Macromol. Symp. **2010**, 294-II, 24–37

DOI: 10.1002/masy.200900027

Changes in the Inter- and Intra- Fibrillar Structure of Lyocell (TENCEL®) Fibers after KOH Treatment[†]

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Summary: Lyocell fibers were treated with KOH up to 8 M which was demonstrated to distribute homogeneously at the *outer zones* of fiber cross section compared to NaOH which accesses more deeply but less homogenously. Both NaOH and KOH solutions can be used to lower significantly the fibrillation of lyocell fibers. However, due to intrafibrillar swelling together with deep penetration ability of alkali seen for NaOH treatments results in great fiber tensile strength loss which is not observed for KOH treatments due to its inability to penetrate the fiber completely. The porous structure of fibers was studied by inverse size exclusion chromatography (ISEC) to identify mean pore diameter, total pore area and accessible pore volume (APV). Mean pore diameter of fibers decreased after KOH treatments which did not change after NaOH treatments. Wide angle X-ray diffraction analyses (WAXD) were applied to identify the crystallinity index and crystallite size. In general, fiber properties such as water retention value, carboxyl content using methylene blue sorption method, depth of color measured after dyeing with C.I. Direct Red 81 and weight loss were distinctly different in the ranges up to 2 M, 2-5 M and 5 to 8 M KOH. KOH treatment suggests new possibilities for the pretreatment of lyocell fibers to lower fibrillation while slightly lowering elongation at break without a distinct loss in tensile strength and with less decrease in carboxyl content and weight loss without changing dyeing properties of fibers compared to NaOH treatment.

Keywords: cellulose; fibers; lyocell; structure; swelling

Introduction

Lyocell is regenerated from cellulose by using wet spinning process where *N*-methylmorpholine-*N*-oxide monohydrate solution is used as dissolving agent.[1] A helical arrangement of the fibrils is present in cotton fibers whereas lyocell fibers have a fibrillar structure with longitudinally arrangement of fibrils along the fiber axis.[2].

Alkali pretreatment is applied during textile processing in order to improve luster, appearance, dye affinity and dimensional stability of cellulosic fibers and also fabric softness or handle, smoothness and resilience of cellulosic fabrics.[3] Alkali treatment consists of three steps: swelling, decrystallization during swelling and then recrystallization by washing off the alkali from the cellulosic material.[4,5]

Swelling decreases the crystallinity by cleavage and rearrangement of hydrogen bonds, but after rinsing and drying crystallinity becomes higher than before for the regenerated cellulosic fibers.[6] Pore structure, crystallinity, unit cell structure, orien-

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tation, mechanical and thermal properties of fibers change by alkali treatments.[7–9] Crystalline-fibril theory is favored than fringe-micelle theory in the publications of Warwicker so that they use the term 'interfibrillar' instead of 'intercrystalline'.[10] In interfibrillar swelling, fibrils move apart, no penetration into the fibrils occurs, i.e. cellulose I structure prevails, whereas intrafibrillar swelling results in penetration into the fibrils resulting in cellulose II. Interfibrillar swelling alone takes place in concentrations less than 3 M of NaOH for cotton fibers, whereas above this concentration intrafibrillar swelling can take place in addition to the interfibrillar swelling.[11] The interfibrillar swelling of various cellulosic fibers in NaOH (4% w/w) is in the order of: cotton < lyocell < modal < viscose and inversely proportional to the crystallinity.[12] Above 9% (2.25 M) concentration of NaOH, NaOH penetrates also into ordered regions of cellulose.[13]

Maximum swelling of a lyocell fiber occurs with a higher concentration of KOH solution (6 M) compared to NaOH solution (2.5 M).[14] Because of its higher basic strength and lower tendency to ion dipole formation resulting in higher affinity for cellulose, KOH penetrates into the semi-crystalline regions of cellulose. Due to its lower hydrated size, KOH is able to penetrate the ordered regions and impart more uniform swelling. KOH with larger cation size can cause greater disorder at the lattice imperfections than NaOH can.[13]

Splitting test, alkali retention value, fiber diameter measurements, weight loss can be conducted *during* the alkali treatment of cellulosic materials.[15,16] Split number indicates the distribution of alkali causing local weakness due to internal stress and loosening of H bonds inside a cellulosic fiber. OH^- ions in alkali solution breaks the hydrogen bonds of cellulose resulting in swelling, but the type of cation defines the place of OH^- ions in the fiber resulting in different split numbers.[15] Splitting of regenerated cellulosic fibers, i.e. lyocell, viscose and modal, into their fibrils was achieved when a shear force was applied on the swollen fiber. While interfibrillar swelling occurred, increase in concentration increased the split number. But above a threshold concentration where intrafibrillar swelling occurred together with interfibrillar swelling, the split number decreased by increase in concentration. Up to 5 M, split number increased in the order of KOH < LiOH ≤ NaOH < TMAH (tetramethyl ammonium hydroxide), which corresponds to the hydrated cation size. On the other hand, irrelevant to either alkali or fiber type no split was observed above 5 M, but the swollen fibers only deformed under applied pressure.[15,17] This region can be deemed as 'deformable, i.e. plasticizable region' for cellulosic fibers due to the homogeneous distribution of alkali and deformable property of the fiber without splitting or fibrillation. This region also refers to the complete mercerization of cellulose I structure mentioned by Dimick 1976.[5]

Compared to other alkali treatments, KOH alkalization yields less negative effects on cellulose which makes KOH attractive to be used in a combination with other textile processes though KOH costs are higher. The substantial improvement in recycling of chemicals, e.g. membrane filtration, re-boiling of chemicals, from waste water streams promises less costs in KOH treatment. A more controlled textile operation of cellulosic materials could be an option to run with KOH where alkali is needed.

The 'Sandoflex' method refers to 250 g/l KOH treatment of lyocell materials in order to decrease its *fibrillation tendency*. The maximum swelling of lyocell in KOH was found to be at a higher concentration (6 M) than cotton, ramie which evidenced the effect of cellulosic fiber type on swelling.[18,19] Mercerization using sole KOH or KOH/NaOH mixtures is applied on mixed yarns made up of pulp and cotton since the solubility (weight loss) of cellulose is much less than that of in sole NaOH.[20,21] Sole KOH or KOH-NaOH mixtures were used as an alkali system during reactive dye fixation on cellulosic material.[22–24] KOH was used in comparison to NaOH and LiOH as a swelling agent before dyeing cotton materials with direct, azo and vat dyes.[25] KOH was applied during vat dyeing in order to increase the solubility of dyestuff[26] and was also used in vat dyeing of cellulose acetate fabrics.[27] The possible substitution of NaOH by KOH was mentioned already in the 30s of the past century to be useful for vat dyeing and alkalization of viscose and cotton.[28]

Significant differences between the effects of a KOH treatment and a NaOH treatment followed by a pad-dry cure operation have been reported for lyocell fabric by Manian et al., who could demonstrate high sensitivity of NaOH pretreated fabric for crosslinking with DMDHEU/$MgCl_2$.[29,30] The effects of NaOH treatment on the lyocell fiber properties also has been studied in detail[31], it is of importance to study the effect of KOH treatment also.

There has not been yet an overall study about the effect of a range of concentrations of KOH on regenerated cellulosic fibers, e.g. lyocell fibers. It is of prime importance to find out the threshold concentration where intrafibrillar swelling takes place together with interfibrillar swelling for KOH with regard to lyocell fibers. While detailed studies about the effects of NaOH and KOH *during* alkali treatment of lyocell fibers have been reported in literature[15], it is also essential to investigate the reactivity, accessibility of lyocell fibers *after* KOH treatment. The present study aims to figure out these important features.

Experimental Part

Materials

Lyocell staple fiber (TENCEL® Standard) without spin finishing was kindly supplied by Lenzing AG Austria. The titer and the length of the fibers were 1.3 dtex and 38 mm, respectively.

Analytical grade potassium hydroxide (KOH, >99%) was from Fluka (Buchs, CH). Uvitex BHT™ (120%) for fluorescent dyeing of fibers was supplied by CIBA (Basel, Switzerland). Embedding resin Technovit7100™ containing a solution based on 2-hydroxyethylmethacrylate (HEMA), hardener I and hardener II for sample preparation of fluorescence imaging was from Kulzer Austria. Isoprene (98%), acetone (99%) and azo-bis-iso-butyronitrile (AIBN) (98%) for sample preparation of TEM samples were obtained from Fluka. NaCl (99.5%) was from Merck (Germany); C.I. Direct Red 81 (50%) from Sigma-Aldrich; acetic acid (100%) from Merck; sodium acetate ($\geq$ 98.5%) from Fluka; methylene blue C.I. 52015 from Merck and boric acid ($\geq$ 99%) from Merck. Polyethylene glycol (PEG) and dextran probes for inverse size exclusion chromatography (ISEC) and gel permeation chromatography (GPC) application were obtained from Fluka.

Methods

Alkali Treatment

Fiber samples in slack form were immersed in aqueous KOH solutions (1 M, 2 M, 3 M, 4 M, 5 M, 8 M) with a liquor ratio of 1:33 at a certain concentration for 2 h at room temperature. The fiber was washed under running tap water and neutralized with an acetate buffer containing 0.01 mol/l of acetic acid and 0.01 mol/l of sodium acetate (pH 5.0). The fiber sample was washed with distilled water sufficiently until the pH value of the solution indicated 7.0 and conductivity was less than 3 mS/m. Then the fibers were dried in an oven at 60 °C for 1 h.[16]

Water Retention Value (WRV)

Swelling of fibers in water was determined by a centrifugal method according to the literature.[19,32] 0.5 g of fiber samples were immersed in water (40 ml) for 2 h at room temperature and then centrifuged at 4000xg for 10 min and weighed (w_w). After washing off the alkali from fiber, the fibers were dried in an oven at 105 °C for 4 h and they were weighed again (w_d). Water retention value was determined according to equation (1). DIN 53 814 was modified in that centrifugation time was taken as 10 min instead of 20 min. The mean value was the result of four measurements.

$$WRV = (w_w - w_d)/w_d \tag{1}$$

Moisture Content (MC)[33]

In order to determine weight loss of fibers during alkali treatment firstly moisture content of fibers were calculated. The moisture content of fibers was calculated according to equation (2). Firstly fibers were conditioned at 20 ± 2 °C at 65 ± 2% relative humidity for 24 h and weighed (w_1). Then they were dried at 105 °C for 4 h. Fibers were weighed again (w_2) after cooling down in a desiccator with P_2O_5.

$$MC\,(\%) = w_1 - w_2/w_2 \tag{2}$$

The measurement was performed three times for each sample to obtain the mean value.

Weight Loss (%)

Weight loss of fibers during alkali treatment was determined. The fibers were conditioned at 65 ± 2% relative humidity and at temperature of 20 ± 2 °C for 24 h. 0.25 g of fibers in the conditioned state (w_m) was swollen in 20 ml of alkali solution for 2 h. Fibers were washed with running tap water and neutralized with an acetate buffer containing 0.01 mol/l of acetic acid and 0.01 mol/l of sodium acetate (pH 5.0). Fibers were washed firstly with running tap water and then distilled water until the pH value of the solution indicated 7.0 and conductivity of fibers was less than 3 mS/m. Then the fibers were dried in an oven at 105 °C for 4 h. The weight of dried fibers was measured (w_3). The weight of dry fibers (w_d) was calculated according to equation (3).

$$w_d = w_m - (w_m \,x\, MC) \tag{3}$$

Weight loss of fibers was calculated according to equation (4).

$$\text{Weight loss} = (w_d - w_3)/\,w_d \tag{4}$$

The measurement was performed three times for each sample to obtain the mean value.[16]

Determination of Carboxyl Content by Methylene Blue Sorption[34]

A weighed cellulose sample with known MC was suspended in a 1:1 mixture of aqueous methylene blue chloride solution (300 mg/l) and borate buffer (pH = 8.5) for 20 h. After filtration, 2.5 ml of the solution was transferred to a calibrated flask with a mixture of 5 ml 0.1 M HCl by diluting up to 50 ml. The visible absorbance of the dye liquor for each sample was measured by a Hitachi U-2000 Spectrophotometer at a wavelength of 664.5 nm. The molar quantity of dye taken up by the fiber was assumed to correspond to the fiber carboxyl content, expressed in mmol/kg (equation 5).

$$\begin{aligned}&\text{mmol COOH/g oven dry sample}\\&\quad = (7.5 - A)x0.00313/E\end{aligned} \tag{5}$$

where A is the total amount of free methylene blue in mg and E is the weight of oven-dry sample in g. The mean value was the result of three measurements.

Inverse Size Exclusion Chromatography (ISEC)

Polyethylene glycol (PEG) and dextran of known molecular weight and diameter were used as probes, and were eluted in a mobile phase through a column packed with the material of interest, which acted as the stationary phase. The ISEC measurements followed Kongdee et al. 2004.[35] The calculations to estimate pore volume, size and surface area were described in the literature.[36–38] The mean value was the result of three measurements.

C.I. Direct Red 81 Dyeing Procedure

The untreated and KOH treated lyocell fibers were dyed with a mixture of 2 g/l

Direct Red Dye 81 and 0.5 g/l NaCl dyeing solution using a liquor ratio of 1:40 by using Werner Mathis AG LABOMAT dyeing machine continuous and alternate agitation of 30 rpm. The samples were dyed by exhaust method. The mean value was the result of three measurements.

The temperature was increased from room temperature to 100 °C with a gradient of 5 °C/min. The temperature was held constant at 100 °C for 30 min and cooled down to 60 °C with a gradient of 3.5 °C/min. The dyed samples were rinsed with running tap water until no color release from fibers to water is observed. Then the fibers were air-dried. The measurement was performed three times for each sample to obtain mean value. Details of the K/S (color strength) measurement can be found in the literature.[16]

Fluorescent Whitening Agent (FWA) Penetration[39,40]

Samples were dyed with fluorescent whitening agent (FWA) Uvitex BHT for different times. After preparing fiber cross sections using an microtome (Reichert, model: 1140/Autocut), the dye penetration depth was measured using an Olympus BX microscope equipped with a mercury burner lamp, monochromatic filters and a digital camera system (Analysis).

Transmission Electron Microscopy (TEM)

Firstly the sample preparation was carried out and then the micrographs were obtained using a Technai G2 12 (FEI Company) microscope equipped with a CCD camera (Gatan Bioscan) at 100 kV.[36,41]

Wide Angle X-ray Diffraction (WAXD)[31,42,43]

Samples were prepared by pressing randomly oriented samples into the form of discs at 50-60 °C. Control experiments showed that temperatures of 50 to 60 °C had no effect on the crystallinity but enabled a more uniform, flatter and denser sample to be produced. X-ray measurements were carried out on a Bruker D5005 diffractometer using copper K alpha radiation of wavelength 1.5418 Å. Slit focus reflection geometry was used. Crystallinity determinations involved optimising the empty holder corrected data to a linear background plus 3 sharp pure Gaussian functions, representing the $1\bar{1}0$, 110 and 020 crystallographic planes, and one broad pure Gaussian feature, representing the amorphous component. Position, width and intensity of all Gaussian functions were allowed to vary independently. Variations in position were due to small errors in the height of samples due to the imperfections in the pressing technique. The data manipulation was carried out using intensity v 2θ data in the Microsoft Excel software package with the Solver add in.

Crystallite sizes corresponding to each sharp diffraction peak and at right angles to the diffracting planes were calculated using the Debye Scherrer equation:

$$\text{Crystallite size} = \{0.9 * \text{X} - \text{ray wavelength}\}/\{\text{corrected peak width} * \cos(\text{q})\}$$

where q is the angle of diffraction.

There are several contributions to the peak width, including instrumental broadening (Binst), lattice distortions (Bdist) and the finite size of the crystals (Bsize) As stated in the literature[44], a correction was only made for the instrumental broadening, using a similar value (0.15) for the integral breadth of the 28.4° peak of the silicon powder standard.

$$(\text{Bobserved})^2 = (\text{Binst})^2 + (\text{Bdist})^2 + (\text{Bsize})^2$$

Tensile Properties

Tensile strength and elongation at break of single fibers was determined according to the method outlined in the literature[31] which is a modification of.[45] The samples were conditioned and measurements were conducted at 65 ± 2% relative humidity and 20 ± 2 °C. Linear density of single fibers was determined by a Vibroskop F113, Lenzing Technik Instruments, before conducting tensile measurements. The tenacity and elongation of single lyocell fibers were determined by a Vibrodyn F120, Lenzing Technik Instruments, according to DIN 53816. Gauge length, pre-loading and cross-head speed were 10 mm, 70 mg, 10 mm/min, respectively. Ten fibers for each sample were tested to obtain a mean value. Fibers having less than 8% elongation to break were deemed to be brittle and a tensile test was not conducted.

Discussion

Swelling Capacity in Water, Carboxyl Content, Weight Loss

Figure 1 shows the changes in WRV, carboxyl content of lyocell fibers *after* KOH treatment and weight loss *during* KOH treatment up to 8 M. Up to 2 M, gradual decrease in WRV and gradual increase in weight loss of lyocell fibers was observed. WRV of lyocell fibers leveled off between 2 M and 5 M, and increased up to the WRV of untreated sample for 8 M KOH treatment. Weight loss increased up to 5 M of KOH by increase in concentration and leveled off beyond this value. Carboxyl content of fibers was found not to change significantly by KOH treatments.

The change in carboxyl content is in accordance with literature where minimal changes reported after treatment with 4.46 M KOH. This was explained by 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.[29]

In the literature carboxyl content of lyocell fibers was reported to be 18.4 ± 1.0, 20.6 ± 0.5, 15 ± 0.9, 12.1 ± 1.1 mmol/kg using potentiometric, conductometric, polyelectrolyte titrations.[46] and methylene blue sorption method[31] respectively. Each method to determine carboxyl group amount accesses to the different parts of the fiber, thus their results differ. In the present study accessible part of the total carboxyl content was characterized by methylene blue sorption.

The gradual changes in WRV, carboxyl content, weight loss of lyocell fibers after NaOH treatment was found to be up to 2.5 M while it is 2 M for KOH in the current study. 2.5 M was found to be the threshold concentration for NaOH, up to which sole inter-fibrillar swelling takes place. Above 2.5 M NaOH the fiber properties leveled off.[31]

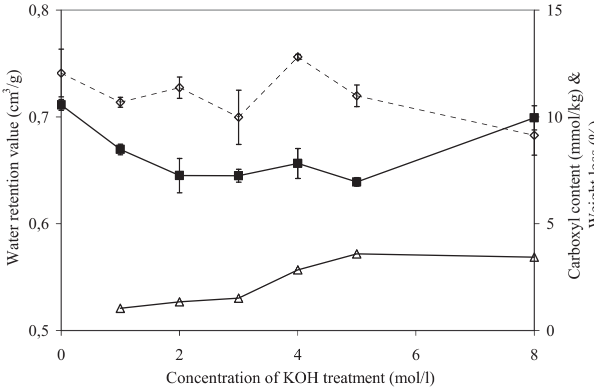

Figure 1.
WRV (■) and carboxyl content (◇) of lyocell fibers after KOH treatment, weight loss (Δ) during KOH treatment.

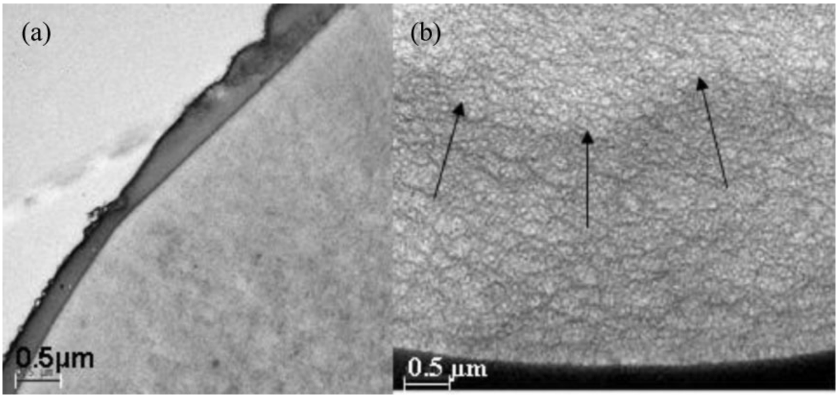

Figure 2.
TEM of (a) untreated lyocell fiber (b) 2 M KOH treated lyocell fiber (The arrows show the uppermost accessibility of water).

Pore Structure

In TEM images of the fibers, pores originally filled with water appear dark or black, due to the electron-opaque osmium stain in the polyisoprene filling the pore, whereas cellulose appears white.[39] Larger bundles of fibrils of the 2 M KOH treated samples (Figure 2b) can be observed compared to the untreated fiber (Figure 2a). Figure 2b also shows the homogenous modification and accessibility of water on the *outer zones* of lyocell fiber as shown by arrows demonstrating the limit of interfibrillar swelling together with intrafibrillar swelling reaching only up to this region across the cross-section.

In a previous study, splitting tendency of lyocell fibers in KOH was found to be less than that of in LiOH, NaOH and TMAH which was attributed to the homogenous distribution of KOH inside the fiber resulting in less stress and split number.[15] During KOH treatment, reorganization to larger bundles of fibrils occurs (Figure 2b) which is assumed to result in reduced stress during wet treatment. Thus lower split numbers are found in KOH.[15]

TEM studies of lyocell fibers showed that homogeneous distribution of fibrils in the untreated sample was changed into small bundles of fibrils after 2.5 M NaOH treatment. The size of a bundle of fibrils is found to be smaller in the case of 2.5 M NaOH treatment[31] compared to 2 M KOH treatment in the current study.

Figure 3 shows the difference between the retention time of each probe (T_e) and the average of totally excluded probes (T_o); DEX 4500000, PEG 511000 and PEG 182000, i.e. (T_e-T_o), as a function of probe size. The T_e-T_o difference decreased as the probe size increased. Kongdee et al. 2004 stated that when the T_e-T_o difference was not significant, (< 1 min), the corresponding pore diameter gave the upper limit of pore size for that sample.[37] Upper limit of pore size of untreated and 1 M KOH treated samples was found as ca. 27-32 Å, whereas ca. 19-22 Å for the rest of the samples. This can be due to the hydrated size of KOH resulting in smaller pores under swelling pressure, which persisted even after washing and drying of the fiber. In the literature, the T_e-T_o difference of NaOH treated samples were found to be comparable with that of the untreated sample.[31]

Accessible pore volume (APV) of untreated and KOH treated lyocell fibers measured by ISEC as a function of concentration was shown in Figure 4. The x-axis was shown up to 35 Å since Figure 3 indicated the upper limit of pore diameter of these samples as 27-32 Å. KOH treatments decreased APV of lyocell fibers except 1 M KOH treatment. APV

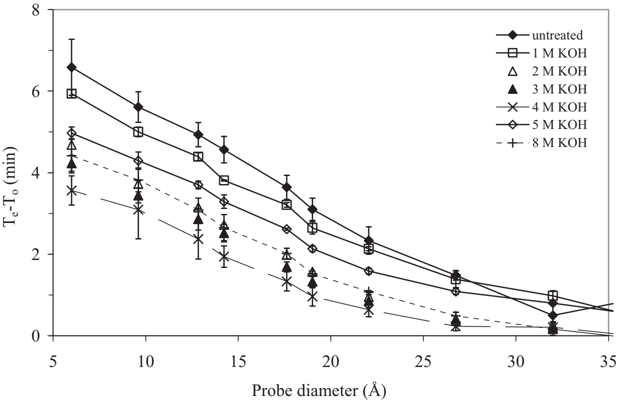

Figure 3.
Retention times for probes in untreated (◆), 1 M (□), 2 M (△), 3 M (▲), 4 M (x), 5 M (◇), 8 M (+) KOH treated lyocell fibers as a function of probe diameter.

decreased ca. 24% by 2 M KOH treatment and leveled off up to 4 M, slightly increased by 5 M KOH treatment (ca. 10% less than untreated sample) and decreased ca. 20% by 8 M KOH treatment compared to the untreated sample. The analogous change in APV (Figure 4) was also observed in WRV (Figure 1). It can be concluded that APV dominantly affect WRV which is consistent with the literature.[47] Similar relation between APV and WRV was found for treatments in NaOH at concentrations of above 2.5 M. Comparable APV between the untreated sample and NaOH treatments up to 2 M was found. 2.5 M NaOH treated sample showed the highest value which is 10% higher than that of the untreated sample, while APV decreased slightly by 3 M NaOH treatment. Above 3 M NaOH, APV of lyocell fibers leveled off.[31]

Table 1 gives the pore volume (Vp), pore area (Op), mean pore diameter (Dp) of lyocell fibers obtained from ISEC. Op values of lyocell fiber did not change significantly after KOH treatments. Between 2 M and 4 M, changes in Vp and Dp were analogous to the change in WRV in that they leveled-off which had lower value than the untreated sample.

10% decrease in pore volume was reported for 4.46 M KOH treated lyocell

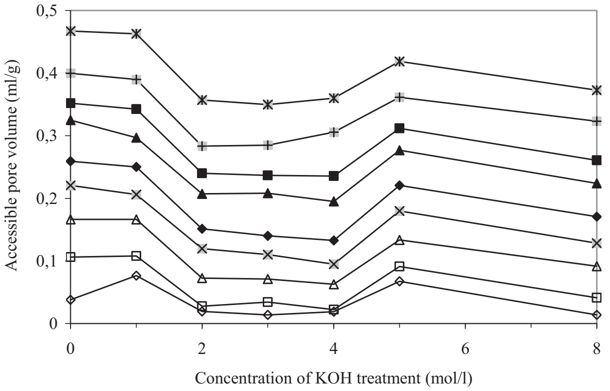

Figure 4.
Accessible pore volume of probes into lyocell fibers as a function of concentration of KOH treatment [6 Å (✱), 9.6 Å (+), 12.84 Å (■), 14.23 Å (▲), 17.62 Å (◆), 19.01 Å (x), 22.05 Å (Δ), 26.75 Å (□), 31.99 Å (◇)].

Table 1.
Average pore diameter (Dp), average total pore area (Op) and accessible total pore volume (Vp) obtained from ISEC, moisture content (%) and crystallinity index (%) obtained from WAXD of untreated and KOH treated lyocell fibers.

KOH concentration (mol/1)	Pore volume, Vp (ml/g)	Pore area, Op (m^2/g)	Mean pore diameter(Å)	Moisture content (%)	Crystallinity index (%)
0	0.58 ± 0.04	369 ± 34	32 ± 1	12 ± 0.2	50.5
1	0.57 ± 0.05	374 ± 9	31 ± 1	9.9 ± 0.6	44.7
2	0.46 ± 0.01	353 ± 4	26 ± 1	9.1 ± 0.2	47.5
3	0.46 ± 0.02	359 ± 6	26 ± 1	10.8 ± 0.1	55.2
4	0.48 ± 0.08	393 ± 78	25 ± 1	9.4 ± 0.4	58.2
5	0.53 ± 0.01	362 ± 9	30 ± 1	11.9 ± 0.1	56.8
8	0.49 ± 0.04	366 ± 37	27 ± 1	9.6 ± 0.2	59.4

fabric[29] which was shown to be around 20% decrease for lyocell fibers in the current study. It is clear that fabric would be less affected by treatments compared to the fibers.

KOH penetrates into the ordered regions of cellulose at lower concentrations than NaOH.[13] In comparison to KOH treatments, NaOH treatments did not affect Dp and Op values of lyocell fibers significantly. Up to 2.5 M NaOH treatment, gradual increase in Vp was observed, above which it leveled off. Similar trend was also observed for changes in WRV, carboxyl content and weight loss of lyocell fibers after NaOH treatments.[31]

Crystallinity and Moisture Content

Table 1 also shows the crystallinity index and moisture content of KOH treated lyocell fibers. Up to 2 M, i.e. the threshold concentration for sole interfibrillar swelling, moisture content and crystallinity index of lyocell fibers showed a decrease. The lowered crystallinity during swelling persists after rinsing and drying. The decrease in moisture content is due to the decreased accessibility to sorption sites in the amorphous region.

The increase in overall crystallinity is said to be responsible for the decreased moisture content, i.e. decrease in easily accessible amorphous region.[47,48]

At higher KOH concentrations (≥3 M) the crystallinity index increased. Due to the intrafibrillar and interfibrillar swelling, amorphous and crystalline regions reorganized. The removal of less ordered parts of the fibers containing low molecular weight polymers also contribute to an increase in crystallinity.

NaOH treatments were found to increase the crystallinity index of lyocell fibers while decreasing the moisture content.[31]

In literature crystallinity index of cotton fibers was reported to decrease gradually when KOH treatment concentration increased up to 2.9 M. Between 3.0-3.4 M KOH treatments, crystallinity index levelled off which had higher value compared to that of observed for 2.9 M KOH treatment. Above 3.5 M KOH treatment the crystallinity index showed an increase similar to that of up to 2.9 M KOH treatment.[49] The distinct lowering effect of KOH on crystallite size of cotton fibers compared to NaOH was found not to be the case for lyocell fibers in the current study. An explanation can be that crystalline parts in the fibrillar structure of lyocell fibers rearrange easier, without a distinct decrease in the crystallite sizes.

Figure 5 shows x-ray diffraction traces for untreated and 3 M KOH treated lyocell fibers, resolved into three sharp peaks corresponding to $1\bar{1}0$, 110, and 020 diffraction planes of cellulose II as well as a broad amorphous background. These three peaks were at the angular positions of $2\theta^\circ$ of approximately 12, 20 and 21.7, respectively.[50]

Changes in crystallite size along the longitudinal direction of fiber, changes

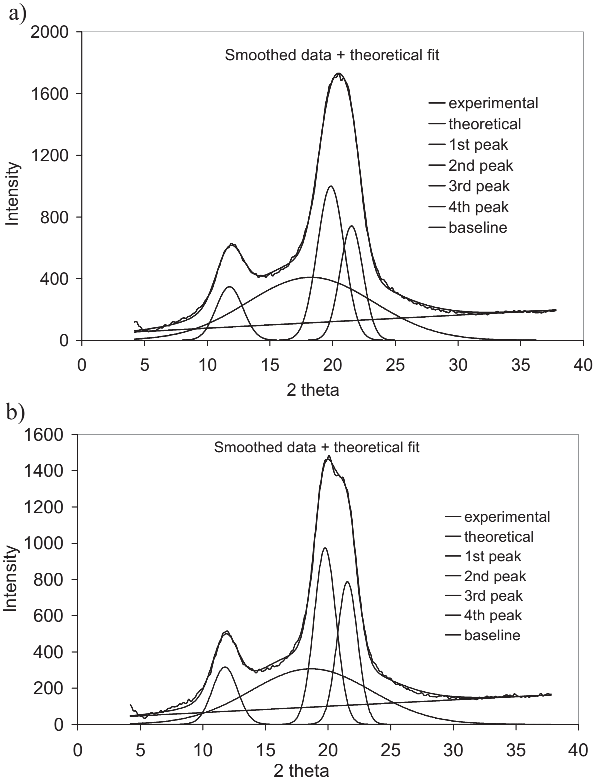

Figure 5.
WAXD of a) Untreated lyocell fiber, b) 3 M KOH treated lyocell fiber

across the cross-section of fiber and changes by an angle in between these planes refer to 110 planes, $1\bar{1}0$ planes and 020 planes respectively. Swelling, i.e. increase in fiber diameter, affects mainly crystallite dimensions normal to the $1\bar{1}0$ and 020 planes.[43]

Figure 6 shows the crystallite size normal to the 110, $1\bar{1}0$ and 020 planes. Crystallite

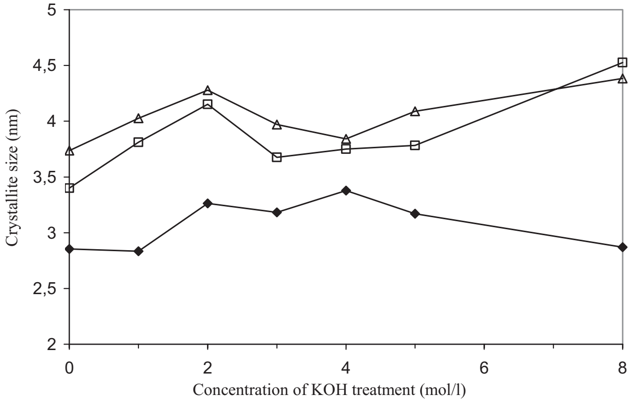

Figure 6.
Crystallite size normal to the 110 planes (◆), planes $1\bar{1}0$ (□) and 020 planes (Δ).

size normal to the $1\bar{1}0$ and 020 planes increased gradually up to 2 M KOH. Lower values of crystallite size were observed at 3-5 M KOH treatments. Highest crystallite size normal to the $1\bar{1}0$and 020 planes are observed at 8 M KOH treatment. Up to 2 M KOH, where sole interfibrillar swelling occurs, increase in crystallite size was observed. At 2-5 M KOH treatment, crystallite size normal to the 110 planes showed a leveled off value which is slightly higher than others.

In the literature it was stated that crystallite width and length of cotton fibers were mostly decreased by KOH treatment followed by NaOH and LiOH treatments under identical conditions of swelling.[51] These results show the effectiveness of KOH in rearranging the amorphous regions.

According to literature, NaOH could not alter the crystallite size normal to the 110 planes which was attributed to the stronger interaction via hydrogen bonding between the cellulose glucose rings. Up to 2.5 M NaOH, the crystallite dimensions size normal to the $1\bar{1}0$ and 020 planes increased correlating with WRV, APV, weight loss. Above 2.5 M NaOH, a decrease was observed.[31]

FWA Penetration

Figure 7 shows the fluorescent whitening agent (FWA) penetration depth in relation to dyeing time. The FWA penetration depth into untreated lyocell fiber increased as the dyeing time increased. The average fiber diameter of lyocell fiber can be taken as 12 μm, which means that the maximum of dye penetration into fiber can be 6 μm as observed from the fluorescence microscopy photos. FWA penetration of 2 M KOH treated sample reached maximum ca. 4 μm in 1440 min of dyeing which was similar to that of the untreated sample.

FWA penetration reached only to the *outer zones* of lyocell fiber after 2 M KOH treatment (Figure 8) which is consistent with its TEM results (Figure 2).

In the literature, following the treatment with 2.5-2.63 M NaOH, both lyocell fabrics and lyocell fibers were dyed with Uvitex BHT and the penetration depth of FWA into the fibers was measured. Fiber cores were dyed with FWA in the case of treatments of *fibers*. But the fiber core of treated *fabrics* was not dyed.[29,31,40] Compared to KOH, NaOH treatment leads to an increase in penetration depth of FWA dye following alkali treatments.

C.I. Direct Red 81 Dyeing

Figure 9 shows the relative color strength expressed as K/S and lightness (L^*) measured by CIELAB of dyed fibers. KOH treatments were found not to change color strength of lyocell fibers significantly. Color strength is related to a complex interaction between fiber properties such as APV, WL,

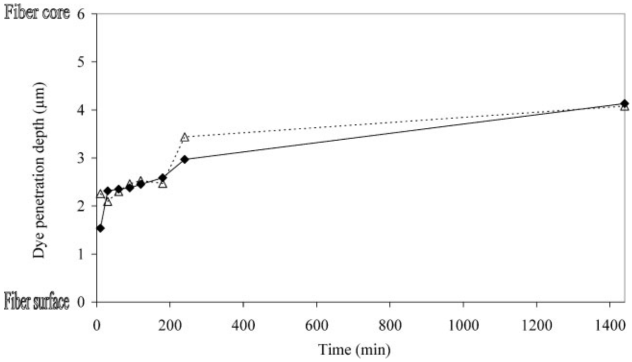

Figure 7.
Dye penetration depth as a function of dyeing time for untreated (◆) and 2 M KOH treated lyocell fibers (Δ).

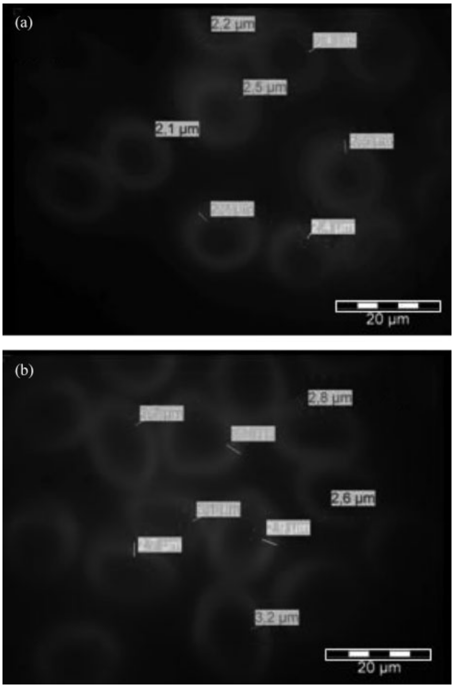

Figure 8.
Dye penetration into (a) untreated and (b) 2 M KOH treated lyocell fibers after 120 min dyeing.

carboxyl group content, accessibility in the *outer* zones of fiber.

In literature, K/S of lyocell fibers increased ca. 30% *after* NaOH treatments at concentrations of up to 2.5 M, levelled off up to 5 M NaOH and further increased ca. 44% up to 8 M NaOH. An inverse relation between color strength and carboxyl content was found for NaOH treated samples which was attributed due to the electrostatic repulsion between carboxyl group of cellulose and negatively charged functional group of the direct dye.[31]

Tensile Mechanical Properties

Tensile strength and elongation at break of single fibers were shown in Figure 10. Tensile strength of KOH treated fibers was found to be comparable with the value of untreated fiber. Elongation at break of KOH treated samples did not change significantly compared to the untreated sample except 8 M KOH treatment which had lower value.

Tensile test of KOH treated samples was able to be conducted up to 8 M (Figure 10). Although intrafibrillar swelling occurs above 2 M KOH, brittleness of fibers did not occur which can be explained by the accessibility of KOH only into the *outer zones* of fiber, i.e. not able to access the fiber thoroughly.

In literature tensile test of NaOH treated samples could only be conducted up to 3 M above which brittleness of fibers due to the interfibrillar swelling together with intrafibrillar swelling and also deep penetration of NaOH occurred. As NaOH treatment concentration increased up to 3 M, tensile strength of lyocell fibers

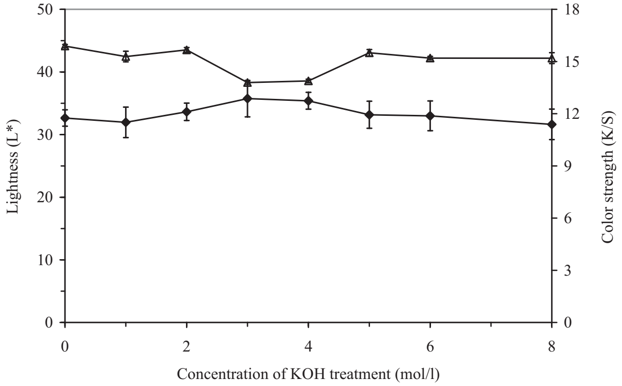

Figure 9.
Lightness (Δ) and color strength (◆) of untreated and KOH treated samples.

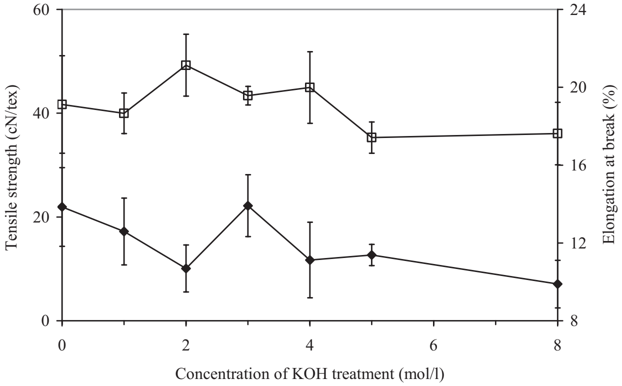

Figure 10.
Tensile strength (□) and elongation at break (◆) values of untreated and KOH treated lyocell fibers.

decreased up to 40%, whereas elongation at break decreased slightly.[31]

Conclusion

KOH treatments on lyocell fibers were conducted up to 8 M. KOH is found to affect slightly the relevant fiber physical properties of lyocell compared to NaOH, LiOH or TMAH treatments which can cause dramatic changes. In a wide range of alkali concentrations, KOH did not affect tensile strength and dyeing properties of the fiber and slightly affected the elongation at break, carboxyl content and weight loss.

Depending on concentration, KOH treatment also changed the fiber properties of lyocell fibers. Up to 2 M KOH, i.e. in the sole interfibrillar swelling region, crystallinity index decreased, above which increased. This shows that due to the smaller hydrated size of KOH, it is more effective to affect the crystalline region than NaOH in that after rinsing and drying the decrease in crystallinity persisted in the interfibrillar swelling region. In the intrafibrillar swelling region, i.e. where homogeneous distribution of alkali occurs, comparable changes in crystallinity index for both KOH and NaOH treated samples were observed. Up to 2 M KOH, pore volume as well as the pore diameter were not affected since this sole interfibrillar swelling region is reversible. During alkali washing off process, the pore structure retains its original structural values. But as the intrafibrillar swelling takes place together with interfibrillar swelling up to the total accessibility of crystalline regions (above 5 M), decrease in pore volume and pore diameter occurred due to the relative smaller hydrated size of KOH. At concentrations of 2 to 5 M KOH, a decrease in upper limit of pore size, APV and WRV was observed. KOH modifies outer regions of fiber leading to higher intensity of FWA.

KOH doesn't have negative influence on lyocell fibers which suggest its usage in reactive, vat dyeing or bleaching processes where alkali is needed without distinct changes in fiber properties as LiOH, NaOH and TMAH can do. A wide range of KOH concentrations can be applied on lyocell fibers without changing fiber properties dramatically compared to other alkali hydroxides.

Current study presented the basic fiber properties which supports the technical usage of KOH solutions for the processing of lyocell fabrics. In the alkali pretreatments to decrease fibrillation tendency, to improve dimensional stability of lyocell fabrics, the negative influence of alkali on the fiber physical properties are minor when KOH is used compared to NaOH.

Acknowledgements: The Authors gratefully acknowledge the Christian-Doppler Research Society and Lenzing AG-Austria for financial and material support, Versuchsanstalt HTL-Dornbirn for equipment, the European Polysaccharide Network of Excellence (EPNOE) for a PhD student exchange program, Dr. Elisabeth Ingolic from the Research Institute for Electron Microscopy (FELMI), the Technical University of Graz for the preparation of ultrathin fiber cross-sections of fibers for TEM measurements and Karl Reiter from Lenzing AG for facilitating the microtome cross-sectioning. We are grateful to Edith Winder and D.Ing. Margit Lenninger for assistance in sample preparation and data analyses for ISEC, respectively.

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