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Carbohydrate Polymers 57 (2004) 39–44

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

The influence of wet/dry treatment on pore structure-the correlation of pore parameters, water retention and moisture regain values

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Received 21 August 2003; revised 23 October 2003; accepted 29 March 2004

Abstract

Three types of regenerated cellulosic fibres, normal lyocell (CLY1), crosslinked lyocell (CLY2 and CLY3), and micromodal (μCMD) were treated with five two-stage cycles comprised of wetting in water at 40 °C for 6 h, and drying at 105 °C for 6 h. The resulting changes in fibre pore characteristics were then estimated with Inverse Size Exclusion Chromatography, water retention values (WRV), and moisture regain values (MRV). Reductions in fibre pore volumes after wet/dry treatments were observed to the extents of 20, 13, 18, and 0% in CLY1, CLY2, CLY3 and μCMD, respectively. Corresponding reductions were also observed in water retention and moisture regain after the treatments. WRVs decreased by 21, 28, 24 and 14%, and MRVs decreased by 48, 43, 34 and 40% in CLY1, CLY2, CLY3 and μCMD, respectively.

The changes observed in pore characteristics, WRVs and MRVs are attributed to changes that occur in the microstructures of fibres. It is proposed that structural rearrangements occur in fibres during repetitive wetting and drying that leads to decreased water sorption.

Keywords: Regenerated cellulose fibres; Inverse size exclusion chromatography; Wet/dry treatment; Structural change; Water retention; Moisture regain

1. Introduction

Regenerated cellulosic fibres, such as lyocell, viscose and modal, offer many advantages over synthetic fibres and have acquired a significant share in the man-made textiles market. The fibre manufacturing process imparts fibres with attractive properties such as softness, and high levels of water absorbency. Water absorbency is a key quality in textile fibres as it determines comfort properties in textile materials, due to its influence on textile characteristics such as stiffness, frictional-mechanical properties and electrical properties (Saville, 1999).

Water sorption and fibre swelling occurs mainly in the amorphous regions of fibres. Pore characteristics, such as volume, size, and surface area, significantly influence water capacity, and absorbency, and therefore water retention and moisture regain in textile substrates (Stana-Kleinschek, Kreze, & Ribitsch, 2001). Hence, changes in pore characteristics leads to changes in the moisture sorption characteristics of fibres. Wet and dry heat treatments change pore characteristics, as have been observed in lyocell fibres using small angle X-ray scattering instruments (Crawshaw & Cameron, 2000). Inverse Size Exclusion Chromatography (ISEC), has also been employed to study changes in pore characteristics, such as size and distribution, in textiles and pulp that underwent chemical, enzymatic, and other physical treatments (Bredereck, Gruber, Otterbach, & Schulz, 1996; Berthold & Salmén, 1997a,b; Bertoniere & King, 1989; Häggkvist, Li, & Ödberg, 1998; Li, Ladisch, & Ladisch, 2001; Rowland, Wade, & Bertoniere, 1984).

In ISEC, molecules of known molecular weight and diameter are used as probes, and are eluted in a mobile phase through a column packed with the material of interest, which acts as the stationary phase. Only such materials that do not have any affinity to the material of interest are used as probes, and hence the elution or retention time of a probe

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doi:10.1016/j.carbpol.2004.03.025

depends on the mean path lengths of its molecules through the packed column. Large probes, which do not have access to all pores in the material, have short mean path lengths and consequently short elution times. Conversely, small probes, as they have access to more pores, have longer mean path lengths and hence longer elution times. Elution profiles may be constructed for materials, with a series of probes of increasing molecular size, and used to estimate their pore characteristics.

Wet and dry treatments are used extensively in pre-treatments of regenerated cellulosic fibres, and it was of interest to us to determine the changes that occur in fibre microstructures due to these treatments. The aim of the present investigation was to evaluate changes in pore characteristics of cellulosic fibres after five wet/dry cycles, with ISEC, and to correlate these with changes observed in moisture regain and water retention.

2. Experimental

2.1. Materials

Three types of regenerated cellulosic fibres: normal lyocell, CLY1 (1.3 dtex), crosslinked lyocell, CLY2 (1.3 dtex) and CLY3 (1.4 dtex), and micromodal, μCMD (1.0 dtex), supplied by Lenzing AG (Austria), were used in this investigation. A series of Dextran and poly(ethylene glycol) polymers, with increasing molecular weights were obtained from Polymer Standard Service (Germany), and used as probes. An anionic surfactant, Leophen MC, supplied by BASF (Germany), was used as a de-aerating agent.

2.2. Methods

2.2.1. Wet/dry treatment

The wet dry treatment was as follows: the fibres were immersed in a 2 g/l aqueous solution of the anionic surfactant at 40 °C for 2 h, removed and then immersed in distilled water at 40 °C. The distilled water was replaced with a fresh supply every hour for 4 h. The wetted fibres were dried in an oven at 105 °C for 6 h. This combination of wetting and drying constituted one cycle of wet/dry treatments. A total of five such cycles of wet/dry treatments (W/D) were applied to each set of fibre samples.

2.2.2. Inverse size exclusion chromatography

The fibre samples, after wet/dry treatments, in dry state were packed into stainless steel columns 25 cm long, with an internal diameter of 0.4 cm. The packing densities in columns were maintained in the range of 0.33–0.35 g/cm^3. At the beginning of each experiment, a 2 g/l aqueous solution of the anionic surfactant was flushed through the packed column at a flow rate of 1.0 ml/min for 12 h using a Jasco PU-1580 HPLC pump. Distilled water was then pumped through, at the same flow rate, for a further 12 h. The column was then connected to a Jasco high-performance-liquid-chromatography system. Using a Jasco AS-1555 auto-sampler, 0.1% solutions of the probes were injected into the column. The detector used in the system was a Jasco RI-1531 differential refractometer type detector. The system was equipped with software for data analysis. All ISEC analyses were performed under ambient conditions, at a flow rate of 0.1 ml/min.

Table 1
Molecular weights and diameters of probes used

Poly(ethylene glycol)	Diameter (Å)	Dextran	Diameter (Å)
Ethylene glycol 62	6.0	Dextran 1080	18.0
Diethylene glycol 108	9.6	Dextran 4400	35.0
Triethylene glycol 150	12.9	Dextran 9900	51.3
PEG 194	14.3	Dextran 21400	73.9
PEG 282	16.6	Dextran 124000	169.8
PEG 400	19.1	Dextran 401000	295.9
PEG 580	22.2	Dextran 4500000	929.1
PEG 940	26.9		
PEG 1470	32.2		
PEG 1960	36.1		
PEG 3060	43.1		
PEG 41500	122.3		

The numbers in the name of polymers correspond to their molecular weights. In calculating molecular diameters for dextran, $M = (M_n M_w)^{1/2}$.

Poly(ethylene glycol) and dextran were used as probes as they have no affinity for cellulosic fibres, and form spherical shapes in aqueous solutions. The relationship between molecular weights and molecular diameters for the polymers used in this investigation are defined by Eqs. (1) and (2) (Haller, 1977; Squire, 1981). The molecular weights and diameters of probes used are listed in Table 1.

$$\text{Dextran} \qquad d = 0.53(M)^{0.5} \tag{1}$$

$$\text{Poly(ethylene glycol)} \qquad d = 1.74(M)^{0.4} \tag{2}$$

2.2.3. Water retention values (WRV)

WRV of fibres were determined with the method described in DIN 53814 Prior to tests all fibre samples were conditioned in a standard atmosphere of 65% RH, at 20 °C for a minimum period of 48 h. Each fibre type of 0.7 g was weighed, and then soaked in water at 20 °C for 2 h. The damp fibres were centrifuged, to remove excess water, at 2790 rpm for 20 min and weighed. The fibres were then dried in an oven at 105 °C for 4 h, and reweighed. Water retention was calculated using the following equation

$$\mathrm{WRV} = [(W_M - W_D)/W_D] \tag{3}$$

where

WRV, water retention value (g/g).
W_M, weight of moist fibre (g).
W_D, weight of dried fibre (g).

2.2.4. Moisture regain values (MRV)

MRV of fibres were determined with the method described in DIN 54351. Approximately, 0.4 g of the cellulosic fibres, conditioned in a standard atmosphere of 65% RH at 20 °C for a minimum of 48 h, were weighed, dried in an oven at 105 °C for 4 h, and reweighed. Moisture regain was calculated using the following equation

$$\mathrm{MRV} = [(W_\mathrm{C} - W_\mathrm{D})/W_\mathrm{D}] \tag{4}$$

where,

W_C, weight of conditioned fibre (g).
W_D, weight of dried fibre (g).

3. Results and discussion

The elution profiles for the fibres analysed are shown in Fig. 1. Retention times decrease with increasing probe size till an upper limit in probe size is reached, after which a plateau is observed in the plot; wherein there are no changes in retention time with increasing probe size. The plateau region, which began at a probe size of 51.3 Å, indicates that probe molecules with sizes 51.3 Å and higher were completely excluded from the pores inside fibres, which implies that the exclusion limit in all fibres lies in the proximity of 51.3 Å.

It is observed in Fig. 1 that the retention times for probes in the plateau region are higher for treated fibres than those for untreated fibres. The differences in retention time maybe attributed to differences in swelling between the two sets of fibres. In the experiment, prior to probe elution, the packed columns were flushed with distilled water for 24 h to remove entrapped air, which would result in fibre swelling. Fibre swelling in columns would change the corresponding packing densities, in proportion to swelling propensity in fibres. Repeated cycles of drying and re-wetting lead to decreased wet swelling in cellulosic fibres (Crawshaw & Cameron, 2000). Hence, the packing densities, in columns with untreated fibres, would be higher than those in columns with treated fibres, since untreated fibres have a greater swelling propensity. Higher packing densities lead to lower inter-fibre volumes and hence lower retention times for large probes.

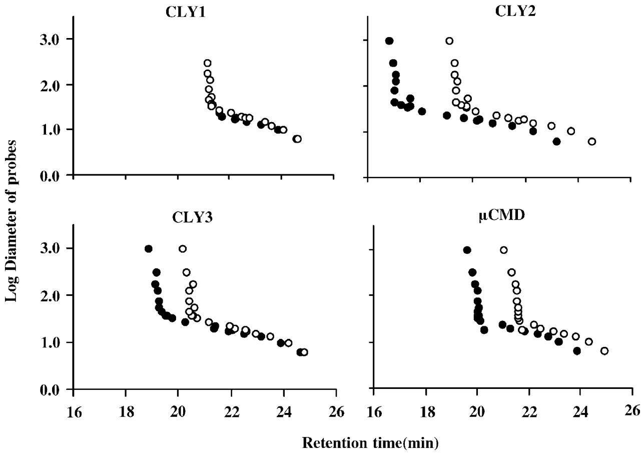

Fig. 1. Retention times for probes in regenerated cellulosic fibres: (●) Untreated (○) Treated. Note: Only eight probe molecules were used for untreated CLY1 fibres.

Accessible pore volumes, V_i, were calculated using Eq. (5):

$$V_i = \frac{(T_\mathrm{e} - T_\mathrm{o})F}{W} \tag{5}$$

In Eq. (5), T_e is retention time for the probe, min; T_o is retention time for a totally excluded component, min; F is the flow rate used, 0.1 ml/min; and W is the weight of the dried material (g). From Fig. 1, Dextran 4500000, the biggest probe molecules used in this investigation, was identified as a totally excluded probe and hence, the retention time obtained for Dextran 4500000 was used as T_o to calculate accessible pore volumes.

The calculations to estimate pore volume, size, and surface area are available in the literature (Bredereck & Blüher, 1992; Bredereck, Meister, & Blüher, 1993; Casassa & Tagami, 1969; Gorbunov, Solovyova, & Pesechnik, 1988), and are reproduced below. The distribution coefficient of probe molecules, between eluent and stationary phase, can be described as shown in Eq. (6)

$$K \approx 1 - n\frac{d}{D_\mathrm{p}} \qquad \text{where } d \ll D_\mathrm{p} \tag{6}$$

where K is the distribution coefficient; (d/D_p) is the ratio of probe radius to pore radius; and n, a constant, is a function of pore configuration. The pores in cellulosic materials are assumed to be of the slit-pore type and hence the value of n is taken to be one (Stone & Scallan, 1968; Nelson & Oliver, 1971; Rowland et al., 1984). If d is probe diameter; O_p, pore surface area (m^2/g); V_p, pore volume (ml/g); and Σ, surface area of pores (m^2/ml); then K is given by Eq. (7):

$$K \approx 1 - \frac{d}{2}\frac{O_\mathrm{p}}{V_\mathrm{p}} \qquad \text{when } \Sigma = \frac{O_\mathrm{p}}{V_\mathrm{p}} \tag{7}$$

Eq. (8) is obtained by multiplying Eq. (7) with V_p :

$$KV_\mathrm{p} = V_\mathrm{p} - \frac{d}{2}O_\mathrm{p} \tag{8}$$

Total pore volume, V_p, is obtained from a plot of V_i against d_i, by extrapolating the plot to $d = 0$, as shown in Eq. (9) (Bredereck & Blüher, 1992; Bredereck et al., 1993; Ladisch, Yang, Velayudhan, & Ladisch, 1992; Li et al., 2001).

$$KV_\mathrm{p} = V_i \approx V_\mathrm{p} - \frac{d}{2}O_\mathrm{p} \tag{9}$$

By introducing the value of K from Eq. (7) into Eq. (6), the following relationship is obtained:

$$1 - \frac{d}{2}\frac{O_\mathrm{p}}{V_\mathrm{p}} = 1 - n\frac{d}{D_\mathrm{p}} \tag{10}$$

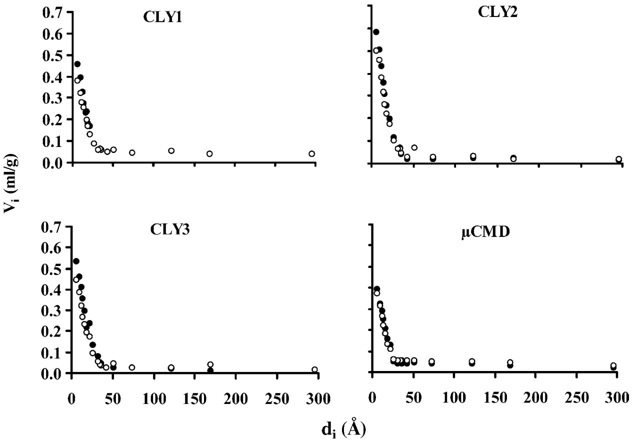

Fig. 2. Accessible pore volumes in regenerated cellulosic fibres. (●) Before treatment and (○) after treatment.

When $n = 1$ (for a slit-pore model), Eq. (10) translates into:

$$\frac{d}{2}\frac{O_\mathrm{p}}{V_\mathrm{p}} = \frac{d}{D_\mathrm{p}} \qquad (11)$$

Hence, mean pore size, $\bar{D}_p$ (ml/m^2), is given by:

$$\bar{D}_p = \frac{2V_\mathrm{p}}{O_\mathrm{p}} \qquad (12)$$

$\bar{D}_p$ maybe estimated in Å units, using Eq. (13):

$$\bar{D}_p(\mathring{A}) = 2 \times 10^4 \frac{V_\mathrm{p}}{O_\mathrm{p}} \qquad (13)$$

The plots of accessible pore volume (V_i) against probe diameter (d_i) in materials, before and after treatment, are shown in Fig. 2.

With increasing probe molecular diameter, an initial decrease was observed in V_i, until a probe molecular diameter of about 50 Å was reached, after which a plateau was observed in the plot. The probe molecular diameter at which the plateau begins is also referred to as the fibre saturation point (Bredereck & Blüher, 1992; Lin, Ladisch, Patterson, & Noller, 1987; Stone & Scallan, 1968), which signifies the upper limit of pore sizes in the substrate. Fibre saturation points vary with fibre type and pre-treatments.

From Eq. (9), it can be seen that in a linear plot of V_i against d_i, the slope of the plot yields the value of the pore surface area (O_p), and the value of the Y-intercept yields the value of V_p, the total pore volume in the substrate (Bredereck & Blüher, 1992; Gruber, 1998; Stone & Scallan, 1968). To obtain linear plots of V_i against d_i, only the initial, linearly decreasing, portions of the plots shown in Fig. 2 were used, and the values derived for total pore volume, pore surface area, and mean pore size for fibres used in this investigation are shown in Table 2.

Distinct differences in pore volumes were observed between fibre types. The lowest values for total pore volume, mean pore size and pore surface area were observed in μCMD fibres. The differences in pore volumes between normal lyocell, CLY1, and micromodal, μCMD, fibres maybe attributed to differences in production processes, especially in spinning, between the fibre types (Kreze & Malej, 2003). All pore parameters in crosslinked lyocell fibres, CLY2 and CLY3, were higher than those in the normal lyocell fibre, CLY1, which is attributed to the presence of the crosslinking agent. The crosslinking reagent, as it is composed of large molecules, may generate large pores in fibre structures.

The reductions observed in total pore volumes upon wet/dry treatments were 20, 13, 18 and 0% for CLY1, CLY2, CLY3 and μCMD, respectively. Overall, in all fibres, wet/dry treatments reduced total pore volume and pore surface area, but did not change mean pore sizes significantly. The mean pore size is a function of the ratio of total pore volume to pore surface area, and since proportionate changes were observed in the two parameters, significant changes in mean pore size were not observed.

The values for water retention and moisture regain of fibres, before and after treatment are listed in Table 3, and represented graphically in Fig. 3.

Lower values of water retention and moisture regain were observed in treated fibres as compared to the corresponding untreated fibres. The WRVs decreased by 21, 28, 24 and 13%, and MRVs decreased by 48, 43, 33 and 40% in CLY1, CLY2, CLY3 and μCMD, respectively. As mentioned previously, there is a correlation between pore volume, and water retention and MRVs in fibres. But in this investigation, an apparent lack of correlation between pore volume and MRVs was observed. From Table 3 and Fig. 3, it is seen that although changes in pore volume and WRVs, as a function of fibre type and wet/dry treatments, are in tandem with each other, MRVs do not change significantly with fibre type. The apparent anomaly with regard to MRVs, also seen in another report (Stana-Kleinschek et al., 2001),

Table 2
Pore parameters in regenerated cellulosic fibres

Fibre	Pore volume (ml/g)		Surface area (m^2/g)		Mean pore size (Å)	
	Before W/D	After W/D	Before W/D	After W/D	Before W/D	After W/D
CLY1	0.59	0.47	430	310	28	30
CLY2	0.71	0.62	462	404	31	31
CLY3	0.70	0.57	490	400	29	28
μCMD	0.49	0.49	332	368	29	26

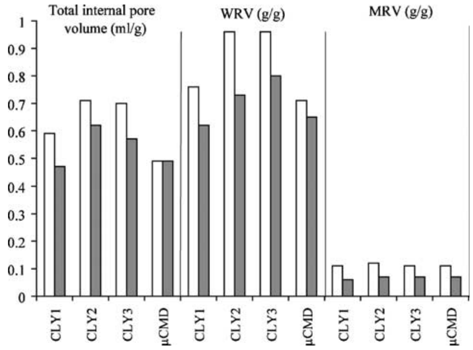

Fig. 3. Pore volumes, water retention and moisture regain in regenerated cellulosic fibres, (▨) before treatment and (☐) after treatment.

may result from the fact that the time period recommended for conditioning, in the test method used for determining moisture regain, maybe insufficient to achieve equilibrium conditions in fibres (Kohler). The lack of equilibrium conditions, in the test for moisture regain, is also probably reflected in the fact that the greatest changes due to wet/dry treatments were observed in MRVs as compared to changes in pore volume and water retention.

Another interesting observation that can be made from Table 3 and Fig. 3 concerns the comparison between WRVs and total pore volumes in fibres. If the density of water in fibres is assumed to be 1.0 g/ml, the values of water retention and total pore volumes can be compared on the same scale; and in such a comparison, the water retention volume is seen to be significantly greater than the corresponding total pore volume. The greater values obtained for water retention is attributed to the fact that water sorption in fibres is not limited only to the pores in fibres, but may also occur on the surface of fibre microstructures; and that the observed water retention is a sum of bound water, pore water and surface water present in fibres (Berthold & Salmén, 1997b). So, though water sorption is a function of the pore characteristics in fibres, it is not sensitive to small differences and hence cannot be used by itself as a reliable measure of pore characteristics in fibres.

In ISEC, on the other hand, there exists a lower limit to estimable pore size, due to limitations in types of materials that can be used as probes (Bredereck & Blüher, 1992). In addition, there has also been some debate on the assumptions made about pore shapes in the material analysed, since they influence the results obtained by this method (Berthold & Salmén, 1997b; Gorbunov et al., 1988). Hence, it maybe stated that a study combining water sorption measurements and ISEC would yield the most reliable information about the pore characteristics in cellulosic fibres.

Table 3
Pore volume, water retention and moisture regain in regenerated cellulosic fibres

Fibre	Pore volume (ml/g)		Water retention (g/g)		Moisture regain (g/g)	
	Before W/D	After W/D	Before W/D	After W/D	Before W/D	After W/D
CLY1	0.59	0.47	0.76	0.62	0.11	0.06
CLY2	0.71	0.62	0.96	0.73	0.12	0.07
CLY3	0.70	0.57	0.96	0.8	0.11	0.07
μCMD	0.49	0.49	0.71	0.65	0.11	0.07

4. Conclusion

The application of ISEC as an instrumental method to study fibre porosity in the swollen state lead to useful insights on changes in pore structures of cellulosic fibres during wet/dry processes. While the mean pore diameter remained almost constant in the fibres, a distinct decrease in accessible pore volume was observed during repeated wetting and drying. For example, after 5 wet/dry cycles, the pore volume in CLY1 decreased from 0.59 to 0.47 ml/g. Due to the crosslinking in CLY2 and CLY3 fibres, the total accessible pore volume was higher, with respective volumes of 0.74 and 0.71 ml/g in untreated fibres, which decreased to 0.62 and 0.57 ml/g after the wet/dry treatments. In contrast, μCMD showed greater stability to wet/dry treatments with regard to changes in pore volume. The changes in fibre pore characteristics, as quantified by ISEC, were also verified by concomitant results from water sorption measurements. Hence, it is believed that wet/dry treatments on cellulosic fibres change their pore characteristics, and that a combination of ISEC and water sorption measurements yields the most reliable information on such changes.

Acknowledgements

Special thanks are extended to the ÖAD (Österreichischer Austauschdienst), Christian-Doppler research society and Lenzing AG for the financial support for this research.

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