples from the sheet laundered 2–4 times and from the sheet laundered >50 times. The same trend was also observed for fibril aggregate size. The initial increase of elementary fibril and fibril aggregate size between the never-laundered sheet and the sheet laundered 2–4 times implies that the degree of hornification increased during the first launderings. Moreover, no clear indication of change in hornification due to further laundering was observed.

Conclusions

The present study is part of a larger project with the aim of investigating different possibilities for textile recycling. Results presented here show that discarded cotton sheets have the potential of becoming a useful cellulose source in production of regenerated cellulosic fibres and cellulose derivatives. The large decrease in molecular mass in combination with small changes in WRV and solid state NMR spectra indicate that cotton textiles can be used for a long time and then recycled. A sample from a sheet that had been laundered more than 50 times had a molecular mass that is in the range of what is preferred by viscose producers (Woodings 2001). Therefore, it is possible that only a light pretreatment may be needed in order to prepare used cotton textiles for recycling. However, the measurement of the specific surface area showed a decreasing trend after long time use and laundering. This decrease in specific surface area may have a negative impact on the reactivity of the cellulose. Consequently, further studies are required to clarify how the reactivity and dissolution behaviour of cellulose in cotton textile is affected after long time use.

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References

Ahn K, Rosenau T, Potthast A (2013) The influence of alkaline reserve on the aging behavior of book papers. Cellulose 20(4):1989–2001. doi:10.1007/s10570-013-9978-3

Atalla RH, VanderHart DL (1999) The role of solid state 13C NMR spectroscopy in studies of the nature of native celluloses. Solid State Nucl Magn Reson 15(1):1–19. doi:10.1016/S0926-2040(99)00042-9

Buisson YL, Rajasekaran K, French AD, Conrad DC, Roy PS (2000) Qualitative and quantitative evaluation of cotton fabric damage by tumble drying. Text Res J 70(8):739–743. doi:10.1177/004051750007000813

Chunilall V, Bush T, Larsson PT, Iversen T, Kindness A (2010) A CP/MAS (13)C-NMR study of cellulose fibril aggregation in eucalyptus dissolving pulps during drying and the correlation between aggregate dimensions and chemical reactivity. Holzforschung 64(6):693–698. doi:10.1515/hf.2010.097

Davidson GF (1948) The acidic properties of cotton cellulose and derived oxycelluloses. Part II. The absorption of methylene blue. J Tex Inst Trans 39(3):T65–T86. doi:10.1080/19447024808659403

Fardim P, Holmbom B, Ivaska A, Karhu J, Mortha G, Laine J (2002) Critical comparison and validation of methods for determination of anionic groups in pulp fibres. Nord Pulp Paper Res J 17(3):346–351

Franzon O, Samuelson O (1957) Degradation of cellulose by alkali cooking. Svensk Papperstidning 60(23):872–877

Goynes WR, Rollins ML (1971) A scanning electron-microscope study of washer-dryer abrasion in cotton fibers. Text Res J 41(3):226–231. doi:10.1177/004051757104100307

Haselton WR (1955) Gas adsorption by wood, pulp, and paper. II. The application of gas-adsorption techniques to the study of the area and structure of pulps and the unbonded and bonded area of paper. Tappi 38:716–723

Henniges U, Kostic M, Borgards A, Rosenau T, Potthast A (2011) Dissolution behavior of different celluloses. Biomacromolecules 12(4):871–879. doi:10.1021/bm101555q

Hubbe MA, Venditti RA, Rojas OJ (2007) What happens to cellulosic fibres during papersmaking and recycling? A review. BioResources 2(4):739–788

Hult E-L, Larsson PT, Iversen T (2001) Cellulose fibril aggregation—an inherent property of kraft pulps. Polymer 42(8):3309–3314

Idström A, Brelid H, Nydén M, Nordstierna L (2013) CP/MAS 13C NMR study of pulp hornification using nanocrystalline cellulose as a model system. Carbohydr Polym 92(1):881–884. doi:10.1016/j.carbpol.2012.09.097

Jayme G (1944) Mikro-Quellungsmessungen an Zellstoffen. Papierfabrikant-Wochenblatt fuer Papierfabrikation 6:187–194

Kato KL, Cameron RE (1999) A review of the relationship between thermally-accelerated ageing of paper and hornification. Cellulose 6(1):23–40. doi:10.1023/a:1009292120151

Kleman-Leyer K, Agosin E, Conner AH, Kirk TK (1992) Changes in molecular size distribution of cellulose during attack by white rot and brown rot fungi. Appl Environ Microbiol 58(4):1266–1270

Knill CJ, Kennedy JF (2003) Degradation of cellulose under alkaline conditions. Carbohydr Polym 51(3):281–300. doi:10.1016/S0144-8617(02)00183-2

Köhnke T, Lund K, Brelid H, Westman G (2010) Kraft pulp hornification: a closer look at the preventive effect gained by glucuronoxylan adsorption. Carbohydr Polym 81(2):226–233. doi:10.1016/j.carbpol.2010.02.023

Laivins GV, Scallan AM (1993) The mechanism of hornification of wood pulps. In: Baker CF (ed) Products of papermaking. Transactions of the 10th fundamental research symposium. Pira International, Oxford, pp 1235–1260

Lindholm C-A (1992) Alkaline extraction of ozone-bleached pulp Part 2. Effect of leachable lignin. Nord Pulp Pap Res J 07(2):095–101. doi:10.3183/NPPRJ-1992-07-02-p095-101

Loon LR, Glaus MA (1997) Review of the kinetics of alkaline degradation of cellulose in view of its relevance for safety assessment of radioactive waste repositories. J Environ Polym Degr 5(2):97–109. doi:10.1007/bf02763593

Morley N, Slater S, Russell S, Tipper M, Ward GD (2006) Recycling of low grade clothing waste. Oakdene Hollins Ltd, Salvation Army Trading Company Ltd. Nonwovens Innovation & Research Institute Ltd. http://www.oakdenehollins.co.uk/pdf/defr01_058_low_grade_clothing-public_v2.pdf. Accessed 14 Sept 2014

Negulescu II, Kwon H, Collier BJ, Collier JR, Pendse A (1998) Recycling cotton from cotton/polyester fabrics. Text Chem Color 30(6):31–35

Nelson R, Oliver DW (1971) Study of cellulose structure and its relation to reactivity. J Polym Sci Part C Polym Symp 36(1):305–320. doi:10.1002/polc.5070360122

Nelson ML, Rousselle MA, Ramey HH Jr, Barker GL (1980) Closed-boll cotton. Part I. Properties of never-dried cotton fibers before and after aqueous formaldehyde treatment. Text Res J 50:491–499. doi:10.1177/004051758005000804

Newman RH (1999) Estimation of the lateral dimensions of cellulose crystallites using 13C NMR signal strengths. Solid State Nucl Magn Reson 15(1):21–29. doi:10.1016/S0926-2040(99)00043-0

Newman R (2004) Carbon-13 NMR evidence for cocrystallization of cellulose as a mechanism for hornification of bleached kraft pulp. Cellulose 11(1):45–52. doi:10.1023/B:CELL.0000014768.28924.0c

Palm D (2011) Improved waste management of textiles. IVL Swedish environmental institute. http://ivl.se/download/18.7df4c4e812d2da6a416800080103/1350484286532/B1976.pdf. Accessed 14 Sept 2014

Park S, Baker J, Himmel M, Parilla P, Johnson D (2010) Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. Biotechnol Biofuels 3(1):10

Pönni R, Vuorinen T, Kontturi E (2012) Proposed nano-scale coalescence of cellulose in chemical pulp fibers during technical treatments. BioResources 7(4):6077–6108

Porter BR, Rollins ML (1972) Changes in porosity of treated lint cotton fibers. I. Purification and swelling treatments. J Appl Polym Sci 16(1):217–236. doi:10.1002/app.1972.070160119

Sugiyama J, Vuong R, Chanzy H (1991) Electron diffraction study on the two crystalline phases occurring in native cellulose from an algal cell wall. Macromolecules 24(14):4168–4175

Timpa JD, Ramey HH (1989) Molecular characterization of three cotton varieties. Text Res J 59(11):661–664. doi:10.1177/004051758905901105

Vaeck SV (1966) Chemical and mechanical wear of cotton fabric in laundering. J Soc Dyers Colour 82(10):374–379. doi:10.1111/j.1478-4408.1966.tb02684.x

Virtanen T, Liisa Maunu S, Tamminen T, Hortling B, Liitiä T (2008) Changes in fiber ultrastructure during various kraft pulping conditions evaluated by 13C CPMAS NMR spectroscopy. Carbohydr Polym 73(1):156–163. doi:10.1016/j.carbpol.2007.11.015

Wakelyn PJ, Bertoniere NR, French AD, Thibodeaux DP, Triplett BA, Rousselle M-A, Goynes WR Jr, Edwards JV, Hunter L, McAlister DD, Gamble GR (2007) Cotton fibers. In: Menachem L (ed) Handbook of fibre chemistry, 3rd edn. Taylor & Francis Group, Boca Raton, pp 521–666

Wang XS, Maloney TC, Paulapuro H (2003) Internal fibrillation in never-dried and once-dried chemical pulps. Appita J 56(6):455–459

Weise U (1998) Hornification: mechanisms and terminology. Pap Ja Puu-Pap Timber 80(2):110–115

Wickholm K (2001) Structural elements in native cellulose. Dissertation, Royal Institute of Technology

Wickholm K, Larsson PT, Iversen T (1998) Assignment of non-crystalline forms in cellulose I by CP/MAS C-13 NMR spectroscopy. Carbohydr Res 312(3):123–129. doi:10.1016/s0008-6215(98)00236-5

Wilson WK, Parks EJ (1979) An analysis of the aging of paper: possible reactions and their effects on measurable properties. Restaurator 3:37–61. doi:10.1515/rest.1979.3.1-2.37

Woodings C (2001) Regenerated cellulose fibres. Woodhead Publishing in association with the Textile Institute, Cambridge