Acid hydrolysis of cellulosic fibres: Comparison of bleached kraft pulp, dissolving pulps and cotton textile cellulose

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ARTICLE INFO

Article history:
Received 6 July 2015
Received in revised form 2 October 2015
Accepted 6 October 2015
Available online 8 October 2015

Keywords:
Cotton
Dissolving pulp
Kraft pulp
Acid hydrolysis
LODP
Hornification

ABSTRACT

The behaviour of different cellulosic fibres during acid hydrolysis has been investigated and the levelling-off degree of polymerisation (LODP) has been determined. The study included a bleached kraft pulp (both never-dried and once-dried) and two dissolving pulps (once-dried). Additionally, cotton cellulose from new cotton sheets and sheets discarded after long-time use was studied. Experimental results from the investigation, together with results found in literature, imply that ultrastructural differences between different fibres affect their susceptibility towards acid hydrolysis. Drying of a bleached kraft pulp was found to enhance the rate of acid hydrolysis and also result in a decrease in LODP. This implies that the susceptibility of cellulosic fibres towards acid hydrolysis is affected by drying-induced stresses in the cellulose chains. In cotton cellulose, it was found that use and laundering gave a substantial loss in the degree of polymerisation (DP), but that the LODP was only marginally affected.

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1. Introduction

Ultrastructural features of cellulose in different raw materials vary depending on origin and on how the material has been handled. Thus, the reactivity of cellulose towards different chemical treatments, such as acid hydrolysis, varies between different cellulose substrates. The present investigation is focused on the reactivity of different cellulosic fibres under acid conditions. Special attention is paid to how the reactivity of cellulose in textiles changes during service life and how the properties of cellulose in used textiles relate to the properties of dissolving pulps.

Acid hydrolysis of cellulose is of interest both from an industrial point of view and as a method to gain understanding of basic properties of cellulosic fibres. Industrially, acid hydrolysis may be used in the production of ethanol from biomass either to liberate glucose directly or as a pre-treatment step prior to enzymatic saccharification (Kamm, Kamm, & Gruber, 2006). The partial degradation of cellulose by acid hydrolysis, leaving crystalline parts unaffected, is also used in the production of CMC and CNC (cellulose micro and nano crystals) (Siró & Plackett, 2010). In pulping and bleaching, the acid catalysed depolymerisation of cellulose cannot be avoided in process steps in which wood material and pulp are treated under acidic conditions, e.g. in acid sulphite pulping and in acidic bleaching stages performed at high temperatures (Sixta, 2006). Acid hydrolysis is also responsible for the deterioration of the strength properties of paper products during ageing (Kato & Cameron, 1999; Wilson & Parks, 1979).

When cellulosic fibres are subjected to acid, the glucosidic linkages in the cellulose are broken and the degree of polymerisation (DP) decreases. Initially, this degradation is fast, but as it proceeds, it slows down and reaches a certain DP level after which the hydrolysis continues at a considerably slower rate. This DP level is called the “levelling-off” degree of polymerisation (LODP) (Battista, 1950; Håkansson & Ahlgren, 2005). Based on this behaviour, the fringed fibril model has been constructed. This model proposes that the cellulose microfibril consists of cellulose chains in well-ordered crystalline parts, which are interconnected with less ordered, amorphous, parts of cellulose (Frey-Wyssling, 1954; Hearn, 1958; Scallan, 1971). The acid only slowly reacts with the crystalline parts, and, thus, degradation primarily occurs in the amorphous cellulose. The LODP is reached when the fast reacting amorphous material has been hydrolysed and mainly cellulose microcrystals are left. This concept is in line with results presented by Davidson (1943), who has shown that hygroscopicity decreases when cotton linters are subjected to acid hydrolysis, and the explanation for this effect is that water is mainly sorbed in the amorphous parts of the cellulose fibres. Davidson has also pointed out that only a very small
part of the glucosidic linkages needs to be hydrolysed to reach LODP. Battista, Coppick, Howson, Morehead, and Sisson (1956) observed a good correlation between the length of cellulose crystals after acid hydrolysis measured with electron microscope, and the DP measured with intrinsic viscosity.

In the present paper, cellulosic materials of different origin have been subjected to acid hydrolysis. Cotton sheets were included, since cellulose from discarded textiles could potentially be used as a raw material for regenerated cellulose or cellulose derivatives (Palme, Jöström, Nordstirna, & Bredl, 2014) and, therefore, knowledge about how the properties of cotton cellulose in textile change during long-time use is of interest. In addition to cotton sheets (new sheets and sheets discarded after long-time use and frequent laundering), the fibre materials included bleached softwood Kraft pulp (both never-dried pulp and once-dried pulp) and two types of once-dried dissolving pulp (softwood sulphite pulp and a hardwood pre-hydrolysis Kraft pulp). The hydrolysis rates as well as the LODP of the different types of fibres were determined. Furthermore, the molecular mass distribution (MMD) and crystallinity of the cellulose samples, before and after an acid treatment, was analysed.

2. Materials and methods

2.1. Materials

Two fractions consisting of five cotton sheets each, made from cotton from Pakistan, were provided by a large Swedish supplier of service textiles. The first fraction contained never used sheets, which had been laundered 2 to 4 times as a general procedure of the textile provider. This fraction is referred to as “New” in the text. The second fraction contained sheets classified as worn out, and this fraction had been laundered more than 50 times, and is referred to as “Discarded”.

The laundering was performed by the service provider using an industrial laundering system with a maximum temperature of 84 °C and the washing agent Clax Hellux free 3EP3, from JohnsonDiversey Sverige AB, an alkaline detergent with a pH between 12 and 12.5 in a 1% solution. The washing agent did not contain any oxidants. After laundering, water was pressed out of the fabric prior to tumble drying. Before all of the analyses, except where noted, the sheets were ripped into approximately 1 cm² pieces and defibrated using a Wiley mill (<1 mm).

Industrial pulp samples were also used in the investigation. The pulp samples consisted of two dissolving pulp samples, and a bleached softwood paper grade Kraft pulp. The dissolving pulps were both once-dried, and consisted of a Scandinavain softwood sulphite pulp (Sulphite pulp) sample and a pre-hydrolysis eucalyptus Kraft pulp (PHK pulp) sample. The bleached softwood paper grade Kraft pulp (BKP) sample was split into two parts; a never-dried and a once-dried sample. In the following, the samples are referred to as the names/abbreviations in brackets above.

2.2. Acid hydrolysis

Prior to acid hydrolysis, all samples were washed with 0.01 M HCl. The acid hydrolysis was performed using a 5 g O.D. sample in 100 ml HCl solution (0.4 M) at 80 °C. The samples were preheated in a water bath before the HCl was added. The samples were treated for 15, 30, 60, 120 and 240 min. After completed hydrolysis, the samples were carefully washed with deionised water at room temperature, in order to remove all acid, and then air-dried before further analysis.

2.3. Analytical methods

2.3.1. Degree of polymerisation

The intrinsic viscosity of the cellulose samples was measured after dissolution in Cuen (copper(II)ethylene diamine), according to the SCAN-C 15:99 standard. The degree of polymerisation was calculated from the correlation formulated by Immergut, as cited in SCAN-C 15:62 (DPK = 0.6, η given in cm²/g) (Immergut, Schurz, & Mark, 1953). This correlation is known to have flaws; however it is a commonly used correlation which facilitates comparisons to other studies.

2.3.2. Water retention value

The water retention value (WRV) 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 at 3000 × g for 15 min. The weight after centrifugation was then compared to the weight of the sample after drying at 105 °C. All tests were carried out in duplicate. The pooled standard deviation was 0.02 g/g.

2.3.3. Levelling-off degree of polymerisation

The LODP was measured as the average degree of polymerisation, determined by intrinsic viscosity, after hydrolysis for 2 and 4 h (two samples at each hydrolysis time). The hydrolysis of a 2 g (dry weight) sample was performed in 100 ml 4 M hydrochloric acid at 80 °C. After hydrolysis, the sample was carefully washed with deionised water, in order to remove all acid, and then air-dried before further analysis. The pooled standard deviation of the samples obtained after 2 and 4 h was 6.5.

2.3.4. X-ray diffractometry

X-ray diffractograms were recorded on a Siemens D5000 krystalloflex between 2θ = 10° and 40°. The crystallinity index (CI) was calculated using the peak height method. In this method the intensity of the crystalline peak (Ih02—Iam) is compared to the total intensity (I002). (Park, Baker, Himmel, Parilla, & Johnson, 2010)

2.3.5. Molecular mass distribution

Molecular mass distributions were determined using size exclusion chromatography after dissolution of the samples in lithium chloride/N,N-dimethylacetamid (Li/DMAC) according to Henniges, Kostic, Borgards, Rosenau, and Potthast (2011). 20 mg (dry weight) of a sample was suspended in deionised 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. Following this procedure, 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 (Pgel 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 Helos-II, λ0 = 658 nm, from Wyatt) were used for the detection process. The value of the dn/dc used was 0.136 ml/g. Data evaluation was performed with standard Astra and Chromeleon software (6.1.17). The BKP samples were not completely dissolved in the DMAC/LiCl, and no attempts were made to quantify the undissolved fraction.
2.3.6. Carbohydrate composition

The neutral carbohydrate composition was analysed after acid hydrolysis (Theander & Westerlund, 1986) using ion chromatography with pulsed amperometric detection. The chromatographic analysis was performed using a Dionex-ICS 3000 system and the separation was performed isocratically in Milli-Q water on a CarboPac PA1 column.

2.4. Modelling

The degradation data from the acid hydrolysis in the present study was fit to the first order degradation model developed by (Calvini, Gorassini, & Merlani, 2008), see the following equation:

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

where \( S \) is the number of scissions per cellulose chain (\( \text{DP}_0/\text{DP} - 1 \)), \( n \) the initial number of scissile bonds per cellulose chain, \( k \) the rate constant of the hydrolytic medium, and \( t \) the time of hydrolysis. In the model it is assumed that one, two or three first order reactions may take place simultaneously. Cellulose fibres have a complex ultrastructure and it is likely that bonds in different parts of a fibre have different reactivities, e.g. the crystalline parts have a very low accessibility compared to amorphous parts of the fibre. The model consists of three components which modulate the degradation of weak links, amorphous cellulose and crystalline cellulose.

For comparison the data was also fit to a pseudo-zero order model, see Eq. (2) proposed by af Ekenstam (1936).

\[ \frac{1}{\text{DP}} - \frac{1}{\text{DP}_0} = kt \]

When utilising the Ekenstam relationship, it is assumed that the degradation takes place in a homogeneous medium, where all the glucosidic bonds are available for hydrolysis. However, in a heterogeneous medium (which is the case when cellulosic fibres are treated in a water solution), the influence of the LODP should be included. By using the expression developed by Calvini et al. (2008), which considers the impact of LODP, a better fit of the model to the data was achieved.

The model (Eq. (1)) was fit to minimise the sum of squared errors of prediction (SSE), using the minimisation function fmincon in Matlab 2013b, for 1, 2 and 3 components. In all of the experiments, one component was enough to describe the degradation, see Eq. (3), and very good fit, with all \( R^2 \) values above 0.99 for all the data sets was achieved.

\[ S = n (1 - \exp(-kt)) \]

After minimisation, the \( S \)-values were recalculated to DP-values.

3. Results and discussion

3.1. Characteristics of the cellulosic fibres

The cellulosic materials were characterised with respect to DP, LODP, carbohydrate composition and WRV, see Table 1. The initial DP values were all on expected levels, i.e. the New sheets (cotton cellulose) had a high DP compared to the dissolving pulps (PHK pulp and Sulphite pulp) as well as the Discarded sheets. The initial DP of the paper pulp (BKP) was in-between that of the other samples. The LODP values ranged from 88 (PHK pulp) to 195 (never-dried BKP). No clear correlation between the DP and LODP of the different samples could be seen. This lack of correlation is mainly related to the fact that cellulose samples from various sources subjected to different treatments were compared. Interestingly, it is evident that the drying of BKP results in a significant decrease in LODP (from 195 to 159). This finding may be somewhat confusing since drying could be anticipated to lower the chemical accessibility of the cellulose due to the coalescence of cellulose fibrils, which has been shown to decrease the rate of enzymatic hydrolysis (Duan, Long, Li, & Qi, 2015; Philipp, Dan, Fink, & Loth, 1981a). However, in the case of acid hydrolysis, the effect seems to be the opposite. Some scattered results in the literature support the finding that drying of cellulosic fibres gives rise to a decrease in the LODP, Lindgren (1956) and Lindgren (1956) have reported that acid hydrolysis of once-dried wood cellulose fibres was faster than that of never-dried fibres and that a lower LODP was reached if the fibres were once-dried. A similar observation was made by Philipp, Dan, and Fink (1981b), who explained the decrease in LODP due to drying in terms of drying-induced stress in cellulosic fibrils, which would favour the chain scission of cellulose polymers through acid hydrolysis. Some thirty years after Philipp et al., Kontturi and Vuorinen (2009) investigated this phenomenon further, and produced cellulose nanocrystals (CNCs) with sulphuric acid, from never-dried and once-dried chemical pulp fibres. Their results show the presence of more long CNCs and fewer short CNCs from the never-dried pulp. They also explain their results with the irreversible stresses built up in the amorphous cellulose during drying. A stress leads to a higher energy level of the bonds and thus a larger susceptibility to acid hydrolysis.

The never-dried BKP had a WRV of 1.29 g/g and the corresponding value for the once-dried BKP was 0.93 g/g. Table 1. A decrease in WRV due to drying is often referred to as hornification (Jayne, 1944), and this loss in swelling capacity is believed to be a consequence of an increase in the degree of coalescence of cellulose fibrils in the fibre wall (Hult, Larsson, & Iversen, 2001; Idström, Breid, Nydén, & Nordstierna, 2013; Pönni, Vuorinen, & Kontturi, 2012; Stone & Scallan, 1968). However, despite hornification, the WRV of the BKP remained on a higher level than that of the other cellulosic fibres. The relatively high WRV is probably mainly an effect of the hemicellulose in the BKP. Hemicellullose (i.e. glucomannan and/or xylan) is known to suppress the tendency of cellulose fibril coalescence during drying, and thus fibres containing high amounts of hemicellulose are less sensible to hornification, cf. (Köhne, Lund, Breid, & Westman, 2010; Oksanen, Buchert, & Viikari, 1997). It has been shown that higher contents of xylan in hardwood Kraft pulps correlate with higher LODP values (Håkansson, Germgard, & Sens, 2005). The proposed explanation was that xylan is closely associated with the cellulose, and that xylan protects amorphous regions in the cellulose fibrils during acid hydrolysis. However, if the decrease in LODP during drying is caused by drying-induced...
stress in amorphous regions of the cellulose (Kontturi & Vuorinen, 2009; Philipp et al., 1981b), the effect of xylan noted by Håkansson and Ahlgren (2005), Håkansson et al. (2005), at least partly, can be explained by the preventive effect of hemicelluloses on hornification.

The LODP of the Sulphite pulp is higher than that of the LODP of the PHK pulp, which is in line with earlier reported values (Håkansson & Ahlgren, 2005; Sixta, 2000). Page (1983) has proposed that one reason for the lower LODP of Kraft pulps is that swelling of non-crystalline parts of the cellulose fibrils in Kraft pulping caused by the alkaline cooking liquor enhances the accessibility of the cellulose and also induces stresses, which would lead to a higher acid hydrolysis reactivity. Furthermore, Kraft cooking is known to induce cellulose fibril aggregation during pulping (Hult, Larsson Per, & Iversen, 2002), which also may induce stresses in the cellulose and thereby increasing the susceptibility towards acid hydrolysis.

Laundering and use of hospital sheets had a major impact on the DP. However, the LODP and the WRV remained virtually unaffected. Cotton fibres consist principally of cellulose, and since there is no hemicellulose or lignin working as blockers during drying, the cellulose fibrils coalesce during drying, partly hindering the rewetting of the fibre. When the cotton fibres are mature they dry on the field, before being picked, and are thus highly hornified even in the virgin state (Fahmy & Mobarak, 1971; Nelson, Rousseau, Ramey, & Barker, 1980). The WRV of the cotton cellulose samples in this study was on the same level, which implies that the degree of hornification of the samples is essentially the same, even though a minor enhancement of fibril coalescence may be expected during the many drying-rewetting cycles the cottons are subjected to during their service life, cf. Fahmy and Mobarak (1971). The large difference in DP between New sheets and Discarded sheets is probably due to autooxidation reactions during the aerobe alkaline laundering process and during tumble drying at elevated temperatures, cf. (Palme et al., 2014). 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 possible stresses built up in the cellulose during the drying and rewetting cycles may be released through the oxidative chain cleavage, leaving the LODP unaffected.

3.2. Molecular mass distributions and crystallinity

In order to further characterise the different cellulosic fibres and their susceptibility to acid hydrolysis, the molecular mass distribution (MMD) of the untreated samples and samples hydrolysed for 60 min at 80 °C in 0.4 M HCl was determined, see Table 2 and Fig. 1. The hydrolysis conditions were milder than in the LODP analysis, which means that the results of the hydrolysed samples represent MMD when only part of the glucosidic bonds available for acid hydrolysis had been cleaved.

Results in Table 2 show that the dispersity of the untreated samples decreased in the order: Sulphite pulp > BKP > PHK pulp > New sheets > Discarded Sheets, cf. also Fig. 1. Furthermore, it can be
noted that the acid hydrolysis gave a substantial decrease in the molecular mass of the samples and that the dispersity of the samples also decreased. In the case of the BKP samples, the 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 Table 2 and Fig. 1 suggest that the once-dried BKP was more degraded after hydrolysis than the never-dried sample.

The Sulphite pulp had a significantly higher dispersity than the PHK pulp, which is in accordance with earlier findings in the literature (Sixta, 2000). Acid hydrolysis of the two dissolving pulps yielded, in both cases, more narrow distributions, Table 2 and Fig. 1. However, the MMD of the Sulphite pulp was still quite broad after hydrolysis, with predominantly higher molecular mass material than the PHK pulp. Hydrolysis of New sheets and Discarded sheets resulted in similar MMDs, which is in line with the results regarding LODP in Table 1.

As shown in Table 2, the crystallinity index (CI) was determined for the initial material and the material subjected to 60 min of hydrolysis, using the peak height method (Segal, Creely, Martin, & Conrad, 1959). This method is known to overestimate the crystallinity, and should therefore only be used to rank the crystallinity of the analysed samples (Park et al., 2010). The crystallinity of the original samples decreased in the order: Discarded sheets > New sheets > PHK pulp > Sulphite pulp > BKP pulp. The results also show a slight increase in crystallinity after 60 min of hydrolysis in all samples. It can be noted that the order of crystallinity differs from that of LODP, see Table 1. This indicates that also other ultrastructural features of the cellulosic fibres than the degree of crystallinity affect their susceptibility towards acid hydrolysis.

### 3.3. Rate of 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 purpose of these trials was to obtain more information regarding the impact of the starting material on the kinetics of the acid hydrolysis. A model was fit to the data points obtained from the hydrolysis, as described in Section 2, see results in Table 3 and Fig. 2. The model used was Eq. (3), and very good fit, with all R² values above 0.99 for all the data sets were achieved. The interpretation of data benefits from modelling, since differences between the degradation rate and the number of scissile bonds can be estimated and compared between data sets. Consequently, information not visible to the eye in the graphs may be detected. Fig. 2 shows the experimental data and the model fit to the data, including the LODP values given by the model.

The modelling results in Table 3 suggest that the difference in the degradation rate between the once-dried and never-dried BKP is mainly a result of the higher amount of scissile bonds, n, in the

<table>
<thead>
<tr>
<th>Sample</th>
<th>n</th>
<th>k x 10^2 (min⁻¹)</th>
<th>LODP (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Never-dried BKP</td>
<td>2.53</td>
<td>0.46</td>
<td>310</td>
</tr>
<tr>
<td>Once-dried BKP</td>
<td>4.02</td>
<td>0.48</td>
<td>218</td>
</tr>
<tr>
<td>PHK pulp</td>
<td>4.43</td>
<td>0.58</td>
<td>107</td>
</tr>
<tr>
<td>Sulphite pulp</td>
<td>3.61</td>
<td>0.63</td>
<td>165</td>
</tr>
<tr>
<td>New sheets</td>
<td>2.43</td>
<td>0.63</td>
<td>104</td>
</tr>
<tr>
<td>Discarded sheets</td>
<td>5.11</td>
<td>0.60</td>
<td>119</td>
</tr>
</tbody>
</table>
Once-dried pulp, since the rate constant, k, is similar for both pulps. The rate constants for the other cellulosic materials are somewhat higher than for the BKP pulps. It is, however, hard to draw any definite conclusions from these relatively minor differences in k.

The number of scissile bonds per cellulose chain, n, is affected by the starting DP. However, a comparison of the results from the Sulphite pulp and the PHK pulp reveals that even though the Sulphite pulp has a higher initial DP, compared to the PHK pulp, the Sulphite pulp still has a lower n. This could be a result of differences in the wood raw material (softwood in the Sulphite pulp and hardwood in the PHK pulp), but it is likely that the effect seen is more related to the conditions during the processing of the wood material, as discussed above.

The difference in n between the New and Discarded sheets was great, 24.3 for the New sheets and 5.11 for the Discarded sheets, Table 3. This difference is probably mainly due to the great difference in the initial DP, and thus the availability of bonds, Table 1. Before hydrolysis, the cotton sheets were cut into pieces and defibrated in a Wiley mill to produce a homogenous material, similar to the pulp. In order to control the effect of defibration, two of the hydrolysis times were repeated with sheets cut into pieces instead of defibration, see Fig. 2. A small difference was observed for the New sheets; however, no difference from the defibrated samples was measured for the Discarded sheets. During defibration, the fibres in the new sheets are exposed to much stronger forces than the discarded sheets, since the new fibres are much stronger. This could be one reason for the difference. However, these results indicate that the general trends in the loss in DP during weak acid hydrolysis were not affected by the defibration.

From the modelling, it is also possible to calculate an LODP. A comparison between calculated values and the actual measured values, see Tables 1 and 3, shows a fairly good correspondence, even though the LODP values obtained from the model are on a higher level than the experimentally determined values in all the cases.

4. Conclusions

The behaviour of different cellulosic fibres during mild acid hydrolysis has been investigated with respect to the kinetics of hydrolysis and differences in LODP. Furthermore, molecular mass distributions and crystallinity of samples before and after hydrolysis have been evaluated. Results from the present investigation, together with results in the literature, emphasise the role of ultrastructural effects on the behaviour of cellulosic fibres during acid hydrolysis.

The observation that never-dried BKP has a higher LODP than once-dried BKP implies that the susceptibility of cellulosic fibres towards acid hydrolysis is affected by the hornification that takes place during drying. The explanation for this may be that hornification induces the coalescence of cellulose fibrils, which builds up stress in the cellulose. This stress may enhance acid hydrolysis reactivity, leading to a lower LODP. Earlier findings in the literature show that higher contents of xylan in cellulosic fibres correlate with a higher LODP. The explanation for this has been that xylan protects cellulose from acid hydrolysis. However, in light of the results from the present investigation and results presented in the literature regarding the role of xylan during hornification, it may be suggested that the effect of xylan on LODP, at least partly, can be ascribed to the lower degree of hornification found in xylan-rich pulps.

The PHK pulp analysed in this study was found to have a lower LODP than the Sulphite pulp, which is in line with comparisons found in the literature. The alkaline conditions during cooking in the production of PHK pulp cause the cellulose to swell more than the acid conditions during sulphite pulping. This swelling introduces stresses in the cellulose, which enhances its reactivity towards acid hydrolysis. The tendency for fibril aggregation during Kraft pulping may also induce stresses in cellulose.

Analyses of MMD showed that the cellulose in both New sheets and Discarded sheets had relatively narrow distributions. Furthermore, it was found that use and frequent laundering of rotten sheets results in substantial loss in DP, but that the LODP was not significantly affected. A tentative explanation for this is that if stresses are built up in the cellulose during laundering and drying, these possible stresses are released by the reactions that lead to the loss in DP during the service life of the cotton sheets.

Acknowledgements

This work was performed within the Mistra Future Programme. Financial support from Mistra—The Swedish Foundation for Strategic Environmental Research and from the Swedish Foundation “Södra Skogssägarnas Stiftelse för Forskning. Utveckling och Utbildning” is gratefully acknowledged. We would also like to thank Textilia for providing the sheets. The staff at Södra Innovation laboratory is thanked for performing the carbohydrate composition analysis. Majid Ghasemi, is acknowledged for performing the HPSEC analysis. Merima Hasani is thanked for fruitful discussions and valuable input. Jonas Wetterling is thanked for modelling expertise.

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