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Miscibility of poly(epichlorohydrin)/poly(*N*-vinyl-2-pyrrolidone) blends investigated with high-resolution solid-state ^{13}C n.m.r.

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The miscibility of poly(epichlorohydrin)/poly(*N*-vinyl-2-pyrrolidone) (PECH/PVP) blends was investigated by ^{13}C cross-polarization combined with magic-angle sample spinning and high-power dipolar decoupling (CP/MAS/DD) techniques. Intermolecular cross-polarization and the downfield shifting of the carbonyl resonance of PVP indicate intermolecular hydrogen bonding. ^{1}H $T_{1\rho}$ relaxation rates monitored at the carbonyl group in PECH/PVP blends were found as the weighted averages between the $T_{1\rho}$ relaxation rate of the carbonyl group in pure PVP and that of the mobile α-hydrogen in pure PECH. A 1.3 ppm downfield shift was found for the carbonyl carbon of PVP in the ^{13}C CP/MAS/DD spectra. These observations provide evidence of strong hydrogen-bonding interactions between the carbonyl group and the α-hydrogen. The polymer components are completely miscible at the molecular level at all compositions. In addition, the methine β-C of PECH is split into two peaks at 80.0 and 76.2 ppm and the methylene γ-C is also split into two peaks at 70.6 and 66.0 ppm. The upfield shifts of the methine and methylene peaks are due to strong dipolar interactions resulting in higher shielding of the ^{13}C nuclei. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

There has been considerable interest in the study of polymer blends due to their importance in academic and technical aspects. Experimentally, various techniques can be explored to characterize polymer blends, such as thermal and mechanical analyses, microscopy, light scattering and spectroscopic methods[1,2]. Solid-state nuclear magnetic resonance (n.m.r.) spectroscopy has proven to be a powerful technique for determining the scale of miscibility and phase structure of polymer blends, and for detecting specific intermolecular interactions[3–16].

Polymer blends composed of poly(epichlorohydrin) (PECH) and poly(*N*-vinyl pyrrolidone) (PVP) have previously been studied by us using differential scanning calorimetry (d.s.c.), and were recognized as miscible since the blends displayed single glass transition temperatures (T_gs), which were intermediate between those of the pure components[17].

In the present study, the blends of PECH and PVP were investigated by high-resolution solid-state n.m.r. spectroscopy to examine the miscibility at the molecular level, and to characterize the specific intermolecular interactions between the two components. In addition, indirect information on the phase structure is provided by dynamic polarization and relaxation experiments. Thus, cross-polarization (CP)/magic angle spinning (MAS)/high-power dipolar decoupling (DD) spectra were obtained, and

the cross-polarization transfer time constant (T_{CH}) and the proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}$) were measured from solid-state ^{13}C n.m.r. spectroscopy. The spatial dimensions of the microstructures of the polymer blends were estimated quantitatively in the light of the spin diffusion processes[4,18,19].

^{13}C CP/MAS/DD and its various extensions offer a vast array of tools to study the miscibility and microstructure in polymer blends[3,20]. Detection of resonance line shift probes miscibility on a length-scale of 0.3 nm or less. Measurements of proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}$) and in the laboratory frame (T_1) probe heterogeneities on the scale of 1 to 3 nm, and of 10 to 100 nm, respectively. We employed ^{13}C CP/MAS techniques in this study to reveal the miscibility of the blends on the segmental scale.

EXPERIMENTAL

Poly(epichlorohydrin) (PECH) was supplied by Shanghai Synthetic Resins Co., Shanghai, China. Judging from the d.s.c. thermograph of PECH, we believe that our sample was mainly atactic for there is no significant crystallization or melting peaks on the thermograph, whereas it was reported that stereoregular PECH is a semi-crystalline polymer[21]. Poly(*N*-vinyl-2-pyrrolidone) (PVP) was purchased from Polyscience, USA, and it has a quoted number-average molecular weight (M_n) of 360 000. Prior to use, PVP was dried under vacuum at 80°C for 48 h.

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PECH/PVP blends were prepared by solution casting from cyclohexanone at 50°C, and the majority of the solvent was evaporated. To remove the residual solvent, all the blend films obtained were dried under vacuum at 80°C for 2 weeks.

^{13}C CP/MAS spectra were measured at ambient temperature using a 9-T JEOL EX-400 n.m.r. spectrometer. Samples were placed into 6-mm rotors. They were spun at the 'magic-angle' (i.e. the angle between the sample spinning axis and the external static field being 54.7°). The ^{1}H 90° pulse width was 5.5 ms. Spinning rates were about 5.7 kHz. The pre-delay time was 5 s. The external reference was adamantane (ADM), which has two peaks at chemical shift values 29.5 and 38.6 ppm relative to tetramethylsilane (TMS).

The cross-polarization transfer time constant (T_{CH}) was measured by varying the contact time. The number of accumulations used was 512. ^{13}C CP/MAS intensity reached a maximum at contact time, $t_m = \{(T_{CH}T_{1\rho})/(T_{1\rho} - T_{CH})\} \cdot \ln(T_{1\rho}/T_{CH})$. T_{CH} may be calculated after t_m and ^{1}H $T_{1\rho}$ are both measured[22].

^{1}H $T_{1\rho}$ was measured by monitoring the cross-polarized ^{13}C intensity after a variable ^{1}H spin-lock time. The strength of the spin-lock field was 45 kHz. The number of accumulations used was 1024. The contact time was set at 1.0 ms. ^{1}H $T_{1\rho}$ measured indirectly at specific ^{13}C CP/MAS resonance line offers higher spectral resolution than the conventional ^{1}H pulsed method.

RESULTS AND DISCUSSION

Figure 1 shows the ^{13}C CP/MAS spectra of PECH, PVP and a 50/50 blend. Peak assignments are shown in the insets based on the literature[12–24]. The methine β-C of PECH is split into two peaks at 80.0 and 76.2 ppm. The methylene γ-C is also split into two peaks, which are at 70.6 and 66.0 ppm. The spectrum of atactic PECH is different from that of isotactic PECH, where there are no peak splittings[23,24]. The methine and methylene resonances of isotactic PECH are at about 80 and 70 ppm, respectively[23,24]. In the solid state, rotation about the C–O–C bond is highly restricted, and so peak splitting due to conformational differences is observed. The higher-field peaks of the doublets, 76.2 and 66.0 ppm, mean higher shielding of the ^{13}C nuclei, and are probably due to γ-*gauche* effects[25] or intermolecular dipolar interactions[26–29]. The upfield shift of 4–5 ppm is a typical value observed in *gauche* shielding effects of the γ-substituents CH$_3$ and Cl[25]. The chloromethyl α-C resonance peak (44.6 ppm) does not split into a doublet, but the ^{1}H $T_{1\rho}$ measured at this peak has two components. The long component belongs to chloromethyl groups that are restricted by strong dipolar interactions with other chloromethyl and C–O–C moieties[28]. The long component $T_{1\rho}$ has the same magnitude as the $T_{1\rho}$s of the shielded β-C and γ-C nuclei; therefore, further substantiating the presence of

Table 1 Cross-polarization transfer times T_{CH} of carbonyl carbon in PECH/PVP blends and glass transition temperatures T_g

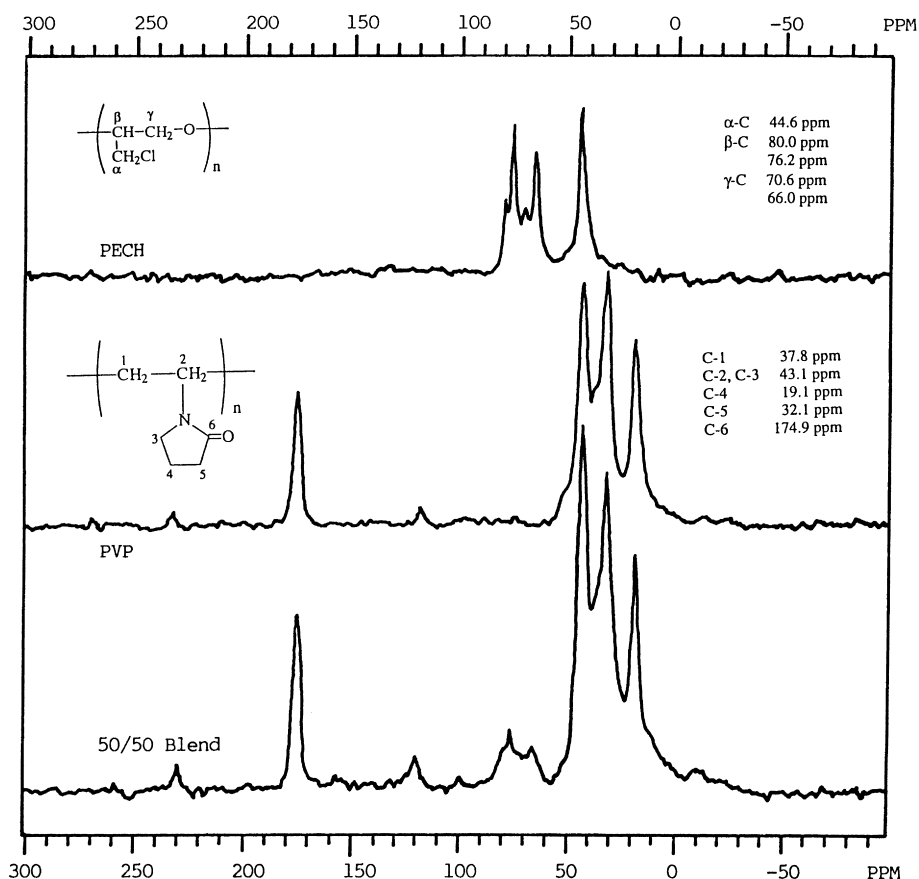| PECH/PVP	T_{CH} (ms)	T_g (°C)
0/100	0.99	180
30/70	0.28	50
50/50	0.66	18
70/30	1.01	−15
100/0	–	−25

Figure 1 ^{13}C CP/MAS spectra and peak assignments for PECH, PVP and 50/50 blend

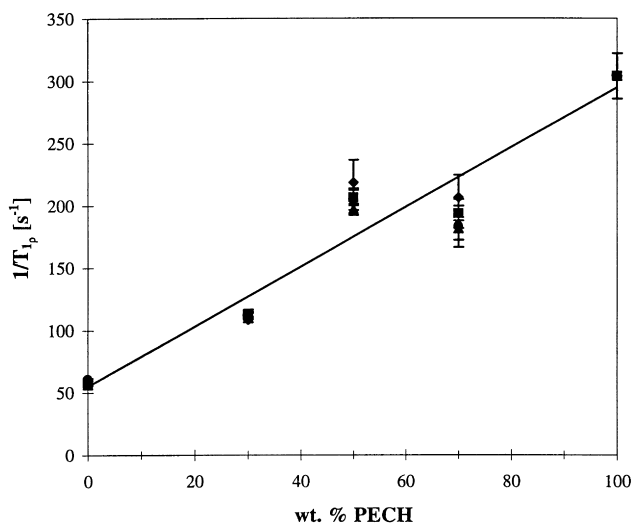**Table 2** ^{1}H T_{1r} (ms) at different carbon sites in PECH, PVP and their blends

Carbon site	0/100	30/70	50/50	70/30	100/0
β-C (80.0 ppm)	–	S/N low	S/N low	S/N low	1.0 ± 0.1
β-C (76.2 ppm)	–	S/N low	7.4 ± 0.5	8.5 ± 0.1	8.9 ± 0.4
γ-C (70.6 ppm)	–	S/N low	S/N low	S/N low	1.4 ± 0.1
γ-C (66.0 ppm)	–	S/N low	S/N low	8.6 ± 0.1	9.2 ± 0.3
α-C/C-1, C-2 and C-3	16.5 ± 0.3	8.9 ± 0.2	4.9 ± 0.2	5.5 ± 0.5	3.3 ± 0.2 (36%) 8.4 ± 0.4 (64%)
C-4	17.7 ± 0.2	8.9 ± 0.3	5.1 ± 0.1	5.5 ± 0.3	–
C-5	17.1 ± 0.5	8.9 ± 0.1	4.9 ± 0.1	5.2 ± 0.3	–
C-6	17.5 ± 0.2	9.2 ± 0.2	4.6 ± 0.4	4.9 ± 0.3	–
Mean	17.2 ± 0.5	9.0 ± 0.3	4.9 ± 0.4	5.3 ± 0.3	
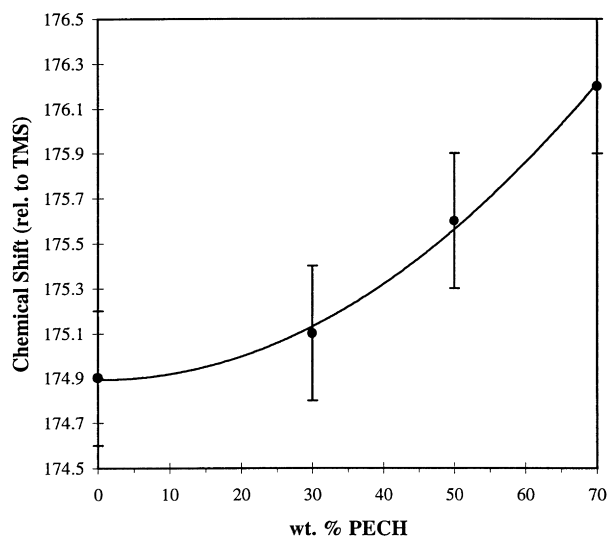
Figure 2 Resonance line of the carbonyl carbon in PVP shifts downfield with increased wt% PECH. This indicates strong intermolecular hydrogen bondings and intimate molecular mixing

Figure 3 ^{1}H $T_{1\rho}$ relaxation rate monitored at carbonyl C-6, pyrrolidone ring carbons C-4, C-5, and at the overlapping peaks of α-C/C-1, C-2, C-3 as a function of PECH composition. The relaxation rate shown at 100 wt% PECH is $1/T_{1\rho}$, short of the α-hydrogen. The linearity of the $T_{1\rho}$ relaxation rate of the PECH/PVP blends indicates that the carbonyl and pyrrolidone methylene groups are strongly coupled to the α-hydrogen of PECH

inter- or intramolecular interactions within PECH. The short component belongs to mobile chloromethyl α-C groups that are not restricted by inter- and intramolecular interactions. Intermolecular dipolar interactions are likely to be stronger in atactic PECH than in isotactic PECH[29].

Table 1 lists T_{CH} values of carbonyl C-6, and glass transition temperatures T_g. We find that T_{CH} of carbonyl C-6 decreases from 0.99 ms (pure PVP) to 0.28 ms (30 wt% PECH). This shows that there is intermolecular cross-polarization between the carbonyl C-6 of PVP and the hydrogens of PECH. Protonated carbon generally has smaller T_{CH} than unprotonated carbon, but chain mobility also affects the magnitude of T_{CH}. A rigid chain has a smaller T_{CH} than a flexible chain. This is clearly demonstrated with the increase in T_{CH} when PECH is greater than 30 wt%. The blend becomes rubbery, and the T_g falls below the ambient temperature.

Table 2 lists the ^{1}H $T_{1\rho}$ of PECH, PVP and their blends monitored at different carbon sites. The α-C resonance (44.6 ppm) overlapped with C-1 (37.8 ppm), and C-2, C-3 peaks (43.1 ppm) in the blends. No attempts were made to deconvolute the peaks by curve fitting. ^{1}H $T_{1\rho}$ values at the overlapping peaks were measured just as they were. The ^{1}H $T_{1\rho}$ relaxations are all single exponential in the blends. By inspecting the magnitudes of ^{1}H $T_{1\rho}$ listed in *Table 2*, we can conclude that β-C and γ-C are not coupled to either α-C or C-6; thus, the observed intermolecular cross-polarization is

between C-6 and α-hydrogens. For each blend, the ^{1}H $T_{1\rho}$ measured at the α-C/C-1, C-2, C-3 overlapping peak and the C-4, C-5, C-6 peaks are averaged to a single $T_{1\rho}$ value by proton spin diffusion. Therefore, the domain size is below the scale of 1 to 3 nm.

Figure 2 shows a downfield shift of the C-6 peak, which is characteristic of strong hydrogen bonding and intimate molecular mixing, with increased weight fraction of PECH. The linearity of the relaxation rate $1/T_{1\rho}$ of PECH/PVP blends *versus* PECH wt%, with the correlation coefficient of 0.97 in *Figure 3*, indicates that the carbonyl C-6 is tightly coupled to the mobile α-hydrogen of PECH. We conclude that PECH and PVP components are completely miscible on the segmental scale due to strong hydrogen bonding between α-hydrogens of PECH and carbonyl groups of PVP.

CONCLUSIONS

The miscibility of poly(epichlorohydrin) (PECH) and poly(*N*-vinyl pyrrolidone) (PVP) was investigated by high-resolution solid-state nuclear magnetic resonance (n.m.r.) techniques. A 1.3 ppm downfield shift was found for the carbonyl carbon of PVP in the ^{13}C cross-polarization combined with magic-angle sample spinning and

high-power dipolar decoupling (CP/MAS/DD) spectra. In addition, the methine β-C of PECH is split into two peaks at 80.0 and 76.2 ppm and the methylene γ-C is split into two peaks at 70.6 and 66.0 ppm. It is further concluded that the higher-field peaks of the doublets, 76.2 and 66.0 ppm, are due to dipolar interactions that shifted the resonances to higher field. In order to obtain information about the phase structure of the blends, we measured the cross-polarization transfer time constant (T_{CH}) and the proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}$). From the relaxation times, we concluded that the PECH and PVP chains are intimately mixed. The relaxation measurement method is complementary to d.s.c. and CP/MAS/DD spectra because relaxation times, especially for ^{1}H $T_{1\rho}$, are more sensitive to structure inhomogeneity in polymer blends.

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