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A dye-adsorption and water NMR-relaxation study of the effect of resin cross-linking on the porosity characteristics of lyocell solvent-spun cellulosic fibre

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Abstract

Complementary isotherm and NMR-relaxation techniques have been used to characterise a controlled series of solvent-spun (lyocell) fibre samples, treated with a methylol-urea type resin. The incorporation of cross-links reduces overall fibre swelling, causing a loss of both large and small pores, a reduction of volume accessible to large dye molecules, and a reduction in the free energy of the dye adsorption. Post-causticisation of resin-treated fibre leads to a dramatic improvement in dyeability, consistent with a recovery in total pore capacity and accessible volume. Structural rearrangement may be associated with relaxation of internal stresses at resin cross-links and the reduction of pore aspect ratios. Contraction may be driven by entropy effects, following the development of elastomeric behaviour in the swelled state, creating new pore spaces that are free of cross-link molecules. Causticisation leads to the extraction of low-molecular weight polymer with a higher proportion of negatively charged carboxylate groups, which also favours higher dye uptake.

Keywords: Lyocell; Cellulose fibre; Dye; Isotherm; NMR relaxation; Porosity; Water behaviour; Morphology; Swelling; Caustic treatment; Resin treatment; Dimethyloldihydroxyethyleneurea; Fibrillation; Dye uptake

1. Introduction

The evaluation of a classical dye isotherm method was reported previously [1]. This is based on one of the comparable theoretical models developed for prediction of the behaviour of dye molecules and other chemicals within cellulosic fibres [2–4]. Such classical thermodynamic techniques can in many cases be applied independently of other property measurements, incorporating parameters that have meaning in terms of the material character of the fibre. The described isotherm method utilises data collected at different electrolyte concentrations, which allows unambiguous fitting to a model accounting for both electropotential and ionic activity effects [5]. Information can be obtained that relates directly to the internal pore volume and internal anionic charge of the fibre, and the strength of dye–fibre interactions, which can be interpreted according to known variations in fibre structure. The approach may also be of value in the interpretation of differences in dyeing behaviour between cellulosic fibre materials from different manufacturing routes [6,7].

This current study explores the isotherm method further and considers its application for the characterisation of a controlled series of solvent-spun (lyocell) fibre samples treated with a methylol-urea type resin. This type of treatment is designed to introduce cross-links between the polymer chains of cellulosic fibres and is well established on a commercial basis, as a way of improving the crease-resistant or easy-care properties of fabrics [8]. In addition, such cross-linking methods have been found to improve the wet-state abrasion resistance of lyocell, which reduces problems due to fabric pilling and scuffing during dyeing or laundering [9]. Previous

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studies of cotton have also demonstrated that resination has a highly exaggerated effect on dyeing efficiency, which is greater than predicted from a simple measurement of the reduction in total wet-state pore volume [10,11]. This suggests that the uptake of dye molecules is sensitive to the distribution of void spaces within the fibre and that the effect of cross-link tie molecules is to subdivide the volume into compartments that are below the accessibility limit [12]. The isotherm technique is ideally suited for the study of this phenomenon, as the data will relate directly to the apparent volume available to the large dye molecules within the cross-linked fibre structure. The method also allows values for the free-energy of dye adsorption to be determined, which may be an indicator of the effect of cross-linking on the chemical nature of the accessible surfaces within the fibre [13].

This study also makes use of a complementary technique based on the measurement of water proton NMR relaxation which is sensitive to the wet-state structure of cellulosic fibres and other heterogeneous systems. Here, water is used as a probe molecule, which explores the internal fibre volume, interacting with cellulose surface sites and with neighbouring molecules in the internal solution [14,15]. Assuming rapid spatial and chemical exchange the transverse (T_2) NMR relaxation time of the water protons is related to the averaged dynamic environment of the molecules. This depends on the intrinsic water rotational rate and the opportunity for binding or proton transfer at static functional groups within the sample [16]. The technique will therefore be sensitive to the effect of resin cross-linking and other treatments that might influence the fibre accessibility and internal porosity characteristics.

Conventional resin application is carried out using a dry-bake cure, which introduces cross-links into the fibre structure in the collapsed state [8]. This dry-bake procedure is believed to create a non-uniform distribution of cross-links within the fibre morphology, which concentrate local stresses during mechanical loading, so resulting in reduced tensile strength [17]. The dry abrasion resistance is similarly reduced and the post-yield tensile modulus of the fibres is expected to increase as the structure becomes more embrittled [18]. Despite these deficiencies, resination techniques have been successfully applied to lyocell to increase the lateral continuity of the fibre structure, in order to reduce problems associated with abrasion in the wet state during processing or laundering. However, the accompanying suppression of dye uptake following resination means that the technique cannot be used to provide fibrillation protection prior to dyeing and can only be applied to lyocell fabrics as a conventional after-treatment [19,20]. In contrast, the use of wet-state cross-linking treatments, where tie molecules are inserted across pore spaces in the fully water-swollen condition, leads to no significant reduction or even an enhancement in dyeability [21]. A better understanding of the way in which resination influences dye uptake will be highly beneficial in the design and evaluation of new cross-linking systems for lyocell. A fuller appreciation of the organisation of tie molecules fixed in the dry state will also be of value in the prediction of the behaviour of resinated fibre.

Previous studies have also shown that alkali swelling treatments applied after resination lead to a full recovery, or even an enhancement in dyeability of both natural and man-made cellulosic fibres [22,23]. The majority of resin cross-links are believed to remain intact after causticistation or mercerisation and work on lyocell has shown that fibrillation resistance is retained. Studies on cotton indicate that dry abrasion resistance may also be improved, which reduces one of the concerns traditionally associated with resin treatments [24,25]. There is limited understanding of the changes in pore structure of resin cross-linked cellulosic fibres as the ingress of sodium hydroxide causes a combination of inter-crystalline and intra-crystalline swelling. The current study may therefore provide new insights into the mechanisms involved. Post-causticisation of resinated lyocell fibre may represent a potential new processing route, delivering the benefits of high dyeability together with both wet and dry abrasion resistance.

2. Experimental

2.1. Samples

Lyocell is the generic name for the man-made cellulosic fibre manufactured by the direct dissolution route, using aqueous *N*-methylmorpholine-*N*-oxide solvent. A sample of a commercial 1.4dtex product was supplied by Lenzing AG, which had been collected and dried without application of soft-finish.

Portions of fibre weighing approximately 15 g each were padded with treatment solutions containing 25, 50, 75 and 100 g/l of a commercial dimethyloldihydroxyethyleneurea resin (Fixapret CP: BASF AG), in liquid concentrate form (approximately 50% solid content). Magnesium chloride hexahydrate catalyst added at a ratio by weight of 1 part catalyst to 5 parts resin concentrate. Wet pick-up was approximately 100% of fibre dry weight. Padded samples were dried at 100 °C in an air-circulated laboratory oven and then baked in a second oven at 180 °C for 5 min. These conditions had previously been optimised for small-scale studies. Samples were washed thoroughly in demineralised water prior to characterisation, to ensure removal of all unfixed resin and catalyst. After washing, the wet fibres were prepared directly for measurement, without further drying, to minimise the possibility of any additional structural reorganisation. Where necessary, the corresponding fibre dry weights were determined by gravimetric analysis, either after characterisation or by using a set of parallel samples.

Portions of the bake-cured samples treated with 50 and 100 g/l resin solutions were then immersed in a 10% by weight solution of sodium hydroxide. The fibres were agitated for several minutes to ensure full and uniform swelling and were then washed in demineralised water. Repeat rinsing was carried out until the wash water was at neutral pH. These post-causticised samples were dried at ambient temperature and rewetted as part of the measurement procedures. Representative portions of all treated fibres were dried in preparation for elemental analysis. Nitrogen contents were measured to determine the amount of resin fixed on fibre on a dry weight basis, assuming the resin atomic formula ($C_5N_2O_5H_{10}$).

2.2. Dye isotherm measurements

Direct Blue 71 dye was used for all isotherm studies (MWt = 1030), available commercially at 95% purity, containing 5% sodium carbonate. The electrolyte from the dye was included in the subsequent model calculations as the sodium chloride equivalent. Solutions of the dye were made up at four concentrations, corresponding to 0.4, 0.8, 1.6 and 2.0 wt% on fibre, using either 2 or 4 g/l stock solutions of sodium chloride electrolyte. Portions of 50 ml of the made-up solutions were transferred to 100 ml stainless-steel dyeing tubes, which were then pre-heated to 80 °C on a laboratory-scale dyeing machine (Labomat: Mathis AG). After temperature equilibration, 2 g equivalent dry weight of fibre was added to each tube, at 25:1 liquor ratio, with dyeings continued at 80 °C for 3 h. At the end of this time, the final solutions from each dye-tube were sampled in turn, avoiding any reduction in temperature below the 80 °C set point. Liquor volume corrections were made to account where necessary for the additional water added with the wet fibre samples. Dye concentrations were determined by visible-light spectroscopy, from the initial and final absorbance of the dye solutions, at 589 nm.

Adsorption isotherms were established by determining the equilibrium dye on fibre $[D_f]$ against the remaining dye in the bath $[D_s]$. Calculation of the apparent fibre accessible volume (V), free energy of dyeing ($-\Delta G^\circ$), and apparent fibre anionic content $[C]$ was carried out according to the previously published method [1], following Eqs. (1–4). Here (A_f) and (A_s) are dye ionic activity products, $[Na_s]$ and $[Na_f]$ are fibre and dye-bath sodium concentrations and $[Cl_s]$ is the chloride (or equivalent) dye-bath anion concentration, and (z) is the total permanent anionic charge of the dye.

$$-\Delta G^\circ = RT \ln \left(A_f/A_s\right) \tag{1}$$

$$A_f = \frac{[D_f][Na_f]^z}{V^{z+1}} \tag{2}$$

$$[Na_f] = 0.5\{z[D_f] + \left(z^2[D_f]^2 + 4V^2[Na_s][Cl_s]\right)^{0.5}\} + [C] \tag{3}$$

$$A_s = [D_s][Na_s]^z \tag{4}$$

The parameter (V) was adjusted to achieve a constant ratio of (A_f) vs. (A_s), as required by Eq. (1), applied to the combined data at both concentrations of added sodium chloride. The parameter $[C]$ was then adjusted to achieve a constant value for ($-\Delta G^\circ$) at all solution concentrations.

2.3. Total fibre water retention

Duplicate fibre samples of 1 g equivalent dry weight were immersed in demineralised water for 5 min, and then transferred immediately to centrifuge tubes containing fritted metal sample supports. Tubes were sealed with cling-film and were then centrifuged for 5 min, at 1400G. Excess water drained from the fibres through the supports into the bottom of the tubes. Samples were weighed to four decimal places, avoiding any change in moisture, to give a wet weight (W). The samples were then reweighed after drying to constant mass at 100 °C, to provide a final weight (D). The water retention (WR), representing the saturated internal pore volume of the fibres was calculated according to Eq. (5)

$$\%\mathrm{WR}\ 100 \times (W - D)/D \tag{5}$$

2.4. NMR relaxation measurements

A 23 MHz low-resolution NMR spectrometer (Maran: Resonance Instruments Ltd) was used to measure the transverse (T_2) relaxation time of the water protons in the saturated fibre samples. Fibres were initially immersed in water and centrifuged following the water retention method. The centrifuged samples were then transferred directly to 10 mm diameter glass NMR tubes, which were sealed to avoid water loss. As before, the water contents after centrifuging were considered to represent the saturated pore volume of the fibres.

Samples were equilibrated in the magnet at 35 °C for 5 min before NMR measurement. A standard CPMG pulse sequence was used with an echo-spacing ($2\times\tau$) of 200 μs and a sequence recycle delay of 3 s [26]. Data points were collected at each echo maximum, with sufficient numbers of echos employed to reduce the magnetisation to baseline. Typically, 16 cycles were sufficient for data averaging purposes.

Proton relaxation times (T_2) were established by iterative error minimisation using commercial software (WinFit: Resonance Instruments Ltd) [27]. Depending on the sample, either a single or two exponential model provided an effective fit to the experimental data. The general form of the decay of magnetisation $M(t)$ is described in Eq. (6) for a two exponential decay, where the time (t) is the product of ($2\times\tau$) multiplied by the number of echos. The proportions of each component (M_1 and M_2) and the weighted mean (T) of the component relaxation times ($T_{\exp1}$) and ($T_{\exp2}$) were also determined from the fitting exercise, where $T = T_{\exp1}$ when M_2 = zero.

$$M(t) = M_1 \times e^{\left(-t/T_{\exp1}\right)} + M_2 \times e^{\left(-t/T_{\exp2}\right)} \tag{6}$$

The simple two-site model originally proposed by Carles and Scallan [28] was used as a basis for the relaxation time analysis. The water molecules were assumed to be in fast exchange between surface and non-surface (bulk) environments within the cellulosic pore structure. The measured relaxation time (T) is considered as a global average of the intrinsic surface (T_s) and bulk (T_b) relaxation parameters characteristic of the sample, according to Eq. (7), where W_s and W_b, respectively, are the weight populations of surface and bulk water at any instant, and $(W_s + W_b) = W_{tot}$.

$$\frac{W_{tot}}{T} = \frac{W_b}{T_b} + \frac{W_s}{T_s} \tag{7}$$

If (T_b) is assumed to be much longer than (T_s) then a simplified Eq. (8) results, which allows the surface water population to be calculated from experimentally determined values for (W_{tot} = WR) and (T), assuming a constant value for the surface relaxation (T_s)

$$W_s = \frac{T_s \times W_{tot}}{T} \tag{8}$$

No method has been reported for calculating the surface relaxation parameter directly for porous solids, although this may be explored in the future [29]. Suitable values have been selected in previous studies of cellulose either on the basis of extrapolation to low water content [28] by measurement of samples where only bound water is believed to exist [30], or where non-bound water has been frozen and is not detected as a liquid species [31]. A value of 1.5 ms was chosen for this work, based on a recent study of wood cell water [30].

3. Results

The dye isotherm plots for the set of resinated fibres at each electrolyte concentration are shown in Figs. 1 and 2, with the curves for the resinated then post-causticised fibres at both electrolyte concentrations shown in Fig. 3 (note change of x-scale). As stated, the fitting procedure for the isotherm data followed the method outlined in previously published work [1]. Four isotherm data points at each of the two electrolyte concentrations were found to be sufficient for accurate error minimisation, as shown in Fig. 4. Firstly, log(A_f) was plotted against log(A_s), with the accessible volume (V) adjusted for best linear fit. After establishing (V), the fibre anionic content [C] was adjusted to achieve a constant value of free energy ($-\Delta G°$) for all values plotted against log(A_s). The results for all fibres are summarised in Table 1.

Both the water retention (WR) and the model accessible volume (V) of the fibres are reduced at increasing resin fixation level, as indicated in Table 1. This is consistent with the observation from the isotherm plots in Figs. 1 and 2 that resination causes a reduction of dye at all bath concentrations. The isotherm plots also show that the additional post-causticiation of the 50 g/l and 100 g/l treated fibres leads to a dramatic recovery in dyeability, which corresponds with an increase in water retention and accessible volume. For the resin-only fibre series, the relationship between (WR) and (V) is linear, as shown in Fig. 5, although this is not the case with the inclusion of the data from the post-causticised samples. A progressive decrease in free-energy of dye adsorption is also noted at increasing resin fixation, shown in Fig. 6, which apparently becomes more significant at the higher resin levels. This graph also shows that the model accessible volume falls most rapidly at lowest levels of resin fixation, suggesting that the first resin cross-links to be incorporated have the most significant influence on the fibre pore texture. The model fitted values for fibre carboxyl content [C] also fall with increasing resin fixation, which may be expected if a greater proportion of the internal fibre volume becomes inaccessible to the dye [1]. The modelled carboxyl contents of the two post-causticised fibres are

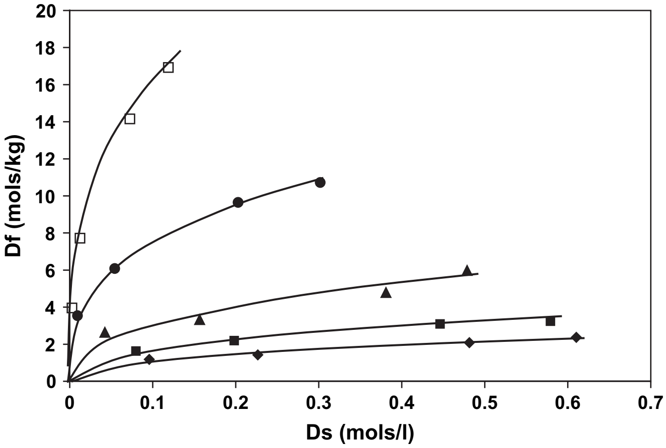

Fig. 2. Isotherm curves for Direct Blue 71 applied to resin-treated lyocell fibre, with 4 g/l of added NaCl electrolyte. Applied resin concentrations of 0 g/l (□), 25 g/l (●), 50 g/l (▲), 75 g/l (■), and 100 g/l (◆).

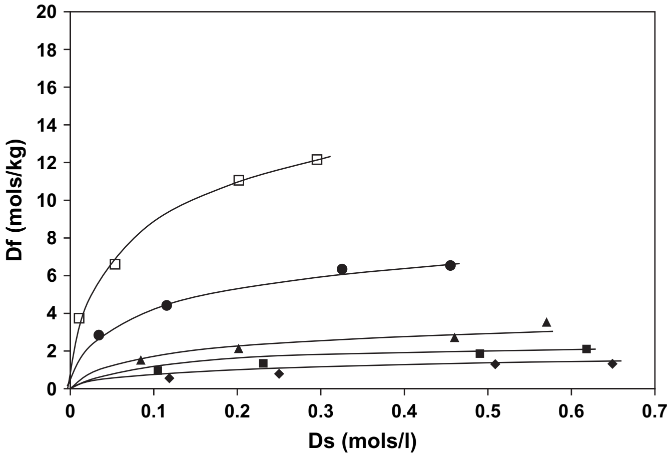

Fig. 1. Isotherm curves for Direct Blue 71 applied to resin-treated lyocell fibre, with 2 g/l of added NaCl electrolyte. Applied resin concentrations of 0 g/l (□), 25 g/l (●), 50 g/l (▲), 75 g/l (■), and 100 g/l (◆).

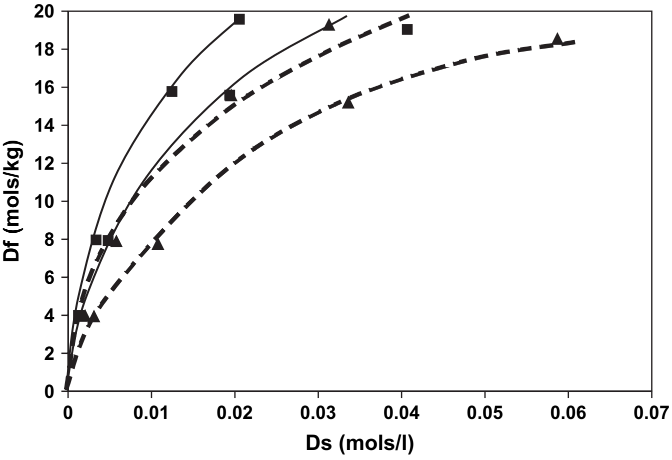

Fig. 3. Isotherm curves for Direct Blue 71 applied to resin-treated, post-causticised lyocell fibre. With 4 g/l (——) or 2 g/l (- - - -) of added NaCl electrolyte. Applied resin concentrations of 50 g/l (■) and 100 g/l (▲).

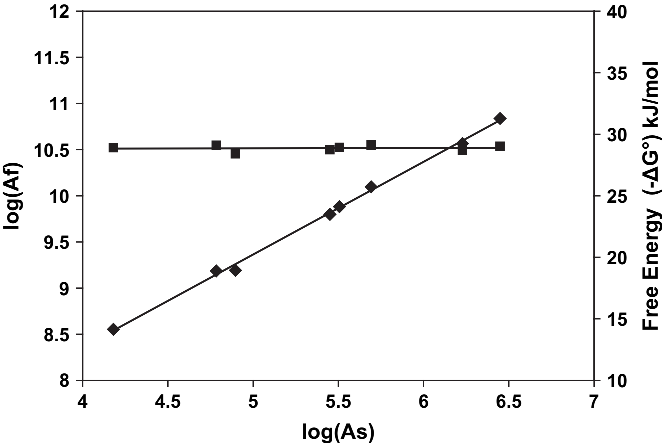

Fig. 4. Example of isotherm model fitting, with adjustment of (V) for linear relationship between log(A_f) (◆) vs log(A_s), and with adjustment of [C] for constant ($-\Delta G°$) (■) at all values for log(A_s).

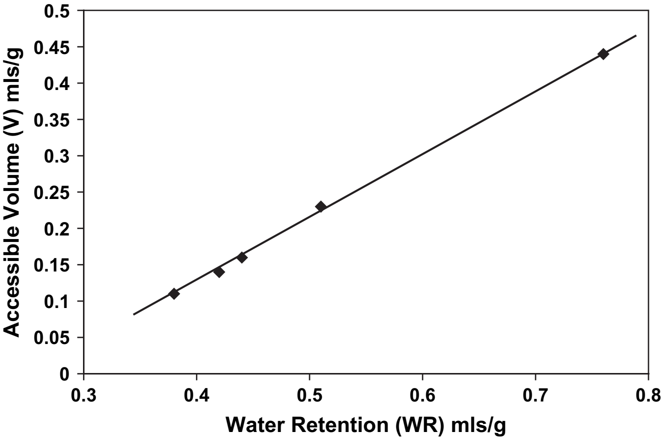

Fig. 5. Relationship between experimental water retention (WR) and isotherm model accessible volume (V), for series of resin-treated lyocell fibres.

both zero, which is anticipated if low-molecular weight material with the highest proportion of endgroups and functional groups is extracted by the alkaline treatment [37].

The results from the water T_2 relaxation time analysis are summarised in Table 2. Single-component relaxation behaviour was observed for the untreated control, the 25 g/l resin-padded sample and the two post-causticised samples. The attempted single-component fits for the other resinated fibres resulted in R^2 values lower than 0.96, suggesting the presence of multi-component behaviour. Two-component fits gave R^2 values better than 0.99 for all fibre samples. However, in physical terms, the water within the fibres was considered to be undergoing fast-exchange on the NMR timescale, as defined by Brownstein and Tarr [16], with rapid interchange between different local surfaces and between surface and bulk environments. The multi-exponential nature of the observed behaviour was therefore not considered to be due to diffusion-relaxation interaction, but was thought more likely to be a result of gross heterogeneity within the pore texture, as might be expected following the dry-bake resination procedure. A distribution of resin cross-link density through the fibre texture, possibly with a greater surface concentration, would lead to a spread of pore sizes, which might not be fully averaged over the macroscopic fibre dimensions. The determination of a weighted-mean relaxation time for the system could then be justified, in order to calculate average porosity parameters for comparison of all fibres in the series.

As described, the simplified analysis proposed by Carles and Scallan [28] was employed in this work, for calculation of a value for the instantaneous surface water population. A similar approach has been used to good effect in a number of studies of natural and regenerated cellulosic materials [29,31]. This basic model has the advantage of establishing a direct relationship between observed relaxation and surface to volume ratio, for comparison with dye uptake results. For the current investigation it has been assumed that the intrinsic surface relaxation parameter (T_s) remains constant, as it can be argued that the fixed resin will have high hydrophilicity and will have a similar interaction with the internal fibre water compared to the cellulose hydroxyl sites.

The weighted averaged experimental relaxation times from the two-component fits were used to determine the instantaneous surface water contents of all fibres (W_s), from Eq. (8). These values were then used to calculate the total internal surface area (S) of the samples, where $S = (W_s \times M_s)$, assuming a monolayer coverage of water, $M_s = 3000\ \mathrm{m^2/g}$ [28].

Table 1
Dye isotherm model parameters and water retention data for resin-treated lyocell fibre

Resin treatment, pad solution (g/l)	Resin fixation (wt% − fibre)	Model free-energy ($-\Delta G°$) (kJ/mol)	Model carboxyl content (C) (equiv/g)	Model accessible volume (V) (mls.g)	log(A_f)/log(A_s) model fit (R^2)	Water retention (WR) (ml/g)
0	0.00	28.86	11	0.44	0.998	0.76
25	0.88	28.02	5	0.23	0.995	0.51
50	1.97	23.65	4	0.16	0.968	0.44
75	3.28	19.16	2	0.14	0.996	0.42
100	3.66	18.09	2	0.11	0.988	0.38
50 (post-NaOH)	1.78	20.2	0	2.6	0.991	1.16
		28.0[a]	0	0.79	0.828	1.16
100 (post-NaOH)	3.48	27.5	0	0.41	0.971	0.94
		28.0[a]	0	0.40	0.970	0.94
NaOH only - Ref. [1]	–	28.0[a]	3	0.56	0.951	0.83

[a] Forced fit to −28.0 kJ/mol.

Table 2
Proton water NMR-relaxation data for resin-treated lyocell fibres, according to the two-site model

	Relaxation times							Surface water content		Total surface area		Pore width (lamellar model)	
No. of relaxation components	1		2					1	2	1	2	1	2
Resin pad solution (g/l)	T (ms)	R^2	M_1 (wt%)	M_2	T_{exp1} (ms)	T_{exp2}	T	W_s (ml/g)		S (m^2/g)		d (nm)	
0	10	0.989	81	19	8	28	12	0.11	0.097	343	291	4.4	5.2
25	11	0.983	78	22	7	27	11	0.07	0.067	207	200	4.9	5.1
50	13	0.943	72	28	5	31	12		0.054		161		5.5
75	10	0.954	73	27	5	27	11		0.057		172		4.9
100	10	0.902	73	27	5	37	14		0.042		126		6.1
50 (post-NaOH)	22	0.996	30	70	10	26	21		0.082		245		9.4
100 (post-NaOH)	20	0.995	36	64	9	26	20		0.071		213		8.8

A lamellar pore model was used to calculate an average pore width (d), according to Eq. (9), with all results summarised in Table 2. From Eqs. (8) and (9) it can be seen that the experimental water T_2 relaxation time is proportional to the mean pore width

$$d = \frac{2(W_{tot})}{(W_s \times M_s)} \tag{9}$$

The dependence of mean pore diameter (d) and wet-state surface area (S) on the amount of fixed resin is shown in Fig. 7, for the resin-only samples. Apparently, the average pore width remains constant at increasing cross-linker content, suggesting a loss of pore volume across the entire size distribution, from both large and small pores. The removal of total water capacity, as indicated from the reduction in water retention (WR), therefore results in a progressive fall in the available internal surface. In contrast, the post-causticised samples display altered characteristics, with higher water T_2 relaxation times compared to the resin-only series, indicating an increase in pore width caused by the swelling treatment. The significantly higher water retention of these fibres leads to the calculation of an increased surface area, with the 50 g/l resin-padded fibre showing the greatest recovery combined with the largest pore width.

4. Discussion

There is excellent correlation between the centrifuged water retention (WR) and model accessible volume (V) of the resin-only fibre series, shown in Fig. 5. The suppression of dyeability must therefore be strongly related to the reduction in total fibre pore capacity. This adds weight to the concept of an internal fibre solution and the dependence of dye adsorption on the activities of the dissolved ionic species. The Peters and Vickerstaff model is shown to be effective in predicting dyeing behaviour as the internal volume of lyocell fibre is reduced through cross-linking, and is able to account for all electrolyte and fibre charge effects. Whilst the relationship between WR and V is linear, it is offset in favour of the water retention, and with continuing reduction in total pore capacity a limit will be reached where the apparent accessible volume is zero. This is consistent with the notion that a residual volume will be available to small water molecules, which

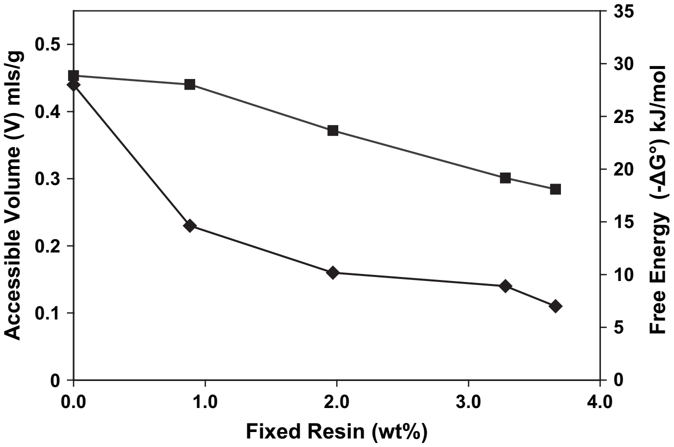

Fig. 6. Relationship between resin fixed on lyocell fibre and isotherm model parameters for accessible volume (◆) and free-energy of dye adsorption (■).

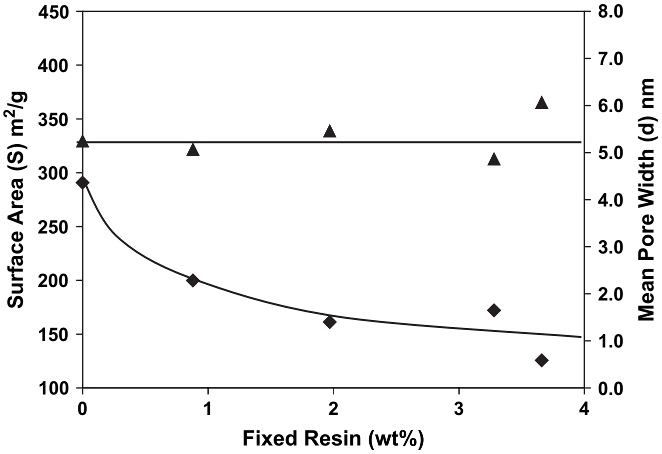

Fig. 7. Influence of fixed resin content on total internal surface area (◆) and mean pore width (▲) from water NMR-relaxation measurements, for resin-treated lyocell series.

cannot be accessed by large direct or reactive dye molecules. Different relationships between (WR) and (*V*) have been noted for other cellulosic fibre series, where variations in pore structure result from changes manufacturing parameters [32]. A comparison of the two parameters (WR and *V*) may have value as an indication of the spread or asymmetry of the pore size distribution.

The relation between fibre water retention (WR) and the amount of fixed resin is not linear, according to Fig. 6, with the greatest suppression in pore capacity occurring at lower resin contents. The tetrafunctional methylol-urea type resin is expected to form rigid, short-range cross-links between the surfaces of the fibrillar crystallites of lyocell [33]. The high temperature bake-cure step occurs when the fibre morphology is fully collapsed meaning that the fibrillar domains will be effectively tied together. Subsequent inter-fibrillar swelling during re-immersion in water will be far less successful, leading to the observed reduction in pore capacity. The first resin molecules to be fixed will have the most significant effect on the potential for reswelling, as these will form the initial inter-fibrillar bridges. Subsequent fixation will introduce further cross-links, which will reinforce these initial ties. The constancy of the mean pore sizes calculated by water NMR relaxation, as shown in Fig. 7, suggests that cross-link addition suppresses swelling across the entire size distribution, with capacity lost evenly from both large and small spaces. The pores in lyocell are believed to have lamellar character, with high aspect ratio and with long tapering fringes. The incorporation of cross-link ties would progressively reduce the lateral expansion of these spaces and would exclude the access of water at their narrowest limits. A progressive reduction in accessible surface area would take place as the total extent of cross-linking was increased. A loss in surface area together with a loss in pore capacity could therefore explain the insensitivity of the mean size calculation m. It can be seen from Table 1 that the resin content for the100 g/l resin-padded sample is about 3.7% of total fibre weight. In contrast, this fibre loses a total of 38% of its original swelling capacity, so assuming equivalent densities, it is unlikely that the incorporation of resin simply fills the volume of the inter-fibrillar spaces, which would otherwise be available for water.

The model of Peters and Vickerstaff is based on the concept of diffuse adsorption, which must account for all material characteristics of the fibre through either the accessible volume (*V*) or the free-energy ($-\Delta G^\circ$) terms in the model equations. The interpretation of the accessible volume term is most straightforward, with a relationship established between this and the physically determined pore capacity of the fibre. Intuitively, the total free-energy of dyeing must depend on the organisation of the dye on the cellulose surface, which could be influenced by the nature of the fibre morphology [34–36]. The internal surface character might also be expected to vary depending on manufacturing or processing conditions. In previous studies, it has been concluded that the free-energy for adsorption to cellulose may be a constant for a particular dye, regardless of the origin of the material [37]. However, from other work there is evidence of a variation in free energy, or other thermodynamic terms, as the dye surface packing is modified by increasing its concentration in the fibre, or as a result of the chemical modification of the internal fibre surface [10,38,39]. The model data from this current study show a distinct reduction in free energy of dyeing with increasing resin fixation, which becomes more exaggerated at higher resin contents, according to Fig. 6. For this controlled fibre series it is reasonable to assume that the effectiveness of the adsorption interaction is reduced as the internal cellulose surfaces become disrupted by fixed resin molecules. Assuming a monolayer area for the resin molecules of 1000 m^2/g, the highest fixation of 3.66 wt% represents an area of approximately 37 m^2, or just over 10% of the original internal surface area of 290–340 m^2/g, according to the measurements by water NMR relaxation. Adsorption surfaces will be available for the incoming dye but will suffer interference from points of resin attachment. This is consistent with the fall in modelled free-energy from −28 kJ/mol for the untreated fibre to −18 kJ/mol for the 100 g/l resin-padded fibre.

Causticisation brings about a dramatic recovery in the dyeability of resin cross-linked lyocell fibre, which according to data from a previous study is actually greater than the improvement introduced by caustication alone [1]. Earlier studies on cotton have concluded that a small proportion of resin may be hydrolytically removed from the fibre under strong caustic conditions [19], which is also confirmed from this work, shown in Table 1. However, the work on cotton demonstrated that the majority of the cross-links are still effective and are contributing to the crease-resistant properties of the fabric substrate [19,24]. The water NMR relaxatioin and water retention data for the post-causticised lyocell samples can be rationalised without difficulty. A large increase in total pore capacity is observed, slightly greater at 1.15 ml/g for the 50 g/l treatment compared to 0.94 ml/g for the 100 g/l treatment. This alone could account for the enhancement in dyeability, according to the sensitivity of the dye equilibrium to the fibre internal volume. In addition, the relaxation data indicate a recovery in internal surface area and also a significant enhancement in average pore size, according to Table 2, from around 5 nm up to 9 nm following caustisation. This would also suggest an improvement in accessibility towards larger dye molecules and an enhancement in equilibrium dye uptake.

The NMR relaxation and water retention data indicate that post-causticistation brings about a major rearrangement of the cross-linked fibre structure. Other research has shown that treatment of lyocell with alkali solutions typically introduces improvements in crystalline order, which is accompanied by a gross relaxation of fibre orientation [40]. It seems that this is enhanced rather than suppressed by the presence of resin cross-links. Probably, the powerful swelling action delivered by sodium hydroxide causes a reduction of pore aspect ratio, which may be driven to a greater extent by the opportunity for relaxation of local stresses at cross-link points. It may be appropriate to think of the swelled cross-linked cellulose network as having elastomeric character, with the intra-crystalline penetration of the alkali solution shifting a significant proportion of polymer chains above their glass-transition temperature. A contraction of the network would be driven by the spontaneous move to a higher state of disorder, or entropy, according to classical theory, leading to a severe morphological reorganisation [17]. The relaxation forces could potentially create new pore spaces, which might be free of the obstructions of resin ties. The effects of a more uniform population of pores, with wider, less elongated shapes and with higher overall capacity would all be expected to improve dyeing performance.

Quantification of the effect of post-caustisation using the Peters and Vickerstaff model is more challenging, with a less obvious relationship shown between model accessible volume (V) and water retention (WR). The accessible volume of the 100 g/l treated fibre increases after caustisation, from 0.11 to 0.41 ml/g, from Table 1, a recovery to the same approximate volume of the untreated sample. However, as discussed, the water retention rises to 0.93 ml/g, which is well above the value for the untreated fibre. The model would therefore imply that the physical accessibility of the dye within the much larger total volume of the post-causticised fibre is still inhibited by the resin network. According to the model, the enhanced dyeability must be accounted for by the reduction of anionic charge of the fibre, as carboxylate functionality is removed by caustic extraction, falling from an apparent 11 to zero meq/g. The importance of the reduction in fibre anionic charge is reasonable, as this parameter that has a strong influence on the electropotential equilibrium at low concentrations of bath electrolyte. A lowering of the number of sodium counterions in the fibre would reduce the ionic imbalance and hence the influence of the Donnan membrane potential, which develops following dye adsorption. However in a further complication, the model accessible volume for the 50 g/l post-causticised fibre rises to an unrealistic 2.6 ml/g, far in excess of the measured water retention, of 1.16 ml/g. The free-energy for this sample is also lower than might be anticipated considering its excellent dyeability, at −20 kJ/mol compared to −28 kJ/mol for the untreated fibre.

Probably at high dye uptake the simple assumptions of the Peters and Vickerstaff model are approaching their useful limits. An earlier study of causticised lyocell also recognised that it was difficult to rationalise a reduction in free-energy of dyeing which apparently accompanied an increase in dyeability [1]. More realistic values for the accessible volume of the resin-treated post-causticised samples can be established if the free energy of dyeing is held constant, although this does reduce the quality of some of the fits. This is shown in Table 1, where for the 100 g/l post-causticised sample the accessible volume at a free-energy of −28 kJ/mol falls only slightly to 0.40 ml/g but for the 50 g/l post-causticised sample reduces to a more reasonable 0.79 ml/g. This new accessible volume established for the 50 g/l post-causticised sample is now more sensibly below that of the water retention value although it is still significantly greater than the accessible volume of the original untreated lyocell fibre. Apparently, at lower levels of resin fixation, the cross-link density does not inhibit movement of dye through the post-causticised structure.

The model applied at constant free-energy shows that the value of accessible volume (V) achieved by caustic relaxation follows a complex relationship with resin content and must describe a maximum at some low but finite cross-link density. The relative increase in accessible volume for the 100 g/l treatment is a factor of 3.6, whilst for the 50 g/l treatment the factor is 4.6. By comparison, the increase without resin pre-treatment is a factor of only 1.25 [1]. The relationship between total pore volume and resin content following caustic relaxation must also display a maximum at a finite cross-link density, which may be at a higher off-set than described by the model accessible volume. These phenomena might be explored in the future by considering statistical theories for the prediction of swelling and entropy contraction of polymer networks. Lastly, in an attempt to improve the model it is possible to separate the volume term (V) in Eq. (2) relating to the dye equilibrium and in Eq. (3) relating to the Donnan equilibrium. This leads to better quality fits but still results in an accessible volume for the dye in the 50 g/l post-causticised sample, which is above the water retention value. This approach also starts to loose the physical significance of the fibre internal solution, and may indicate that the Donnan theory is insufficient to describe the internal sodium concentration at high levels of dye uptake.

5. Conclusions

Dye isotherm and water NMR relaxation measurements provide complementary information, allowing a more complete interpretation of the wet-state porosity characteristics of lyocell cellulosic fibres. The isotherm model developed by Peters and Vickerstaff provides an intuitive interpretation of the effect of resin cross-linking, predicting a loss of internal fibre volume accessible to the dye and a reduction in the energy of the dye-surface interaction. This is consistent with the blocking of pore channels caused by inter-fibrillar cross-link ties, inhibiting dye accessibility. NMR-relaxation data support the view that the incorporation of tie molecules leads to a reduction of overall fibre swelling causing a loss of porosity at both large and small size scales. Post-causticisation of resinated lyocell fibre leads to a dramatic improvement in dyeability, consistent with a recovery in accessible volume and an enhancement in total pore capacity. The mechanism of the structural rearrangement of the fibre may be associated with the relaxation of internal stresses at resin cross-links and the reduction in pore aspect ratios. Reorganisation leading to an increase in pore widths may follow the development of elastomeric behaviour in the swelled state, driven by entropy effects. Causticisation is also expected to lead to the extraction of low-molecular weight polymer with a higher proportion of carboxylate endgroups.

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