Macromol. Symp. 2008, 262, 39–49 DOI: 10.1002/masy.200850205

Treatment in Swelling Solutions Modifying Cellulose Fiber Reactivity – Part 1: Accessibility and Sorption

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Summary: Of prime importance in reactions involving insoluble cellulosic fibers is the sorption of reagents, which is governed by their degrees of accessibility in substrates. Swelling treatments of cellulosics in alkali solutions alter substrate accessibility leading to changes in their reactivity. In this paper, the first of a two-part series, we collate and examine the results from various studies involving different techniques to characterize modifications in cellulosic fibers after swelling treatments in alkali solutions. Results from measurements of structure and accessibility in fibers with techniques such as water retention, inverse size exclusion chromatography (ISEC), iodine sorption, fiber diameters, and fiber-splitting propensities indicate that the influence of swelling treatments on fiber structure/accessibility is differs with alkali type. The results show that a non-uniform rather than uniform distribution of reagents within structures is a more accurate representation of reactions involving swollen cellulosic fibers. Hence, the observed changes in cellulose-fiber reactivity are governed by the degrees of fiber swelling, and reagent sorption and accessibility during swelling treatments.

Keywords: cellulose; fibers; structure-property relations; surfaces; swelling

Introduction

Cellulosic substrates are subjected to swelling treatments in alkali solutions in order to improve their luster, dimensional stability, wrinkle resistance, and/or dyeability. The most common method is mercerization with sodium hydroxide,[1] although mercerization with liquid ammonia[2,3] is also practiced to limited extents. The strong swelling propensity of cellulosics in alkali solutions[4] may lead to changes in substrate properties such as pore structure,[5,6] fibrillation tendency,[7] crystallinity,[8] and surface characteristics[9] in fibers; and yarn crimp and stiffness in fabrics.[10] Such changes in substrate properties may also lead to alterations in the accessibility and reactivity of cellulosic substrates to chemicals and reagents in subsequent treatments.

The swelling process and resulting changes in sorption and accessibility of cellulosics may be monitored with a number of methods. The degrees of swelling may be estimated from measurements of fiber diameter, or from the amount of water retained in wet substrates after centrifugation at high speeds, termed the water retention value (WRV). The pore structure in substrates (*viz.* accessible pore volume, pore surface area, pore size) may be estimated with Inverse Size Exclusion Chromatography (ISEC). The pore structure exerts an influence on the mechanical

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properties, reactivity and wear comfort of textiles.[11] The degrees of reagent sorption in substrates (salts, alkali, ions) may be used as measures of substrate accessibility.

In this paper, the first of a two-part series, we present a collation of selected results from extensive studies on cellulosic substrates (fibers and fabrics) to characterize their swelling in alkali solutions and to assess the resulting changes in substrate sorption and accessibility. The swelling of fibers in solutions of inorganic salt,[12,13] alkali, and their mixtures were estimated from measurements of their diameter. The splitting-tendency of fibers in presence of alkali solutions were determined to characterize the swollen structures. The pore structure in alkali treated fibers was determined with ISEC. The influence of alkali treatments on substrate accessibility was studied by determinations of salt and alkali sorption in fibers from salt-alkali mixtures; and, from the propensity of alkali-treated fabrics for Fe(III)-complexation and iodine sorption.

Experimental Part

Materials

All regenerated-cellulosic fibers were kindly provided by Lenzing AG (Austria). The different fiber types were: Lyocell – CLY (TENCEL® Standard), and Viscose – CV (Lenzing Viscose®), of 38 mm length with a titer of 1.3 dtex.

The cotton (Co) substrates were kindly provided by Getzner Textil AG (Austria). The substrates were: yarn (69 Nm/1; scoured and bleached), and plain woven fabric of specific weight 125 g/m^2 with 44 ends and 26 picks per cm (untreated, liquid-ammonia treated, and liquid-ammonia treated and bleached with H_2O_2).

Methods

Swelling in Alkali-salt Solutions

Table 1.
Composition of swelling solutions.

Solution	LiSCN (mol/L)	NaOH (mol/L)	Solution pH
B1	0.65	–	5.9
B3	2.31	–	6.2
B5	3.85	–	6.5
A1	–	1	–
A3	–	3	–
A5	–	5	–
M1	0.65	1	12.6
M3	0.65	3	12.4
M5	0.65	5	12.4

The swelling of Co and CV fibers in solutions of salt (LiSCN), alkali (NaOH), and their mixtures were determined by measurements of their diameter. The Co fibers were obtained from the scoured and bleached yarn. Analytical grade reagents were used to prepare the swelling solutions, as listed in Table 1.

A minimum of 10 fibers were placed on a glass-slide and 1–2 drops of swelling solution were placed on the specimens. After two minutes, a cover-slip was placed on top of specimens, and the slides were placed under a Reichert projection microscope equipped with built-in ruler at 500× magnification for measurements of fiber diameter. Ten measurements were performed per combination of solution and fiber type. The diameter was measured at random places along fiber-lengths for CV; while for Co fibers, due to their non-uniform flat-ribbon-like shape, the diameter was measured at the narrowest point along fiber lengths. For comparison, these measurements were also conducted using immersion oil and water in place of swelling solutions.

Fiber Splitting-propensity and Porosity

The influence of swelling on splitting-propensity and porosity was determined on CLY fibers using alkali solutions of different concentrations formulated with analytical grade reagents in deionized water. The different alkali types used in this investigation were NaOH, KOH, LiOH, and TMAH (tetramethyl ammonium hydroxide).

Fiber Splitting-propensity

The splitting-propensity was determined with a method developed at this laboratory.[14] A single fiber was placed on the

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middle of a glass-slide, and a few drops of alkali solution were placed on the fiber. After two minutes, a cover-slip was placed on the specimen followed by a second glass-slide. This assembly was then placed in an AATCC Crockmeter with the rubbing arm resting on top of the assembly with a downward force of *ca.* 14 N. The rubbing arm was moved to-and-fro along the length of top glass-slide for ten times, then the specimen was removed from the assembly and examined under an optical microscope to determine the degree of splitting.

The degree of splitting was quantified numerically: the number '0' was assigned when there were no splits; the number of '1' was assigned when there were no splits, but striations were observed along the fiber length indicating a limited separation between fiber elements; and numbers '2' and greater quantify the number of separated elements. Three replicate determinations were conducted using fresh fiber specimens at each instance.

Porosity

The principle and methodology of ISEC is described in a previous communication from this laboratory.[15] In essence, the material of interest is packed in a chromatography column to act as the stationary phase and probe molecules (substances of known molecular size that have no affinity for the material) are eluted through the column in a mobile phase. The pore parameters (total pore volume, pore surface area, and pore size) are derived from the elution profiles. The experimental procedure described previously[15] was followed in characterizing the porosity of alkali-treated CLY fibers using as probes a series of polyethylene glycols and dextrans of increasing molecular weight. Two replicate measurements were conducted with specimens from each alkali treatment.

The alkali treatments consisted of immersing CLY fibers in alkali solutions for 2 h at room temperature after which the solution was filtered through a G4 sintered-glass crucible. The fibers were then washed with cold water at 60 °C for 5 min, followed by neutralization with 0.1 mol/L acetate buffer. The fibers were then rinsed thoroughly with water until the wash-water reached a pH of 7.0, after which the fibers were dried in an oven at 60 °C for 1 h.

Water Retention Value (WRV)

Approximately 0.5 g of fiber specimens was immersed in deionized water for a minimum of 2 hours. The specimens were then removed, centrifuged at 4000G for 10 min in a laboratory centrifuge, and the wet samples were weighed (*Ww*). The wet specimens were then dried in a laboratory oven at 105 °C for 4 h, then allowed to cool to room temperature in a P_2O_5 desiccator and reweighed (*Wd*). The water retention value (WRV) was calculated with Equation 1.

$$WRV = \frac{Ww - Wd}{Wd} \tag{1}$$

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

Accessibility Studies - Salt/alkali Sorption In Fibers

The degrees of salt and alkali sorption were determined in CLY and CV fibers immersed in aqueous solutions of salt-alkali mixtures (combinations of NaOH with NaCl, and of KOH with KCl).[16]

The fibers were conditioned in a standard atmosphere of 20 °C ± 2 °C and 65% ± 4% relative humidity for a minimum period of 48 h prior to use. About 0.5 g of conditioned fiber specimens were accurately weighed and immersed in solutions of salt-alkali mixtures in deionized water for 24 h (treatment), then removed and centrifuged at 4000 G for 10 min in a laboratory centrifuge, and immersed in deionized water for a further 24 h (washing). Analytical grade reagents were used to formulate salt-alkali mixtures (MX + MOH) of: NaOH with NaCl, and KOH with KCl. The salt concentration in mixtures was maintained at 0.02 mol/L, while the alkali concentration ranged from 0-8 mol/L. The volumes of treatment liquor

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retained in fibers after centrifugation, and the salt and alkali contents in wash liquor were determined as described below.

Solution Retention Value (SRV)

The volumes of treatment liquor retained in fibers (SRV) were determined from fiber weights after centrifugation (W_W) and their initial dry weights (W_D) derived from their conditioned weights and moisture content with Equations 2 and 3.

$$SRV = \left(\frac{W_W - W_D}{W_D}\right) \times \frac{1}{\rho} \tag{2}$$

$$W_D = (1 - MC) \times W_C \tag{3}$$

where, SRV = solution Retention Value (mL/g); W_W = wet weight of fibers (g); W_D = initial dry weight of fibers (g); ρ = density of treatment solution (g/mL); MC = fractional moisture content of fibers; and W_C = weight of conditioned fiber (g).

The moisture content in fibers was measured by accurately weighing about 0.5 g of conditioned fibers (W_C) and drying them in an oven at 105 °C for 4 h, after which they were placed in P_2O_5 desiccators and allowed to cool to room temperature. The fibers were then reweighed every 2 h until a stable value for the weight of oven-dried fiber (W_S) was obtained. The moisture content was then calculated with Equation 4.

$$MC = \left(\frac{W_C - W_S}{W_C}\right) \tag{4}$$

where, MC = fractional moisture content; W_C = weight of conditioned fiber (g); and W_S = weight of oven-dried fiber (g).

Analysis of Salt/alkali Contents

The amounts of salt and alkali in wash liquors were measured by volumetric titrations; alkali contents by pH titration with 0.1 mol/L HNO_3 on an ORION EA 940 auto-titrator, and salt contents by potentiometric titration with 0.005 mol/L $AgNO_3$ on a METTLER DL 25 auto-titrator.

The degrees of alkali/salt sorption by fibers from treatment liquors were estimated from their SRV with Equation 5.

$$[X]_f = (SRV) \times [X]_s \times 0.001 \tag{5}$$

where, $[X]_f$ = alkali or salt sorbed by fiber (mol/g Fiber); SRV = solution retention value of fiber (mL/g); and $[X]_s$ = alkali or salt content in treatment liquor (mol/L).

The degrees of alkali/salt desorption from fibers in wash liquors were determined from the alkali/salt contents in wash liquors with Equation 6.

$$[Y]_f = \frac{[Y]_s \times V}{W_D} \times 0.001 \tag{6}$$

where, $[Y]_f$ = alkali or salt desorbed by fiber (mol/g Fiber); $[Y]_s$ = alkali or salt content in wash liquor (mol/L); V = volume of wash liquor (mL); and W_D = initial dry weight of fibers (g) obtained from Equation 3.

The alkali/salt sorption values ($[X]_f$) calculated from the volumes of treatment solution retained in fibers (SRV) are what would be expected if the solution composition in fiber were the same as that in bulk liquor and there were no effects of affinity or accessibility on alkali/salt sorption. The degrees of alkali/salt desorption ($[Y]_f$) from fibers in wash liquors are a measure of the true alkali/salt contents in fibers after immersion in treatment liquors. Hence, the ratio of desorption to sorption ($[Y]_f/[X]_f$) may be used to estimate the affinity or accessibility of alkali/salt in fibers.

Accessibility Studies – Fe(III)-Complexation and Iodine Sorption

The influence of de-swelling by drying and swelling with alkalis on accessibility was measured in Co fabrics treated at laboratory- and technical-scales as listed in Table 2.

The technical-scale treatments were performed in a process house (Getzner Textil AG, Austria), and the samples were used as received. The laboratory-scale treatments were performed in this laboratory with analytical grade reagents. The swelling treatment with NaOH (No. 6) was performed by immersing untreated Co fabric samples in 250 mL of 7.5 mol/L

Table 2.
Treatment applied on plain-woven Co fabrics.

No.	Treatment
1.	Untreated control
2.	Untreated sample dried 60s at 130 °C (lab-scale)
3.	Untreated sample dried 60s at 130 °C, followed by 60s at 160 °C (lab-scale)
4.	Liquid NH_3 (technical-scale)
5.	Liquid NH_3 treatment followed by bleaching with H_2O_2 (technical-scale)
6.	NaOH (7.5 mol/L, lab-scale)

NaOH at room temperature for 75 s, then padding at a nip pressure of 3 bar with a roller speed of 1 m/min. The samples were then padded three more times with deionized water under the same conditions. The fabric samples were then rinsed twice in soft water for 15 min each, neutralized in a 1 mL/L solution of 80% acetic acid, and line-dried at room temperature.

Fe(III)-Complexation

The propensity of cellulosic fibers to complex with Fe(III) ions from Fe(III)-sugar acid complexes through ligand-exchange reactions in aqueous alkaline solutions may be used as a measure of substrate accessibility.[17]

About 1.00 g of fabric samples were accurately weighed and immersed in a solution containing 1.8 mmol/L of Fe(III)-D-gluconate (DGL) and 1 mol/L of NaOH, and subjected to a temperature of 60 °C for 24 h in a shaking water bath. The samples were then removed from the treatment solution, centrifuged in a laboratory centrifuge at 4000 G for 10 min, and the iron content in fibers estimated by extraction in hydrochloric acid followed by photometric quantification of Fe(II)-1,10-phenanthroline complex according to DIN 38406.

Analytical grade reagents were used in these tests, and three replicate determinations were conducted with samples from each treatment.

Iodine Sorption Value (ISV)

The iodine sorption value (ISV) is an empirical method of measuring accessibility in cellulosic substrates.[18] In essence, cellulosic specimens are immersed and mixed in a concentrated iodine-potassium iodide solution for 3 min. Then a solution of Na_2SO_4 is added and the mixture stirred for a further 1 h, after which the supernatant is analyzed for iodine content. The quantity of iodine taken up by the cellulose is quantified in terms of milligram I_2 per gram of dry cellulose from the difference in iodine contents between that of the supernatant solution and of a blank solution.

The ISV was determined on the untreated and treated fabric specimens cut finely into small pieces with the method described by Nelson et al.[18] Analytical grade reagents were used in these tests, and three replicate determinations were conducted with samples from each treatment.

Discussion

Swelling in Alkali-salt Solutions

The differences in swelling propensities between CV and Co fibers upon treatment with two different swelling agents: alkali (NaOH) and inorganic salt (LiSCN), and their mixtures, offer insights into the interactions between cellulosic structures and solvents. In Figure 1 are shown the changes in the diameter of CV and Co fibers immersed in the treatment solutions (B1-B5; A1-A5; and M1-M5) as compared to their diameters when immersed in oil and water.

Both fiber types showed greater swelling when immersed in solutions of salt, alkali, and their mixtures as compared to the oil and water; and the extent of swelling in Co fibers was generally lower than that in CV in all solutions. The increase in concentration of salt in B-solutions did not influence the degree of swelling in CV fibers, but Co

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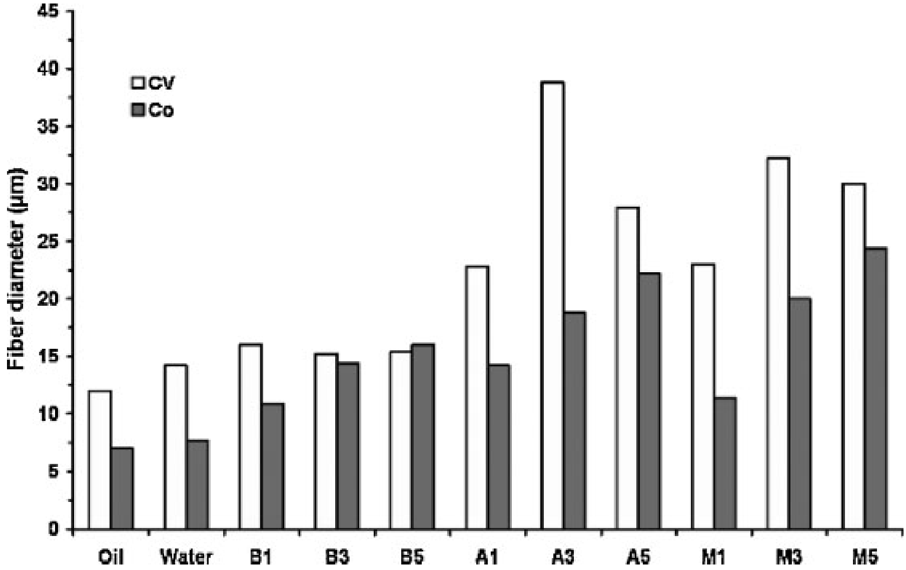

Figure 1.
The diameters of CV and Co fibers in: immersion oil, deionized water, solutions of salt (B1, B3, B5), alkali (A1, A3, A5), and their mixtures (M1, M3, M5). Please refer Table 1 for treatment solution compositions.

fiber swelling increased with increasing salt concentration. The swelling extents in both fiber types increased with increasing alkali concentration both in A- and M-solutions; but while there was a continuous increase in Co fiber diameters, a peak was observed in CV fiber diameters at an alkali concentration of 3 mol/L in solutions (A3 and M3). When comparing fiber diameters in solutions of alkali with those in solutions of salt-alkali mixtures, there appeared no influence of salt in mixtures (M-solutions) on the swelling extents of the two fiber types apart from the reduced swelling observed in CV fibers in salt-alkali mixtures containing 3 mol/L alkali.

There are significant differences in structure between Co and CV fibers,[19] such as: a greater degree of polymerization (DP) and of crystallinity/order in Co as compared to CV; and, differences in crystal morphology between Co (Cellulose I) and CV (Cellulose II), where Cellulose II is characterized by a greater density of intermolecular hydrogen bonds as compared to Cellulose I. These factors, both individually and in combination, exert significant influences on fiber swelling extents.

The greater extents of swelling in CV as compared to Co fibers may be attributed to the lower degree of polymerization and lower extent of crystallinity/order in CV fibers. It is possible that the relative insensitivity of CV fiber swelling compared to Co fiber swelling to salt concentration in B-solutions results from the differences in density of inter-molecular hydrogen bonds between the crystal structures in the two fiber types. The reduced swelling of CV in presence of salt (as observed in the higher swelling of CV in A3- as compared to M3-solutions) may be attributed to lower availability of water for swelling due to greater binding of water molecules in the hydration shells of the salt ions.[13]

Cellulosics exhibit maximum swelling in NaOH solutions at the concentration range of 2-3 mol/L,[19] which was reflected in this work by the peak in CV fiber diameters with 3 mol/L NaOH solutions (A3 and M3). However, similar peaks in swelling were not observed in Co fiber diameters. It is worth pointing out that diameters were measured only at the narrowest points in Co fibers due to their non-uniform shapes, while the uniform cylindrical profiles of CV

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fibers allowed for diameter measurements at random points along fiber lengths. Hence, it is likely that the measured Co fiber diameters are not truly representative of the overall changes in fiber swelling extents. This highlights an inherent limitation of using only fiber diameters as measures of fiber swelling.

Fiber Splitting-Propensity and Porosity

Splitting-Propensities

The splitting-propensity of CLY fibers in alkali solutions as a function of alkali type and concentration is shown in Figure 2. In general, the fiber exhibited high splitting-propensities in alkali solutions up to concentrations of 5 mol/L, but exhibited little or no splitting in solutions with alkali concentrations greater than 5 mol/L. At comparable concentrations, in the range of concentrations below 5 mol/L, fiber splitting-propensities changed with alkali type and in general decreased in the order: TMAH > NaOH ≥ LiOH > KOH.

The high fiber-splitting propensities in alkali solutions of concentrations less than 5 mol/L is attributed to the build-up of localized stresses within fiber structures as a result of non-homogenous fiber swelling due to non-uniform alkali distribution within fibers.[21] It is believed that the strong sorption of alkali in fibers from solutions of concentrations greater than 5 mol/L leads to more uniform distribution of alkali within fibers and therefore to more homogenous fiber swelling.[20] The greater homogeneity in fiber swelling results in reduced stress within fibers, which leads to reductions in fiber splitting-propensities.

The differences in fiber splitting-propensities as a function of alkali type are indicative of differences between the alkali types in uniformity of distribution within fibers. Among the alkali types studied in this work, the low fiber splitting-tendency in KOH solutions appears indicative of a more uniform distribution of the alkali within fibers, while the high fiber splitting-propensities in TMAH solutions appears indicative of a greater non-uniformity in distribution of this alkali within fibers. The differences in uniformity of distribution within fibers among the different alkali types, as reflected in the order of change in fiber splitting-propensities, appears related to the hydrated-ion size among cations in the series of inorganic alkalis and to the bulky nature of cation in the organic alkali.

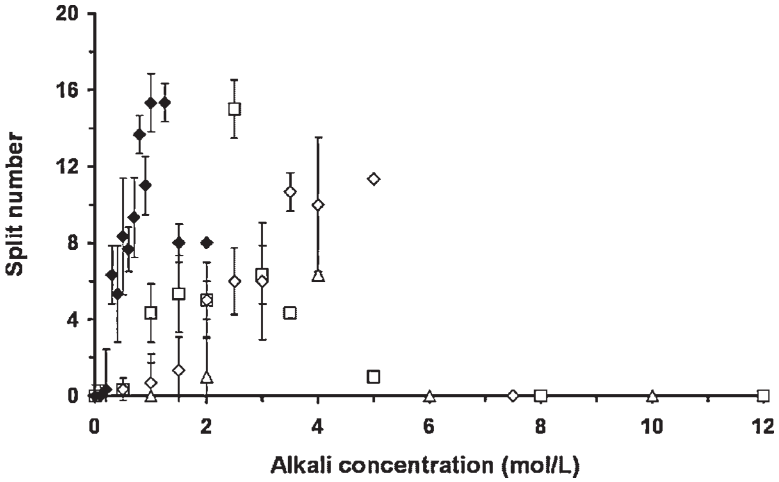

Figure 2.
Splitting propensity of CLY fibers in alkali solutions as function of concentration for alkali types: TMAH (◆); LiOH (◇); NaOH (□); and, KOH (△).[20]

Porosity

The WRV measured on alkali treated CLY fibers is plotted against the corresponding total pore volumes obtained with ISEC for the same fibers in Figure 3. The fractional water retention (g/g) calculated with Equation 1 was converted to units of 'mL/g' by dividing the measured values with the density of water (1 g/mL).

A direct and linear correlation was obtained between the WRV and total pore volumes of CLY fibers treated with the different alkali types over a range of concentrations. However, the measured WRV was greater than the corresponding total pore volumes by approximately 0.1 mL/g for all treated fibers. The WRV represents the volume of water retained in swollen fibers, while the total pore volume is indicative of the volumes accessible to chemical reagents in water-swollen fibers. The difference between the WRV and total pore volumes suggests that in alkali-treated CLY fibers about 10% of the volume in water-swollen fibers remains inaccessible to reagents which may be regarded as the 'non-reactive' fraction in fibers.

Accessibility Studies - Salt/alkali Sorption in Fibers

The desorption/sorption (D/S) ratios of salt and alkali in CLY and CV fibers from solutions of salt-alkali mixtures are shown in Figure 4. The values of reagent D/S ratios reflect their degrees of affinity or accessibility in fibers. A value of 1 indicates that the reagent content is that expected from the volume of treatment solution retained in fibers. Values greater than 1 indicate greater than expected reagent contents, indicative of reagent affinity for fibers. Values less than 1 indicate lower than expected reagent contents, and reflect reagent exclusion from fibers.

The characteristic swelling peak of cellulose in NaOH solutions at the concentration range of 2–3 mol/L NaOH[19] resulted in the gelation of CV fibers leading to high variability in the corresponding D/S ratios. No conclusions could be drawn from the D/S ratios of CV fibers obtained with 2 mol/L NaOH and these values were ignored.

There were no significant differences in D/S ratios of salt or alkali between the two fiber types CLY and CV. At low alkali

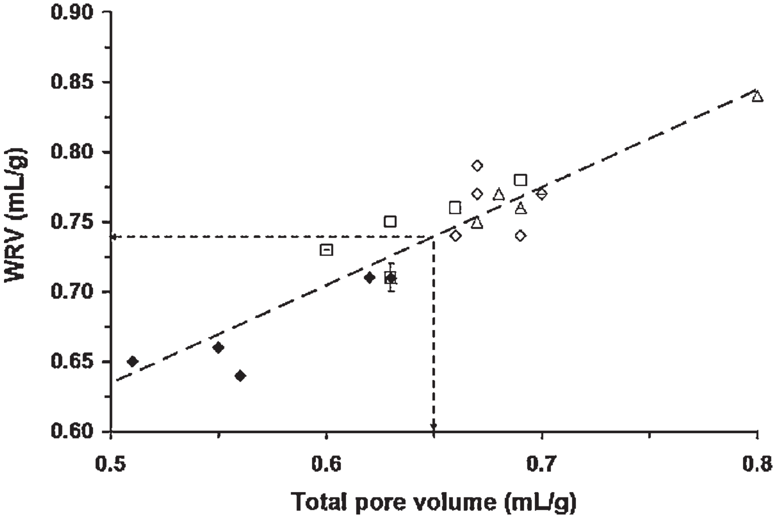

Figure 3.
Correlation between WRV and total pore volumes (from ISEC measurements) obtained for CLY fibers after treatments with: TMAH (△); LiOH (□); NaOH (◇); and KOH (◆).

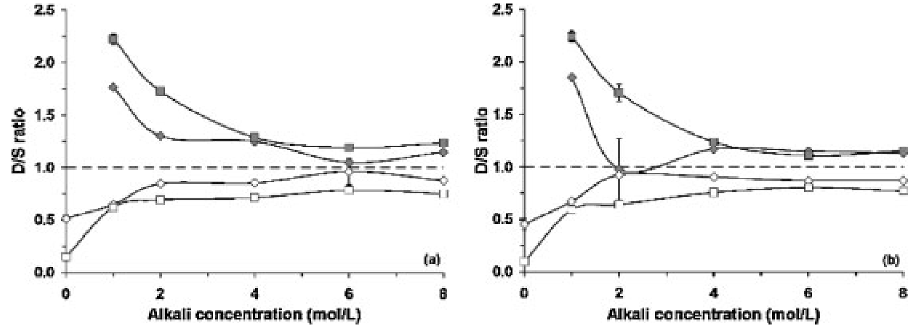

Figure 4.
The desorption/sorption (D/S) ratios of alkalis: NaOH (◆), KOH (■); and salts: NaCl (◇), KCl (□); in (a) CLY and (b) CV fibers from aqueous solutions of the mixtures: NaOH + NaCl and KOH + KCl.

concentrations, alkali D/S ratios were distinctly higher than unity reflecting the strong affinity of alkalis for cellulose. With increasing alkali concentration in solutions, alkali D/S ratios decreased and the values tended towards unity. This trends may result from the fact that with increasing alkali concentration, the composition of the solution in fiber approaches that of bulk solution thereby reducing the differences between the expected and measured values of alkali content in fibers. The D/S ratios of KOH were greater than those of NaOH in solutions with alkali concentrations up to 4 mol/L, beyond which the D/S ratios of NaOH were greater than those of KOH. The differences in D/S ratios reflect differences in alkali affinity to cellulose: KOH exhibits a greater affinity for cellulose up to concentrations of 4.4 mol/L, while that of NaOH is greater at higher concentrations.[13]

The salt D/S ratios were less than unity with all treatment solutions, indicating that there was exclusion of salts from fibers. In general, salt D/S ratios increased with increasing alkali concentration up to 2 mol/L beyond which the values did not change significantly. The D/S ratios of NaCl were greater than those of KCl at all levels of alkali concentration in solution, indicating a greater accessibility of the Na^+ salt than the K^+ salt in fibers. These results indicate that in aqueous treatments of cellulosics involving chemical reactions in presence of alkali, such as in crosslinking with sodium hydroxy dichloro-triazine (NHDT) or in dyeing with reactive dyes, the reactivity may change with cation type due to differences in accessibility and distribution. The reactivity of cellulosic structures is thus directly coupled to the degrees of access and distribution of reagents. However, the magnitude and relevance of such changes in reactivity will vary with the type of reaction and/or reaction conditions.

Accessibility Studies – Fe(III)-complexation and Iodine Sorption

The results from measurements of ISV, Fe(III)-complexation, and WRV on untreated and treated Co fabrics are shown in Table 3.

The drying treatments employed did not result in substantial changes to substrate accessibility as estimated in this work since there were no significant differences in any of the measured parameters between the untreated and heat-treated fabrics.

There were no significant differences in WRV between the untreated and NH_3-treated samples, but the WRV was significantly higher in the NaOH-treated samples. The ISV increased in the order: Untreated $<$ NH_3-treated $\approx$ NH_3-treated and bleached $<$ NaOH-treated samples. The Fe(III)-complexation propensities increased in the order: Untreated $<$ NaOH-treated $\leq$ NH_3-treated $<$ NH_3-treated and bleached samples.

Treatments with NaOH or liquid NH_3 cause decrystallization in cellulosics to

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Table 3.
Results of ISV, Fe(III)-complexation, and WRV measurements on untreated and treated Co fabrics.

No.	Treatment	ISV (mg/g substrate)	Fe(III) (mmol/kg)	WRV (g/g)
1.	Untreated	47.2 ± (5.55)[a]	29.5 ± 0.50	0.40 ± 0.007
2.	Untreated sample dried 60s at 130°C	47.0 ± 2.09	28.5 ± 1.98	0.39 ± 0.001
3.	Untreated sample dried 60s at 130°C, followed by 60s at 160°C	45.6 ± 4.03	26.4 ± 1.12	0.38 ± 0.002
4.	Liquid NH_3	91.3 ± 5.37	41.1 ± 0.82	0.38 ± 0.003
5.	Liquid NH_3 treatment followed by bleaching with H_2O_2	82.7 ± 5.54	46.1 ± 1.41	0.36 ± 0.004
6.	NaOH	128.9 ± 2.75	37.3 ± 1.37	0.51 ± 0.006

[a] 95% confidence intervals.

extents that depend on treatment conditions, but in general, mercerization treatments with NaOH result in comparatively greater reductions of substrate crystallinity and greater improvements of water regain in substrates.[13] These trends were observed in the results from the WRV and ISV measurements. However, despite the greater accessibility in NaOH-treated samples as evinced by the results from ISV measurements, the Fe(III)-complexation propensities were significantly higher in the NH_3-treated and bleached samples. Apart from substrate accessibility, the Fe(III)-complexation propensities in cellulosics is also influenced by the carboxyl content of substrates. Bleaching treatments of cellulosics, being oxidative, tend to increase the carboxyl content of substrates. Hence, the higher Fe(III)-complexation propensity of the NH_3-treated and bleached samples as compared to the NaOH-treated samples likely arise due to a higher carboxyl content in the bleached substrates.

These results highlight the fact that although swelling treatments generally improve the level of accessibility in substrates, such improvements will not always translate into increased levels of sorption for all reagents. The level of changes in accessibility and reactivity of substrates will also depend on sorbate properties.

Conclusion

The degree of swelling in Co and CV fibers were assessed from their diameter in solutions containing LiSCN, NaOH, and their mixtures. The swelling extents increased with increasing concentrations of NaOH in solutions with a peak in swelling extents being observed in CV fibers with 2 mol/L NaOH solutions. The swelling extents of Co fibers appeared to increase with increasing concentration of LiSCN in solutions, but this was not evident for CV fibers. The presence of salt in solutions of salt-alkali mixtures appeared to reduce the peak swelling extent in CV fibers, but did not exert a significant influence on Co fiber swelling. The differences in swelling between the two fiber types may be attributed to differences in their structure.

The splitting-propensities of CLY fibers were examined in solutions of different alkalis over a range of concentrations. Fiber specimens exhibited little or no splitting in alkali solutions of concentrations greater than 5 mol/L, but exhibited significant splitting in alkali solutions of lower concentrations where splitting-propensities changed with alkali type. The propensity of fibers to undergo splitting in alkali solutions is attributed to the inhomogenous distribution of alkali in fibers that results in non-uniform swelling producing localized stresses within fiber structures. The difference in fiber splitting-propensities between solutions of different alkalis is attributed to differences in uniformity of alkali distribution within fibers, which appears related to the alkali cation.

In correlating the measured WRV with total pore volumes obtained with ISEC measurements on CLY fibers treated with

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solutions of different alkalis over a range of concentrations, the WRV were consistently greater than the corresponding total pore volumes by approximately 10%. The WRV represents the total volume of water in water-swollen fibers, while the total pore volume represents the volume of water-swollen fibers accessible to reagents. Hence, it appears that 10% of the volume in alkali-treated water-swollen fibers may be regarded as a 'non-reactive' fraction.

Significant differences were observed in the accessibility of salts in CLY and CV fibers immersed in salt-alkali mixtures. In comparisons between NaCl and KCl, the Na^+ salt exhibited greater accessibility than the K^+ salt. Such differences may play a significant role in chemical reactions involving cellulosic fibers and other chemical reagents, such as crosslinkers, by influencing the overall extent and efficiency of reactions.

Different trends were observed in results when estimating the accessibility of alkali-treated Co fabrics using different reagents. These differences, related to the sorbates used in the different methods, highlight the fact that an increase in accessibility of substrates after alkali-treatments will not always translate into an increased sorption or reactivity towards all reagents and that any changes in accessibility or sorption will also depend on sorbate properties.

Acknowledgements: The authors gratefully acknowledge the Christian-Doppler Research Society and Lenzing AG for the financial and material support. We are grateful to HTL-Dornbirn and Versuchsanstalt-Textil-Dornbirn for the use of their facilities. We also wish to thank Ms. Edith Winder for help with sample preparation, DI. Margit Lenninger for help with ISEC measurements, and MSc. Huong Mai Bui for help with measurements of fiber swelling.

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