Carbohydrate Polymers 87 (2012) 361–367

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Water interaction in paper cellulose fibres as investigated by NMR pulsed field gradient

E.L. Perkins, W.J. Batchelor*

Australian Pulp and Paper Institute, Department of Chemical Engineering, Monash University, Wellington Road, VIC 3800, Australia

ARTICLE INFO

Article history:
Received 3 June 2011
Received in revised form 27 July 2011
Accepted 28 July 2011
Available online 5 August 2011

Keywords:
NMR
Pulsed field gradient
Paper fibres
Cellulose
Water interaction
Fibre structure
Cellulose nanofibre

ABSTRACT

In this paper, water diffusion coefficients were measured using NMR pulsed field gradient, on a variety of paper materials made from predominantly cellulose fibre and nanofibres, derived from wood, with different dimensions, internal porosity, and chemical composition. The moisture content ranged from 0.2 to 1.2 g of water/g of dry fibre. Diffusion measurements were made both in the plane and through the thickness of the sheet. All data was generally well fitted by a simple two component diffusion model. For moisture contents less than 0.55 and 0.85 g/g for measurements in the plane and through the thickness, respectively, it was found that both diffusion components increased approximately linearly with moisture content, with the faster diffusion coefficient being approximately five times larger than the smaller. The water appeared, within errors, to be evenly split between two components. The measured diffusion coefficients were not affected by fibre dimensions, internal structure or chemical composition, but were consistently higher when measured in the plane.

1. Introduction

Water plays a significant role in the formation and physical properties of paper; changes in moisture content affect the physical strength of paper and paperboard products. The removal of water during the drying process in papermaking significantly affects process economics and final paper strength, which is further reduced by the repetition of drying and recycling of fibres (Park, Venditti, Jameel, & Pawlak, 2007). After manufacture, changes in temperature and humidity can have profound effects on the performance of these products (Haslach Jr, 2000). It is well known that cardboard boxes that are subjected to cyclic humidity within warehouses collapse more readily than if stored under constant conditions (Considine & Laufenberg, 1992).

Traditional methods of water retention value (WRV), fibre saturation point (FSP), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been extensively used to study moisture in paper fibres (Park, Venditti, Jameel, & Pawlak, 2006; Weise, Maloney, & Paulapuro, 1996). WRV is a measure of the water that remains trapped in a fibre pad after centrifugation, reflecting the swellability of a pulp on rewetting (ISO Standard, 2007) and is a commonly used parameter within the paper industry. Through ageing and repeated drying and re-wetting cycles, the porosity and swellability of the fibres decrease (Östlund, Köhhnke, Nordstierna, & Nydén, 2009) and a corresponding loss in strength of products made from these fibres is observed. FSP is a measure of the porosity of the fibres. TGA is a measure of the absorbance of water on the fibres surface and thus a measure of the surface area exposed to moisture. DSC is commonly used to thermodynamically determine the water types in the fibre. Water bound within the fibre wall has a depressed freezing point compared to that of bulk water due to its location in small pores within the wall. Not all bound water is able to freeze; a layer two to three molecules thick in direct contact with cellulose fibrils does not freeze, even at temperatures well below 0 °C (Overloop & Vangerven, 1993). Independent of the experimental technique used, three types of water are generally identified, free water (FW), bound freezing water (BW_f) and bound non-freezing water (BW_{nf}). Another concept used to categorize water types has also been defined by TGA as “easy-to-remove” and “hard-to-remove”, where the first category includes only the true free water, the second category includes free water that is trapped in the fibre network and all bound water (Park et al., 2007). During drying, these types of water are thought to be removed in sequence according to the strength of their interaction with the fibres, with some overlap at the boundary between two types (Weise et al., 1996).

Within a typical paper sheet, cellulose fibres have average dimensions in the range of 10–50 μm widths and lengths of 0.7–4 mm, depending on the species. These fibres form a porous

---

* Corresponding author. Tel.: +61 03 9905 3452; fax: +61 03 9905 3413.
E-mail addresses: Warren.Batchelor@Monash.edu, warren.batchelor@eng.monash.edu.au (W.J. Batchelor).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.07.065

network where intra-pore dimensions are tens of microns to millimetres. This porous system made by the spaces between fibres contains some of the “free water”, so-called “trapped water”. The fibres themselves are formed from bundles of microfibrils, the microfibrils are made of an array of cellulose chains and are around ten to twenty nanometres in diameter and hundreds of microns in length (O’Sullivan, 1997). Within the fibres, therefore, there are pores on the nanometre scale. Both “bound water” components are within the fibre porous network and on the surface of the fibres in close contact with the cellulose microfibrils. Both crystalline and amorphous regions of cellulose are expected within the fibres. For more details on the structure and crystallinity of cellulose see the review by O’Sullivan (1997). In addition, paper prepared from wood pulp fibres will also contain hemi-cellulose and lignin, the balance between the three polymers depending on species and method of pulping.

Whilst these methods have been used to describe and quantify the water types present in the fibre network of paper based materials, the interaction and changes in interaction at different moisture content between these water types and the cellulose polymers has yet to be investigated. Nuclear magnetic resonance techniques are applied here to investigate the relative interaction of water within different environments and with the cellulose fibres by means of studying the diffusion of water at different moisture contents.

Nuclear magnetic resonance pulsed field gradient (NMR PFG) studies have previously been used to examine the transport of water within paper fibre structure networks (Harding, Wessman, Stenström, & Kenne, 2001; Li, Henriksson, Klason, & Ödberg, 1992; Li, 1991; Topgaard & Soderman, 2001, 2002b, 2002c). Studies evaluating porosity have also been conducted with NMR PFG (Foston & Ragauskas, 2010; Li, Henriksson, & Ödberg, 1995; Topgaard & Soderman, 2002a). The advantages of NMR techniques are that they are non-invasive and non-destructive, and able to study the structure, porosity and environmental situation of an imbibed liquid within a porous medium. The study of diffusion by NMR can also have directional dependence based on the orientation of the sample within the applied field gradient.

In the early 1990s Li et al. (1992) studied water diffusion in paper sheets with very high water content, greater than 4 g (water)/g (fibres). They measured diffusion both in the plane (which will be called the *X*–*Y* direction for the rest of the paper) of the sheet and perpendicular to the plane, or through the sheet (hereafter called the *Z*-direction). At these high moisture contents, Li and co-workers observed two distinct diffusion coefficients. One coefficient was around half that of bulk water at the same temperature, approximately $1.3 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$, and the second coefficient was approximately $4 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$. These two components were identified as the diffusion coefficient of bulk water between the fibres and the diffusion coefficient of the water within the fibres and within the pores of the fibres. In complimentary work, the diffusion of water in cellulose fibres was measured at very low moisture content, less than 0.25 g/g (Topgaard & Soderman, 2001). These workers found at low moisture content there was significant influence of cross-relaxation between water and cellulose during the measurement of the diffusion coefficient. A single phase of water was identified, having a continuous distribution of diffusion coefficients, from which a value for the diffusion coefficient of highest probability for the given moisture content was determined. This phase of water was said to be within the fibril network that makes up the cellulose fibres. Typical values of diffusion coefficient measured were of the order of 10^{-10} to $10^{-11}\,\mathrm{m^2\,s^{-1}}$.

In this work we examine the diffusion of water in the cellulose fibre structure for paper systems with intermediate moisture contents, between 1.2 g/g and 0.20 g/g, to expand our understanding of moisture content and diffusion of water over the complete range of moisture contents. Knowledge of water transport behaviour in this water content range will be advantageous in understanding the drying of fibre sheets, a process that, in part, determines final sheet strength. Diffusion at the lower end of this range is also critical in the performance of packaging materials under high and variable atmospheric humidity. A further significant contribution of this work is that water diffusion has been examined with a range of different fibre morphologies.

2. Theory

The first NMR PFG measurements of liquid diffusion coefficients were made in 1965 (Stejskal & Tanner, 1965), with further work developing the use of stimulated echo measurements for nuclei with short transverse relaxation rates (Tanner, 1970). The diffusion coefficient is calculated from the measured signal attenuation over a series of stimulated echo experiments, where the spatial locations of the nuclei are mapped and decoded using an increasing strength, or length of applied magnetic field gradient. The relationship between signal attenuation and diffusion coefficient is given in Eq. (1):

$$\mathrm{Ln}\left(\frac{I}{I_0}\right) = -D\gamma^2\delta^2 g^2\left(\Delta - \frac{\delta}{3}\right) \tag{1}$$

where I is the measured signal intensity, I_0 is the signal intensity if no diffusion occurred, D is the calculated diffusion coefficient, γ is the gyromagnetic ratio of the nucleus being observed, δ is the length and g is the strength of the applied magnetic field gradient and Δ is the time between the two applied gradients, often called ‘big delta’. If δ is small then Δ is the approximate diffusion time. For simplification, α is defined as $\alpha = \gamma^2\delta^2 g^2(\Delta - \delta/3)$. For simple liquid self diffusion, the log – attenuation plot, Ln (I/I_0) against α, is linear with a negative gradient equivalent to the self-diffusion coefficient. However, for a non-linear log-attenuation plot the interpretation of NMR data can be complex and often requires additional knowledge of the system or comparison with a complimentary technique. When the liquid is contained within a porous system a non-linear log-attenuation plot is often observed; the causes of non-linearity include, multi component systems (Hollewand & Gladden, 1995), cross-relaxation effects (Goldman & Shen, 1966) and restricted diffusion (Callaghan, Jolley, & Lelievre, 1979). Often a combination of these effects is present within a system. For the system studied here, it has been shown that NMR diffusion measurements produce non-linear log-attenuation plots (Perkins & Batchelor, 2010), with the best approximation being a discrete two-component system, two components of water having different mobility due to location within and thus interaction with cellulose fibres. No consistent effect of cross-relaxation between cellulose and water was observed.

3. Materials and methods

Measurements were made on four different cellulose fibre materials. Two of the materials were NIST reference materials of Northern (Canadian) Softwood Bleached Kraft (labelled NSBK), reference material 8495, and Eucalypt Hardwood Bleached Kraft (labelled EHBK), reference material 8496 (Ampulski, 2001). Both fibre materials had been chemically pulped, then bleached to remove almost all lignin and supplied as once dried sheets.

The third material was a Radiata Pine Unbleached Never dried Kraft (labelled RPUNK), kindly donated by Australian Paper and supplied as wet fibres with a water content of 6.59 g/g. Radiata pine is a softwood with coarser fibres than the NSBK pulp. The lignin content of the fibres measured using the kappa number method was approximately 10%. Whilst the dimensions of these samples were not measured for the work here, values measured on dry fibres from the literature (Kibblewhite, 1993) are fibre lengths of 0.75, 2.45 and 2.45 mm for the EHBK, RPUNK and NSBK fibres, respectively, with corresponding fibre widths of 13, 30 and 25 μm, respectively and fibre thicknesses of 7, 12 and 9 μm, respectively.

The fourth material was cellulose nanofibres (CNF), derived from the mechanical refining of NSBK fibres in a Valley beater at 15.7 g of solid per litre of suspension. This process opens up the porous structure of the fibres and separates cellulose fibrils from the fibres. The CNF was then prepared by filtration to separate the nano-sized fibrils from the rest of the material. Further details of the method employed to produce the nanofibres is discussed in Batchelor, Gras, Lee, and Wang (2009).

4. Experimental

To prepare the pulp fibres from dried fibre sheets of NSBK and EHBK, the samples were soaked overnight in deionised water and fibres then separated by agitation for 30,000 revolutions.

A NSBK sample was also refined in a Valley beater reducing the drainage properties of the pulp, measured as a reduction in the Canadian standard freeness (CSF) from 670 ml to 400 ml (Australian and New Zealand Standard, 2002). This sample is denoted NSBK-R. An unrefined NSBK (labelled NSBK-U) was also used. The NSBK-R thus differs from NSBK-U by an increase in the internal porosity of the fibres. The EBHK, RPUNK and CNF samples were given no further treatment. All paper sheets, except the nanofibre sheets, were formed on the moving belt sheet former (Li & Parker, 2000) to a target weight of 60 grams per square metre (gsm), and an area of 22 cm × 22 cm. The moving belt sheet former simulates the industrial paper making process, with the exception that sheets are produced with isotropic fibre orientation within the sheet plane. Once formed, the sheets were lightly pressed to remove bulk water and then stored in sealed bags at around 5 °C to prevent sample deterioration. CNF sheets, target weight of 40 gsm, were made using a circular 31 mm diameter vacuum filtration system.

Samples were partially dried to different moisture contents under constant conditions of temperature (23 ± 0.2 °C) and relative humidity (50 ± 2%). Diffusion coefficients in the *X*–*Y* and *Z* directions were measured using different sample orientations within the NMR receiver coil (only vertical gradients were available.) For *X*–*Y* tests a strip of approximately 1 cm by 2 cm was cut and rolled into a cylinder and placed between two susceptibility plugs within a 5 mm outside diameter NMR tube. For *Z*-direction tests, between ten and twenty disks of 4 mm diameter were cut using a hole punch and placed between two susceptibility plugs within the NMR tube. The susceptibility plugs are used to reduce the sample volume required to cover the receiver coils within the spectrometer. They are designed to have negligible magnetic susceptibility. Sample moisture content was measured by weighing the sample off-cut immediately after sample preparation, then weighing again after drying in an oven at 105 °C for at least 4 h. The moisture content was calculated by Eq. (2):

$$\text{moisture content (g/g)} = \frac{\text{wet mass} - \text{oven dried mass}}{\text{oven dried mass}} \quad (2)$$

NMR PFG experiments were conducted in a Bruker 300 MHz spectrometer, equipped with a Diff30 diffusion probe. A stimulated echo pulse sequence was used with applied gradients between 5 and 740 G/cm and gradient duration of 1 ms. The time between gradient pulses was varied between 10 and 50 ms. Experiments were carried out at 20 °C, the equilibrium temperature within the coil when no internal heating is applied, thus reducing any convection currents within the sample. Only diffusion in the liquid state, within the fibre and on the fibre surface is being examined.

Lignin content was measured using the kappa number method (Tappi Standard, 1999).

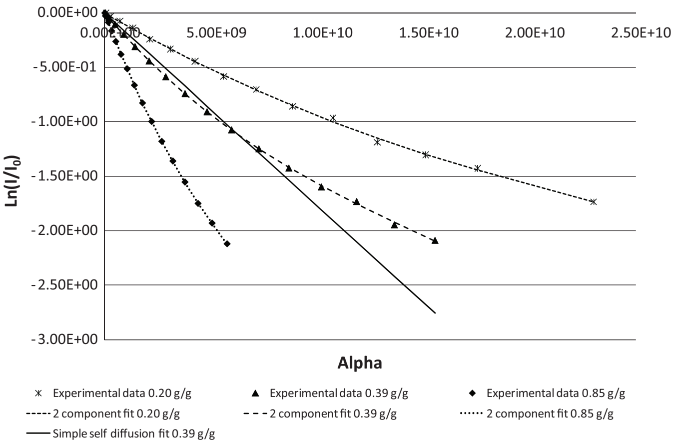

Fig. 1. Example of experimental data for refined bleached Kraft softwood sample at 0.20, 0.39 and 0.85 g/g moisture content, diffusion measured in the plane of paper sheet. Data displayed as a log-attenuation plot.

5. Results and discussion

5.1. Measurements and fitting

Non-linear log-attenuation plots were obtained for water diffusion measured by NMR PFG. Some example data are shown in Fig. 1, for NSBK-R. The figure shows in plane diffusion measured at 0.20, 0.39 and 0.85 g/g moisture contents and a diffusion time of 20 ms. All three data sets show non-linearity, attributable to some combination of multi-component diffusion, restricted diffusion and cross-relaxation. The causes of non-linearity and reasons behind the choice of a two component model are discussed in detail in previous work (Perkins & Batchelor, 2010). Briefly, the two component model provides a simple, but good fit to experimental data that enables a straightforward physical interpretation of a complex and dynamic system. Experimental data is fitted to Eq. (3):

$$I = I_0\{(1-p)\exp(-D_1\gamma^2\delta^2 g^2(\Delta - \delta/3)) + p\exp(-D_2\gamma^2\delta^2 g^2(\Delta - \delta/3))\} \quad (3)$$

where p is the fraction of water in the slow component and D_1 and D_2 are the diffusion coefficients of the fast and slow components respectively. All other symbols are as defined in Eq. (1).

It can be seen that the two component model provides an excellent fit to all three data sets. The simple single component diffusion model fit, of Eq. (1), is also shown for the 0.39 g/g moisture content data. From Fig. 1 it is seen that the two component model significantly improves the fit to the experimental data from the simple single component, straight line, diffusion model. The fit to the experimental data may be improved slightly by adding more components, but the number of free variables increases compared to the number of data points thus, the fitting parameters become less reliable. It is important to note that the diffusion behaviour measured is the average diffusion behaviour within the system and, therefore, the two component model is a best approximation to explain the overall behaviour of the water diffusion. The diffusion coefficients calculated for the two components, shall be identified as a “fast component” and a “slow component”, and the sum of the fractions of water in each component shall be 1. The definition of water in two components will now be discussed.

5.2. Distribution of two phases of water

At low moisture content the significance of cross-relaxation between protons in the water phase and those of the cellulose has been discussed (Topgaard & Soderman, 2001), but as water content increases, the significance of both nuclear and spin exchange between the protons of water molecules in different components,

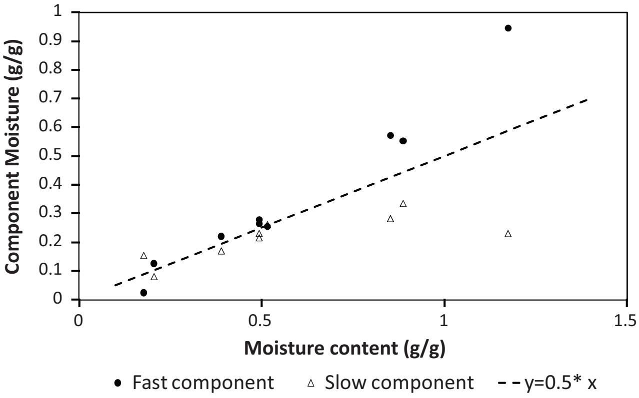

Fig. 2. Mass of water in each component against moisture content for *X–Y* diffusion of all materials.

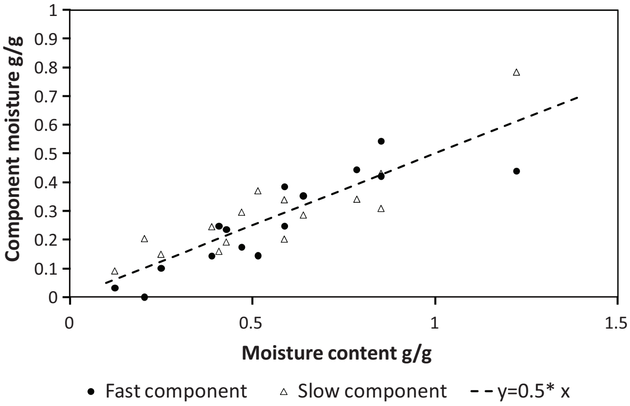

Fig. 3. Mass of water in each component against moisture content for *Z* diffusion of all materials.

or environments, is thought to be less important; the dominating effect observed for the mobility of water is its direct interaction with cellulose. At high moisture content the two components observed by Li and co-workers were described as bulk water and water contained within the fibre structure, where the fast component, or free water, has a reduced diffusion coefficient from bulk due to effects of tortuosity (Li et al., 1992).

In the intermediate moisture regime studied here, the two components may be suggested to represent the two water types present, i.e. the fast component corresponds to the bound freezing water (BW_f) and the slow component corresponds to the bound non-freezing water (BW_{nf}). Such a literal explanation of the two water components, however, does not fit with the quantified assessment of these water types found by others using DSC or TGA (Park et al., 2007; Weise et al., 1996). Therefore, further thought to determine a definition of the water types and the relationship between them, as observed by diffusion behaviour is considered.

The amount of water in each component for a range of moisture contents is shown in Fig. 2, for in plane, labelled *X–Y*, diffusion and Fig. 3 for through plane, labelled *Z*, diffusion, for all available data with the different samples measured at a diffusion time of 20 ms. The fractions of water in the two components are calculated from Eq. (3). These fractions are used to estimate the amount of water in each component using the moisture content measured directly from the mass of the sample off-cut as described in Eq. (2). The key observation of both figures is that as moisture content increases, the split between fast and slow components seems to be constant at approximately 50%, for moisture contents less than 0.55 g/g and 0.85 g/g, for the measurements in the *X–Y* and *Z* directions, respectively. The significance and possible implications of this are discussed next.

As it has previously been discussed that the FW, BW_f and BW_{nf} are sequentially lost during the drying process with only some overlap (Weise et al., 1996), the near equal mass of fast and slow component at moisture contents below 1 g/g suggests that the fast and slow component are not directly related to the BW_f and BW_{nf}. Instead, the interaction and fast exchange of water molecules between these two water types appears to influence the distribution of the components and hence the diffusion behaviour observed.

As an alternative to the BW_f and BW_{nf} classification, a water layer hypothesis is proposed to describe the change in diffusion behaviour with moisture content increase. At very low moisture contents, which were not measured for the work reported here, all the water within the fibres is expected to be in close proximity to the cellulose microfibril surface and thus the diffusion behaviour is strongly affected by the interaction between the cellulose and water. The water layer may only be a few molecules thick and a single characteristic diffusion coefficient is expected (Topgaard & Soderman, 2001).

The minimum moisture content we measured was 0.20 g/g. For all of our measurements, the data showed more complex diffusion, which was modelled as two components of water, as is seen in Figs. 1–3. The question then remains as to the location of these two phases within the cellulose fibril and fibre structure, consistent with the observation, that at lower moisture contents studied here, the water is equally split between the two phases.

Fig. 4A shows a simple diagrammatic representation of the suggested arrangement of the two components of water as layers and how these layers increase in thickness with increasing moisture content. The layers are described as the close layer and outer layer, the grey area represents the cellulose fibril. It is not thought that these layers have a direct physical meaning, but more that they represent the closeness of water to the cellulose interaction influence. As moisture content increases, the water layers thicken, the closest layer to the cellulose shields the outer layer from the influence of the cellulose and thus the outer layer begins to show a more mobile phase present, a second different diffusion coefficient can be observed. The closest layer still has some interaction with the cellulose, but is now also interacting with the outer layer. The net effect is an increase in the observed diffusion coefficient of this slow component layer also. As moisture content continues to increase, the shielding effect of the closest layer increases until a maximum shielding level is reached and the outer, fast component, diffusion coefficient continues to rise. Likewise the increasing mobility of the outer layer continues to interact with the close layer, increasing the diffusion coefficient observed for the slow component, up to a maximum limit. At the upper limit of moisture content studied here, the maximum diffusion coefficient for the outer layer is still significantly less than that of bulk free water, due to its interaction with the close layer. The short observation times do not indicate any effects of structural influence at this point.

The boundary between the fast and slow component is not rigidly defined, therefore, fast and numerous exchange of molecules is expected to occur between the layers, such that the mass of water in each layer appears equal. At very high moisture content, above the water retention value where bulk water starts to be present the close layer and outer layer are observed as one component and the bulk, or free water, is observed as a second component. This is a mathematical anomaly caused by the change in magnitude of the diffusion coefficient of free water compared to water influenced by the fibres, thus the signal contribution from the more tightly bound, or close layer becomes insignificant when compared to the large contribution to signal made by the faster moving free water. This leads to the two component system observed by

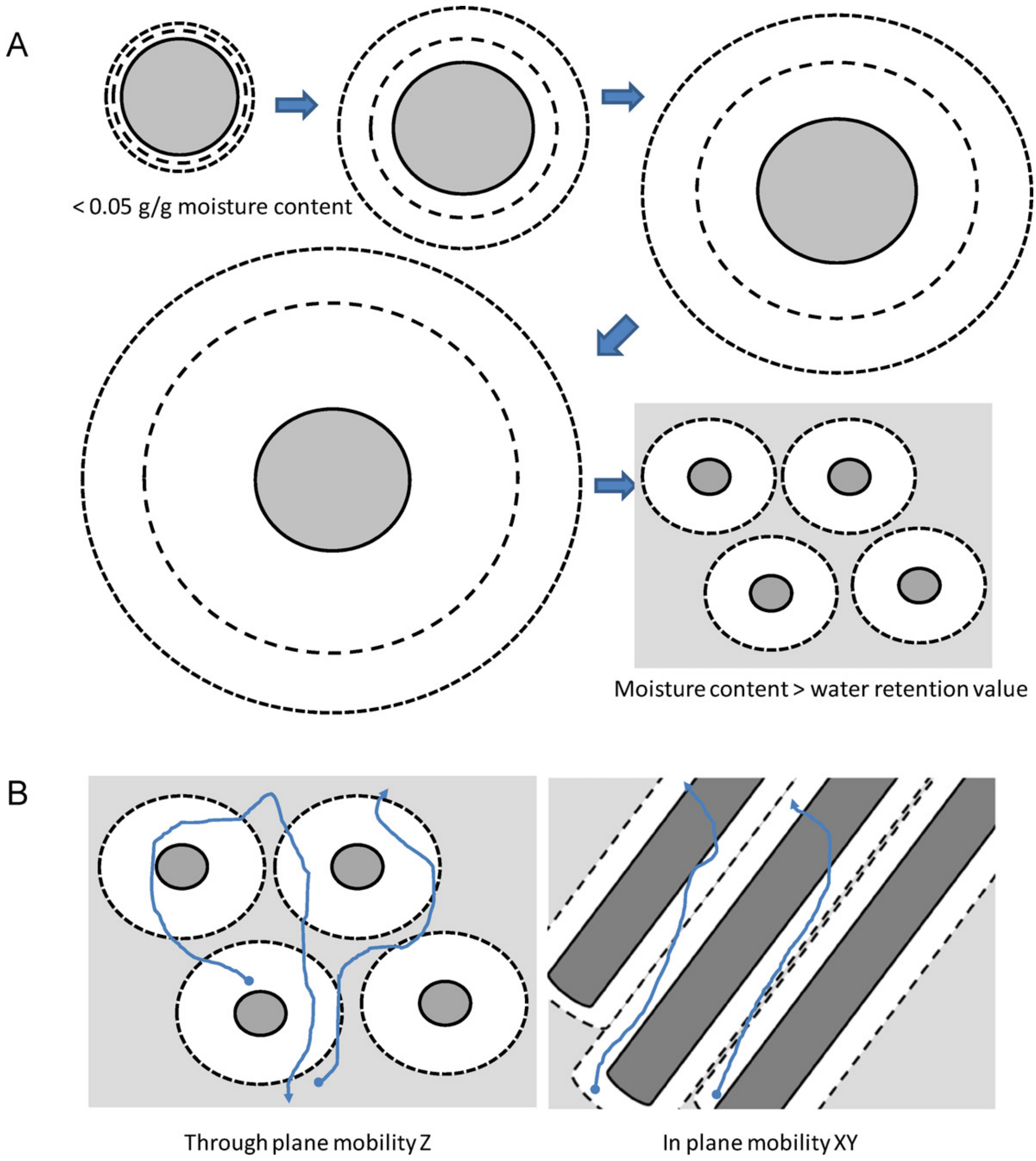

Fig. 4. (A) Diagrammatic representation of water layer build up with moisture content increase in direction of arrows. (B) Comparison of *Z* and *X*–*Y* motion at the fibril level.

Li and co-workers for bulk and water contained in fibres moisture contents over 4 g/g (Li et al., 1992).

At moderate moisture content, the relative mass of each component of water is equal, however Fig. 2 shows that at high moisture content a definite diversion from this equality is observed. This divergence in mass fraction corresponds to the approximate moisture content of the water retention value. Therefore, it is suggested that this significant increase in the fast component at this moisture content is representative of the free water. This increase in the fast component, coupled with the comparative low mass of the slow component fraction suggests a reduction in the interaction between the two components from what was previously observed at lower moisture content. In contrast, for the diffusion observed in the *Z*-direction, this divergence is not observed, Fig. 3. The lack of this change in relative mass fraction of the two components for *Z*-direction diffusion highlights an effect of orientation on the diffusion behaviour. The change in tortuosity expected, shown in Fig. 4B, is a possible cause for this change. Further discussion of the change in observed diffusion for *X*–*Y* and *Z* direction diffusion is discussed in Section 5.3.

This model of water layers around cellulose fibrils is further supported in Fig. 5, which combines the data in Figs. 2 and 3 and breaks down the data points by fibre type. The water fractions for different fibres types are independent of fibre type, as shown in Fig. 5. This lack of dependence of water fraction on the fibre type shows that the interaction between the two water components is not affected by the ultra structure of the fibres studied, or the structural arrangement of the fibres to form the sheet. SEM measurements were used to measure the fibre diameters of the nanofibres, using the procedure discussed in Zhang, Tsuzuki, and Wang (2010). The material was found to be quite heterogeneous with fibre diameters ranging from 20 nm to 1 μm. The average diameters of the other fibres from the literature (Kibblewhite, 1993) range from 12, 21.6 and 26 μm for the EHBK, NSBK (unrefined) and RPUNK fibres, respectively. The

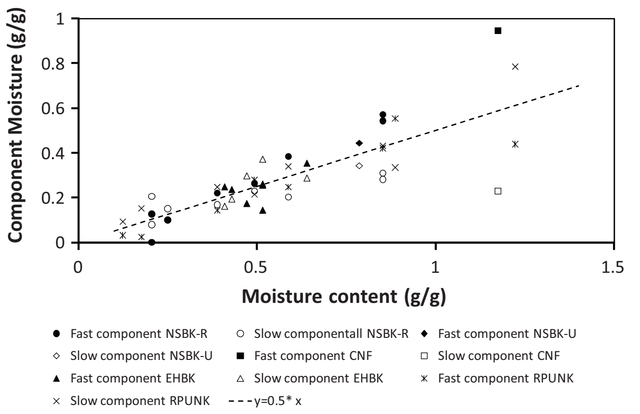

Fig. 5. Fast and slow component water contents for different fibre types and moisture contents both in plane and through plane.

refining of the NSBK is expected to increase internal porosity of the fibres. The fact that none of these ultrastructural arrangements of the cellulose microfibrils appears to have influenced the split of water in the fast and slow components is a strong argument that the origin of the fast and slow components arises in the interaction and diffusion of water around the cellulose microfibrils, as the primary feature of the interaction of the water and the cellulose polymer.

5.3. *Diffusion coefficients*

This picture of two interacting layers discussed in Section 5.2 is further supported when the diffusion coefficients are plotted in Fig. 6 for diffusion measured in the plane (*X*–*Y*) and in Fig. 7 for diffusion measured through the plane (*Z*). The two diffusion coefficients at different moisture contents for a range of materials show negligible dependence on the fibre dimensions, chemical composition or mechanical treatment. Whilst there is a significant difference in the magnitude of the corresponding diffusion coefficients in the plane versus through the plane, the overall trends of decreasing diffusion coefficient with decreasing moisture content can be observed for both diffusion directions and for both fast and slow components. This pattern of decreasing diffusion coefficient with decreasing moisture content follows well with the suggested water layer hypothesis described in Section 5.2. The ratio between fast and slow component diffusion coefficients changes only slightly with moisture content and is similar both in plane and through plane, with an average value of around 5. This is a further indication that diffusion in either fast or slow component does not occur in isolation of the other component.

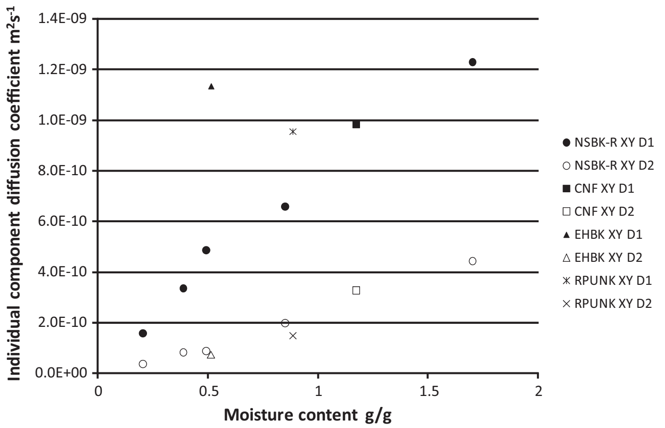

Fig. 6. Fast (D_1) and slow (D_2) diffusion coefficients measured in the plane of the paper for all materials.

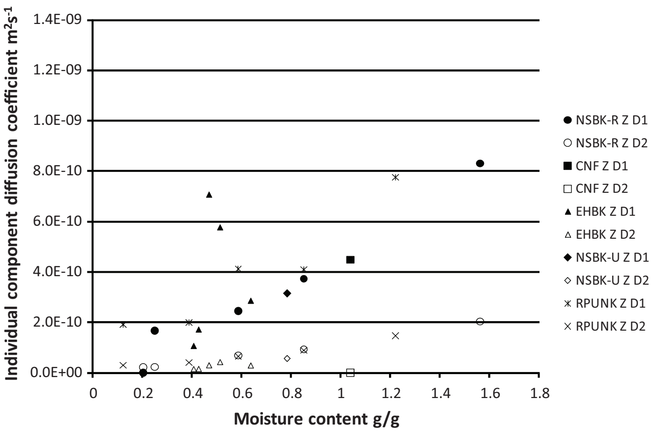

Fig. 7. Fast (D_1) and slow (D_2) diffusion coefficients measured through the plane of the paper for all materials.

Initially it was thought that the root-mean-square (RMS) displacement distance as derived by the Stokes–Einstein relation could be used to probe the structure of the fibres and fibre network containing the water. The calculated RMS displacement values for all materials studied are shown in Fig. 8. However, the investigated diffusion distances did not highlight any differences in fibre structure between different materials and moisture content histories. WRV and CSF will depend on the fibre size and the fibre network porosity of the compacted fibre pad. The range of diffusion distances probed were approximately 2–12 μm. The main feature of interest in this order of magnitude is the fibre wall thickness. However, even at longer diffusion times, the definition of absolute diffusion boundaries was not sufficiently significant to determine structural information. No difference in diffusion distance was observed for the refined versus unrefined samples where an opening of the pore wall structure is expected. It is thought that the complex nature of the fibril bundles that make up the fibre structure may be the cause of the lack of an absolute boundary. Thus, the water molecules are more sensitive to the tortuosity of the fibril network that describes the path through which they travel to exit the fibre wall, observing non-continuous fibre wall boundaries, see Fig. 4B.

The differences in the tortuosity of the network of cellulose fibrils are why the trends between diffusion in the *X*–*Y* and *Z* directions are the same, but the numbers are different.

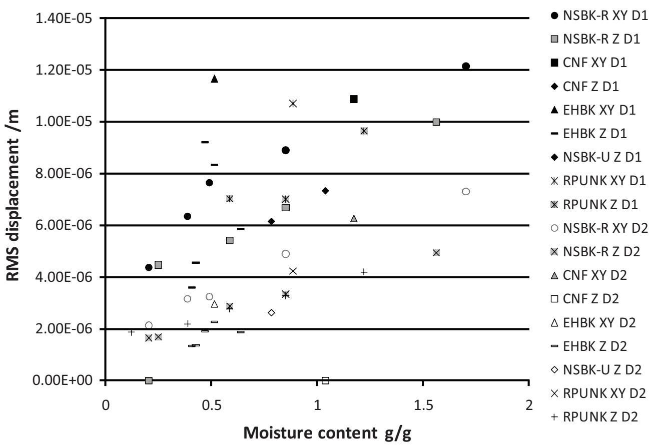

Fig. 8. Root mean square displacement against moisture content for all materials and both sheet orientations measured at a diffusion time of 20 ms.

All of the materials were manufactured such that the orientation of the cellulose fibres was isotropic within the plane of the sheet. Under such circumstances, the cellulose microfibrils are predominantly oriented within the plane of the sheet. Thus diffusion within the plane of the sheet, where some fraction of water will be diffusing along the cellulose microfibrils, will be higher than through the thickness of the sheet, where diffusion will require movement around the circumference of the cellulose microfibrils.

6. Conclusion

NMR PFG experiments were used to investigate the diffusion behaviour of water within the cellulose fibre structure of paper sheets at intermediate moisture contents. The diffusion data was fitted by a two component diffusion model and an alternate classification of the two components was discussed in combination with traditional definitions of water types within such systems.

At intermediate moisture contents, the diffusion coefficients of both components of water are observed to decrease with decreasing moisture content. The relative mass fractions of water in each component are near equal and the ratio between the two diffusion coefficients remains near constant, implying that there is interaction between the two water components under these moisture conditions. Through plane and in plane studies show an increase in the interaction effects and tortuosity of the diffusion motion for water through the sheet compared to within the plane of the sheet.

The fibre ultrastructure had no measured effect on the diffusion behaviour.

Funding

ARC Linkage Grant No. LP0989823. With industry partners: Amcor, SCA, Visy, Australian Paper and Norske Skog.

Acknowledgements

Liyuan Zhang is thanked for her estimates of the nanofibre size distributions. A. Prof Wei Shen is thanked for his critical review of the manuscript.

References

Ampulski, R. S. (2001). *Report of Investigation Reference Materials 8495 Northern Softwood Bleached Kraft 8496 Eucalyptus Hardwood Bleached Kraft*. Gaithersburg, MD: National Institute of Standards and Technology.

Australian/New Zealand Standard. (2002). *AS/NZS 1301.206s:2002 Australian/New Zealand Standard*$^{\mathrm{TM}}$ *Methods of test for pulp and paper—Freeness of pulp AS/NZS*.

Batchelor, W., Gras, S., Lee, R., & Wang, S. (2009). *Cellulose nanofibre nonwovens (Paper 206). Chemeca 2009*. Perth: Institute of Engineers Australia.

Callaghan, P. T., Jolley, K. W., & Lelievre, J. (1979). Diffusion of water in the endosperm tissue of wheat grains as studied by pulsed field gradient nuclear magnetic resonance. *Biophysical Journal*, *28*, 133–142.

Considine, J., & Laufenberg, T. L. (1992). Literature review of cyclic humidity effects on paperboard and packaging. *Proceedings of the Cyclic Humidity Effects on Paperboard Packaging*,. Madison WI: Forest Products Laboratory.

Foston, M., & Ragauskas, A. J. (2010). Changes in the structure of the cellulose fiber wall during dilute acid pretreatment in Populus studied by ^{1}H and ^{2}H NMR. *Energy and Fuels*, *24*(10), 5677–5685.

Goldman, M., & Shen, L. (1966). Spin-spin relaxation in LaF3. *Physical Review*, *144*(1), 321–331.

Harding, S. G., Wessman, D., Stenström, S., & Kenne, L. (2001). Water transport during the drying of cardboard studied by NMR imaging and diffusion techniques. *Chemical Engineering Science*, *56*(18), 5269–5281.

Haslach, H. W., Jr. (2000). Moisture and rate-dependent mechanical properties of paper: a review. *Mechanics Time-Dependent Materials*, *4*(3), 169–210.

Hollewand, M. P., & Gladden, L. F. (1995). Transport heterogeneity in porous pellets.1 Pgse NMR-studies. *Chemical Engineering Science*, *50*(2), 309–326.

International Standard. (2007). *ISO 23714:2007(E) Pulps-Determination of water retention value (WRV)*. Switzerland: ISO., p. 8.

Kibblewhite, R. P. (1993). Effects of refined softwood: Eucalypt pulp mixtures on paper properties. In C. F. Baker (Ed.), *Products of papermaking transactions of the tenth fundamental research symposium* (pp. 127–157). Oxford: PIRA International.

Li, T. Q. (1991). Interaction between water and cellulose fibers. Ph.D. Thesis, Department of Physical Chemistry. Stockholm: KTH.

Li, T. Q., Henriksson, U., & Ödberg, L. (1995). Determination of pore volume in cellulose fibers by the pulsed gradient spin-echo NMR technique. *Journal of Colloid and Interface Science*, *169*(2), 376–379.

Li, T. Q., Henriksson, U., Klason, T., & Ödberg, L. (1992). Water diffusion in wood pulp cellulose fibers studied by means of the pulsed gradient spin-echo method. *Journal of Colloid and Interface Science*, *154*(2), 305–315.

Li, X., & Parker, I. (2000). Simulating the forming process with the moving belt drainage former. *Appita Journal*, *53*(4), 282–286.

O'Sullivan, A. C. (1997). Cellulose: The structure slowly unravels. *Cellulose*, *4*(3), 173–207.

Östlund, Å., Köhhnke, T., Nordstierna, L., & Nydén, M. (2009). NMR cryoporometry to study the fiber wall structure and the effect of drying. *Cellulose*, 1–8.

Overloop, K., & Vangerven, L. (1993). Freezing phenomena in adsorbed water as studied by NMR. *Journal of Magnetic Resonance Series A*, *101*(2), 179–187.

Park, S., Venditti, R. A., Jameel, H., & Pawlak, J. J. (2006). Hard to remove water in cellulose fibers characterized by high resolution thermogravimetric analysis—Methods development. *Cellulose*, *13*(1), 23–30.

Park, S., Venditti, R. A., Jameel, H., & Pawlak, J. J. (2007). Hard-to-remove water in cellulose fibers characterized by thermal analysis: A model for the drying of wood-based fibers. *Tappi Journal*, *6*(7), 10–16.

Perkins, E. L., & Batchelor, W. J. (2010). Water diffusion behaviour in paper cellulose structure at different moisture content studied by nuclear magnetic resonance (NMR). Chemeca 2010. In *The 40th Australasian chemical engineering conference (p. 10)* Adelaide, Australia.

Stejskal, E. O., & Tanner, J. E. (1965). Spin diffusion measurements: spin echoes in the presence of a time dependent field gradient. *Journal of Chemical Physics*, *42*, 288–292.

Tanner, J. E. (1970). Use of stimulated echo in NMR diffusion studies. *Journal of Chemical Physics*, *52*, 2523–2526.

Tappi Standard (1999). T 236 om-99 Kappa Number of pulp.

Topgaard, D., & Soderman, O. (2001). Diffusion of water absorbed in cellulose fibers studied with 1H-NMR. *Langmuir*, *17*(9), 2694–2702.

Topgaard, D., & Soderman, O. (2002a). Changes of cellulose fiber wall structure during drying investigated using NMR self-diffusion and relaxation experiments. *Cellulose*, *9*(2), 139–147.

Topgaard, D., & Soderman, O. (2002b). Self-diffusion in two- and three-dimensional powders of anisotropic domains: An NMR study of the diffusion of water in cellulose and starch. *Journal of Physical Chemistry B*, *106*(46), 11887–11892.

Topgaard, D., & Soderman, O. (2002c). Self-diffusion of nonfreezing water in porous carbohydrate polymer systems studied with nuclear magnetic resonance. *Biophysical Journal*, *83*(6), 3596–3606.

Weise, U., Maloney, T., & Paulapuro, H. (1996). Quantification of water in different states of interaction with wood pulp fibres. *Cellulose*, *3*(4), 189–202.

Zhang, L., Tsuzuki, T., & Wang, X. (2010). Preparation and characterization on cellulose nanofiber film. *Materials Science Forum*, 1760–1763.