Nanoheterogeneity of a Polymer Blend and the Effect of Humidity as Characterized by Solid-State NMR

Stuart A. Brewer,*,† David C. Apperley,‡ and Corinne A. Stone†

DSTL Chemical and Biological Sciences, Porton Down, Salisbury, Wiltshire, United Kingdom, SP4 0JQ, and Department of Chemistry, Durham University, South Road, Durham, United Kingdom, DH1 3LE

Received July 11, 2007. Revised Manuscript Received September 20, 2007

A material that potentially displays both breathability and chemical barrier properties has been the center of this study. This material is based on a hydrogel formed between polyvinyl alcohol, polyethyleneimine, and water. An important aspect of this study has been a need to obtain a greater understanding of the solid-state structure adopted by the material. Consequently, a detailed investigation of the polymer blend was conducted by solid-state NMR. A combination of high-resolution carbon-13 cross-polarization and fast-recycle direct-polarization experiments, together with ^{1}H wide-line measurements, has yielded a wealth of information on the domain structure of the material and the characteristics of those domains. The effects of environmental humidity on the polymer blend have also been studied.

Introduction

Protective clothing that utilizes a moisture-vapor permeable (breathable) membrane allows the wearer to lose heat through sweating. Potentially, this offers a means by which protection against chemical hazards can be balanced with the user burden associated with wearing such garments. Importantly, breathable garments would occupy a position in between air-permeable clothing systems and air-impermeable clothing systems in terms of the protection/physiological balance. Although breathable membranes exist, the challenge is to develop a breathable membrane that affords an adequate level of protection to toxic chemical agents. A material that potentially displays both breathability and chemical barrier properties has been the center of a detailed investigation conducted by us.[1] This material is based on a hydrogel formed between polyvinyl alcohol (PVOH), polyethyleneimine (PEI), and water. PVOH is a much studied polymer that has been investigated for a range of applications,[2] including pervaporation membranes,[3] packaging materials, barrier laminates, and even ionic conductors.[4] PEI has also been used for applications such as alcohol/water separation[5] and as a cationic polyelectrolyte. However, the majority of the work conducted on this polymer is associated with its ability to chelate heavy metals,[6] its ability to act as a scavenger of a wide variety of organic compounds,[7] and its ability to impart antimicrobial activity.[8]

Relatively few references exist for formulations that contain both PVOH and PEI. One of the most recent is concerned with an ion-exchange membrane that contains a semi-interpenetrating network of PVOH (used as a cross-linked matrix) and a variety of polyelectrolytes to impart a specific ion-exchange property. In that study, one of the cationic polyelectrolytes investigated was PEI.[9]

Although not restrictive, the standard formulation that is used in our investigations is composed of equal proportions (by weight) of PEI and PVOH. The polymers are mixed as aqueous solutions, cast as a film, and allowed to dry under either ambient conditions or at a controlled temperature and relative humidity (RH). Thermogravimetric analysis revealed that a significant amount of water (approximately 10% by weight) is retained in the resulting films. The amount of water in the films is believed to be determined by the environmental conditions to which the films are exposed and was observed to be reasonably constant regardless of the curing regime employed.

An important aspect of our study of this material has been the need to obtain a greater understanding of the solid-state structure adopted by a membrane formed from this hydrogel. A differential scanning calorimetry (DSC) investigation of this material reveals only one glass transition temperature, T_g (Table 1).

---

* To whom correspondence should be addressed. E-mail: sabrewer@mail.dstl.gov.uk.

† DSTL.

‡ Durham University.

(1) Brewer, S. A.; Stone, C. A.; Willis, C. R.; Beadle, B. A. Patent number: US2004166350, August 26, 2004.

(2) Finch, C. A. *Polyvinyl Alcohol*; Wiley: London, 1973. Finch, C. A. *Properties and Applications of Polyvinyl Alcohol*; Society of Chemical Industry: London, 1968; S. C. I. Monograph No. 30. Pritchard, J. G. *Poly(Vinyl Alcohol), Basic Properties and Uses*; Macdonald Technical and Scientific: London, 1970. Sakurada, I.; *Polyvinyl Alcohol Fibres*; Marcel Dekker, Inc: New York, 1985; International Fiber Science and Technology Series, 6.

(3) Gozzelino, G. *Sep. Sci. Technol.* **2005**, *40*, 2265.

(4) (a) Vargas, R. A.; Zapata, V.; Delgado, M. L.; Palacios, I. *Solid State Ionics* **2004**, *175*, 729. (b) Jinli, Q.; Takeo, H.; Tatsuhiro, O. *Chem. Mater.* **2005**, *17*, 2413. (c) Finch, C. A. *Polyvinyl Alcohol: Developments*; Wiley: Chichester, U.K., 1992.

(5) Ali, T.; Lutz, K.; Bernd, T. *Colloids Surf., A* **2002**, *198–200*, 881. Zhaoqi, Z.; Xianshe, F. *Mater. Sci. Eng.* **2006**, *26*, 1.

(6) Juang, R. S.; Chen, M. N. *Ind. Eng. Chem. Res.* **1996**, *35*, 1935.

(7) Birkart, P.; Lang, H.; Dautzenberg, H. *Faserforsch. Textiltech.* **1970**, *21*, 49.

(8) Lin, J.; Murthy, S. K.; Olsen, B. D.; Gleason, K. K.; Klibanov, A. M. *Biotechnol. Lett.* **2003**, *25*, 1661.

(9) Lebrun, L.; Da Silva, E.; Metayer, M. *J. Appl. Polym. Sci.* **2002**, *84*, 1572.

10.1021/cm071822z CCC: $40.75

Table 1. DSC Data

sample	T_g/°C	T_m/°C
PVOH powder	38.2 (1st hc[a]) 76.5 (2nd hc[a])	223.1
PEI liquid	−52.9	
PVOH film + neat PEI liquid (1:1)	−49.2 36.8	217.3
PVOH−PEI blend air-dried	−14.8	222.8

[a] hc = heating cycle.

PVOH exhibits a glass transition temperature that is dependent on the amount of water present. With up to 5% water by weight, PVOH exhibits a T_g at 35 °C. At a lower water content, the T_g increases to 76 °C. PEI exhibits a considerably lower T_g at −52 °C. The DSC data also reveal that a melting temperature, T_m, of 223 °C, consistent with the T_m for PVOH, is also present. Since the polymer blend exhibits one T_g at −14 °C, it is likely that, solely on the basis of this, these polymers would be considered miscible, certainly on the micrometer scale. However, there is growing evidence that glass transition temperatures cannot be used to indicate miscibility on the molecular level.[10] It is suggested that dynamic mechanical thermal analysis (DMTA) data should be obtained on polymer systems where an understanding of polymer miscibility on the submicron scale is required. For our system, this reveals only a single tan δ peak at 5 °C. Although this is 20 K higher than the T_g determined by DSC, this is quite typical of the two techniques. No separate peaks in the vicinity of −55 and +38 °C were seen. The evidence from both the DSC and DMTA data suggests that the polymer system is phase-mixed.

In our studies, we have used solid-state NMR to elucidate how the two specific polymers interact at the molecular level and on the nanometer scale. Solid-state NMR is a powerful tool for the study of heterogeneous systems such as semicrystalline polymers.[11,12] High-resolution carbon-13 magic-angle spinning (MAS) spectra and wide-line ^{1}H measurements provide a wealth of information on the chemical nature and morphology of materials, both individually and when used in combination. Importantly, specific ^{13}C NMR experiments can be conducted which will probe either relatively mobile or immobile environments.[13]

To observe rigid crystalline phases and, to a potentially lesser extent, amorphous phases, a carbon-13 cross-polarization (CP) MAS spectrum is recorded. This NMR experiment preferentially observes phases where there is strong dipolar coupling between protons and between protons and carbon, a situation which occurs in more rigid environments. Cross-polarization becomes much less efficient in highly mobile phases where there is a motionally averaged dipolar coupling. Spectra can be obtained from such phases with a direct-polarization (DP) MAS experiment, and if the recycle delay is kept short, the experiment will favor phases with short carbon relaxation times and discriminate against those rigid phases observed in the CPMAS experiment—where the relaxation times are usually much longer.

With this combination of techniques, we have studied PVOH and PEI raw materials to give us information, on which we have based a characterization of the polymer blend. We have then studied the effects of environmental humidity on the system.

Experimental Section

Carbon-13, ^{15}N, and ^{1}H measurements were carried out using a Varian Unity Inova spectrometer operating at 299.82 MHz for ^{1}H, 75.40 MHz for ^{13}C, and 30.39 MHz for ^{15}N. Carbon and nitrogen spectra were obtained using either a 7 mm (rotor o.d.) Doty Scientific MAS probe or a 7.5 mm Varian Apex-style probe. Proton measurements were made using a static, 5 mm horizontal coil probe. Except where otherwise stated, ^{13}C CPMAS spectra were obtained with a 2 s recycle delay, a 0.2 ms contact time, and spin-lock fields of 50–60 kHz. The ^{15}N spectrum was obtained with a 2 s recycle delay and 1 ms contact time. Fast-recycle direct-polarization (FRDP) spectra were obtained using a 1 s recycle delay and a 90° excitation pulse (of 4–5 μs duration). Sample spin rates were between 4.3 and 5 kHz, and typically, 1000−1600 repetitions were recorded for the carbon spectra, 27 920 repetitions for the nitrogen. The carbon spectra were referenced with respect to tetramethylsilane (by setting the high-frequency signal from adamantane to 38.4 ppm) and the nitrogen to nitromethane (by setting the nitrate signal from solid ammonium nitrate to −5.1 ppm). In addition to the traditional CPMAS experiment, a spectrum was also obtained using a delayed contact experiment where a delay is inserted between the start of the ^{1}H spin-lock pulse and the contact period. Further experimental details are given in the figure captions. Static ^{1}H spectra were obtained using a 90°-spin-lock experiment (incorporating a solid echo after the spin lock)[14] with a 50 kHz spin-lock field, a 2 μs 90° excitation pulse, and a 2 s recycle delay.

Samples provided as films were cut into small (1–2 mm) squares and packed into rotors without further manipulation. All rotors were packed in air. The polymer film discussed in the text was made from an aqueous solution of 10 wt % PVOH and 10 wt % PEI, which was then dried at room temperature and ambient humidity. Typically, the films were left to dry overnight at ambient temperature, whereupon the polymer film could be easily removed from the glass plate. Information on the other samples used in this study is given in the text. Storage environments with different relative humidities were produced from saturated salt solutions: 76% RH from NaCl, 33% from $MgCl_2$, and 6% from NaOH (all at ambient laboratory temperature, ~21 °C).

Spectral deconvolutions were carried out using VNMR software (Varian Inc., Palo Alto, CA) with either Gaussian (CP spectra) or Lorentzian (FRDP spectra) line shapes.

Results and Discussion

Solid-State NMR of PVOH. The carbon-13 CPMAS spectrum from PVOH consists of four lines (Figure 1): one broad one centered at 45–46 ppm from the methylene carbon and a group of three lines at 64.9, 70.7, and 76.7 ppm from the methine carbon (designated III, II, and I, respectively).[15]

---

(10) Wagler, T.; Rinaldi, P. L.; Han, C. D.; Chun, H. *Macromolecules* **2000**, *33*, 1778.

(11) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: New York, 1994.

(12) Komoroski, R. A. *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; VCH Publishers Inc.: New York, 1986.

(13) Ha, M.-A.; Vietor, R. J.; Jardine, G. D.; Apperley, D. C.; Jarvis, M. C. *Phytochemistry* **2005**, *66*, 1817.

(14) McBrierty, V. J.; Packer, K. J. *Nuclear Magnetic Resonance in Solid Polymers*; Cambridge University Press: Cambridge, 1993.

(15) Terao, T.; Maeda, S.; Saika, A. *Macromolecules* **1983**, *16*, 1535.

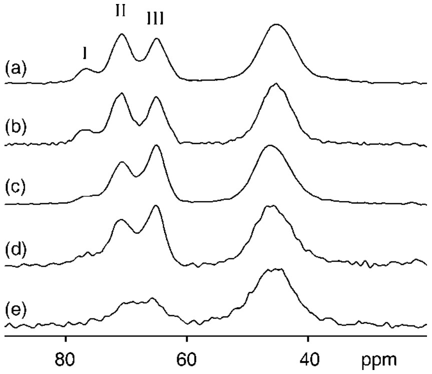
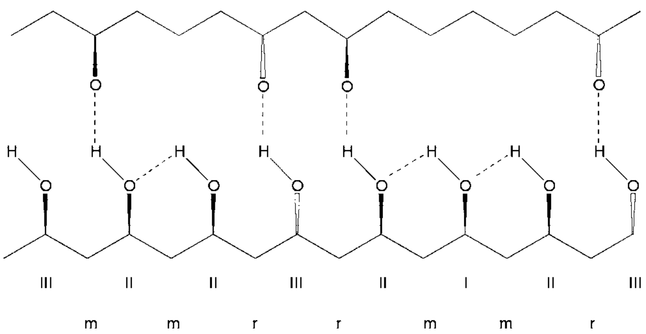


Figure 1. Carbon-13 spectra from PVOH. (a−c) CPMAS spectra from (a) powdered raw material, (b) film dried at 150 °C and 50% RH (from 448 repetitions with a 5 s recycle delay and 1 ms contact time), and (c) air-dried film. (d) Long-recycle (176 repetitions with 120 s recycle delay) DPMAS spectrum from air-dried film. (e) Fast-recycle (1920 repetitions with 1 s recycle delay) DPMAS spectrum from air-dried film.

Scheme 1. Hydrogen-Bond Formation in PVOH



Line I arises from carbons where the hydroxyl is involved only in intramolecular hydrogen bonds.

Such bonding can occur for the hydroxyl groups of meso−meso (mm in Scheme 1) triad sequences in the polymer where there is a short (0.252 nm) O−O separation. The O−O separation in rr triads is longer (0.341 nm), which precludes intramolecular hydrogen-bond formation, and one such bond can be formed for an mr triad. Relative to the intramolecular hydrogen bonds, weaker intermolecular hydrogen bonds can also form. These, however, do not produce such large (∼6 ppm) differences in the chemical shifts but may lead to a smaller distribution in shifts which broadens the lines. Line II arises from methine carbons where either the hydroxyl has one intramolecular hydrogen bond (mr triad) or is from a carbon in a mm triad where the hydroxyl undergoes one intra- and one intermolecular hydrogen bond. Line III arises from carbons where the hydroxyl group is not involved in intramolecular hydrogen bonding, so this may include signals from all three triads depending on the extent of intermolecular hydrogen bonding. The intensities of the II and III lines do not, therefore, give a direct indication of the tacticity of the polymer. There is also some evidence in the literature for a low-frequency shoulder (III$_\mathrm{f}$) on the 64.9 ppm signal that is attributable to an environment with no intra- or intermolecular hydrogen bonding.[16] It is worth noting that PVOH adopts the same planar-zigzag conformation irrespective of tacticity, so these shift differences do not relate to changes in conformation.[13]

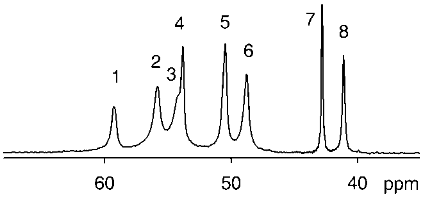


Figure 2. Carbon-13 DPMAS spectrum from neat PEI obtained from 2944 repetitions with a 1 s recycle delay. The numbering refers to Scheme 2.

Scheme 2

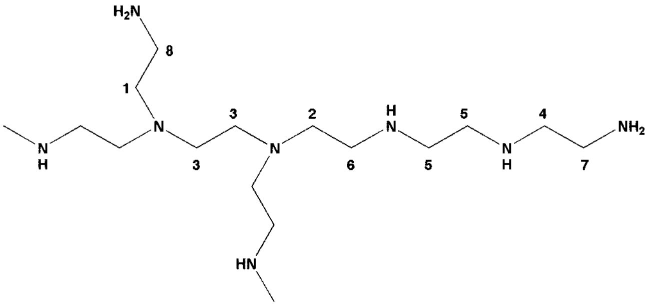


Figure 1a shows the ^{13}C CPMAS spectrum from a powdered parent material. The form of the spectrum is as discussed above. There is no clear evidence for a III$_\mathrm{f}$ signal. Film dried at 150 °C and 50% RH gives a methine peak intensity distribution similar to that of the powder (Figure 1b) but different from that from an air-dried film (Figure 1c). Analysis of the intensity as a function of contact time showed that these differences do not arise from variation in the cross-polarization behavior.[17] As both films are made from the same parent material, the polymer tacticity must be the same, so the films must differ in the nature of the hydrogen bonding. Furthermore, experiments on the air-dried film showed that the relative humidity of the storage environment (18 days at 76% RH and 15 days at 6% RH) had little effect on the spectrum. The CP spectrum from the air-dried film has a similar appearance to that obtained from a long-recycle (120 s) direct-polarization spectrum (Figure 1d). This suggests that the CP spectrum is largely representative of the sample as a whole. Nevertheless, we are able to demonstrate, Figure 1e, using a FRDP experiment, that the air-dried film does contain a component that is less well ordered and gives broader signals than that contributing to the bulk of the CP spectrum. The total signal intensity in the spectrum shown in Figure 1e is 16% of that shown in Figure 1c. The storage environment also had little effect on the FRDP spectrum from the air-dried film.

Solid-State NMR of PEI. The PEI used in this study was a viscous liquid. A ^{13}C spectrum, shown in Figure 2, was obtained from the neat liquid using a direct-polarization magic-angle spinning experiment. It can be inferred immediately from the number of signals that the material is not a simple linear sequence of $(-CH_2CH_2NH-)_n$ units. Scheme 2 gives the numbering sequence, and Table 2 lists

---

(16) Horii, F.; Hu, S.; Ito, T.; Odani, H.; Kitamura, R.; Matsuzawa, S.; Yamaura, K. *Polymer* **1992**, *33*, 2299.

(17) Mehring, M. *Principles of High-Resolution NMR in Solids*; Springer-Verlag: New York, 1983.

Table 2. Chemical Shift Values for PEI

carbon number (Scheme 1)	neat PEI	5% w/w solution in water	polymer blend
1	59.3	56.7	55.2
2	55.8	53.8	53.8
3	54.2[a]	51.7	52.3
4	53.7	51.4	50.1
5	50.4	48.5	48.4
6	48.7	46.4	46.9
7	42.8	40.7	40.5
8	41.0	38.7	38.9

[a] Appears as a shoulder on the 53.7 ppm line.

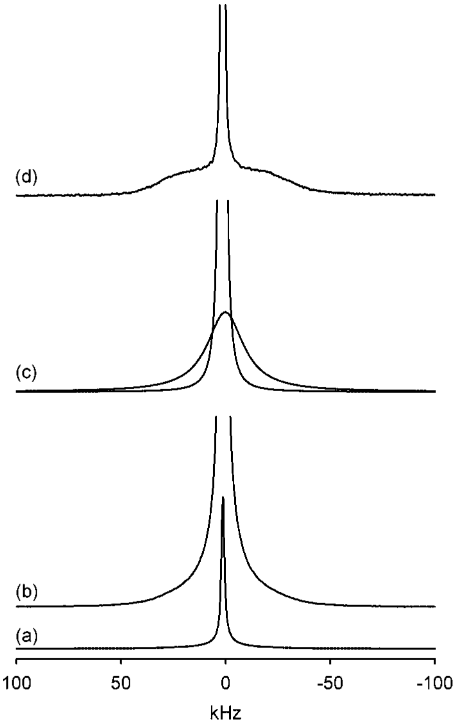


Figure 3. Wideline ^{1}H spectra from the air-dried polymer blend conditioned at 76% RH. (a) Full spectrum, with (b) × 10 vertical expansion, (c) simulated components, and (d) the spectrum acquired after a 2.84 ms spin-lock pulse. All spectra were obtained with a solid echo to minimize the effect of the spectrometer dead time (~12 μs).

the chemical shifts and solution state-state assignments.[18] It is assumed that the order in which the lines appear is the same in solution and in the neat liquid (and subsequently in the polymer blend). Chemical shift values similar to the neat liquid were obtained from a sample containing approximately 2% by weight of water; however, significant changes in shift were observed for a sample containing 95% water. No signals were detected outside the range shown in Figure 2.

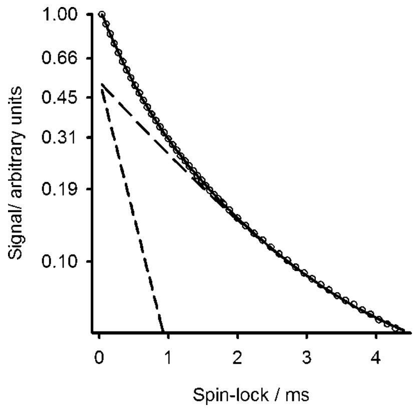


Figure 4. The ^{1}H signal from the air-dried polymer blend conditioned at 76% RH (open circles) as a function of spin-lock time, with a least-squares fit (solid line) comprised of two exponential decays (dashed lines) plus a baseline (added to the slower decay).

Solid-State NMR of the Polymer Blend. Wideline proton spectra obtained from a static sample of the polymer blend are shown in Figure 3, and a $T_{1\rho}(H)$ relaxation plot is shown in Figure 4. The band shape shown in Figure 3a cannot be accurately simulated with a single line with a Lorentzian shape, but a close fit can be obtained using two such lines with line widths at half-height of 1.76 and 20.78 kHz, with relative intensities of 2:1, respectively, as illustrated in Figure 3c. The signal as a function of spin-lock time also cannot be simulated with a single exponential decay but can be modeled with a two-component decay (one with a time constant of 0.38 ms and a population of 52% and the other with a time constant of 1.32 ms and a population of 48%). Immediately, then, there is evidence for heterogeneity within the blend. However, this is not the full picture. A spectrum acquired after a spin-lock time of 2.84 ms (Figure 3d) shows a band shape quite different from that illustrated in Figure 3a. The narrow Lorentzian line is retained, but the broader one is missing. Instead, a broad, flat-topped line can now be seen. This must be present in Figure 3a, but at a relative intensity too low to make it easily detectable in the presence of the other signals. This broad component has a width at half-height of approximately 63 kHz and is consistent with a rigid, ordered component. The Lorentzian line with the high line width is interpreted as being associated with a relatively rigid but amorphous component and the narrow line with a highly mobile component. The two components of Figure 3d could not be separated on the basis of $T_{1\rho}(H)$, which implies either that they have a strong association (with spin-diffusion averaging the individual $T_{1\rho}$ values) or that they have coincidentally similar $T_{1\rho}$ values.

The multiexponential $T_{1\rho}$ behavior contrasts with that observed for $T_1(H)$ measured using a saturation-recovery experiment. For this, the recovery can be accurately modeled with a single exponential with a time constant of 0.6 s. This single-exponential T_1 behavior suggests that the blend is homogeneous over domains with a characteristic dimension over about 30 nm, so the heterogeneity detected in the $T_{1\rho}$ measurement must occur over a smaller scale than this.[11]

Heterogeneity within the blend can be further demonstrated with a combination of two-dimensional wideline separation (WISE),[19] relaxation-filtered cross polarization, and direct polarization carbon-13 magic-angle spinning measurements. The ^{1}H$-$^{13}C WISE spectrum is shown in Figure 5a, with a projection onto the carbon axis shown in Figure 5b. The signal at ~71 ppm, through comparison with Figures 1 and 2, can *only* arise from the PVOH in the blend; a shoulder centered at ~54 ppm can only arise from PEI, and a broad band between 35 and 50 ppm contains contributions from both components. Slices taken parallel to the proton axis at

---

(18) St. Pierre, T.; Geckle, M. *J. Macromol. Sci., Chem.* **1985**, *A22*, 877.

(19) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273.

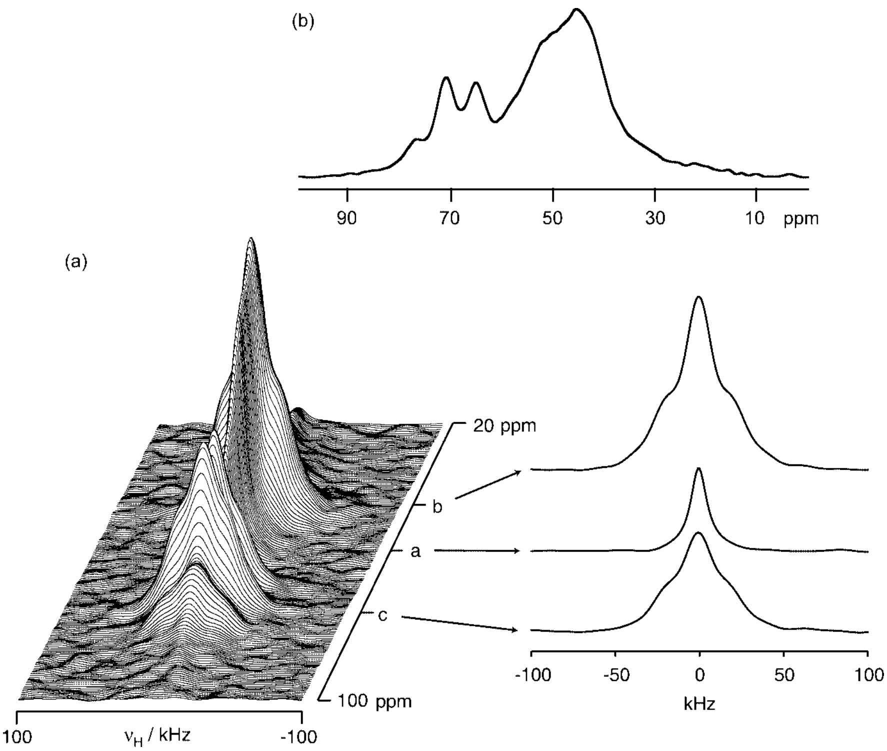


Figure 5. (a) ^{13}C−^{1}H correlation (WISE) spectrum from the air-dried polymer blend and obtained without any sample preconditioning. The experiment consisted of 48 increments of 1 μs in t1. For each increment, 160 repetitions with a 2 s recycle delay and 0.2 ms contact were acquired. The experiment was carried out in hypercomplex fashion and processed with a linear prediction of 256 additional points in t1. (b) Skyline projection onto the ^{13}C axis.

these three positions give line shapes indicative of the nature of the material giving rise to these regions in the spectrum. The slice at 54 ppm (“a” in Figure 5a) gives a relatively narrow line with a width at half-height of 14 kHz (similar to the value for the broader of the two Lorentzian lines in the ^{1}H spectrum). Given that the signal here can only arise from the PEI, this indicates that the PEI detected by the cross-polarization experiment occurs in an amorphous domain. A slice taken at ~71 ppm (position “c”) reveals a composite band shape with a narrow component similar to that observed in the first slice and a broad line with a width at half-height of about 45 kHz. This suggests that the PVOH occurs both in a PVOH-rich, rigid, ordered domain and in an amorphous domain (it would seem likely that this is the domain containing PEI as well, although there is no proof of that here). The slice taken at ~46 ppm (position “b”), as might be expected, shows both broad and narrow lines, with the narrow component enhanced due to the presence of the signal from the PEI in this part of the spectrum.

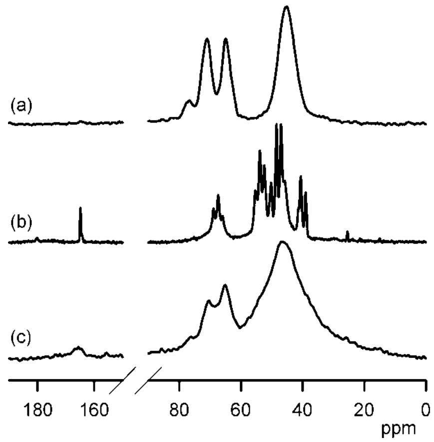


Figure 6. Carbon-13 spectra from the air-dried polymer blend conditioned at 76% RH. (a) CPMAS spectrum obtained with a 2.2 ms $T_{1\rho}(H)$ filter. (b) DPMAS spectrum obtained with 1 s recycle delay. (c) CPMAS spectrum obtained with 15 μs $T_2(H)$ filter.

The proton relaxation data can be used to design a relaxation-filtered CPMAS experiment. If the proton spin-lock pulse in the CP experiment is applied but the contact period delayed, then the resulting spectrum will be $T_{1\rho}(H)$-filtered. Using a delay of 2.2 ms allows the proton magnetization associated with the shorter $T_{1\rho}$ component (0.38 ms) to fully decay. Cross-polarization from the remaining magnetization will reveal the nature of the material associated with the longer $T_{1\rho}$ component(s). The result of such an experiment is shown in Figure 6a. This is a spectrum of ordered PVOH with no evidence of any signal from PEI. The proton magnetization associated with the narrow Lorentzian line should still be present under these experimental conditions, yet there is no evidence in the ^{13}C spectrum of any narrow lines that could be associated with a highly mobile domain. However, highly mobile materials have a poor cross-polarizaton efficiency and may simply not be detectable with a CP experiment. It is also feasible that this narrow ^{1}H line belongs to water, in which case it does not have an associated ^{13}C spectrum. A proton MAS spectrum obtained at a spin-rate of 8 kHz revealed a line at 2.1 ppm which can be attributed to the CH/CH$_2$ protons and an intense line at 4.4 ppm which is consistent with water (presumably in exchange with the labile protons in the polymer). The resolution in the spectrum was not sufficient to yield any other information on the proton speciation. If this mobile domain does not cross polarize, then it should be possible to detect it with a direct-polarization experiment, and if a short recycle delay is used, it will discriminate against any rigid carbon with typically long relaxation times (mobile carbon is likely to have a relatively short relaxation time). The result of such an experiment is shown in Figure 6b, and this indeed reveals a narrow-lined spectrum containing a signal from both PVOH and PEI.

The spectrum shown in Figure 6a has had the signal associated with the 0.38 ms $T_{1\rho}(H)$ component filtered out. So what does the carbon spectrum from this component look like? The difference between Figure 6a and a spectrum recorded with no delay before contact would reveal this. However, the spectrum can also be obtained directly by using a $T_2(H)$ filter to remove the signal from the ordered PVOH. The result of such an experiment is shown in Figure 6c (and is consistent with the difference spectrum discussed above). This has much broader lines than those shown in Figure 6a, and the band ranging from 35 to 60 ppm encompasses a signal from both PVOH and PEI. The spectrum from amorphous PVOH shown in Figure 1e does not cover this whole range, so it is concluded that there must be a signal from PEI present in this spectrum. Additionally, the low-intensity signal at 164 ppm has only been observed in association with the PEI component, providing further evidence that this domain does indeed contain PEI. The origin of this signal is discussed below. This domain, then, is amorphous and contains both PVOH and PEI.

The highly resolved spectrum shown in Figure 6b shows signals from both PVOH and PEI. In the absence of intramolecular hydrogen-bond-induced shifts, the PVOH methine signals appear between 65 and 69 ppm, which is their range in solution,[20] and their intensity relates more simply to the tacticity of the material in this domain. Deconvolution of this region of the spectrum suggests that the atactic form is the dominant one and gives a result close to that obtained from a solution-state spectrum of the parent PVOH. This indicates that the order/disorder within the blend is independent of the tacticity of the PVOH. Spectral deconvolution also suggests that a shoulder at 45.8 ppm comes from a broader line than any of its near neighbors, so this is likely to be the PVOH methylene. The remaining, intense lines between 38 and 56 ppm arise from the PEI component. Their positions are listed in Table 2. All of the lines are shifted by more than 1.5 ppm from their values in neat PEI, but six of the lines are within 0.6 ppm of their values in aqueous solution. This might indicate that this is a water-rich domain. The other two lines, from carbons 1 and 4 in the terminal groups, are shifted by 1.5 and 1.3 ppm, respectively. The reason for the larger shift differences for these two carbons is unclear.

In addition to the signals discussed above, there are others which do not appear in the spectra from either neat PEI or PVOH. One occurs as a shoulder (at 41.3 ppm) and one at 25.3 ppm. Low-intensity signals also occur at 164.8 and 180.2 ppm. As far as we have been able to establish, their intensity relative to the other lines arising from this phase does not change with time, so they do not relate to an ongoing aging process. A potential explanation for the origin of the most intense pair (41.3 and 164.8 ppm) is the formation of carbamate species during the manufacture of the film. It is known that amines can react with carbon dioxide to form carbamate species, particularly in the presence of water, as illustrated in eq 1.[21,22]

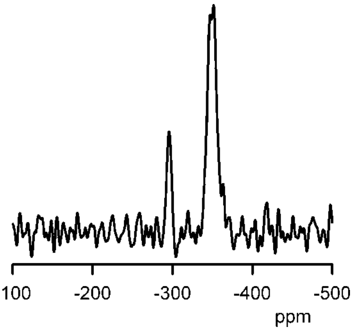


Figure 7. Nitrogen-15 CPMAS spectrum from the air-dried polymer blend conditioned at 35% RH and obtained with a 2 s recycle and 1 ms contact time.

$$2RNH_2 + CO_2 \rightleftharpoons RNHCOO^- + RNH_3^+ \qquad (1)$$

Both of these chemical shifts are consistent with the formation of such species.[23] To investigate this further, a nitrogen-15 CPMAS spectrum was recorded, and this is shown in Figure 7. The amine signals from the PEI are expected to contribute to the broadband around −350 ppm, but the spectrum shows a further signal at −295 ppm. Such a signal is consistent with the presence of carbamate species.[24] The signal at 164.8 ppm has also been observed in some cross-polarization spectra recorded from the blend (Figure 6c), so the carbamate species are not exclusive to the highly mobile phase.

The shift at 180.2 ppm is midrange for a carboxyl carbon as is the 25.3 ppm signal for CH_3 (including CH_3COO).[25] This is consistent with the presence of a small amount of residual polyvinylacetate from the manufacturing process.

During the investigation of the polymer blend, it was observed (see Figure 8a and b) that any fine structure in the FRDP spectrum from as-received material was lost when the experiment was repeated after the sample had been in storage for several months (in a closed plastic bag, in the dark under ambient laboratory conditions: 21 °C and ~40% RH). To investigate this further, spectra were recorded from a freshly prepared film and again after the film had been stored at 76% RH for two weeks.

The forms of the spectra are as discussed above. For the FRDP spectrum there is a general increase in resolution and a 40% increase in the total amount of intensity in the spectrum on storage at high-humidity relative to the as-made

---

(20) Katsuraya, K.; Hatanaka, K.; Matsuzaki, K.; Amiya, S. *Polymer* **2001**, *42*, 9855.

(21) Zou, J.; Ho, W. S. W. *J. Membr. Sci.* **2006**, *286*, 310.

(22) Donaldson, T. L.; Nguyen, Y. N. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 260.

(23) National Institute of Advanced Industrial Science and Technology. http://www.aist.go.jp/RIODB/SDBS/ (accessed May 25, 2005).

(24) Gouesnard, J.-P.; Martin, G. J.; Martin, M. L. *NMR Basic Principles and Progress*; Springer-Verlag: New York, 1981; Vol. 18.

(25) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden & Son Ltd.: London, 1976.

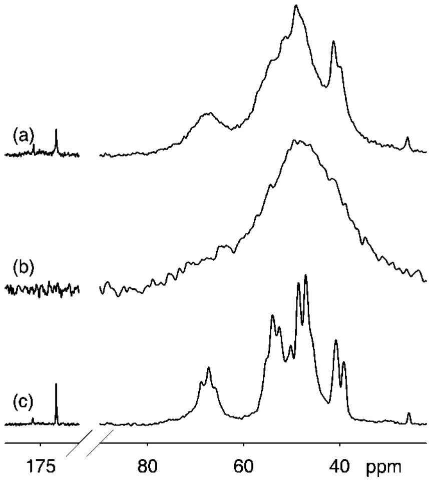


Figure 8. Carbon-13 FRDP spectra from the air-dried polymer blend (a) as-received, (b) after storage in the laboratory for 4 months (see text), and (c) after storage at 76% RH.

material. Together, these suggest a substantial overall reduction in the ^{13}C T_1 resulting from increased molecular motion.

After two weeks at 76% RH, the film was transferred to a 33% RH environment for two weeks and then a 6% one. After four weeks in this environment, the process was reversed and the material rehydrated. Spectra were recorded throughout this sequence. No change in the relative intensities of the minor components in the spectra was found, so there is no evidence for any ongoing chemical change within the blend. The total intensity in the highly resolved FRDP spectrum decreased upon storage at low RH and increased again upon rehydration. The line widths from the FRDP experiment also reflected the storage environment: higher at low RH and lower at high RH. It was concluded that the most likely explanation for the featureless spectrum shown in Figure 8b was a loss of molecular motion resulting from a loss of water on storage. A concomitant increase in carbon T_1 would explain the loss (through saturation) of the signal from quaternary carbons such as those giving the 164 ppm signal.

We have established that the polymer blend contains an ordered, PVOH-rich component and that a rigid, amorphous component containing PVOH and PEI coexists with a highly mobile component also containing PVOH and PEI. From the study with variable humidity, it would seem likely that the relative amount of these latter two components depends on the water content of the blend.

Conclusion

It has been shown that solid-state NMR is an excellent tool for the study of this PVOH/PEI polymer blend. While the single T_g value for the blend suggests that the components are miscible on the micrometer scale, the NMR measurements reveal heterogeneity on a nanometer scale. The NMR experiments can be designed to demonstrate the existence of three distinct domains within the polymer blend. One of these is rigid and ordered and predominantly contains PVOH. A second domain shows a high level of molecular mobility. This is a domain containing both PEI and PVOH and is potentially water-rich, and its nature depends on the environmental conditions under which the blend is stored. The third component is relatively rigid and disordered and also contains both PVOH and PEI. It would seem likely that this domain and the second one are present in an equilibrium determined by the environmental conditions.

Acknowledgment. We thank Dr. A. M. Kenwright for obtaining the solution-state spectrum and Mr. A. F. Markwell for carrying out many of the solid-state measurements.

CM071822Z