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Polymer 41 (2000) 1873–1881

polymer

The hydration of TENCEL® cellulose fibres studied using contrast variation in small angle neutron scattering

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Received 30 November 1998; received in revised form 12 April 1999; accepted 5 May 1999

Abstract

A small angle neutron scattering (SANS) contrast variation study was performed to investigate the presence of air filled voids in fully hydrated Tencel® cellulose fibres. The data indicate that there are very few, if any, air filled voids within the water swollen fibres. A three phase scattering power analysis together with additional information from water imbibtion measurements show that the volume fraction of air filled voids in water swollen Tencel fibres is probably zero, but has an upper limit of 0.02.

In a complementary experiment, a H_2O/D_2O mixture was prepared with the same neutron scattering length density as air. The difference between the SANS patterns from air and water swollen fibres persists when the fibres are swollen in an air/water contrast matched H_2O/D_2O mixture. The data qualitatively agrees with the analysis of time resolved SAXS data which indicated that the void size increases on drying, and the void volume fraction decreases on drying water swollen Tencel fibres (Crawshaw J, Cameron RE. Polymer, in press, Crawshaw J. PhD thesis. Changes in cellulose microstructure during processing. University of Cambridge, 1997). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Small angle neutron scattering; Contrast variation; Cellulose

1. Introduction

Tencel[1] is a lyocell fibre. Such fibres have a high degree of crystallinity and are composed of elementary fibrils about 80 Å in diameter, oriented roughly parallel to the fibre axis. The elementary fibrils consist of cellulose II crystallites, separated in the fibre axis direction by highly oriented amorphous regions [1,2]. Between some of the fibrils are long thin voids, which can be characterised by small angle scattering [3,4]. When the fibre as a whole in hydrated, swelling occurs, which changes the void size shape and orientation.

Elsewhere [5,6] we report time resolved small angle X-ray scattering (SAXS) during the dehydration of Tencel fibres. The data show that the void size increases and the void volume fraction decreases on drying. The water swollen fibre apparently consists of a network of small voids between many of the elementary fibrils. As the water is driven out of the fibre, smaller voids collapse leaving dense regions and a few large voids. Implicit in such analysis of SAXS data is the assumption that in the water swollen fibre the fraction of air filled voids is very small or zero.

While it is clear that many voids fill with water during hydration of the fibre, there has been, to date no evidence to prove that all are filled. It is possible that some remain isolated and filled with air. This paper addresses this question using contrast variation and small angle neutron scattering (SANS). Tencel fibres swollen in the water/cellulose match point mixture will give zero SANS contrast if all the voids in the fibres are water filled. However, if some air filled voids remain in the water swollen fibres, then the SANS signal will not be zero throughout the sample and a scattering pattern will be seen.

2. Experimental

2.1. Materials

Tencel fibres are produced from a solution of cellulose in *n*-methyl morpholine oxide (NMMO). The fibres were supplied by Courtaulds Corporate Technology (now Akzo Nobel).

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[1] Tencel® is a registered trademark of Akzo Nobel.

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PII: S0032-3861(99)00331-6

Table 1
Scattering Length densities of water deuterated water, cellulose and air

Molecule	Neutron scattering length density (cm^{-2})
H_2O	-0.56×10^{10}
D_2O	6.35×10^{10}
Cellulose–glucose unit $C_6H_{10}O_5$	1.86×10^{10}
Air–ideal gas composed of N_2 and O_2	0.008×10^{10}

2.2. Calculation of scattering length densities

The scattering length density of cellulose was estimated assuming 100% crystalline cellulose of mass density 1.6 g cm^{-3}, using a single monomer unit, $C_6H_{10}O_5$ of rmm 162 using standard equations and known values of elemental scattering lengths [7,8]. The scattering length density of Tencel fibres was assumed to be approximately that estimated for crystalline cellulose. This is a reasonable assumption as they are highly crystalline cellulose II fibres. The scattering length density of air was calculated by treating air as 80% nitrogen and 20% oxygen to estimate a rmm of 14.4. Air was assumed to be an ideal gas, occupying a molar volume of 24l at s.t.p. The values of scattering length density used are in Table 1.

2.3. Calculation of match points

The scattering length density of a mixture of D_2O and H_2O, δ_w may be calculated from

$$\delta_w = F \times \delta_{D_2O} + (1 - F) \times \delta_{H_2O} \quad (1)$$

where F is the volume fraction of D_2O in the mixture and δ_{D_2O} and δ_{H_2O} are the scattering length densities of D_2O and H_2O, respectively. Thus, a value of F may be chosen such that the scattering length density of the water mixture is equal to that of another phase of the system. The match point between water and Tencel fibres is approximately $F = 0.35$. The water/air match point was calculated similarly and found to be at a D_2O fraction of 0.08.

2.4. Neutron experiments

The experiments were carried out on the LOQ station of the ISIS spallation source at the Rutherford Appleton Laboratory which has been described in detail elsewhere [8].

The Tencel fibres were carefully packed into quartz sample cells, ensuring that as far as possible the fibres were parallel to each other and to the long sides of the sample cells. Care was taken to ensure that a similar number of fibres was packed into each cell. They were then hydrated with H_2O/D_2O mixtures with fractions of D_2O of 0.00, 0.08 (the water/air match point), 0.25, 0.35 (the approximate water/cellulose match point), 0.45 and 1.00. A dry sample was also prepared.

To minimise problems due to exchange between the hydrogen within the cellulose and the deuterium in the H_2O/D_2O mixture, the Tencel fibres were pre-swollen in the H_2O/D_2O mixture for at least 3 h, after which most of the H/D exchange was expected to have occurred [9]. The water was then removed just before SANS data were to be collected, and replaced with a fresh H_2O/D_2O mixture of the correct contrast.

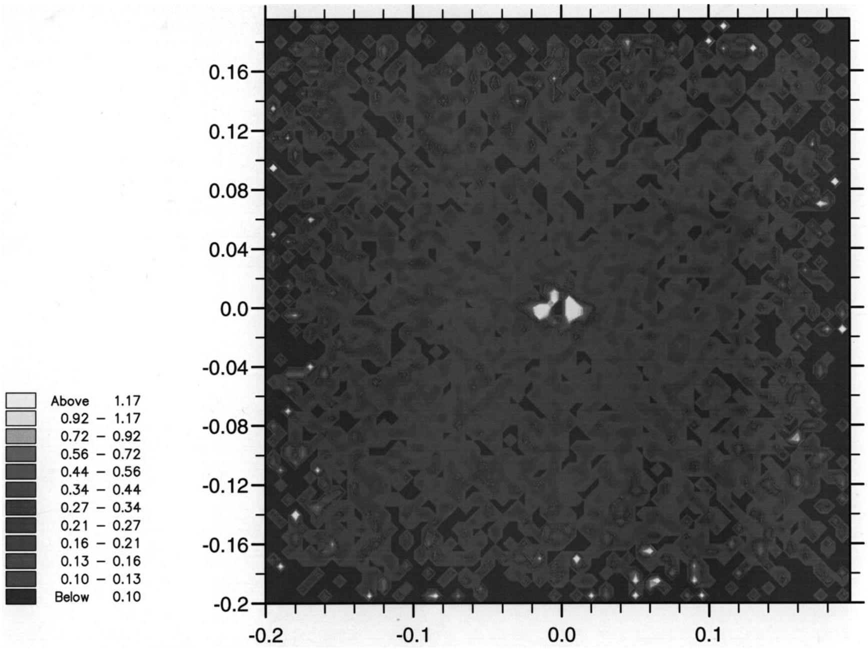

Fig. 1. Two-dimensional contour plot of approximate differential cross-section in cm^{-1} in the q_x q_y plane from dry Tencel fibres. Scattering angles, q, are in $Å^{-1}$. The fibre axis is vertical.

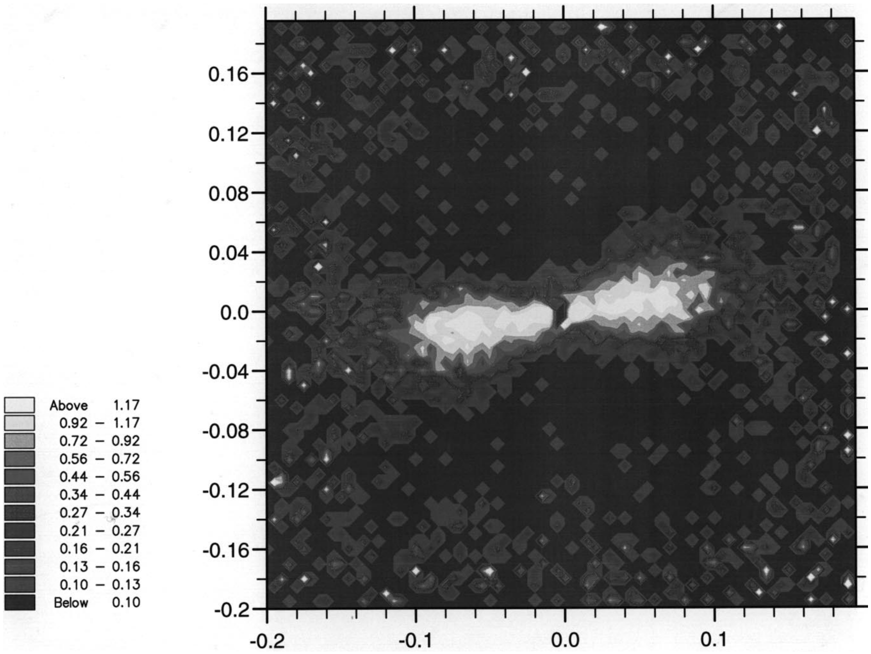

Fig. 2. Two-dimensional contour plot of approximate differential cross-section in cm^{-1} in the $q_x\, q_y$ plane from Tencel fibres swollen in H_2O. Scattering angles, q, are in $Å^{-1}$. The fibre axis is vertical.

These samples and a cell of dry Tencel fibres were exposed in the beam for a minimum of 2 h. Scattered intensity was recorded on a two-dimensional position sensitive gas filled detector and sample transmission data were collected. Data from an empty cell and from the six H_2O/D_2O mixtures were also collected for background subtraction.

2.5. Water imbibtion measurements

Approximately 1 g of the Tencel fibres was soaked in distilled water for 30 min. The excess water was removed by centrifugation for 5 min at 1490 g, and the wet weight of fibre was recorded. The samples were air dried at 107°C for 180 min, reaching constant weight.

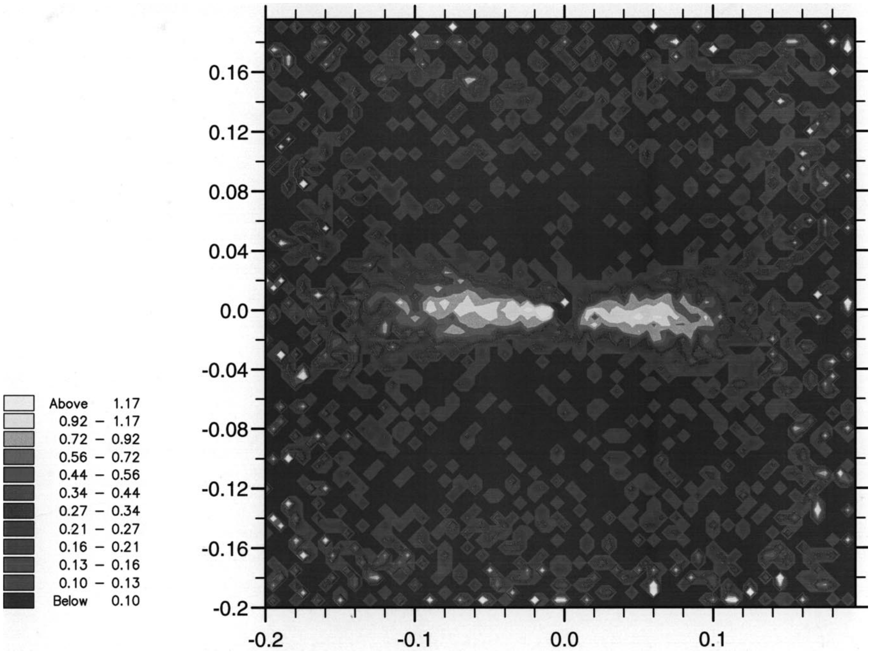

Fig. 3. Two-dimensional contour plot of approximate differential cross-section in cm^{-1} in the $q_x\, q_y$ plane from Tencel fibres swollen in 0.92 H_2O/0.08 D_2O. Scattering angles, q, are in $Å^{-1}$. The fibre axis is vertical.

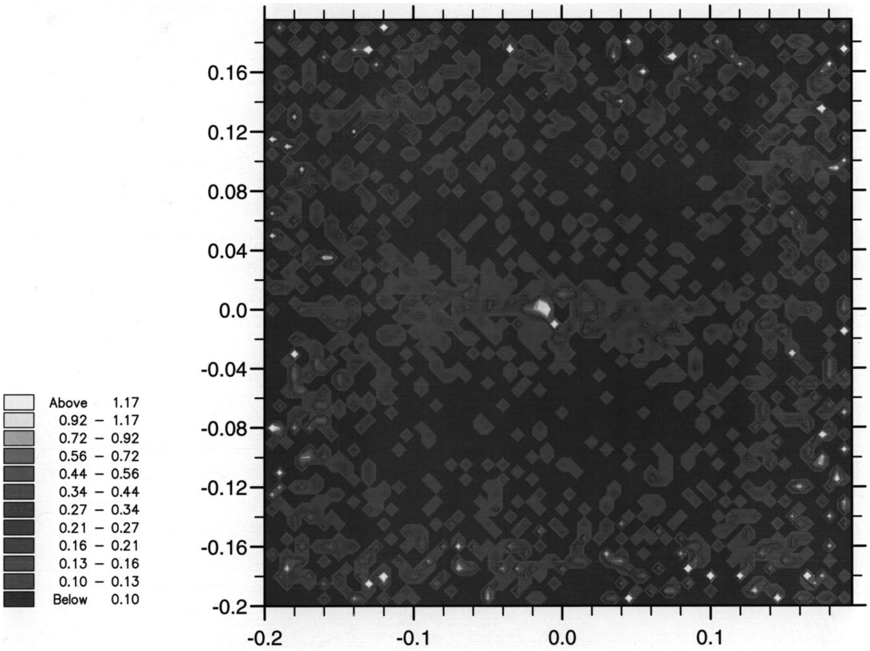

Fig. 4. Two-dimensional contour plot of approximate differential cross-section in cm^{-1} in the q_x q_y plane from Tencel fibres swollen in 0.75 H_2O/0.25 D_2O. Scattering angles, q, are in $Å^{-1}$. The fibre axis is vertical.

3. Results and data analysis

3.1. Data processing

The raw time-of-flight cross-section data were reduced to two dimensions, calibrated in scattering vector, using standard programs described elsewhere [8,10] to give data in the form of differential cross-section, $d\sigma/d\Omega$, as a function of the scattering vector. It was assumed that the same amount of fibre was in the beam for each sample. Since this will not be exactly true, the differential cross-sections obtained will have an additional element of uncertainty. The appropriate H_2O/D_2O mixture or empty cell background was then subtracted. Figs. 1–7 show the data obtained.

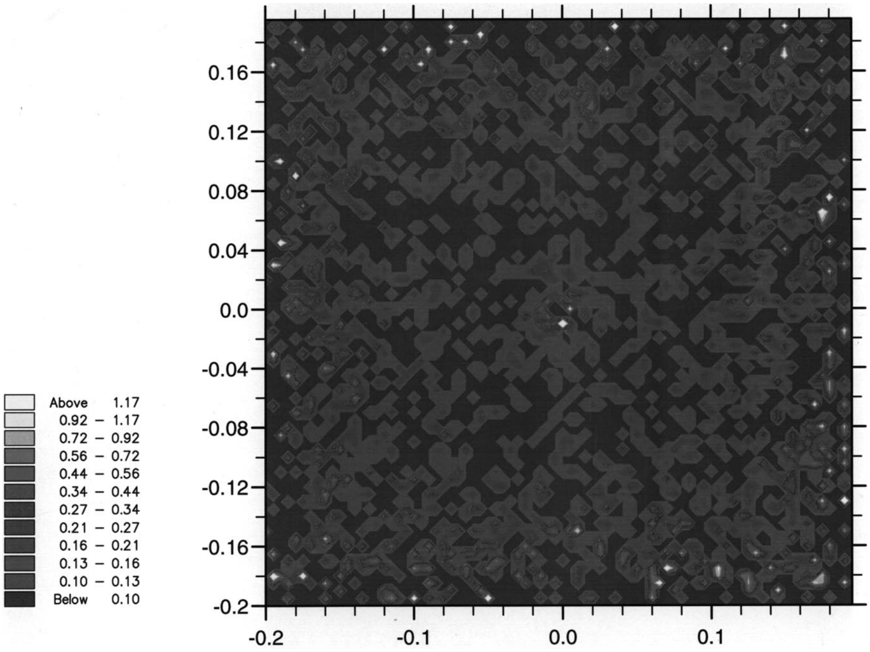

Fig. 5. Two-dimensional contour plot of approximate differential cross-section in cm^{-1} in the q_x q_y plane from Tencel fibres swollen in 0.65 H_2O/0.35 D_2O. Scattering angles, q, are in $Å^{-1}$. The fibre axis is vertical.

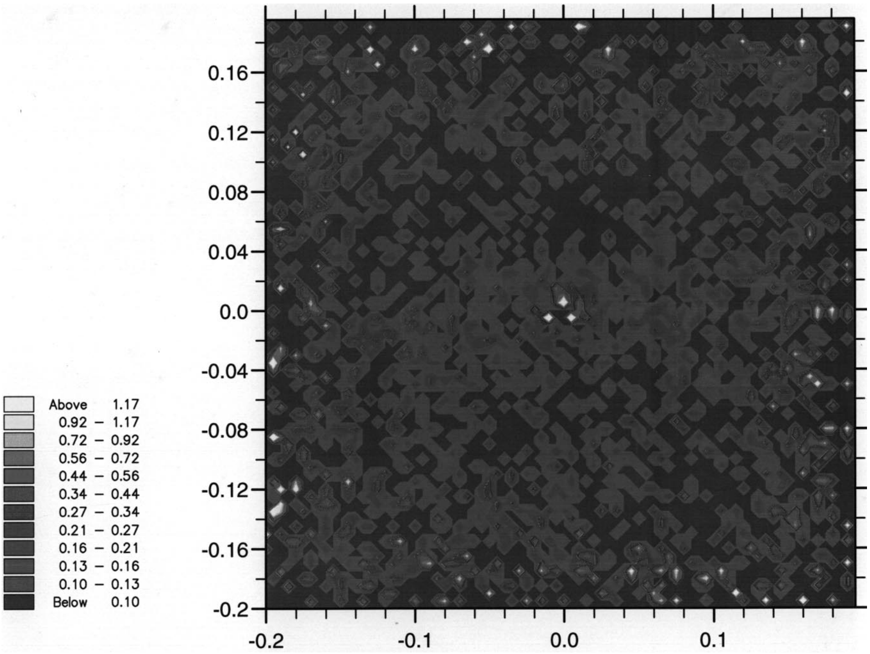

Fig. 6. Two-dimensional contour plot of approximate differential cross-section in cm^{-1} in the $q_x\, q_y$ plane from Tencel fibres swollen in 0.55 H_2O/0.45 D_2O. Scattering angles, q, are in Å^{-1}. The fibre axis is vertical.

3.2. The integrated equatorial intensity

For simplicity of notation, and since these terms are directly proportional, equations will be expressed in terms of scattered intensity $I(\mathbf{q})$ rather than differential cross-section, $\mathrm{d}\sigma/\mathrm{d}\Omega$. The SANS integrated equatorial intensity, $\tilde{I}(q_x)$, was extracted from the 2D data, $I(\mathbf{q})$, by meridionally summing intensities at each equatorial point according to

$$\tilde{I}(q_x) = \int_{-\infty}^{\infty} I(\mathbf{q})\, \mathrm{d}q_z \tag{2}$$

where q_x, is the scattering vector in the equatorial direction and q_z the scattering vector in the meridional direction. The integration was performed over the limits of reliability of the detector.

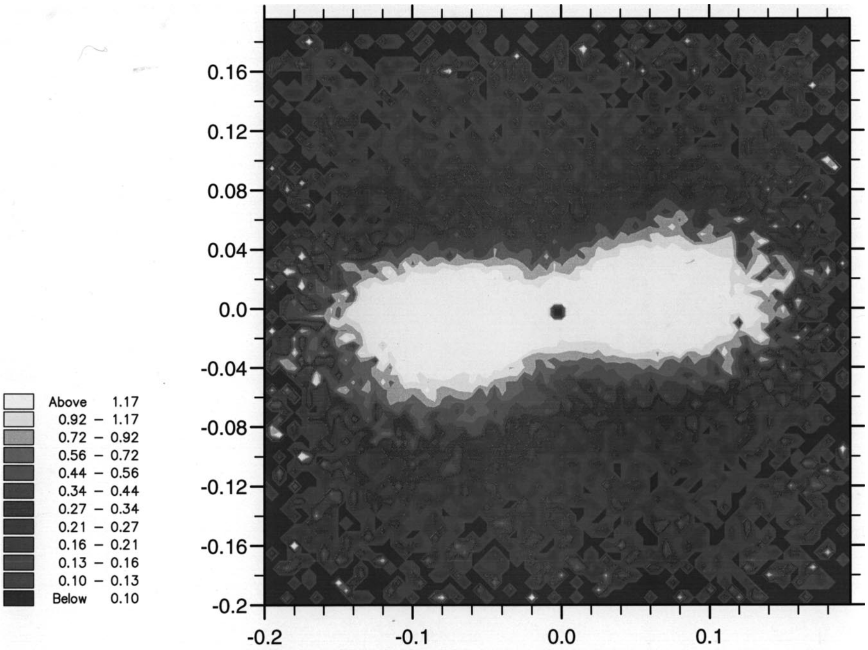

Fig. 7. Two-dimensional contour plot of approximate differential cross-section in cm^{-1} in the $q_x\, q_y$ plane from Tencel fibres swollen in D_2O. Scattering angles, q, are in Å^{-1}. The fibre axis is vertical.

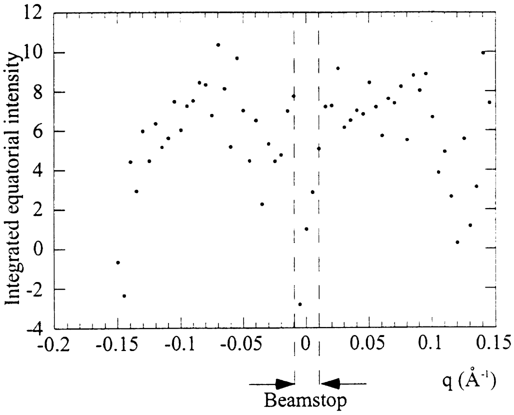

Fig. 8. The corrected integrated equatorial intensity, $\tilde{I}_c(q_x)$ in cm^{-1} Å^{-1} demonstrated for Tencel fibres swollen in a 0.08 D_2O, 0.92 H_2O mixture. Negative values near the beamstop are unphysical and should be disregarded. The negative values at high q are a consequence of uncertainties in the background subtraction, and detector edge effects.

Although the simple subtraction of the scattering from the solvent gives a reasonable background subtraction, it does not take into account problems arising from incoherent scatter from H and D. For Tencel fibres swollen in H_2O/D_2O mixtures, the H_2O/D_2O background subtractions were incorrect because there is actually a higher proportion of H in the swollen Tencel fibre sample than in the H_2O/D_2O sample. This is due to the contribution to scattering from the H in cellulose.

This problem was addressed in the calculation of the integrated equatorial intensity, $\tilde{I}(q_x)$, by estimating the extent to which the pure solvent background subtraction was too high, or too low, from a section of the two-dimensional image which contained no Tencel fibre scattering. This area of the image should have zero intensity if the correct incoherent background subtraction is used. The resulting intensity was multiplied by the ratio of the whole detector area used in the calculation of $\tilde{I}(q_x)$ to the area of the background section used to give the background correction. This constant was then subtracted from the already background subtracted $\tilde{I}(q_x)$ to give the corrected integrated equatorial scattering intensity, $\tilde{I}_c(q_x)$. This method of correcting the pure solvent background subtraction is reasonable since the incoherent scattering from water was found to be approximately constant with angle.

Table 2
The scattering power of water swollen Tencel fibres, Q_{expt} in cm^{-1} Å^{-3} for each percentage of D_2O in the water mixture

Fraction of D_2O in the water mixture	Q_{expt} (cm^{-1} Å^{-3})
0.00	0.100
0.08	0.061
0.25	0.009
0.35	0.001
0.45	0.019
1.00	0.282

Fig. 8 shows the corrected integrated equatorial scattering intensity for Tencel fibres swollen in the 0.08 D_2O/H_2O mixture, and illustrates the nature and quality of the data obtained.

3.3. The scattering power

The scattering power (also known as the invariant), Q_{expt}, was calculated from the corrected integrated equatorial intensity after the method of Shioya and Takaku [11] for cylindrically symmetric scatterers

$$Q_{\mathrm{expt}} = \int_0^\infty \tilde{I}_c(q_x) q_x \, dq_z \tag{3}$$

The integration was performed over the limits of the available range.

Table 2 shows the scattering power of the samples swollen in D_2O/H_2O mixtures of varying concentration.

3.4. Imbibtion measurements

Imbibtion measurements for three Tencel fibre samples indicated a mean dry weight of $m_c = 1.01 \pm 0.01$ g, and an imbibed water content of $m_w = 0.69 \pm 0.01$ g. The centrifugation step is designed to remove all water except that within the voids. Therefore, the relationship between the volume fraction of water, w_w, and the volume fraction of cellulose, w_c, can be estimated using

$$\frac{w_w}{w_w + w_c} = \frac{m_w/\rho_w}{(m_w/\rho_w) + (m_c + \rho_c)} = \frac{0.69/1.0}{(0.69/1.0) + (1.01/1.6)} \cong 0.52 \tag{4}$$

where, ρ_w is the mass density of water set at 1.0 g cm^{-3} for all mixtures, and ρ_c is the mass density of cellulose, approximated by 1.6 g cm^{-3}, the value for crystalline cellulose. Re-arranging Eq. (4) shows that

$$w_c \cong 0.92 w_w \tag{5}$$

4. Discussion

4.1. Contrast matching air and water

Figs. 1 and 3 show the SANS area patterns for dry Tencel fibres and for Tencel fibres in the water/air matched, 0.08 D_2O/H_2O mixture. The contrast between the phases in each pattern is thus the same, and differences between them are thus solely a consequence of changes in the void size shape and number. These patterns clearly demonstrate the effect of water on the structure of the fibre. Dry Tencel fibre SANS appears as a small diamond shape pattern, showing slight equatorial elongation. Water swollen fibres give scattering broadened in a meridional direction, and elongated on the

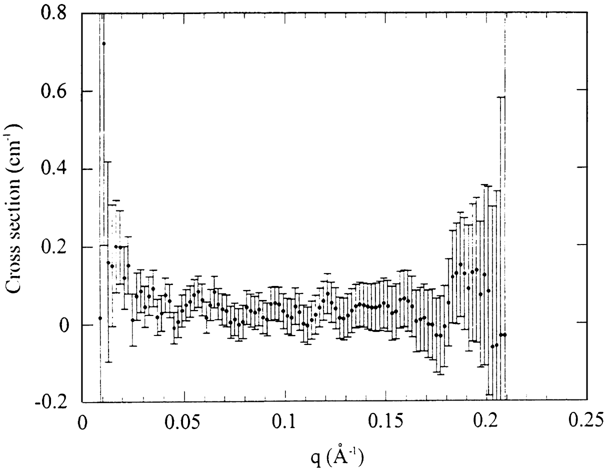

Fig. 9. An equatorial slice of the 2D SANS pattern from Tencel fibres swollen in the approximate cellulose/water match point mixture of 0.35 D_2O and 0.65 H_2O. The slice was produced by adding intensities around a contour of constant *q*, between 20° both above and below the equator. Negative values near the beamstop are unphysical and should be disregarded. The negative values at high *q* are a consequence of uncertainties in the background subtraction, and detector edge effects.

equator. The scattering at very low angles is less intense in the wet fibres than in the dry. This result qualitatively agrees with the analysis of SAXS data which indicates that the void size increases on drying, and the void volume fraction decreases on drying water swollen Tencel fibres [5,6].

4.2. Contrast matching cellulose and water

Figs. 2–7 show the two-dimensional SANS for Tencel fibres swollen in the six different H_2O/D_2O mixture concentrations. The contrast does indeed fall very close to zero at the calculated water/cellulose match point of approximately 0.35 D_2O.

Indication of the error in these data can be seen from Fig. 9, which shows an equatorial slice of the two-dimensional SANS data for Tencel fibres swollen in the 0.35 D_2O mixture. This equatorial slice was produced by adding intensities around a contour of constant *q*, between 20° both above and below the equator. There is statistical uncertainty in the data. Further, the calculated value of the match point is approximate as it does not take into account the (small) density difference between amorphous and crystalline cellulose or the possibility that water in the void might have a difference density from bulk water. These factors mean that the results do not prove complete absence air filled voids within the water swollen Tencel fibres, but the results are consistent with there being no air filled voids.

4.3. Estimation of the volume fractions of water and air filled voids and cellulose

If air filled voids persist in water swollen Tencel fibres, the fibre will form a three-phase small angle scattering system consisting of cellulose, water filled voids and air filled voids. For such a system the experimentally determined scattering power obeys

$$Q_{\mathrm{expt}} \propto (w_{\mathrm{w}} w_{\mathrm{a}}(\delta_{\mathrm{w}} - \delta_{\mathrm{a}})^2 + w_{\mathrm{c}} w_{\mathrm{w}}(\delta_{\mathrm{c}} - \delta_{\mathrm{w}})^2 + w_{\mathrm{a}} w_{\mathrm{c}}(\delta_{\mathrm{a}} - \delta_{\mathrm{c}})^2) \qquad (6)$$

where w_{w} is the volume fraction of the H_2O/D_2O mixture, w_{a} is the volume fraction of air, w_{c} is the volume fraction of cellulose, δ_{w} is the neutron scattering length density of the H_2O/D_2O mixture, δ_{a} is the neutron scattering length density of air and δ_{c} is the neutron scattering length density of celluose [12].

The constant of proportionality, *k*, will depend on the constant relating intensity to differential cross-section, and other factors relating to the volume of material in the beam, the geometry of the scattering particles and approximations made in the calculation of Q_{expt}. The scattering length densities are all known. Since δ_{a} is much smaller than the other scattering length densities it may be set to zero. Eq. (6) can be simplified by considering two relationships between the volume fractions of the constituent phases. First, by definition, the three volume fractions obey:

$$w_{\mathrm{w}} + w_{\mathrm{a}} + w_{\mathrm{c}} = 1 \qquad (7)$$

Secondly, from Eqs. (5) and (7) it can be seen that

$$w_{\mathrm{a}} \cong 1 - 1.92 w_{\mathrm{w}} \qquad (8)$$

Substituting into the expression for Q_{expt} in Eq. (6) can gives a quadratic equation in w_{w}

$$Q_{\mathrm{expt}} \propto (w_{\mathrm{w}}(1 - 1.92 w_{\mathrm{w}})(F\delta_{\mathrm{D_2O}} + (1 - F)\delta_{\mathrm{H_2O}})^2 + 0.92 w_{\mathrm{w}}^2(\delta_{\mathrm{c}} - F\delta_{\mathrm{D_2O}} - (1 - F)\delta_{\mathrm{H_2O}})^2 + 0.92 w_{\mathrm{w}}(1 - 1.92 w_{\mathrm{w}})(\delta_{\mathrm{c}})^2) \qquad (9)$$

with all parameters known except the constant of proportionality, *k*. If the ratio of Q_{expt} shown in Eq. (9) is taken for pairs of H_2O/D_2O mixtures, then the constant of proportionality is eliminated leaving w_{w} as the only unknown. Therefore, w_{w}, and hence w_{c} and w_{a} may be estimated from pairs of SANS data and the additional information provided by the water imbibtion measurements. The advantage of this method of analysis is that no fitting parameter is introduced: the parameters are all calculated directly from the data. This calculation was performed for all possible pairings of the six H_2O/D_2O mixtures and the values obtained listed in Table 3. The pairs of H_2O/D_2O mixtures have been represented by the percentage of D_2O in each H_2O/D_2O mixture of the pair.

From Table 3 it can be seen that the values of w_{w}, w_{c}, and w_{a} are broadly similar for every pairing, except 0.25 D_2O with 0.45 D_2O. (This exception was found to be the result of a rather high Q_{expt} obtained for 0.45 D_2O. If Q_{expt} for 0.45 D_2O is set at $0.01\ \mathrm{cm}^{-1}\ \text{Å}^{-3}$, which is similar to that obtained for 0.25 D_2O, then w_{w}, w_{c}, and w_{a} fall within the same range as was found for all the other pairs of mixtures. The values obtained for this pairing gives a curve, which

Table 3
Estimated volume fractions of water, cellulose, and air in water swollen Tencel fibres, calculated from pairs of data, indicated by the fraction of D_2O in the water mixture

Fraction of D_2O, F	Fraction of D_2O, F	w_w	w_c	w_a
0.08	0.25	0.515	0.474	0.010
0.08	0.35	0.519	0.477	0.003
0.08	0.45	0.509	0.468	0.023
0.25	0.35	0.519	0.478	0.003
0.25	0.45	0.216	0.199	0.585
0.35	0.45	0.520	0.478	0.002
0.00	0.08	0.490	0.451	0.059
0.00	0.25	0.514	0.473	0.012
0.00	0.35	0.519	0.477	0.004
0.00	0.45	0.508	0.467	0.024
0.00	1.00	0.563	0.518	−0.080
1.00	0.08	0.577	0.531	−0.108
1.00	0.25	0.500	0.460	0.040
1.00	0.35	0.518	0.477	0.005
1.00	0.45	0.492	0.453	0.055

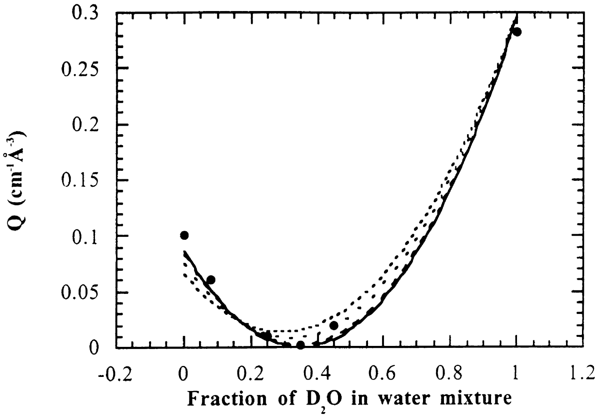

Fig. 11. The scattering power of water swollen Tencel fibres, Q_{expt} in cm^{-1} Å^{-3} plotted against percentage of D_2O in the water mixture (closed circles), and the calculated curves obtained from fitting Eq. (6) to the data and allowing the constant of proportionality k to vary, but fixing w_a as 0.00, (solid line) 0.01 (long dashes) 0.05 (short well-separated dashes) and 0.1 (short, close spaced dashes).

does not fit the remaining Q_{expt} values at all.) Confidence in the estimated volume fractions is supported by calculation of the constant of proportionality, k, which was found to be roughly constant for all pairings except 0.25 D_2O with 0.45 D_2O.

Fig. 10 shows the values of Q_{expt} together with the curve obtained from the average of the parameters in Table 3: $w_a = 0.004 \pm 0.012$, $w_c = 0.477 \pm 0.006$, $w_w = 0.519 \pm 0.006$, $k = 7.37 \times 10^{-22} \pm 0.47 \times 10^{-22}$ (omitting data from the 0.25/0.45 pair).

The above results in Table 3 indicate that the volume fraction of air filled voids in water swollen Tencel fibres lies in the approximate range 0.00–0.02. This estimation is consistent with the possibility that there are no air filled voids in water swollen fibres. The negative values for the volume fraction of air filled voids appearing in Table 3 are obviously unphysical and arise from the experimental errors in Q_{expt}.

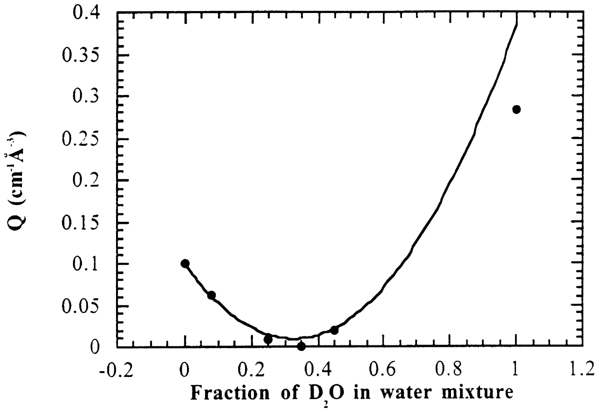

Fig. 10. The scattering power of water swollen Tencel fibres, Q_{expt} in cm^{-1} Å^{-3} plotted against percentage of D_2O in the water mixture (closed circles), and the calculated curve obtained from the average of the parameters obtained from the pairwise analysis (solid line): $w_a = 0.004$,$w_c = 0.477$ and $w_w = 0.519$, (omitting data from the 0.25/0.45 pair).

An alternative analysis of the values of $Q_{expt}$was performed in order to take into account the full shape of the curve, rather than only two points as in the pairwise analysis. The relative height of the minimum in Q_{expt}, at the "match point", $\delta_w = \delta_c$ will depend on w_a. Fits of Eq. (9) to Q_{expt}, adjusting only the scaling parameter, k, by least squares, provide an estimate of w_a. Density variations within the cellulose or water regions mean that for SANS a perfect match point; is rarely attained, thus the w_a determined will be an upper limit. Curves on Fig. 11 show the calculated Q using (6) for $w_a = 0.00, 0.01, 0.05$ *and* 0.10. (Fitted values of k are 5.91×10^{-22}, 5.32×10^{-22} and 4.89×10^{-22}, respectively). Like the pairwise analysis, these curves suggest that w_a is probably less than 0.02 and may well be zero.

5. Conclusions

The SANS data obtained are consistent with a complete absence of air filled voids in water swollen Tencel fibres. Water imbibtion experiments indicate that the ratio of the volume of cellulose to the volume of water filled voids is about 0.92. Three-phase scattering power analysis suggests that the void fraction of air lies between 0.00 and 0.02. The very small or non-existent fraction of air filled voids in water swollen fibres validates SAXS analysis which requires this assumption [5,6]. Contrast matched SANS data between air and water indicates that dry fibres have larger voids than wet fibres and that the volume fraction is much higher in wet fibres. This is consistent with data from SAXS [5,6].

Acknowledgements

The authors are grateful to Courtaulds Corporate Technology (now part of the Akzo Nobel group) for samples and financial support and the EPSRC for funding. Neutron experiments were performed at the ISIS facility at the Rutherford Appleton Laboratory.

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