

Alkali Pretreatment and Resin Finishing of Lyocell: Effect of Sodium Hydroxide Pretreatments

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ABSTRACT: Lyocell fabric samples were pretreated with 2–8 mol/L sodium hydroxide (NaOH) and then resin-finished with dimethyloldihydroxyethylene urea, dimethyl dihydroxyethylene urea, and dimethylol urea based products. The resin-finishing treatments caused changes in the substrate properties, such as reduced accessibility, improved crease recovery, and reduced work of rupture and abrasion resistance. Differences were observed between resin-finished substrates as a function of the crosslinker type, and they were attributed to the influence of the crosslinker content and crosslink length in the substrates. The alkali pretreatments influenced the effects of resin finishing. A significant enhancement of the crosslinker penetration appeared within the substrates pretreated with 4 mol/L NaOH. Pretreatments with 6 and 8

mol/L NaOH also enhanced the crosslinker penetration, but the depth of catalyst penetration appeared to exceed that of the crosslinker; leading to demixing between the two components within the substrates. The penetration depth of a direct dye, C.I. Direct Red 81, appeared lower than that of the crosslinker in the alkali-pretreated substrates. Pretreatments with NaOH in the range of 4–8 mol/L appeared to create gradients of accessibility within fibers and yarns of lyocell fabrics, with the depth of reagent penetration increasing in the following order: C.I. Direct Red 81 < crosslinker < catalyst. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2898–2910, 2010

Key words: accessibility; alkali pretreatment; crosslinking; fibers; swelling

INTRODUCTION

Fabrics made of lyocell, a regenerated cellulosic fiber manufactured from a solution of wood pulp in *N*-methyl-morpholine-*N*-oxide, are susceptible to the formation of permanent crease marks in the course of wet processing; to counter this, alkali pretreatments are recommended as remedial measures.^{1,2} However, the strong swelling propensity of lyocell fibers in alkali solutions³ changes substrate properties and may lead to alterations in the accessibility and reactivity of lyocell for chemicals and reagents and influence its performance in subsequent treatments.^{4,5}

In earlier work,^{6,7} we examined the influence of alkali pretreatments on the performance of lyocell fabrics in subsequent resin finishing treatments. Fabric samples were pretreated with sodium hydroxide (NaOH; 120 g/L) or KOH (250 g/L) and resin-

finished with a dimethyloldihydroxyethylene urea (DMDHEU) based product. Lyocell fibers appeared to be characterized by transitions of porosity with accessibility lower at the fiber centers than at the peripheral regions. The pretreatments appeared to enhance accessibility at the peripheral regions and possibly reduce accessibility at the fiber centers. These changes were believed responsible for some observed effects of alkali pretreatment on resin finishing, such as a predominant presence of the crosslinker on the surface of samples resin-finished after alkali pretreatments versus a more uniform distribution of the crosslinker through samples resin-finished without a pretreatment. However, some other aspects of the effects were not understood, such as why samples resin-finished after alkali pretreatments exhibited greater strength loss than samples resin-finished without a pretreatment.

The previously described work was limited to pretreatments with only two alkali types, each at one concentration. To further explore the observed phenomena, it was considered necessary to expand the study to include more alkali types, a greater range of alkali concentrations, and more crosslinker types. These investigations were pursued and are the subject of this series of communications. Lyocell fabric

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TABLE I
Crosslinking Reagents Used in the Resin Finishing Treatments

Reagent	Commercial product	Solid content (% w/w) ^a
DMDHEU	Fixapret CP	~ 75
DMeDHEU	Fixapret NF	~ 45
DMU	Kaurit S	~ 100

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

samples were pretreated with the alkalis NaOH, KOH, and LiOH (1–8 mol/L) and were further resin-finished with the reagents DMDHEU, dimethyl dihydroxyethylene urea (DMeDHEU), and dimethyl urea (DMU).

In this communication, we describe the first set of results from our experiments examining the effects of pretreatments with 2–8 mol/L NaOH on the performance of lyocell fabrics subsequently resin-finished with DMDHEU, DMeDHEU, and DMU.

EXPERIMENTAL

Materials

The fabric used in this work, supplied by Lenzing AG (Lenzing, Austria), was a desized and scoured 1/1 plain-woven 100% lyocell (Tencel), with a specific weight of 138 g/m² and with 36 ends/cm and 29 picks/cm, composed of 20-tex yarns. Analytical-grade NaOH, KOH, and LiOH were used in alkali treatments. Commercial crosslinking reagents, listed in Table I, were obtained from BASF AG (Ludwigshafen, Germany) for use in resin finishing treatments, with analytical-grade magnesium chloride used as a catalyst and Kieralon Jet B Konz (BASF) used as a nonionic wetting agent. Analytical-grade acetic acid and sodium bicarbonate were used in the neutralization of fabrics after alkali and crosslinking treatments, respectively.

Experimental scheme

The experimental scheme is shown in Figure 1. Lyocell fabric samples (30 cm × 35 cm) were subjected to pretreatments with alkali solutions (NaOH, KOH, or LiOH), neutralized, washed, dried, and then subjected to resin finishing treatments with DMDHEU, DMeDHEU, or DMU; this was followed by neutralization, washing, and drying. In one set labeled control A, fabric samples were subjected to no pretreatment, and in another set labeled control B, fabric samples were pretreated with only deionized water. Control B samples did not undergo the neutralization step with acetic acid.

Pretreatment

Fabric samples were treated with a pad–batch process: they were padded through solutions of NaOH, KOH, LiOH, or deionized water on a laboratory padder at a roller speed of 1.0 m/min and a nip pressure of 1.0 bar. After padding, the samples were rolled around glass rods, enveloped in plastic sheets, and stored at ambient temperature for 4 h; then, the samples were removed from the glass rods, rinsed in hot running water for 5 min, immersed in 5% acetic acid at ambient temperature for 60 min, rinsed in cold running water for 5 min, and line-dried overnight at the ambient temperature. Samples treated with deionized water, that is, the control B samples, were only line-dried after removal from the glass rods.

The alkali concentration in the solutions ranged from 2 to 8 mol/L in treatments with NaOH and KOH and from 1 to 4 mol/L in treatments with LiOH. The limited solubility of LiOH prevented us from formulating solutions of greater concentrations. In all, 24 samples were treated at each alkali concentration, and pad liquors were renewed after every 6 samples to mitigate the effects of alkali depletion in liquors due to sorption by fabrics.

Resin finishing

The formulations used in the resin finishing treatments are listed in Table II. The amounts of the commercial products were adjusted to achieve a solid content of about 42 g/L in all resin treatment formulations. The catalyst amounts were adjusted to 30, 35, and 20% of the commercial product in the formulations of DMDHEU, DMeDHEU, and DMU,

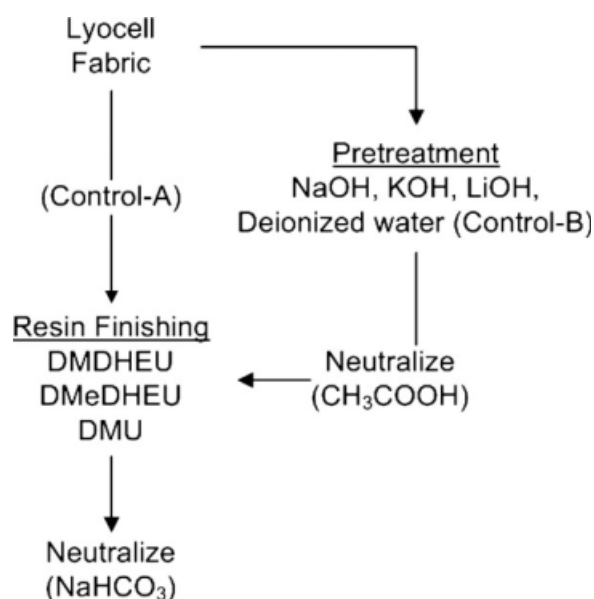


Figure 1 Experimental scheme.

TABLE II
Compositions (g/L) of the Resin Treatment Formulations

	DMDHEU	DMeDHEU	DMU
Commercial product	56	93.3	42
Catalyst (MgCl ₂)	16.8	32.7	12.6
Wetting agent	0.5	0.5	0.5

respectively, on the basis of recommendations of the supplier.⁸ An exception to the supplier recommendations was the use of only MgCl₂ as a catalyst in formulations of DMeDHEU when a stronger catalyst (a mixture of inorganic salts) was recommended. The catalyst mixture was not used to avoid influences arising from differences in the catalyst type.

Samples were padded through treatment formulations on a laboratory padder at a roller speed of 2.0 m/min and a nip pressure of 2.0 bar, dried at 100°C for 3 min, and cured at 180°C for 65 s. The drying and curing steps were performed in a laboratory stenter. To neutralize any residual acidity after the resin finishing treatments, samples were immersed in 1 g/L NaHCO₃ at the ambient temperature for 30 min, rinsed in cold running water, and line-dried overnight.

In all, a set of 6 samples from each pretreatment was subjected to every resin finishing treatment, and the treatment liquors were renewed after each set. It was ensured that every set included samples treated at different points (from first to last) between renewals of the alkali liquor in the pretreatment. One set of samples from each pretreatment (including controls A and B) was subjected to no resin finishing treatment and was retained as no-resin samples.

Evaluations

All samples were conditioned in a standard atmosphere of 20 ± 2°C and 65 ± 2% relative humidity for a minimum of 48 h before testing, which was performed in the same atmosphere. The breaking strength and elongation at break along the warp direction of the samples was tested with the strip method according to ISO 13934-1:1999 with an 18-cm gauge length at a 2 cm/min rate of extension. The abrasion resistance was assessed from the mass loss in specimens after 6000 abrasion cycles under 9 kPa of pressure on a Martindale abrasion tester (Halifax, England) according to ISO 12947-3:1999, and the crease recovery angle (CRA) along the warp direction of the samples was determined according to DIN 53890 after 30 min of recovery. The flexural rigidity of the samples was determined from the specimen bending lengths measured according to ISO 9073-7:1998 on a laboratory-built apparatus. The specimens were then padded through deionized water at 2 m/min at a nip pressure of 1 bar and tested again for the wet

flexural rigidity (WFR). The initial weights of the specimens and their wet weights after padding were recorded to determine the water pickup as a percentage of their initial weights.

The wet pickup of the samples during the pretreatment and resin finishing treatments was calculated with eq. (1) from sample weights measured before and immediately after padding:

$$\text{Wet pickup (\%)} = \left(\frac{W_f - W_i}{W_i} \right) \times 100 \quad (1)$$

where W_i is the sample weight before padding (g) and W_f is the sample weight immediately after padding (g).

Before the pretreatments, benchmarks were drawn on samples 26 cm apart along both the warp and fill directions. The distance between benchmarks was remeasured after the pretreatment to determine the dimensional change [ΔL (%)] in samples with eq. (2):

$$\Delta L (\%) = \left(\frac{L_i - L_f}{L_i} \right) \times 100 \quad (2)$$

where L_i is the distance between the benchmarks before the pretreatment ($L_i = 26$ cm) and L_f is the distance between the benchmarks after the pretreatment (cm).

The dimensional changes in the samples were also estimated from sample specific weights (mass/area) measured on fabric discs with a 100-cm² area. The crosslinker content in the samples was determined from their nitrogen contents, which were analyzed by the Dumas method in a Leco FP 328 nitrogen analyzer, and the resin distribution was estimated by the negative-staining method with C.I. Direct Red 81, as described previously.⁹ The dye content in the specimens was estimated by extraction in a 25% (v/v) aqueous solution of pyridine at 90°C for 45 min, and this was followed by spectrophotometric measurements of the extracts at 520 nm.

The moisture content of the samples was determined by the accurate weighing of approximately 0.2 g of conditioned fabric samples and drying in a laboratory oven at 105°C for 4 h, after which they were placed in P₂O₅ desiccators to cool to ambient temperature and were reweighed. The moisture content was calculated with eq. (3):

$$\text{Moisture content (\%)} = \left(\frac{W_C - W_D}{W_C} \right) \times 100 \quad (3)$$

where W_C is the weight of the conditioned samples (g) and W_D is the weight of the oven-dried samples (g).

The degree of yellowing in the samples was evaluated from their yellowness indices measured

TABLE III
Results of the Evaluations for the Samples That Were Only Pretreated (No-Resin Samples)

Pretreatment	WPU (%) ^a	Dimensional change (%)		Specific weight (g/m ²) ^b	Moisture content (%)	Yellowness index	CRA (°)	Break force (N)	Break elongation (%)
		Warp	Fill						
Control A	—	—	—	138.01	9.70	6.19	98	726	15.6
Control B	106	3.5	0.3	143.78	10.38	5.67	98	689	15.0
2 mol/L NaOH	110	10.0	2.8	154.63	9.99	4.51	97	700	12.4
4 mol/L NaOH	117	14.6	8.7	175.96	9.67	7.23	58	532	16.3
6 mol/L NaOH	119	19.4	10.2	187.92	9.27	6.41	66	489	16.3
8 mol/L NaOH	123	19.9	11.5	193.58	9.23	6.74	71	565	17.8

^a Wet pickup in the pretreatment.

^b Fabric specific weight (mass/area).

according to DIN 6167 with a Minolta Chroma Meter (Osaka, Japan) CR-200 d/0° spectrophotometer using the illuminant D₆₅ with a 10° field of observation. The yellowness index (G) was calculated with eq. (4):

$$G = \left(\frac{a \times X - b \times Z}{Y} \right) \times 100 \quad (4)$$

where *a* and *b* are standard factors with values of 1.301 and 1.149, respectively, for the illuminant D₆₅ and *X*, *Y*, and *Z* are measured tristimulus values.

Statistical analysis of the data was performed with SPSS software at a 0.05 level of significance. The error bars in graphs represent data variability in terms of ±1 standard deviation. To include results from control A and control B samples in the plots, these samples were assigned nominal alkali concentrations in pretreatment of 0 and 0.5 mol/L, respectively.

RESULTS AND DISCUSSION

The mean values of the wet pickup in the pretreatment (*n* = 24), the dimensional changes after the pretreatment (*n* = 18), the wet pickup in the resin finishing treatment (*n* = 6), the nitrogen content

(*n* = 3), the specific weight (*n* = 3), the moisture content (*n* = 3), the yellowness index (*n* = 9), CRA (*n* = 9), and the breaking force and elongation (*n* = 6), where *n* = sample size, measured on no-resin and resin-finished samples, are shown in Tables III–VI.

Pretreatments

The wet pickup during the pretreatment increased with alkali concentration of the solutions, and this can be attributed both to increased alkali sorption by cellulose with rising alkali concentrations¹⁰ and to the increasing density of the alkali solutions. The pretreatments resulted in fabric shrinkage, which was evidenced by the dimensional changes in the samples along the warp and fill directions. The dimensional change is caused by fiber swelling, which in turn causes yarn swelling leading to an increase in yarn crimp and therefore a contraction in the fabric dimensions.^{2,11} Warp shrinkage was greater than that along the fill and increased with the alkali concentration up to 6 mol/L NaOH but leveled off thereafter; whereas the fill shrinkage increased continuously with the alkali concentration of the pretreatment solutions. Shrinkage was also reflected in sample specific weights, which increased continuously with rising alkali concentrations in the liquors.

TABLE IV
Results of the Evaluations for the Samples That Underwent the Resin Finishing Treatment with DMDHEU

Pretreatment	WPU (%) ^a	N content (wt %)	Specific weight (g/m ²) ^b	Moisture content (%)	Yellowness index	CRA (°)	Break force (N)	Break elongation (%)
Control A	79.5	0.436	139.99	9.27	6.74	105	631	10.6
Control B	78.6	0.434	142.08	9.16	6.16	111	630	10.0
2 mol/L NaOH	76.9	0.449	145.28	8.41	5.25	108	593	9.8
4 mol/L NaOH	73.1	0.429	160.90	8.28	8.79	90	361	9.3
6 mol/L NaOH	76.8	0.459	164.35	8.32	7.00	93	306	9.4
8 mol/L NaOH	77.5	0.442	161.91	8.15	6.79	99	366	8.9

^a Wet pickup in the resin finishing treatment.

^b Fabric specific weight (mass/area).

TABLE V
Results of the Evaluations for the Samples That Underwent the Resin Finishing Treatment with DMedHEU

Pretreatment	WPU (%) ^a	N content (wt %)	Specific weight (g/m ²) ^b	Moisture content (%)	Yellowness index	CRA (°)	Break force (N)	Break elongation (%)
Control A	78.1	0.271	140.96	9.32	6.41	99	643	10.7
Control B	77.9	0.261	142.72	9.21	6.63	100	613	10.2
2 mol/L NaOH	75.8	0.249	147.31	8.99	5.61	104	613	10.4
4 mol/L NaOH	75.9	0.259	165.09	9.25	7.31	73	434	10.7
6 mol/L NaOH	78.6	0.254	168.66	9.03	6.92	83	358	9.4
8 mol/L NaOH	76.9	0.234	168.51	9.15	7.21	85	361	9.4

^a Wet pickup in the resin finishing treatment.

^b Fabric specific weight (mass/area).

Resin finishing treatments

The average wet pickup of the samples during the resin finishing treatments ranged from 73 to 80% with no effect of the crosslinker type or pretreatment. The crosslinker content (estimated from the fabric nitrogen contents) decreased in the following order of the resin finishing treatments: DMU > DMDHEU > DMedHEU. Within the individual resin finishing treatments, the pretreatment did not influence the crosslinker content in the samples. Nitrogen contents were also measured in control A and control B samples subjected to no resin finishing treatments and were found to be 0.010 and 0.008 wt %, respectively.

The nitrogen contents, measured on fabrics neutralized and washed after resin finishing treatments, reflect the degree of crosslinker fixation on treated fabrics. The order of the decreases in the crosslinker content may to some extent reflect differences of reactivity, which also decreases in the order of DMU > DMDHEU > DMedHEU.¹² However, it is likely that other factors also played a role. The resin treatment formulations were adjusted to contain a concentration of active solids of about 42 g/L for each resin type. On this basis, the formulations of DMU contained greater molar amounts of the crosslinker because of its low molecular weight, which may have contributed to the higher DMU content

observed in the treated fabrics. The very low DMedHEU content may have arisen in part from the sub-optimal formulation of the treatment liquor with respect to the catalyst type.

Specific weight

Apart from control A and control B, specific weights were lower in the resin-finished samples versus the corresponding no-resin samples, and the differences increased with the alkali concentration of the pretreatment. There were no significant differences in the fabric specific weight between the no-resin and resin-finished control samples. The specific weights were similar in the samples treated with DMedHEU and DMU but were lower after treatments with DMDHEU in samples pretreated with 4–8 mol/L NaOH.

The differences in the specific weight between the no-resin and resin-finished samples may stem primarily from three factors. Resin-finished samples exhibited lower moisture content than no-resin samples, and this may have exerted a degree of influence on the measured specific weights. Another reason may be mass loss in the samples due to hydrolysis during the resin finishing treatments. Fabrics contracted after alkali treatments expand on subsequent rewetting.¹¹ It is possible that there was

TABLE VI
Results for the Evaluations for the Samples That Underwent the Resin Finishing Treatment with DMU

Pretreatment	WPU (%) ^a	N content (wt %)	Specific weight (g/m ²) ^b	Moisture content (%)	Yellowness index	CRA (°)	Break force (N)	Break elongation (%)
Control A	75.3	0.718	141.61	9.27	6.45	104	644	10.2
Control B	78.9	0.740	142.52	9.20	5.87	108	620	9.4
2 mol/L NaOH	76.3	0.760	145.49	8.53	4.98	109	625	10.2
4 mol/L NaOH	74.9	0.725	163.14	8.59	7.23	85	360	8.9
6 mol/L NaOH	77.0	0.746	170.16	8.46	7.04	93	316	9.4
8 mol/L NaOH	75.5	0.744	167.42	8.70	7.03	100	328	8.9

^a Wet pickup in the resin finishing treatment.

^b Fabric specific weight (mass/area).

a relaxation in the samples when they were padded through resin formulations, and the expanded dimensions were retained as the samples were then dried and cured under tension on a pin frame. An expansion of the fabric dimensions would result in reduced specific weights.

The differences in the moisture content were too small to completely account for differences in the specific weight between the resin-finished and no-resin samples. There was also no evidence of substantial hydrolysis in the samples due to the resin finishing treatments (as discussed later). Hence, the lower specific weight of the resin-finished samples can be attributed predominantly to the expansion of the fabric dimensions. Unfortunately, the distance between benchmarks along the warp and fill directions on resin-finished samples were not measured before destructive tests, so it was not possible to determine the dimensional changes in the fabrics after resin finishing.

Moisture content

The moisture content was higher in the no-resin sets versus the resin-finished sets. Differences between the resin-finished sets appeared only among samples pretreated with 2–8 mol/L NaOH, where the values of the DMEdHEU set were higher than those of the DMDHEU or DMU sets. No differences in the moisture content were observed between samples from the DMDHEU and DMU sets. The pretreatment exerted only a marginal influence on the moisture content in the no-resin set and no influence in the DMEdHEU set. Among the DMDHEU and DMU sets, the moisture content was lower in samples pretreated with 2–8 mol/L NaOH versus samples from control pretreatments.

The moisture regain (or content) of cellulosic substrates at a given relative humidity is a function of both their accessibility and their degree of swelling under prevailing conditions.¹³ The moisture regain decreases upon resin finishing to extents directly related to the degree of crosslinking,¹⁴ as the introduction of crosslinks reduces both the degree of substrate swelling and its accessibility.^{12,15}

The following observations are of particular interest. Although the crosslinker content in resin-finished fabrics decreased in the treatment order of DMU > DMDHEU > DMEdHEU, there were no significant differences in the moisture content between control samples treated with different resin types or between alkali-pretreated samples treated with DMDHEU or DMU. On the other hand, although the crosslinker content did not vary between samples treated with an individual resin type, the moisture content was lower in the alkali-pretreated sam-

ples versus the controls among samples treated with DMDHEU or DMU.

In other words, for a set of samples treated with the same crosslinker type and exhibiting similar crosslinker contents, there were differences in the extents of swelling/accessibility reduction that were influenced by the pretreatment. In a sample set treated with different crosslinker types and exhibiting different crosslinker contents, the reductions of swelling/accessibility were similar. These observations point to qualitative differences in the effectiveness of crosslinking, which was influenced by both the pretreatment and the crosslinker type.

Yellowness index

An indicator of degradation during the curing step in resin finishing is substrate yellowing.¹² Heat-induced substrate yellowing is believed to be the result of a complex hydrolysis and dehydration reaction sequence followed by self-polymerization among the reaction products yielding colored compounds.¹⁶ Hence, a rough estimate of the hydrolysis or tendering during treatment may be obtained from the degree of yellowing in resin-finished substrates.

The yellowness was marginally lower in the no-resin sets compared to the resin-finished sets. The pretreatment did not exert a significant influence on the yellowness of the samples, apart from a dip in values observed for those pretreated with 2 mol/L NaOH. The crosslinker type exerted little influence on yellowness values among the resin-finished sets, apart from a peak observed in the DMDHEU set in samples pretreated with 4 mol/L NaOH.

The marginal differences in yellowness between the samples from the no-resin and resin-finished sets indicate that the resin finishing did not result in substantial hydrolysis of the substrates. There also appeared to be no difference between the resin finishing treatments on the resulting degree of substrate hydrolysis. The yellowness was relatively high in samples treated with DMDHEU after the pretreatment with 4 mol/L NaOH, but this did not appear related to greater substrate hydrolysis. Higher extents of substrate hydrolysis should be reflected in a loss of overall strength, but this was not observed. As discussed later, among samples treated with DMDHEU, those pretreated with 4 mol/L NaOH exhibited the highest abrasion resistance with a work of rupture similar to that of samples from other resin finishing treatments. The reasons for the high yellowness values are not clear at this time.

Crease recovery

There was no pretreatment effect on the sample CRA up to an alkali concentration of 2 mol/L

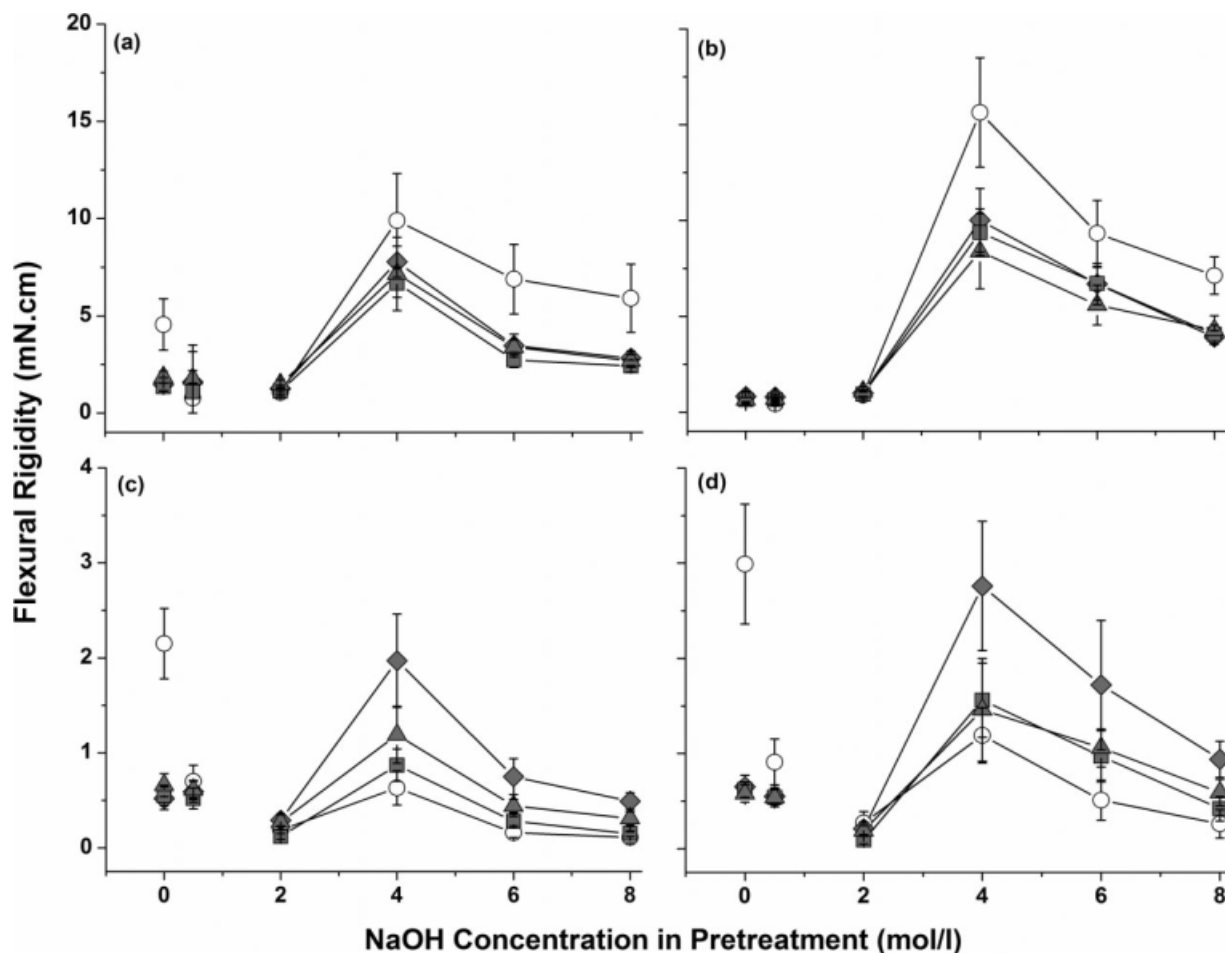


Figure 2 Average flexural rigidity ($n = 24$) (a) in the conditioned state along the warp, (b) in the fill direction, and in the wet state along the (c) warp and (d) fill directions measured on (○) no-resin, (◆) DMDHEU-treated, (■) DMEdHEU-treated, and (▲) DMU-treated samples. The first two data points in each series, at NaOH concentrations of 0 and 0.5 mol/L, represent the results from the control A and control B samples, respectively.

NaOH. Pretreatments with 4 mol/L NaOH caused sharp reductions in CRA, but there was a gradual increase in the values thereafter as the alkali concentrations rose to 8 mol/L NaOH. The lowest CRA was exhibited by the no-resin set. Resin finishing improved crease recovery, and the improvements generally increased in the treatment order of DMEdHEU < DMU = DMDHEU. An exception was observed in samples pretreated with 2 mol/L NaOH, in which there were no significant differences in crease recovery between resin-finished sets.

Crease recovery improvements after resin finishing were also influenced by the pretreatment. The largest improvement was observed in samples pretreated with 4 mol/L NaOH, and they were followed by those pretreated with 6 and 8 mol/L NaOH. Samples from the control and 2 mol/L NaOH pretreatments exhibited the lowest improvements in crease recovery after the resin finishing treatments.

Crease recovery is inversely related to rigidity and directly related to elastic recovery in fabrics.¹⁷ In

resin-finished fabrics, the crease recovery improves with the crosslinker content but is also influenced by the distribution of the crosslinker within the fabric structures. For the same crosslinker content, better crease recovery is obtained if greater penetration and more uniform distribution of the crosslinker exist through fiber/yarn cross sections than if the crosslinker is restricted to their surfaces.^{18–20}

The dip in CRA values exhibited by the samples pretreated with 4 mol/L NaOH is indicative of high rigidity and low elastic recovery. The large crease recovery improvements in the resin-finished samples pretreated with 4–8 mol/L NaOH may be attributed to the greater penetration of the crosslinker within the fibers and yarns in the samples. The low crease recovery improvements in samples from the control and 2 mol/L NaOH pretreatments suggest that the crosslinker distribution was limited to the surfaces of the samples.

The lower CRA values of the DMEdHEU-treated samples may stem from the lower crosslinker

contents in these samples. However, the greater crosslinker contents in the samples after DMU treatments did not result in higher CRA values in comparison with the DMDHEU-treated samples.

Flexural rigidity

The conditioned flexural rigidity (CFR) and WFR values of samples along the warp and fill directions, which exhibited similar trends in values, are shown in Figure 2. CFR values remained low up to the pretreatment with 2 mol/L NaOH but rose significantly in samples pretreated with 4–8 mol/L NaOH. Peaks of CFR were observed in samples pretreated with 4 mol/L NaOH. Although there were generally no differences between treatment sets up to the pretreatment with 2 mol/L NaOH, CFR values were greater in the no-resin sets compared to the resin-finished sets among samples pretreated with 4–8 mol/L NaOH. There were no significant differences in CFR between the resin-finished sets.

The highest WFR was observed in control A samples from the no-resin set, whereas the lowest values were observed in samples pretreated with 2 mol/L NaOH. Samples from all other pretreatments exhibited intermediate WFR values, again with peak values for the samples pretreated with 4 mol/L NaOH. Differences in WFR were observed among samples pretreated with 4–8 mol/L NaOH (DMDHEU > DMU = DMedHEU > no resin), but there were generally no such differences among samples from control B or 2 mol/L NaOH pretreatments.

When specimens were padded through deionized water for measurements of WFR, there was no significant effect of the pretreatment on the water pickup (values not shown). The water pickup in no-resin specimens ranged from 82 to 104% and was on average 8% higher than that in specimens from the resin-finished samples. There were no significant differences in water pickup between specimens subjected to different resin finishing treatments.

The WFR/CFR ratios along the warp and fill directions of the samples are shown in Figure 3. The WFR/CFR ratios along the fill direction were greater than those along the warp direction in the samples subjected to control pretreatments, but no such differences were observed in samples subjected to alkali pretreatments.

The WFR/CFR ratios were greater in samples subjected to control pretreatments versus those subjected to alkali pretreatments and in general decreased gradually with increasing alkali concentration of the pretreatment. Apart from the no-resin set, there were generally no differences in the WFR/CFR ratios between samples from control A or control B pretreatments. Among the alkali-pretreated samples, the WFR/CFR ratios decreased in the fol-

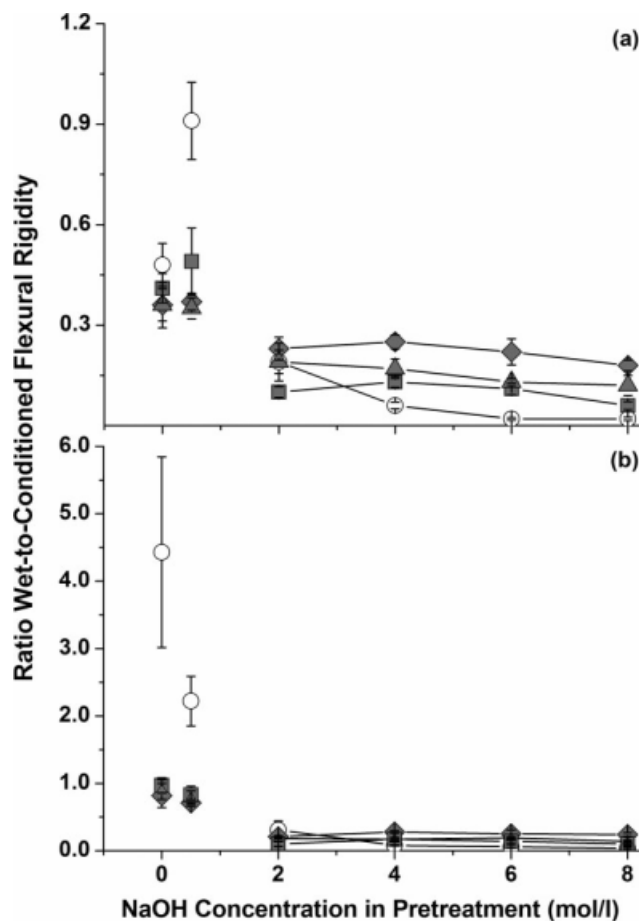


Figure 3 Average WFR/CFR values ($n = 6$) along (a) warp and (b) fill directions in (O) no-resin, (◆) DMDHEU-treated, (■) DMedHEU-treated, and (▲) DMU-treated samples. The first two data points in each series, at NaOH concentrations of 0 and 0.5 mol/L, represent the results from the control A and control B samples, respectively.

lowing treatment order: DMDHEU > DMU = DMedHEU > no resin. Among samples from the control pretreatments, the WFR/CFR ratios were greater in the no-resin sets compared to the resin-finished sets, with generally no differences between resin-finished sets.

The flexural rigidity of fabrics is influenced by the ability of yarns to move past one another at points of interlacement or crossover in the weave:² close contact among yarns reduces mobility because of friction and enhances flexural rigidity, whereas interyarn spaces enhance mobility and reduce flexural rigidity. In untreated fabrics, the swelling of fibers and yarns in water reduces interyarn spaces at crossover points, reduces yarn mobility, and increases WFR. In alkali-treated fabrics, the increase in yarn crimp due to swelling in alkali solutions is retained even after yarns deswell upon neutralization and drying, and there is increased interyarn

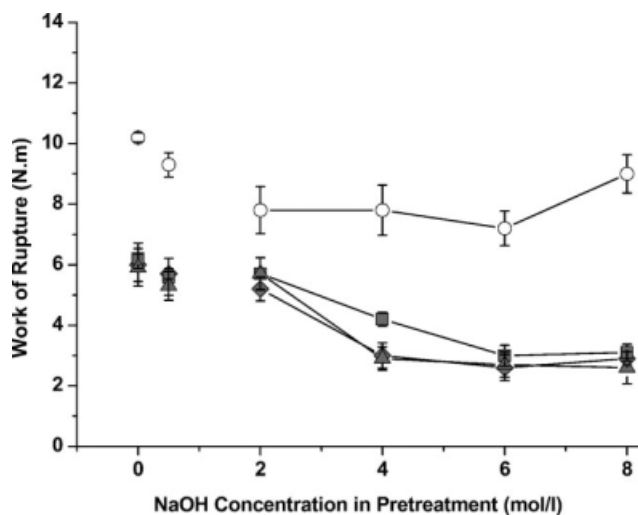


Figure 4 Average work of rupture ($n = 6$) calculated from measurements on (○) no-resin, (◆) DMDHEU-treated, (■) DMeDHEU-treated, and (▲) DMU-treated samples. The first two data points in each series, at NaOH concentrations of 0 mol/L and 0.5 mol/L, represent the results from the control A and control B samples, respectively.

space at crossover points. Upon rewetting in water, the yarn swelling does not reach levels attained during alkali treatment; hence, interyarn spaces are maintained at crossover points, and WFR is reduced.

In no-resin samples, the high WFR/CFR ratios after control pretreatments and the low WFR/CFR ratios after alkali pretreatments reflect the previously described phenomena. Among samples subjected to control pretreatments, the lower ratios in the resin-finished set versus the no-resin set may be attributed to reduced substrate swelling as a result of crosslinking.¹² Among alkali-pretreated samples, the greater WFR/CFR ratios in the resin-finished set versus the no-resin set reflect the higher WFR values observed in the resin-finished sets [Fig. 2(c,d)]. The higher WFR values in the resin-finished sets presumably resulted from the increased Young's modulus of the fibers,²¹ to which the differences in WFR between the resin-finished sets may also be attributed.

High flexural rigidity is accompanied by low crease recovery and low abrasion resistance.^{18,22,23} However, samples from the no-resin set and all samples pretreated with 4 mol/L NaOH, which exhibited low crease recovery along with high flexural rigidity, also exhibited high abrasion resistance (discussed later). Hence, the flexural rigidity peaks in samples pretreated with 4 mol/L NaOH and the high CFR exhibited by the no-resin set may be attributed to a temporary setting known to occur in lyocell fabrics after alkali treatments,²⁴ which dissipates as fabrics are worked on in the course of further processing or handling.

Fabric strength

The work of rupture, calculated from values of the breaking force and elongation [work of rupture = $0.5 \times$ breaking force (N) \times elongation at break (m)], is shown in Figure 4. All resin-finished samples exhibited lower work of rupture than the corresponding no-resin samples. There were no significant differences between the resin finishing treatments, apart from the comparatively higher work of rupture in samples treated with DMeDHEU after the pretreatment with 4 mol/L NaOH.

In the no-resin set, there were minor differences between controls A and B, but the work of rupture in the alkali-pretreated samples was significantly lower. Among the resin-finished samples, the work of rupture did not change significantly up to the pretreatment with 2 mol/L NaOH, decreased significantly with a rise in the pretreatment alkali concentration to 4 mol/L NaOH, and leveled off thereafter.

The mass loss in samples from abrasion resistance tests is shown in Figure 5. Among the controls, there were no significant differences between the no-resin, DMeDHEU-treated, and DMU-treated samples, but the DMDHEU-treated samples exhibited greater mass loss. Among the alkali-pretreated samples, the mass loss decreased in the treatment order of DMDHEU > DMU > DMeDHEU > no resin.

The pretreatment strongly influenced the abrasion resistance in samples subjected to the DMDHEU and DMU treatments: high mass loss was exhibited by samples pretreated with 2, 6, or 8 mol/L NaOH. Pretreatments with 4 mol/L NaOH resulted in the lowest mass loss for samples from the DMDHEU

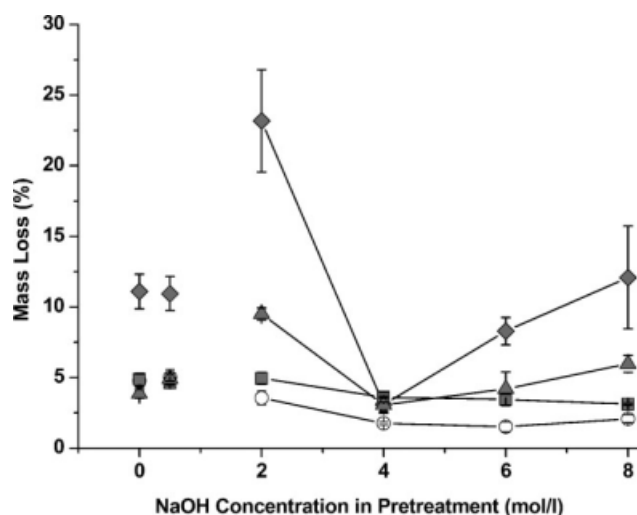


Figure 5 Average mass loss ($n = 3$) measured in the abrasion resistance tests on (○) no-resin, (◆) DMDHEU-treated, (■) DMeDHEU-treated, and (▲) DMU-treated samples. The first two data points in each series, at NaOH concentrations of 0 and 0.5 mol/L, represent the results from the control A and control B samples, respectively.

and DMU treatments, and the values matched those of the DMeDHEU-treated samples. The pretreatment exerted little to no influence on the abrasion resistance of the no-resin and DMeDHEU-treated samples.

Strength loss in cellulose after resin finishing is attributed to substrate hydrolysis by the catalyst and/or substrate embrittlement due to the formation of crosslinks.^{18,25} Substrate hydrolysis leads to an overall reduction in strength, whereas embrittlement may lead to different types of strength loss depending on the distribution of the crosslinking reagent in the substrate. A higher surface concentration of the crosslinker leads to reduced abrasion resistance but preserves tenacity, whereas greater penetration leading to a more uniform distribution of the crosslinker through the fabric structure preserves abrasion resistance but reduces tenacity.^{20,26}

The amounts of $MgCl_2$ used as a catalyst in the resin finishing treatments ranged from 12.6 to 32.7 g/L, but there were generally no differences in the work of rupture between the resin-finished sets. There were also no differences in the abrasion resistance between the no-resin, DMeDHEU, and DMU sets among samples from control pretreatments. In contrast, although all samples within individual resin-finished sets were subjected to identical crosslinking treatments, the pretreatment was observed to significantly influence the work of rupture and abrasion resistance.

These observations lead us to conclude that the loss in strength-related properties among resin-finished samples was not influenced by the amounts of the catalyst used in the treatments. Combinations of low abrasion resistance with high tensile properties or vice versa, illustrated by samples resin-finished after a pretreatment with 2 mol/L NaOH and all samples from DMeDHEU treatments, evidence the lack of overall strength loss characteristic of general hydrolysis in substrates due to a catalyst. There was no evidence in the results of yellowness measurements to indicate substantial hydrolysis in the samples. In another work,²⁷ when lyocell fabrics were subjected to resin finishing treatments with a DMDHEU-based product with 0–36 g/L $MgCl_2$ as a catalyst, there was also no evidence that amounts of $MgCl_2$ in that range caused significant hydrolysis in the substrates.

Samples resin-finished after control pretreatments exhibited high abrasion resistance and high work of rupture, with the exception of DMDHEU-treated samples, for which the abrasion resistance was lower. The samples also exhibited low crease recovery improvements after resin finishing treatments. The low crease recovery improvements and high work of rupture values suggest a large presence of the crosslinker on the surface rather than within the

fabric structures. However, the high surface concentration of the crosslinker appeared to lower the abrasion resistance only among samples treated with DMDHEU.

Samples resin-finished after the pretreatment with 4 mol/L NaOH exhibited high abrasion resistance and low work of rupture. These samples also exhibited the largest improvements in crease recovery over the corresponding no-resin samples. This combination of properties suggests a preponderant presence of the crosslinker within rather than on the surface of the fabric structures. Such a distribution of the crosslinker through substrates will lead to lowered tensile properties because of greater embrittlement at fiber/yarn cores and preserve abrasion resistance because of low surface embrittlement. It will also lead to improvements of the crease recovery.

Samples from the DMDHEU and DMU sets pretreated with 2, 6, or 8 mol/L NaOH exhibited low abrasion resistance. The work of rupture was high in samples pretreated with 2 mol/L NaOH but was among the lowest in samples pretreated with 6 or 8 mol/L NaOH. The abrasion resistance of DMeDHEU-treated samples was uniformly high across all pretreatments, but the pattern of loss in the work of rupture was similar to that observed after DMDHEU and DMU treatments. The crease recovery improvement was low in samples pretreated with 2 mol/L NaOH but greater in samples pretreated with 6 or 8 mol/L NaOH.

The combination of low crease recovery improvement, low abrasion resistance, and high work of rupture in samples resin-finished after the pretreatment with 2 mol/L NaOH suggests a preponderant presence of the crosslinker at the surface of the samples. The larger crease recovery improvements in the samples resin-finished after the pretreatment with 6 or 8 mol/L NaOH suggest greater penetration of the crosslinker within the fabric structures. However, the samples treated with DMDHEU and DMU also exhibited poor abrasion resistance, which was indicative of high extents of surface embrittlement and therefore a significant concentration of crosslinks at the surface of the samples. The possibility that these results indicate overall strength loss in the samples is negated by the lack of such evidence in the DMeDHEU set.

One possible explanation for the apparent perplexity of these results may be that in samples resin-finished after the pretreatment with 6 or 8 mol/L NaOH, there was some increase in the degree of crosslinker penetration within the substrates, but there was a greater increase in the extent of catalyst penetration. A level of demixing between the catalyst and crosslinker molecules within substrates, in which the depth of catalyst penetration exceeds that of the crosslinker, will result in hydrolysis at fiber/

yarn cores due to the catalyst and embrittlement at the substrate surface due to the crosslinker and lead to the combination of crease recovery and strength properties described previously.

There were no differences in the work of rupture between resin-finished samples as a function of the crosslinker type. The higher abrasion resistance exhibited by the DMeDHEU set can be attributed to the low crosslinker content in the samples, but the DMU set exhibited greater abrasion resistance than the DMDHEU set despite the greater crosslinker content in the samples treated with DMU.

Negative staining with C.I. Direct Red 81

The negative staining method is based on the principle that in resin-finished fabrics dyed with C.I. Direct Red 81, the dye content and color depth in substrates are functions of the crosslinker content and distribution.^{26,28} The dye content is inversely proportional to the crosslinker content, and the color depth is inversely proportional to the surface concentration of the crosslinker in the substrates. The uptake of C.I. Direct Red 81 has also been used as a measure of substrate accessibility.^{29,30} The shade depth (corrected for the reflectance of the undyed substrate) and dye content of the samples are shown in Figure 6.

In general, sample dye contents decreased in the treatment order of no resin > DMeDHEU > DMU > DMDHEU. An exception was observed with control A samples from the no-resin set, which exhibited low dye content values for reasons that are not clear at this time. Small peaks of the dye content were observed in the no-resin and DMeDHEU sets for samples pretreated with 2 mol/L NaOH; apart from this, samples pretreated with alkali generally exhibited lower dye contents than those subjected to control pretreatments. There were no peaks of dye content in the DMDHEU and DMU sets, and the dye content values in alkali-pretreated samples were lower than those in samples from control pretreatments.

In parallel with the dye content values, the shade depth in the samples decreased in the treatment order of no resin > DMeDHEU > DMU > DMDHEU, with the exception of control A samples from the no-resin set. In the no-resin and DMeDHEU sets, the shade depth in the alkali-pretreated samples was greater than that in samples from control pretreatments, with strong peaks observed in samples pretreated with 4 mol/L NaOH. Such trends were also observed in the DMDHEU and DMU sets, except that samples pretreated with 2 mol/L NaOH exhibited lower shade depth than samples from control pretreatments.

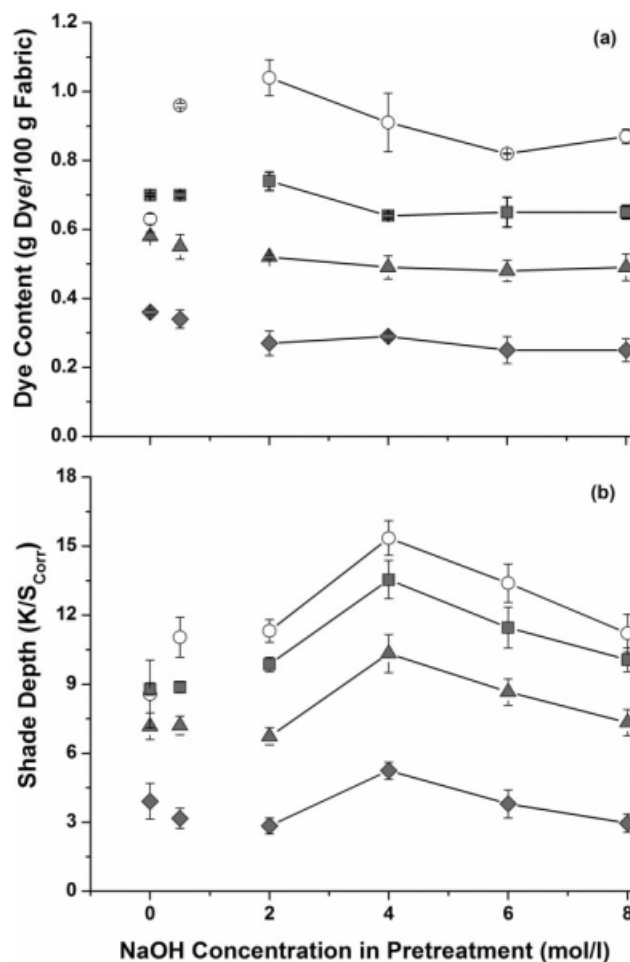


Figure 6 Results from the negative staining tests with C.I. Direct Red 81 on (○) no-resin, (◆) DMDHEU-treated, (■) DMeDHEU-treated, and (▲) DMU-treated samples: (a) average dye content ($n = 3$) and (b) average shade depth ($n = 9$). The first two data points in each series, at NaOH concentrations of 0 and 0.5 mol/L, represent the results from the control A and control B samples, respectively.

Alkali treatments are known to increase accessibility in cellulosic substrates,^{4,5} but strong evidence of this was not observed in dye content values, apart from the sometimes higher dye content in samples pretreated with 2 mol/L NaOH. However, there was evidence that crosslinking decreased accessibility in samples, as the dye contents in the resin-finished sets were lower than those in the no-resin set. The greatest reduction of accessibility was observed after DMDHEU treatments, and this was followed by DMU treatments, despite the higher crosslinker content in the samples treated with DMU. The smallest reduction of accessibility was observed in samples treated with DMeDHEU, and this was in line with their low crosslinker contents.

The dye contents of the controls were greater than those of the alkali-pretreated samples within resin-finished sets, and this indicated that resin finishing after alkali pretreatment resulted in greater

reductions of accessibility than resin finishing without an alkali pretreatment, even though the crosslinker content did not vary between samples from control and alkali pretreatments.

The shade depth is a function of both the dye content and the dye distribution in substrates. The shade depth increases with the dye content and, for a given dye content, rises with a greater presence of the dye at or near the substrate surface. The differences in the shade depth between treatment sets may be attributed to differences in the dye content. However, the higher shade depths in the alkali-pretreated samples may be attributed only to differences in the dye distribution as there were no corresponding parallels in the dye content. Shade depth peaks were observed in all treatment sets, with ratios of the shade depth between the resin-finished and no-resin sets nearly uniform across the range of pretreatment alkali concentrations: the values were 0.29 ± 0.04 , 0.64 ± 0.03 , and 0.88 ± 0.03 in samples treated with DMDHEU, DMU, and DMeDHEU, respectively. Hence, the differences in the dye distribution, reflected in the shade depth peaks, cannot be attributed to the crosslinker and appear to be related to changes in the substrate structure due to the alkali pretreatment.

The higher shade depth values in the samples pretreated with 4–8 mol/L NaOH, especially the peak values, indicate the presence of greater proportions of the dye at or near the surface of these samples and therefore suggest changes in the substrate structure that lowered dye penetration within the fiber/yarn cores of these samples and prevented uniform dye distribution. However, the lowering of dye accessibility did not appear correlated with a similar reduction of crosslinker accessibility because the results from strength tests and the crease recovery improvements suggested greater penetration of the crosslinker within these substrates.

It appears that pretreatments with NaOH in the range of 4–8 mol/L created gradients of accessibility within fibers/yarns of lyocell fabrics, with the depth of reagent penetration increasing in the order of C.I. Direct Red 81 < crosslinker < catalyst.

Effect of the crosslinker type

In the previous discussions, we observed differences between resin-finished sets as a function of the crosslinker type. In some cases, it was possible to attribute these differences to the crosslinker content; in particular, the high moisture content and dye uptake, low crease recovery, and high abrasion resistance exhibited by the DMeDHEU set may be attributed to the low crosslinker content in these samples.

However, it was not possible to attribute differences between the DMDHEU and DMU sets to the crosslinker content. In comparison with samples treated with DMDHEU, those treated with DMU exhibited similar moisture contents, lower crease recovery, higher abrasion resistance, higher dye uptake, and lower WFR, despite the greater crosslinker content in the DMU-treated samples.

The propensity for self-condensation is greater in DMU compared to DMDHEU,¹² and hence crosslink lengths are expected to be greater in DMU-treated samples versus those treated with DMDHEU. Smaller crosslink lengths promote greater improvements of crease recovery but also result in greater losses of strength.^{31,32} Smaller crosslink lengths may also be expected to lead to greater reductions of accessibility. Hence, the differences between the DMU and DMDHEU sets with respect to the mechanical properties and accessibility appear to be influenced more by the crosslink length than the crosslinker content in the samples.

CONCLUSIONS

Woven lyocell fabric samples were subjected to pretreatments with deionized water or solutions of 2–8 mol/L NaOH or no pretreatment, and they were subsequently resin-finished with DMDHEU, DMeDHEU, or DMU as a crosslinking reagent. The crosslinker content in the samples, which was not influenced by the pretreatment, decreased in the following order of resin finishing treatments: DMU > DMDHEU > DMeDHEU.

The resin-finishing treatments caused changes in the substrate properties, such as reduced accessibility (measured by the moisture content and dye uptake), improved crease recovery, reduced work of rupture and abrasion resistance, improved WFR, and reduced CFR. Differences were observed in properties of the resin-finished substrates as a function of the crosslinker type that were attributed to the effects of both the crosslinker content and the crosslink lengths in the treated substrates.

Alkali pretreatments strongly influenced the effects of resin finishing on the substrate properties. Treatments with NaOH, especially in the concentration range of 4–8 mol/L, appeared to cause changes in the substrate structure that influenced the accessibility of the crosslinker and catalyst within the substrates. There appeared to be a significant enhancement of the crosslinker penetration within substrates pretreated with 4 mol/L NaOH. Pretreatments with 6 or 8 mol/L NaOH also enhanced crosslinker penetration, but the depth of catalyst penetration appeared to exceed that of the crosslinker; leading to demixing between the two components within the substrates. The depth of penetration of C.I. Direct

Red 81 appeared lower than that of the crosslinker in the alkali-pretreated substrates. It appears that pretreatments with NaOH in the concentration range of 4–8 mol/L created gradients of accessibility within fibers/yarns of lyocell fabrics, with the depth of reagent penetration increasing in the order of C.I. Direct Red 81 < crosslinker < catalyst. Further experiments are needed to confirm the formation of accessibility gradients in lyocell substrates after alkali pretreatments; such experiments are underway and will be reported at a later time.

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