

# NaOH/Urea Aqueous Solutions Improving Properties of Regenerated-Cellulosic Fabrics

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**ABSTRACT:** The application of sodium hydroxide and sodium hydroxide containing urea solutions has been utilized for regenerated-cellulosic material activation. The treatments resulted in the reorganization of cellulose fibers, hence accessibility and reactivity. In this study, sodium hydroxide–urea solutions were applied to lyocell and viscose-knitted fabrics as finishing treatment to improve the accessibility and physical properties of textiles. Besides the mixtures, different concentrations of sole sodium hydroxide and sole urea treatment were applied. The different concentrations of urea, sodium hydroxide, and sodium hydroxide–urea mixtures were used with small increment to detect suitable concentrations and mixture ratios applied for fabrics modification. The results

showed the effectiveness of applying the mixture solutions of alkali–urea particularly to CV-knitted fabrics for improving pilling behavior, whereas for CLY fabrics, the standard alkali solutions showed the best pilling performance. The utilization of urea and sodium hydroxide–urea mixture played an important role for regenerated-cellulosic fabrics where high alkali concentrations is not preferred to avoid fabric damages and where a mixture system could inhibit some of these aspects. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2865–2874, 2010

**Key words:** fibers; polysaccharides; solution properties; structure–property relations; swelling

## INTRODUCTION

Activation of cellulose is an important treatment of raw cellulosic materials with the aim of increasing the accessibility and reactivity of cellulose for subsequent reactions by structural changes. Change of fibers accessibility is considered as an important part of change in chemical reactivity. Swelling agents most frequently used for cellulose activation include sodium hydroxide and sodium hydroxide containing urea solutions.<sup>1</sup> The reorganization of cellulosic fibers by swelling treatments in sodium hydroxide solutions results in numerous changes in fibers structure, causing changes in chemical reactivity in the fiber-solution heterogeneous system.<sup>2,3</sup> The effectiveness of sodium hydroxide at high concentrations and sodium hydroxide–urea–water aqueous solutions at room

temperature to dissolve cellulose has been reported as a potential low cost and simple processing to produce cellulosic fibers.<sup>1,4</sup> In recent years, it was found that sodium hydroxide–urea at cold temperature can dissolve cellulose better than sole sodium hydroxide alone.<sup>5,6</sup> By adjusting the composition of sodium hydroxide and urea as well as controlling the temperature of the solvent, the easy and simple method to dissolve cellulose has been investigated. The dissolution of cellulosic raw material has great effects on the structure and properties of regenerated-cellulosic fibers/fabrics.<sup>5</sup> Generally, the treatment of cellulose results in changes in the degree of polymerization (DP), crystallinity degree, interfibrillary bonds, and fiber morphology. These factors influence mechanical properties in both conditioned and wet state, therefore influence the final physical performance of textile fabrics. In addition, it was stated that sodium hydroxide containing urea solutions has a considerably stronger effect on the cellulose structure than sole sodium hydroxide solution.<sup>1</sup>

Zhou Jinping et al. studied the molecular parameters on cellulose dissolution using sodium hydroxide–urea solution where a solution of 10 wt %

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sodium hydroxide showed the same chemical shifts than did 6 wt % sodium hydroxide – 4 wt % urea. The chemical shifts of C=O indicated an interaction between sodium hydroxide and urea in the solution as well playing an important role in the solvation of cellulose, which effectively improves the dissolution of cellulose and brings the cellulose into the aqueous solution.<sup>7</sup> In addition, Cai and Zhang demonstrated that sodium hydroxide–urea in aqueous solution precooled to  $-12^{\circ}\text{C}$ , rapidly dissolve cellulose at ambient temperature.<sup>8</sup> The addition of urea and the low temperature play an important role in the improvement of the cellulose dissolution, because low temperature creates a large inclusion complex associated with cellulose, sodium hydroxide, urea, and water clusters, which brings cellulose into aqueous solution.<sup>9</sup> Zhou Qui et al. reported the homogeneity of alkali–urea medium when used as a solvent for cellulosic by the chemical shift of sodium hydroxide–urea solution followed by  $^{13}\text{C}$ -NMR spectrum. The spectrum indicated an interaction between sodium hydroxide and urea, breaking the inter- and intramolecular hydrogen bond of cellulose and enhancing the interaction between cellulose and urea molecules, which effectively prevented the self-association of cellulose macromolecules in sodium hydroxide aqueous solution and improved the stability of the cellulose solution.<sup>10</sup>

In this investigation, different low-concentration solutions of sole urea, sole sodium hydroxide, and their mixtures with specific-concentration ratios were applied on lyocell and viscose-knitted fabrics. The changes in fibers accessibility were evaluated by swelling behavior, water retention value, and dye uptake. The effect of treatment on the final physical properties of fabrics was assessed by shrinkage and pilling in cellulosic fabrics. Pilling is one of the most important properties reflecting the quality of textile fabrics, as the formation and removal of pilling are related to any chemical and mechanical effects on fibers and fabrics. The significant influence of low-solution concentrations, as described in our previous paper<sup>11</sup> and ratio of mixtures has been noticed, opening further possibilities to study the correct selection of sodium hydroxide–urea treatment processes to achieve the desired behaviors in cellulosic fabrics.

## EXPERIMENTAL

### Fabrics

Regenerated-cellulosic fabrics supplied by Lenzing AG, Austria were used for this investigation. The fabrics included Tencel<sup>®</sup> Standard (CLY) and Lenzing Viscose<sup>®</sup> (CV). All materials are single jersey fabrics knitted from ring yarns. The fabric specifications for CLY are 1.3 dtex count, 39-mm fiber length, 50/1

**TABLE I**  
**Description of Sodium Hydroxide–Urea Mixtures**

Mixture name	Mixture composition
Mix A	0.05M NaOH + 4.9M Urea
Mix B	0.5M NaOH + 4.9M Urea
Mix C	1M NaOH + 4.9M Urea

Nm yarn, 140 g/m<sup>2</sup> specific weight, and 280 loops/cm<sup>2</sup> loop density. The specifications for CV are 68/1 Nm ring yarn, 1.3 dtex count, 39 mm fiber length, 148 g/m<sup>2</sup> specific weight, and 324 loops/cm<sup>2</sup> loop density.

### Chemicals and solutions

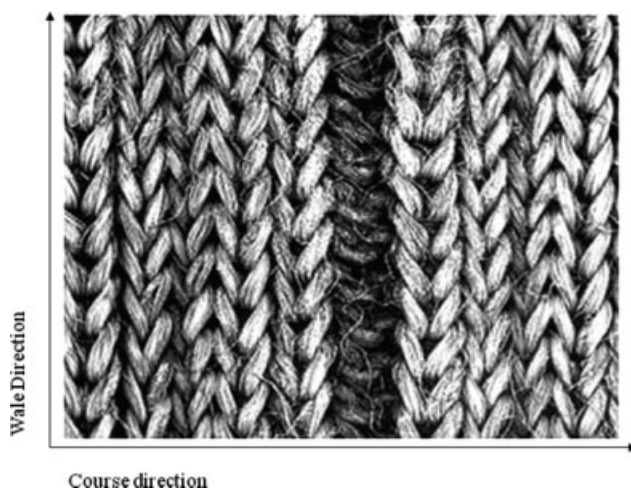
The analytical grade sodium hydroxide (>98%) was purchased from Riedel-de Haën (Seelze, Germany) and technical grade urea was used. The sodium hydroxide was prepared in different concentrations solutions of 0.05M, 0.5M, and 1M, and the urea was prepared in different concentration solutions of 1.7M, 3.3M, and 4.9M. The sodium hydroxide and urea solution were mixed as described in Table I. The mixtures (Mix A, B, C) were applied for all CLY and CV fabrics.

The fabrics were used as received, cut into 800 × 400 mm pieces, kept 24 h in standard atmosphere ( $20 \pm 2^{\circ}\text{C}$ , relative humidity-RH 65%), and treated following the pad batch procedure. The samples were immersed in different sole sodium hydroxide concentration solutions (0.05M, 0.5M, and 1M), sole urea solutions (1.7M, 3.3M, and 4.9M), and their mixtures (Mix A, B, C) for 5 min. The wet samples were padded once at 3.5 bar nip pressure and speed of 1 m/min in Mathis padder laboratory module. The padded fabrics were batched 4 h at room temperature, rinsed with hot and cold running tap water, neutralized with commercial 5% citric acid solution, three times water rinsed, and line-dried overnight and weighed.

### Methods for physical and chemical properties measurements

#### Swelling test

For swelling test, loose fibers were withdrawn from untreated fabrics. The swelling of the cellulosic fibers was investigated following the changes in fibers diameter. A minimum of 10 fibers were placed on a microscope glass with 1–2 drops of the selected solutions, including deionized water, sole sodium hydroxide solutions (0.05M, 0.5M, 1M), sole urea solutions (1.7M, 3.3M, 4.9M), and their mixtures (Mix A, B, C) as described in Table I. After 2 min in contact with the solutions, samples were covered with a glass cover. A Reichert projection microscope, using



**Figure 1** Description of wale and course directions of knitted fabric.

an objective of 40/0.65 and reproduction scale of 500, with an attached ruler, was used for measuring fibers diameter. For comparison reasons, immersion oil for microscopy (Merck, Germany) was used for measurement of nonswollen diameter of fibers.

**Wet pickup**

The fabrics were weighed in dry-state ( $W_d$ ) and in wet-state after padding ( $W_w$ ) to obtain the wet pickup values. The wet pickup value was calculated according to chemical finishing of textiles, described in eq. (1).<sup>12</sup> The fabrics were treated with sole sodium hydroxide, with sole urea, and with the Mix A, B, and C following the pad batch procedure. After washing-off the solvents and line-dried overnight, the fabrics were kept 24 h in room climate ( $25 \pm 2^\circ\text{C}$ ) for use in further tests.

$$\text{Wet pickup} = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

**Shrinkage**

The shrinkage was determined in wale and course direction of knitted fabric as described in Figure 1. A permanent pen was used to mark the fabrics before treatment with three 30-cm pairs of bench marks parallel to the wale direction of fabric and with three 30-cm pairs of bench marks parallel to the course direction of fabric, with a 5-cm distance from all borders. Measurement of the distance were done before and after treatment, and the shrinkage values for wale and course directions were calculated as described in eq. (2).<sup>13,14</sup>

$$S(\%) = \frac{d_u - d_t}{d_u} \times 100\% \quad (2)$$

where  $S\%$ , shrinkage in wale and course directions;  $d_u$ , distance between two marks of untreated fabrics, measured in mm;  $d_t$ , distance between two marks of treated fabrics, measured in mm.

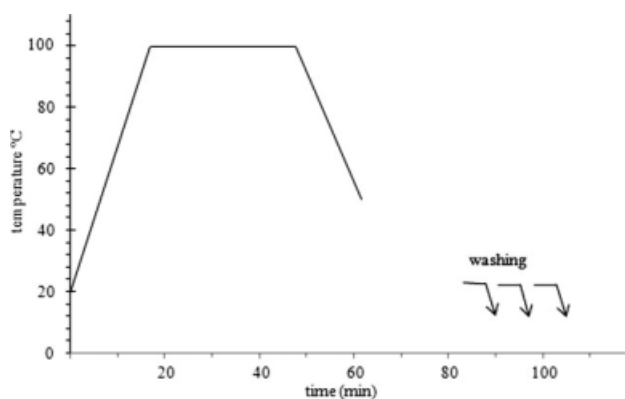
**Water retention values (WRV)**

A 0.5 g of untreated and treated fabric were added into 50 mL of distilled water and stood at room temperature for 24 h. The wet fabric was placed in a plastic centrifuge tube containing a filter, centrifuged at  $4000 \times g$  (Heraeus Multifuge 1 L) for 10 min and weighted ( $W_w$ ). For each sample, four repetitions were done. The drying step was carried out at  $105^\circ\text{C}$  for 4 h ( $W_d$ ). The water retention values (WRV) were calculated as described in eq. (3).<sup>15</sup>

$$\text{WRV} = \frac{W_w - W_d}{W_d} \times 100\% \quad (3)$$

**Dyeing procedures**

The changes in accessibility in the treated fabrics caused by different solution mixtures and concentrations were assessed by dye uptake in the samples dyed with Direct Red 81 (CI Direct Red 81, 50% dye content from Sigma-Aldrich).<sup>16,17</sup> The dyeing solution contained 0.5 g/L of NaCl and 2 g/L of dye-stuff. The dyeing was performed using a liquor ratio of 1 : 40 with untreated and treated fabrics of CLY and CV cut in  $100 \text{ cm}^2$  pieces. The samples were dyed at a Werner Mathis AG LABOMAT dyeing machine, with continuous and alternate agitation of 30 rpm. The dyeing profile followed the steps: the temperature increased from room temperature to  $100^\circ\text{C}$  with a gradient of  $5^\circ\text{C}/\text{min}$ , kept at  $100^\circ\text{C}$  for 30 min, and decreased to  $50^\circ\text{C}$  with a gradient of  $3.5^\circ\text{C}/\text{min}$ . The dyeing diagram is given at Figure 2. After dyeing, the unfixed dyestuff was removed by rinsing until colorless in running water and the samples were line-dried overnight.



**Figure 2** Temperature-time diagram of dyeing process with CI Direct Red 81.

### Color measurements

The color differences ( $\Delta E$ ) of the dyed samples were determinate using the CIELab coordinates by a tristimulus colorimeter (Minolta Chromameter CR 210, geometry  $d/0^\circ$ , sample diameter 50 mm). The color difference ( $\Delta E$ ) was calculated with the obtained CIELab coordinates as described in eq. (4)–(7).<sup>18</sup>

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (4)$$

where  $\Delta E$  = relative perceptual difference of untreated and treated samples,  $\Delta L^*$  = lightness difference of untreated and treated samples [eq. (5)],  $\Delta a^*$  = redness (+)/greenness (-) difference of untreated and treated samples [eq. (6)],  $\Delta b^*$  = yellowness (+)/blueness (-) difference of untreated and treated samples [eq. (7)].

$$\Delta L^* = L^*_u - L^*_t \quad (5)$$

where  $L^*_u = L$  value of untreated sample and  $L^*_t = L$  value of treated sample.

$$\Delta a^* = a^*_u - a^*_t \quad (6)$$

where  $a^*_u = a$  value of untreated sample and  $a^*_t = a$  value of treated sample.

$$\Delta b^* = b^*_u - b^*_t \quad (7)$$

where  $b^*_u = b$  value of untreated sample and  $b^*_t = b$  value of treated sample.

### Rapid pilling test (RPT)

The fabrics were cut in 140/180-mm diameter for upper/lower sample holders. The samples were kept in a standard atmosphere room ( $20 \pm 2^\circ\text{C}$ , RH 65%) for 24 h and immersed in 1000 mL of DI water for 1 h, padded at 3.0 bar nip pressure and 1 m/min speed. The padded samples were weighed and immediately placed in the Martindale abrasion tester and were abraded under 250 g loading weight. Short abrasion cycles (50 and 500 cycles) were applied with two repetitions for each cycle type. The samples were flat-dried overnight before rating to avoid the light reflection on the wet samples during the pill rating test.

### Pill rating test (PRT)

The samples were rated by visual estimation according to the International Standard ISO12945 Part 2:

Modified Martindale Method. The samples were scrutinized in a viewing cabinet under day light illumination, rated from 1 to 5, where 1 indicates the highest level of pilling. Two observers rated all samples once, where samples of each cycle type had four repetitions. Consequently, a mean value from eight ratings was recorded for each type of cycles.

### Image analysis

A series of scanning microscope images (SEM) of fabrics surface were done at a Environmental Scanning Electronic Microscope XL30 ESEM-FEG, from Philips, at 30 kV acceleration voltage,  $\text{H}_2\text{O}$  mode ( $P = 0.9$  Torr and Beam = 16.0 kV), with magnification of 3500 $\times$ .

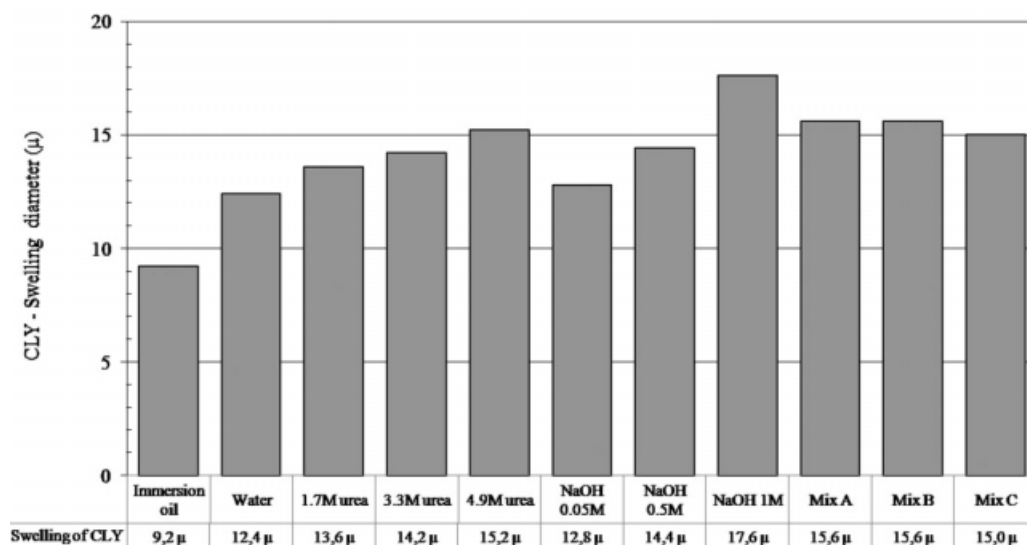
## RESULTS AND DISCUSSION

### Swelling behavior

Aqueous sodium hydroxide is a strong swelling agent for cellulose and the swelling effects are highly concentration and temperature dependent.<sup>19,20</sup> In ambient temperature, the swelling increases following the increasing of solution concentrations until optimum swelling concentration. In the case of sodium hydroxide–urea mixture, the reaction mechanism was proposed that sodium hydroxide hydrates – urea hydrates – free water–cellulose form a special complex in the solution. Sodium hydroxide destroys inter- and intrahydrogen bonds between cellulose molecules and urea hydrates functioning as hydrogen bonds donor and receptor between solvent molecules and prevents the reassociation of cellulose molecules. It was concluded that the DP of cellulose plays a more important role in cellulose dissolution in sodium hydroxide–urea solutions than cellulose with high crystallinity does.<sup>5</sup> That might serve the explanation for the different swelling behavior of CLY and CV, where the DP of CLY (600–800) is higher than the DP of CV (200–250).<sup>21</sup>

The swelling behavior of cellulosic fibers was investigated following the changes in fiber diameter. The changes in fiber diameter caused by sodium hydroxide, urea, and their mixture solutions are illustrated in Figure 3 for CLY fibers and in Figure 4 for CV fibers.

Figure 3 shows that lyocell fiber swelled 35% in water, 65% in 4.9M urea, 91% in NaOH 1M when compared with the nonswollen diameter of fibers measured in immersion oil. The swelling in sole sodium hydroxide and sole urea solutions increased, in general, following the increase in molar concentration of solutions. The lyocell fibers treated in sodium hydroxide–urea mixtures showed similar

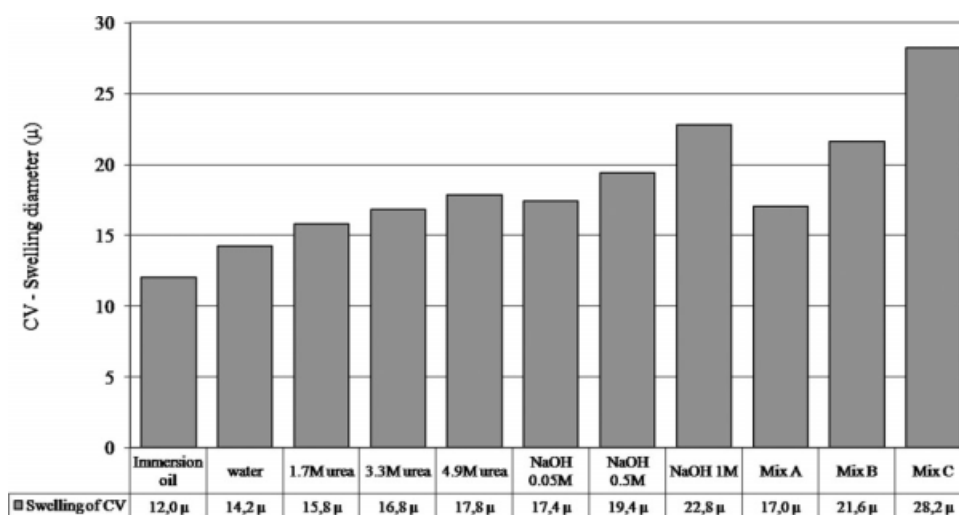


**Figure 3** Influence of sodium hydroxide, urea, and their mixture solutions on CLY fiber swelling, in the order of increasing concentrations.

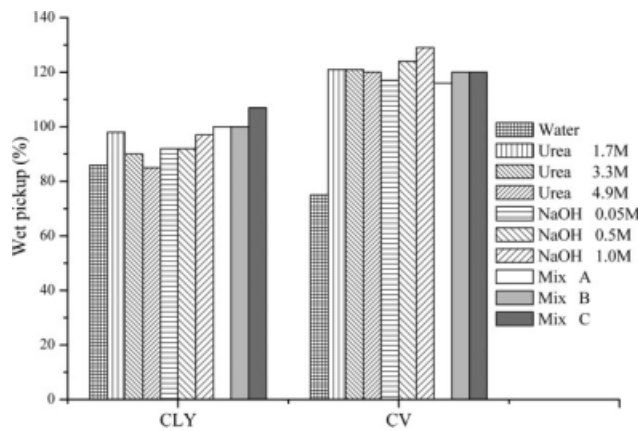
swelling values, where the Mix A, Mix B, and Mix C swelled fibers ~ 65–70%. Following the increase in the solution concentration, lyocell fibers exhibited the following swelling tendency: increased with increasing urea solution concentrations, increased with increasing alkali solution concentrations, and decreased with increasing mixture solution concentrations. Moreover, the mixture solutions containing lower concentrations of NaOH (Mix A and Mix B) gave the fabrics similar or higher swellings – boosted by the urea addition – when compared with the ones treated with sole alkali in the same concentrations (0.05M and 0.5M), which permits to a reduction in the costs profile of swelling solution. Posteriorly,

these values can be taken into account for dyeing conditions, where a higher swelling can be inputting deeper shades due to higher amounts of dye penetration

Figure 4 shows that viscose fibers swelled 17% in water, 48% in 4.9M urea, 90% in NaOH 1M when compared with the nonswollen diameter of fibers measured in immersion oil. The swelling in sodium hydroxide, urea, and their mixtures increased following the increase of solution concentrations. The sodium hydroxide–urea mixture seems to be the most effective swelling agents for viscose fibers, especially for Mix C, where viscose fibers presented a swell of 135%.



**Figure 4** Influence of sodium hydroxide, urea, and their mixture solutions on CV fiber swelling, in the order of increasing concentrations.



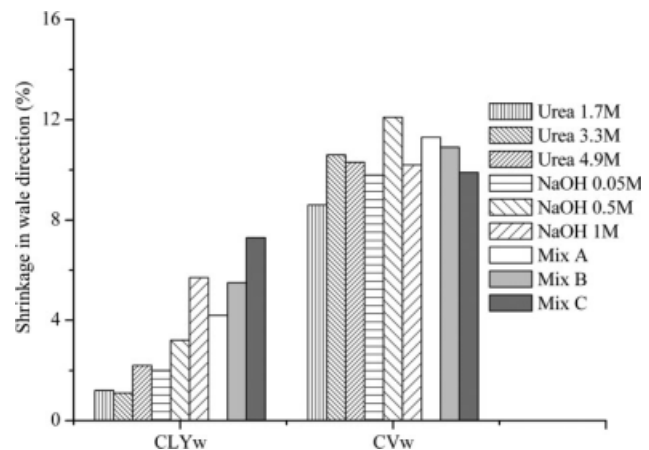
**Figure 5** Wet pickup values of CLY and CV fabrics treated with sodium hydroxide, urea, and sodium hydroxide–urea mixtures.

### Wet pickup

Resulting from fibers swelling, the wet pickup values exhibited differences for CLY and CV fabrics. In general, CV fabrics retained higher amount of liquid compared with CLY fabrics. For CLY and CV fabrics, the urea, alkali, and their mixture solutions permeate better than water. The pickup values increased following the increase of solution concentrations, except for urea solutions where the pickup value slightly decreased at higher concentrations, where the viscosity state of the solution can draw back the pickup values. CLY fabrics had the highest pickup rates with the mixtures solutions; nevertheless, CV showed very similar pickup rates for solely or mixed solutions, which conferred to the mixture solution the same performance than solely solution, but with the half concentration of alkali. The pickup values are very important during finishing processes and the mixture solutions can half-reduce the alkali consume. The pickup values of CLY and CV fabrics are described in Figure 5.

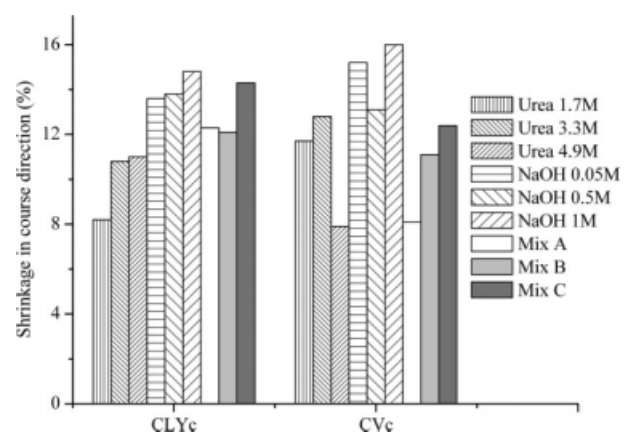
### Shrinkage

The expansion in fibers leads to fabrics shrinkage, which might reduce the planar dimensions and increase the fabrics thickness. Fabric structural changes during subsequent wetting and drying are normally explained using swelling–shrinkage and hygral expansion–contraction model.<sup>20</sup> The shrinkage of knitwear originates from dimensional changes, particularly stitches.<sup>22</sup> In addition, the changes in loop length, the wale, and course spacing values are determinant factors for the shrinkage of knitted fabrics and the effect on loop shape is apparently widthwise.<sup>23</sup> The shrinkage of CLY and CV fabrics in wale and course directions are shown in Figures 6 and 7.

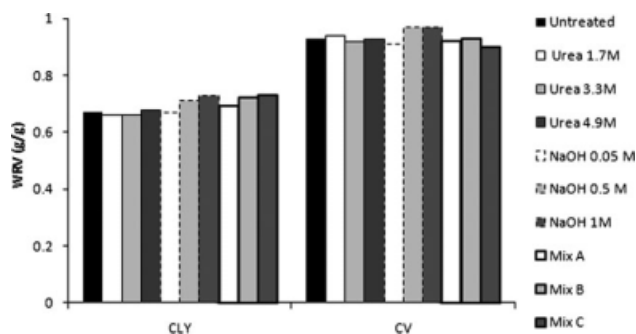


**Figure 6** Influence of sodium hydroxide, urea, and their mixture solutions and concentrations in wale shrinkage of knitted CLY (CLYw) and CV (CVw) fabrics.

Figures 6 and 7 illustrate that fabrics shrank more in course direction than in wale direction, with remarkable differences for CLY fabrics. The structural changes in CLY and CV fabrics were influenced by specific solutions and concentrations. For CLY fabrics, the wale/course shrinkage in three types of solutions is prominent and grows with increasing concentration, indicating regular textile structure stabilization. For CV fabrics, the wale shrinkage reduction and course shrinkage increase at high-concentration solutions can be attributed to the higher density of CV fabrics in contrast with CLY fabrics, which will allow less fabric penetration. The shrinkage will be intrinsic related to fiber type and fabric construction, and absorbency. It can be assumed that loop length did not significantly change while the spaces between loops reduced. However, CV fabrics treated with high-concentration urea solutions showed almost the same shrinkage value for wale direction and decreased in course direction, which



**Figure 7** Influence of sodium hydroxide, urea, and their mixture solutions and concentrations in course shrinkage of knitted CLY (CLYc) and CV (CVc) fabrics.



**Figure 8** Influence of sodium hydroxide, urea, and their mixture solutions and concentrations on the water retention values (WRV) of treated and untreated CLY and CV fabrics.

can be attributed to the low amount of “available” water in the high-concentration urea solely solution.

**Water retention values (WRV)**

The water retention values (WRV) of fabrics after treatment insignificantly changed, as shown in Figure 8. For both CLY and CV fabrics, sole urea treatment almost had no effect on WRV; sole sodium hydroxide treatment showed minor increase in WRV; sodium hydroxide–urea mixtures resulted in minor increase of WRV in lyocell fabrics, nevertheless showed negligible variations in WRV of viscose fabrics. The slight changes of WRV in untreated and treated fabrics within the three types of solutions can illustrate the absence of damage in the fabrics during/after the treatment. Probably, due to low concentration of treatment solutions, the treated fabrics had little pore collapse and maintained the average space between fibers. For comparative results, the results of untreated fabrics submitted to WRV are plotted for CLY and CV fabrics.

**Accessibility**

The uptake of dyestuff is often used to monitor the changes in fibers properties and the small variation

**TABLE II**  
CIELab and  $\Delta E^*$  Color Values of Untreated and Treated CLY Fabrics

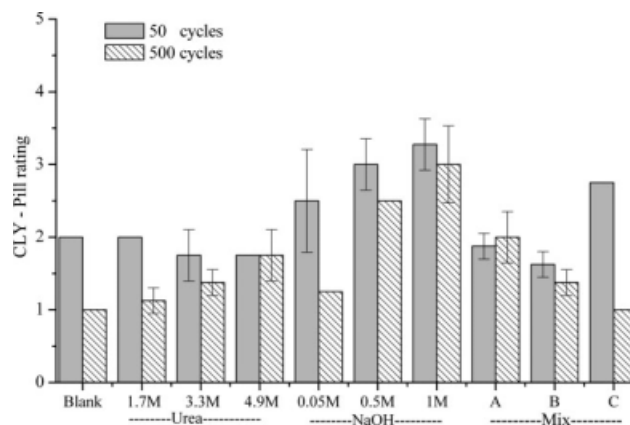
Sample	$L^*$	$a^*$	$b^*$	$\Delta E^*$
Blank (undyed)	87.06	-2.23	3.64	-
Untreated dyed	37.36	47.69	12.67	-
Urea 1.7M	40.84	49.34	12.88	3.86
Urea 3.3M	41.68	49.94	12.92	4.87
Urea 4.9M	41.58	49.12	12.52	4.46
NaOH 0.05M	42.45	49.68	12.72	5.47
NaOH 0.5M	41.58	50.12	13.08	4.89
NaOH 1M	41.00	49.18	12.60	3.93
Mix A	41.94	49.74	12.78	5.02
Mix B	40.95	49.29	12.74	3.93
Mix C	38.51	49.08	12.69	1.80

**TABLE III**  
CIELab and  $\Delta E^*$  Color Values of Untreated and Treated CV Fabrics

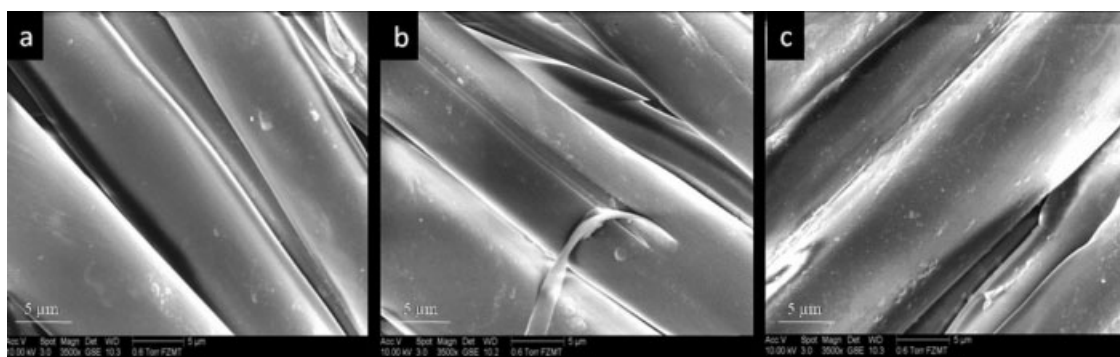
Sample	$L^*$	$a^*$	$b^*$	$\Delta E^*$
Blank (undyed)	94.95	-2.68	5.25	-
Untreated dyed	44.42	51.40	11.59	-
Urea 1.7M	45.58	50.66	10.42	1.80
Urea 3.3M	45.39	50.97	10.63	1.43
Urea 4.9M	46.65	50.73	10.10	2.76
NaOH 0.05M	47.16	50.81	10.09	3.18
NaOH 0.5M	46.97	51.31	10.45	2.79
NaOH 1M	45.86	50.69	10.23	2.10
Mix A	47.83	51.00	10.14	3.73
Mix B	47.88	50.95	10.23	3.74
Mix C	46.86	51.09	10.34	2.76

in fiber color is the first indication of some alteration to process variables.<sup>24</sup> Dyes can be considered as colored probe molecules. When selecting a dye to use as a probe for studies on the accessible surface and pore size of cellulose, care has to be taken on dye structure, dyeing conditions, and dye substantivity as well as molecular volume.<sup>25</sup> In this investigation, the CI Direct Red 81 was applied for untreated and treated fabrics. The color differences between untreated and treated fabrics, which are expressed via CIELab and  $\Delta E^*$  values, can be assumed as a measurement for differences/changes in fibers accessibility. The  $L^*$ ,  $a^*$ ,  $b^*$  (CIELab) values, and  $\Delta E^*$  of untreated and treated fabrics are shown in Table II for CLY fabrics and in Table III for CV fabrics.

Tables II and III showed that, with the same dye conditions, lyocell had higher accessibility compared with viscose fabrics. The great accessibility of lyocell, consistent with its high-dye uptake, has been found and rationalized in terms of the known fibrillar structure of lyocell fibers.<sup>24</sup> For CLY fabrics, high  $\Delta E^*$  values were obtained in fabrics treated with sodium hydroxide 0.05M, with urea 3.3M, and with the Mix A. For CV fabrics, high  $\Delta E^*$  values were



**Figure 9** Pill rating in untreated and treated CLY fabrics.



**Figure 10** SEM images of CLY fabrics treated with Mix A (a), Mix B (b), and Mix C (c), with magnification of  $\times 3500$ .

obtained in fabrics treated with sodium hydroxide 0.05M, with urea 4.9M, and with the Mix A and B.

The lightness of CLY fabrics presented similar values to all concentrations and mixtures, except for CLY fabrics treated with Mix C, that had the highest diffusion CI Direct Red 81, corroborated by the decrease in the  $L^*$  values and imparting darker shades. Contrary to CLY fabrics, the  $L^*$  values of CV fabrics treated with Mix C displayed increasing values and imparted the lightest shades compared with the other treatments. The accessibility of CLY and CV fabrics is compatible with swelling degree indicated by WRV in Figure 8. The dye uptake behavior of cellulosic fabrics reflected the accessible volume of fibers, modified by sodium hydroxide, urea, and sodium hydroxide–urea mixtures. The effective concentrations for improving the accessibility of both CLY and CV fabrics could be referred to sodium hydroxide and sodium hydroxide–urea mixture with high ratio of alkali.

### Pilling

The effect of treatment on final physical properties of textile products was assessed by pill formation. The fabrics were subjected to rapid pilling test (RPT), where 50 and 500 wet abrasion cycles were chosen as illustrative cycles for CV and CLY fabrics.<sup>26</sup> The pill ratings of untreated and treated fabrics after RPT are displayed in Figure 9 for CLY fabrics and Figure 11 for CV fabrics.

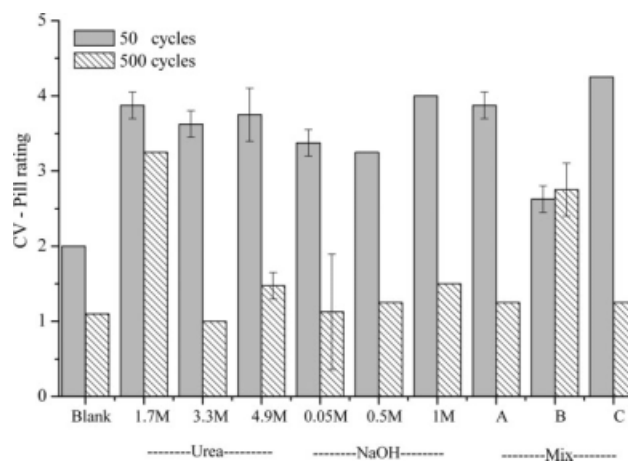
Figure 9 showed that at low-wet abrasion of 50 cycles, the improvement of pill rating were recorded for CLY fabrics treated with sodium hydroxide and with the Mix C, where the pill rating increased following the increase in sodium hydroxide concentrations. CLY fabrics treated with different concentrations of sole urea exhibited the equivalent or lower pill rating values of untreated fabrics. However, at high-wet abrasion of 500 cycles, all treatment proved to have a beneficial effect on pill rating, except for Mix C that decreased the pill rating and presented

similar rates of untreated CLY fabrics. Sole sodium hydroxide solutions with concentrations of 0.5M, 1.0M, and Mix A with low-sodium hydroxide content seems to be the most effective treatment for improving pilling in CLY fabrics in long cycles of abrasion (500 cycles), among the investigated concentrations and mixtures of solutions.

Figure 10 shows representative series of SEM images of CLY fabrics treated with Mix A, B, and C with magnification of 3500 $\times$ . The images of single fibers after sodium hydroxide–urea treatment showed that fabrics treated with Mix A [Fig. 10(a)] and Mix B [Fig. 10(b)] have a smooth surface with less surface damage or course shrinkage than fabrics treated with Mix C [Fig. 10(c)].

Consequently, the pilling formation illustrated at Figure 10(a,b) is high (low pill rating) and increased with increasing the cycles of abrasion. However, the brittleness of the fiber surface of Figure 10(c) can hinder the pill formation, leading to lower amount of pills at 50 cycles. At long abrasion cycles of 500, the fabrics treated with Mix C presented the highest pilling formation (low pill rating).

In our previous work, the same pill tendency at short (50) and long (500) cycles of abrasion was



**Figure 11** Pill rating in untreated and treated CV fabrics.



found and reported.<sup>11</sup> That could explain the high-pill formation (low rating) at short cycles of abrasion (50) for smooth surfaces illustrated at Figure 10(a,b). The initial fibrils originated from the fabric surface could be easily gapped and joined to form the pills, beside the pill tendency follows the increase in increasing abrasion cycles.

On the other hand, while the brittle surface illustrated at Figure 10(c) will not release fibrils at short abrasion cycles (50), consequently it will form fewer pills. At long cycles of abrasion (500), it can be draw that the superficial brittle condition has been eliminated after long cycles, causing the pill formation, justifying the reported higher amount of pills (low pill rating) at 500 cycles.

Figure 11 showed that at low-wet abrasion of 50 cycles, sodium hydroxide, urea, and sodium hydroxide-urea treatment presented higher pill rating (less pilling) when compared with untreated CV fabrics. At high-wet abrasion of 500 cycles, almost all treatments indicated an adequate improvement in pilling formation for CV fabrics. The 1.7M urea and Mix B solutions provided the more stable conditions for pilling prevention in CV fabrics. It might be caused by combined effect of fibers swelling and the changes of dimensional structure in knitted fabrics after treatment. For CV fabrics, the sole urea and sodium hydroxide-urea mixtures are more suitable than the sole sodium hydroxide solution for pilling improvement.

The high fibers swelling and the weaker fiber tenacity in swollen state can result in the rapid pill formation and rapid pill removal in cellulosic fabrics. As described by Bui et al., the low-wet abrasion resistance of CV fibers (~ 33 counts) may be responsible for the faster pill formation in CV fabrics than in CLY fabrics.<sup>26</sup> Therefore, the effectiveness of treatment on pilling can be seen in CV fabrics at 50 wet abrasion cycles, whereas in CLY fabrics at 500 wet abrasion cycles.

Currently, the mixing of sodium hydroxide-urea system, turned out to modify physical properties of lyocell and viscose fabrics. Furthermore, the described treatment of regenerated-cellulosic fabrics in sodium hydroxide-urea mixtures indicates new variations in processing of cellulose textiles and their influence on the pill formation that has been investigated with an outlook on the fabric appearance and wearing wellness.<sup>27</sup> For lyocell fabrics, sole sodium hydroxide was outlined to higher influence in the pill formation rate at short and long cycles of abrasion. For viscose fabrics, no differences in pill formation were reported at short abrasion cycles for all solutions. Nevertheless, at high-abrasion cycles, viscose fabrics treated with sole urea (1.7M) and Mix B showed a favorable/advantageous increase in the pill rating (less pill formation).

## CONCLUSIONS

The effect of sole urea, sole sodium hydroxide, and their mixtures with different concentration ratio on accessibility, physical properties, and pill formation in lyocell and viscose-knitted fabrics were assessed in this investigation. The results showed that a suitable alkali-urea mixture treatment for cellulosic fabrics depends on solution concentration and type of cellulosic fabric.

The changes in knitted fabric morphology after treatment were estimated by shrinkage. While viscose-knitted fabrics show similar rates of shrinkage in wale and course direction, lyocell fabrics indicated the higher shrinkage in wale direction than in course direction. The shrinkage of lyocell and viscose fabrics was less in sole urea than in sole alkali in both wale and course direction. Viscose fabrics treated with sodium hydroxide-urea profiled to be less influenced by the mixture in the course shrinkage when compared with lyocell fabrics.

The useful treatments to improve accessibility were detected via direct dye uptake, where sodium hydroxide-urea mixture with high ratio of alkali (Mix C) showed the most effectiveness for lyocell fabrics, while sole urea (1.7M) for viscose fabrics.

The changes in fiber properties and dimensional structure of fabrics resulted in pilling behaviors of treated fabrics tested with rapid pilling test. The outcome pilling behaviors in lyocell fabrics suggested the feasibility of applying sodium hydroxide with higher concentrations (i.e., >1M) and Mix A for pilling improvement at short and long cycles of abrasion. For viscose fabrics, improved pilling behavior was observed with sole urea (1.7M) and Mix B for long cycles of abrasion.

Each, solely or mixture, selected solution interacted with the selected cellulosic fabrics imparting distinct behaviors in the physical tests; it is not possible to pinpoint the best solution for improvement of all physical properties simultaneously. However, it is possible to identify the best solution for each case of desired physical improvement. Nevertheless, in most cases, the mixture solution of alkali-urea with half-alkali concentration showed the same performance than single alkali solution in double-concentration, where the cost-benefit profile can be the selecting factor for fabric treatment solutions. Further investigations with different mixture concentrations would be needed to acquire the desired improvement for regenerated fabrics.

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