Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Polymers 71 (2008) 664–671
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

The influence of alkali pretreatments in lyocell resin finishing – Fiber structure

Avinash P. Manian [a], Mohammad Abu-Rous [a,c], Margit Lenninger [a], Thomas Roeder [b], K. Christian Schuster [c], Thomas Bechtold [a,*]

[a] *Christian-Doppler Laboratory for Textile and Fiber Chemistry in Cellulosics, Institute of Textile Chemistry/Physics, University of Innsbruck, Hoechsterstrasse 73, 6850 Dornbirn, Austria*
[b] *Department of Zellstoff Forschung, BU Pulp, Lenzing AG, 4860 Lenzing, Austria*
[c] *Textile Innovation, Lenzing AG, 4860 Lenzing, Austria*

Received 11 April 2007; received in revised form 12 July 2007; accepted 16 July 2007
Available online 28 July 2007

Abstract

The fiber structure was investigated in lyocell fabrics treated with NaOH (120 g/l), or KOH (250 g/l), and compared with that in untreated fabrics. The alkali treatments caused some degree of degradation in fibers, but no significant changes in carboxyl contents or crystallinity. There were indications of transitions of porosity in the morphology of lyocell fibers, with accessibility at the fiber centers being distinctly lower than that at the outer edges. Both alkali treatments appeared to increase accessibility at the peripheral region in fibers, though to different extents; but there were no evident changes of accessibility at fiber centers. A model is proposed of changes in fiber structure due to the two alkali treatments.

Keywords: Accessibility; Alkali pretreatment; Crosslinking; Lyocell; Pore structure; Resin finishing

1. Introduction

In a previous communication (Manian, Abu-Rous, Schuster, & Bechtold, 2006), we described the influence of two *specific* alkali pretreatments on the resin finishing of lyocell – a regenerated cellulosic spun from a solution of wood pulp in *N*-methyl-morpholine-*N*-oxide. Woven lyocell fabric samples were awarded pretreatments with NaOH (120 g/l), KOH (250 g/l), or remained untreated. A half of the pretreated samples (including the untreated) were awarded resin finishing treatment by a pad-dry-cure process with a dimethylol dihydroxyethyleneurea (DMDHEU) based product. In comparisons between samples, it was observed that: (a) there was a small but measurable increase in accessibility (measured by dye uptake) of samples pretreated with NaOH, as compared to the untreated or the KOH pretreated samples; (b) there were no significant differences in resin content between samples finished with or without pretreatment; (c) there was a greater concentration of resin on fiber/yarn surfaces in samples finished after alkali pretreatments, as opposed to a more uniform distribution of resin across fiber/yarn cross-sections in samples finished without pretreatment; (d) the crease recovery was highest in samples resin finished without pretreatment; and (e) while there were no significant differences in strength between samples subjected to pretreatments alone, both tensile strength and abrasion resistance were lower in samples resin finished after alkali pretreatment as compared to those resin finished without pretreatment.

There was little difference in wet pickup after padding, hence similar resin contents were observed in all samples. Some properties of treated samples could be correlated with resin distribution. Higher surface concentrations of

---

[*] Corresponding author. Tel.: +43 (0) 5572 28533; fax: +43 (0) 5572 28629.
E-mail address: textilchemie@uibk.ac.at (T. Bechtold).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2007.07.020

resin result in lower abrasion resistance (Grant, Andrews, Weiss, & Hassenboehler, 1968; Lickfield et al, 2001) while a more uniform distribution of resin through substrates results in greater crease recovery (Bertoniere, King, & Rowland, 1981; Rowland, Bertoniere, & King, 1983), as observed respectively in samples resin finished with and without pretreatments. A uniform distribution of resin is also correlated with decreased tenacity, but was not found to hold true for the samples in this work. Hence, some questions remained to be answered. In particular: (i) why did alkali pretreatments result in a greater surface concentration of resin; and (ii) why was the tensile strength lower in samples resin finished after alkali pretreatments, despite a higher surface concentration of resin.

Investigations were undertaken of the fiber structure in untreated and alkali pretreated fabric samples in an effort to answer the questions raised above. In this communication, we report the results of our investigations.

2. Experimental

2.1. Alkali pretreatments

Samples of plain-woven lyocell fabric (137 g/m^2, 36 × 29 threads/cm, 50/1 Nm yarns comprised of 1.3 dtex fibers) were padded through treatment formulations containing alkali and surfactant. The padded samples were rolled around glass rods and enveloped in plastic sheets to be stored at room temperature: for 30 min in NaOH pretreatments, and for 4 h in KOH pretreatments. After the respective time periods, the samples were rinsed in running hot water for 5 min, immersed in a solution of 5% acetic acid at room temperature for 60 min, rinsed again in running cold water for 5 min, and line-dried overnight. The ‘untreated’ fabric samples received no treatments.

More details on the resin finishing of samples may be obtained from our previous communication (Manian et al., 2006). The measurements performed on the pretreated fabric samples are described below.

2.2. Carboxyl content

The carboxyl (COOH) content in samples was measured with the TAPPI Test Method T 237 (TAPPI Test Methods, 1989) on 0.250–0.510 g specimens cut finely into pieces of approximately 1 mm in size. Three replicate measurements were conducted on samples from each treatment.

2.3. IR crystallinity

The degree of crystallinity was determined from the ratio of absorbance intensities at 1370 cm^{-1} to those at 2900 cm^{-1} in specimens as measured by KBr transmission FT-IR spectroscopy with the method of Baldinger, Moosbauer, and Sixta (2000), who reported a good correlation between the absorbance ratio and wide-angle X-ray scattering (WAXS) values in determinations of cellulose II crystallinity. About 5 mg of finely cut fiber specimens were mixed with 1.5 g KBr, pressed into pellets, and measured in transmission mode with a Bruker IFS 66 spectrometer (Bruker, Germany). Four replicate measurements were conducted on samples from each treatment.

2.4. Degree of polymerization (DP)

The degree of polymerization in samples was determined by Gel Permeation Chromatography (GPC) as described by Schelosky, Roeder, and Baldinger (1999), using as eluant 0.9% (w/v) DMAc/LiCl filtered through a 0.02 μm filter. The test specimens were injected automatically, eluted through four serial GPC columns, and monitored with MALLS and refractive index (RI) detectors. The molecular weight distribution and related parameters were calculated on the basis of a RI increment of 0.140 ml/g for cellulose in 0.9% (w/v) DMAc/LiCl. Two replicate measurements were conducted on samples from each treatment.

2.5. Pore characterization with inverse size exclusion chromatography (ISEC)

The principle and methodology of ISEC is described in a previous communication from this laboratory (Kongdee, Bechtold, Burtscher, & Sheinecker, 2004). In essence, the material of interest is packed in a chromatography column to act as the stationary phase and probe molecules (substances of known molecular size that have no affinity for the material) are eluted through the column in a mobile phase. The accessible pore volumes are derived from the residence times of probes as shown in Eq. (1), and plotted as a function of probe diameter. The slope and y-intercept from regression analysis of the linear portion of the plot yield values of the pore parameters: total pore volume, pore surface area, and mean pore size in material as shown in Eqs. (2) and (3).

$$V_{\mathrm{i}} = \frac{(T_{\mathrm{e}} - T_{\mathrm{o}})F}{W} \tag{1}$$

$$V_{\mathrm{i}} \approx V_{\mathrm{p}} - \frac{d_{\mathrm{i}}}{2} O_{\mathrm{p}} \tag{2}$$

$$\bar{D}_{\mathrm{p}} = \frac{V_{\mathrm{p}}}{O_{\mathrm{p}}} \times 2 \times 10^4 \tag{3}$$

where V_{i} = accessible pore volume (ml/g); T_{e} = retention time of probe (min); T_{o} = retention time for a totally excluded component (min); F = flow rate of mobile phase (0.1 ml/min); and W = dry weight of material (g); V_{p} = total pore volume (ml/g); d_{i} = probe diameter (Å); O_{p} = pore surface area (m^2/g); and $\bar{D}_{\mathrm{p}}$ = mean pore size (Å).

The experimental procedure described previously (Kongdee et al., 2004) was followed in characterizing the pore structure of samples by ISEC using as probes a series of polyethylene glycols and dextrans of increasing molecular weight. Four replicate measurements, two each on specimens from warp and fill yarns, were conducted on samples from each treatment.

2.6. Diffusion studies

The diffusion rates and distribution of a given dye may be used for semi-quantitative comparisons of pore structures between substrates. In this work, the diffusion and distribution of a fluorescent whitening agent (FWA), C.I. Fluorescent Brightener 252 (Uvitex BHT; Ciba, Basel, Switzerland), was used as the basis for comparisons of pore structures between the samples. An aqueous solution was prepared by dissolving 1 g Uvitex BHT 120% in 1 l deionized water and filtered through a microfilter (0.45 μm HV). Fiber specimens, 0.2 g in weight, were immersed in 40 ml of the 1 g/l solution for 10 min, 4 h, or 24 h at room temperature; then removed, rinsed twice for 10 min each with running cold water, and dried under ambient conditions. Fiber cross-sections were then observed with fluorescence microscopy, photographed, and the depth of FWA diffusion within fibers measured on the photographic images; as described elsewhere (Abu-Rous, Varga, Bechtold, & Schuster, 2007). Five to seven measurements were conducted on fiber specimens from each treatment.

Statistical analyses of data were performed with the software SPSS® at a 0.05 level of significance. The error bars in graphs represent data variation in terms of ±1 standard deviation.

3. Results and discussion

The mean values of results from the different measurements on untreated and alkali treated samples are listed in Table 1.

3.1. Carboxyl content and DP

No significant differences were observed in carboxyl content between the untreated and alkali treated samples. Substantial differences were not observed in molecular weight distribution profiles obtained by GPC between the different samples, shown in Fig. 1. In comparisons of molecular weight distribution parameters, there was evidence of a small decrease in the proportion of short chain-length polymers as well as some degradation of longer chain-length polymers in alkali treated samples.

Oxidative degradation of cellulose, to which it is susceptible in alkaline conditions, results in the generation of carboxyl groups in the polymer (Klemm, Philipp, Heinze,

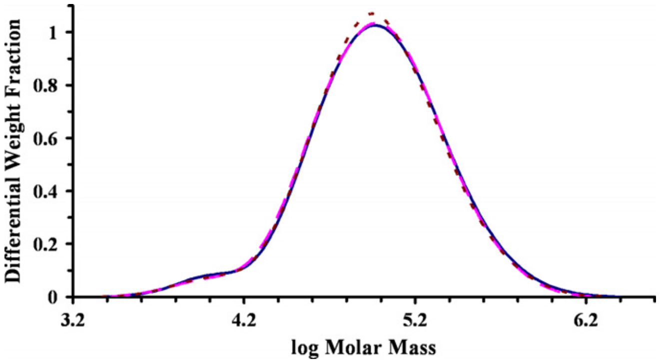

Fig. 1. Molecular weight distribution profiles obtained by GPC in specimens from: (——) untreated; (— —) NaOH treated; and (— —) KOH treated samples. (color reproduction in web, but black-and-white in print).

Table 1
Results of sample evaluations

Measurement	Treatment		
	Untreated	NaOH	KOH
Carboxyl content (meq/100 g substrate)	2.81 (0.41)[a]	2.45 (0.90)	3.31 (0.44)
IR crystallinity index (A_{1370}/A_{2900})	0.630 (0.013)	0.599 (0.023)	0.623 (0.004)
Degree of polymerization			
Mn (×1000 g/mol)	57.3 (0.0)	57.0 (0.3)	57.0 (0.1)
Mw (×1000 g/mol)	142.2 (0.3)	136.4 (3.3)	137.0 (2.5)
Mz (×1000 g/mol)	313.3 (3.7)	282.2 (1.4)	295.3 (1.5)
Mw/Mn	2.48 (0.00)	2.40 (0.05)	2.41 (0.05)
DP (<50)	1.3 (0.0)	1.3 (0.1)	1.3 (0.1)
DP (<100)	4.0 (0.1)	3.8 (0.2)	3.8 (0.2)
DP (>2000)	8.8 (0.2)	8.1 (0.3)	8.1 (0.2)
Pore parameters[b]			
V_P (ml/g)	0.596 (0.078)	0.671 (0.041)	0.544 (0.023)
$\bar{D}_p$ (Å)	37.52 (6.79)	33.45 (1.51)	32.56 (1.59)
O_p (m^2/g)	320 (16)	402 (29)	335 (29)
FWA diffusion (μm)[c]			
10 min	1.02 (0.05)	1.88 (0.17)	1.27 (0.17)
4 h	2.29 (0.11)	2.82 (0.21)	1.90 (0.13)
24 h	3.23 (0.29)	3.94 (0.19)	3.23 (0.19)

[a] 95% Confidence intervals.

[b] V_P, total pore volume; $\bar{D}_p$, mean pore size; O_p, pore surface area.

[c] Extents of FWA diffusion within fibers after 10 min, 4 h, and 24 h of immersion.

Heinze, & Wagenknecht, 1998; Trotman, 1984). Alkali treatments of cellulose also cause a limited dissolution in the polymer, mainly of short-length chains and hemicelluloses (Klemm et al., 1998). To these short chain-length components are attributed a large proportion of the carboxyl groups in cellulose (Ibbett, Phillips, & Kaenthong, 2006a, 2007). The alkali treated samples in this work exhibited evidence both of dissolution of short chain-length polymers, and of polymer degradation. Hence, the lack of significant differences in carboxyl content between the untreated and alkali treated samples may possibly result from a compensation of the increase in carboxyl content due to oxidative degradation during alkali treatment, by a coincident decrease in carboxyl content due to dissolution of short chain-length components from the cellulose.

3.2. Crystallinity

An increase in crystallite dimensions but a reduced degree of orientation among crystallites and amorphous regions is observed in lyocell fibers after alkali treatment (Lenz, Schurz, & Wrentschur, 1992, 1993; Zhu, Ren, & Wu, 2004). A decrease in fiber crystallinity is observed *during* treatment with alkali, but recrystallization occurs in subsequent washing and neutralization to extents which depend on process conditions. Hence, under different treatment conditions, the crystallinity in alkali treated lyocell has been found to be higher, lower, or not very different from that in untreated substrates (Lenz, Schurz, & Wrentschur, 1992; Zhu et al., 2004). In our work, there were no significant differences in IR crystallinity indices between the untreated and alkali treated samples.

3.3. Pore characterization with ISEC

A comparison of elution profiles (semi-log plots) obtained with the different samples in ISEC measurements are shown in Fig. 2. There were no significant differences in elution profiles between specimens from a given treatment, so average retention times are shown for each sample.

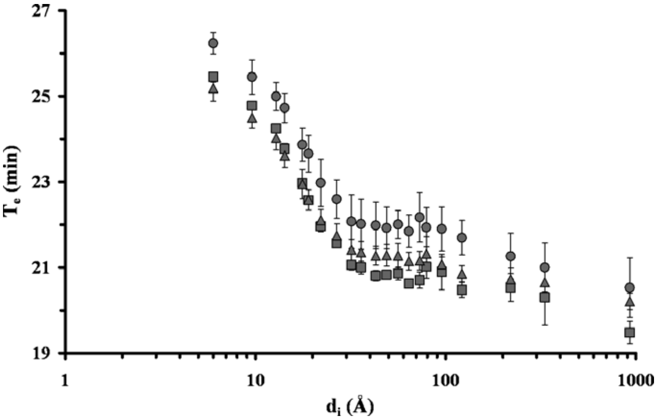

Fig. 2. Results from ISEC measurements: average retention times (T_e) of probes as a function of their diameter (d_i) in (●) untreated; (■) NaOH treated; and (▲) KOH treated samples.

Retention times decrease continuously with increasing probe diameter until a certain probe size beyond which changes in retention times are minimal and a plateau is observed in plots. The probe size at which the plateau region begins is designated the exclusion limit and signifies the smallest probe to be completely excluded from all pores in the material (Kongdee et al., 2004). Exclusion limits may be used as approximations of the largest pore size in materials, but the degree of scatter in data (Fig. 2) did not allow for a precise estimation of exclusion limits among the different samples.

The plots of accessible pore volumes against probe diameters obtained with Eq. (1) from the elution profiles of individual specimens are shown in Fig. 3, and average values of pore parameters derived with Eqs. (2) and (3) from the linear portions of these plots are listed in Table 1.

In general, alkali treatments of cellulose increase total pore volume but decrease the average pore diameter in substrates (Heinze & Wagenknecht, 1998). Again, the treatment conditions employed can exert a significant influence on the results obtained and examples may be found in literature of both increased and decreased pore volume in cellulosic fibers after alkali treatments (Bredereck, Stefani, Beringer, & Schulz, 2003; Kasahara, Sasaki, Donkai, & Takagishi, 2004).

In our work, the total pore volume in samples treated with NaOH was significantly higher than in those treated with KOH, with intermediate values being observed in the untreated samples. But the differences in total pore volume between the untreated and alkali treated samples were not statistically significant. The values of $\bar{D}_p$ appeared to be lower in the alkali treated as compared to untreated samples, but the differences were not statistically significant. Similar values of pore surface area were obtained for the untreated and KOH treated samples, but that in NaOH treated samples was significantly higher.

Despite the uncertain differences in $\bar{D}_p$ between the different samples, a significant presence of smaller sized pores may be discerned in NaOH treated samples from the significantly higher pore surface area. Such indications though were not evident for the KOH treated samples. The slopes of change in accessible pore volume (V_i) with change in probe size (d_i) maybe used for rudimentary assessments of differences in pore size distribution between substrates (Bertoniere & King, 1989). The magnitudes of these negative slopes (ml/g/Å): 0.016 ± 0.001, 0.020 ± 0.002, and 0.017 ± 0.001 for untreated, NaOH treated and KOH treated samples respectively; indicate a higher gradient of change in pore size and thereby a different pore size distribution in the NaOH treated samples as compared to the untreated or KOH treated samples.

3.4. FWA diffusion studies

Photomicrographs of fiber cross-sections from FWA diffusion studies on specimens from the untreated, NaOH treated and KOH treated samples are shown in Fig. 4;

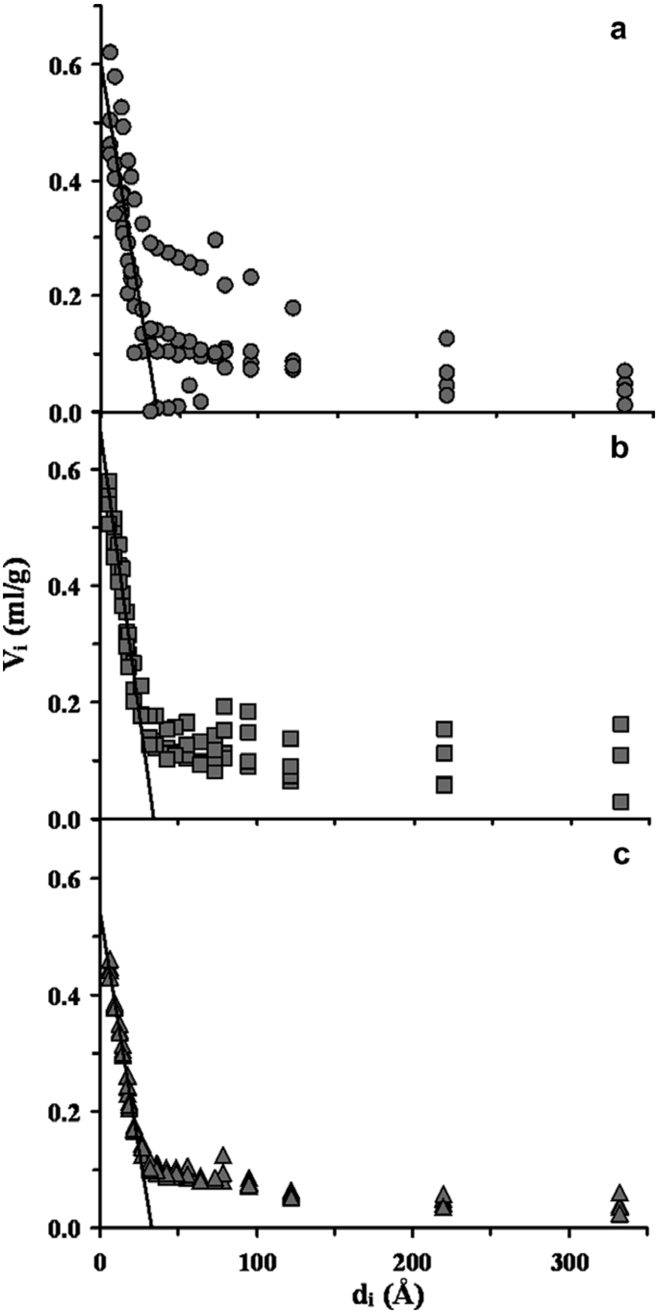

Fig. 3. Results from ISEC measurements: plots of accessible pore volume (V_i) against probe diameter (d_i) obtained with individual specimens from (a) Untreated; (b) NaOH treated; and (c) KOH treated samples.

and the extents of FWA diffusion within fibers after 10 min, 4 h, and 24 h of immersion as measured on the images are listed in Table 1.

It may be worth pointing out that the parameter quantified in this test was only the depth of FWA diffusion within fibers, and not the amounts of FWA taken up by samples. Hence, these results will not be useful for quantitative comparisons of overall accessibility but may be used for assessing relative differences in accessibility across fiber structures.

The extent of FWA diffusion within fibers increased with immersion time in all samples. In comparing the depth of FWA diffusion in fibers between alkali treated and untreated samples, we observed the following: at 10 min, the values were higher for alkali treated samples by close to 85% and 24% in the NaOH and KOH treated samples, respectively, at 4 h, the value for NaOH treated samples was higher by 23%, but that for KOH treated samples was lower by 17%; and at 24 h, the diffusion extent in NaOH treated samples was 22% greater, while that in KOH treated samples was not significantly different. In addition, it was observed that for all samples, there was a lack of FWA presence at fiber centers even after 24 h of immersion in test solutions.

In taking photographs of specimens for measurements of diffusion extents, the exposure times were adjusted to obtain the sharpest possible image at each instance. In images taken at a set exposure time of 1.2 ms of fiber cross-sections from specimens immersed in the FWA solution for 4 h (shown in Fig. 5), the fluorescence intensity was observed to be higher in the alkali treated as compared to untreated samples, with the highest intensity being observed in samples treated with KOH. The differences in fluorescence intensity likely result from differences in FWA content between samples from the different treatments.

In other work (Abu-Rous et al., 2007), it was found that a complete diffusion of FWA across cross-sections was observed only in 'never-dried' lyocell fibers, and that tests on fibers dried after spinning revealed a lack of FWA presence at fiber centers. Transmission electron microscopy (TEM) images of lyocell fiber cross-sections reveal a thin highly-porous skin, a compact center of low porosity, and an intervening area of intermediate porosity (Abu-Rous, Ingolic, & Schuster, 2006).

The results from FWA diffusion measurements and observations from TEM images appear to indicate transitions of porosity in the morphology of lyocell fibers, where accessibility at the center is distinctly lower than that at the periphery. Both alkali treatments appear to have resulted in higher accessibility at the peripheral regions in fibers (NaOH more than KOH). The consistently high levels of FWA diffusion in fibers from the NaOH treated samples appear to indicate an increased accessibility up to greater depths in fiber peripheral regions; while the initially high then lower extents of FWA diffusion in fibers from the KOH treated samples, as well as the higher fluorescence intensity in these samples as observed in Fig. 5, appear to indicate increased accessibility up to shallower depths.

Other evidence of changes in fiber structure due to alkali treatments may be obtained from reports in literature. In water or its mixtures with *N*-methylmorpholine-*N*-oxide (NMMO), the fibrillation in lyocell appears to be limited primarily to fiber surfaces (Ducos, Biganska, Schuster, & Navard, 2006). However, lyocell fibrillation in NaOH-water mixtures appears to result from a splitting of the whole fiber into fibrils. Lyocell exhibits a greater fibrillation tendency in solutions of NaOH as compared to KOH in tests on alkali-swollen fibers (Zhang, Okubayashi, & Bech-

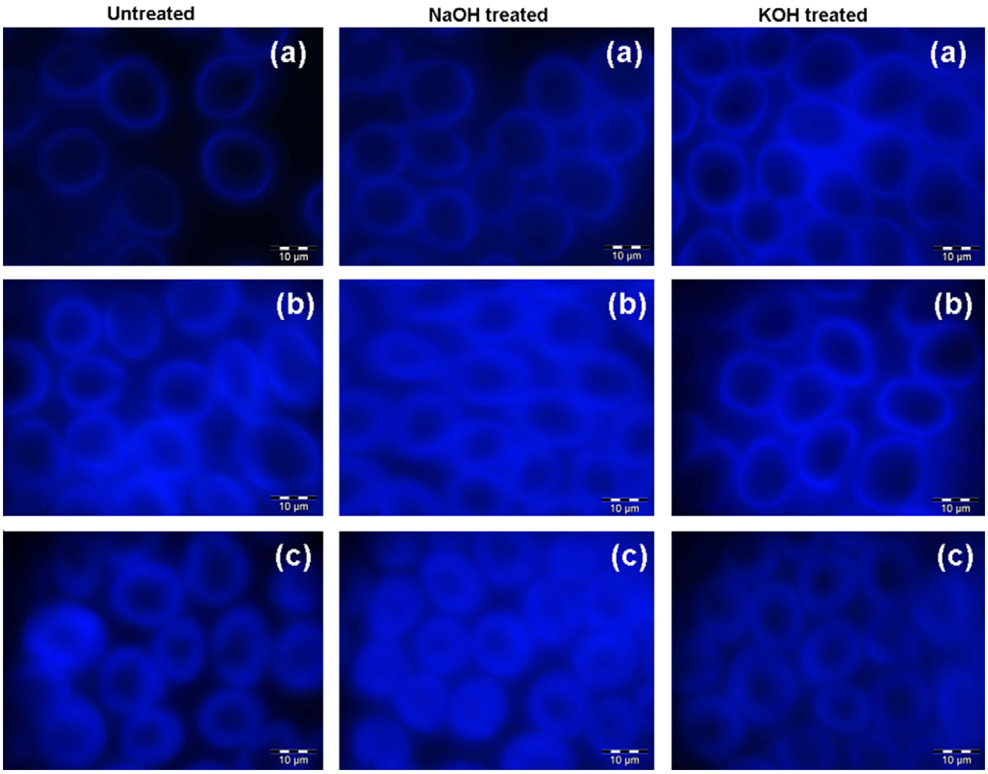

Fig. 4. Cross-section of fiber specimens from untreated, NaOH treated and KOH treated samples after immersion in 1 g/l Uvitex BHT 120% for: (a) 10 min; (b) 4 h; and (c) 24 h (color reproduction in web, but black-and-white in print).

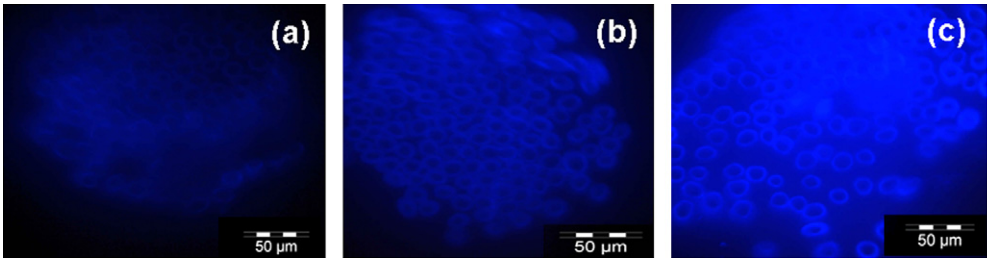

Fig. 5. Diffusion of FWA across fiber cross-sections after 4 h immersion in 1 g/l Uvitex BHT 120%, as observed in images taken at an exposure time of 1.2 ms in specimens from: (a) untreated; (b) NaOH treated; and (c) KOH treated samples (color reproduction in web, but black-and-white in print).

told, 2005a). The splitting tendency of alkali-swollen lyocell is also greater in solutions of NaOH as compared to KOH, and this order is found to persist despite a similarity in fiber swollen diameters (Öztürk, Okubayashi, & Bechtold, 2006). In tests of fibrillation tendencies in water on lyocell fibers after alkali pretreatment, the fibrillation is found to be greater in fibers pretreated with NaOH as compared to KOH at pretreatment concentrations comparable to those used in this work (Zhang, Okubayashi, & Bechtold, 2005b).

The results of this work and of others reported in literature indicate that there are differences between the two alkali types (NaOH and KOH) in the changes they bring about in lyocell fiber structure during/after treatments. From available evidence, it appears that there may be a deeper extent of NaOH diffusion through fibers, which results in changes to fiber structure/accessibility to greater depths. On the other hand, the extent of KOH diffusion in fibers appear to be limited to shallower depths, which limits the changes in fiber structure/accessibility to shallower depths. There is no definitive evidence of changes or lack thereof in structure/accessibility at fiber centers during/after alkali treatments. A schematic illustration of this tentative model is shown in Fig. 6.

4. Conclusions

The primary objective of this work was to explore reasons for the varied behavior in lyocell fabrics resin finished after alkali pretreatments as compared to those resin finished without pretreatment. Investigations of the fiber structure in alkali pretreated and untreated fabric samples

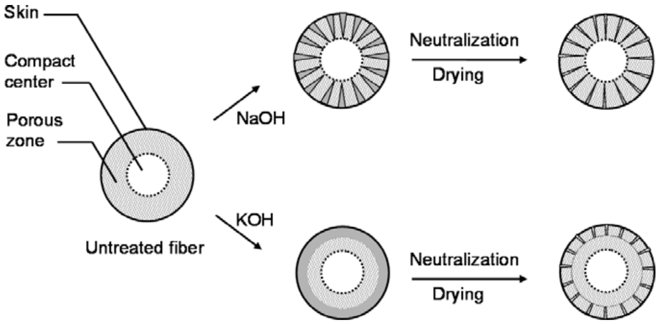

Fig. 6. Schematic illustration of tentative model of change in lyocell fiber structure during and after treatments with NaOH and KOH (Abu-Rous, 2006).

revealed some differences that may be attributed to the alkali treatments. We shall now attempt to correlate the differences in fiber structure among the different samples to the differences observed in resin distribution and mechanical properties between the same samples after resin finishing.

Lyocell fiber morphology appears to be characterized by transitions of porosity with accessibility at fiber centers being lower than that in the peripheral regions. Evidence was obtained of increased accessibility in fiber peripheral regions after alkali treatment, but there were no visible changes of accessibility at fiber centers. There were also indications of a decrease in pore size in alkali treated substrates. The predominant presence of resin on substrate surfaces in samples resin finished after alkali treatment may possibly result from a reduced pore size at or near fiber centers leading to an exclusion of resin from fiber centers.

There was some evidence of degradation in fibers from the alkali treated samples. There were no significant differences in crystallinity, but it may be expected that there is a reduced degree of orientation among crystallites and amorphous regions in fibers from the alkali treated samples. These changes alone may be expected to cause strength loss in samples after alkali treatment; but no significant differences were observed in strength among samples awarded pretreatments alone (Manian et al., 2006). Hence, it is at present unclear why there was a greater reduction in strength among samples resin finished after alkali pretreatments in comparison to those resin finished without pretreatment.

More work is required to gain a better understanding of the influence of alkali pretreatments in lyocell resin finishing. The scope of this work was limited to two *specific* alkali treatments. It is necessary to expand the study to include a wider range of alkali concentrations, more alkali types, and more types of resin finishing reagent. It will also be interesting to evaluate the influence of alkali treatments on the accessibility of lyocell to resin finishing reagents and catalysts. In addition, it is necessary to conduct FWA diffusion tests on lyocell substrates treated with a wider variety of alkalis over a greater range of concentrations. All these investigations are underway and will be reported at a later time.

Acknowledgements

We are grateful to the Versuchsanstalt-Textil of HTL-Dornbirn for the use of their testing facilities, and to Ms. Edith Winder for her gracious assistance in sample preparation for ISEC measurements. This work was made possible by the financial and material support received from the Christian-Doppler Research Society (Vienna, Austria), and Lenzing AG (Austria).

References

Abu-Rous, M. (2006). Characterisation of the Wet-State Pore Structure of Lyocell and Other Man-Made Cellulosic Fibres by Fluorescence and Electron Microscopy. Ph.D Thesis, University of Innsbruck, Austria.

Abu-Rous, M., Ingolic, E., & Schuster, K. C. (2006). Visualisation of the fibrillar and pore morphology of cellulosic fibres applying transmission electron microscopy. *Cellulose, 13*(4), 411–419.

Abu-Rous, M., Varga, K., Bechtold, T., & Schuster, K. C. (2007). A new method to visualize and characterise the pore structure of TENCEL® (Lyocell) and other man-made cellulosic fibres using a fluorescent dye molecular probe. *Journal of Applied Polymer Science, 106*(3), 2083–2091.

Baldinger, T., Moosbauer, J., & Sixta, H. (2000). Supermolecular structure of cellulosic materials by Fourier transform infrared spectroscopy (FT-IR) calibrated by WAXS and ^{13}C NMR. *Lenzinger Berichte, 79*, 15–17.

Bertoniere, N. R., King, W. D., & Rowland, S. P. (1981). Reagent migration and the performance of durable-press fabrics. *Textile Research Journal, 51*(4), 242–251.

Bertoniere, N. R., & King, W. D. (1989). Effect of scouring/bleaching, caustic mercerization, and liquid ammonia treatment on the pore structure of cotton textile fibers. *Textile Research Journal, 59*(2), 114–121.

Bredereck, K., Stefani, H.-W., Beringer, J., & Schulz, F. (2003). Alkali- und Flüssigammoniak-Behandlung von Lyocellfasern. *Melliand Textilberichte, 58*(1/2), 58–64.

Ducos, F., Biganska, O., Schuster, K. C., & Navard, P. (2006). Influence of the lyocell fibers structure on their fibrillation. *Cellulose Chemistry and Technology, 40*(5), 299–311.

Grant, J. N., Andrews, F. R., Weiss, L. C., & Hassenboehler, C. B. Jr., (1968). Abrasion and tensile properties of cross-linked cotton fabrics. *Textile Research Journal, 38*(3), 217–225.

Heinze, U., & Wagenknecht, W. (1998). In *Comprehensive cellulose chemistry*. *Functionalization of cellulose* (Vol. 2). Weinheim: Wiley-VCH.

Ibbett, R. N., Phillips, D. A. S., & Kaenthong, S. (2006a). Evaluation of a dye isotherm method for characterisation of the wet-state structure and properties of lyocell fibre. *Dyes and Pigments, 71*(3), 168–177.

Ibbett, R. N., Phillips, D. A. S., & Kaenthong, S. (2007). A Dye-Adsorption and Water NMR-Relaxation Study of the Effect of Resin Cross-Linking on the Porosity Characteristics of Lyocell Solvent-Spun Cellulosic Fibre. *Dyes and Pigments, 75*(3), 624–632.

Kasahara, K., Sasaki, H., Donkai, N., & Takagishi, T. (2004). Effect of processing and reactive dyeing on the swelling and pore structure of lyocell fibers. *Textile Research Journal, 74*(6), 509–515.

Klemm, B., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W. . In *Comprehensive cellulose chemistry*. *Fundamentals and Analytical Methods* (Vol. 1). Weinheim: Wiley-VCH.

Kongdee, A., Bechtold, T., Burtscher, E., & Sheinecker, M. (2004). The influence of wet/dry treatment on pore structure – the correlation of pore parameters, water retention and moisture regain values. *Carbohydrate Polymers, 57*(1), 39–44.

Lenz, J., Schurz, J., & Wrentschur, E. (1992). Comparative characterization of solvent spun cellulose and high wet modulus viscose fibres by their long periods. *Acta Polymerica, 43*(6), 307–312.

Lenz, J., Schurz, J., & Wrentschur, E. (1993). Properties and structure of solvent-spun and viscose-type fibres in the swollen state. *Colloid and Polymer Science, 271*(5), 460–468.

Lickfield, G.C., Yang, C.Q., Drews, M.J., Aspland, J.R., Chen, W., Feng, N., & Hu, C. (2001). Abrasion Resistance of Durable Press Finished Cotton. National Textile Center Annual Reports. http://www.ntcresearch.org/pdf-rpts/AnRep01/C00-01-A1.pdfAccessed September 16, 2003.

Manian, A. P., Abu-Rous, M., Schuster, K. C., & Bechtold, T. (2006). The influence of alkali pretreatments in lyocell resin finishing – resin distribution and mechanical properties. *Journal of Applied Polymer Science, 100*(5), 3596–3601.

Öztürk, H. B., Okubayashi, S., & Bechtold, T. (2006). Splitting tendency of cellulosic fibers. Part 2: Effects of fiber swelling in alkali solutions. *Cellulose, 13*(4), 403–409.

Rowland, S. P., Bertoniere, N. R., & King, W. D. (1983). Assessment of fabric performance versus reagent location from lick roller application of DMDHEU. *Textile Research Journal, 53*(3), 187–196.

Schelosky, N., Roeder, T., & Baldinger, T. (1999). Molecular mass distribution of cellulosic products by size exclusion chromatography in DMAc/LiCl. *Das Papier (Darmstadt), 53*(12), 728–738.

TAPPI Test Methods, Volume One. (1989). T 237 om-88 – Carboxyl Content of Pulp. Atlanta: TAPPI.

Trotman, E. R. (1984). In *Dyeing and chemical technology of textile fibers* (6th ed., pp. 39–40). Great Britain: Charles Griffin and Company Ltd.

Zhang, W., Okubayashi, S., & Bechtold, T. (2005a). Fibrillation tendency of cellulosic fibers. Part 1: Effects of swelling. *Cellulose, 12*(3), 267–273.

Zhang, W., Okubayashi, S., & Bechtold, T. (2005b). Fibrillation tendency of cellulosic fibers. Part 3: Effects of alkali pretreatment of lyocell fiber. *Carbohydrate Polymers, 59*(2), 173–179.

Zhu, Y., Ren, X., & Wu, C. (2004). Influence of alkali treatment on the structure of newcell fibers. *Journal of Applied Polymer Science, 93*(4), 1731–1735.