Alkali pretreatments and crosslinking of lyocell fabrics

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Abstract Lyocell fabrics were pretreated with NaOH, KOH and LiOH and subsequently crosslinked with three urea–formaldehyde based crosslinkers DMDHEU, DMedHEU and DMU. The mechanical properties varied with the alkali concentration in fabrics crosslinked after pretreatment with 2–8 mol/l NaOH and 4 mol/l LiOH. In fabrics crosslinked after pretreatment with 2–8 mol/l KOH and 1–3 mol/l LiOH, in contrast, the mechanical properties were relatively insensitive to the alkali concentration. The difference in effects is attributed to the alkali influence on the accessibility of crosslinker in fiber structures. The NaOH and 4 mol/l LiOH pretreatments increase the accessibility of crosslinker but the KOH and 1–3 mol/l LiOH pretreatments do not appear to change accessibilities to the same extent. The results underscore the importance of alkali choice and process control in the pretreatments of lyocell. Both NaOH and KOH may be used to good effect. However,

lyocell is more sensitive to changes of alkali concentration in NaOH treatments as compared to KOH pretreatments. Thus, the use of NaOH in pretreatments of lyocell will require a greater degree of monitoring and control of alkali concentrations as compared to when KOH is used.

Keywords Lyocell · Crosslinking · Alkali pretreatment

Introduction

Lyocell is a regenerated cellulosic fiber that is manufactured from wood pulp dissolved in *N*-methyl-morpholine-*N*-oxide. The fibers exhibit high swelling in water (Bredereck and Hermanutz 2005), and due to that, woven fabrics made of the fiber are susceptible to the formation of permanent crease marks when processed in rope form (Burrow 1998). The fiber swelling in water causes the yarns to swell and push up against each other. If the fabric is folded, the swelling stress exerted on the yarns curved around folds causes them to pull past their original positions at interlacement points, and creases are formed. Such yarn displacements cannot be reset, and hence the formed creases are permanent.

If woven fabrics are treated with alkali in open-width form before wet processing, it prevents the formation of such creases (Burrow 1998; Taylor 2015). In alkali, the

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levels of fiber/yarn swelling are far greater than with water, and that increases the yarn crimp. The crimp is retained even as the yarns de-swell when the alkali is washed off, and thus larger spaces are created between yarns at interlacement points. Now when the fabric is wetted with water, as the yarn swelling does not reach the same level as with alkali, and as the inter-yarn spaces are greater, the yarns are not pushed up against each other. It prevents the stress-induced displacement of yarns, and thus creases are not formed.

The swelling of cellulotics in alkali can change their supramolecular structure, viz., the crystallinity, porosity and accessibility, and therefore alter their sorption abilities and reactivity (Rojo et al. 2013; Xu et al. 2017). As a result, the alkali pretreatment step has the potential to influence the results of subsequent chemical processing of fabrics. A common step in cellulosic fabric processing is a treatment with crosslinker to enhance their wrinkle resistance, which is often referred to as the “durable press” or “easy care” finishing. Thus, it was of interest to determine if alkali pretreatments of lyocell exerted any influence on its subsequent crosslinking.

The alkalis commonly used in commercial-scale pretreatments of lyocell are NaOH (120 g/l) and KOH (250 g/l). We examined their effects on later crosslinking with a widely used agent, dimethyldihydroxyethylene urea (DMDHEU) (Manian et al. 2006, 2008). Fabric pieces crosslinked after alkali pretreatment exhibited lower tensile strength, lower abrasion resistance and lower crease recovery as compared to pieces crosslinked without pretreatment, although all pieces were treated with the same crosslinker formulation and all exhibited the same crosslinker content. The differences between the results from no pretreatment and KOH pretreatment were small, but the differences with NaOH pretreatment were larger. Furthermore, the NaOH pretreatment appeared to have changed the pore size distribution in fibers, and the distribution of DMDHEU through fibers in the pieces crosslinked after NaOH pretreatment was different as compared to the non-pretreated and KOH-pretreated pieces.

To further explore these differences, the investigation was expanded to include three alkali types: NaOH, KOH and LiOH; over a wider range of concentrations: 2–8 mol/l of KOH and NaOH, and 1–4 mol/l of LiOH; and three crosslinkers: DMDHEU, dimethyldihydroxyethylene urea (DMeDHEU) and dimethyl urea

(DMU). The maximum solubility of LiOH in water is about 5 mol/l at ambient temperature, and hence its concentration range was smaller. It is not commonly used in fabric pretreatments but LiOH is known to influence lyocell structure such as the porosity and fibrillation propensity (Öztürk et al. 2011; Zhang et al. 2005), and hence was included in this work to better understand the effect of alkali type.

A subset of the work, viz. the effect of NaOH pretreatments on crosslinking with the three agents, has been reported on previously (Kongdee et al. 2010). Here, we present the remainder of the results. In the main part of the paper, we discuss the effects of pretreatments with NaOH, KOH and LiOH on crosslinking with DMDHEU. In the supplementary section (Tables S1–S2 and Figures S1–S5), we show the pretreatment effects on crosslinking with DMeDHEU and DMU.

Experimental materials and methods

Materials

A 100% lyocell, 1/1 plain-woven fabric, of 138 g/m² basis weight, with 36 ends and 26 picks per centimeter comprised of 20-tex yarns was kindly supplied by Lenzing AG (Austria) and was used in the work. The crosslinking agents (see Table 1) and the wetting agent (Kieralon Jet B Conc.) were commercial products kindly provided by BASF AG (Ludwigshafen, Germany). The alkalis, crosslinking catalyst (MgCl₂·7H₂O), acetic acid, and sodium bicarbonate, were all analytical grade reagents, and the solutions were all formulated in deionized water.

Treatments

The alkali pretreatments were performed on fabric pieces of dimensions 30 cm × 35 cm with a pad-batch method. The pieces were padded through the alkali solutions at 1.0 m/min with a nip pressure of 1 bar, rolled around glass rods, enveloped in plastic sheets, and stored at ambient temperature for 4 h. They were then rinsed in running hot water for 5 min, neutralized by immersion in 5% acetic acid for 60 min, rinsed again in running cold water for 5 min, and line-dried overnight. The samples were then padded through crosslinker formulations at

Table 1 The crosslinkers and formulations used in treatments

	DMDHEU	DMU	DMeDHEU
Commercial product	Fixapret CP	Kaurit S	Fixapret NF
Solids content (% w/w) ^a	ca. 75	ca. 100	ca. 45
Concentrations used in crosslinking treatments (g/l)			
Commercial product	56	93.3	42
Catalyst (MgCl ₂ ·7H ₂ O)	16.8	32.7	12.6
Wetting agent	0.5	0.5	0.5

^a The data were obtained in a personal communication from the supplier

2.0 m/min with a nip pressure of 2 bar, dried at 100 °C for 3 min, and cured at 185 °C for 65 s. To neutralize any residual acidity, the pieces were immersed in 1 g/l sodium bicarbonate for 30 min, rinsed in running cold water, and line-dried overnight.

The alkalis employed in the pretreatments were 2–8 mol/l of NaOH and KOH, and 1–4 mol/l of LiOH. A set of 24 pieces were pretreated at each alkali concentration, and the solutions were changed after every six pieces to minimize the effects of alkali depletion. The compositions of the crosslinker formulations are shown in Table 1, where the amounts of commercial products were adjusted to achieve a solids content of about 42 g/l. The catalyst and crosslinker amounts are derived from recommendations of the supplier (BASF AG). A set of six pieces from each alkali type/concentration went into each crosslinker treatment, and the liquors were changed after each set.

There were two sets of controls: (A) where the pieces were awarded no pretreatment, and (B) where the pieces were pretreated with deionized water (under the same conditions as with alkali except there was no neutralization).

Measurements

The wet pickup in padding was calculated from the mass change on padding as percentage of the initial mass. The dimensional change was measured by drawing 26 cm × 26 cm benchmarks on the pieces before pretreatment and re-measuring the distance between them after. It was also determined from the change in mass per area measured on 100 cm² discs punched from the non-pretreated and pretreated pieces.

The nitrogen content was determined on specimens from the crosslinked pieces on a Leco FP 328 nitrogen analyzer as a measure of their crosslinker content. Its distribution was determined by the method of negative

staining with the dye C.I. Direct Red 81 (De Boer 1980), as described previously (Manian and Bechtold 2005). The carboxyl content was measured with the methylene blue dye sorption method (Klemm et al. 2004).

The breaking force and elongation at break was measured with an 18 cm gauge length at a 2 cm/min rate of extension with the ISO 13934-1:1999 strip method. The values were then used to calculate the work of rupture, or toughness, with Eq. 1. The abrasion resistance was measured with the ISO 12947-3:1999 mass loss method after 6000 abrasion cycles under 9 kPa pressure on a Martindale Abrasion Tester (Halifax, England). The wrinkle or crease recovery angle (CRA) was measured along the warp direction according to DIN 53890 after 30 min of recovery. The flexural rigidity was determined from bending lengths according to ISO 9073-7:1999. The specimens were then padded through deionized water at 2.0 m/min through a nip pressure of 1 bar, and tested again for wet flexural rigidity.

$$\text{Work of rupture (N m)} = 0.5 \times \text{force at break (N)} \times \text{elongation at break (m)} \quad (1)$$

The fabric pieces were all conditioned at (20 ± 2) °C and (65 ± 2)% relative humidity for a minimum of 48 h before any measurements were performed on them. All comparisons were assessed with Analysis of Variance (ANOVA) and Bonferroni tests at a 0.05 level of significance with the software SPSS® (IBM Software, USA). The error bars in plots and parenthetical values in tables denote ±1 SD.

Results

The following results are available in Table 2 (from pretreated pieces) and III (from pretreated and

Table 2 Results of measurements on pretreated (non-crosslinked) samples

Pretreatment	Alkali wet pickup (%)	Dimensional change (%)		Mass/area (g/m ²)	Carboxyl content (10 ⁻³ mmol/g)	Breaking force (N)	Elongation at break (%)	Dye content (g/100 g)	Color depth (K/S _{Corr})
		Warp	Fill						
Controls									
A	—	—	—	138.01 (3.35) ^a	6.09 (0.97)	726 (11)	15.6 (0.0)	0.63 (0.02)	8.57 (1.48)
B	106 (3)	3.5 (0.6)	0.3 (0.5)	143.78 (1.53)	7.49 (0.52)	689 (10)	15.0 (0.6)	0.96 (0.01)	11.04 (0.86)
NaOH									
2 mol/l	110 (3)	10.0 (1.0)	2.8 (0.6)	154.63 (1.31)	11.20 (1.32)	700 (22)	12.4 (1.6)	1.04 (0.05)	11.31 (0.49)
4 mol/l	117 (4)	14.6 (1.3)	8.7 (0.3)	175.96 (1.75)	13.80 (2.27)	532 (40)	16.3 (0.6)	0.91 (0.08)	15.35 (0.76)
6 mol/l	119 (3)	19.4 (1.4)	10.2 (0.1)	187.92 (3.71)	12.68 (0.11)	489 (29)	16.3 (0.6)	0.82 (0.00)	13.39 (0.83)
8 mol/l	123 (2)	19.9 (0.8)	11.5 (0.4)	193.58 (0.97)	13.33 (1.18)	565 (43)	17.8 (1.0)	0.87 (0.02)	11.21 (0.82)
KOH									
2 mol/l	114 (3)	9.5 (0.5)	2.4 (0.5)	152.15 (0.87)	12.83 (0.95)	712 (22)	18.9 (0.8)	0.91 (0.01)	9.81 (0.41)
4 mol/l	129 (5)	10.9 (1.0)	4.7 (0.2)	160.12 (2.94)	14.39 (0.13)	700 (15)	15.9 (0.9)	0.84 (0.00)	9.84 (0.40)
6 mol/l	137 (2)	12.7 (0.8)	5.8 (0.6)	166.89 (2.03)	15.18 (0.74)	718 (27)	15.6 (0.7)	0.92 (0.04)	10.90 (0.56)
8 mol/l	141 (3)	14.0 (0.6)	6.3 (0.8)	167.48 (0.69)	14.93 (0.73)	698 (19)	16.4 (0.6)	0.87 (0.01)	10.08 (0.96)
LiOH									
1 mol/l	110 (15)	5.5 (2.0)	2.1 (1.9)	150.00 (1.83)	4.92 (0.47)	730 (19)	14.4 (0.7)	0.97 (0.02)	10.50 (0.41)
2 mol/l	109 (2)	9.9 (0.5)	2.6 (1.1)	155.87 (1.05)	4.44 (0.00)	723 (22)	16.5 (0.8)	1.07 (0.00)	11.90 (0.76)
3 mol/l	115 (2)	6.3 (0.6)	2.8 (0.3)	149.79 (0.94)	4.02 (0.29)	760 (22)	16.3 (1.2)	1.02 (0.02)	12.26 (1.38)
4 mol/l	114 (1)	10.9 (0.7)	6.4 (0.6)	164.57 (1.88)	12.33 (2.15)	637 (31)	16.3 (0.6)	0.96 (0.05)	14.62 (1.34)

^a Standard deviation

crosslinked pieces): wet pickup during pretreatment and crosslinker treatment, dimensional change as measured with benchmarks, mass/area, carboxyl content, force and elongation at break, and shade depth and dye content from the C.I. Direct Red 81 negative staining test.

The wet pickup in pretreatment increased with the concentration for all alkalis, and while there were no differences between LiOH and NaOH, the levels with KOH were greater. The following effects may account for these observations: both the density of alkali solutions and the degree of alkali sorption by cellulose increase with the concentration (Hitchcock and McIlhenny 1935); and, at the same molar concentrations, the densities of KOH solutions are greater than those of NaOH and LiOH (Sipos et al. 2000). Both measurements of shrinkage in alkali pretreatment—the dimensional changes and the changes of mass per area—yielded the same results. The shrinkage was greater along the warp direction than fill, and the levels increased with the alkali concentration. There were no differences between the alkalis up to 2 mol/l, but at higher concentrations the shrinkage with NaOH was greater than with KOH and LiOH.

The carboxyl content in the pieces increased with concentration of alkali in the NaOH and KOH pretreatments. In the LiOH pretreatment, the carboxyl content initially decreased with alkali concentration up to 3 mol/l, but then rose up to the levels of the other two alkalis at 4 mol/l.

The wet pickup in crosslinker pretreatment was significantly greater in the controls as compared to the alkali-pretreated pieces. Among the pretreated samples, there was no difference between LiOH and NaOH, but the crosslinker wet pickup was lower in the KOH pretreated pieces. Despite this, there were no significant differences of crosslinker content (as determined with the nitrogen content) between the control and pretreated pieces. One exception was a marginally greater crosslinker content in the samples pretreated with NaOH as compared to KOH at 6 mol/l of alkali.

The work of rupture (i.e. toughness) values calculated from the force and elongation at break are shown in Fig. 1a, a'. The values were significantly lower in the crosslinked as compared to the non-crosslinked pieces. In the non-crosslinked set, there were no differences between the controls and the pieces

pretreated with LiOH and KOH, but the toughness was significantly lower in the pieces pretreated with NaOH. In the crosslinked set, the toughness in all alkali-pretreated pieces was lower than in the controls, and the toughness in the KOH pretreated pieces was greater than in the LiOH and NaOH pretreated pieces. The following order was observed in reduction of toughness on crosslinking: controls < KOH < NaOH < LiOH.

The mass loss in abrasion resistance tests are shown in Fig. 1b, b'. The mass loss in the non-crosslinked pieces was low and in the range of 1.5–5.3%. The mass loss was generally much higher in the crosslinked pieces, and the levels varied widely with the alkali type and concentration in the pretreatment. For example, the lowest mass loss in the crosslinked set (of $3.1 \pm 0.5\%$) was observed in the pieces pretreated with 4 mol/l NaOH, and the highest mass loss (of $29.8 \pm 3.8\%$) was observed in the pieces pretreated with 1 mol/l LiOH.

The crease recovery angles (CRA) after 30 min of recovery are shown in Fig. 1c, c'. As expected, the crosslinked pieces exhibited greater crease recovery than the non-crosslinked pieces. In both sets, the crease recovery was greater in the controls as compared to the alkali-pretreated pieces. In the KOH pretreatments, the crease recovery decreased gradually with alkali concentration. In the NaOH pretreatments, the values fell sharply as the alkali concentration rose from 2 to 4 mol/l, and then increased again when the alkali concentration rose further to 6 and 8 mol/l. The pieces pretreated with LiOH also showed a reduction of crease recovery in the range of 2–4 mol/l alkali.

The percent improvement in crease recovery on crosslinking was highest in the pieces pretreated with 4 mol/l NaOH and LiOH (of 51–55%), followed by the pieces pretreated with 6 and 8 mol/l NaOH (of 39–41%), and then by the pieces pretreated with 2–8 mol/l KOH and 1–3 mol/l LiOH (of 17–21%). The control pieces showed a crease recovery improvement of only 7–13% on crosslinking.

The results of flexural rigidity measurements in the conditioned state are shown in Fig. 2. In the non-crosslinked set, the controls exhibited lower rigidity as compared to the alkali-pretreated pieces, especially those pretreated with 4–8 mol/l alkali; and, the rigidity was greater in the pieces pretreated with NaOH as compared to LiOH and KOH. In the crosslinked set,

the rigidity was similar in the controls and in the pieces pretreated with KOH and LiOH, but greater in the pieces pretreated with NaOH. In both the non-crosslinked and crosslinked sets, the pieces pretreated with 4 mol/l NaOH and LiOH exhibited significantly greater rigidity than all other pieces. The crosslinked rigidity was greater than the non-crosslinked rigidity in the controls and in the pieces pretreated with up to 2 mol/l alkali, but in pieces pretreated with alkali at concentrations of 4 mol/l and higher, the non-crosslinked rigidity was greater.

The results of wet flexural rigidity measurements are shown in Fig. 3. In the non-crosslinked set, the controls exhibited greater rigidity than the alkali-pretreated pieces. In the crosslinked set, the rigidity was generally similar in the controls and the pieces pretreated with LiOH and KOH, but the rigidity of the NaOH-pretreated pieces were higher. Peak rigidity in the pieces pretreated with 4 mol/l of NaOH and LiOH were observed also in all the wet rigidity measurements. In contrast to the conditioned-state measurements, the non-crosslinked rigidity was higher than the crosslinked rigidity in the controls and in the pieces pretreated with up to 2 mol/l alkali, and the crosslinked rigidity was higher in the pieces pretreated with alkali at concentrations of 4 mol/l and higher.

The ratios of the wet rigidity to the corresponding conditioned-state rigidity are shown in Fig. 4. In the non-crosslinked set, the ratios were much higher in the controls as compared to the alkali-pretreated pieces, and there were no significant differences between the alkali types. In the crosslinked set, the differences between the controls and the alkali-pretreated samples were smaller, and the ratios in the KOH-pretreated pieces were lower than in the pieces pretreated with NaOH and LiOH.

The principle of the negative staining test is that in crosslinked cellulose, the Direct Red 81 dye content is inversely proportional to the crosslinker content; and for the same dye content, the color depth varies with crosslinker distribution (De Boer 1980; Rowland et al. 1983). A low color depth indicates a greater surface presence of crosslinker and a high color depth indicates a low surface presence of crosslinker. The dye contents and the corresponding color depths were both lower in the crosslinked as compared to the non-crosslinked pieces (see Tables 2, 3), but the ratios of color depth-to-dye content were remarkably similar (see Fig. 5). Among the pieces pretreated with 4 and

Fig. 1 The work of rupture (**a**, **a'**), abrasion mass loss (**b**, **b'**), and crease recovery angle (**c**, **c'**) in the controls (*open circle*), NaOH-pretreated (*diamond*), KOH-pretreated (*inverted triangle*) and LiOH-pretreated (*triangle*) pieces. The values from the controls are shown at the arbitrary alkali concentrations of 0.25 mol/l (control A) and 0.5 mol/l (control B). The plots in the *left column* (**a**, **b**, **c**) show values from the non-crosslinked pieces and those in the *right column* (**a'**, **b'**, **c'**) from the pieces crosslinked with DMDHEU

6 mol/l NaOH and 4 mol/l LiOH, the values were on average 16.1 ± 0.9 in the non-crosslinked set and 16.7 ± 1.5 in the crosslinked set. Among all other

alkali-pretreated pieces and the controls, the values were on average 11.7 ± 0.9 in the non-crosslinked set and 10.5 ± 1.2 in the crosslinked set.

Fig. 2 The flexural rigidity measured in the conditioned state along the warp (a, a') and fill (b, b') directions in the controls (open circle), NaOH-pretreated (diamond), KOH-pretreated (inverted triangle) and LiOH-pretreated (triangle) pieces. The values from the controls are shown at the arbitrary alkali

concentrations of 0.25 mol/l (control A) and 0.5 mol/l (control B). The plots in the left column (a, b) show values from the non-crosslinked pieces and those in the right column (a', b') from the pieces crosslinked with DMDHEU

Discussion

A high flexural rigidity in fabrics results from reduced mobility of yarns past one another at crossover points, and it is accompanied by low crease recovery and poor abrasion resistance (Reeves et al. 1967; Grant et al. 1968, 1973). In the non-crosslinked set, the pieces pretreated with 4 mol/l NaOH and LiOH exhibited high rigidity and low crease recovery as compared to the controls, but the abrasion resistance did not differ. Therefore, the high rigidity is attributed to a temporary “setting” that is known to occur in lyocell fabrics after alkali pretreatments, which dissipates when the fabric is worked on in subsequent processing and handling.

A rise in carboxyl content of cellulose after alkali treatments, which was observed in the pieces pretreated with NaOH and KOH and to some degree with LiOH, is an indicator of oxidation. But it appears that the degree of oxidation did not reach detrimental levels as there were generally no differences of strength between the controls and the alkali-pretreated pieces in the non-crosslinked set. Both exhibited the same level of abrasion resistance and, apart from the pieces pretreated with 4 and 6 mol/l NaOH, the toughness levels did not differ between the controls and the alkali-pretreated pieces.

Crosslinking treatments can reduce the strength of cellulose for two primary reasons: the introduction of crosslinks leads to reduced stress dissipation in

Fig. 3 The flexural rigidity measured in the wet state along the warp (a, a') and fill (b, b') directions in the controls (open circle), NaOH-pretreated (diamond), KOH-pretreated (inverted triangle) and LiOH-pretreated (triangle) pieces. The values from the control are shown at the arbitrary alkali concentrations

of 0.25 mol/l (control A) and 0.5 mol/l (control B). The plots in the left column (a, b) show values from the non-crosslinked pieces and those in the right column (a', b') from the pieces crosslinked with DMDHEU

fibers (embrittlement), and there is molecular degradation due to hydrolysis by catalyst (Wakelyn et al. 1998). The former is proportional to the crosslinker content in substrates, while the latter is a function of the catalyst amount in formulations and the curing conditions. The distribution of crosslinks within fiber structures also has an influence. For the same crosslinker content, the crease recovery is greater if there is a uniform distribution of crosslinks through the fiber bulk than if the crosslinks are localized at the fiber surface (Joarder et al. 1969; Grant et al. 1968; Bertoniere et al. 1981). But, a uniform distribution of crosslinks also tends to reduce tensile strength while preserving abrasion resistance, and a greater surface localization of crosslinks preserves the tensile strength

but reduces the abrasion resistance (Bertoniere et al. 1981; Rowland et al. 1983).

As seen in the results above, the crease recovery and strength loss in the crosslinked pieces varied significantly with the alkali type and its concentration in pretreatment. All pieces were crosslinked under the same treatment conditions with identical formulations, and all exhibited very similar crosslinker contents. Thus, the variations in crease recovery and strength loss are attributed to differences of crosslinker distribution within the substrates.

In the crosslinked set, the pieces crosslinked after pretreatment with 4 mol/l NaOH and LiOH exhibited the highest percent improvement in crease recovery, their abrasion resistance was amongst the

Fig. 4 The ratios of wet-to-conditioned flexural rigidity along the warp (a, a') and fill (b, b') directions, in the controls (*open circle*), NaOH-pretreated (*diamond*), KOH-pretreated (*inverted triangle*) and LiOH-pretreated (*triangle*) pieces. The values from the controls are shown at the arbitrary alkali concentrations of 0.25 mol/l (control A) and 0.5 mol/l (control B). The plots in the left column (a, b) show values from the non-crosslinked pieces and those in the right column (a', b') from the pieces crosslinked with DMDHEU. Note the different scales on the ordinate in each plot

highest, and their toughness was amongst the lowest. In addition, their color depth/dye content ratios were the highest. The same combination of properties, though to lower extents than with 4 mol/l alkali, were also observed in the pieces crosslinked after pretreatment with 6 and 8 mol/l NaOH. In comparison, the pieces crosslinked after pretreatment with 1–3 mol/l LiOH and 2–8 mol/l KOH exhibited generally lower crease recovery improvement, lower abrasion resistance, lower color depth/dye content ratios and higher toughness.

All of these observations suggest that in the pieces crosslinked after pretreatment with NaOH (and 4 mol/l LiOH), there was a greater penetration of the crosslinker within the fiber bulk as compared to a greater surface presence in the pieces crosslinked after KOH and 1–3 mol/l LiOH. Further evidence in

support of this inference may be observed in the flexural rigidity results. The ratios of wet/conditioned rigidities in the crosslinked set were greater in the pieces pretreated with NaOH and 4 mol/l LiOH as compared to the pieces pretreated with KOH and 1–3 mol/l LiOH, which indicates that the Young's modulus was greater in the former as compared to the latter (Matsuo 1969). An improvement of the Young's modulus on crosslinking is observed with increase in the degree of crosslinker penetration in the fiber bulk (Frick et al. 1960).

The trends observed in the DMDHEU crosslinked pieces as discussed above were also observed in the pieces crosslinked with DMU and DMedHEU (see supplementary tables S1-S2 and figures S1-S5), and hence the above discussion applies for all three crosslinkers.

Table 3 Results of measurements on DMDHEU-crosslinked samples

Pretreatment	Crosslinker wet pickup (%)	Nitrogen content (%)	Breaking force (N)	Elongation at break (%)	Dye content (g/100 g)	Color depth (K/S _{Corr})
Controls						
A	79.5 (0.4) ^a	0.436 (0.025)	631 (41)	10.6 (0.6)	0.36 (0.01)	3.91 (0.78)
B	78.6 (0.9)	0.434 (0.013)	630 (19)	10.0 (0.0)	0.34 (0.03)	3.17 (0.44)
NaOH						
2 mol/l	76.9 (1.5)	0.449 (0.003)	593 (41)	9.8 (0.5)	0.27 (0.04)	2.84 (0.35)
4 mol/l	73.1 (1.2)	0.429 (0.006)	361 (17)	9.3 (0.9)	0.29 (0.01)	5.24 (0.37)
6 mol/l	76.8 (0.5)	0.459 (0.013)	306 (22)	9.4 (0.9)	0.25 (0.04)	3.80 (0.61)
8 mol/l	77.5 (0.6)	0.442 (0.001)	366 (23)	8.9 (0.7)	0.25 (0.03)	2.96 (0.39)
KOH						
2 mol/l	73.2 (2.1)	0.469 (0.011)	523 (23)	9.4 (0.6)	0.19 (0.02)	2.14 (0.13)
4 mol/l	71.0 (1.5)	0.433 (0.011)	550 (31)	9.1 (0.5)	0.27 (0.03)	3.04 (0.33)
6 mol/l	70.6 (1.3)	0.394 (0.051)	549 (39)	9.6 (0.9)	0.65 (0.16)	4.97 (1.33)
8 mol/l	70.5 (0.6)	0.422 (0.007)	450 (50)	7.8 (0.7)	0.42 (0.07)	4.23 (0.98)
LiOH						
1 mol/l	78.4 (0.9)	0.465 (0.005)	600 (43)	9.6 (0.6)	0.23 (0.03)	2.53 (0.45)
2 mol/l	76.4 (2.3)	0.464 (0.009)	540 (100)	9.3 (1.2)	0.28 (0.02)	2.87 (0.52)
3 mol/l	73.8 (0.6)	0.458 (0.006)	477 (36)	8.5 (0.6)	0.24 (0.03)	2.61 (0.15)
4 mol/l	74.1 (0.9)	0.446 (0.003)	343 (18)	8.5 (0.6)	0.24 (0.06)	4.11 (0.54)

^a Standard deviation

Fig. 5 The ratio of color depth to dye content in the controls (*open circle*), NaOH-pretreated (*diamond*), KOH-pretreated (*triangle*) and LiOH-pretreated (*triangle*) pieces, from the non-crosslinked set (**a**) and from the DMDHEU-crosslinked set (**b**). The values from the control pieces are shown at the arbitrary alkali concentrations of 0.25 mol/l (control A) and 0.5 mol/l (control B)

Conclusions

Lyocell fabrics were pretreated NaOH, KOH and LiOH and then crosslinked with the urea–formaldehyde based crosslinkers, DMDHEU, DMeDHEU and DMU. Significant influences were observed of the pretreatments with 2–8 mol/l NaOH and with 4 mol/l

LiOH on the crosslinking results. In contrast, the pretreatments with 2–8 mol/l KOH and with 1–3 mol/l LiOH did not exert a strong influence on the results of the subsequent crosslinking treatment. These results indicate that the pretreatments with 2–8 mol/l NaOH and 4 mol/l LiOH significantly alter the accessibility of crosslinker in the fibers.

Both NaOH and KOH may be used to good effect in pretreatments to reduce the wet stiffness of lyocell fabrics, but the results indicate that greater care is required in pretreatments with NaOH. Like all celluloses, lyocell exhibits high affinity for alkali, and thus there is a tendency of alkali depletion from process liquors during the course of the pretreatment. Lyocell is more sensitive to the changes in concentration of NaOH as compared to KOH, and thus concentration differences in pretreatments with NaOH may exert a greater negative impact on subsequent processing than pretreatments with KOH. Thus, it is more important to monitor and control alkali concentrations in treatments with NaOH as compared to KOH.

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