Cellulose and Cellulose/Poly(vinyl alcohol) Blends. 2. Water Organization Revealed by Solid-State NMR Spectroscopy

D. Radloff, C. Boeffel, and H. W. Spiess*

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

Received March 24, 1995; Revised Manuscript Received August 1, 1995⊗

ABSTRACT: Cellulose as well as two cellulose/poly(vinyl alcohol) blends with compositions 60/40 and 80/20 w/w exposed to water are investigated by ^{1}H-, ^{2}H-, and ^{13}C solid-state NMR spectroscopy. For pure cellulose, the lower temperature, secondary dielectric relaxation process can be attributed to the onset of motion of adsorbed water molecules as revealed by ^{2}H-NMR spectroscopy. This water is not crystalline below 270 K. Three distinct kinds of water bound to the polymer matrix are detected, as far as dynamic behavior is concerned. First there is nonfreezable, strongly bound water that is rigid but amorphous at low temperatures. The second component is highly mobile and exhibits isotropic motion even below 270 K. Interestingly, there is a third component of water molecules that undergo well-defined 180° flips around their bisector axis with a rate greater than 10^{5} s^{-1} due to anisotropic constraints. In contrast to the first two kinds, this component cannot be removed from the polymer matrix by drying even at elevated temperatures and its motional process is observed over the whole temperature range, investigated from 190 to 370 K. All three kinds of matrix water coexist in a wide temperature range. In the blends, 2D ^{1}H−^{13}C heteronuclear wide line separation (WISE) NMR spectroscopy shows that at our low concentrations the water is predominantly associated with the cellulose backbone. No water can be detected in the immediate vicinity of the poly(vinyl alcohol). Applying spin diffusion, we detected nanoheterogeneities in the range of about 3 nm within these systems.

Introduction

Blends of synthetic and natural polymers are of considerable interest for various reasons. There is the need to balance the high performance of natural polymers like cellulose, with the ability to accommodate environmental concerns. Important to note here is the good biodegradability, which is a problem for most of the synthetic materials, and the “self-renewal” of natural polymers.

A drawback in the use of unmodified cellulose is its poor solubility in all common solvents and the thermal degradation below its melting point,[1] which makes blend preparation by solvent casting or extrusion difficult. This problem can be overcome by the use of solvent systems like *N,N*-dimethylacetamide (DMAc)/lithium chloride (LiCl) or *N*-methyl-2-pyrrolidinone (NMP)/lithium chloride, which are suitable for several synthetic polymers as well. By this method, various compatible as well as phase-separated blends were prepared.[2,3]

It is well-known that cellulose has a tendency to adsorb water, which drastically influences this material's properties.[4] The amount of water adsorbed and, therefore, the mechanical peoperties of cellulose strongly depend on the atmospheric humidity. This may lead to serious problems as far as applications of cellulose-containing materials are concerned. For this reason, a better understanding of the water organization in cellulose and cellulose blends is needed to combine the advantages of natural and synthetic polymers.

Concerning water adsorbed in a polymer matrix, different states have been identified in polymers.[5] Although no general nomenclature exists to describe these different components of matrix water, a basic distinction can be made between freezing and nonfreezing water.[6−8] In thermal analysis like DSC measurements, nonfreezing water exhibits more of a glass transition than a first-order transition like melting or crystallization. At low temperatures, well below the freezing point of bulk water, it behaves like a viscous liquid. Because these effects are due to polymer−water interactions, this component is named bound water. Furthermore, it can be divided into strongly and loosely bound water, depending on its thermal and dynamic behavior. In contrast, freezable water exhibits all the properties of bulk water. Because no polymer−water interactions can be detected, it is also called free water. This kind is present after the saturation point of the polymer matrix and can coexist with the bound water.

The systems studied here are cellulose and two different cellulose/poly(vinyl alcohol) blends prepared as films from NMP/LiCl. Dielectric measurements in the frequency range from 20 Hz to 1 MHz on these systems, described in detail in the companion paper,[9] exhibit a secondary relaxation in the temperature range from 140 and 290 K and a primary relaxation in the range from 330 to 470 K. The low-temperature process is strongly influenced by the water content of the samples. In the blends, the secondary relaxation is identical to the one in pure cellulose, except for an asymmetric broadening of the relaxation time distribution. The secondary relaxation observed in pure poly(vinyl alcohol) seems to be suppressed. Dynamic processes involving the adsorbed water molecules will be detected in dielectric relaxation because of their large dipole moments. However, this technique does not provide information about the geometry of the motions involved.

In this paper we report on ^{1}H-, ^{2}H-, and ^{13}C solid-state NMR experiments performed on these systems. The mobility of water molecules within a polymer matrix can be investigated in detail by ^{2}H-NMR. This technique has been shown to yield unique information about the time scale and geometry of rotational motions in polymers.[10] The water content of the blends as well as the dynamic behavior of the systems can be probed by standard ^{1}H-NMR experiments, while ^{13}C-CP/MAS NMR spectroscopy gives valuable information about the molecular structure and the blend composition of the samples under investigation.[11] In addition, it is possible to correlate the dynamic information to specific sites

⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1996.

0024-9297/96/2229-1528$12.00/0

within a system by the 2D-heteronuclear wide line separation (WISE) experiment.[12] This experiment is particularly useful for the investigation of matrix water in natural polymers, as shown recently for starch.[13]

Experimental Section

Sample Preparation. The blends were prepared from a mixed solution of cellulose (Hoechst Dunafil) and poly(vinyl alcohol) (Hoechst Mowiol 8-88) in NMP/LiCl by coagulation in ethanol, details are described elsewhere.[9] Before the measurements, the films were powdered under cooling with liquid nitrogen in a polymer mill and then dried under vacuum at 100 °C for 24 h. The cellulose samples for ^{2}H-NMR measurements were prepared as follows: to exchange the water present with D_2O, the cellulose films were dried first at 80 °C under vacuum for about 24 h. Then, the samples were exposed to a saturated D_2O atmosphere at 70 °C for about 24 h and then 12 h at room temperature. Four distinct samples were prepared: the "equilibrium1" and "equilibrium2" samples, prepared as described above but additionally dried for 1 and 2 h, respectively, at room temperature under vacuum in order to remove surface water. The "dry" sample was dried again after 2 weeks, and the "wet" sample was immersed in pure D_2O after the treatment. The resulting water content is about 2 wt % in the sample "equilibrium1" and 1 wt % in the sample equilibrium2"; the "dry" sample contains no excess water. All samples were sealed in a glass tube. In all cases chemical exchange between the cellulose $-$OH groups and D_2O takes place at room temperature and leads to an isotopic labeling of the cellulose as well. This fact is important for the interpretation of the spectra; see below.

NMR Measurements. The ^{1}H and ^{13}C measurements were performed on a Bruker MSL 300 spectrometer, equipped with a standard Bruker double resonance 7 mm MAS probe, operating at a frequency of 300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively. All samples were spun at frequencies of 4.5 kHz and the 90° pulse length for protons was about 3.7 μs. The cross-polarization time in all cases was 2 ms. The 2D-WISE spectra were recorded with 512 complex data points in the t_2 dimension and the 64 increments in the t_1 dimension. Dwell times of 5 and 20 μs were used in the t_1 and the t_2 dimension, corresponding to spectral widths of 200 and 25 kHz, respectively.

The ^{2}H-NMR spectra were recorded on a Bruker ASX 500 spectrometer operating at a frequency of 76.75 MHz, equipped with a Bruker single tuned variable temperature probehead. Two different pulse sequences were used: A solid echo $90°-\tau-90°-\tau-$acquire sequence was used to obtain the fully relaxed undistorted spectra, and a saturation echo $[90°]_{n\text{-times}}-\tau_1-90°-\tau_2-90°-\tau_2-$acquire pulse sequence with $n = 20$ and $\tau_1 = 10$ ms was applied to selectively excite the fast relaxing species. The 90° pulse length was about 2.9 μs; the pulse delay of the solid echo sequence τ, τ_2, was 30 μs. A total of 1K data points with a dwell time of 0.5 μs were acquired for each scan with a repetition rate of 2 s and 100 ms.

Results and Discussion

I. ^{2}H-NMR Investigations of Amorphous Cellulose Films. As mentioned above, dielectric studies show two distinct relaxations for cellulose and cellulose/PVA blends. In the frequency range from 20 Hz to 1 MHz a secondary relaxation in the temperature range from 140 to 290 K and a primary relaxation in the range from 330 to 470 K are seen. The low-temperature process is mainly influenced by the presence of water in the case of the pure cellulose as well as in the blends,[9] suggesting that this relaxation is related to the motion of water molecules within the polymer matrix. To check this conjecture, ^{2}H-NMR is the appropriate method. The dynamic behavior of matrix water, which is always present in cellulose and other natural polymers as well as certain synthetic polymers, can be investigated specifically and in detail by this means. This was shown in the case of water-containing epoxy resins[14,15] and poly(benzimidazole)[16] which contains matrix water as well. Therefore, cellulose was equilibrated with D_2O in order to isotopically label the matrix water. Figure 1a shows the temperature dependence of the ^{2}H-NMR spectra obtained from the "equilibrium2" sample. For comparison, the T_1 selective spectra of this sample, emphasizing the mobile components with $T_1 < 10$ ms, are plotted in Figure 1b. All spectra are scaled to the same height.

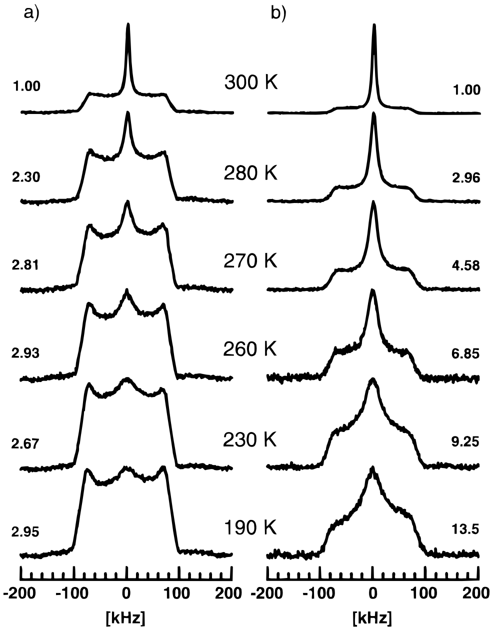

Figure 1. Cellulose/D_2O ^{2}H-NMR spectra of the "equilibrium2" sample recorded in the temperature range from 190 to 300 K. All spectra are scaled to the same height. Scaling factors are printed on the right and left side. (a) Solid echo spectra recorded with a repetition time of 2 s. (b) T_1-selective solid echo spectra recorded after saturation of the slow relaxing components by 20 rapidly repeated 90° pulses and a delay of $\tau_1 = 10$ ms, repetition time 100 ms. The line shape reveals 180° flips of one part of the mobile D_2O molecules.

At 190 K a broad Pake pattern is observed (Figure 1a) with a line splitting of about 145 kHz, the value for a rigid O$-$D component in the absence of any motional narrowing.[17] This Pake pattern is due to two different components which cannot be distinguished at one given temperature, namely the D_2O and the $-$OD components of the isotopic labeled cellulose. The cellulose is labeled due to chemical exchange between the D_2O and the $-$OH groups, leading covalently to the rigid cellulose backbone bonded ^{2}H nuclei. Two important features are observed at this temperature: First, there is no indication of crystallinity, which would lead to a Pake pattern with sharp singularities and edges. Crystallinity would be expected in the case of bulk water and is also observed in crystalline hydrates as a matrix.[18] Second, a partially narrowed component is visible throughout. This indicates the presence of water that is highly mobile as compared to frozen free water at this low temperature. In comparison, the spectrum of "wet" cellulose which contains frozen excess water as well highly mobile water is shown in Figure 3c and discussed below.

Detailed information about this component can be extracted from the T_1 selective spectra plotted in Figure 1b. Important here is the result that the motion of this mobile component is not isotropic. The spectrum at 190 K clearly exhibits a line shape typical for tetrahedral jumps with a reorientation angle of 109°. For such a motional process, three distinct possibilities exist within this system: (1) 180° flip process of water molecules around their bisector axis; (2) reorientations of the cellulose backbone; (3) intramolecular chemical exchange between different cellulose OD groups.

Reorientations of the cellulose backbone itself, which would lead also to this flip spectrum, can be ruled out because they would cause large changes of the dipole moment. Such a process must be observed with dielectric spectroscopy. However, this is not the case. From these data, it cannot be excluded that the flip spectrum is due to fast intramolecular ^{2}H exchange processes, even though this is very unlikely. We conclude that this spectrum is due to water molecules undergoing fast 180° flips around their bisector axis with a rate exceeding 10^7 s^{-1}. Such an anisotropic behavior of water molecules associated with a matrix observed here was found before in crystalline hydrates like $Ba(ClO_3)_2 \cdot H_2O$[18] and in silicate glasses.[19] Therefore, two components of matrix water can be distinguished at 190 K: The rigid amorphous one, which seems to be very strongly bound to the polymer matrix and for this reason cannot crystallize, and the highly mobile "flipping" one, whose motion is hindered due to anisotropic constraints.

With increasing temperature, starting around 260 K, the narrow part of the T_1-selective spectra becomes more intense while the broad part of the flip spectrum remains unchanged. This indicates the presence of a third component which is highly mobile as well, but with isotropic motions.

If the temperature is further increased, the integral intensity of this isotropic component increases while the intensity of the rigid amorphous component decreases. Interestingly, there is no change detected for the intensity of the flipping species. This indicates an equilibrium between the rigid amorphous and the isotropic mobile component, while the dynamic behavior of the anisotropic constrained water shows no temperature dependence. The equilibrium is visualized in Figure 2a. Plotted is the integral intensity of the mobile component as a fraction of the overall intensity for the "equilibrium1" and the "equilibrium2" samples, data extracted from the solid echo spectra seen in Figure 1a. The overall intensity includes the broad signal of the isotopic labeled cellulose as well. This is the reason why the maximum value for the "equilibrium1" and "equilibrium2" samples at 370 K is about 55% and 40%, respectively. The loss of intensity above 370 K is due to the evaporation of water above its boiling point.

Not only the intensity depends on the temperature, but also the line width at half-height of the narrow component decreases as the temperature increases (Figure 2b). This means that not only more molecules become mobile but also the motional rate of the mobile parts increases with temperature.

Since line narrowing in ^{2}H-NMR spectroscopy requires motional dynamics with a rate exceeding the frequency of the quadrupolar interaction of 210 kHz in the case of water, the presented ^{2}H-NMR spectra should be compared to the dielectric data acquired at a frequency of 200 kHz. They exhibit a secondary relaxation maximum at 250 K, which correlates very well with the temperature range where the water molecules become mobile on the ^{2}H-NMR time scale. This gives evidence tht the dielectric secondary relaxation is due to the onset of motion of the matrix water and explains the strong dependence of the dielectric relaxation strength on the water content of the sample. The 180° flip process of the water molecules observed via ^{2}H-NMR for the component with intermediate mobility is highly symmetric and therefore does not involve a change of the dipole moment. Therefore this motion is not detected by dielectric measurements.

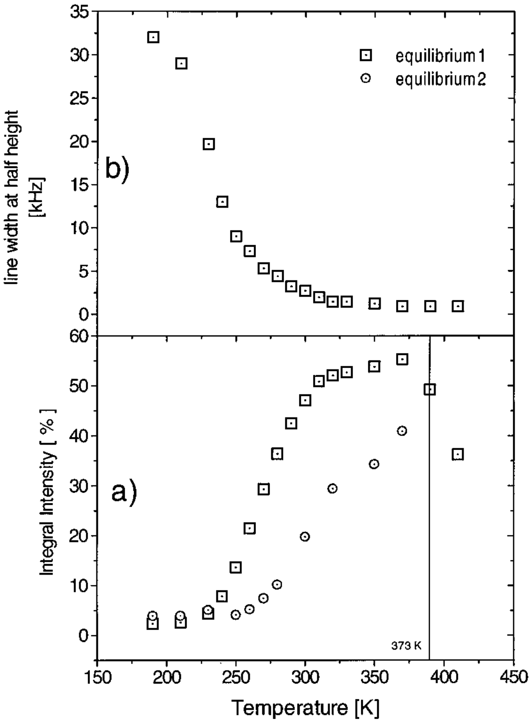

Figure 2. Relative intensity and line width at half-height of the narrow component extracted by integration of the solid echo spectra for samples "equilibrium1" (Figure 1a) and "equilibrium2". (a) Temperature dependence of the equilibrium between mobile and amorphous matrix water. Plotted is the integral intensity of the narrow component as a fraction of the overall intensity. (b) The decreasing line width in the range from 210 to 330 K shows the increasing mobility of the matrix water. The temperature range is in good agreement with the temperature range of the dielectric secondary relaxation at a frequency of 100 kHz.

At room temperature, the line width at half-height of the narrow peak within sample "equilibrium1" is of the order of 1000 Hz. This is considerably broader than the line width of liquid water at this temperature which in our magnet is of the order of 10 Hz. Hence, the water within the polymer matrix is partially immobilized. This is further shown by spin-diffusion measurements described below. The immobilization can be attributed to attractive forces between water molecules and the polymer matrix due to the ability of cellulose to form hydrogen bonds. This inhibits the crystallization of water even at temperatures as low as 190 K on one hand, and the same interaction immobilizes the molecules at room temperature on the other hand. However, these interactions do not prevent the water from evaporation above 373 K, as evident from Figure 2a with a strong decrease of the intensity of the mobile component above 373 K.

To check whether the observed mobile component is due to mobile polymer components or due to D_2O molecules, spectra of the "dry" sample were recorded (Figure 3a). The low-temperature spectrum at 190 K looks very similar to the one of the "equilibrium1" sample. But when the temperature is raised, no sharp line shows up. There is no temperature dependence observed in the spectra up to 300 K. This confirms that

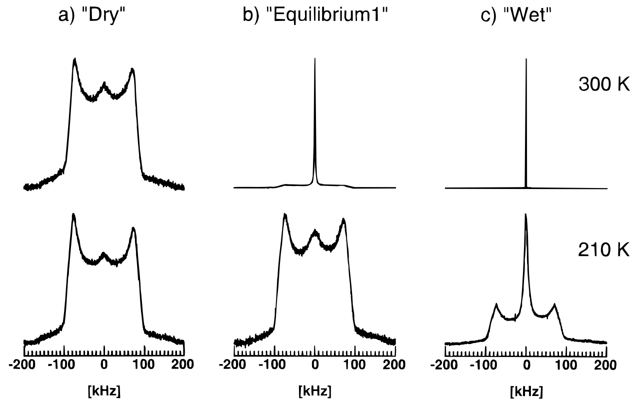

Figure 3. Solid echo ^{2}H-NMR spectra of three different samples at 210 and 300 K. (a) Spectra of the "dry" sample, showing a Pake pattern of amorphous deuterated cellulose arising from H−D exchange at room temperature. Remarkable is the small narrow component in the center, due to matrix water which undergoes 180° flips and is still present after drying for 24 h at 370 K in vacuum. (b) Spectra of the "equilibrium1" sample, showing at 210 K the same features as the dry sample but exhibiting a strong signal from mobile water at 300 K. (c) Spectra of the "wet" sample, containing bulk water. Clearly seen is the Pake pattern of crystalline water at 210 K and the intense signal of mobile water at this temperature which is unable to crystallize because of the strong association with the cellulose backbone. At 300 K the spectrum exhibits only one narrow peak, revealing the high-frequency motions of bulk water as compared to the restricted motion of the bonded water seen in the equilibrium sample at 300 K.

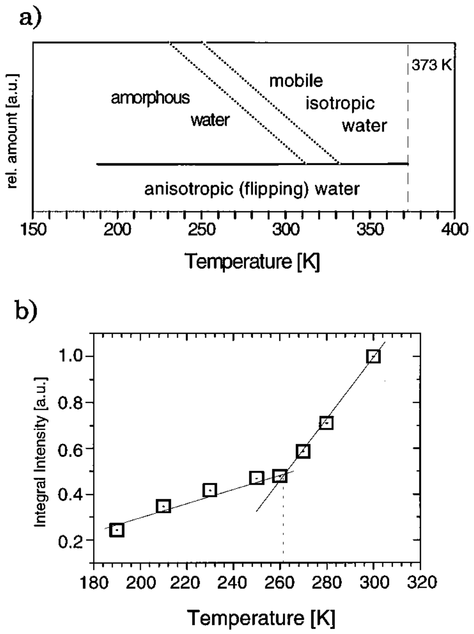

Figure 4. (a) The three different kinds of matrix water adsorbed to cellulose: Mobile water that undergoes well-defined 180° flips indepenent of temperature and the equilibrium between rigid, nonfreezable amorphous water and highly mobile water which starts to evaporate above 373 K. (b) Integral intensity of the T_1 selective spectra from Figure 1b, showing behavior comparable to a glass transition. The onset of motion of the matrix water is clearly seen at 260 K.

the observed sharp line in the case of the "equilibrium1" sample, plotted for direct comparison in Figure 3b, is due to water. Remarkably, the central peak, attributed to the "flipping" water (Figure 1), is present even in the spectra of this "dry" sample. This shows tht this component cannot be removed from the polymer matrix under the conditions we used. If occluded, crystallizable water would still be present within this sample and a well-defined line shape for a crystalline component would be present. This is not observed.

The ability of cellulose to adsorb water has a limit that is not reached in the "equilibrium" samples. This can be shown by the spectra recorded from the "wet" sample, shown in Figure 3c. A comparison to the spectra of the "equilibrium1" sample recorded at 210 K, as shown in Figure 3, shows distinct differences. The line due to mobile water that is adsorbed to the cellulose is much more intense and narrower even at this low temperature. This indicates that the "equilibrium1" cellulose is not saturated. At the same time a sharp well-defined Pake pattern is observed in the "wet" case, showing the features of a crystalline material. This shows the presence of excess water that cannot be adsorbed by the cellulose matrix and therefore crystallizes.

The three different states of water bonded to cellulose which are found here are summarized in Figure 4a. There is adsorbed water that cannot be removed from the cellulose matrix and undergoes relatively well-defined 180° flips around the bisector axis. The flip rate is above 10^7 Hz throughout. Its temperature dependence could be determined through measurement of the spin−lattice relaxation time,[18] which is beyond the scope of this paper. In addition, there is an equilibrium between rigid amorphous water and highly mobile isotropic water which changes drastically with temperature and depends on the water content of the sample. The onset of motion of the water molecules bound to the polymer matrix exhibits a glass transition like behavior. The increasing amount of the mobile component above this temperature leads to an increase in the overall integral intensity of the T_1-selective spectra, as seen in Figure 4b. On the ^{2}H-NMR time scale, a dynamic T_g of around 260 K can be extracted from these data, which is in good agreement with data reported in the literature. Previous DSC and NMR relaxation time measurements performed on poly(*N*-vinyl-2-pyrrolidone-*co*-methyl methacrylate) copolymers and poly(hydroxyethyl methacrylate)[7,20] revealed equivalent properties of the matrix water, except for the anisotropic behavior. An equilibrium between rigid glass-like and mobile components of bound water far below 273 K is found there as well with a process comparable to a glass transition of water in the range from 170 to 200 K.[20]

II. ^{1}H- and ^{13}C-NMR Investigations of Cellulose and Cellulose/Poly(vinyl alcohol) Blends. Detailed information about the molecular dynamics of water within the cellulose matrix is obtained from ^{2}H-NMR investigations. But for a better understanding of the water organization in natural polymers, additional knowledge is needed. For pure cellulose and its derivatives, several investigations concerned with matrix water are found in the literature. However, no information is available on the localization and organization of water even for the particularly interesting cellulose-containing multicomponent systems. In the case of blends, most of the scientific work is concerned with blend preparation and compatibility, e.g. cellulose/poly(vinyl alcohol) blends were prepared and investigated by Manley and co-workers.[1−3] The blends are described as compatible although heterogeneities of the order of 1−36 nm are detected by ^{1}H relaxation time measurements and dynamic-mechanical investigations. The miscibility of both components seems to increase with increasing cellulose content of the blends. But still, little is known about the water present within these

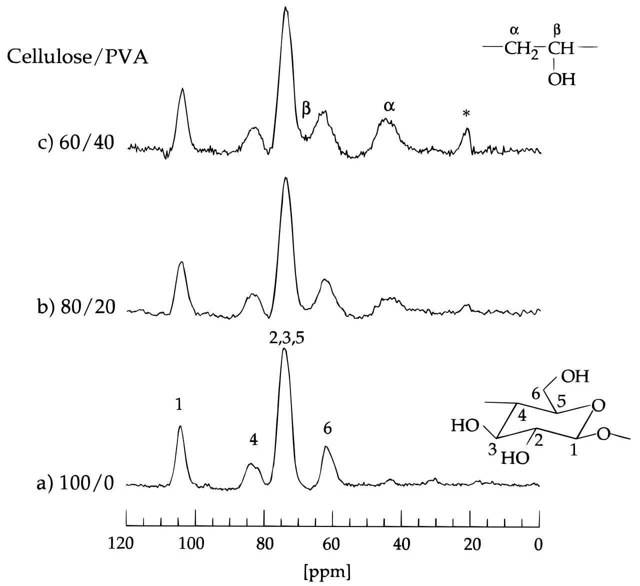

Figure 5. ^{13}C-CP/MAS spectra of cellulose, the cellulose/poly(vinyl alcohol) 80/20 w/w blend, and the cellulose/poly(vinyl alcohol) 60/40 w/w blend. (a) shows the characteristic spectrum of amorphous cellulose; (b) and (c) show the different poly(vinyl alcohol) contents of the blends and the presence of remaining acetyl groups from unhydrolyzed vinyl acetate groups. Peak assignment: 104.6 ppm, C_1; 83.9 ppm, C_4; 74.5 ppm, $C_{2,3,5}$; 62.2 ppm, C_6 and CHOH in PVA; 45.1 ppm, CH_2 of PVA; 21.4 ppm, CH_3 of remaining acetyl groups (*).

systems. Important questions to be addressed are: Is there a direct influence of the blend composition on the water content of the systems and is there a preference for the water molecules to be located within the cellulose or the poly(vinyl alcohol) rich phase, if such phases exist?

In the case of truly compatible blends all three components—cellulose, poly(vinyl alcohol), and water—should be mixed on a molecular level and no separated domains are expected. Furthermore, both blend components are hygroscopic due to the presence of hydroxy groups and should therefore be capable of adsorbing water.

^{1}H and ^{13}C solid-state NMR experiments are performed to answer these questions. ^{13}C-CP/MAS NMR spectra give information about the structure and the composition of the samples, which is particularly important in our case.[11] Figure 5 shows the ^{13}C-CP/MAS spectra of pure cellulose and two cellulose/PVA blends.

The spectrum of pure cellulose is characteristic of a completely amorphous material[21] and shows four well-separated peaks which can be attributed to the corresponding structural elements: 104.6 ppm, C1; 83.9 ppm, C4; 74.5 ppm, C2,3,5; 62.2 ppm; C6. In the case of the blends (Figure 5b,c) the C6 peak at 62.2 ppm is overlayed by the CH_2OH signal of the poly(vinyl alcohol). Nevertheless, the poly(vinyl alcohol) is easily identified by the separated peak at 45.1 ppm due the CH_2 group. The peak at 21.5 ppm is due to the acetyl CH_3 group, remaining from nonhydrolyzed poly(vinyl acetate).

^{1}H one-pulse MAS spectra, acquired at room temperature with a spinning speed of 4.500 Hz are plotted in Figure 6. The spectra are scaled to the same integral intensity of the broad component, reflecting the polymer matrix. Because the narrow component is exclusively due to the adsorbed water, its integral intensity reflects directly the water content of the sample. A correlation between the amount of cellulose and the amount of water is found within the blends. It is clearly seen that the water content can be related to the blend composition in the order: cellulose > cellulose/poly(vinyl alcohol) 80/20 > cellulose/poly(vinyl alcohol) 60/40. The water content therefore decreases with decreasing cellulose content. This result shows that the ability of the blends to adsorb water is dominated by the cellulose in accord with the dielectric measurements,[9] where the relaxation strength of the secondary relaxation decreases with decreasing cellulose content. This result reflects the different tendencies for the two different polymers PVA and cellulose to adsorb water. Because of the higher concentration of OH groups, cellulose adsorbs more water water than PVA.

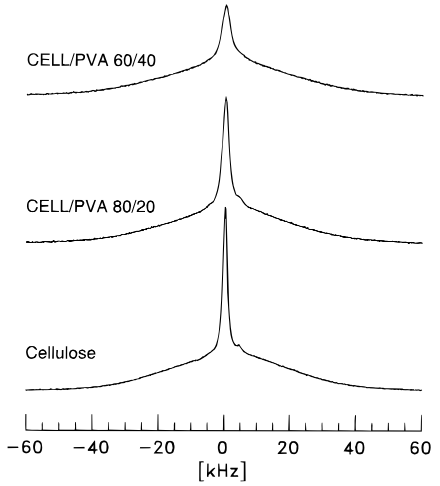

Figure 6. ^{1}H one-pulse MAS spectra (ν_{rot} = 4.500 Hz) of cellulose, the cellulose/poly(vinyl alcohol) 80/20 w/w blend, and the cellulose/poly(vinyl alcohol) 60/40 w/w blend. All spectra are scaled to the same integral intensity of the broad component, representing the polymer matrix. The intensity of the narrow components reflects directly the water content of the samples, which decreases with decreasing cellulose content.

It should be mentioned that no influence of magic spinning on the water content of the samples was detected even after the long measuring time of a 2D experiment of 24 h.

A deeper insight into the water localization and organization within the blend matrix is obtained using the 2D-wide line separation (WISE) experiment.[12,22] Here, the spectroscopic information about the dynamic behavior within a system, reflected in the ^{1}H one pulse experiments (Figure 6), can be directly related to structural elements resolved in the ^{13}C-CP/MAS spectrum (Figure 5). If the water were equally distributed throughout the sample, the narrow line in the ^{1}H dimension is expected at all positions in the ^{13}C dimension. Indeed, recently, a similar experiment with minor modifications was performed on a starch-*g*-poly(acrylonitrile) copolymer by Ganalpathy and co-workers.[23] These authors could detect water with a different dynamic behavior at the backbone and the poly(acrylonitrile) side chains.

Figures 7a–9a show the 2D-WISE spectra of cellulose at room temperature and the 60/40 and the 80/20 w/w cellulose/poly(vinyl alcohol) blends. Interestingly, all components exhibit the same line width at half-height of 40 kHz in the ^{1}H dimension and no sharp signal is observed at all. It should be noted that because of the short CP time of 2 ms, the spectra are dominated by the signals of the CH and the CH_2 groups. Thus, the 2D-WISE spectra first of all confirm our earlier conclusion that the polymer backbones are rigid at room

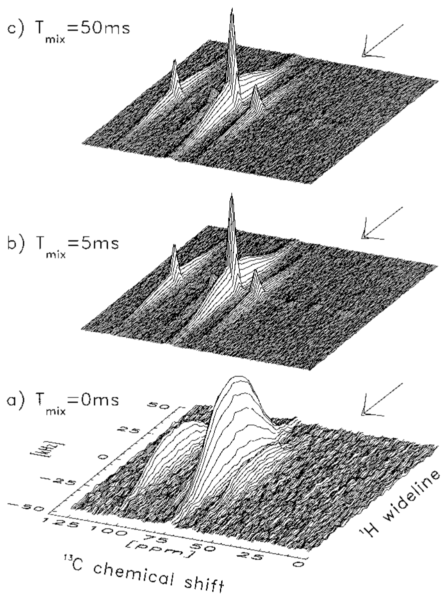

Figure 7. 2D-WISE spectra of pure cellulose, recorded at room temperature (CP time: 2 ms): (a) spectrum without a mixing time before cross-polarization; (b) spectrum after insertion of 5 ms mixing time, the mobile component due to mobile water is now seen; (c) spectrum after insertion of 50 ms mixing time. The arrows mark the position at 45 ppm where the PVA CHOH signal is expected for the blends.

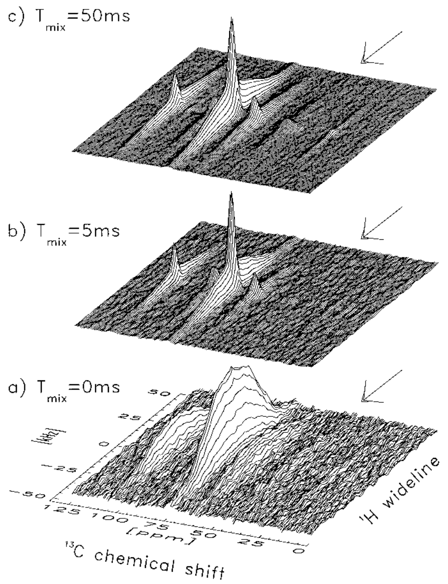

Figure 8. 2D-WISE spectra of the cellulose/poly(vinyl alcohol) blend 80/20, recorded at room temperature (CP time: 2 ms): (a) spectrum without a mixing time before cross-polarization; (b) spectrum after insertion of 5 ms mixing time (the mobile component due to mobile water is now seen, but just at the cellulose signals); (c) spectrum after insertion of 50 ms mixing time (the mobile water is now seen even at the poly(vinyl alcohol) signals). The arrows mark the PVA CHOH signal at 45 ppm, where the water signal appears after T_{mix} = 50 ms.

temperature, as already shown by ^{2}H-NMR spectroscopy; see above. The mobility is ascribed to the water molecules. The absence of a narrow line shows that there exists no sufficient heteronuclear dipolar interaction between the mobile water protons and the ^{13}C nuclei of both the cellulose and the PVA. There can be two reasons for this finding: first, it is possible that the inverse correlation time of the matrix water exceeds the frequency of the heteronuclear dipolar interaction. However, the matrix water is significantly immobilized at room temperature, as revealed by ^{2}H-NMR; see above. Therefore, this explanation can be ruled out. Second, the dipolar coupling strength of a given pair of nuclei scales with $1/r^3$, where r is the length of the vector connecting these nuclei. Therefore, it is likely that the distance between the water protons and the ^{13}C nuclei of the polymer matrix is too large. In this case, information about the dynamic behavior of displaced regions can be transferred to the ^{13}C nuclei by spin diffusion via the polymer protons.[11,12] Then, a narrow line is expected to appear after the introduction of a mixing time in the WISE experiment[22] during which ^{1}H spin diffusion can occur.

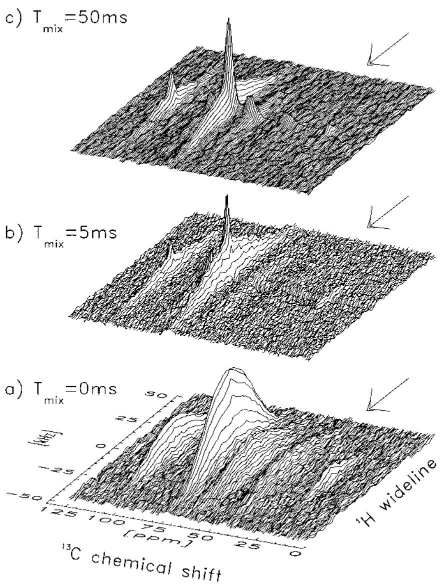

Figure 9. 2D-WISE spectra of the cellulose/poly(vinyl alcohol) blend 60/40, recorded at room temperature (CP time: 2 ms): (a) spectrum without a mixing time before cross-polarization; (b) spectrum after insertion of 5 ms mixing time (the mobile component due to mobile water is seen now, but just at the cellulose signals); (c) spectrum after insertion of 50 ms mixing time (the mobile water is now seen even at the poly(vinyl alcohol) signals). The arrows mark the PVA CHOH signal at 45 ppm, where the water signal appears after T_{mix} = 50 ms.

Spectra with insertion of a spin diffusion time of T_{mix} = 5 ms and T_{mix} = 50 ms are plotted in Figures 7b−9b and 7c−9c, respectively. Now, the narrow component due to mobile water is observed in all spectra. First, this observation proves directly the immobilization of the matrix water. Spin diffusion requires the presence of dipolar couplings, here between the water and the cellulose protons. These couplings were not present if the correlation time of the matrix water would be less than 10^{-7} s, which is the case for free water.

Particularly informative are the spectra recorded with a mixing time of 5 ms. Here, in the case of the blends, the narrow line is detected only at the cellulose signals. They are absent at the signals of the PVA CH_2 group at 45.1 ppm in the ^{13}C dimension, marked by arrows. This gives evidence that the water molecules are predominantly associated with the cellulose polymer and not with PVA. Again, this is somewhat surprising since PVA is hydrophilic and even water soluble. Furthermore, this result reveals microheterogeneities of the blends. With T_{mix} = 50 ms the equilibrium is reached and, in Figures 8c and 9c, the narrow line can be located at the poly(vinyl alcohol) signals as well. From spin diffusion behavior, the length scale $\langle x \rangle$ of the heterogeneities in the cellulose/poly(vinyl alcohol) bends can be estimated by the following equation:[12]

$$\langle x\rangle = \sqrt{4/\pi D T_{\mathrm{mix}}} \tag{1}$$

The spin diffusion coefficient D as determined from the line width of the mobile component of the proton spectra[24] is about 0.15 $\mathrm{nm}^2\,\mathrm{ms}^{-1}$. Thus, the length scale of the water−cellulose disatnce can be estimated to be less than 1 nm in all cases. This reveals that the water is associated with the cellulose backbone on a molecular level and that no domains of bulk water exist. For the blends, a distance of about 3 nm between the water molecules associated with the cellulose and the poly(vinyl alcohol) backbone is found in both systems. This clearly shows that the two polymer components and water are not mixed on a molecular level but rather exhibit nanoheterogeneities in the range of 3 nm, consistent with the SAXS measurements reported in the companion paper.[9]

Conclusion

The water organization in pure cellulose and two cellulose/poly(vinyl alcohol) blends was investigated by solid-state NMR spectroscopy. Three distinct kinds of matrix water are detected by ^{2}H-NMR in pure cellulose: First, there is adsorbed water that is highly mobile even at 190 K and not removable from the polymer matrix at elevated temperatures under vacuum. Its motional process involves a 180° flip around the bisector axis of the water molecules. This process seems to be largely independent of temperature.

Secondly, there is adsorbed nonfreezable amorphous water and adsorbed water that is very mobile even far below 270 K. Between these two kinds, a temperature dependent equilibrium exists.

In the blends, the ability to adsorb water is mainly influenced by the cellulose component. The matrix water is located in the vicinity of the cellulose, as determined by the 2D-WISE experiment with spin diffusion. No water adsorbed by the poly(vinyl alcohol) is detected. This reveals nanoheterogeneities between the cellulose and the poly(vinyl alcohol) components in the range of 3 nm.

Acknowledgment. The samples were kindly provided by Dipl. Chem. C. Meckel-Jonas. Financial support by the Bundesministerium für Forschung und Technologie (BMFT Grant 03 M 4068 7) is gratefully acknowledged.

References and Notes

(1) Nishio, Y.; Roy, S. K.; Manley, R. St. J. *Polymer* **1987**, *28*, 1385.
(2) Masson, J. F.; Manley, R. St. J. *Macromolecules* **1992**, *25*, 589.
(3) Nishio, Y.; Manley, R. St. J. *Macromolecules* **1988**, *21*, 1270.
(4) Hatakeyama, T.; Ikeda, Y.; Hatakeyama, H. *Makromol. Chem.* **1987**, *188*, 1875.
(5) Rowland, S. P., Ed. *Water in Polymers*; ACS Symposium Series 127; American Chemical Society: Washington, DC, 1980.
(6) Hofmann, K.; Hatakayama, H. *Polymer* **1994**, *35*, 2749.
(7) Smyth, G.; Quinn, F. X.; McBrierty, V. J. *Macromolecules* **1988**, *21*, 3198.
(8) Kinard, D. A.; Hoeve, C. A. J. *J. Polym. Sci., Polym. Symp.* **1984**, *71*, 183.
(9) Schartel, B.; Wendling, J.; Wendorff, J. *Macromolecules* **1996**, *29*, 1521 (preceding paper in this issue).
(10) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
(11) McBrierty, V. J.; Packer, K. J. *Nuclear Magnetic Resonance in Solid Polymers*; Cambridge University Press: Cambridge, U.K., 1994.
(12) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: New York, 1994.
(13) Kulik, A. S.; de Costa, J. R. C.; Haverkamp, J. *J. Agric. Food Chem.* **1994**, *42*, 2803.
(14) Jelinski, L. W.; Dumains, J. J.; Stark, R. E.; Ellis, T. S.; Karasz, F. E. *Macromolecules* **1983**, *16*, 1019.
(15) Jelinski, L. W.; Dumains, J. J.; Cholli, A. L.; Ellis, T. S.; Karasz, F. E. *Macromolecules* **1985**, *18*, 1091.
(16) Egger, Norbert. Ph.D. Thesis, Mainz, 1992.
(17) Spiess, H. W.; Garrett, B. B.; Sheline, R. K.; Rabideau, S. W. *J. Chem. Phys.* **1969**, *51*, 1201.
(18) Griffin, R. G.; et al. In *The Time Domain in Surface and Structural Dynamics*; Long, G. J., Grandjean, F., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1988; pp 81−105.
(19) Eckert, H.; Yesinowski, J. P.; Stolper, E. M. *Solid State Ionics* **1989**, *32/33*, 298.
(20) Quinn, F. X.; Kampff, E.; Smyth, G.; McBrierty, V. J. *Macromolecules* **1988**, *21*, 3191.
(21) Atalla, R. H.; Gast, J. C.; Sindorf, D. W.; Bartuska, V. J.; Maciel, G. E. *J. Am. Chem. Soc.* **1980**, *102*, 3249.
(22) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273.
(23) Ganalpathy, S.; Rajamohanan, P. R.; Siddharth, S. R.; Mandhare, A. B.; Mashelkar, R. A. *Macromolecules* **1994**, *27*, 3432.
(24) Spiegel, S.; Schmidt-Rohr, K.; Boeffel, C.; Spiess, H. W. *Polymer* **1993**, *34*, 4566.

MA950405H