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# AN EXPERIMENTAL STUDY BY NMR AND SANS OF THE AMBIENT HYDRATION OF PAPER

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# ABSTRACT

The structural changes in fibre polymers and dispersion of water in the polymer have been studied at length scales less than 400 Å with contrast variation small angle neutron scattering (SANS) and solid state nuclear magnetic resonance (NMR). The SANS of hydrating paper samples is discussed in different angular regions in terms of a scattering wavenumber vector,  $q (q = 4\pi/\lambda . \sin \theta/2)$ where  $\lambda$  is the wavelength of the neutrons and  $\theta$  is the scattering angle). At low q close to the neutron beam, the Guinier region, voids in the structure are found to disappear as the microfibrils swell with water. The lateral dimensions of the cellulose crystallite are calculated from x-ray diffraction data and there is a good qualitative correlation with relative size of the crystallites and the appearance of short range of order in the SANS in the mid-range of the q studied. The range of the length scale of the SANS feature is slightly larger than the elementary crystallite which is consistent with layers of swollen cellulose and water around the crystallite. In the high q region, the angular region furthermost from the beam, the scattering is discussed in terms of deviation

from Porod scattering. According to this interpretation the interface between cellulose and water is not clearly defined and there is an increase in the amount of surface area for water to bind to. These results are consistent with water disrupting the hydrogen bonding in fibre polymers. The NMR spin diffusion experiment monitors the exchange of magnetisation between water and polymer protons. A simplistic model of this transfer process is justified and indicates that water is not uniformly dispersed in the polymer as a function of moisture content.

#### INTRODUCTION

Water plays a major role in the formation and properties of the fibre network. When paper is formed it is the medium in which the fibres are dispersed. It causes fibres to swell and plasticizes them. When water is removed during sheet forming, its surface tension brings the fibres into close proximity, and as more water is removed it is the medium through which the fibre surfaces interact as water participates in hydrogen bonding between and within fibres. The removal of water causes the fibres to shrink, develop dried in stresses, and undergo the densification associated with hornification. Once the paper web is formed, its properties are strongly influenced by the concentration of water in the atmosphere, and past levels of this concentration.

The paper web is a network of fibres which have been wound by nature from strands known as fibrils. These fibrils can be further sub-divided into units called microfibrils. The major component of fibrils is the polymer cellulose. In order to understand the nature of the molecular interactions that affect properties at each structural level of paper, it is important to understand the intimacy of mixing between the cellulose polymer and the sorbed water.

In a review of the structure of cellulose, O'Sullivan [1] concluded that cellulose is complex with continuing research gradually unraveling its secrets. Cellulose exists in a number of crystalline forms but only Cellulose I is present in natural sources, including paper. However this does not entirely remove the complexity associated with the crystal structure as cellulose exists in two slightly different forms Cellulose Ia and Cellulose I $\beta$ , the relative amounts of each depending on the source of the cellulose. The belief was long held that cellulose is composed of crystalline and amorphous regions with the crystal-line region being in the form of crystallites, but the spatial relationship between the two regions was uncertain. O'Sullivan [1] pointed out that the

concept of amorphous regions was probably not accurate as the so-called 'amorphous material' would still retain some degree of order. Following Krässig [2], O'Sullivan also noted that there is a close correspondence between the surface area of cellulose crystallites in a particular material and its amorphous content *i.e.* a material with a measured crystallinity that is high is composed of large crystallites. This model has been supported experimentally by Muller *et al.* [3], among others [2 and references therein], who agree that the disordered cellulose molecules exist on the microfibril surface. Muller *et al.* [3] prefer the concept of 'accessibility to guest molecules, particularly water', rather than crystallinity.

The crystallites, or microfibrils, are packed loosely into a volume with spaces between them. These spaces may be empty in fibres with a high cellulose content but they may also contain varying amounts of lignin and hemicellulose in unbleached wood pulp fibres. Thus, if mainly the lignin has been removed, the microfibrils will interact through regions of disordered cellulose which can contain varying amounts of hemicellulose. If lignin is present it also may take part in interactions between the microfibril surfaces. The arrangement of the microfibrils into the architecture described above is illustrated in Figure 1.

It has been established that water does not have access to hydroxyl groups in the crystallite core of the microfibril [2,4]. Water will preferentially interact with hydroxyl groups on polysaccharides, competing for hydrogen bonds with hydroxyl groups which form bonds between polysaccharide chains. The chains may belong to cellulose or hemicellulose on neighbouring microfibrils, or within a microfibril. In this way the sorption of moisture can mediate the interactions and dynamics along the polymer chain and the interactions between microfibrils. Since crystalline cellulose is not particularly permeable to water [2], water is absorbed through the area between crystallites. Water can lower the temperature at which the onset of long-range co-operative motions of cellulose molecules occurs, it can drastically change the ability of chains to undergo structural relaxation [3,5,6] and it can affect the diffusion of small molecules into the disordered regions of polymers [7].

There are a number of experiments which have revealed that when water is absorbed in paper its dynamics are perturbed. In cellulose there appears to be some water that is relatively immobile and some whose dynamics resemble those of liquid water [8,9,10]. The pool of immobile water is constantly exchanged with the mobile phase [8]. Some experiments further separate the immobile phase into a glassy-like phase, and one that is more structured [9]. The relative amount of water in the two phases has been found to be a function of moisture content. This has been demonstrated by freezing and then gradually heating fully hydrated samples to remove water [9,10]



Figure 1 A schematic of the model of fibres used in this work: a) A cross-section of a cellulose microfibril which consists of a fixed number of cellulose chains (ovals) which run in a direction normal to the paper. The interior of the microfibrils exhibit order (crystalline region) and the exterior less order ('amorphous' region). b) The microfibrils are loosely arranged in hydrogen-bonded bundles. The spaces between the microfibrils may be voids or contain varying amounts of an amorphous matrix (lignin/hemicellulose).

A number of experimental techniques can be used to probe the structure of fibres and their interaction with water at the molecular level. The width of the crystallite in a particular crystallographic direction,  $\tau$ , can be measured by x-ray diffraction (Figure 2). In this technique the intensity of scattered x-rays is measured at a series of known angles between the incident x-rays and the surface of the sample. Peaks are observed as a function of the angle of incidence and they provide information about the crystalline structure of the material. The breadth of peaks is related to the size of crystallites. The Bragg peaks, as they are known, result from scattered x-rays that constructively interfere because of the periodic spacing of atoms in an ordered material [11]. Gjonnes and Norman [12] showed that the diffraction pattern of cellulose can be fitted by assuming four reflections from the unit cell [13]. This analysis assumes that a reflection is broadened only by the size of the crystallite [14] and that lattice distortions [15] do not play a role. The size broadening of the cellulose crystallite can be estimated by simply using the Scherrer



Figure 2 The crystallographic planes through which  $\tau$  is measured according to the lattice parameters of Meyer and Misch (1937). Each ellipse represents a cellulose chain normal to the paper.

Equation [16,17]. Scherrer formulated an expression for the integral breadth at half height  $\beta$ :

$$\beta = \frac{k\lambda}{\tau \cos \theta_{max}} \tag{1}$$

where  $\tau$  is the x-ray crystallite width (Figure 2) and k is a constant whose value is close to one [11]. The prominent Bragg reflections (peaks), which are clear enough for an accurate fit, all measure the 'width' in a particular direction across the crystallite. The measurements can therefore provide estimates of cross sectional dimensions, as illustrated in Figure 2.

The above technique looks at large scattering angles and is referred to as wide angle x-ray scattering (WAXS). Small angle scattering (SAXS for x-rays and SANS for neutrons) is a technique that is used to investigate shorterrange order. In the same way that dispersed particulate matter in the atmosphere at sunset bends light through an angle that depends on wavelength [18], waves incident at small angles to a material (illustrated in Figure 3) are scattered by variations (contrast) in the scattering length density,  $\delta$ , of the medium. X-rays are scattered by electrons and so small angle x-ray scattering (SAXS) is the result of variations in electron density. The electron density variations in cellulose fibres and wood have been extensively investigated using SAXS [19,20,21,22,23]. The electron density difference between amorphous and crystalline cellulose is low [24]. The chief density variations in cellulose fibres are due to small, elongated voids of the order of 15 Å in



area detector

Figure 3 A schematic representation of the small angle neutron scattering experiment. A collimated beam of neutrons passes through the sample and the distribution of the intensity of neutrons scattered at small angles to the direction of the primary beam is measured by means of an area detector at the rear of the sample. The intensity measured as a function of  $\theta$  is converted to intensity as a function of the magnitude of the scattering vector, q.

length [22]. In the case of neutron scattering, the neutrons sense the nuclear spin [25], which can vary considerably for atoms of similar atomic number and for isotopes of the same element (Table 1). This enables small angle neutron scattering to probe variations in bulk density, isotopic content and the chemical composition of the scattering regions. Small angle neutron scattering has been used to study changes in polymers brought about by water sorption, using a technique called contrast variation.

Contrast variation is the deliberate control of the difference in the neutron scattering length density (contrast) of specific regions of a sample by isotopic

Nucleus	$b_i$ (×10 <sup>12</sup> cm) [25]
<sup>1</sup> H	-0.374
D ( <sup>2</sup> H)	0.667
$^{12}C$	0.665
$^{16}\mathrm{O}$	0.58

 Table 1
 Values of neutron scattering length used in calculations in this work.

substitution. In particular, differences in the scattering length of hydrogenated and deuterated materials have been exploited to study the structure of solid polymers and blends [25] and porous materials [26]. In a heterogeneous material, contrast variation allows the experimenter to manipulate the nature of the scattering [25,26]. It is possible to adjust the scattering length of water by changing the H<sub>2</sub>O : D<sub>2</sub>O ratio. The scattering length can then be selected to remove the contrast between water and voids, *i.e.*  $\delta_{water} = \delta_{void} = 0$ , or between water and polymer *i.e.*  $\delta_{water} = \delta_{polymer}$ . Using this experimental technique, the simplifying assumption is made that scattering results from the contrast between two phases only *i.e.* the experiment is reduced to a two-phase problem. When water matches the voids the contrast is between the bulk polymer ( $\delta_{vp}$ ) and a combination of the water and voids.

Another technique which probes the structure of materials through nuclear spins is nuclear magnetic resonance spectroscopy (NMR), but in this case it is via resonant absorption of energy rather than scattering. NMR is really a broad category covering a number of experimental techniques based on the same fundamental phenomenon [27,28]. NMR spectra are determined by the fundamental spin states of nuclei and the local magnetic environments of the nuclear spins. NMR spectra provide information about the chemistry and dynamics within the medium under study. In an NMR experiment, a radio frequency magnetic field is applied as a pulse to populations of spins aligned by the intensity and duration of the pulse. The return of spins to their equilibrium distribution generates a signal, called the free induction decay (FID), in a detector coil. The Fourier transform of this signal converts the time dependant signal to the familiar intensity versus frequency spectra [29].

A number of available NMR techniques are able to observe spin diffusion. Spin diffusion is the spatial transport of magnetisation (nuclear magnetic dipole polarisation) between neighbouring nuclei by dipole/dipole interactions. These interactions are short range, and are confined to nuclei in the immediate environment of the spin [30]. When two separate phases exist in a medium it is possible to generate a spatial gradient by selective excitation of the spins of one phase (Figure 4). The process of equilibration between the two phases can be followed as a function of the mixing time,  $t_{mix}$  [32]. Assuming the two phases are the two states of water in a polymer, a bound and a mobile state, with the relative amounts of each depending on moisture content; as outlined above, spin diffusion can be used to study the distribution of water between these states as a function of relative humidity. Referring to the distribution of spins between states as a temperature, in the Boltzmann sense [31], one phase can be thought of as being at a higher temperature than the other with dipolar couplings between adjacent nuclei allowing the system to



Figure 4 The thermal diffusion model for the spin diffusion experiment. In the permanent magnet of the spectrometer the nuclear dipoles (<sup>1</sup>H nuclei) align themselves with the field  $(\tilde{B}_o)$ . The population in each state  $(N_{up} \text{ or } N_{down})$  defines a spin temperature [31] according to the energy separation between the states,  $\Delta E$ . In the Boltzman sense of temperature, a spin temperature,  $T_{spin}$ , is defined such that  $N_{up}/N_{down} = \exp - (\Delta E/kT_{spin})$  where k is the Boltzmann constant. Selective excitation leads to a gradient in spin temperature with the interface being the region of communication between the two phases.

move towards thermal equilibrium. As communication between the two phases occurs at the interface, spin diffusion in polymers is a powerful probe of the structure of the interface and the morphology and size of domains [30].

Protons in cellulose can be identified on the basis of their spin-spin relaxation times,  $T_2$  [10,33]. The spin-spin relaxation time is shorter in less mobile protons leading to broader peaks. In solids, NMR peaks are very broad because dipolar couplings are very efficient and atoms exist in a range of surrounding spin environments. In liquids these environments are motionally averaged and the lines are narrow [34]. The proton NMR spectrum of paper, a cellulosic material, consists of a narrow spectral line superimposed over a much broader one [10,32]. The dipolar filter pulse sequence NMR technique has been used to study the exchange of magnetisation between mobile protons (relaxation time  $T_2^m$ ) and rigid protons (relaxation time  $T_2^r$ ) in hydrated cellulose/polyvinyl-alcohol blends [9] and water/starch mixtures [35]. The magnetisation is selected from the component with the longer  $T_2$ , in this case mobile water.

In the approach used in the work described in this paper, the proton fraction belonging to water was selectively excited and the magnetisation then exchanged with the protons belonging to the polymers (lignin, cellulose and hemicellulose). The initial rate of this type of process is controlled by the interface between the two phases (water and polymers). A comprehensive analysis of spin diffusion is a complicated multi-body problem. The description of the flow of magnetisation from one phase to another, can be simplified using a simple heat diffusion analogy [32,37] and Fick's second law [7]:

$$\frac{\partial M(r, t_{mix})}{\partial t} = \nabla (D(r) \nabla M(r, t_{mix}))$$
(2)

where D(r) is the spin-diffusion coefficient and  $M(r,t_{mix})$  is the spatially varying magnetisation which starts solely in one phase, but can diffuse into other phases. D also varies spatially since the materials under consideration are heterogeneous.

In using this experiment to investigate the intimacy of water/polymer mixing we have made the following assumptions:

- The water sorbed to the polymer is in two dynamically exchanging states, one in which the dynamics resemble those of bulk water, and the other which exists between the bulk water and the cellulose or hemicellulose and is bound to hydroxyl groups on the polysaccharides.
- It is this bound water which is able to communicate via dipolar interactions with the polymer.
- It is the relative amount of bound water which determines the initial rate of magnetisation transfer.

This model can be justified by considering the relative magnitudes of the spin diffusion co-efficient, D, for the polymer, free water and bound water.

The estimation of D for each phase is an important step in the use of the spin diffusion experiment to evaluate the structure of the mixture. This can be done by solving the partial differential equation, Equation 2, to estimate domain sizes. In solids the value of D is related to the strength of dipolar couplings, and can be estimated directly from  $T_2$  [37] or by calibration with SAXS [38]. In the more mobile regions, dipolar couplings between nuclei become weaker, however magnetisation may also be transported spatially by molecular diffusion in combination with dipolar couplings [39,40].

Using the empirical relation of Mellinger *et al.* [38], the value of the spin diffusion coefficient for water is calculated to be approximately 0.001 nm<sup>2</sup>/ms, when the value of  $T_2$  is of the order of seconds. By contrast the value obtained for a rigid polymer such as polystyrene is 0.8 nm<sup>2</sup>/ms [37]. The self diffusion (mass transport) co-efficient of water is  $2 \times 10^6$  nm<sup>2</sup>/ms at  $25^{\circ}$ C [41]. From a comparison of these values we can conclude that, while

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magnetisation can be very efficiently transported by molecular diffusion, the magnetisation of a mobile proton cannot be efficiently exchanged to another until the two molecules are bound. When a water molecule is immobile relative to the polymer fraction dipolar coupling is much stronger than when it is mobile but separated by the same distance. Thus changes in the initial rate of exchange reflect the relative amount of bound water to free water in a system.

#### EXPERIMENTAL

#### Paper samples

The paper samples used in this study were: Whatman number 4 filter paper; handsheets produced from a commercial eucalypt NSSC pulp; and handsheets produced from a commercial bleached eucalypt kraft pulp (BEK). The two pulps were beaten to 2000 revs in a PFI mill according to Australian Standard AS1301.005 before processing into handsheets. To equilibrate the paper samples in a known relative humidity, they were exposed to the atmosphere above water saturated with an inorganic salt for at least 3 hours in the case of SANS experiments and for at least two days in the case of the NMR experiments. The relative humidity depended on the actual inorganic salt selected (Table 2).

Salt	Humidity (%RH:23°C)	
LiCl	9	
NH <sub>4</sub> NO <sub>3</sub>	56	
NaCl	75	
$K_2SO_4$	97	

Table 2         Salt solutions used to generate known relative humiditie	s [42].
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# X-ray diffraction

The measurement of x-ray diffractograms has been outlined elsewhere [14]. The experiments described in this work were designed to reduce the relative contribution of instrumental broadening to the Bragg reflections. The source of x-rays was a copper tube with selection of the x-ray K $\alpha$  line made using a Scintag Peltier-cooled solid state detector that collected intensity versus angle data. Profiles from this experiment were fitted with four peaks using Peakfit<sup>®</sup> software [43] using a Voigt function [44] for each peak (Figure 5). Following



Figure 5 An example of the fit of four peaks, each Voigt functions, to the x-ray diffraction profiles (eucalypt NSSC handsheet).

Gjonnes and Norman [12], no subtraction was made for the amorphous background. This approach gave an excellent fit to the data ( $r^2 > 0.999$ ).

#### Small angle neutron scattering

Small angle neutron scattering (SANS) experiments were carried out at the National Institute of Standard and Technology's Center for Neutron Research (NCNR) (Gaithersburg, USA) on the 8 m SANS instrument on beamline NG1. A schematic of the experiment is outlined in Figure 3. Experiments were carried out using a neutron wavelength of 7 Å, accumulating each data set for 2 hours. A 64 cm × 64 cm position sensitive detector is located approximately 8 m from the sample. In the instrument configuration used here the available q range was 0.01 to 0.2 Å<sup>-1</sup>. Further details of this instrument can be found at http://www.ncnr.nist.gov/8msans.html.

For SANS experiments, the sample consisted of a piece of paper which was suspended above the saturated salt solution, in a sealed aluminum container, orthogonal to the neutron beam (Figure 3). To determine a suitable equilibration time, a piece of paper was first equilibrated overnight in an atmosphere at the lowest relative humidity (9%). It was then immediately placed in the highest relative humidity (97%) in the neutron beam. It took 3 hours before the SANS results, collected at 5 minute intervals, became constant. Thus each sample was equilibrated for at least 3 hours before placing it in the neutron beam.

The intensity, *I*, of neutrons measured in the SANS experiments is a function of  $\lambda$  and  $\theta$ :

$$I(\lambda,\theta) = I_o(\lambda) \Delta \Omega \eta(\lambda) T V \frac{\partial \sigma}{\partial \Omega} (q)$$
(3)

where  $I_o(\lambda)$  is the incident flux of radiation,  $\Delta\Omega$  is the incident angle subtended by one pixel of the detector,  $\eta(\lambda)$  is the detector efficiency, *T* is the sample transmission, *V* is the volume of the sample illuminated and the function  $(\partial\sigma/\partial\Omega)(q)$  is the microscopic differential cross-section. On the 8 m SANS instrument at NCNR the intensity is measured as a function of angle,  $\theta$ .

The first three terms of Equation 3 are dependent on the instrument and the last three are related to the sample. The magnitude of the wave vector, q, through which a neutron is scattered is given by

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \tag{4}$$

where  $\theta$  is the scattering angle. By subtracting the scattering from an empty sample container and applying the appropriate corrections to the intensity measured by the area detector, the data are reduced to the variation in scattered intensity as a function of the wave vector, q, (i.e. I(q) versus q). The interpretation of the SANS experiment is based on a simple representation of the microscopic differential cross-section for scattering particles, with a number concentration,  $N_p$ , and volume  $V_p$ , in a second phase:

$$\frac{\partial\sigma}{\partial\Omega}(q) = N_p V_p^2 (\Delta\delta)^2 P(q) S(q) + B_{inc}$$
(5)

where P(q) is the shape or form factor of the particles, S(q) is a factor which takes into account the distribution of particles in the second phase and  $B_{inc}$  is the incoherent background scattering. The term  $(\Delta \delta)^2$  is the contrast factor. If  $(\Delta \delta)^2 = 0$  there can be no scattering as there is no contrast between the

two phases. For ease of notation the quantity  $(\partial \sigma / \partial \Omega)(q)$  will be referred to as I(q).

If two regions of scattering length density  $\delta_a$  and  $\delta_b$  exist,  $(\Delta \delta)^2$  is given by

$$(\Delta \delta)^2 = (\delta_a - \delta_b)^2 \tag{6}$$

For neutrons the scattering length density of a phase,  $\delta_b$ , is calculated from the bulk density of the material,  $\rho$ , the sum of the atomic weights,  $m_i$ , weighted for their number fractions in the phase,  $a_i$ , and the sum of the atomic scattering factors of the atoms,  $b_i$ , weighted for their number fractions in the phase

$$\delta_b = \frac{\sum a_i b_i \times \rho}{\sum a_i m_i \times 1.66 \times 10^{-24}} \tag{7}$$

There is an equivalent expression for the small angle scattering of x-rays (SAXS) where  $b_i$  of each nucleus is replaced by a term for the electron density [45].

The values of the neutron scattering length density of water,  $\delta_{water}$ , for various mixtures of H<sub>2</sub>O and D<sub>2</sub>O have been calculated using Equation 7 and the values of  $b_i$  in Table 1. The values of  $\delta_{water}$  are plotted in Figure 6. There is a large difference between  $b_H$  and  $b_D$ , thus mixtures of H<sub>2</sub>O and D<sub>2</sub>O from 100% H<sub>2</sub>O to 100% D<sub>2</sub>O span a large range of values of  $b_i$ , including those for most of the components of fibres: voids, cellulose and lignin.

Using a range of literature values for the density of cellulose [2,46] a range of values for the scattering length density of cellulose,  $\delta_{cell}$ , has been calculated. This range has been plotted in Figure 6 to show the mixtures of  $D_2O$ and H<sub>2</sub>O that give matching values for the scattering length density. The calculation of  $\delta_{lignin}$  is not straight forward due to the ill-defined nature of lignin chemistry. Taking a value of the density of lignin from the literature, and using the chemistry of the three major monomers that form lignin, three values were calculated for  $\delta_{lienin}$  and these are plotted in Figure 6. The value of  $\delta_{lienin}$  is not very sensitive to the variation in chemistry but, as with  $\delta_{cell}$ , the variation in the value for the density is the major source of uncertainty in this calculation. The contrast factors for water and cellulose and for water and lignin are plotted as a function of the percentage of H<sub>2</sub>O in the mixture in Figure 6. There is overlap in the ranges of contrast factors for cellulose and lignin contrasted with different water mixtures. The density of hemicellulose in fibres is unknown. It is mixed with lignin and may be complexed with the cellulose crystallite surfaces [47].



**Figure 6** The scattering length density  $(\delta)$  of  $D_2O/H_2O$  mixtures and the contrast  $(\Delta \delta^2 = (\delta_a - \delta_b)^2)$  between cellulose and lignin and these mixtures. For reference the coherent scattering length density of cellulose, monomers of lignin and a mixture of  $8\% D_2O$  in  $H_2O$ , where  $\delta_{water} = 0$  (at **X**) are shown.

Hemicellulose is a polysaccharide and therefore is expected to have a similar chemical composition and density to cellulose. Thus it is assumed that  $\delta_{polymer} \approx \delta_{cell} \approx \delta_{hemi} \approx \delta_{lignin}$ . This allows simplification of small angle neutron scattering in paper through isotopic substitution if the D<sub>2</sub>O:H<sub>2</sub>O ratio is chosen so that the scattering length density of the moisture in the sample is equal to that of either the polymer or the voids. In the experiments described in this paper a D<sub>2</sub>O:H<sub>2</sub>O ratio of 8:92 was chosen so that there was no contrast between the water and the voids.

#### Proton NMR

Spin diffusion experiments were conducted on an MSL-300 spectrometer operating at a proton frequency of 300.13 MHz. The dipolar filter pulse sequence [48] was used to selectively excite the mobile fraction of the proton spectra based on differences in spin-spin relaxation times,  $T_2$  [32]. The sequence consists of 12 90° pulses separated by 10 µs cycled 7 times. The filter is followed by a time delay,  $t_{mix}$ , to allow exchange before a 90° pulse is used to read the magnetisation (Figure 7). The 90° pulses were 4 µs long and the time between points on the FID was 0.5 µs.

Each experiment consisted of a series of free induction decays (FIDs) accumulated for each value of  $t_{mix}$ . The free induction decay is a digitized signal from the detector coil. Details of the method for processing solid state free induction decays into spectra can be found elsewhere [49]. A linear baseline was then subtracted from each spectrum. Each spectrum consisted of two peaks, one broad from rigid protons in the polymer and the other narrow from mobile (water) protons. The spectra were integrated to obtain the magnetisation in each phase as a function of  $t_{mix}$ .

The interpretation of the spin diffusion experiment is based on an understanding of the exchange of magnetisation between the polymer and water phases. During  $t_{mix}$  there is a loss of the total amount of magnetisation to the lattice and it is necessary to correct for this loss [32]. This loss can be estimated by expressing the magnitude of the third point of the digitised free induction decay as a function of  $t_{mix}$  [49]. The resulting decay,  $M_z(t_{mix})$ , can be fitted by a biexponential decay:

$$M_{z}(t_{mix}) = A + X_{fast} \exp\left(\frac{-t_{mix}}{T_{1}^{fast}}\right) + X_{slow} \exp\left(\frac{-t_{mix}}{T_{1}^{slow}}\right)$$
(8)

where A is an experimental offset, X is the relative number of protons in each decay and  $T_1$  is the characteristic decay time of a two component



**Figure 7** The dipolar filter sequence. After 7 filter sequences  $(12 \times \pi/2 \ (90^\circ) \text{ pulses})$  the distribution of magnetisation is monitored with a 90° pulse after a delay,  $t_{mix}$ . During  $t_{mix}$  magnetisation diffuses back into the rigid proton region.



Figure 8 The loss of magnetic polarization to the lattice during the spin diffusion experiment for eucalypt NSSC handsheets equilibrated in a 97%RH atmosphere.

system, one relaxing more slowly that the other (Figure 8). The two values of  $T_I$  used to fit the data fell in the range: 4 ms  $< T_1^{\text{fast}} < 20$  ms and 400 ms  $< T_1^{\text{slow}} < 900$  MS. Generally it has been found that polymer spin-lattice relaxations in paper are of the order of 100 ms and water 10 ms. The short  $T_I$ component is attributed to water and the longer to polymer. Often this set of data is the subject of detailed analysis [33]. The analysis of the spin-lattice relaxation is complicated greatly by the combined effects of spin-diffusion between phases and the spin-lattice relaxation in each component [50,51]. The effects of spin lattice relaxation can be removed by estimating them using the fit to Equation 8 for the data set. The characteristic times for each phase can then be used to correct the integral intensities according to the method of Clauss *et al.* [48].

#### **RESULTS AND DISCUSSION**

#### **X-ray Diffraction**

X-ray scattering profiles were obtained for the filter paper and eucalypt kraft and NSSC handsheets. An example of an x-ray diffraction profile fitted with Voigt functions is shown in Figure 5. Table 3 contains the angular position and the integral breadth of each reflection. There is a slight variation in the peak positions from one sample to another that can be attributed to slight differences in the average lattice spacing for the various samples [12]. The angular width of each reflection and the wavelength of CuKa (1.542 Å [17]) have been inserted into Equation 1 to calculate the crystallite widths (Table 3). Following Newman [52] we used the 002 spacing (200 in the lattice of Sugiyama *et al.* [53]) to estimate the size of the crystallites because it is the most clearly resolved of the three x-ray reflections. The relationship of each reflection to a monoclinic lattice [13] is shown in Figure 3. All these

**Table 3** The position of the maximum  $(2\theta_{max})$ , width at half maximum integral intensity ( $\beta$ ) and crystallite width ( $\tau$ ) (obtained using Equation 1) for lattice reflections after Meyer and Misch [13].

Reflection		101			101			002	
	$2\theta_{max}$	β	τ	$2\theta_{max}$	β	τ	$2\theta_{max}$	β	τ
Sample	(±0.05°)	(±0.05°)	(±2 Å)	(±0.05°)	(±0.05°)	(±2 Å)	(±0.05°)	(±0.05°)	(±2 Å)
Filter paper	14.95	1.58	56	16.58	1.61	55	22.80	1.18	75
BEK	15.14	2.25	39	16.64	2.73	32	22.83	1.72	51
NSSC	15.28	2.73	32	16.68	2.57	34	22.68	1.87	47

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measurements relate to dimensions that lie perpendicular to the axis of the microfibril and are therefore measurements of lateral dimensions.

It can be seen that the cellulose microfibrils of filter paper are larger than those of the other two samples. The values for the crystallite sizes are slightly higher than those found for similar materials [52]. This is entirely attributable to the different values of k used here and in that work. Although Scherrer originally suggested that the value of k is close to one and is dependant on the aspect ratio of the crystallites, subsequent treatments have fixed the value at one [11]. Filter paper has the largest crystallites and therefore the smallest surface to volume ratio of the crystallites. The eucalypt NSSC handsheets have the smallest crystallites. The relative difference in the two eucalypt crystallite sizes is no greater than that previously observed between NSSC pulps from different eucalypt species [52,53]. Thus the difference cannot be ascribed to general differences between kraft and NSSC pulps as the mix of species used for the two pulps is not identical.

Assuming the model we have adopted for the cellulose crystallite, some workers [2,3] have used the lateral crystallite dimensions to estimate the fraction of crystalline cellulose. An additional feature is imposed where an arbitrary number of layers of cellulose chains on the surface of the microfibrils are designated as amorphous and the cellulose chains in the interior are considered crystalline. The latter assumption implies a greater understanding of the nature of the broadening of cellulose reflections than is evident in the literature. A simpler and more general interpretation is that smaller crystallites have more surface area and therefore contain more disordered cellulose.

#### SANS

Small angle neutron scattering profiles were obtained for the three paper samples described in the Experimental Section with no contrast between the water and the voids. The values of I(q) are shown as a function of q for the three samples in a number of relative humidities in Figure 9. From duplicate runs we found that the absolute intensity for a given q-value on the same sample can vary by as much as 5% in different experimental runs. The main uncertainty appears to reside in the transmission of the sample, the factor T in Equation 3. With a simple re-scaling of T (multiplication by a constant factor) it was found that the curves from duplicate runs can be made to closely match.

The log-log plots are linear in the low and high q-ranges in these experiments. All curves show an initial linear region ( $q < 0.02 \text{ Å}^{-1}$ ), the gradient of which decreases in magnitude with increasing relative humidity. At high

relative humidity an additional feature appears in each of the curves. For filter paper this feature appears as a distinct maximum in the small angle scattering. In the other two materials this peak is not as distinct, appearing as a change in concavity of the curve. It also appears to be shifted to higher q. The higher portion of the scattering curves ( $q > 0.1 \text{ Å}^{-1}$ ) is also linear. The counting statistics of neutrons in the region of low q is much better and as a consequence the relative precision of calculated slopes is much better close to the beam direction.

In principle it is possible to model the data across the entire q-range of the experiment. In practice this is only achieved for systems of well-defined and understood form and structure [25]. In this work we have analysed the data in terms of scattering laws which predict the limiting behaviour at high and low q. A simple observation from each curve in Figure 9 is that more neutrons are scattered as the sample hydrates. This means that there are more density fluctuations in the q-range studied. Rearranging the Bragg diffraction equation in terms of q can reveal the length scales involved:

$$d = \frac{2\pi}{q} \tag{9}$$

where *d* is the length scale.

The Guinier Law [45] interprets the initial slope of a log I(q) versus  $q^2$  curve.

$$I(q) = (\Delta\delta)^2 v^2 \exp\left(\frac{-q^2 R_g^2}{3}\right)$$
(10)

where v is the volume of the scattering particles and  $R_g$  is the radius of gyration of the particle.

The main assumptions of the Guinier Law are that:

- q is much smaller than  $1/R_g$ .
- Particles scatter independently of each other.
- The scattering bodies are isotropically distributed in the sample.

These conditions are best satisfied in the low q-range that can be referred to as the Guinier region. The radius of gyration is a convenient means of characterizing a particle irrespective of its shape. It is the root-mean-square distance of all the points in the scattering particle from its centre of mass [56]. Given this, it is possible to interpret  $R_g$  as an average for a polydisperse system. However it is not possible to determine polydispersity of the particles



Figure 9 The small angle neutron scattering from a) filter paper, b) BEK handsheet, and c) eucalypt NSSC handsheet as a function of the wave vector q at a number of humidities (8% D<sub>2</sub>O in H<sub>2</sub>O).



Figure 10 The radius of gyration of voids in filter paper, BEK handsheets and eucalypt NSSC handsheets as a function of relative humidity (8%  $D_2O$  in  $H_2O$ ). Lines are to aid the eye only.

from the SANS experiment in the Guinier region [45], and as a simplifying assumption we assume the system is monodisperse.

 $R_g$  has been calculated from the initial slope of the ln(I(q)) versus  $q^2$  curve, with all initial slopes giving  $r^2 > 0.99$ . These high  $r^2$  values are not surprising if the system obeys the Guinier Law since this region is close to the primary beam where the counting statistics are good. Guinier Law behaviour has been found in the low q range for SAXS of rayon [21] and plant fibres [19,20] and SANS of rayon fibres [4]. The calculated values of  $R_g$  are shown as a function of ambient relative humidity in Figure 10. At low relative humidities the radius of gyration of these voids is similar in all samples. There is a general decrease in  $R_g$  with increasing moisture content. The greatest effect is found in the bleached material. The filter paper and the BEK and eucalypt NSSC handsheets, all exhibit voids of approximately the same dimensions at low relative humidity. As the relative humidity increases the BEK voids are affected most by the sorption of moisture. The reduction in void size could be the result of swelling of the microfibrils or of the opening of new small pores by water molecules forcing microfibrils further apart, thus creating new



**Figure 11** Small angle neutron scattering from filter paper in a 97% RH atmosphere (8% D<sub>2</sub>O in H<sub>2</sub>O) replotted to include *d*, the repeat distance (Equation 9).

scattering centres. A possible reason for the difference in behaviour of BEK and NSSC sheets is that the lignin matrix around cellulose microfibrils in the NSSC sheets is able to restrict the swelling of the microfibrils whilst the hemicellulose associated with the microfibrils in BEK sheets promotes swelling.

The intercept of the ln(I(q)) versus  $q^2$  plot is related to the volume fraction of scattering "particles" (voids) and the contrast factor (i.e. the scattering length density of cellulose  $(\Delta \delta)^2 = \rho_{cellulose}^2$ , Equation 10). It is possible to use the volume of the particle obtained from the intercept of the Guinier plot with the Y axis and relationships between the dimensions of a known geometry and  $R_g$  to determine the absolute dimensions of the scattering body [56]. However we have found that the values of I(0) obtained by extrapolation are experimentally noisy and no trends could be identified. This is attributed to the transmission uncertainty discussed above. Additionally, it would be expected that where the voids run parallel to microfibrils, as in the model in Figure 1, changes to  $R_g$  as the long thin voids become thinner will be subtle and difficult to resolve.

The length scales, d, for the filter paper were calculated using Equation 9.

The data for this material at 97% RH have been replotted in Figure 11 with d on the top X-axis. The hump in the plot is broad and ill-defined and falls at approximately 100 Å. It appears in all samples at high relative humidity. In the two samples in which the crystallites were found to be smaller, the NSSC and BEK handsheets, the feature is shifted to larger q values, i.e. smaller length scales. The feature would appear to be associated with microfibrils and, because it is a maximum in intensity, to be a repeat structure of variations in  $\delta_i$ . Similar features, short range order (interference maximum) have been seen in wood fibres [23] and in chemically swollen [19] and moisture swollen cellulose fibres [20]. These features are attributed to the formation of repeat structures based around the microfibril. In the case of wood, the microfibril is surrounded by a layer of hydrated polymer. In cellulose fibres layers of water surround the crystalline region. We conclude that this structure is layers of water, a layer of hydrated cellulose and the crystalline core of the microfibril (Figure 12).

In the high *q*-region Porod [57] showed theoretically that for an ideal twophase system bounded by a clear interface of area *S*, as  $q \rightarrow \infty$ :

$$I(q) \to \frac{2\pi (\Delta \delta)^2 S}{q^4} \tag{11}$$

In scattering which obeys the Porod Law  $I(q).q^4$  plotted against  $q^4$  the plot is parallel to the X-axis at high q, and the Y-axis intercept is proportional to the surface area. Luzzati *et al.* [58] modified this approach to include the effects of the lack of homogeneity of the two phases. When  $I(q).q^4$  is plotted against  $q^4$  the result at high q is a straight line of the form:



Figure 12 The proposed unit of short range order, a swollen cellulose microfibril and a layer of water.

$$I(q).q^4 = K_1 + K_2 q^4 \tag{12}$$

where  $K_1$  and  $K_2$  are constants. The slope,  $K_2$ , is a constant at high q that determines the correction  $(K_2, q^4)$  that is subtracted from the scattering curve  $I(q).q^4$  to obtain  $I_{corr}(q).q^4$ .

In the limit of the high q-range of this study, the eucalypt NSSC and BEK handsheets show the effect of the diffraction peak due to a periodic structure and are quite noisy in I(q). The following discussion is therefore confined to the high q scattering of filter paper as a function of moisture content. The value of  $K_2$  for filter paper was the same,  $0.22 \pm 0.01$ , for all relative humidities.  $I_{corr}(q).q^4$  versus  $q^4$  has been plotted for a range of relative humidities to give a qualitative indication of the changes in surface area as the sample hydrates (Figure 13). The surface area is proportional to the y-intercept of the high-q region of the plot. The surface area of filter paper clearly increases as a function of relative humidity. The quantitative interpretation of this data is hampered by the large scatter of points at high  $q^4$  due to poor counting statistics at high q, the uncertainty in the absolute intensity and the lack of a clear interfacial region (reflected in the value of  $K_2$ ). Nevertheless it does



**Figure 13**  $I_{corr}(q).q^4$  as a function of  $q^4$  for filter paper in various relative humidity atmospheres (8% D<sub>2</sub>O in H<sub>2</sub>O).

indicate that water is able to access increasing surface area for further water binding as moisture content increases. This must occur through the disruption of hydrogen bonding between polymer molecules.

#### Proton NMR

To study the dispersion of water through the polymer matrix, the process of magnetisation exchange between polymer and water spins, after selective excitation by the dipolar filter pulse sequence, was followed for samples of differing moisture content. Figure 14 plots the spectra for each time delay,  $t_{mix}$ , for samples of NSSC handsheet equilibrated with 97% RH. At the shortest time delay, there is a single narrow peak. As the  $t_{mix}$  increase the relative intensity of this peak decreases and a broader peak evolves. The narrow peak is due to water whilst the broad peak is due to protons in the polymer which are more rigid and therefore have more efficient spin-spin relaxation. The interpretation of this experiment is based on the evolution of exchange of magnetisation between the two protons which comprise the narrow peak (mobile) to the protons which comprise the broad peak (rigid). No discernable difference was found in the position of the broad peak for eucalypt NSSC, BEK and filter



Figure 14 The proton spectra from the dipolar filter pulse sequence for a range of values of  $t_{mix}$  for a eucalypt NSSC handsheet equilibrated in a 97% relative humidity atmosphere.

paper. Chemical differences in the samples are lost in the dispersion of the chemical shifts and the efficient dipolar coupling.

A series of spectra for each sample at different relative humidities has been deconvoluted and the integral of each spectrum plotted as a function of  $(t_{mix})^{1/2}$ . Figure 15 illustrates one such plot and the features general to each sample will be discussed. As  $t_{mix}$  increases the magnetisation in the mobile proton phase (water),  $M^{\nu}$ , decreases and the magnetisation in the rigid phase,  $M^{p}$ , increases. At longer time periods the overall magnetisation in the solid phase decreases. Significant loss of magnetisation due to spin-lattice relaxation in the time scale of ms is commonly observed in hydrated polymeric systems [30].

The model under which the data is analyzed is illustrated schematically in Figure 16. There are two pools of magnetisation that can clearly be exchanged (Figure 15). Each of the magnetisation reservoirs is connected to the lattice, allowing magnetisation to leak from the system. The transport between the magnetisation pools occurs via a layer of water which exhibits dynamics more like that of a solid. This allows dipole interactions to



**Figure 15** Magnetisation, *M*, as a function of  $(t_{mix})^{1/2}$  for the two proton fractions, mobile (water) and rigid (polymer), of eucalypt NSSC handsheets equilibrated in a 97% RH atmosphere.



Figure 16 A schematic of the nuclear spin system considered in this work. It consists of two reservoirs of magnetisation (water and polymer). The exchange between reservoirs is by spin diffusion (Equation 2), and the loss from each reservoir has a characteristic time constant,  $T_1$  (Equation 8).

exchange magnetisation. It is assumed that this proton fraction is in diffusional exchange with a more mobile water fraction which, by virtue of its motional dynamics, has very poor communication with the polymer protons. The interpretation of the experiment is based on the initial rate of transport where it is assumed that the transport of magnetisation is controlled by the relative amount of bound water.

The initial rate is determined from the  $T_1$  corrected data (Figure 17). The intensity at  $t_{mix} = 0$  is normalized to 1, plotted against  $(t_{mix})^{0.5}$  (see Equation 2), and the initial slope is taken. The initial rate approximation [32,59] predicts that the initial slope of  $M^w(t_{mix}^{1/2})$ ,  $\Delta M^w/\Delta t_{mix}^{1/2}$ , is linear. This was found to be the case for all samples. The values for the slope of the  $T_1$  corrected magnetisation curves are plotted against the relative humidity in Figure 18.

In the initial rate approximation the slope,  $\Delta M^{\nu}/\Delta t_{mix}^{1/2}$  is a function of  $D_{water}$  and the area of the interface between the two domains *i.e.* the size and morphology of the domains [48]. Using the heat flow analogy, heat (magnetisation) is introduced in a dispersed phase. The rate at which the dispersed phase (water) transfers heat to the surrounding medium (polymer) is related to the diffusivity ( $D_{water}$ ) of the phase and the size of the interfacial region (see Figure 4). As previously noted, the efficiency of dipolar coupling drives spin diffusion, however in liquid-like water (as demonstrated by



Figure 17 The raw data, and data corrected for spin lattice relaxation, for the magnetisation from the mobile phase as a function of  $t_{mix}$  for a eucalypt NSSC handsheet equilibrated in a 97% RH atmosphere. The line is the initial slope of the corrected data.



Figure 18 The initial slope,  $\Delta M^{\nu}/\Delta t_{mix}^{1/2}$ , for the three paper samples with increasing relative humidity. Lines are to aid the eye only.

motional narrowing of lines) the process is much slower. It seems likely that mobile water exchanges mass with a bound layer which is less mobile and can thus exchange magnetisation with the solid phase more easily. Indeed mass exchange between bound water and free water has been demonstrated experimentally [8]. It can also be shown that the diffusion of a liquid to an exchange surface in a very small pore can be approximated by an effective diffusion co-efficient [28].

For all materials, the initial value of  $\Delta M^{\nu}/\Delta t_{mix}^{1/2}$  decreases in magnitude between 9 and 97% RH. This trend contains information about changes in the distribution of water with increasing relative humidity. If water is sorbed to handsheets in regions of uniform size and dimensions,  $\Delta M^{\nu}/\Delta t_{mix}^{1/2}$  will remain constant since bound water can exchange magnetisation much more efficiently than free water. This quantity reflects the ratio of bound to free water. For more disperse water, smaller regions and greater surface area, the magnitude of  $\Delta M^{"}/\Delta t_{mix}^{1/2}$  increases. Since the value decreases, in this model water must condense into larger aggregates where there is a larger proportion of free water. For filter paper and the NSSC handsheet the slope remains constant up to 97% RH. This is consistent with the analysis of water sorption curves using the Zimm-Lundberg [60] cluster model which predicts a large increase in the cluster size near saturation [61]. The slope for BEK decreases steadily with increasing relative humidity. This material consists largely of pure cellulose but there may be some hemicelluloses that modify the interaction between polymer and water

#### CONCLUSIONS

A poorly resolved diffraction peak appears at high humidities in all three samples. The repeat distance is slightly larger than the crystallite size in all cases. The presence of this peak has been noted in other small angle scattering studies of the swelling of cellulosic fibres. This peak is attributed to a structural unit consisting of a cellulose crystallite surrounded by a layer of swollen cellulose and a layer of water. The widths (in terms of molecules of cellulose and water) of these layers is unknown. Lignin in the NSSC sheet that restricted the swelling of the microfibril does not affect the appearance of this peak.

X-ray diffraction and small angle neutron scattering have proven powerful tools to study the changes in morphology due to the sorption of water. A layer of disordered cellulose surrounds the cellulose crystallite. When the fibre is dry, the structure is consolidated (exhibits no short range order) with pores formed from the non-ideality of the packing of microfibrils into fibres. Microfibrils interact with each other, presumably through hydrogen bonding, at the disordered crystallite surface. With increasing humidity the fibres swell and the voids are filled. The relative swelling of the lignified NSSC material was less than that of either the bleached eucalypt kraft, or filter paper, and it is concluded that the presence of lignin restricts the swelling of disordered cellulose.

In terms of the model adopted moisture first causes the disordered layer around the microfibril to swell. This swelling appears to be affected by the presence of lignin and hemicellulose. NSSC hand sheet containing both lignin and cellulose seems to swell less than filter paper and the BEK hand sheet. Clearly interactions between the disordered cellulose and these polymers is important in the swelling behaviour. At the high humidity a layer of liquid water between the microfibrils explains the appearance of a periodic structure larger than the microfibril. This happens in all materials and does not appear to be affected by the presence of other wood polymers in the paper. The analysis of NMR spin diffusion experiments is consistent with this interpretation.

The ability of water to swell and open up the structure of paper at microscopic length scales has been demonstrated. Scattering in the high q range indicates an increase in the effective surface area, and therefore exposed hydroxyl groups of cellulose. These experimental results indicate that water first swells the amorphous material around the microfibril. In doing this water must displace hydrogen bonds between cellulose molecules. This will plasticise the polymer chains and may displace hydrogen bonds between neighbouring microfibrils. Spin diffusion results studying the transfer of magnetisation between polymer and water indicate that the dispersal of water in the matrix is not uniform and are qualitatively consistent with changes in the arrangement of microfibrils inferred from SANS.

The ability of water to expose potential binding sites and presumably open up the structure of cellulosic fibres is not universal. Any hydroxyl group on a carbohydrate molecule has the opportunity to hydrogen bond with its neighbors or water. In some situations exposure to moisture can cause a more dense structure to form. Amorphous cellulose had the tendency to recrystallize to cellulose II when exposed to moisture. Hornification while marked with specific changes in macroscopic fibre properties is also associated with changes in fibre density perhaps to due to recrystallisation of cellulose [62]. In the case of plasticisation hydrogen bonding between cellulose chains is facilitated by water and in other cases cellulose chains are free to undergo both cooperative long range and segmental motions. Water in effect competes for binding sites with cellulose chains. As Nissan [63] points out, the kinetics of this process have important implications for macroscopic behaviour, in terms of formation or dissolution of load bearing bonds, and also in accessibility of cellulose for further disruption of cellulose/cellulose bonding.

Finally it is interesting to speculate on the nature of the interactions which cause microfibrils to separate at high humidities. Two microfibrilar surfaces are forced apart by the inclusion of water between them to produce the short-range order observed here. The intercalation of water between microfibrils interactions has important implications for the number of load bearing structures in fibres [64]. The interaction between cellulose surfaces at short length scales will also become important as water is removed from the fibres during the formation of the sheet. Certainly long range electrostatic forces are of primary importance between cellulose surfaces, but as surfaces are brought into contact, an attractive and a short range repulsive interaction are experienced [65]. In all fibres, including the NSSC material, water was able to force apart surfaces.

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# **Transcription of Discussion**

# AN EXPERIMENTAL STUDY BY NMR AND SANS OF THE AMBIENT HYDRATION OF PAPER

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#### Thad Maloney JM Huber

I'm a little confused about one figure, in your neutron scattering experiment you have one figure (Figure 10, Page 379) where you show the voids between microfibrils as a function of RH and at zero RH the voids have a radius of gyration of about 16 *nm*, does this means that in dry cellulose you are suggesting that there are 32 *nm* diameter pores in the cell wall?

#### Ian Parker

Yes in the dry cellulose there obviously appears to be significant voids between the fibrils, and that's certainly something that has been observed in other eg Tercell fibres.

#### Thad Maloney

I have to say that I disagree that in dry cellulose there are any pores in the cell wall because why don't we see these, we should be able to measure these with Mercury porosimetry or on density measurements, and we don't.

#### Ian Parker

They may not be readily accessible to the Mercury, as they may be in the interior of the fibres.

#### Discussion

# Thad Maloney

OK, but the density of the cell wall is around  $1.55 \text{ kg/m}^3$ , which is the density of pure cellulose so there are no mysterious voids inside the cell wall, that is my opinion.

#### Ian Parker

All we can do is quote what the neutron scattering experiments are indicating; something is doing the scattering there. Perhaps we are seeing fibrils and 'voids' at the surface of fibres.

#### Jonathan Phipps Imerys Minerals

You showed how you made the voids and the water appear the same to the neutrons by adjusting the Hydrogen/Deuterium ratio of the water (contrast matching). How important is it to get the Hydrogen/Deuterium ratio absolutely right, and what would you expect to see if there were a slight error in the ratio obtained – how would that influence the scattering?

#### Ian Parker

There would be something similar to what you would observe if you were using matching of refractive indices in microscopy, the further you go from the match of course, the larger the amount of scattering that occurs but as long as you are reasonably close there is minimal scattering. In these cases you can match very accurately to the voids.

#### Jonathan Phipps

And can you see that from the experiments that you have hit a good match?

#### Ian Parker

Yes you can very accurately produce the mix of the Deuterium based, *i.e* the heavy, and the normal water.

#### John Peel Retired

If I understood this paper correctly, and there was a lot to take in, you referred to the water penetrating between microfibrils, which cause the

collection of microfibrils to swell and thereby decrease the volume between the large macrofibrils. Is there a point reached eventually where the whole structure begins to swell, where the gap between the macrofibrils then begins to enlarge. Is that likely to happen if the RH goes above 97%?

#### Ian Parker

I think at 97% we are close to the maximum RH at which you can actually do an experiment. Obviously if you put a lot of water into the structure you get swelling of the fibres so that the whole structure is swelling and you are forcing the fibrils apart, so yes certainly that occurs.

#### Derek Page Institute of Paper Science & Technology

I have to agree with Thad Maloney, there is an awful lot of experimental data which suggests that there aren't any voids in the dry cell wall. I am not familiar with the techniques that you have used. I am however familiar with the techniques which show pretty conclusively to my mind, that there aren't any voids in the cell wall. For example in addition to what Thad has suggested there is the evidence of specific surface by nitrogen absorption. There is no internal surface in dry fibres. Also there is the question of what would be the surface energy of a fibre that had this enormous quantity of surface area inside it? I would like to suggest a mechanism for the shrinkage of fibres upon drying, in the extremely dry regime and subsequent re-swelling by water. When the cell wall dries the surface tension forces become enormous as the last remnants of water evaporate. We have seen diagrams and indeed micrographs of crystallites which cannot, without deformation pack into a voidless structure. They are too irregular and dissimilar. But the modulus of the fibrils in the transverse direction is guite low, being dependent only on hydrogen bonds. I propose that the fibrils deform elastically under the forces of surface tension to allow pushing with no void space. This when water is reintroduced into the fibre, swelling is driven by the stresses in the fibrils. As the voids open up and are filled with water, the stresses in the fibrils relax to zero. I was wondering if you could check whether this hypothesis is supported by your data?

#### Ian Parker

Thank you for the suggestion.

#### Discussion

# Lars Ödberg AssiDomän

I have a more technical question. I guess you mix heavy water and ordinary water and then you equilibrate the fibres with that mixture. Can you be sure that in the fibres you have the same ratio of  $H_2O$  to  $D_2O$  as you had in your liquid phase, because I think it is known that that the hydrogen bond strength is not the same for ordinary water and  $D_2O$ ?

# Ian Parker

Contrast matching with mixtures of  $D_2O$  and  $H_2O$  is a well established technique.