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Miscibility and Specific Interactions in Blends of Poly(4-vinylphenol) and Poly(2-ethoxyethyl methacrylate)

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ABSTRACT: The properties of the hydrogen-bonded polymer blends of poly(4-vinylphenol) and poly(2-ethoxyethyl methacrylate) are presented. Spectroscopic techniques such as ^{13}C solid-state NMR and FT-IR are used to probe specific interactions of the blends at various compositions. Spectral features from both techniques revealed that site-specific interactions are present, consistent with a significant degree of mixing of the blend components. Changes in chemical shift and line shape of the phenolic carbon and carbonyl resonances in the ^{13}C CPMAS spectra of the blends as a function of composition are interpreted as resulting from changes in the relative intensities of two closely overlapped signals. A quantitative measure of hydrogen-bonded carbonyl groups using ^{13}C NMR has been obtained which agreed well with the results from FT-IR analyses. It is also shown that ^{13}C NMR can be used to measure the fraction of hydroxyl groups associated with carbonyl groups, which was not possible previously using FT-IR due to extensive overlapping of bands in the hydroxyl stretching region. The results of measurements of ^{1}H T_1 and ^{1}H $T_{1\rho}$ indicate that PVPh and PEEMA are intimately mixed on a scale less than 2−3 nm.

Introduction

The term "polymer blend" refers to mixtures of two or more polymers. Blending offers an attractive alternative to create new materials rather than developing totally new polymers. Many polymer producers are developing new blended products because this strategy is usually cheaper, less time-consuming to get a product into the market, and without the exorbitant cost of capital investment into a new plant. As new requirements arise, the details of blending can be tailored to achieve a combination of favorable characteristics.[1]

A large number of blends have been studied in the literature; however, only a limited number of blends form a single-phase material.[1] This is due to the unfavorable enthalpy of mixing and very small entropy of mixing. Only when there is a significant interaction between the constituent polymers is miscibility observed. Dipole−dipole, charge transfer, hydrogen bonding, and acid−base neutralization interactions therefore play a key role in polymer−polymer miscibility.[1−3]

Hydrogen-Bonded Polymer Blends. Among miscible polymer blends, hydrogen-bonded systems have played a prominent role. There exists a great structural variety of miscible hydrogen-bonding polymer pairs.[4−8] In particular, a considerable amount of literature concerns the miscibility of poly(4-vinylphenol) (PVPh) with other polymers.[9−13] Poly(4-vinylphenol) is a proton donor that has an easily accessible hydroxyl group in the fourth position of the aromatic ring (Figure 1). It undergoes strong hydrogen-bonding interactions with proton-acceptor polymers such as poly(ethylene oxide),[14] poly(methyl methacrylate),[15] and poly(vinyl methyl ketone).[16] In the past 10 years or so, miscibility of poly(4-vinylphenol) with poly(ether)s[17,18] and poly(*n*-alkyl methacrylate)s[19] has been studied using Fourier transform infrared (FT-IR) spectroscopy. These studies were concerned primarily with the quantitative analysis of the carbonyl stretching region of the infrared spectrum.

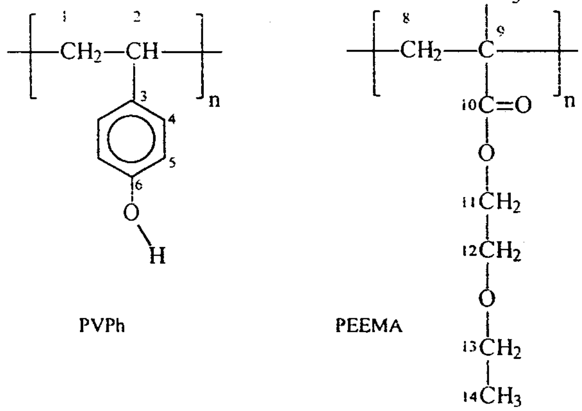

Figure 1. Structures of PVPh and PEEMA and atom numbering scheme.

Poly(2-ethoxyethyl methacrylate) (PEEMA) is a side-chain polyester with two hydrogen-bonding sites on the side chain (Figure 1). In addition to the ester carbonyl group, there is also an ether group which is available for hydrogen bonding. The types of possible specific interactions in a blend system such as this are self-association of PVPh and interassociation of PVPh and PEEMA as illustrated in Figure 2.

The aim of this paper is to measure quantitatively the number of units in blends of PVPh and PEEMA participating in specific interactions shown in Figure 2. In addition, the degree of mixing is studied using measurements of NMR relaxation times.

Experimental Section

PVPh was obtained from Polysciences with a reported molecular weight (M_w) of 30 000. PEEMA was synthesized in our laboratory by free radical polymerization.[20] The weight-average molecular weight (M_w) of PEEMA was measured by gel permeation chromatography (GPC) in tetrahydrofuran

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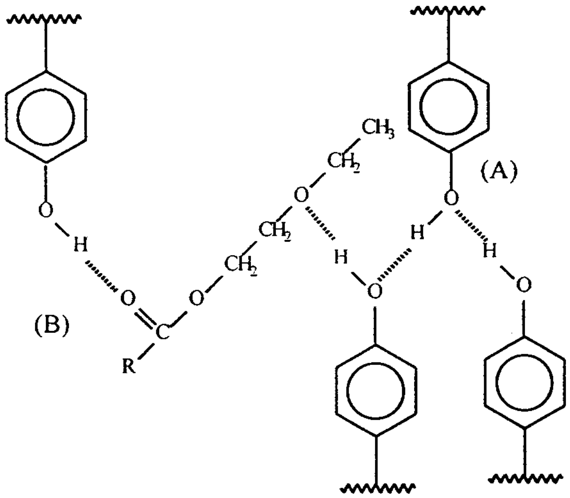

Figure 2. Schematic diagram showing possible types of interactions in the blends: (A) self-association between different PVPh units; (B) interassociation between PVPh and carbonyl or ethoxy group of PEEMA.

solution and was found to be 735 000 (PD index = 3.1). PVPh was used without further purification, and PEEMA was purified using solvent/nonsolvent, THF/methanol reprecipitation three times. The purity of the polymers was confirmed by ^{1}H and ^{13}C NMR spectroscopy.

Infrared spectra were obtained on a Perkin-Elmer-2000 infrared spectrometer using a minimum of 64 co-added scans at a resolution of 2 cm^{-1}. Nitrogen was used to purge the detector and sample compartments prior to and during scans to avoid interference from gaseous water bands.

Thermal analyses were performed on a Perkin-Elmer DSC-7 instrument, which was calibrated using indium and dodecane standards. A heating rate of 20 °C/min was used in all experiments. The glass transition temperature was taken as the midpoint of the heat flow change during a second heating. The weight of the sample used was typically 5−10 mg.

^{13}C CPMAS spectra were carried out on a Bruker MSL300 spectrometer operating at resonance frequencies of 300.15 and 75.048 MHz for ^{1}H and ^{13}C, respectively. ^{13}C CPMAS spectra of samples were obtained with the normal CPMAS pulse sequence with a spinning speed of 6 kHz. The ^{1}H−^{13}C $\pi/2$ pulse time were both 5 μs. The CP contact time was 1 ms. The chemical shifts of the carbon resonance were referenced to the methine carbon of solid adamantane (38.23 ppm). ^{1}H T_1 and ^{1}H $T_{1\rho}$ measurements were made using the inversion recovery and ^{1}H spin-lock sequences with a spin-locking field of 50 kHz.

Sample Preparation. All polymer blends were prepared by solvent-casting into Petri dishes. Appropriate weights of polymers were dissolved in acetone at a concentration of approximately 1 g of polymer/100 mL of solvent. The solvent was evaporated in an oven at 40 °C under an N$_2$ atmosphere. The solution-cast films were then dried in a vacuum oven at 60 °C for 5 days and then 1 day at 130 °C to remove all residual solvent. FT-IR samples were prepared by casting the polymer solution onto KBr disks and dried as described above.

Results and Discussion

Thermal Analysis. A common method to assess the miscibility of polymer blends is to measure the glass transition temperature of the blend component which represents the onset of the cooperative segmental motion of the component polymers. In a polymer mixture, a single compositionally dependent glass transition is an indication of miscibility on the order of 20−40 nm. A number of equations have been proposed to predict the variation of the glass transition temperatures of copolymers and blends as a function of composition. These are the Fox equation,[21]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

the Gordon−Taylor equation,[22]

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}$$

and the Kwei equation:[23]

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2$$

where w_i is the weight fraction of polymer component i, and k and q are constants. These equations have been used in the past to describe the correlations between the composition and the glass transition temperatures, depending on the entropy of mixing and specific interactions between the components present in the blends. The T_g of PVPh and PEEMA differ by about 140 °C, which indicates that there is a large difference in the free volumes, and hence also in the details of the motions, of the two polymers. Upon blending, the PEEMA/PVPh blends exhibit a single glass transition temperature at all of the compositions studied (Figure 3). Deviations from the Fox and Gordon−Taylor equations are to be expected, because of the strong hydrogen bonding between the components, and a least-squares fit to the Gordon−Taylor equation gave a value of k of 1.2 ± 0.5 (95% confidence). The Kwei equation is applicable to polymer blends with specific interactions, such as those which apply in these blends. The nonlinear least-squares "best fit" values obtained for this relationship were $k = 3.2 \pm 0.8$ and $q = -144 \pm 42$, with the relatively large value for q reflecting the strength of the interchain hydrogen bonding. Similar values for k and q were obtained for comparable blends of PVPh/poly(vinyl methyl ketone)[16] where $k = 3.5$ and $q = -95$.

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy is used extensively in the study of polymer blends. This method is useful for determining the presence of interactions between various groups due to the sensitivity of the force constants to inter- and intramolecular interactions.[4]

Figure 4 shows the changes in the carbonyl stretching region of the infrared spectra with increasing composition of PEEMA. The carbonyl stretching region of these blends is characterized by two bands which may be attributed to absorption by "free" and hydrogen-bonded carbonyl groups. Quantitative analysis is feasible using the curve-fitted areas of the respective hydrogen-bonded and "free" carbonyl bands from a knowledge of the ratios of the molar absorptivities (extinction coefficients) for the hydrogen-bonded and "free" carbonyl bands.[3] Typical values for this ratio of the molar absorptivities have been reported to fall within the range 1.2−1.5,[4] and a value of 1.5 has been determined for the poly(methacrylate)s.[3] Coleman et al.[24] have reported that Beer's law applies to PVPh blends with acrylates provided that the absorbance of the films is less than 0.6, which was the case for all of the films studied here.

It has been previously determined by Coleman et al.[19] that, for systems such as that studied here, a relationship exists between the fraction of hydrogen-bonded

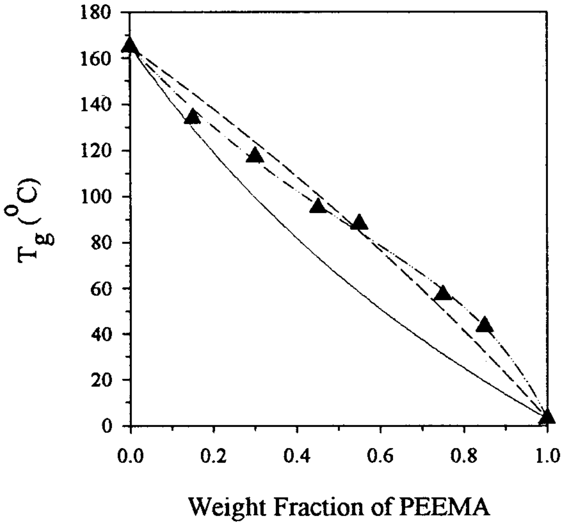

Figure 3. T_g–composition curve: (▲) experimental data; (—) Fox equation; (- - -) Gordon–Taylor equation; (– • –) Kwei equation.

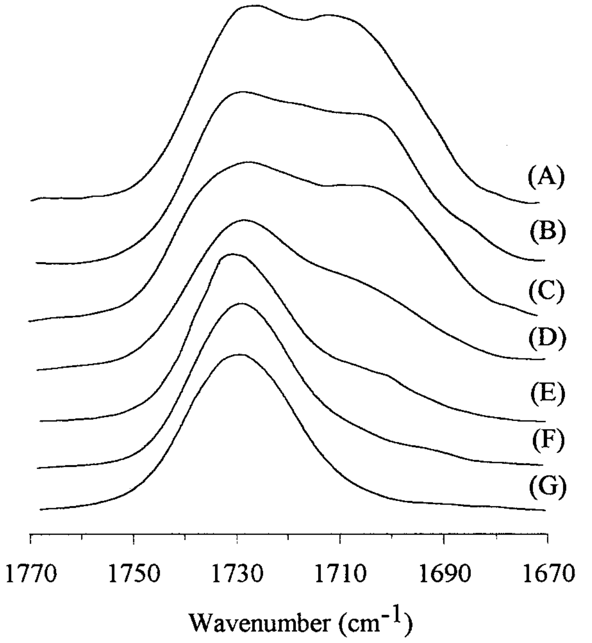

Figure 4. FT-IR spectra in the carbonyl stretching region (1660–1780 cm^{-1}) recorded at room temperature for PVPh–PEEMA blends cast from acetone: (A) 15%, (B) 30%, (C) 45%, (D) 55%, (E) 75%, (F) 85%, (G) 100% PEEMA.

carbonyl groups in component A, $f_{HB}^{C=O}$, the volume fraction of the non-hydrogen-bonded PVPh, component B, and the equilibrium constants that describe the competing equilibria within the system:

$$f_{HB}^{C=O} = 1 - \frac{\Phi_{A1}}{\Phi_A} = 1 - \frac{1}{1 + K_A\Phi_{B1}(1 - K_2/K_B) + (K_2/K_B)(1/(1 - K_B\Phi_{B1}))} \quad (1)$$

where ϕ_A is total volume fraction of A and ϕ_{A1} and ϕ_{B1} are the volume fractions of "free" or non-hydrogen-bonded A and B species in the mixture, respectively; K_A, K_B, and K_2 are the equilibrium constants describing interassociation, self-association for multimers of PVPh, and self-association for dimers of PVPh, respectively.

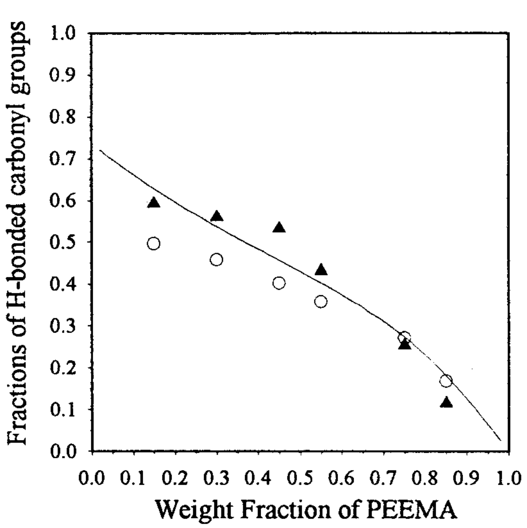

Figure 5. Fractions of hydrogen-bonded carbonyl groups vs composition: (○) FT-IR data, (▲) NMR data, (—) theoretical fraction calculated.

Therefore, with knowledge of the equilibrium constants between the polymers involved (i.e., K_2, K_B, and K_A), taking into account the changes in molar volume, the fraction of hydrogen-bonded carbonyl groups in the blend can be calculated by solving the above equation using the iterative least-squares method described by Coleman and co-workers.[25] Alternatively, measurement of the fractions of hydrogen-bonded carbonyl groups in blends having various compositions at different temperatures will allow the interassociation constant, K_A, be calculated. Using equilibrium constants previously reported by Coleman et al.[19] for blends of poly(methacrylate)s and PVPh, the predicted hydrogen-bonded fractions of carbonyl groups have been calculated and compared with that obtained experimentally from the deconvolution of the infrared spectra. A good correlation between experimental data and the predicted fractions is shown in Figure 5. In this calculation, we have made the assumption that equilibrium is attained and that the ether linkage did not affect the interassociation equilibrium constant of the ester carbonyl group or the fraction of hydrogen-bonded carbonyl groups to any significant extent. The agreement between experimental and predicted values supports the validity of this assumption.

Figure 6 shows typical FT-IR spectra of PEEMA/PVPh blends in the hydroxyl stretching region, which is also a region of interest because of the involvement of hydroxyl groups in hydrogen bonding. In the spectrum of pure PVPh, the band at around 3525 cm^{-1} is that attributed to non-hydrogen-bonded hydroxyls, and a broad band at around 3370 cm^{-1} is assigned to the wide distribution of hydrogen-bonded hydroxyl groups (self-association). In the spectra for the blends, two additional components appear. These third and fourth components are those due to interassociation of the hydroxyl with the carbonyl and ether groups occurring at around 3420 and 3200 cm^{-1}, respectively. Inspection of the spectra shows that the relative intensity of each band changes as a function of blend composition.

Quantitative analysis of the hydroxyl stretching region of polymer blends in the FT-IR spectrum had not been possible as was previously documented.[26] The difficulties lie in (1) the extensive overlap of the bands of interest, (2) the molar absorptivities of the compo-

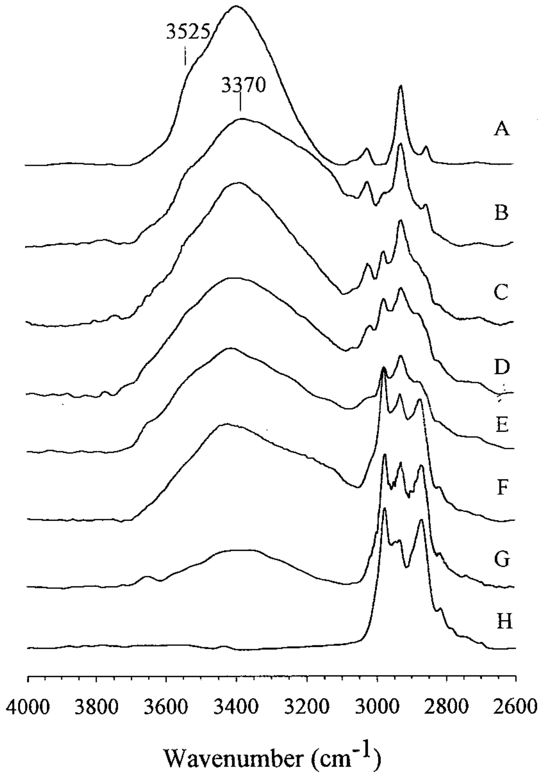

Figure 6. FT-IR spectra in the region (2700−3900 cm^{-1}) for PVPh/PEEMA blends recorded at room temperature: (A) 0%, (B) 15%, (C) 30%, (D) 45%, (E) 55%, (F) 75%, (G) 85%, (H) 100% PEEMA.

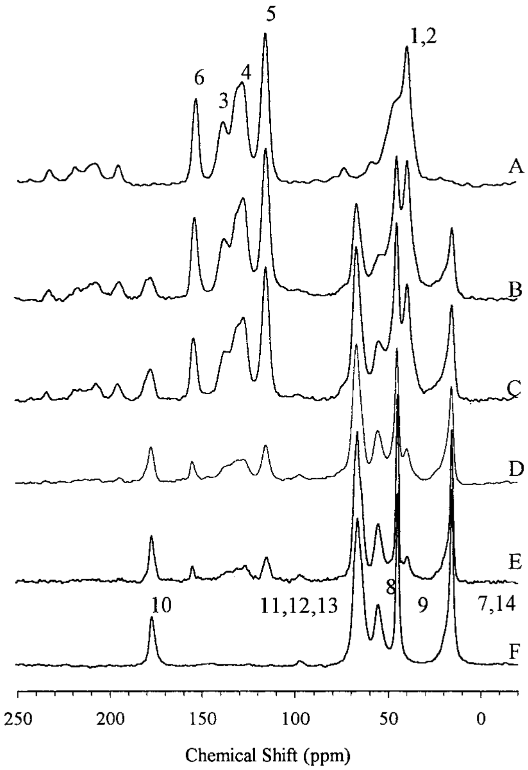

Figure 7. ^{13}C CPMAS spectra of PVPh/PEEMA blends at room temperature: (A) pure PVPh, (B) 15% PEEMA, (C) 45% PEEMA, (D) 75% PEEMA, (E) 85% PEEMA, (F) 100% PEEMA.

nents being a strong function of wavenumber and temperature, and (3) the stretching region being very broad.

To reiterate, the miscibility of PEEMA/PVPh blends is anticipated due to the favorable interactions observed in the FT-IR. Quantitative analysis of the carbonyl stretching region showed that a considerable number of carbonyl groups are interacting with the hydroxyl proton through hydrogen bonding.

^{13}C CPMAS Spectra and Hydrogen-Bonding Interaction. Solid-state NMR spectroscopy was used to understand better the phase behavior and morphology of the polymer blend in relation to hydrogen bond formation. Selected ^{13}C CPMAS spectra of PEEMA/PVPh blends of various compositions are shown in Figure 7. Assignments of the peaks in the ^{13}C spectra of PVPh and PEEMA to the structures (in Figure 1) are as shown in Figure 7. Figure 8 shows an expansion of the ^{13}C carbonyl resonance as a function of composition. The increasing contribution of a second signal as the amount of PVPh is increased is similar to that observed in the FT-IR spectra. At 30% PEEMA, the carbonyl resonance is partially resolved into two peaks. This change in line shape has also been observed by Belfiore et al., who assigned the additional signal to the contribution of the hydrogen-bonded carbonyl groups.[27] However, apart from mentioning that the assignment is based on comparison with the FT-IR spectra, no further evidence was given to support the assignment.

The rates of cross-polarization and spin−lattice relaxation in the rotating frames were measured to ensure that the conditions under which the spectra were collected give rise to quantitative peak intensities. The rate of cross-polarization, R_{CH}, is proportional to the strength of heteronuclear dipolar coupling, which is in turn proportional to r^{-6} , where r is the internuclear distance and also proportional to n, where n is the number of protons.[28] The values of R_{CH} for the two poorly resolved carbonyl peaks were measured for the 45% blend to be 1.4 and 1.5 ms^{-1}; these values are the same within experimental errors, and so it appears that the two types of carbonyl groups (the “associated” and the “free” carbonyl) have very similar dipolar couplings. Hence, the methylene protons in the side chain or even those in the main chain play a much more dominant role in the dipolar coupling with the carbonyls, compared with the H-bonded protons. Examination of the structure of the EEMA monomer (Figure 2) and calcula-

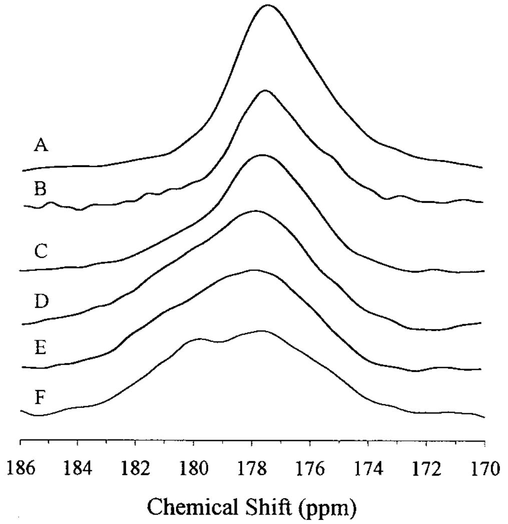

Figure 8. ^{13}C CPMAS spectra for the C=O resonance in the blends: (A) 100% PEEMA, (B) 85% PEEMA, (C) 75% PEEMA, (D) 55% PEEMA, (E) 45% PEEMA, (F) 30% PEEMA.

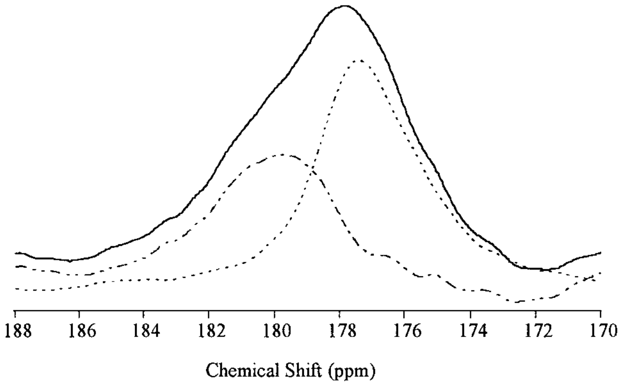

Figure 9. ^{13}C CPMAS spectra for (—) 55% PEEMA/PVPh; (- - -) 100% PEEMA; (- • -) difference spectrum 55% PEEMA − PEEMA.

tion of the contribution of the H-bonded proton to the dipolar coupling show that this is not an unexpected result. The values of ^{1}H $T_{1\rho}$ for each of these peaks were also found to be identical within the experimental error, and therefore the CPMAS spectra recorded using a CP contact time of 1 ms give rise to quantitative peak intensities. Such a conclusion is important for the ongoing discussion.

Considering the resemblance of the carbonyl region in the FT-IR and NMR spectra, the fractions of hydrogen-bonded groups may also be determined using CPMAS NMR using a similar method. Figure 9 shows the spectra of pure PEEMA and a 55% PEEMA blend and the spectrum obtained by subtracting that of the pure PEEMA from that of the blend. By integrating the respective areas of the contributions due to hydrogen-bonded and "free" carbonyl groups, the fractions of hydrogen-bonded carbonyl groups were estimated and plotted in Figure 5. The NMR results agree well with those obtained from the FT-IR analyses. This agreement supports the assignment of the additional signal in the carbonyl region to be that of the hydrogen-bonded carbonyl groups.

In addition to having an effect on the carbonyl resonance, blending also effects the other interaction sites, for example the peak due to the phenolic carbon (carbon 6). The phenolic peak in the solid-state ^{13}C spectrum of pure PVPh resonates at 152.7 ppm. Upon addition of PEEMA, the resonance shifts approximately 2.5 ppm downfield (Figure 10) This change has been interpreted as being caused by the change in electron density/shielding experienced by the phenolic carbon, which is adjacent to interacting groups.[14,15] A closer examination of the line shape of the phenolic carbon in, for example, the spectrum of the blend with 30% PEEMA content shows that the line is composed of two or more overlapping peaks. Previously, Qin et al.[29] have remarked on the line shape of the phenolic carbon in the blend of PVPh/PEO and believed it consisted of two poorly resolved signals. It was suggested that one of those signals was due to the phenolic groups in PVPh undergoing self-association.

As discussed earlier, there are three possible types of hydroxyl groups in a system such as this: the "free", the self-associated, and the interassociated. The phenolic peak in the ^{13}C spectrum of PVPh is due to contributions from the self-associated and the "free" hydroxyl groups. On blending, an additional contribution from interassociated phenolic carbons appears. The difference spectrum between the spectrum of the blend and pure PVPh is due to interassociated hydroxyl groups (Figure 11). The intensity of the spectrum of PVPh was adjusted so that on subtraction from the spectrum of the blend the mean intensity on the low field side of the peak was equal to the mean baseline intensity prior to subtraction. Integrating the spectra to obtain the areas will give the fractions of the hydrogen-bonded hydroxyl groups present. The experimental results are plotted (Figure 12) with predicted data using the same iterative least-squares procedure as for carbonyl groups;[24] the good agreement between the two indicates that the fractions of hydroxyl groups can be estimated using the CPMAS NMR spectrum. In this analysis, errors could arise due to subtraction and from the assumption that the relative proportion of "free" hydroxyl and self-associated hydroxyl groups is constant across the blend composition and therefore is represented by the line shape of pure PVPh. However, these errors should be relatively small at high PVPh content and become slightly larger as the content of PEEMA increases. This expectation is reflected in the

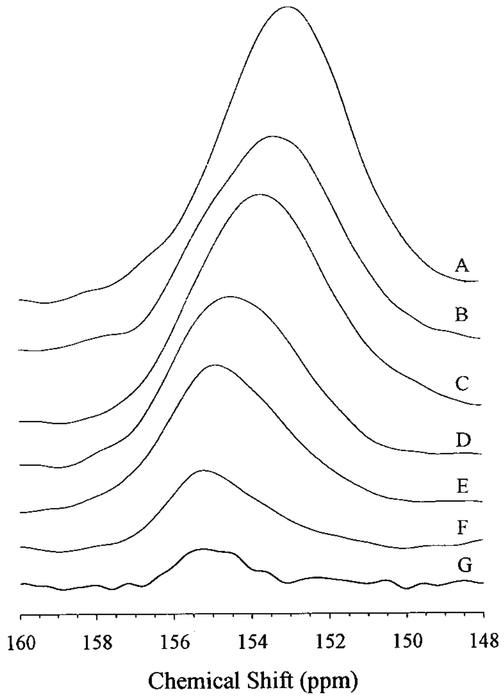

Figure 10. ^{13}C CPMAS spectra for the phenolic carbon resonance for PVPh/PEEMA blends. (A) 100% PVPh, (B) 15% PEEMA, (C) 30% PEEMA, (D) 45% PEEMA, (E) 55% PEEMA, (F) 75% PEEMA, (G) 85% PEEMA.

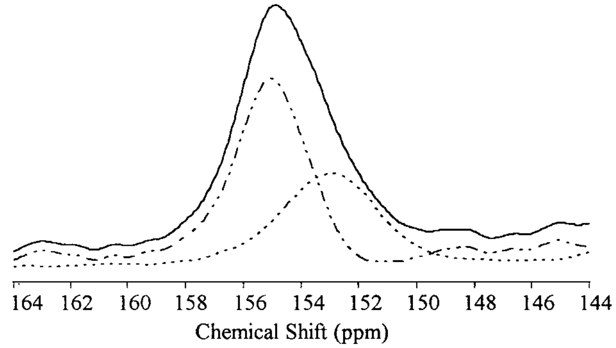

Figure 11. ^{13}C CPMAS spectra for (—) 55% PEEMA/PVPh; (- - -) 100% PVPh; (- • -) difference spectrum 55% PEEMA − PVPh.

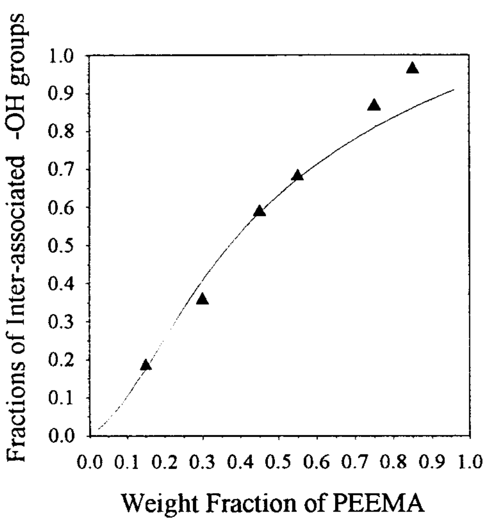

Figure 12. Experimental fractions of interassociated hydroxyl groups as a function of composition: (▲) experimental data, (—) predicted fractions.

Table 1. ^{1}H T_1 and ^{1}H $T_{1\rho}$ of PVPh/PEEMA Blends at 298 K

sample	^{1}H T_1 (s)	^{1}H $T_{1\rho}$ (ms)
PVPh	1.43 ± 0.02[a]	9.0 ± 0.2
PEEMA	0.68 ± 0.03	5.5 ± 0.4
45% PEEMA/PVPh[b]	1.16 ± 0.07	8.3 ± 0.6
45% PEEMA/PVPh (pred)	0.93	7.2

[a] ±2 × standard deviation. [b] ^{13}C detection.

Figure 12 as the experimental data agree less well with the predicted curve at high PEEMA content.

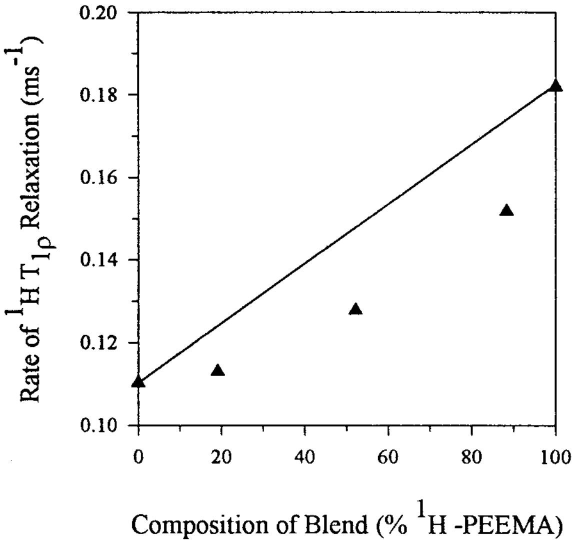

Figure 13. Plot of the rate of ^{1}H $T_{1\rho}$ relaxation of the blend as a function of the proton density of the PEEMA in the blend: (▲) experimental data, (—) calculated values.

^{1}H Relaxation Times and Miscibility. The above results show that the proportions of hydrogen-bonded and non-hydrogen-bonded carbonyl and hydroxyl carbons change systematically as a function of the composition of the blends. The excellent agreement of the NMR results and those from FTIR, and with calculated proportions, strongly supports the assignment of the peaks to carbonyl and hydroxyl carbons in the two environments. It may be argued, however, that the changes in the peak intensities merely reflect changes in the phase structure across the composition range, with partial phase separation occurring. DSC measurements, however, of a single T_g for all of the blends strongly suggests that these are indeed single-phase blends. We have performed measurements of the ^{1}H spin–lattice relaxation time both in the laboratory frame and in the rotating frame to provide this information. The ^{1}H relaxation times in blends of PEEMA/PVPh were measured using ^{1}H as well as ^{13}C detection to allow the relaxation in the homopolymers to be determined separately. The use of cross-polarization to the ^{13}C nuclei greatly increases the ability to identify changes to the values of T_1 and $T_{1\rho}$ on blending. Typical results for the blend containing 45% PEEMA are given in Table 1. Both PVPh and PEEMA showed a single-exponential T_1, and a single-exponential T_1 was also observed for the 45% PEEMA blend. Very similar results were obtained using detection of both ^{1}H and ^{13}C NMR signals. This indicates that fast spin diffusion occurs among all the protons from different chemical constituents equilibrating the magnetization. By simulating the effect of spin diffusion,[30] the polymers were estimated to be miscible on a scale less than 70–80 nm. The ^{1}H $T_{1\rho}$ values were measured using with both ^{13}C and ^{1}H detection. Again the homopolymers and the 45% blend showed single-exponential decays, and using the same approach to simulate the effect of spin diffusion, the polymers were shown to be miscible on a scale less than 2 nm.

Also shown in Table 1 are the values of ^{1}H T_1 and $T_{1\rho}$ predicted from relaxation times of the homopolymers, assuming complete mixing of the types of polymer chains. Figure 13 shows the values of ^{1}H $T_{1\rho}$ for blends across the whole composition range measured using both ^{1}H and ^{13}C detection. The solid line shows the calculated values predicted from the rates of relaxation of the homopolymers and the proton densities of the component polymers in the blends.[15] The decrease in the rates of relaxation compared to the predicted values demonstrates that the intrinsic rates of relaxation of the homopolymers at 50 kHz frequencies must be changed on blending, A similar observation for the values of ^{1}H T_1 shows that motions at 300 kHz are also affected by blending.[31]

Conclusion

Both FT-IR and NMR have been used to investigate specific interactions and miscibility in PEEMA/PVPh blends. Solid-state NMR has been shown to be able to measure the fractions of hydrogen-bonded carbonyl groups and hydroxyl groups in the blend systems. The latter measurement is only possible with ^{13}C NMR. Spin–lattice relaxation measurements in both laboratory frame and rotating frame have shown that the blends are homogeneous down to a scale of 2 nm. The miscibility of the blends was also supported by results from FT-IR and thermal analysis, which probes mixing on a macroscopic level.

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