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The hydration of paper studied with solid-state magnetisation-exchange ^{1}H NMR spectroscopy

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Abstract

The wide-line ^{1}H nuclear magnetic resonance (NMR) spectrum of paper in equilibrium with ambient humidity consists of super-imposed relatively broad and narrow lines. The narrower line is of the order of 2 kHz wide at half the maximum height, while the broader line is of the order of 40 kHz in width at half height. On the basis of these line widths, the narrow line is assigned to water sorbed to the paper, and the broad line to the polymeric constituents of the paper. It was not possible to distinguish between the various polymeric components of paper contributing to the ^{1}H NMR spectra. A modified Goldman-Shen pulse sequence was used to generate a spatial magnetisation gradient between the polymer and water phases. The exchange of magnetisation between protons associated with water and those associated with the macromolecules in paper was observed. The exchange of magnetisation is discussed within a heat transfer model for homonuclear dipolar coupling, with exchange being characterised by a spin-diffusion coefficient. Consideration of the magnitude of the initial rate of the exchange process and estimates of the spin-spin relaxation times based on ^{1}H line widths indicate that some water must exist in a sufficiently immobile state as to allow homonuclear dipolar interactions between adjacent polymer and water protons. Thus, water sorbed onto paper must exist in at least two states in mass exchange with each other. This observation allows certain conclusions to be drawn about the ratio of free/bound water as a function of moisture content and the dispersal of water within the polymer matrix.

Keywords: hydration; NMR spectroscopy; paper; spin diffusion.

Introduction

Paper is quite hydrophilic and under normal ambient conditions, water is sorbed to paper and constitutes a significant weight fraction. If the relative humidity increases, the weight fraction of water increases until it reaches equilibrium. Conversely, if the relative humidity decreases, paper loses sorbed moisture until it once again attains an equilibrium moisture content. The mass content of water is a function of both the ambient humidity and the path by which equilibrium was approached (Venkateswaran 1970). The sorption of water has a profound effect on the mechanical properties of the structure. This observation can be rationalised at a molecular level by considering the preponderance of polysaccharide chemistry in these materials and the ability of water to disrupt hydrogen bonding. Having previously directly demonstrated the ability of water to disrupt hydrogen bonding between polymer chains as a function of the moisture content (Garvey et al. 2004), in this study we examined the interaction between mobile water molecules and the polymer.

In a review, McBrierty et al. (1999) outlined the complexity of the terminologies used to describe the motional states of water sorbed into polymeric systems. They classified the models used to describe water as either discrete or continuum models. A discrete model of water postulates different classes or states of water that may exist and potentially undergo mass exchange with each other. The simplest of these models has two types of water, one that is motionally constrained by interactions (bound) with the surface and another that behaves much like liquid water (unbound; Resing 1972).

Bound water is thought to be hydrogen-bonded to the hydroxyl groups on exposed surfaces of the cellulose fibres. Nissan (1976) presented a general theory describing the effects of moisture on hydrogen-bonded materials and the kinetics of this effect based on the ability of water to displace hydrogen bonds between load-bearing polymer chains. An alternate perspective for the effects of moisture on cellulosic fibres is the concentration-dependent ability of moisture to lower the glass transition temperature of amorphous cellulose towards its own glass transition temperature (Salmén and Back 1977, 1980). The former approach involves a very specific interaction between the polymer and water; the latter treats the amorphous region of a semi-crystalline polymer as a mixture of water and polymer. However, the discrete and continuum models are clearly related. For example, increasing the degree of acetylation of cellulose results in a decrease in the degree of hydrogen bonding between the cellulose chains, and also lowers the glass-to-rubber transition temperature compared with unacetylated cellulose (McBrierty et al. 1996).

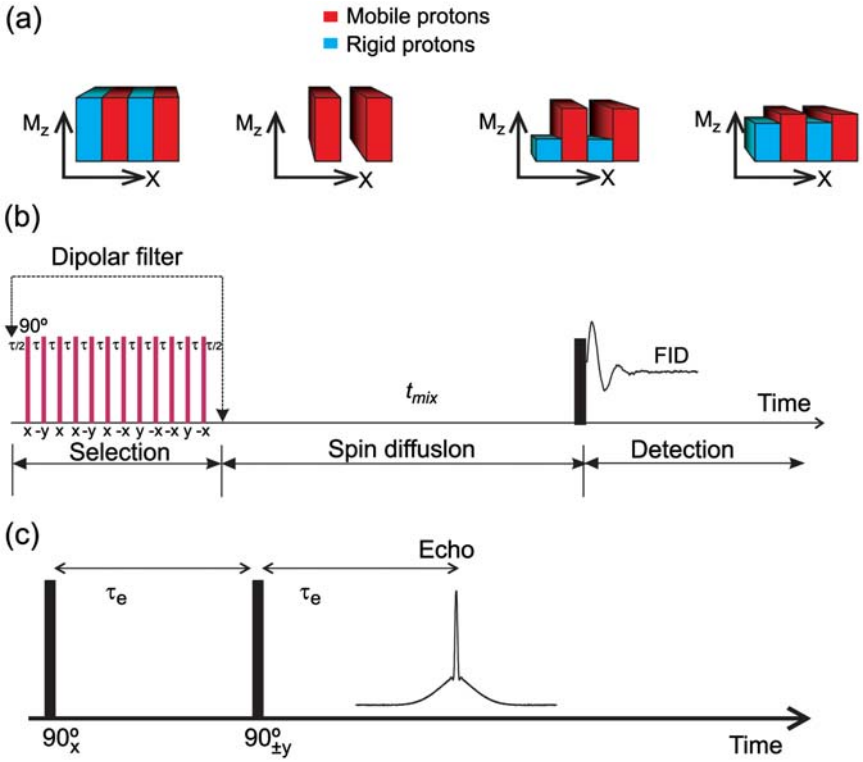

Figure 1 The NMR pulse sequence used to selectively excite one component of a multiphase system and (a) allow its return to equilibrium during (b) a delay t_{mix} is called the dipolar filter, as shown with a pulse sequence and phase cycle. Detection of the magnetisation after t_{mix} was carried out via a 90° pulse. (c) The solid-echo sequence was used to obtain a proton solid-echo.

To understand these states of water, measurements sensitive to the dynamics of water are usually employed. Suitable techniques include differential scanning calorimetry (Deodhar and Luner 1980), deuterium NMR (Radloff et al. 1996), ^{1}H NMR (Froix and Nelson 1975; Capitani et al. 1996) and inelastic neutron spectroscopy (Czihak et al. 1999). In general it is observed that there is water that resembles free water in its dynamics, as well as a fraction of water that may exist in one of many less mobile states. The number of states determined usually depends on the technique used and the time scale of the motion that the experimental technique probes (McBrierty et al. 1999). The relative population in each state also depends on the moisture content and the temperature of the sample (Froix and Nelson 1975; Radloff et al. 1996). It is not known if these states may undergo exchange with each other.

A particular approach to understanding the states of water in materials such as paper is to observe the transport of magnetisation from one state of water to the others, and to the polymer substrate. This transport can occur through a combination of molecular and spin diffusion. The first type of transport involves Brownian motion of water molecules and exchange of protons between water and the polymer substrate. Spin diffusion, on the other hand, involves the transfer of magnetisation between near-neighbour protons by dipole-dipole interactions (Abragam 1961).

A number of available NMR techniques are able to observe transport of magnetisation. The basic experiment involves generation of a spatial gradient in the magnetisation by selective excitation of the spins of one phase (Figure 1a) with a series of radio-frequency pulses (Figure 1b). Homonuclear dipolar coupling between adjacent spins in solids leads to a very efficient exchange process (Bloembergen 1949). The process of equilibration between the two phases can be followed as a function of the mixing time, t_{mix} (Schmidt-Rohr and Spiess 1994). In multi-phase systems such as polymer blends, the magnetisation exchange process is particularly sensitive to the amount of interfacial area between two phases (i.e., the surface/volume ratio or the phase morphology; Schmidt-Rohr and Spiess 1994) and the nature of the interface (degree of mixing) between the two phases (Wang 1996). The exchange process is energy-conservative in terms of magnetisation, but there will be some loss of magnetisation to the lattice due to spin-lattice relaxation during the experiment (Packer et al. 1984; Friebel et al. 1997).

Detailed descriptions of the use of the spin diffusion experiment as a structural probe are found elsewhere (Schmidt-Rohr and Spiess 1994) and only a brief summary is presented here. While a comprehensive analysis of spin diffusion is a complicated multi-body problem (Abragam and Goldman 1982), the description of the flow of magnetisation from one phase to another can be simplified using a simple heat-diffusion analogy (Schmidt-Rohr and Spiess 1994) and Fick's second law (Crank 1975):

$$\frac{\partial M(\mathbf{r},t_{mix})}{\partial t} = \nabla\,(D(\mathbf{r})\nabla M(\mathbf{r},t_{mix})), \qquad (1)$$

where **r** is a vector that describes position, t_{mix} is the time from the start of the experiment, $D(\mathbf{r})$ is the spin diffusion coefficient and $M(\mathbf{r},t_{mix})$ is the spatially varying magnetisation. D also varies spatially since the materials under consideration are heterogeneous. In the spin diffusion experiment illustrated in Figure 1, the magnetisation starts solely in one phase, but can diffuse into other phases.

There are a number of pulse sequences that are able to generate spatial magnetisation gradients in solids. Selection can be based on differing chemical shifts in the proton spectrum (Caravatti et al. 1985), T_1 relaxation times (Packer et al. 1984) or rotating frame spin-lattice relaxation times (Schmidt-Rohr and Spiess 1994). Goldman and Shen (1966) reported a pulse sequence used to select magnetisation on the basis of differences in T_2. The Goldman-Shen pulse sequence has been successfully applied to select magnetisation of mobile protons in heterogeneous polymeric solids (Packer et al. 1984; Kenwright and Packer 1990; VanderHart and McFadden 1996; Friebel et al. 1997) but multiple quantum coherences may lead to distortions of spectral line shapes (Schmidt-Rohr and Spiess 1994). The dipolar filter pulse sequence (Figure 1b; Schmidt-Rohr and Spiess 1994; Clauss et al. 1998) is similar to the Goldman-Shen experiment, but consists of multiple cycles of a similar pulse sequence. The effect is a filter that can be adjusted in strength (Landfester and Spiess 1998). It has been used to select the magnetisation from water protons in experiments on various hydrated polymers (Kulik et al. 1994; Radloff et al. 1996; Mellinger et al. 1998).

Estimation of the spin diffusion coefficient D for each phase is an important step in the use of spin diffusion experiments to evaluate the structure of the mixture. In solids, the value of D is related to the strength of dipolar couplings, and can be estimated directly from T_2 (Spiegel et al. 1993) or by calibration of domain sizes using small-angle X-ray scattering (Mellinger et al. 1999). In the more mobile regions of heterogeneous materials, dipolar couplings between nuclei become weaker; however, magnetisation may also be transported spatially by molecular diffusion in combination with dipolar couplings (Fisher et al. 1997; Fatkullin et al. 1998).

In this study, we investigated the states of water in various hydrated paper samples using the NMR experiments described above. Rather than simply categorising the states of water, we draw some conclusions about the gross morphology of the condensed water phase and exchange of water between a mobile and bound state based on the time-scales of magnetisation exchange.

Experimental methods

The paper samples used in this work were: Whatman number 4 filter paper; hand sheets produced from a commercial eucalypt neutral sulfite semi-chemical pulp (NSSC); 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 (Standards Australia 2001) before processing into handsheets. Samples were equilibrated with a known humidity atmosphere inside a glass tube (outer diameter 7 mm) and then sealed at either end with Teflon tape. The glass tube containing the piece of paper in equilibrium with known relative humidity (RH) was inserted into the detector coil of the spectrometer probe.

Wide-line ^{1}H NMR experiments were conducted on an MSL-300 spectrometer operating at a proton frequency of 300.13 MHz. Two separate pulse sequences were used. The solid-echo sequence (Powles and Mansfield 1962; Powles and Strange 1963) was used to collect proton spectra (Figure 1c). Each free induction decay (FID) from the solid-echo sequence was accumulated for 64 scans and consisted of 4000 complex data points. After removing the data points before the solid-echo maximum, the FID was then zero-filled to 4000 points to avoid truncation effects (Auñón and Chandrasekar 1997).

The dipolar filter pulse sequence (Figure 1b), used here to generate a spatial magnetisation gradient, consists of 12 90° pulses separated by 10 μs (τ) cycled seven times. The delay between pulses is sufficient to allow the ^{1}H signal from the polymer to dephase. The effect is to maintain magnetisation in the water or mobile phase (Landfester and Spiess 1998). The filter is followed by a time delay, t_{mix}, to allow exchange of magnetisation between mobile and rigid phases before a 90° pulse is used to read the magnetisation. The 90° pulses were 4 μs long and the time between points on the FID was 0.5 μs. Data acquisition for each spin diffusion experiment consisted of a series of 64 FIDs for each value of t_{mix}. A recycle delay of 5 s was used between proton spectra/value of t_{mix}. With the exception of having to remove points before the echo maximum in the case of the solid echo, processing of FIDs from the dipolar filter sequence is the same as for the solid echo. The baseline of the spectrum far from the polymer peak was clearly on a slope and thus a linear baseline was then subtracted from each spectrum.

Each spectrum consisted of two peaks, a broad peak attributed to rigid protons in the polymer and a narrow peak attributed to mobile (water) protons. The spectra were deconvoluted into two separate peaks and the areas of these peaks were used to obtain the magnetisation in each phase as a function of t_{mix}.

Results and discussion

The FID and spectrum resulting from a solid-echo experiment on a piece of NSSC hand sheet equilibrated at 97% RH is shown in Figure 2. Both the FID and the spectrum are typical of those found for all materials in a range of humidities. The FIDs consists of two regions: one region marked by a rapid decay of magnetisation and a longer-lived component. When the FID is processed and Fourier-transformed from the time to the frequency domain according to the method outlined above, the ^{1}H spectrum consists of a narrow line superimposed upon a broader line.

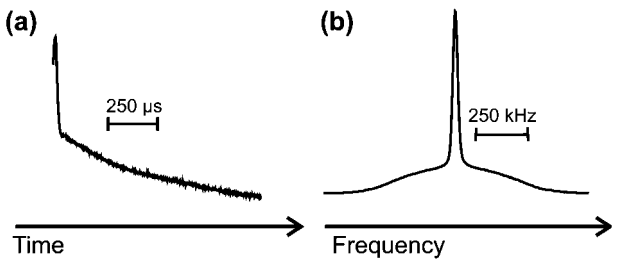

Figure 2 (a) Solid-echo FID from an NSSC hand sheet equilibrated at 97% RH and (b) the resulting Fourier-transformed spectrum.

Using a Gaussian line shape for the broad (polymer) component and a Lorentzian line shape for the narrow, more liquid-like line shape (Fukushima and Roeder 1981), the spectrum was deconvoluted using the PeakFit software (Jandel Scientific 1995). There were no resolvable differences in the line widths of either the narrow or broad components in the spectra of any of the materials at any humidity. The narrow line component had a line width of 2 kHz, while the broad component had a width of 42 kHz. A spin-spin relaxation time of 7 μs was calculated for the polymer fraction (Fukushima and Roeder 1981). This value is the same order of magnitude as found for rayon fibres (Froix and Nelson 1975) and saturated wood (Filbotte et al. 1990). In the work of both Filbotte et al. (1990) and Froix and Nelson (1975), multiple T_2 components were fitted to the decay. They found that the distribution of ^{1}H spin-spin relaxation times for hydrating cellulosic fibres (Froix and Nelson 1975) and wood (Filbotte et al. 1990) is complex and can in some cases be well approximated by four exponential decays.

The shortest decay time is attributed to solid polymer, where strong dipolar coupling between relatively immobile spins leads to rapid dephasing of the magnetisation. Paper is a composite material consisting of varying amounts of unitary semi-crystalline cellulose fibres (microfibrils) in an amorphous matrix of hemicellulose and lignin (Garvey et al. 2001). The exact chemical composition depends on the source of the paper (Garvey et al. 2001). Amorphous and crystalline regions of polymers often yield multi-component line shapes, especially when the amorphous phase is plasticised (Wilson and Pake 1953; Callaghan 1993). We could find no difference in the widths of the peaks from the polymers in paper from various sources or water phase at any humidity; only the relative intensities of each line shape changed. We therefore assume that the experiment is not able to differentiate between amorphous or crystalline cellulose, lignin and hemicellulose polymer components of paper. In the case of wood, a similar T_2 component to the overall relaxation has been reported for lignin and polysaccharide components of the plant cell wall (Filbotte et al. 1990).

Using other pulse sequences more suited to studying the distribution of T_2 values, a number of other T_2 components of the FID have been attributed to freely diffusing water in various confining geometries (Filbotte et al. 1990) or motionally constrained states (Froix and Nelson 1975) in cellulose-based fibres and wood. It is well known that both effects reduce the T_2 of water protons in porous solids (Cory and Garroway 1990; Callaghan 1993) and polymers (McBrierty and Packer 1993) from their bulk value. Radloff et al. (1996), in an analysis of the ^{2}H NMR spectra of deuterium oxide sorbed onto cellulose, constructed a phase diagram for D_2O absorbed on amorphous cellulose as a function of both moisture content and temperature. In common with earlier work, they suggested that in the ambient temperature range studied, there is some water that is bound, which is in exchange with free water.

The longer T_2 component evident in the FID and narrow line shape in the spectrum are attributed to water. On the basis of the literature observations cited above, we conclude that the narrow line is due to protons that belong to water that is in exchange between the bound and free states. The time-scale of this exchange is such that it causes a single line shape to be evident for both water components.

The ^{1}H NMR line widths can be used to estimate the order of magnitude of the spin diffusion coefficient (McBrierty and Packer 1993; Spiegel et al. 1993, 1994). The probability of the dipolar transitions is directly related to the distribution (density) of spins and, importantly, is modulated by molecular motion. An estimate of the spin diffusion coefficient, D, can be obtained from the transition rate, Ω, and the average separation between nuclei, a:

$$D = \Omega a^2. \tag{2}$$

The probability of the flip-flop transition is related to the strength of the dipolar coupling and the line width. Thus, Bloembergen (1949) has written for a rigid system:

$$D \propto \mathrm{FHWM} \cdot \langle a^2 \rangle, \tag{3}$$

where $\langle a^2 \rangle$ is the average of the square mean displacements between protons and FHWM is the width of the peak at half height. This relationship has been used by Spiegel et al. (1993) to estimate the spin diffusion coefficient for polystrene-polybutadiene diblock copolymers. For example, for polystyrene that has a similar line width (40 kHz) to the broad line for a paper sample, they calculated a value of 0.8 nm^2 s^{-1}.

While it is possible in principle to use the transfer of magnetisation to the rigid phase to elucidate aspects of the size and contact between two polymer phases (Schmidt-Rohr and Spiess 1994), the situation here is somewhat more complicated. The mobile water phase is sorbed onto the surface of the cellulose microfibrils, so the water is in contact with the polymer phase and voids within the microfibrils. As the humidity increases, moisture fills the voids between the microfibrils and the contact between water and the polymer increases (Garvey et al. 2001). It is therefore difficult to use this experiment to determine the size of the water domains because the area of contact between the polymer and water is a function of moisture contact.

Figure 3a shows the spectra for each time delay, t_{mix}, after the dipolar filter pulse sequence for a sample of NSSC hand sheet equilibrated at 97% RH. The spectrum for the first delay, 0.2 ms, is shown in Figure 3b. Only the narrow component of the spectrum shown in Figure 2 is observed. This indicates that the pulse sequence is able to selectively excite the longer T_2 component of the spectrum that arises from water. Some further spectra at longer mixing times are shown separately to highlight the evolution of the spectral line shape with increasing t_{mix}.

At $t_{mix} = 20$ ms (Figure 3b), it is clear that the broader peak re-emerges underneath the narrow peak due to mobile protons. Figure 3b shows the spectrum at longer values of t_{mix} (2000 ms). This spectrum is dominated by the broad component and a significant loss of intensity of the narrow peak due to spin-lattice relaxation. To consider the evolution of the line shape and the magnetisa-

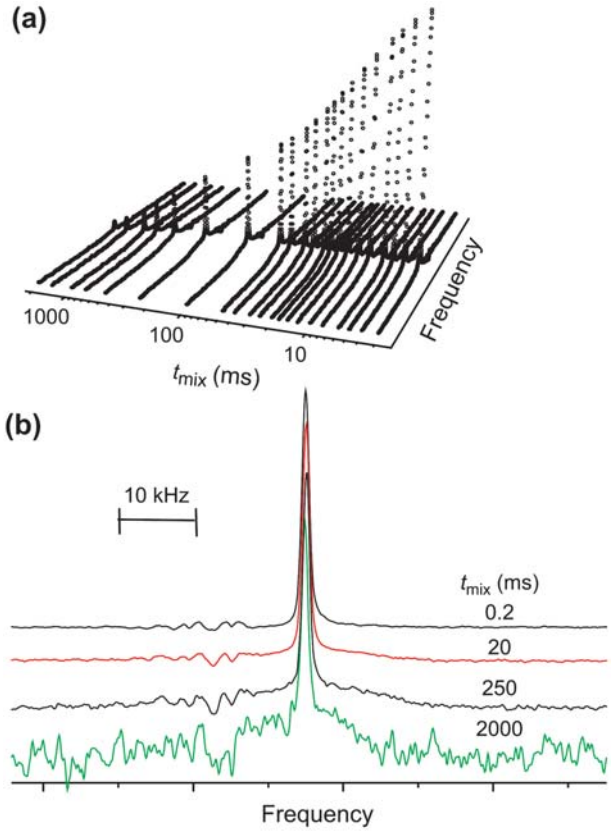

Figure 3 (a) Proton spectra from the dipolar filter pulse sequence for a range of t_{mix} values from a sheet of NSSC paper equilibrated at 97% RH. (b) Selected spectra (not to scale) indicate the change in line shape.

tion in each phase, $M(t_{mix})$, the spectrum for each sample at different relative humidities has been deconvoluted into signals from the water and solid polymer protons, and the integrated intensities of each component plotted as a function of $(t_{mix})^{1/2}$. The use of $t_{mix}^{1/2}$ reflects the diffusional nature of the model adopted for the spin diffusion process [see Eq. (1)]. Figure 4 illustrates such a plot and the features general to each sample are discussed. As t_{mix} increases, the magnetisation in the mobile proton phase (water), M^w, decreases and the magnetisation in the rigid phase (polymer), M^p, increases. At longer time periods the overall magnetisation in the solid phase decreases. A significant loss of magnetisation due to spin-lattice relaxation on a time scale of milliseconds is commonly observed in hydrated polymeric systems (McBrierty and Packer 1993).

Hydrated paper contains a greater weight fraction of polymer than water. The signal in the spectra obtained from the dipolar filter pulse sequence attributed to the water fraction is greater in intensity than that for the polymer. Landfester and Spiess (1998) observed the non-stoichiometric nature of peak ratios obtained from dipolar filter pulse sequences for polymer blends of differing mobility. When the results are interpreted and conclusions drawn about the structure of the system by numerical simulation of the diffusion model outlined in Eq. (1), the intensity of the peaks must be normalised for the volume fraction of protons in each phase (Wang 1996). Experimentally the relative intensity of the two peaks can be adjusted by applying more cycles of the dipolar filter sequence to adjust the strength of the filter (Landfester and Spiess 1998). In the case studied here, it is only the loss of magnetisation from the mobile phase that is of interest, and such corrections have not been applied.

At the start of the experiment, it is evident that magnetisation decreases in the mobile fraction and increases in the rigid fraction. At the longest time scales, magnetisation decreases in both phases, which indicates a loss of magnetisation to the lattice during t_{mix}. To estimate the initial rate of magnetisation transfer, it is necessary to correct for this T_1 relaxation (Schmidt-Rohr and Spiess 1994). The decrease due to T_1 relaxation can be estimated by expressing the magnitude of the third point of the digitised FID as a function of time from the start of last pulse of the filter sequence (Figure 1b), t_{mix} (Fukushima and Roeder 1981). The resulting decay, $M_z(t_{mix})$, can be fitted by the exponential:

$$M_z(t_{mix}) = A + M_z(0)\exp\left(\frac{-t_{mix}}{T_1}\right), \quad (4)$$

where A is an experimental offset, $M_z(0)$ is the time-zero magnetisation and T_1 is the characteristic decay time. The values of T_1 used to fit the data fell in the range $500\ \text{ms} < T_1 < 1200\ \text{ms}$.

Detailed analysis of spin-lattice relaxation in cellulose (Froix and Nelson 1975; Capitani et al. 1996) is greatly complicated by the combined effects of spin diffusion between phases and the spin-lattice relaxation in each component. This is the probable reason for the observation of a single exponential for spin-lattice relaxation rather than a bi-exponential, which might be expected for the quite different spin-lattice relaxation characteristics of polymer and water (McBrierty and Packer 1993). Similarly, the presence of spin-lattice relaxation in the spin diffusion experiment limits the length scales the magnetisation exchange experiment can probe (Vander-Hart and McFadden 1996; Friebel et al. 1997). For the purpose of this study, the effects of spin-lattice relaxation were estimated using a fit to Eq. (4) for each data set. This is an empirical correction, whereby the corrected $M_z(t_{mix})$ for rigid and mobile phases has a slope that is

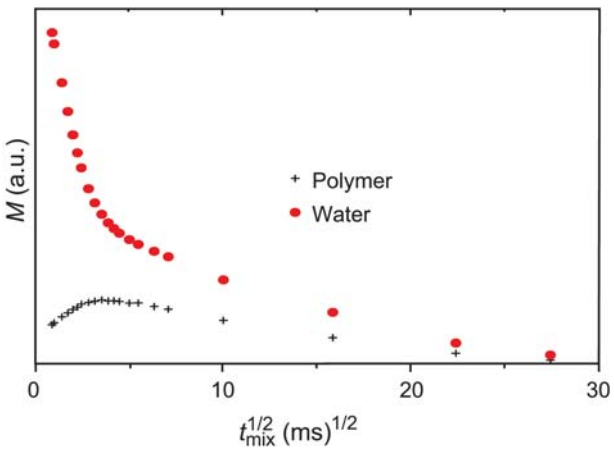

Figure 4 Magnetisation, M, as a function of $(t_{mix})^{1/2}$ for the two proton fractions, mobile (water) and rigid (polymer), of NSSC hand sheets equilibrated at 97% RH.

indicative of equilibrium between the rigid and mobile protons (i.e., slope = 0). Figure 5, which shows a limited region of the corrected and uncorrected data, indicates that this correction has little effect on the initial slope.

Mellinger et al. (1999) used small-angle X-ray scattering measurements to calibrate the value of the spin diffusion coefficient D. Using this calibration they derived an empirical relationship between T_2 and D ($D = 8.2 \times 10^{-6} + (T_2)^{-1.5} + 0.007$), and calculated a value for the spin diffusion coefficient of water of ~ 0.001 nm^2 ms^{-1} when the value of T_2 is of the order of seconds. In contrast, the value obtained for a rigid polymer such as polystyrene is 0.8 nm^2 ms^{-1} (Spiegel et al. 1993). The self-diffusion (mass transport) coefficient of bulk water is 2×10^9 nm^2 ms^{-1} at 25°C (Cory and Garroway 1990). From a comparison of these values, we can conclude that, while 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 average distance.

A summary of the model under which the data were analysed is illustrated schematically in Figure 6. In this model there are two pools of magnetisation, with each reservoir being connected to the lattice, allowing magnetisation to leak from the system. Interpretation of the experiment is based on the initial rate of transport, whereby it is assumed that the transport of magnetisation is controlled by the relative amount of bound water.

The initial rate of exchange of magnetisation was determined from the data corrected for T_1 relaxation (Figure 5). The intensity at $t_{mix} = 0$ was normalised to 1 and plotted against $t_{mix}{}^{1/2}$, and the initial slope was measured. The initial rate approximation (Abragam and Goldman 1982; Clauss et al. 1993; Landfester and Spiess 1998) 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 7. Errors were estimated from the linear regression.

A negative slope is evident for all plots of $M^w(t_{mix}^{1/2})$. For all materials, the initial value of $\Delta M^w/\Delta t_{mix}^{1/2}$ decreases in magnitude between 7% and 97% RH. This trend contains information about changes in the distribution of water with increasing relative humidity. If water is sorbed to hand sheets in regions of uniform size and dimensions, $\Delta M^w/\Delta t_{mix}^{1/2}$ will remain constant, since bound water can exchange magnetisation much more efficiently than free water. This quantity reflects the ratio of bound/free water. For more disperse water, smaller regions and greater surface area, the magnitude of $\Delta M^w/\Delta t_{mix}^{1/2}$ increases as exchange of magnetisation from the mobile phase becomes more efficient. Over the range of humidity 7–97% RH, there is a general decrease in the efficiency of the exchange for all the materials studied. As the value decreases, in this model, water must increasingly condense into larger aggregates, in which there is a larger proportion of free water.

There are many models of the energetics of sorption of a small molecule to a substrate, which have been applied to water molecules sorbing to cellulose-based materials (Venkateswaran 1970). A general feature of these models is that water molecules that interact most directly with hydroxyl groups are the most energetically favourable. In terms of our model, this is bound water. As the moisture content increases, water molecules may either be modelled as forming layers or clusters of water molecules (unbound water; Hill 1986). In either case the bound/free water ratio decreases with increasing humidity.

At humidities below 60% RH for the filter paper and NSSC hand sheet, it was found that $\Delta M^w/\Delta t_{mix}^{1/2}$ remains constant or that the bound/free water ratio is similar. This is consistent with the analysis of water to cellulose sorption curves using the Zimm and Lundberg (1956) cluster model. This model also predicts a large increase in the cluster size near saturation (Starkweather 1975), and it is found that $\Delta M^w/\Delta t_{mix}^{1/2}$ decreases in magnitude as the humidity increases to 97% RH. The initial slope obtained from experiments on BEK decreases steadily with increasing relative humidity, suggesting that the cluster size gradually increases with moisture content. This material consists largely of pure cellulose, but may also con-

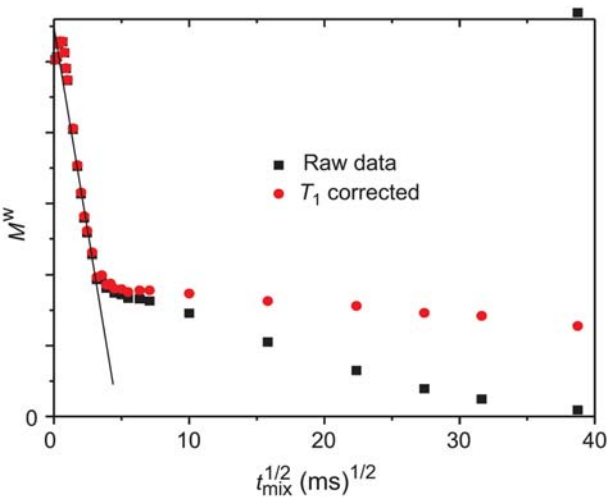

Figure 5 Raw data representing magnetisation from the mobile phase, and data corrected for spin-lattice relaxation from data collected from a NSSC hand sheet in equilibrium with 97% RH.

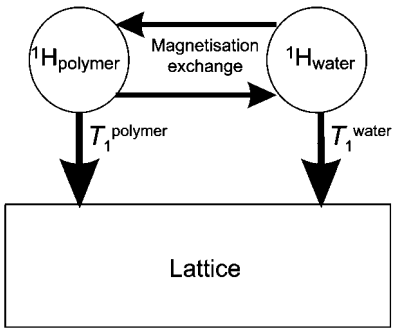

Figure 6 A schematic representation of the model adopted for magnetisation exchange between two phases of protons connected to the lattice.

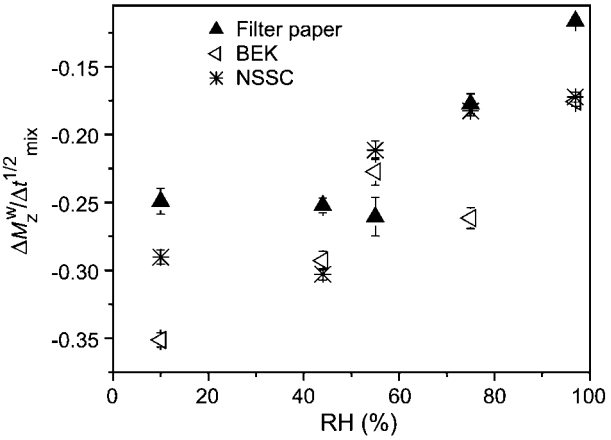

Figure 7 The initial slope, $\Delta M^w/\Delta t_{mix}^{1/2}$, for the three paper samples with increasing relative humidity.

tain hemicelluloses. The NSSC hand sheet has a similar composition, but with much greater amounts of lignin.

Conclusions

The dipolar filter pulse sequence was effective for selective excitation of the narrow component in the ^{1}H spectrum of humidified paper. The simplified line shape obtained after selective excitation changes as a function of the delay between the filter and the read pulse, t_{mix}. There are two effects that change the relative amounts of the wide line signal of the polymer and the narrower line of water in the ^{1}H spectra. The initial behaviour is dominated by the exchange of magnetisation between the two phases. The later behaviour is determined by a loss of magnetisation to the lattice through spin-lattice relaxation.

Although the spin-lattice relaxation has been characterised by a single exponential, the relaxation processes are likely to be far more complicated. The intrinsic relaxation times of bulk polymers and liquids are of the order of seconds (Callaghan 1993). It is unlikely that significant relaxation to the lattice occurs in either phase. A more likely scenario is that bound water acts as a relaxation sink for both phases. Unfortunately it is not easy to define the area of contact between the two phases.

Brownstein and Tarr (1979) examined the spin-lattice relaxation behaviour of water in a pore and modelled the behaviour with an interface between the fluid and solid phase acting as a magnetisation sink for water in the pore. The values of T_1 and T_2 for such systems are often characterised by a single exponential. This behaviour is common for fluids in a range of biological and geological materials (Callaghan 1993). Thus, although it is likely that there are two distinct time scales for relaxation in the sample, the fast exchange of magnetisation between regions of slow and fast relaxation produces a single average behaviour.

Changes in the proton NMR spectra as a function of t_{mix} are due to the exchange of magnetisation between the polymer and water phases. The initial slope of $M^w(t_{mix}^{1/2})$corrected for T_1 effects is negative and linear. The negative slope indicates that magnetisation is exchanged with the mobile phase. The slope of $M^p(t_{mix}^{1/2})$ is positive and linear. The positive slope indicates that some of the magnetisation lost from the mobile phase is exchanged with the polymer phase. Thus, as a function of t_{mix}, the broad component of the ^{1}H spectrum becomes more pronounced.

Previously, changes in the spin-lattice and spin-spin relaxation times of water have been interpreted as an indication of bound water. A layer of water that undergoes hindered dynamics is essential to this model (Resing 1965, 1972). After considering the magnitude of the spin diffusion coefficient for bulk water, it was concluded that, although thermal motion was very efficient at transferring magnetisation spatially in a liquid, transfer of magnetisation to the polymer phase from bulk water would be very slow and would not be observed in the time-scales of this experiment. Therefore, the presence of motionally hindered water is a necessary condition for exchange to occur, and the exchange of magnetisation from the mobile to the rigid phase indicates that there are protons in exchange with free water. The decrease in $|\Delta M^w/\Delta t_{mix}^{1/2}|$ with increasing moisture content was interpreted as a change in the free/bound water ratio.

The behaviour of $|\Delta M^w/\Delta t_{mix}^{1/2}|$ as a function of the moisture content was quite similar for the NSSC hand sheet and filter paper. This indicates that the surface/volume ratio of the regions of water was similar in these two materials up to a humidity of approximately 60% RH, at which the size of the water clusters seemed to increase. This observation is consistent with theoretical interpretations of moisture sorption to cellulosic fibre curves. If the behaviour of the NSSC hand sheet is significantly different, it may be that the cross-linked polymer, lignin, is able to restrict access of water to the hemicellulosic polymers. Certainly this is consistent with current knowledge of the phase morphology of cellulose fibres from the cell walls of higher plants, in which lignin is intimately mixed on a molecular scale with the hemicellulosic polymers (Garvey et al. 2001). The use of ^{13}C detection of the ^{1}H magnetisation in a two-dimensional NMR experiment may be able to resolve this issue, since there are separate and easily identified signals from each polymer constituent.

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