Treatment in Swelling Solutions Modifying Cellulose Fiber Reactivity – Part 2: Accessibility and Reactivity

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Summary: The reorganization of cellulose fibers by swelling treatments in alkali solutions results in numerous changes to fiber structure, causing changes of chemical reactivity in the fiber-solution heterogeneous system. An important part of the change in chemical reactivity is the change of fiber accessibility because it results in exclusion of chemicals such as reagents or catalysts from the fiber. In the second of a two-part series of papers, we examine the influence of changes in fiber accessibility and/or reactivity due to treatment in swelling solutions on the performance or behavior of substrates during and after chemical finishing treatments. Changes in fiber accessibility due to alkali treatments are visualized with fluorescence microscopy. The effect of alkali treatments on enzymatic hydrolysis and pad-dry-cure crosslinking treatments of cellulose substrates are discussed as representative examples to demonstrate the effects of swelling processes on fiber reactivity and accessibility. Model calculations indicate that a considerable redistribution of chemicals in substrates occurs during dry-cure operations resulting from molecule-specific exclusion effects. Pilling tests on lyocell knit-fabrics show the impact of preceding alkali processes on the final physical performance of textile fabric highlighting the importance of correct selection of alkali processes to achieve desired behavior.

Keywords: alkali; cellulose; crosslinking; enzymes; fluorescence; structure-property relationships; swelling

Introduction

In the first paper of this two-part series,[1] we examined the results from various investigations aimed at characterizing the changes of accessibility and sorption in cellulosic fibers after swelling treatments with aqueous alkali solutions. The results indicated that the influence of alkali treatments on fiber accessibility and sorption differ with alkali type, and that alkali-cellulose fiber interactions were characterized by a non-uniform distribution of reagents within fiber structures.

In this second paper, we present selected results from extensive studies in a common discussion to give an overview about the wide range of impacts that result from alkali pre-treatments on cellulosic substrates. The effects are demonstrated by a number of changes in completely different aspects of substrate properties, including:

- Porosity and accessibility as indicator for accessibility of chemicals.
- Rate of enzymatic hydrolysis as a measure of cellulose reactivity.

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- Crosslinking in textile finishing as example of chemical reactivity.
- Pilling propensities as representative of physical properties.

By examining the extent of sorption or intrusion of the Fluorescent Whitening Agent (FWA) Uvitex BHT across fiber cross-sections with fluorescence microscopy it is possible to discriminate between different porous zones in regenerated cellulosic fibers, partly confirming earlier models of fiber structure.[2] Measurements of dye intensity and its penetration depth are promising tools to not only differentiate between fibers spun under different conditions, but also to follow changes in the pore network of fibers after alkali treatments.[3]

Viscose, a man-made cellulosic fiber, is found to be more easily degraded by cellulases as compared to other cellulosics, which is attributed to the more open and homogenous fiber structure.[4,5] Alkali treatments of cellulosic substrates such as mercerization which is commonly employed in the textile industry, results in a more open and homogenous fiber structure and thereby enhances enzymatic hydrolysis of cellulose by cellulases.[6,7] By examining the effects of caustic soda pre-treatments of regenerated cellulosics on the observed levels of hydrolytic activity in subsequent treatments with *Trichoderma* cellulases, as will be discussed in following sections, it is possible to observe the impact of swelling treatments on fiber structure and reactivity. Assessments of changes in substrate accessibility due to swelling treatments may be observed in examinations of the influence of alkali pre-treatments on the behavior of cellulosic substrates after subsequent crosslinking treatments, as elaborated in later sections.

Treatments with caustic soda have been in use for many years to modify fiber structure and properties such as swelling extents, crystallinity, and orientation of fibrils in cellulosic fibers,[8] all of which have a bearing on the physico-mechanical properties of substrates. These characteristics are reflected strongly in the pilling propensities of cellulosic fabrics where fiber swelling, fibrillation tendency, and inter-fiber friction govern the pilling mechanism, pill structure, and pilling propensities.[9,10] Therefore, the impact of swelling treatments on substrate physical properties may be assessed from studies of the influence of alkali pretreatments on pilling in lyocell fabrics as a function of alkali type and concentration.

Experimental Part

Materials

All regenerated-cellulosic substrates (fibers and fabrics) were kindly provided by Lenzing AG, Austria. The different fiber types used in these investigations were: Lyocell – CLY (TENCEL®), Modal – CMD (Lenzing Modal®), and Viscose – CV (Lenzing Viscose®).

Methods

Fluorescence Microscopy On Fiber Cross-Sections

An aqueous solution of the FWA Uvitex BHT 120% (Ciba, Basel, Switzerland) was prepared by dissolving 1 g of the commercial product in 1 L deionized water. Fiber specimens, 0.2 g in weight, were dyed by immersion in 40 mL of the 1 g/L solution for specific time periods. After immersion, the specimens were removed from solution, rinsed twice for 10 min in running cold water, and dried at room temperature.

The dried fiber specimens were embedded in a 2-hydroxyethylmethacrylate resin (Technovit7100™, Kulzer, Vienna, Austria), and fiber cross-sections of 8 μm thickness were prepared using a Reichert microtome (model: 1140/Autocut). The fiber cross-sections were observed and photographed under a fluorescence microscope (Olympus BX microscope equipped with mercury burner lamp and monochromatic filters) as described elsewhere,[11] and the depth of FWA penetration across fiber cross-sections were measured on the photographs.

These measurements were done on untreated CLY, CV, and CMD fibers; on fiber specimens from CLY and CMD fabrics (plain weave, 50/1 Nm ring-spun yarns, 1.3 dtex fibers) treated with 105 g/L and 49 g/L NaOH respectively by dipping in the alkali solutions, passing through a padding mangle at 1 bar nip pressure, followed by neutralization and washing; as well as on fiber specimens from fabrics treated with NaOH and KOH as described in the section 'Alkali treatment – crosslinking'.

Alkali Treatment - Enzymatic Hydrolysis

Woven fabrics of CV, CLY and CMD fiber types (38 mm staple fibers of fineness 1.3 dtex), as described in Table 1, were subjected to treatments with NaOH followed by enzymatic hydrolysis. Analytical grade NaOH, and a commercial cellulase formulation (provided by Genencor International, USA) were used in treatments. The cellulase formulation was used as received without further purification. The total culture filtrate had a nominal activity of 3500 IU/g (IU, International unit = 1 μmol/min), and on analysis yielded the following activities: cellulase activity of 91 FPU/g (FPU, Filter paper Unit) and carboxymethylcellulose activity of 3100 CMC Units/g according to the methods described by Ghose;[12] activity on Avicel of 7.4 IU/g according to the method described by Wood and Mahlingeshwara.[13]

Treatment Method

Fabrics were immersed in alkali solutions (1-3.5 mol/L NaOH) at a liquor ratio of 1:3 (w/v) for 1–2 min at room temperature in slack condition before being passed through a padding-mangle with roller speed of 2 m/min to obtain alkali-solution uptake values of 100–250% (depending on alkali concentration). Immediately after padding, the samples were rinsed twice with deionized water, once in a solution of 20 mmol/L acetic acid, again with deionized water, and line-dried. The control samples received no pretreatment.

The commercial enzyme formulation was diluted with 50 mM sodium acetate buffer (pH 4.8) to a protein concentration of 30 mg/mL for enzymatic-hydrolysis treatments of the samples. The treatment was carried out with a liquor ratio of 1:25 (w/v) at 55 °C ± 1 °C for 1 h in a laboratory dyeing unit (Pretema Multicolor Type MC 360; Caromatic, Switzerland), where fabric samples were wound around perforated cores and treatment solution was repeatedly flushed through the sample at a controlled rate.

The degree of substrate hydrolysis was assessed from the amount of reducing sugar released in treatment liquor determined with the neocuproine method in terms of the glucose content of solutions (cG) [mg/mL].[14]

Alkali Treatment - Crosslinking

The substrate used in this work was a desized and scoured 100% CLY plain-woven fabric, with 36 ends and 29 picks per cm, and a weight of 137 g/m^2. The alkalis used in treatments were analytical grade NaOH and KOH. Leonil SRP and Sandoflex A (Clariant, Basel, Switzerland) are commercial surfactant formulations designed for use under highly alkaline conditions and were used as wetting agents in alkali treatments. The crosslinking

Table 1.
Fabric Parameters.

Fabric	Weave Type	Mass/area [g/m^2]	Thread density [threads/cm]		Yarn linear density [tex]		Yarn twist [tpi]	
			Warp	Fill	Warp	Fill	Warp	Fill
CV	plain	143	36.6	28.8	20.2	24.0	19	19
CLY	poplin	145	37.9	29.1	20.6	23.0	19	19
CMD	plain	142	34.9	29.1	21.5	23.0	19	19

reagent used was a modified dimethylol dihydroxyethyleneurea (DMDHEU) based commercial product, Fixapret ECO (BASF, Ludwigshafen, Germany); Kieralon Jet B Konz. (BASF, Ludwigshafen, Germany) was used as the non-ionic wetting agent, and analytical grade magnesium chloride used as the catalyst.

Alkali Treatments

Fabric samples (30×30 cm^2) were treated at room temperature in a pad-batch process with formulations comprised of 120 g/L NaOH and 3 g/L Leonil SRP, or 250 g/L KOH and 50 ml/L Sandoflex A. The samples were padded through formulations at a nip pressure of 1.0 bar and roller speed of 2.0 m/min and batched for 30 min (NaOH treatment) or 4 h (KOH treatment). 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 were line dried overnight. The wet pickup after padding through NaOH and KOH formulations were 106–111% and 113–120% respectively. The control samples received no alkali treatment.

Crosslinking Treatment

The treatment formulation contained 60 g/L crosslinking reagent, 18 g/L catalyst, and 0.5 g/L wetting agent. Samples awarded crosslinking treatments were padded through treatment 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 fabric after treatment, the samples were immersed in a solution of 1 g/L $NaHCO_3$ at room temperature for 60 min, rinsed with running cold water, and were line dried overnight.

Evaluations

All treated fabric samples were conditioned in a standard atmosphere of 20 °C ± 2 °C and 65% ± 4% relative humidity for over 24 h before testing, and the evaluations 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 pre-tension at a gauge length of 10 cm and 5 cm/min rate of extension, and the crease recovery angle (CRA) determined after 30 min recovery period according to DIN 53890. The abrasion resistance was estimated from the mass loss after 6000 abrasion cycles on a Martindale abrasion tester according to ISO 12947-3:1999. The crosslinker content in samples was estimated from their nitrogen contents analyzed by the Dumas method in a LECO FP 328 Nitrogen analyzer.

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 re-measured after alkali treatments and after resin finishing, and the dimensional change was determined with Equation 1:

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

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

Alkali Treatment - Pilling

Samples, 100×40 cm^2, of a single-jersey knit CLY fabric (of 140 g/m^2 specific weight with 280 loops/cm^2, made of 50/1 Nm ring yarns comprised of fibers of fineness 1.3 dtex and 39 mm length), and analytical grade reagents were used in this investigation. The knit-fabric samples were immersed in NaOH solutions of different concentrations (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mol/L) for 5 min, then padded once at a nip pressure of 3.5 bar and roller speed of 1 m/min, and batched for 4 h at room temperature. At the end of the batching period, samples were rinsed with running hot and cold water, neutralized with acetic acid buffer (pH 5), rinsed again with running cold water, and line-dried overnight.

Wet Pilling-Propensity

Tests of wet pilling-propensity were conducted with a procedure developed at our laboratory.[15] Specimen-pairs from alkali-treated samples were immersed for 1 h in deionized water, then padded at a nip pressure of 3.0 bar and roller speed of 1 m/min. Immediately after padding, individual pieces from specimen-pairs were mounted on the upper and lower holders of a Martindale Abrasion Tester (James. H. Heal & Co. Ltd, UK), and awarded 50–1000 abrasion cycles under a normal load of 250 g.

The specimens after abrasion cycles were observed in a viewing cabinet under daylight illumination to assign pill-ratings from 1-5 according to ISO 12945-2 (1 – high pilling; 5 – low pilling). A mean of 8 rating values from two observers was recorded.

Water Retention Values (WRV)

Dry specimens of approximately 0.5 g weight, from untreated and alkali-treated samples were immersed in 50 ml deionized water for 24 h. The samples were then removed, centrifuged at 4000 G for 10 min in a laboratory centrifuge, and the wet samples were weighed (Ww). The wet samples were then dried in a laboratory oven at 105 °C for 4 h, and the dried samples were reweighed (Wd). The water retention value (WRV) was calculated with Equation 2.

$$WRV = \frac{Ww - Wd}{Wd} \times 100 \tag{2}$$

where, WRV = water retention value (%); Ww = wet weight of specimen (g); Wd = dry weight of specimen (g).

Fiber Physical Properties

Yarns from the wale direction were separated from untreated and treated fabric samples and untwisted to yield individual fibers for measurements of tenacity, elongation at break, diameter, and wet abrasion resistance.

The wet abrasion resistance was measured on an abrasion tester (DELTA 100, Lenzing Technik Instruments). A pretension of 50 mg was attached to individual fiber specimens, which were then suspended from a frame such that they hung freely across a rotating aluminum bar with a roughened surface. A stream of water was allowed to flow along the surface of the aluminum bar as it rotated at a speed of 100 rpm, and the number of rotations required to break each fiber specimen was recorded. Replicate measurements were conducted with 60 fiber specimens per sample, and the mean value was used as a measure of fiber wet abrasion resistance.

The tenacity/elongation at break of single fibers was measured on a Vibroskop integrated with Vibrodyn (Lenzing Technik Instruments) according to DIN 53816 under a pretension of 70 mg, across a 10 mm gauge length, at 100 mm/min rate of extension. The tests were conducted both in dry and wet states, with 30 replicate measurements per sample type.

Results and Discussion

Fluorescence Microscopy

The principle of fluorescence microscopy tests is illustrated in Figure 1, which shows photomicrographs of cross-sections of untreated CLY fiber specimens immersed in the FWA solution for different periods of time. Semi-qualitative comparisons of porosity/accessibility in fiber structures may be obtained from comparisons of FWA diffusion and distribution within/across fiber cross-sections. A distinct outer skin is observed in CLY fibers, which is most evident in cross-sections of fiber specimens immersed in the FWA solution for 10 min. The depths of FWA diffusion increases with increase in immersion time, but the rate of diffusion appears greater across fiber bulk than through the fiber skin, indicating that the outer skin in lyocell fibers may act as a semi-permeable membrane. The lack of FWA presence at fiber centers, even in specimens immersed for 24 h, is indicative

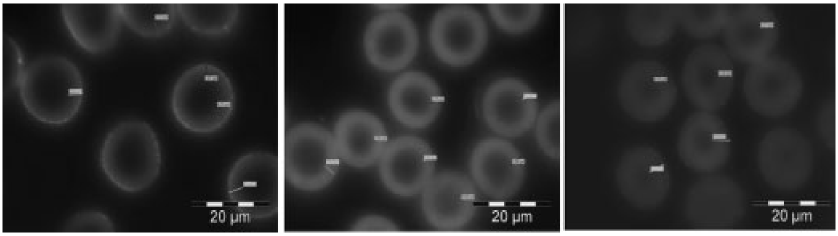

Figure 1.
FWA intrusion into CLY fiber cross-sections after 10 min (left), 4 h (center) and 24 h (right).[3]

of transitions in porosity/accessibility across fiber structures, with porosity/accessibility at the middle being significantly lower than that at the peripheral regions in fibers.

Comparisons Between Regenerated-Cellulosic Fibers

Distinct differences are observed in comparisons of FWA diffusion and distribution across the cross-sections of untreated CLY, CV, and CMD fibers; shown in Figure 2.

In CLY specimens, the FWA diffusion across fiber cross-sections increased with increasing time of specimen immersion in FWA solutions, and the depth of FWA was greater in CLY as compared to CV and CMD fiber types. In CV specimens, the FWA diffusion across fiber cross-sections was limited to shallower depths, but the intensity of fluorescence at the peripheral regions in fibers increased with time of immersion. In CMD specimens, there was a

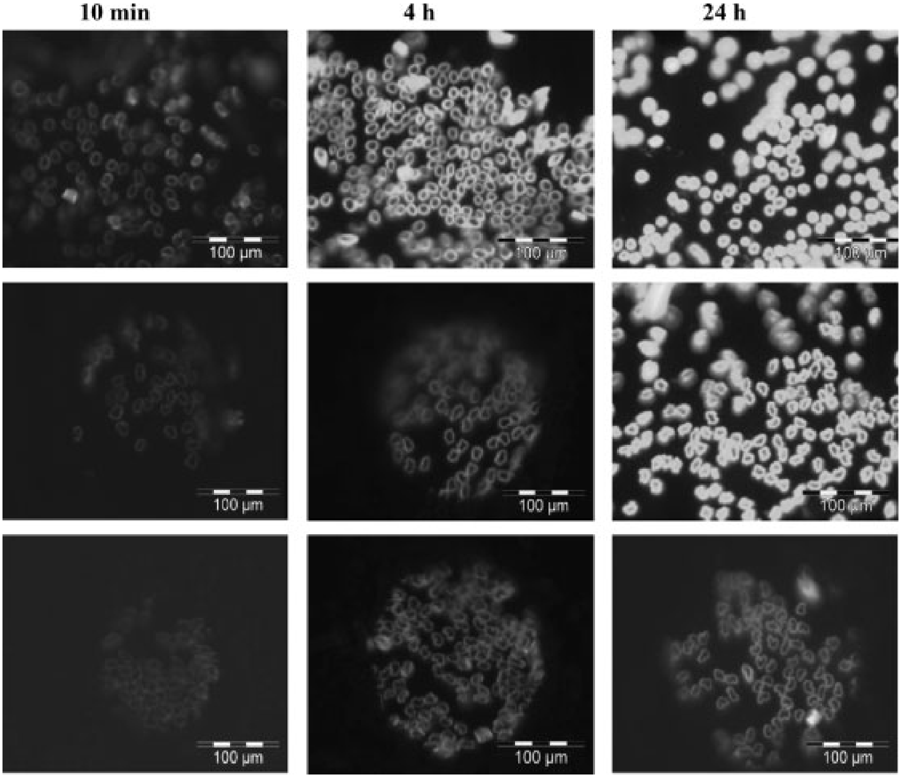

Figure 2.
Diffusion of FWA into CLY (top), CV (middle) and CMD (bottom) fibers immersed in the FWA solution for 10 min, 4 h, and 24 h.[3]

limited diffusion of FWA in fiber cross-sections, but there was also a limited increase in fluorescence intensity with time. There was a lack of FWA presence at fiber centers in all fiber types, even after immersion for 24 h in the FWA solution.

The differences in FWA distribution across fiber cross-sections are indicative of differences in morphology between the three fiber types. CLY fibers exhibit greater porosity/accessibility within the fiber bulk compared to CV and CMD. CV and CMD exhibit similar depths of FWA diffusion within the fiber bulk, but the increased fluorescence at fiber peripheries in CV indicates a greater porosity/accessibility at the peripheral region as compared to CMD. In all fiber types, the porosity/accessibility at the middle appears to be distinctly lower than that at the peripheral regions.

Effect of Alkali Treatments On Fabrics

The depths of FWA penetration within cross-sections of fiber specimens from untreated and alkali-treated (105 g/L and 49 g/L NaOH respectively) CLY and CMD fabrics after 10 min, 4 h, and 24 h immersion in FWA solution are plotted in Figure 3.

In general, a greater depth of FWA penetration was observed in CLY as compared to CMD fiber specimens. There appeared no significant influence of either alkali treatment or immersion time in FWA solution on FWA penetration depths in CMD fiber specimens. However, the fluorescence intensity was higher in the cross-sections of fiber specimens from the alkali-treated as compared to untreated CMD fabric. The FWA penetration depths were greater in fibers from the alkali-treated as compared to untreated CLY fabric, among specimens immersed in the FWA solution for 4 h and 24 h. A higher intensity of fluorescence was also observed in CLY fiber specimens from the alkali-treated as compared to untreated fabric. In all instances, there was a lack of FWA presence at fiber centers.

These results indicate that, under the respective conditions of treatment, there was a greater change in porosity/accessibility to greater depths in fiber specimens from the CLY as compared to CMD fabric. The increased fluorescence in cross-sections of fibers from alkali-treated CMD fabrics indicates increase in porosity/accessibility that is limited to shallower depths in the fiber.

Comparisons Between NaOH and KOH Treatments on CLY Fabrics

The FWA penetration depths in fiber specimens from untreated, NaOH-treated, and KOH-treated CLY fabrics are plotted in Figure 4. Significantly higher FWA penetration depths were observed in specimens from NaOH-treated as compared to KOH-treated and untreated CLY fabrics at all time-periods of fiber immersion in FWA solution. In comparisons of FWA penetration depths between fiber specimens from untreated and KOH-treated fabrics, the values were greater in KOH-treated specimens after 10 min immersion, that in the

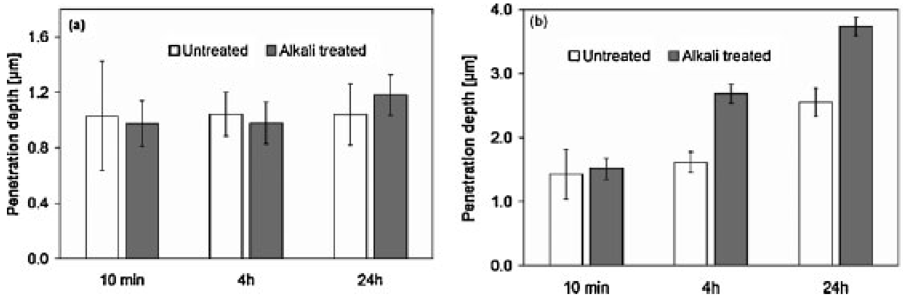

Figure 3.
Depth of FWA diffusion within cross-sections of fiber specimens from untreated and alkali-treated fabrics: (a) CMD (49 g/L NaOH), and (b) CLY (105 g/L NaOH). Please note the different y-axis scales in the two plots.

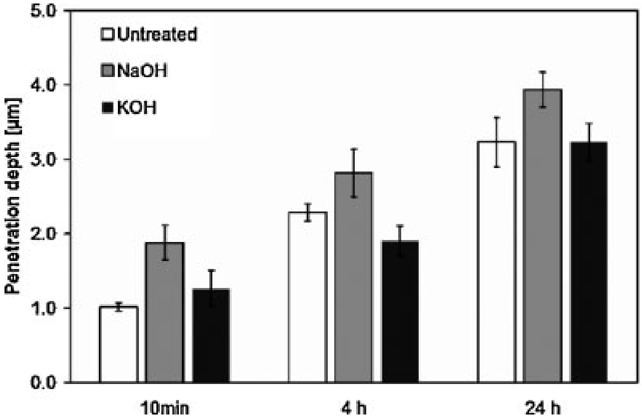

Figure 4.
FWA penetration depths in fiber specimens from untreated, NaOH-treated, and KOH-treated CLY fabrics, immersed for 10 min, 4 h, and 24 h in FWA solution.

untreated were greater after 4 h immersion, and there were no significant differences between the two specimens after immersion for 24 h. There was a lack of FWA presence at centers of all fiber specimens, even after 24 h immersion in the FWA solution. In addition, the fluorescence intensity among fiber cross-sections was higher in the alkali-treated specimens as compared to untreated, with the greatest intensity being observed in KOH-treated specimens.

These results indicate that both alkali treatments increased porosity/accessibility in fiber peripheral regions. The consistently high levels of FWA penetration in NaOH-treated specimens indicates increased porosity/accessibility to greater depths in fiber peripheral regions. On the other hand, the initially high then lower extents of FWA penetration (as compared to untreated) in the KOH-treated specimens as well as the higher fluorescence intensities in these samples indicate greater accessibility/porosity to shallower depths.

Hence, it appears there are differences between the two alkali types (NaOH and KOH) in the changes they bring about in

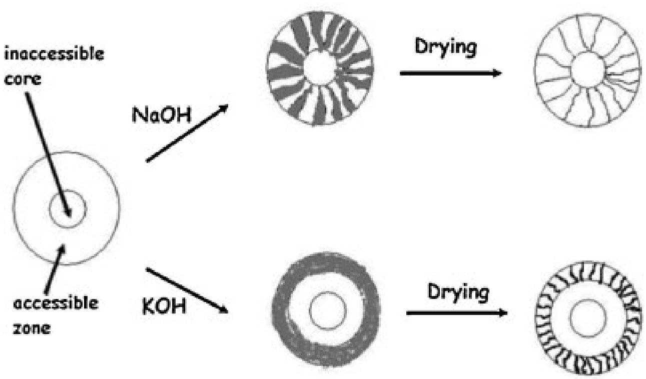

Figure 5.
Schematic illustration of tentative model of change in CLY fiber structure during and after treatments with NaOH and KOH.[16]

CLY fiber structure during/after treatments. It appears there may be a deeper extent of NaOH diffusion through fibers, resulting in changes to fiber porosity/accessibility to greater depths. The extent of KOH diffusion in fibers appears limited to shallower depths, thus limiting the changes in porosity/accessibility to shallower depths in fibers. There is no definitive evidence of changes or lack thereof in porosity/accessibility at fiber centers. A schematic illustration of this tentative model is shown in Figure 5.

Alkali Treatment – Enzymatic Hydrolysis

The reducing sugar content in treatment liquors after enzymatic hydrolysis as functions of fiber type in fabrics and NaOH concentration in alkali treatment is shown in Figure 6. In general, in comparisons of fiber type in fabrics, the degree of substrate hydrolysis decreased in the order: CV > CMD > CLY.

The content of reducing sugars in treatment liquors after enzymatic hydrolysis in pretreated samples, as relative percentages of their respective controls, as function of alkali-solution uptake in fabrics is shown in Figure 7. The uptake of alkali-solutions in fabric increased with increase in alkali concentration of treatment liquor, ranging from *ca*. 100% (w/w) at treatment concentrations of 1 mol/L NaOH to 260% (w/w) at 3.5 mol/L NaOH. Samples pretreated with 1 mol/L NaOH exhibited a lower degree of hydrolysis as compared to control samples, with CV and CMD exhibiting 90% and CLY 71% of the reducing sugar contents observed with their respective controls. Samples pretreated with 2.2 mol/L NaOH exhibited a substantially greater degrees of hydrolysis as compared to control samples and those pretreated with 1 mol/L NaOH. The pretreatment with 3.5 mol/L NaOH further increased the degree of hydrolysis in CV and CLY, but not in CMD.

Enzymatic hydrolysis is believed to occur predominantly at accessible amorphous regions in substrates.[5] The crystallinity among different fiber types decreases in the order CLY > CMD > CV,[17] indicating that the proportion of amorphous regions in the different fiber types decreases in the reverse order. The differences in degree of hydrolysis between the different fiber types may be attributed to differences in their proportions of amorphous regions.

Swelling treatments in aqueous solutions of alkali increase accessibility at amorphous regions in cellulosics and are thus used for 'activation' of substrates.[18] The solubility, and hence swelling, of cellulosics in NaOH solutions passes through a maximum in the concentration range of 2-3 mol/L alkali.[19] The degree of swelling in substrates during pretreatments in this work, estimated from their values of alkali-solution uptake,

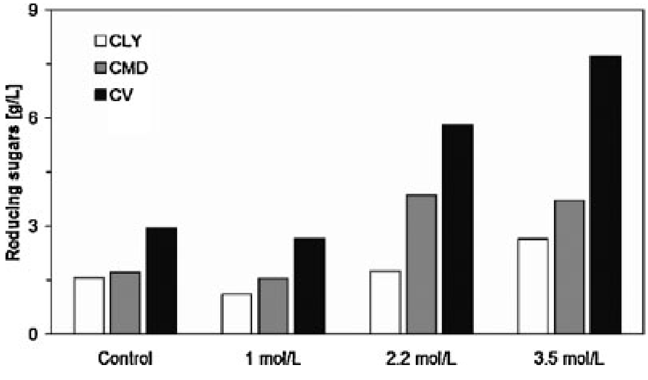

Figure 6.
Produced reducing sugars after one hour enzymatic hydrolysis as function of concentration in alkaline pretreatment fiber type.

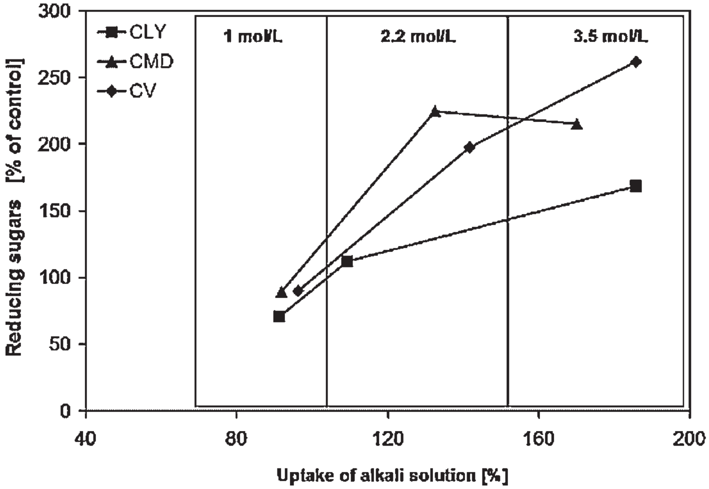

Figure 7.
Coherence between degradation rate and alkali uptake. Rectangles indicate the alkali concentration in pre-treatment solution.

indicate greater substrate swelling during treatments with 2.2 mol/L and 3.5 mol/L NaOH as compared to treatments with 1 mol/L NaOH. The higher extents of hydrolysis in samples pretreated with 2.2 and 3.5 mol/L NaOH may be attributed to increased accessibility due to greater substrate swelling during these treatments. The reasons for the lack of differences in hydrolysis extents between CMD substrates pretreated at 2.2 and 3.5 mol/L NaOH are not clear.

Alkali treatment - crosslinking

The mean values of dimensional change (ΔL), nitrogen content, yarn strength, crease recovery angle (sum of values obtained in warp and fill directions), and mass loss in abrasion tests on untreated and alkali-treated CLY fabrics before and after crosslinking treatment are shown in Table 2.

The alkali treatments resulted in sample shrinkage, with the KOH treatment causing greater shrinkage than the NaOH treatment. There was little difference in wet pickup between samples during crosslinking treatment; hence there were no significant differences in crosslinker-content between samples. Crosslinking increased crease recovery in all samples, but the alkali pretreated-crosslinked samples exhibited lower crease recovery than the crosslinked-control. The crosslinking treatment reduced yarn strength and abrasion resistance, with greater losses observed in samples crosslinked after alkali pretreatment compared to samples crosslinked

Table 2.
Results of sample evaluations.

Treatment	ΔL [%]		N-content	Strength [N]		CRA_{W+F}	Mass loss
	Warp	Fill	[wt%]	Warp	Fill	[°]	[%]
Before crosslinking							
Control	–	–	0.009	5.2	5.4	170	4.41
NaOH	6.6	3.0	–	5.1	5.0	203	4.72
KOH	12.0	4.7	–	5.1	5.2	224	4.46
After crosslinking							
Control	–	–	0.301	4.1	4.9	243	5.51
NaOH	0.8	4.1	0.306	2.5	3.0	222	12.01
KOH	0.8	5.3	0.295	2.9	2.5	231	8.24

without alkali pretreatment. A high concentration of crosslinker was observed on fiber/fabric surfaces in the alkali pretreated samples in contrast to a more uniform distribution of crosslinker through substrate in control samples.[20]

Strength loss in cellulosics due to crosslinking 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 and catalyst in the substrate. A higher surface concentration of crosslinker leads to decreased fabric abrasion resistance[21,22] while a more uniform distribution of crosslinker through fabric structures improves crease recovery but decreases tenacity.[23,24]

In this investigation, the correlation of high surface concentration of crosslinker with low abrasion resistance and crease recovery was observed to hold true. But the correlation of uniform crosslinker distribution with decreased tenacity did not hold true as the yarn strength in crosslinked-control samples was higher than that in samples crosslinked after alkali pretreatments. The samples crosslinked after alkali pretreatments exhibited greater overall reduction in strength as compared to the crosslinked-control. Hence, the strength loss in the alkali-pretreated and crosslinked 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 greater overall reduction of strength in the pretreated and crosslinked samples is suggestive of a greater hydrolysis in these samples as compared to the crosslinked-control.

Model Calculations For Estimations of Reagent Distribution During Pad-dry-cure Operations

In pad-dry-cure crosslinking treatments with N-methylol reactants, catalyst (*e.g.* $MgCl_2$) and crosslinker (*e.g.* DMDHEU) are padded with a certain liquor add-on, dried, and subjected to dry heat (curing) at temperatures of *ca.* 160–180 °C. In such treatments, the distribution of reagents in fabric is a critical aspect that governs the resulting properties of the final product. When the knowledge about substrate accessibility to chemicals presented in Part 1 of this series is considered along with literature data on sorption and exclusion of reagents, it is to be expected that there is redistribution of chemicals within fabrics during the drying step in pad-dry-cure treatments. The relevance of such chemical redistributions within fabrics may be demonstrated with model calculations.

The accessibility of $MgCl_2$ in regenerated cellulosic fibers is estimated at 0.6 (*i.e.* 60% of the total volume of water in substrate); which after NaOH treatments increases to 0.9.[25] This implies that even after NaOH treatment, $MgCl_2$ is excluded from 10% of the total water present in the swollen fiber. The crosslinker DMDHEU accesses only 40% of the total water present in substrate, and this is not altered after alkali treatment of fibers.

When a treatment formulation containing 0.1 mol/L of reagent is padded onto a fabric at a wet pickup of 75% the resulting amount of reagent on the fabric will be 0.075 mol/kg. This value represents the overall content of the chemical in fabric; however, depending on the degree of accessibility, the actual local concentrations of reagent will be higher as molecular filtration limits the distribution of chemicals through substrate.

The concentration of a reagent in the accessible proportion of water within substrates can be calculated according to Equation 3.

$$c_f = \frac{c_p \times p}{(w - n)} \tag{3}$$

with

$$n = WRV \times E \times 100 \tag{4}$$

where, c_f = concentration of reagent in accessible solution within substrate (mol/L); c_p = concentration of reagent in pad-liquor (mol/L); p = pickup of pad-liquor

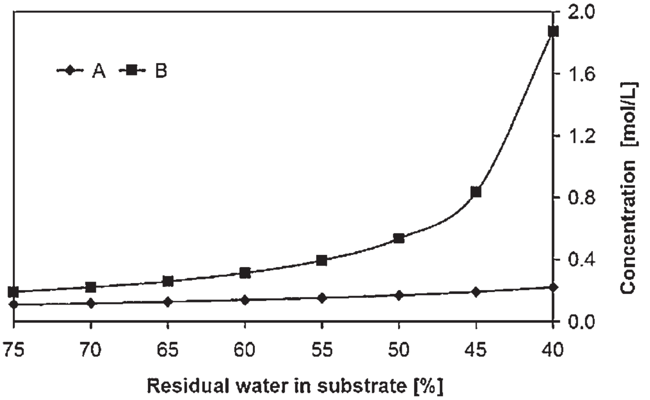

Figure 8.

Change in concentrations of finishing chemicals as function of residual water content in a cellulosic substrate during drying. Initial concentration of both regants 0.1 mol/L (A = $MgCl_2$, B = DMDHEU).

on substrate (%); w = water content in substrate during/after drying (%); n = proportion of water in substrate not accessible to reagent (%); WRV = substrate water retention value (%); E = fraction of WRV not accessible to reagent.

Using Equation 3 and 4 for model calculations to simulate the change in solution concentrations within substrate of the reagents $MgCl_2$ ($E = 0.1$) and DMDHEU ($E = 0.6$) during the drying step in pad-dry-cure crosslinking treatments yields remarkable results, plotted in Figure 8 as a function of residual water content in substrate.

Even though both reagents have been added onto the cellulosic fabric from the same pad-liquor, the volumes of water-in-substrate accessible to the two reagents is restricted to different degrees and the resulting molecular filtration causes a redistribution of chemicals within the substrate structure. As seen in Figure 8, with decrease in water content of substrate due to evaporation during drying there is an increase in concentration of $MgCl_2$ and DMDHEU as there is a decrease in their respective volumes of accessible water. While the increase in concentration of $MgCl_2$ is gradual due to its greater accessibility, that of DMDHEU is substantially more rapid due to its lower accessibility. At a residual water content of 40% in substrate, the DMDHEU concentration within its accessible water volume is nearly 2 mol/L, while that of $MgCl_2$ reaches is close to 0.2 mol/L, and this is in spite of the fact that both reagents were present in the pad-liquor at a concentration of 0.1 mol/L.

Another important fact related to the above mentioned changes in concentrations is reagent redistribution within substrates. Assuming there is sufficient time for diffusion-controlled leveling out of concentration differences due to evaporation of water from substrate during drying, a major proportion of the dissolved $MgCl_2$ will reside in areas within the substrate to which DMDHEU has no access. Hence, during the curing step, the $MgCl_2$ present in regions with no DMDHEU will cause hydrolysis of the substrate leading to strength losses. Thus, any changes of porosity, structure, and/or accessibility in substrates due to alkali pretreatments can be expected to exert a significant influence on the outcomes of later chemical treatments, especially if the treatments involve a pad-dry-cure operation such as in crosslinking treatments.

Alkali Treatment - Pilling

The intensive restructuring of cellulose fibers during alkali treatment can also be

Table 3.
Physico-mechanical properties of fiber specimens from untreated and NaOH-treated knit CLY fabrics.

Property	Untreated	NaOH concentration in treatment (mol/L)					
		0.5	1.0	1.5	2.0	2.5	3.0
Wet Tenacity (cN/tex)	25.6	30.5	30.0	30.7	30.9	30.7	29.0
Dry Tenacity (cN/tex)	41.8	38.7	36.9	36.8	35.8	34.2	31.8
Wet Elongation (%)	14.8	14.4	13.4	13.0	10.8	11.8	12.1
Dry Elongation (%)	11.4	9.0	8.4	9.2	9.2	8.0	6.7
Fiber diameter (μ)	13.2	14.2	14.1	14.3	14.7	14.8	14.0
WRV (g/g)	0.61	0.68	0.71	0.73	0.7	0.72	0.68
Wet abrasion resistance ±95% Confidence interval (counts)	37.3 ± 8.7	66.1 ± 15,0	60.9 ± 10.5	71.5 ± 13.4	69.7 ± 14.1	68.0 ± 12.0	57.1 ± 10.3

observed in changed physical properties, which is reflected in pilling propensities of knit materials. The physico-mechanical properties of fiber specimens obtained from untreated and NaOH-treated knit CLY fabric are shown in Table 3.

The dry tenacity was lower in fiber specimens from alkali-treated samples as compared to the untreated sample, but the reverse was true for the corresponding wet tenacities. There was a decrease in both the dry and wet elongation with NaOH treatment and the losses increased with increase in NaOH concentration in treatment. The rate of decrease was greater in the dry than in wet elongation. Both fiber diameter and water retention values increased with NaOH treatments. The greatest changes were observed in fiber wet abrasion which was greater in specimens from alkali-treated samples as compared to the untreated sample. In general, the wet abrasion increased with increase in NaOH concentration up to 1.5 mol/L beyond which there was little change in fiber wet abrasion with further increase in NaOH concentration.

Fabric pilling propensities increase with increase in fiber fibrillation, which in turn decreases with increase in fiber wet abrasion resistance. The fabric wet pilling propensities, shown in Figure 9, increased with increase in abrasion cycles; and in concordance with increased wet abrasion resistance the pilling propensities decreased with increase in NaOH concentration.

Conclusion

The internal pore structure and accessibility of CLY, CV and CMD fibers were assessed with fluorescence microscopy, by comparing the diffusion and distribution

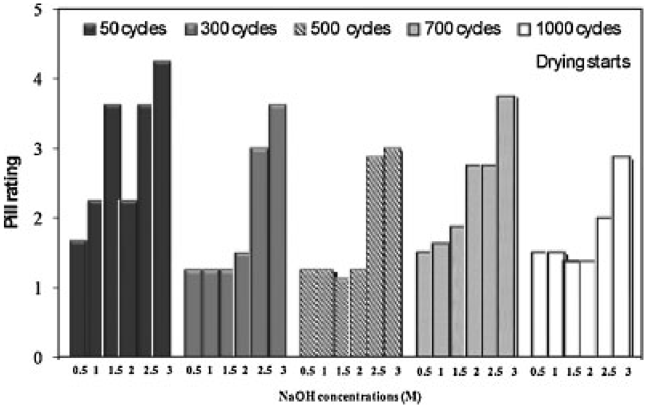

Figure 9.
Effect of sodium hydroxide concentrations on pilling of CLY knit fabrics.

of a FWA across cross-sections of specimens from the three fiber types. The three regenerated-cellulosic fibers studied in this work, CV, CMD and CLY, exhibited similar patterns of porosity/accessibility in that the accessibility/porosity at fiber centers appeared to be significantly lower than at the peripheral regions. CLY fibers appeared to have greater accessibility/porosity through the fiber bulk as compared to CV and CMD, while CV fibers exhibited greater porosity/accessibility at peripheral regions than CMD fibers.

An increase in porosity/accessibility was observed in fiber specimens from CLY and CMD fabrics after treatments with NaOH solutions. Swelling treatments of CLY fabrics with NaOH and KOH solutions brought about increases in their porosity/accessibility, but there were qualitative differences in the changes caused by the two different alkali types. The diffusion of NaOH appeared to reach greater depths within fiber structures thereby resulting in porosity/accessibility changes at greater depths within fibers. In comparison, the diffusion of KOH within fibers appeared limited to shallower depths thereby limiting changes in porosity/accessibility to fiber peripheral regions.

The pretreatment of CLY, CV, and CMD fabrics with NaOH solutions was observed to increase the degree of substrate degradation in subsequent enzymatic hydrolysis steps. The increased degree of degradation is most evident on substrates pretreated with NaOH solutions at concentrations in the region where cellulosics exhibit the maximum degree of swelling and solubility. Enzymatic hydrolysis of cellulosics involves the sorption of high-molecular weight proteins (the enzymes) onto accessible regions in cellulose. Hence, pretreatments of cellulosics with alkali concentrations in the region of their swelling/solubility maxima will significantly enhance accessibility in fiber structures and thereby promote the sorption of enzymes onto the substrate.

The influence of swelling pretreatments with NaOH solutions pretreatment of CLY knit fabrics with NaOH solutions was observed to influence the pilling propensities in treated fabrics due to changes in physico-mechanical properties of the constituent fibers.

The pretreatment of CLY woven fabrics with NaOH and KOH solutions was observed to influence the final performance of these fabrics after subsequent pad-dry-cure crosslinking treatment. The alkali pretreated fabrics exhibit greater strength losses after crosslinking as compared to samples crosslinked without pretreatment. Differences were also observed in crosslinker distribution between samples crosslinked after and without alkali pretreatment, where the pretreated samples exhibited a greater surface concentration of the crosslinker while the non-pretreated samples exhibited a more uniform distribution of crosslinker. It was shown with model calculations that the differences in performance between substrates crosslinked after and without alkali pretreatments could be attributed to enhanced substrate accessibility of catalyst after pretreatments.

This communication highlights different aspects of the changes in properties of cellulosic substrate brought about after swelling treatments with alkali solutions. The wide-ranging changes in substrate properties highlight the need for careful selections of variables during treatment to achieve desired end-properties in treated substrates. More work is required to gain better understanding of the results discussed in this communication, which is ongoing and will be reported in future communications.

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