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The influence of alkali pretreatments in lyocell resin finishing—Changes in fiber accessibility to crosslinker and catalyst

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ABSTRACT

The aim of the work was to examine reasons behind the detrimental effects of alkali pretreatments on resin finishing of lyocell, a regenerated cellulosic. The accessibility of DMDHEU and $MgCl_2$, which are typically used crosslinker and catalyst in resin finishing treatments of cellulosics, were determined in lyocell fibers treated with 0–8 mol/l alkali (NaOH and KOH). The accessibility of $MgCl_2$ was found to exceed that of DMDHEU in the original, untreated fibers. The differences were further enhanced on alkali treatments; attributed to a reduction of the pore size in fibers after alkali treatments. The changes to pore size, and the resultant rise in differences between catalyst and crosslinker accessibility, appeared related to fiber swelling extents during alkali treatments. The widening of differences between crosslinker and catalyst accessibility in alkali treated lyocell, is believed responsible for the detrimental effect of alkali pretreatments on resin finishing of lyocell fabrics.

Viscose fibers, subjected to the same alkali treatments, did not exhibit a similar widening of differences between crosslinker and catalyst accessibility. Although, as in lyocell, the untreated viscose fibers exhibited greater accessibility to $MgCl_2$ compared to DMDHEU, the alkali treatments did not change the levels of these differences. The lack of changes was attributed to the fact that viscose fibers do not exhibit pore size changes on alkali treatments.

1. Introduction

Swelling treatments with alkali are recommended for fabrics made of lyocell, a regenerated cellulosic fiber manufactured by direct dissolution of wood pulp in *N*-methyl-morpholine-*N*-oxide, to prevent the formation of permanent crease marks during wet processing (Burrow, 1998; Hohberg & Thumm, 1998). However, the swelling of lyocell fibers in alkali solutions can change many of their properties such as pore structure, crystallinity, accessibility and reactivity (Bui et al., 2008; Jaturapiree et al., 2008). Such changes may influence the performance of lyocell fabrics in subsequent treatments.

Cellulosics are commonly imparted 'resin finishing' treatments to improve crease-resistance. Fabrics are dipped through solutions of crosslinker and catalyst, squeezed through a mangle to remove excess liquor, dried, and subjected to dry heat at 150–170 °C for 0.5–3 min (Schindler & Hauser, 2004). *N*-methylol reactants such as *N*,*N*′-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) are typically used as crosslinkers and lewis-acid salts such as $MgCl_2$ are used as catalysts.

Previously, we examined the influence of alkali pretreatment on resin-finishing of lyocell fabrics. Resin finishing after alkali pretreatments caused greater losses of tenacity and abrasion resistance compared to resin finishing without pretreatment, and the losses were greater with NaOH compared to KOH pretreatments (Manian, Abu-Rous, Schuster, & Bechtold, 2006). Staining tests showed evidence that the crosslinker was located predominantly on the surfaces of fibers and/or yarns in alkali pretreated samples. In contrast, there was a more uniform distribution of crosslinker through fiber and yarn cross-sections in samples that were not pretreated. From the available evidence, we surmised that alkali treatments of lyocell fabrics created accessibility gradients within fibers and/or yarns and that the accessibility at fiber/yarn edges was greater than towards their core (Kongdee, Manian, Lenninger, Schlangen, & Bechtold, 2010). As a result, the depth of catalyst penetration exceeded that of crosslinker, and lead to de-mixing between the two within the substrate, when resin finishing formulations were applied on lyocell fabric after an alkali pretreatment step. The de-mixing was believed responsible for the greater strength losses observed in fabrics resin finished after

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alkali pretreatment compared to those resin finished without alkali pretreatment.

Goswami, Blackburn, Taylor, and White (2009) demonstrated that alkali pretreatment of lyocell fabrics can reduce accessibility within the yarns. Yarns in fabrics dyed after pretreatments with alkali at certain concentrations exhibited ‘ring dyeing’, where the color depth (proportional to dye content) was greater at yarn edges than at the core. It was of interest to determine if similar changes of accessibility could be observed also in fibers. To this end, we subjected lyocell fibers to pretreatment with alkali (NaOH and KOH) over a range of concentrations, and evaluated the changes in their accessibility to $MgCl_2$ and DMDHEU. The study also included viscose fibers, another regenerated cellulosic, to determine if the results obtained were typical only of lyocell, or were generally common in regenerated cellulosics.

2. Experimental

2.1. Materials

The regenerated cellulosic fibers used in experiments: lyocell – “CLY” (Standard Tencel®) and viscose – “CV” (Lenzing Viscose®), were supplied by Lenzing AG (Lenzing, Austria); all with linear density 1.3 dtex and 38 mm length. The fibers were used as received after being conditioned in a standard atmosphere of 65 ± 2% RH and 20 ± 2 °C for a minimum of 48 h.

A commercial formulation of the crosslinker DMDHEU (Fixapret® CP conc.) was obtained from BASF AG (Ludwigshafen, Germany) and used as received, while all other reagents were of analytical grade. Deionized (DI) water was used in preparation of solutions.

2.2. Experimental procedure

The experimental procedure is illustrated schematically in Fig. 1. In step 1, about 0.5 g of conditioned fiber specimens were accurately weighed (W_C) and subjected to ‘pretreatment’ by immersion in 50 ml solution of alkali at ambient temperature for 24 h. The alkali in solutions ranged between 1 and 8 mol/l of NaOH or KOH. A control set was also included where fiber specimens were immersed in 50 ml DI water (0 mol/l alkali). The fiber specimens were then placed in filtration tubes (mesh size 10 μm) and centrifuged at 4000 g for 10 min to remove excess solution. The wet mass of specimens after centrifugation (W_1) was recorded.

The specimens were then neutralized in step 2 by immersion overnight in 50 ml solution of 1 mol/l acetate buffer at pH 5 (composed of CH_3COOH and CH_3COONa at concentrations of *ca.* 0.37 and 0.64 mol/l respectively), rinsed in DI water, immersed in DI water overnight, and rinsed again until the pH and conductivity of the rinse water were close to that of fresh DI water (pH 6–7, conductivity <30 μS/cm). The fibers were then centrifuged as above, and their wet mass (W_2) recorded.

Prior to step 3, one half of specimens from step 2 were dried in a laboratory oven at 50 °C for 12 h, while the other half were not dried. Treatments with the intervening drying stage between steps 2 and 3 were labeled ‘*dry*’, while those without were labeled ‘*no-dry*’ treatments.

In step 3, fiber specimens were immersed in 50 ml ‘treatment’ solutions at ambient temperature for 24 h. The solutions contained: (a) 0.01 mol/l $MgCl_2$ (pH 5.08), (b) 4.75 g/l of the commercial DMDHEU formulation (pH 4.25), or (c) mixture of 0.01 mol/l $MgCl_2$ and 4.75 g/l commercial DMDHEU formulation (pH 4.56). The solids content in the commercial formulation of the crosslinker was estimated by the supplier at *ca.* 75% (personal communication), and on this basis, treatment solutions (b) and (c) contained *ca.* 0.02 mol/l DMDHEU. After treatment, the specimens were centrifuged as above and their wet mass (W_3) was recorded.

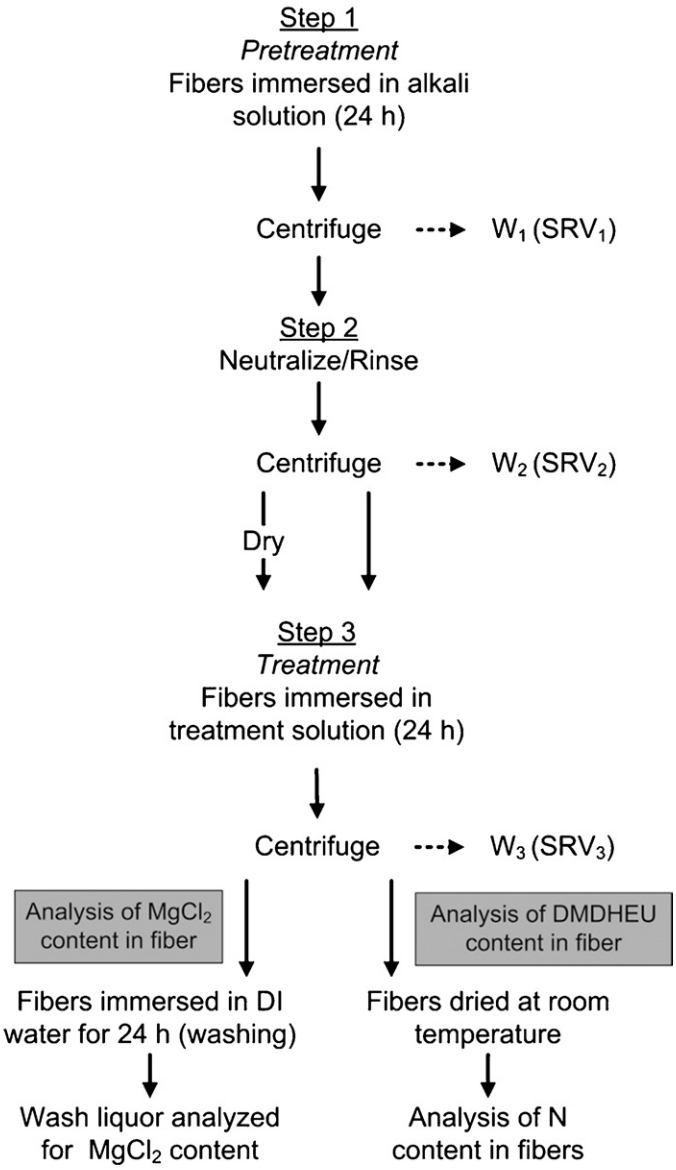

Fig. 1. Schematic illustration of experimental procedure.

After Step 3, the contents of $MgCl_2$ and DMDHEU were determined in fibers. There were no significant differences between $MgCl_2$ contents measured in treatment solutions before and after fiber immersion. Hence, fiber specimens were ‘washed’ by immersion in 50 ml DI water for 24 h and the $MgCl_2$ amounts in wash liquors were quantified by potentiometric titration with $AgNO_3$ as titrant. In preliminary experiments, no residual content of $MgCl_2$ could be detected in ‘washed’ specimens. For determinations of DMDHEU content, the fiber specimens were dried at room temperature, and their nitrogen content quantified by the Dumas method in a Leco FP 528 nitrogen analyzer.

2.3. Moisture content

About 0.5 g of conditioned fibers were accurately weighed (W_C) and placed in a laboratory oven to dry at 105 °C for 4 h, then allowed to cool to ambient temperature in a P_2O_5 desiccator. The fibers were reweighed every 2 h until a stable value for the mass of oven-dried fibers (W_S) was obtained. The moisture content was calculated with Eq. (1).

$$MC = \frac{W_C - W_S}{W_C} \tag{1}$$

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

The fractional moisture contents were determined to be 0.085 and 0.096 in CLY and CV respectively.

2.4. Solution retention value (SRV)

The volume of solution retained in fibers after steps 1, 2 and 3, *i.e.* solution retention values (SRV), were determined with Eqs. (2) and (3).

$$SRV_i = \frac{W_i - W_D}{W_D} \times \frac{1}{\rho_i} \tag{2}$$

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

where SRV_i = solution retention value (ml/g) in experimental step i (i = 1, 2 or 3); W_i = wet mass (g) of specimens after centrifugation in step i; W_D = initial dry mass (g) of specimens; ρ_i = density of solution (g/ml) in step i; MC = fractional moisture content of fiber; and W_C = initial conditioned mass (g) of specimens.

The SRV is generally used as a measure of fiber swelling (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998a), but in this work it was used also in estimations of reagent accessibility as described below.

2.5. 'Fractional uptake' values

Reagent accessibility was estimated with fractional uptake values computed as the ratio of 'true' to 'expected' reagent sorption in fibers. The expected (or theoretical) reagent sorption was estimated from fiber SRV in step 3, on the assumption that solution composition and density in fiber was the same as that in bulk liquor. The true reagent sorption was determined from quantifications of reagent content in fibers.

The expected $MgCl_2$ sorption in fibers was estimated with Eq. (4).

$$[X]_f = SRV_3 \times [X]_s \times 0.001 \tag{4}$$

where $[X]_f$ = expected $MgCl_2$ sorption in fiber (mol/g); SRV_3 = solution retention value (ml/g) of fibers in experimental step 3; and $[X]_s$ = $MgCl_2$ content in treatment liquor (mol/l).

The true $MgCl_2$ sorption in fibers was determined as shown in Eq. (5).

$$[Y]_f = \frac{[Y]_s \times V}{W_D} \times 0.001 \tag{5}$$

where $[Y]_f$ = true $MgCl_2$ content in fiber (mol/g); $[Y]_s$ = $MgCl_2$ content in wash liquor (mol/l); V = volume of wash liquor (ml); and W_D = initial dry mass of specimens (g) as estimated with Eq. (3).

The expected DMDHEU sorption in fibers was estimated with Eq. (6).

$$[P]_f = SRV_3 \times \frac{N_s}{100} \times \rho_3 \times \frac{1}{m_N} \tag{6}$$

where $[P]_f$ = expected DMDHEU sorption by fiber (mol/g); SRV_3 = solution retention value (ml/g) of fibers in experimental step 3; N_s = nitrogen content of treatment solution (wt%); ρ_3 = density of treatment solution (g/ml); m_N = mass of nitrogen per mole of DMDHEU (g N/mol DMDHEU).

The true DMDHEU sorption in fibers was determined as shown in Eq. (7).

$$[Q]_f = \frac{N_f}{100} \times \frac{1}{m_N} \tag{7}$$

where $[Q]_f$ = true DMDHEU content in fiber (mol/g); N_f = nitrogen content of fiber (wt%); m_N = mass of nitrogen per mole of DMDHEU (g N/mol DMDHEU)

Fractional uptake values (*i.e.* $[Y]_f/[X]_f$ or $[Q]_f/[P]_f$) greater than unity indicate preferential sorption (or affinity) of a component, while values less than unity indicate component exclusion from fibers. A fractional uptake of unity indicates that components were neither excluded nor preferentially sorbed, and that the composition of treatment solution in fibers was the same as that in the bulk.

2.6. Mass loss

In a parallel set of experiments, about 0.5 g conditioned fiber specimens were accurately weighed (W_C) and subjected to experimental steps 1 and 2. They were dried at 105 °C for 4 h in a laboratory oven, and allowed to cool to ambient temperature in a P_2O_5 desiccator. The specimens were then reweighed until a stable value for the mass of post-alkali-treatment dried fibers (W_P) was obtained. The mass loss in fibers as a result of alkali pretreatment was then determined with Eq. (8).

$$ML = \frac{W_D - W_P}{W_D} \times 100 \tag{8}$$

where ML = mass loss in fibers (%); W_D = initial dry mass of fiber specimens (g) estimated from their initial conditioned mass with Eq. (3); and W_P = dry mass of fibers (g) after alkali pretreatment and neutralization.

2.7. COOH content

The carboxyl group content in alkali treated specimens was measured by the methylene blue (C.I. Basic Blue 9) dye sorption method (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998b). About 0.25 g conditioned fiber specimens were accurately weighed (W_C) and subjected to experimental steps 1 and 2. The specimens were then dried in ambient atmosphere, immersed in 50 ml solutions of 150 mg/l methylene blue buffered to pH 8.5 with borate buffer, and agitated for 20 h at ambient temperature. The residual methylene blue content in solutions was determined with the aid of calibration plots from photometric measurements of the exhausted dye liquor at 664.5 nm, and the carboxyl group content in specimens determined with Eq. (9).

$$\text{COOH Content} = \frac{(7.5 - A) \times 0.00313}{W_D(1 - (ML/100))} \tag{9}$$

where COOH Content = carboxyl group content (mmol COOH/g fiber), A = residual content of methylene blue in solution (mg) after fiber immersion; W_D = initial dry mass of fiber specimens (g) estimated from their initial conditioned mass with Eq. (3); ML = mass loss (%) in specimens due to pretreatment.

2.8. Effect of mass loss on SRV and fractional uptake values

Fiber specimens exhibited mass loss in pretreatment of 1.6–13% as discussed later. To be strictly accurate, the mass loss should be accounted for when computing SRV. However, SRV magnitudes increased only by small amounts when accounting for mass loss. Moreover, the relative differences between values did not change. In addition, there was no influence of mass loss on fractional uptake

Table 1
Solution retention values (ml/g) in fibers during the course of treatments with NaOH.

NaOH (mol/l)	CLY				CV			
	SRV_1	SRV_2	SRV_3[a]		SRV_1	SRV_2	SRV_3[a]	
			No-dry	Dry			No-dry	Dry
0	0.657 (0.014)	0.657 (0.014)	0.646 (0.022)	0.604 (0.015)	0.865 (0.009)	0.865 (0.009)	0.841 (0.012)	0.827 (0.012)
1	1.189 (0.021)	0.768 (0.022)	0.743 (0.026)	0.616 (0.015)	1.624 (0.045)	0.888 (0.026)	0.868 (0.041)	0.804 (0.010)
2	2.188 (0.143)	0.817 (0.038)	0.820 (0.067)	0.603 (0.022)	–[b]	–	–	–
4	2.648 (0.091)	0.915 (0.029)	0.908 (0.058)	0.560 (0.009)	3.467 (0.051)	1.116 (0.027)	1.069 (0.039)	0.743 (0.013)
6	2.121 (0.051)	0.777 (0.030)	0.755 (0.039)	0.555 (0.033)	2.730 (0.081)	0.996 (0.041)	0.970 (0.073)	0.756 (0.041)
8	2.238 (0.043)	0.713 (0.022)	0.722 (0.060)	0.529 (0.011)	2.524 (0.065)	0.901 (0.035)	0.870 (0.051)	0.730 (0.019)

[a] Average of values from specimens immersed in solutions of $MgCl_2$, DMDHEU, and their mixtures.

[b] Pre-treatments of CV with 2 mol/l NaOH resulted in fiber gelation, leading to highly inconsistent values. Therefore results from this fiber-pretreatment combination are omitted from discussions.

values. Hence, the SRV reported in this work are values neglecting mass loss.

Statistical analyses of data were conducted at a 0.05 level of significance. In tables, the values in parentheses denote 95% confidence intervals, while the error bars in graphs represent ±1 standard deviation.

3. Results and discussion

The levels of fiber swelling at different stages in the course of the experiment may be estimated from the SRV listed in Tables 1 and 2 for NaOH and KOH treatments respectively.

3.1. Fiber swelling in pretreatment

Fiber swelling initially increased and then decreased with rising alkali concentration in pretreatment, with distinct peaks at 2–4 mol/l NaOH and 6 mol/l KOH. The swelling profiles of cellulosic fibers in alkali solutions result from a combination of two contrasting effects of rising alkali concentration: decrease in hydration radius of alkali cations, and increase in alkali penetration into the cellulose structure (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998c). The initial increase in fiber swelling results from the second effect being predominant at low alkali concentrations, and the subsequent decrease in fiber swelling is because the first effect is predominant at higher alkali concentrations.

While some sources cite peak swelling of cellulosics to be at *ca.* 4 mol/l alkali with both NaOH and KOH (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998c), the differences observed in our experiments tally with other reports, such as from Voronova et al. (2004), Zhang, Okubayashi, and Bechtold (2005), and Bredereck, Stefani, Beringer, Schulz, and Commarmot (2003). Voronova et al. (2004) deduced that cellulose swelling peaks occur when all water in solution is bound to the hydrate shells of the alkali cations, which they report as occurring at 3.08 mol/l of NaOH and 6.5 mol/l of KOH.

The SRV_1 in NaOH pretreatments were generally greater than those in KOH pretreatments, except at 6 mol/l alkali where the values were similar. The greater swelling of cellulosics in NaOH compared to KOH solutions is attributed to the greater hydration radius of Na^+ compared to K^+ ions (Kielland, 1937; Voronova et al., 2004).

CV fibers consistently exhibited greater SRV_1 than CLY, which may be attributed to the lower degree of polymerization (DP) and lower crystallinity that characterizes CV in comparison to CLY (Bredereck & Hermanutz, 2005; Smole et al., 2003). The high swelling of CV in 2 mol/l NaOH led to fiber gelation and made it difficult to obtain consistent results in any test. Therefore the results from this particular combination of fiber and pretreatment are omitted from the present discussions.

3.2. Fiber de-swelling upon neutralization/rinse

The SRV_2 were significantly lower than SRV_1, indicating that neutralization and rinsing after alkali pretreatment caused fiber de-swelling. The de-swelling was quantified from percent changes in SRV as shown in equation 10, and the results plotted against fiber swelling in pretreatment (SRV_1), as shown in Fig. 2.

$$\Delta SRV_{1-2} = \frac{SRV_1 - SRV_2}{SRV_1} \times 100 \tag{10}$$

where ΔSRV_{1-2} = fiber de-swelling upon neutralization and rinsing (%), SRV_1 = SRV after alkali pretreatment (ml/g), SRV_2 = SRV after neutralization and rinsing (ml/g).

There was no influence of fiber or alkali type on de-swelling, and all values followed the same profile. The de-swelling initially increased with fiber swelling, from SRV_1 values of 0.7–0.9 ml/g (with water) up to *ca.* 2 ml/g (with alkali), but then reached a plateau in the range of 63–68%, even as SRV_1 values increased to 3.5 ml/g. The plateau region occurred with alkali amounts at or beyond concentrations of peak fiber swelling, while the rising part of the curve corresponds to lower alkali amounts.

Fiber swelling in alkali solutions is accompanied by the cleavage of inter- and intra-molecular hydrogen bonds as cellulosic hydroxyl groups interact preferentially with the alkali ion dipoles

Table 2
Solution retention values (ml/g) in fibers during the course of treatments with KOH.

KOH (mol/l)	CLY				CV			
	SRV_1	SRV_2	SRV_3[a]		SRV_1	SRV_2	SRV_3[a]	
			No-dry	Dry			No-dry	Dry
0	0.657 (0.014)	0.657 (0.014)	0.646 (0.022)	0.604 (0.015)	0.865 (0.009)	0.865 (0.009)	0.841 (0.012)	0.827 (0.012)
1	1.092 (0.040)	0.712 (0.020)	0.704 (0.032)	0.605 (0.030)	1.290 (0.042)	0.799 (0.033)	0.793 (0.052)	0.733 (0.032)
2	1.277 (0.034)	0.650 (0.036)	0.650 (0.051)	0.543 (0.042)	1.431 (0.047)	0.712 (0.035)	0.694 (0.053)	0.622 (0.032)
4	1.472 (0.077)	0.677 (0.046)	0.660 (0.070)	0.535 (0.032)	1.886 (0.113)	0.793 (0.039)	0.788 (0.037)	0.648 (0.034)
6	1.944 (0.192)	0.717 (0.063)	0.711 (0.083)	0.544 (0.055)	2.724 (0.134)	0.888 (0.060)	0.862 (0.094)	0.709 (0.039)
8	1.660 (0.113)	0.681 (0.052)	0.673 (0.070)	0.542 (0.047)	2.197 (0.093)	0.821 (0.058)	0.770 (0.092)	0.699 (0.035)

[a] Average of values from specimens immersed in solutions of $MgCl_2$, DMDHEU, and their mixtures.

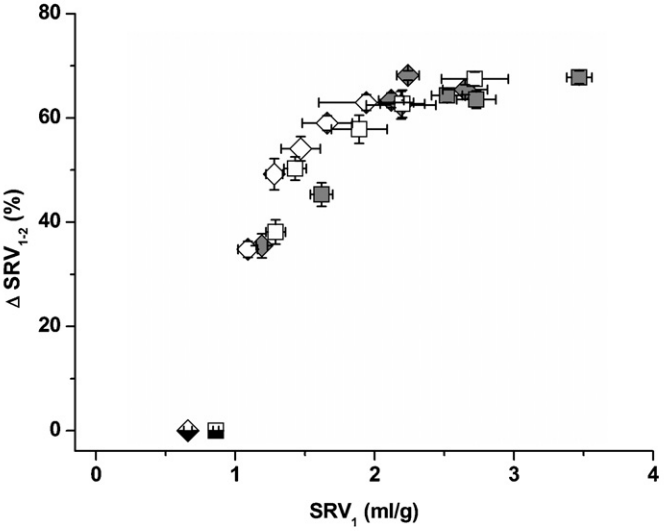

Fig. 2. Fiber de-swelling upon neutralization and rinse: CLY fibers after (⬘) DI water pretreatment, (◆) NaOH pretreatment, (◇) KOH pretreatment; and CV fibers after (⬓) DI water pretreatment, (■) NaOH pretreatment, and (□) KOH pretreatment. Results from CV fibers pre-treated with 2 mol/l NaOH omitted due to fiber gelation which led to inconsistent results.

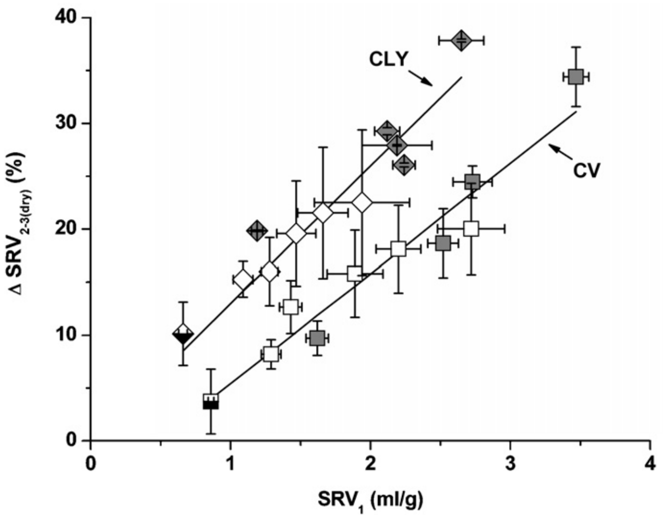

Fig. 3. Fiber hornification as result of drying: CLY fibers after (⬘) DI water pretreatment, (◆) NaOH pretreatment, (◇) KOH pretreatment; and CV fibers after (⬓) DI water pretreatment, (■) NaOH pretreatment, and (□) KOH pretreatment. Results from CV fibers pre-treated with 2 mol/l NaOH omitted due to fiber gelation which led to inconsistent results.

(Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998d). The de-swelling, as calculated with equation 10, is a measure of the extent to which hydrogen bonds reform as swollen structures contract, when alkali is replaced with water. The profile in Fig. 2 suggests that the reformation of hydrogen bonds depends on the degree of prior swelling, and is not influenced by either fiber morphology and supramolecular structure, or the alkali cation. The plateau also suggests a maximum to the degree to which hydrogen bonds are reformed upon de-swelling, which is reached when fibers attain peak swelling levels.

3.3. *Fiber hornification–no-dry vs. dry treatments*

The treatment solution composition ($MgCl_2$, DMDHEU or their mixtures) did not significantly influence the SRV_3 in specimens, so the values shown in Tables 1 and 2 are overall averages. In comparison to SRV_2, there was little or no change in SRV_3 (*no-dry*) but the values of SRV_3 (*dry*) were significantly lower. The lowered fiber swelling as a result of drying may be attributed to 'hornification'—a term used to describe the irreversible reductions in swelling and pore (or void) volume of cellulosics that occurs upon drying. It is attributed variously, to the formation of hydrogen bonds, covalent bonds or lactone bridges between chains or to increase in cellulose crystallinity (Brancato, 2008; Hubbe, Venditti, & Rojas, 2007).

The hornification in fiber specimens subjected to the drying step was quantified from the percent change in SRV as shown in Eq. (11).

$$\Delta SRV_{2-3(dry)} = \frac{SRV_2 - SRV_3(dry)}{SRV_2} \times 100 \qquad (11)$$

where $\Delta SRV_{2-3(dry)}$ = fiber hornification as a result of drying (%), SRV_2 = SRV after neutralization/rinse (ml/g), $SRV_3(dry)$ = SRV (ml/g) after immersion in treatment solutions, in specimens dried after neutralization/rinse.

When hornification was plotted against fiber swelling in pretreatment (SRV_1), as shown in Fig. 3, the data points clustered along quasi-linear relationships that differed with fiber type but were not influenced by alkali type. The hornification in CLY was greater compared to CV at similar levels of initial swelling, and the rate of change in hornification with fiber swelling was greater in CLY as well.

As water evaporates from inside pores, capillary pressures are created at the vapor/liquid interface that pull pore walls together and lead to their collapse (Park, Venditti, Jameel, & Pawlak, 2006; Walsh, 2006). The degree of pore collapse depends on: the magnitude of capillary pressures, which increase with decreasing pore radii; and the resistance of pore walls to collapse pressures, which decreases with increasing pore radii. Pore geometry or shape will also influence resistance to collapse pressures. Spherical vessels exhibit greater collapse resistance compared to cylindrical vessels, and cylinders with circular cross-sections exhibit greater collapse resistance than those with oval cross-sections (Fryer & Harvey, 1997).

The average pore diameters in CV are similar to CLY (Kreze, Stana-Kleinschek, & Ribitsch, 2001; Öztürk, 2008), but there are significant differences of pore geometry between the two fiber types. The pores in CV are more spherical compared to the long, thin, ribbon-like pores in CLY (Crawshaw & Cameron, 2000; Schurz, 1994). Perhaps the differences in hornification between CV and CLY described above are related to their different pore geometries.

3.4. *Mass loss and carboxyl content*

The mass loss and carboxyl contents in CLY and CV fibers are listed against the alkali concentration of pretreatment in Tables 3–6. It may be observed from Fig. 4, that the mass loss increased continuously with fiber swelling in pretreatment, without being influenced by either fiber or alkali type. Exceptions were observed with CLY fibers treated with 2, 6 and 8 mol/l NaOH, where a comparatively wide range in mass loss of 3.1–9.4%, was observed across a narrow span of swelling between 2.12 and 2.24 ml/g.

The carboxyl content in CLY was lower than in CV fibers. For better comparisons of changes in carboxyl content, the values were calculated as percentage of the average of their respective controls, and plotted against the corresponding mass loss, as shown in Fig. 5. The carboxyl content decreased with mass loss in both fiber types. The rate of change with mass loss was similar in all except CLY pretreated with NaOH, where there was a sharp reduction in carboxyl content with mass loss of up to 3% followed by no further changes.

The greater carboxyl content in CV compared to CLY may be attributed to differences in fiber-manufacturing—in particular, to cellulose oxidation during the steps of activation and pre-aging

Table 3
Mass loss, carboxyl contents, and fractional uptake values (dry and no-dry) in CLY fibers treated with NaOH.

NaOH (mol/l)	Mass loss (%)	Carboxyl content (10^{-3} mmol COOH/g fiber)	Fractional uptake[a]			
			$MgCl_2$		Resin	
			No-dry	Dry	No-dry	Dry
0	1.56 (0.18)	13.42 (0.34)	0.61 (0.02)	0.62 (0.02)	0.43 (0.01)	0.44 (0.03)
1	2.80 (0.19)	10.96 (1.26)	0.76 (0.04)	0.69 (0.02)	0.46 (0.02)	0.52 (0.05)
2	9.40 (0.14)	9.62 (1.34)	0.79 (0.03)	0.74 (0.05)	0.54 (0.03)	0.58 (0.02)
4	6.77 (0.48)	9.23 (1.34)	0.87 (0.03)	0.83 (0.04)	0.50 (0.02)	0.53 (0.04)
6	4.38 (0.28)	9.28 (0.54)	0.82 (0.02)	0.74 (0.05)	0.49 (0.03)	0.48 (0.03)
8	3.09 (0.23)	8.82 (0.08)	0.74 (0.03)	0.70 (0.05)	0.48 (0.04)	0.51 (0.06)

[a] Average of values from specimens immersed in solutions of single components and their mixtures.

Table 4
Mass loss, carboxyl contents, and fractional uptake values (dry and no-dry) in CV fibers treated with NaOH.

NaOH (mol/l)	Mass loss (%)	Carboxyl content (10^{-3} mmol COOH/g fiber)	Fractional uptake[a]			
			$MgCl_2$		Resin	
			No-dry	Dry	No-dry	Dry
0	1.61 (0.41)	17.79 (0.54)	0.60 (0.02)	0.59 (0.02)	0.40 (0.01)	0.40 (0.01)
1	4.72 (0.28)	16.43 (1.07)	0.73 (0.02)	0.69 (0.04)	0.43 (0.01)	0.42 (0.02)
2	–[b]	–	–	–	–	–
4	13.18 (0.65)	13.96 (0.37)	0.84 (0.03)	0.81 (0.05)	0.54 (0.01)	0.61 (0.03)
6	8.23 (0.61)	14.54 (0.56)	0.72 (0.02)	0.68 (0.03)	0.48 (0.01)	0.47 (0.02)
8	5.58 (0.80)	17.38 (0.45)	0.66 (0.02)	0.61 (0.05)	0.47 (0.02)	0.43 (0.01)

[a] Average of values from specimens immersed in solutions of single components and their mixtures.

[b] Pre-treatments of CV with 2 mol/l NaOH resulted in fiber gelation, leading to highly inconsistent values. Therefore results from this fiber-pretreatment combination are omitted from discussions.

Table 5
Mass loss, carboxyl contents, and fractional uptake values (dry and no-dry) in CLY treated with KOH.

KOH (mol/l)	Mass loss (%)	Carboxyl content (10^{-3} mmol COOH/g fiber)	Fractional uptake[a]			
			$MgCl_2$		Resin	
			No-dry	Dry	No-dry	Dry
0	1.56 (0.18)	13.42 (0.34)	0.61 (0.02)	0.62 (0.02)	0.43 (0.01)	0.44 (0.03)
1	2.27 (0.45)	13.02 (0.24)	0.66 (0.02)	0.68 (0.04)	0.40 (0.04)	0.50 (0.02)
2	2.52 (0.12)	14.00 (0.32)	0.66 (0.03)	0.65 (0.04)	0.50 (0.05)	0.51 (0.06)
4	3.82 (0.44)	12.98 (0.23)	0.69 (0.05)	0.65 (0.04)	0.47 (0.04)	0.56 (0.05)
6	4.95 (0.17)	11.71 (0.22)	0.73 (0.06)	0.68 (0.05)	0.46 (0.04)	0.59 (0.04)
8	4.24 (0.12)	11.79 (0.81)	0.69 (0.05)	0.68 (0.07)	0.43 (0.03)	0.47 (0.03)

[a] Average of values from specimens immersed in solutions of single components and their mixtures.

that form part of the viscose process but are absent from the lyocell process (Bredereck & Hermanutz, 2005). Alkali treatments of cellulose cause a limited dissolution in the polymer, mainly of short-length chains and hemicelluloses (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998d). To these short-length chains are attributed a large proportion of the carboxyl groups present in cellulose (Ibbett, Phillips & Kaenthong, 2006, 2007). Hence, it follows that the mass loss and related changes in carboxyl content should be proportional to fiber swelling in alkali. These relationships are evident in Figs. 4 and 5. The values from NaOH-pretreated CLY diverged from general trends for reasons that are not clear at the present time.

3.5. *Fractional uptake of $MgCl_2$ and DMDHEU*

The fractional uptake of $MgCl_2$ and DMDHEU are listed against alkali concentration of pretreatment in Tables 3–6, and plotted against the corresponding fiber swelling levels in Fig. 6. At

Table 6
Mass loss, carboxyl contents, and fractional uptake values (dry and no-dry) in CV treated with KOH.

KOH (mol/l)	Mass loss (%)	Carboxyl content (10^{-3} mmol COOH/g fiber)	Fractional uptake[a]			
			$MgCl_2$		Resin	
			No-dry	Dry	No-dry	Dry
0	1.61 (0.41)	17.79 (0.54)	0.60 (0.02)	0.59 (0.02)	0.40 (0.01)	0.40 (0.01)
1	3.21 (0.79)	17.74 (0.31)	0.65 (0.04)	0.64 (0.02)	0.37 (0.01)	0.40 (0.01)
2	3.40 (0.53)	17.56 (0.71)	0.60 (0.05)	0.57 (0.03)	0.44 (0.06)	0.40 (0.02)
4	6.69 (0.72)	16.58 (0.16)	0.68 (0.02)	0.64 (0.07)	0.48 (0.06)	0.46 (0.02)
6	8.43 (0.62)	15.40 (3.07)	0.72 (0.03)	0.70 (0.03)	0.46 (0.04)	0.48 (0.03)
8	5.70 (0.42)	16.26 (0.46)	0.68 (0.06)	0.61 (0.04)	0.41 (0.02)	0.45 (0.03)

[a] Average of values from specimens immersed in solutions of single components and their mixtures.

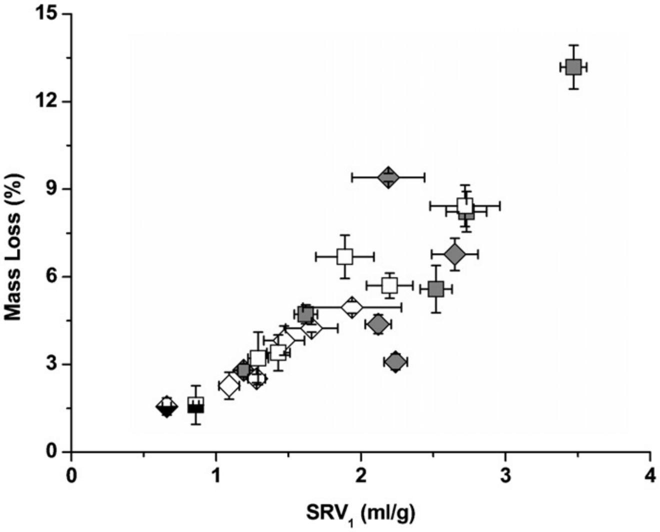

Fig. 4. Mass loss in fibers due to pretreatment: CLY fibers after (⬙) DI water pretreatment, (◆) NaOH pretreatment, (◇) KOH pretreatment; and CV fibers after (⬓) DI water pretreatment, (■) NaOH pretreatment, and (□) KOH pretreated CV. Results from CV fibers pre-treated with 2 mol/l NaOH omitted due to fiber gelation which led to inconsistent results.

high concentrations, the diffusion of DMDHEU from solution into cellulose may be retarded in presence of catalyst, due to self-condensation among crosslinker molecules (Meyer, Wattenwyl, & Zollinger, 1976). Such effects were not evident in this work, as there were no significant differences between fractional uptake values of DMDHEU or $MgCl_2$ measured from solutions of single components or component mixtures. Hence the reported values of fractional uptake are the average of results from the two solutions. There was also no significant difference between values measured from dry or no-dry treatments, except in KOH pretreated CLY where the fractional uptake of DMDHEU in dry treatments was greater than in no-dry treatments. The reasons for these differences are not evident at the present time.

The fractional uptake of both $MgCl_2$ and DMDHEU were lower than unity, but the values for the catalyst was greater than that for the crosslinker. This indicates exclusion of both components from fibers, but that DMDHEU was excluded to a greater extent than $MgCl_2$. The fractional uptake increased for both components with fiber swelling in pretreatment (*i.e.* SRV_1), but at rates that differed with component and fiber type. The DMDHEU fractional uptake was similar in both CV and CLY fibers across the range of swelling measured in this work. The $MgCl_2$ fractional uptake was similar in both fibers at low swelling, but the rate of change with swelling was greater in CLY than in CV. Hence, the fractional uptake of $MgCl_2$ was greater in CLY than in CV at higher fiber swelling. In CV, the rate of change in $MgCl_2$ fractional uptake matched that of DMDHEU, so the differences between the two remained unchanged across the measured range of fiber swelling. But in CLY, the rate of change in $MgCl_2$ fractional uptake was greater than that of DMDHEU, so the differences between the two increased with fiber swelling.

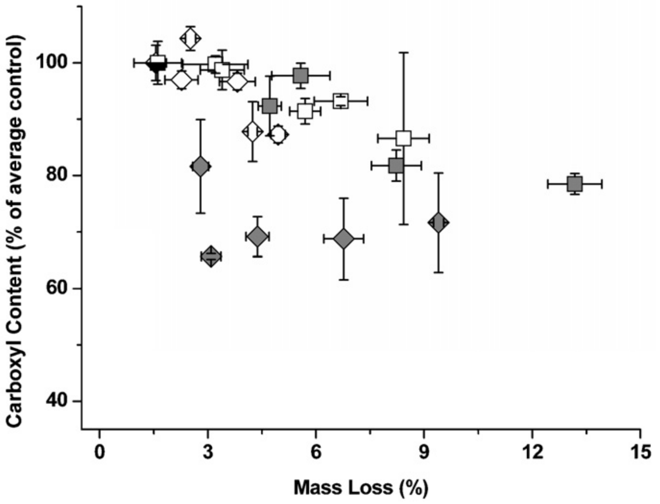

Fig. 5. Change in fiber carboxyl content with mass loss: CLY fibers after (⬙) DI water pretreatment, (◆) NaOH pretreatment, (◇) KOH pretreatment; and CV fibers after (⬓) DI water pretreatment, (■) NaOH pretreatment, and (□) KOH pretreated CV. Results from CV fibers pre-treated with 2 mol/l NaOH omitted due to fiber gelation which led to inconsistent results.

There appeared no influence of alkali type on fractional uptake. However, results from KOH pretreatments were found predominantly at the lower end and those from NaOH pretreatments at the higher end of fiber swelling. As a result, in CLY fibers, the differences in fractional uptake between $MgCl_2$ and DMDHEU were greater with NaOH compared to KOH pretreatments. This was not observed in CV fibers, as the differences in fractional uptake between crosslinker and catalyst were uniform across the swelling range measured in this work.

The uptake of both $MgCl_2$ and DMDHEU by cellulose may be modulated through ion-exchange with dissociated carboxyl groups (Fitz-Binder & Bechtold, 2009; Shet & Yabani, 1982). However, as the $MgCl_2$ fractional uptake in fibers always exceeded that of DMDHEU at a given carboxyl content, and the increase in fractional uptake of both components coincided with decreasing carboxyl content of fibers (*cf.* Figs. 5 and 6), it appears that the fractional uptake values were governed primarily by the pore size in fibers.

The effective size of molecules and ions in aqueous solutions, which defines the minimum pore size in substrates to which they have access, have been estimated at 10 Å for DMDHEU (Bertoniere & King, 1989), and in the range 5.1–5.8 Å and 3.62–4.21 Å for Mg^{2+} and Cl^- respectively (Eliad, Salitra, Soffer, & Aurbach, 2001). Hence, DMDHEU molecules will be excluded from pores of size lower than 10 Å, while the catalyst will be excluded from pores of size lower than *ca.* 5.8 Å. Treatments with NaOH and KOH are found to increase the total pore volume in CV fibers, but to not significantly change the average pore diameter (Öztürk, 2008). In CLY fibers, the total pore volume increases on treatments with NaOH and changes only marginally with KOH, but there is a reduction of the average pore diameter with both alkali types (Manian, Abu-Rous, Lenninger, Roeder, Schuster, & Bechtold, 2008; Öztürk, Abu-Rous, MacNaughtan, Schuster, Mitchell, & Bechtold, 2010; Öztürk et al., 2009).

The difference in fractional uptake between DMDHEU and $MgCl_2$ even in untreated fibers, both CV and CLY, indicates that generally in both fibers, the proportion of pores accessible to the catalyst exceeds that of crosslinker. The increase in fractional uptake with swelling indicates a general rise in accessible pore volume for both components; a reflection of the increase in total pore volume after alkali treatments that is reported for both fibers. The increase with swelling, of the differences between fractional uptake of $MgCl_2$ and DMDHEU in CLY, suggests a reduction in the proportion of pores accessible to DMDHEU as compared to $MgCl_2$. This is corroborated by the reported reduction of average pore diameter in CLY fibers after alkali treatment. The lack of changes with swelling, in the differences between fractional uptake of $MgCl_2$ and DMDHEU in CV, suggests no change in the relative proportions of pores accessible to DMDHEU and $MgCl_2$. This is corroborated by the reported absence of changes in average pore diameter of CV fibers after alkali treatments. It is not certain why alkali treatments cause significant changes to the pore size distribution in lyocell when they do not

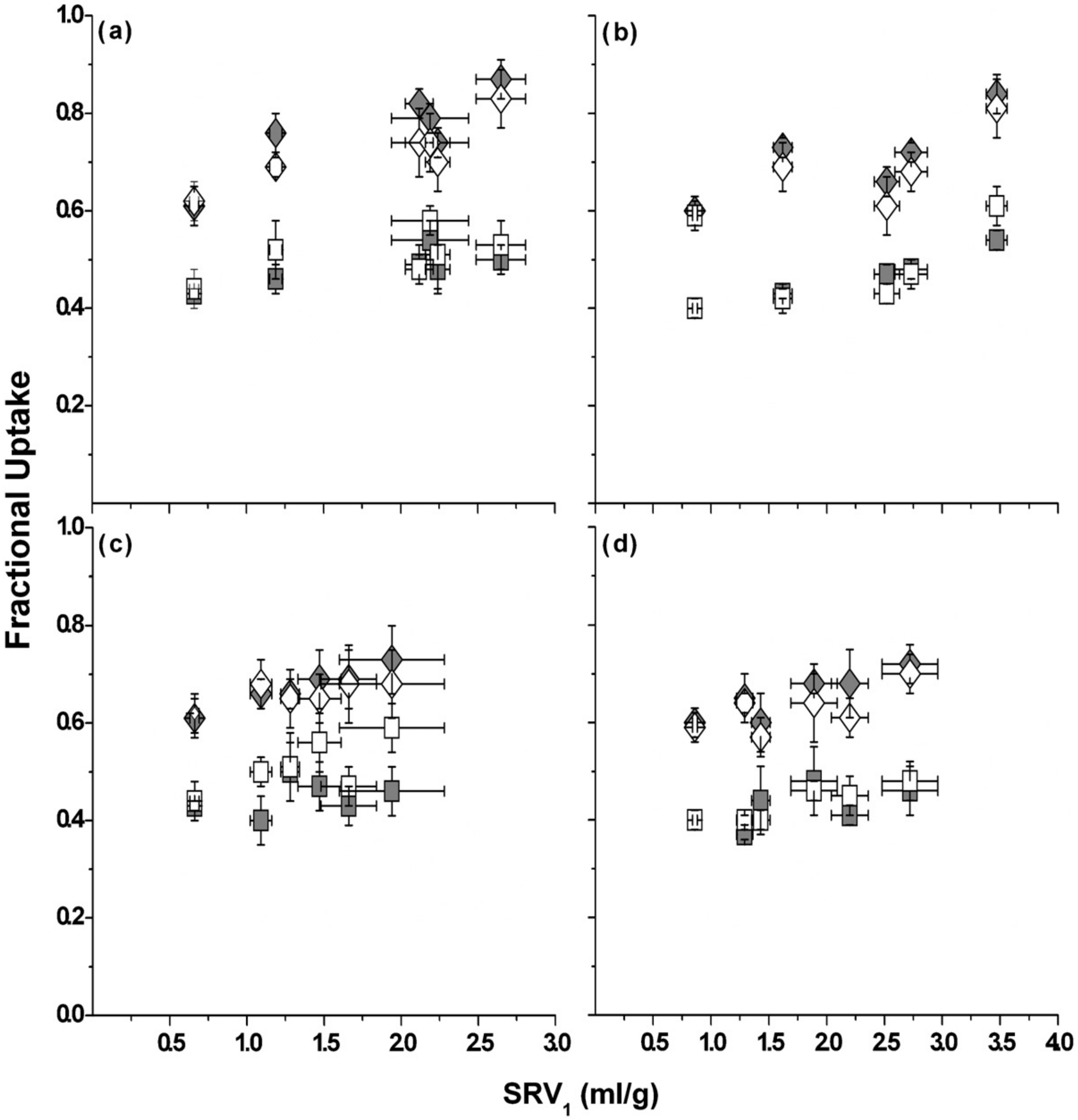

Fig. 6. Fractional uptake values in (a) NaOH pretreated CLY, (b) NaOH pretreated CV (c) KOH pretreated CLY, and (d) KOH pretreated CV, of: (◆) MgCl$_2$ from no-dry treatments, (◊) MgCl$_2$ from dry treatments, (■) DMDHEU from no-dry treatments, and (□) DMDHEU from dry treatments.

appear to exert a similar effect on viscose. However, drawing parallels from the trends in hornification, the differences between the fiber types may stem from their different pore geometries.

From these results, it is difficult to identify the location where pore size reductions occur in CLY fibers. The results of our previous work (Kongdee, Manian, Lenninger, Schlangen, & Bechtold, 2010; Manian, Abu-Rous, Schuster, & Bechtold, 2006; Manian et al., 2008) suggest that the reductions occur most likely towards the center or core of fibers. That the degree of de-mixing between crosslinker and catalyst in CLY was lower after KOH compared to NaOH pretreatments, was previously attributed to smaller changes in accessibility of CLY after KOH pretreatments, and is also supported by the results of this work. However, we had also inferred that the mode of KOH action on CLY perhaps differed from that of NaOH (Manian et al., 2008). Such inference is not supported by the results from this work. The indications are that the accessibility changes relate primarily to the levels of fiber swelling reached in alkali treatment, rather than differences in mode of action between the alkali types.

4. Conclusions

The effect of alkali pretreatments on cellulose reactivity, through their influence on substrate crystallinity, is widely recognized. The results of this work highlight an additional avenue through which alkali pretreatments may affect cellulose reactivity, *viz.* through their influence on cellulose porosity.

Alkali pretreatments may reduce the pore diameter in cellulosics. Such changes in porosity may alter the accessibility of chemical reagents in substrates. On subsequent treatments with solutions of reagent mixtures, there may be a de-mixing between the mixture components within the substrates. The reagent concentrations, at local regions within the substrate, may differ from that in the treatment solution, leading to unexpected results.

Our results suggest that changes in the porosity and accessibility observed in cellulosics after alkali treatments are related strongly to the swelling attained during treatment. The original pore geometry (*i.e.* shape) in fibers also appears to be a determinant factor, as they may dictate the extent to which pore sizes change upon swelling and de-swelling. The effect of alkali types and their concentrations on the accessibility changes in fibers appeared to stem only from their influence on how much the substrate swells. However, the scope of this work was limited only to accessibility studies of DMDHEU and $MgCl_2$. The results of accessibility tests often vary with the probe molecule, and it is possible that other effects of alkali type may be discerned with different probes.

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