

The Influence of Alkali Pretreatments in Lyocell Resin Finishing—Resin Distribution and Mechanical Properties

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ABSTRACT: Lyocell fabric samples were pretreated with NaOH and KOH and resin finished. The treated samples were tested to determine the influence of alkali pretreatments on the tenacity, abrasion resistance, and crease recovery of resin-finished lyocell. Alkali pretreatments resulted in a higher surface concentration of the crosslinking reagent in fabrics, leading to lowered crease recovery and abrasion resistance. The pretreatments also exerted a deleterious influence on the tensile strength in resin-finished samples.

However, the differential distribution of crosslinking reagent within the textile structure does not appear to be the only factor responsible for the changes observed in substrate properties; other factors also appear to be responsible for the results observed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3596–3601, 2006

Key words: lyocell; alkali pretreatments; resin finishing; crosslinking; mechanical properties

INTRODUCTION

Alkali pretreatments are recommended as remedial measures against the formation of permanent crease marks to which lyocell fabrics are susceptible during wet processing.^{1,2} However, the strong swelling propensity of lyocell fibers in alkali solutions³ changes substrate properties such as the pore structure,^{4,5} fibrillation tendency,⁶ crystallinity,⁷ and surface characteristics⁸ in fibers, and yarn crimp and stiffness in fabrics.⁹ Such changes in substrate properties lead to alterations in the accessibility and reactivity of lyocell with chemicals and reagents, and may influence substrate performance in subsequent treatments. The objective of this research was to determine if alkali pretreatments of lyocell exerted an influence on its performance during subsequent resin finishing.

EXPERIMENTAL

Materials

The fabric used in this investigation, supplied by Lenzing AG, was a desized and scoured 100% lyocell plain-weave fabric, with 36 ends and 29 picks/cm, and a weight of 137 g/m². The alkalis used in pretreat-

ments were analytical grade NaOH and KOH, with Leonil SRP (Clariant) and Sandoflex A (Clariant), which are commercial surfactant formulations designed for use under highly alkaline conditions, being used as wetting agents. The crosslinking reagent used in resin finishing was a modified dimethylol dihydroxyethyleneurea (DMDHEU)-based product, Fixapret ECO (BASF); Kieralon Jet B Konz (BASF) was used as the nonionic wetting agent, and analytical grade magnesium chloride was used as the catalyst.

Methods

Fabric samples, 30 × 30 cm² in dimension, were subjected to alkali pretreatments followed by resin finishing.

Alkali pretreatments

The treatment conditions used for alkali pretreatments in this investigation were derived from the recommendations of the supplier for full-scale operations.

NaOH pretreatment.

The treatment formulation consisted of 120 g/L NaOH and 3 g/L Leonil SRP in deionized water. Samples were treated in a pad-batch process by padding through the formulation at a nip pressure of 1.0 bar and roller speed of 2.0 m/min to obtain wet pickup values of 106–111%, and batched for 30 min.

KOH pretreatment.

The treatment formulation consisted of 250 g/L KOH and 50 mL/L Sandoflex A in deionized water. Sam-

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ples were treated in a pad-batch process by padding through the formulation at a nip pressure of 1.0 bar and roller speed of 2.0 m/min to obtain wet pickup values of 113–120%, and batched for 4 h.

Batching consisted of rolling padded samples around glass rods and enveloping them in plastic sheets. After the required time period for batching elapsed, the samples were removed from glass rods, rinsed in running hot water for 5 min, immersed in 5% acetic acid at room temperature for 60 min, rinsed again in running cold water for 5 min, and line-dried overnight.

Resin treatment

The treatment formulation contained 60 g/L resin, 18 g/L catalyst, and 0.5 g/L wetting agent. Samples subjected to resin treatments were padded through resin formulation at a nip pressure of 2.0 bar and roller speed of 2.0 m/min, dried at 130°C for 30 s, and cured at 180°C for 65 s. To neutralize any residual acidity in the fabric after treatment, the samples were immersed in a solution of 1 g/L NaHCO₃ at room temperature for 60 min, rinsed with running cold water, and line dried overnight.

Evaluations

All treated fabric samples were conditioned in a standard atmosphere of 20 ± 2°C and (65 ± 4)% relative humidity for over 24 h before testing, and the evaluations were performed in the same conditions. The breaking strength in warp and fill yarns from samples were tested on an Instron Tensile Tester according to DIN 53834 with 5 cN pretension at a gauge length of 10 cm and a crosshead speed of 5 cm/min. The abrasion resistance in samples was tested according to ISO 12947-3: 1999, with minor modifications made to the method as described previously,¹⁰ and the crease recovery angle (CRA) was determined according to DIN 53890.

Prior to alkali treatments, benchmarks were drawn on fabric samples, 27 cm apart, along the warp and fill directions. The distances between these benchmarks were remeasured after alkali treatments and after resin finishing, and the dimensional change was determined using eq. (1):

$$\Delta L = \left(\frac{L_i - L_f}{L_i} \right) \times 100 \quad (1)$$

where ΔL is dimensional change (%); L_i , the distance between benchmarks before treatments (= 27 cm); and L_f is the distance between benchmarks after treatment (cm).

The dimensional change in samples was also estimated from their specific weights (mass/area), but this measure was used only prior to resin finishing. The resin content in samples were estimated from their nitrogen contents analyzed by the Dumas method in a LECO FP 328 Nitrogen analyzer, and resin distribution was estimated by the negative-staining method with C.I. Direct Red 81 as described earlier.¹⁰ The dye content in specimens dyed with the direct red dye was estimated by extraction in a 25% (v/v) aqueous solution of pyridine at 90°C for 45 min, followed by spectrophotometric measurements of the extracts at 520 nm.

The resin distribution in samples was also visualized by the positive-staining method with Rhodamine B¹¹ by immersing resin-finished fabric specimens in a $1 \times 10^{-4}M$ solution of the cationic dye and maintained at pH 9.3 with NH₄Cl/NH₃ buffer for 24 h at room temperature. The samples were then rinsed twice for 10 min in the buffer solution, rinsed once for 5 min in deionized water, and line dried at room temperature. Cross sections of the stained fabric specimens were observed by fluorescence and confocal microscopy as described previously.¹²

The evaluations were conducted on samples that were (a) alkali pretreated, (b) alkali pretreated and resin finished, (c) not subjected to treatments whatsoever (untreated control), and (d) subjected to no pretreatments but resin finished (resin-finished control). Statistical analyses of the data were performed with the software SPSS[®] at a 0.05 level of significance. The error bars in graphs represent data variability in terms of ± 1 standard deviation.

RESULTS AND DISCUSSION

In alkali treatments of cellulose, alkali type and its concentration, among other variables, exert a strong influence on the swelling behavior of cellulosic materials and thereby on other macroscopic properties of the treated substrates.^{13,14} As the conditions in the two pretreatments were different, it is not possible to compare the properties in treated samples with reference to a common pretreatment condition. The scope of the present investigation was limited to studying the influence of specific alkali pretreatment processes, which are designed to inhibit the formation of permanent crease marks in substrates during wet processing, on the performance of substrates in subsequent treatments. Hence, the results obtained in this investigation pertain only to substrates pretreated as described, and may change if the pretreatment conditions are varied.

The mean values of dimensional change ($n = 6$), specific weight ($n = 3$), wet pickup during resin treatment ($n = 6$), nitrogen content ($n = 6$), yarn strength ($n = 15$), and CRA ($n = 15$) are shown in Table I. The

TABLE I
Results of Sample Evaluations

Treatment	ΔL (%)		Sp. weight (g/m ²)	Resin WPU (%)	N-content (wt %)	Yarn strength (N)		CRA _{W+F} (°)	
	Warp	Fill				Warp	Fill	5 min	30 min
Before resin finishing									
Control	—	—	137	—	0.009	5.2	5.4	150	170
NaOH	6.6	3.0	149	—	—	5.1	5.0	184	203
KOH	12.0	4.7	159	—	—	5.1	5.2	203	224
After resin finishing									
Control	—	—	—	78.9	0.301	4.1	4.9	218	243
NaOH	0.8	4.1	—	78.6	0.306	2.5	3.0	202	222
KOH	0.8	5.3	—	74.4	0.295	2.9	2.5	211	231

CRA of samples was measured at 5 and 30 min from the beginning of the recovery process, and the reported values are the sum of the values obtained along the warp and fill directions.

Dimensional change

Alkali pretreatments caused significant shrinkage in samples, which is attributed to the swelling of lyocell in alkali solutions. The KOH pretreatments caused greater shrinkage than the NaOH pretreatments. No attempt was made to control sample dimensions during pretreatment, and apart from any incidental stresses that might have incurred during treatment, the samples were maintained in a relaxed state during pretreatment.

In resin finishing the samples were stretched along the warp direction as they were fixed on metal frames before being passed through drying and curing chambers, and so a large part of the warp shrinkage was recovered. However, as the samples were not held along the fill direction during drying and curing, fill shrinkage increased during resin finishing.

Resin content

The wet pickup during resin treatment in the control and NaOH pretreated samples was similar. The wet pickup in the KOH pretreated samples was marginally lower, but the differences were statistically significant. However, there were no significant differences in nitrogen content, and therefore resin content, among the resin-finished samples.

Yarn strength

Prior to resin finishing, there were no significant differences in strength among the control and alkali pretreated samples in either the warp or fill yarns. Resin finishing significantly reduced yarn strength in samples, with pretreatment exerting a significant influence on the values obtained. After resin finishing, alkali

pretreated samples exhibited lower strength than the control samples in both the warp and fill yarns. While there were no significant differences in warp yarn strength between samples from the two different alkali pretreatments, greater losses in fill yarn strengths were caused by KOH pretreatments as compared with the NaOH pretreatments.

Crease recovery

The samples were found to be crumpled after neutralization and rinsing, so all test specimens for crease recovery determinations were lightly ironed, and reconditioned in the standard atmosphere for further 24 h before measurements.

The results obtained at both measurement times were similar. The alkali pretreatments alone were observed to enhance crease recovery in samples, which is attributed to an increase in fabric resilience due to shrinkage. After resin finishing, the CRA increased significantly in all samples but the alkali pretreated samples exhibited lower CRA values than the resin-finished control samples. Among alkali pretreated and resin-finished samples, the KOH pretreated samples exhibited greater crease recovery than the NaOH pretreated samples.

Abrasion resistance

The results of the abrasion resistance tests are shown in Figure 1. Prior to resin finishing, similar degrees of weight loss were exhibited by the control and alkali pretreated samples indicating that the alkali pretreatments did not exert a significant influence on fabric abrasion resistance. Resin finishing alone caused some loss in abrasion resistance as evinced by the marginally higher, but statistically significant, weight loss observed in the resin-finished control samples. However, resin finishing after alkali pretreatments resulted in substantial losses in abrasion resistance, evinced by the high degree of weight loss exhibited by the alkali pretreated resin-finished samples. Among these sam-

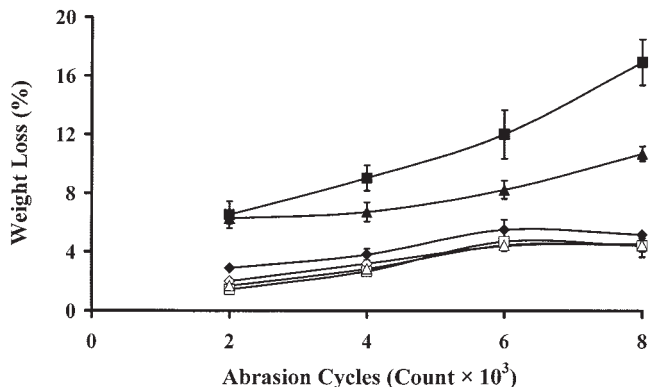


Figure 1 Mean weight loss ($n = 3$) in control (\diamond, \blacklozenge), NaOH pretreated (\square, \blacksquare), and KOH pretreated ($\triangle, \blacktriangle$) samples, in abrasion resistance tests. Hollow symbols represent samples that were only pretreated, and filled symbols represent samples that were pretreated and resin finished.

ples, NaOH pretreatments resulted in lower abrasion resistance as compared with KOH pretreatments, and the differences increased with increasing number of abrasion cycles.

Negative staining with C.I. Direct Red 81

The principle of the negative-staining method is based on the fact that in resin-finished samples dyed with C.I. Direct Red 81, dye content and color depth in substrate are functions of its resin content and distribution.^{15,16} The dye content is inversely proportional to resin content and the color depth is inversely proportional to the surface concentration of resin in samples. The degree of C.I. Direct Red 81 uptake has also been used as a measure of accessibility in substrates.^{17,18} The shade depth (corrected for reflectance from the undyed substrate) and dye content obtained

in samples dyed with the direct red dye, are shown in Figure 2.

Among samples that were only pretreated, there were no significant differences in dye content between samples from the two alkali pretreatments. The dye content in the NaOH pretreated samples was significantly higher than that in control samples, but the difference in dye content between the control and KOH pretreated samples was not statistically significant. The shade depth was significantly higher in the alkali pretreated samples as compared with the control samples, and there were no significant differences in shade depth between samples from the two alkali pretreatments.

Resin finishing resulted in substantial reductions in both dye content and shade depth in all samples as compared with samples awarded pretreatments alone. The dye content in all resin-finished samples was similar, but a significantly higher shade depth was observed in the resin-finished control as compared with the alkali pretreated samples. There were no significant differences in shade depth among the alkali pretreated resin-finished samples. The lower shade depth in the alkali pretreated and resin-finished samples as compared with the resin-finished control despite the similar dye contents in all resin-finished samples denotes a higher surface concentration of resin in the alkali pretreated samples (Basel, Switzerland).

Positive-staining test with rhodamine B

When cellulosic fabrics crosslinked with urea-based resins are dyed with Rhodamine B (Ludwigshafen, Germany), the dye selectively stains the crosslinking reagent¹¹ and hence this technique helps in visualizing resin distribution through the fabric structure. The cross sections of resin-finished fabric specimens stained with the cationic dye are shown in Figure 3.

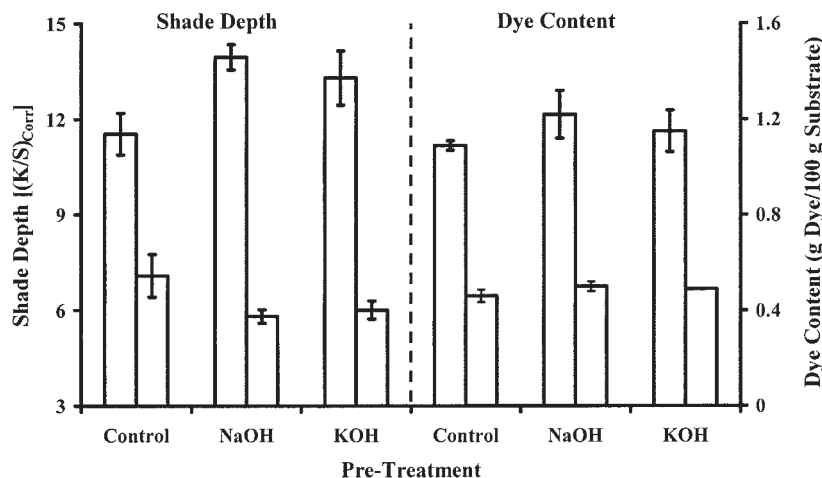


Figure 2 Mean shade depth ($n = 15$) and dye content ($n = 3$) in samples dyed with C.I. Direct Red 81: after pretreatment alone (\square) and after pretreatment and resin finishing (\blacksquare).

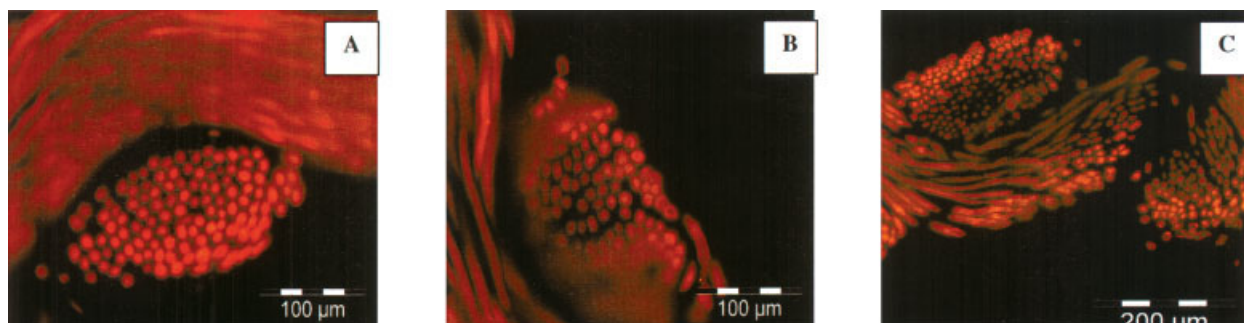


Figure 3 Cross-sections of fabric specimens stained with rhodamine B, from samples resin finished after: no pretreatments (control) (A), NaOH pretreatments (B), and KOH pretreatments (C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The cationic dye stained fabric cross sections confirmed the results of the negative-staining test. In samples resin-finished without pretreatments the crosslinking reagent was distributed through fiber cross sections, but in samples resin-finished after alkali pretreatments the crosslinking reagent was observed to be present predominantly at fiber surfaces and was not distributed through the cross sections.

In full scale alkali pretreatment operations, fabrics are tensioned along both warp and fill directions either by holding them to fixed dimensions during treatment or by stretching them to desired dimensions in subsequent washing and drying steps.¹ In this work, the samples were not tensioned at any stage during pretreatments. The degree of tension imparted during alkali treatments may exert a significant influence on the changes occurring in substrate properties, and so this investigation may not have an immediate or direct relevance to technological practice. However, we believe that the results obtained in these experiments offer some interesting insights into the changes that occur in lyocell due to alkali treatments.

Alkali treatments change the pore structure in lyocell, and increase or decrease total pore volume in substrate depending on alkali type, its concentration, and treatment conditions^{4,5}, and thereby change substrate accessibility. In this work, the NaOH pretreatment appeared to increase substrate accessibility as evinced by the higher dye content in NaOH pretreated samples compared with the untreated control in the negative-staining test with C. I. Direct Red 81. However, there was little evidence of change in substrate accessibility due to the KOH pretreatment.

Despite the apparent differences in substrate accessibility due to pretreatment type, all resin-finished samples exhibited similar resin content. However, the pretreatment type strongly influenced the distribution of resin in samples. A high concentration of resin was observed on fiber/fabric surfaces in the alkali pretreated samples in contrast to a more uniform distribution of resin through the substrate in control samples.

The pretreatment type also exerted a significant influence on properties of the resin-finished samples. The abrasion resistance and yarn strength were lower in samples resin-finished after alkali pretreatments as compared with the resin-finished control, while there were no significant differences in strength among substrates subjected only to pretreatments. Hence, it appears unlikely that the differences observed among the resin-finished samples were caused by alkali pretreatments alone.

Strength loss in cellulose due to resin finishing is attributed to substrate hydrolysis during the process and/or to substrate embrittlement due to the formation of crosslinks. Substrate hydrolysis leads to an overall reduction in strength, while embrittlement may lead to different types of strength loss depending on the distribution of crosslinking reagent in the substrate. A higher surface concentration of resin leads to decreased fabric abrasion resistance^{19,20} whereas a more uniform distribution of resin through fabric structures improves crease recovery but decreases tenacity.^{16,21}

In this investigation, the correlation of high surface concentration of resin with low abrasion resistance and crease recovery was observed to hold true. But the correlation of uniform resin distribution with decreased tenacity did not hold true as the yarn strength in resin-finished control samples was higher than that in the samples resin finished after alkali pretreatments. The samples resin finished after alkali pretreatments exhibited an overall reduction in strength as compared with the resin-finished control. Hence, the strength loss in the pretreated and resin-finished samples cannot be attributed only to the differential distribution of resin in the substrates; it appears that other factors may also be responsible for the results observed. The overall reduction in strength in the pretreated and resin-finished samples is suggestive of a greater hydrolysis in these samples as compared with the resin-finished control; but there is no evidence of such differences at this time. The reasons for the differential resin distribution observed in the alkali

pretreated and resin-finished samples are also not clear at present.

More work is required to elucidate the results obtained in this investigation. An investigation of the internal structure of fibers from the treated samples may lead to a better assessment of the nature and extent of any changes caused by the different treatments, and lead to a better understanding of the influence exerted by alkali pretreatments on the properties of resin-finished lyocell. These studies are underway and their results will be reported in a future communication.

CONCLUSIONS

The resin finishing of alkali pretreated samples resulted in a higher concentration of reagent on the fabric surface, in contrast to a more uniform distribution of reagent in the control samples. Among resin-finished samples, alkali pretreatments resulted in lowered crease recovery, abrasion resistance, and tensile strength. The differences in distribution of crosslinking reagent among the resin-finished substrates offer only a partial explanation for the differences observed in substrate properties. More work is being conducted in an attempt to better understand the influence of alkali pretreatments on the properties of resin-finished lyocell and will be reported in a future communication.

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