A high resolution solid-state n.m.r. and d.s.c. study of miscibility and crystallization behaviour of poly(vinyl alcohol)/poly(*N*-vinyl-2-pyrrolidone) blends

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Blends of crystallizable poly(vinyl alcohol) (PVA) with poly(*N*-vinyl-2-pyrrolidone) (PVPy) were studied by ^{13}C cross-polarization/magic angle spinning (CP/MAS) n.m.r. and d.s.c. The ^{13}C CP/MAS spectra show that the blends were miscible on a molecular level over the whole composition range studied, and that the intramolecular hydrogen bonds of PVA were broken and intermolecular hydrogen bonds between PVA and PVPy formed when the two polymers were mixed. The results of a spin-lattice relaxation study indicate that blending of the two polymers reduced the average intermolecular distance and molecular motion of each component, even in the miscible amorphous phase, and that addition of PVPy into PVA has a definite effect on the crystallinity of PVA in the blends over the whole composition range, yet there is still detectable crystallinity even when the PVPy content is as high as 80 wt%. These results are consistent with those obtained from d.s.c. studies.

(Keywords: solid-state n.m.r.; miscibility; crystallization)

INTRODUCTION

The miscibility of the semicrystalline polymer poly(vinyl alcohol) (PVA) with the amorphous polymer poly(*N*-vinyl-2-pyrrolidone) (PVPy) has been investigated by Eguiazabal *et al.*[1] and Ping *et al.*[2]. Eguiazabal *et al.* found that with the vinyl alcohol unit content in poly(VA-VAc) being ~70 wt% or more P(VA-VAc)/PVPy blends were fully miscible. From d.s.c. results Ping *et al.* indicated that blends of PVA and PVPy were miscible over the whole composition range. The results of d.s.c. and density measurements have shown that when the PVPy content was >50 wt% in the blends, there were no detectable PVA crystallites. *FT*i.r. spectra showed that small organized regions were still present over the whole composition range of the blends.

High resolution solid-state n.m.r.[3–16] and d.s.c. have been widely used to characterize the heterogeneity or crystallinity of solid polymers. Since the ^{13}C spin-lattice relaxation time, T_1(C), can provide detailed information on the overall molecular and segmental motion[3,4], the T_1(C) value can be used to characterize the structure and motion of both the crystalline and non-crystalline portions of semicrystalline polymers. T_1(C) values from 2 to 4500 s have been found in semicrystalline polymers[3,5–11,15,16].

In this study, the spin relaxation times and cross-polarization/magic angle spinning (CP/MAS) ^{13}C spectra of PVA, PVPy and their blends are determined, and d.s.c. is also used to investigate the miscibility and crystalline morphology of PVA/PVPy blends.

EXPERIMENTAL

The polymers used in this study were all commercial products. PVPy ($M_w = 360\,000$) was obtained from Janssan Chimica and PVA ($M_w = 25\,000$, 98.5% hydrolysed) from Polyscience. Solution blending was used with water as the solvent, and the solution concentration was 10% (wt/v). Specimens with different compositions were cast from the solution at 60°C and then dried under vacuum at 110°C for 1 week.

Solid-state ^{13}C CP/MAS n.m.r. experiments were performed on a Bruker MSL-400 NMR spectrometer at 25°C. The total sideband suppression (TOSS) method was used for suppressing spinning side bands. The hydrogen resonance frequency was 400.13 MHz and the carbon resonance frequency was 100.63 MHz. The Hartman–Hahn CP matching and dipolar decoupling field was ~49 kHz, while a 5.5 μs 90° pulse for the ^{13}C nucleus and a 4.8 μs 90° pulse for ^{1}H were used. The contact time was 1.0 ms and the MAS rate was 4.000 kHz. ^{13}C spin-lattice relaxation times were measured by the T_1 CP method[17], and ^{1}H spin-lattice relaxation times in the rotating frame, $T_{1\rho}$(H), were obtained from the

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^{13}C CP/MAS intensity with increasing contact time at long contact times[18–20]. ^{13}C spectra are referred to the chemical shift of methyl group carbons of hexamethylbenzene (16.9 ppm).

A Perkin-Elmer DSC-7 apparatus was used to determine the glass transition temperature (T_g) and melting points (T_m) of the blends. D.s.c. curves of samples were recorded at a heating rate of 20 K min^{-1}. The temperature at the midpoint of the heat capacity transition and the temperature at the maximum of the melting endothermic peak of the d.s.c. curves were taken as the T_g and T_m of a specimen, respectively.

RESULTS AND DISCUSSION

Miscibility and interaction between PVA and PVPy

Figure 1 shows the CP/MAS ^{13}C n.m.r. spectra of PVA, PVPy and their blends. A lot of useful information can be drawn from these spectra. For example, the methine carbon resonance of PVA is split into three peaks. We designate these peaks peak 1, peak 2 and peak 3 in order of decreasing frequency. The intensity of peak 3 is the strongest, hence the PVA used in this study is slightly syndiotactic[21]. According to Terao *et al.*[21] the splitting of the methine carbon resonance reflects the stereoregularity of the PVA, but the relative intensities of the three peaks in the solid state are not consistent with isotactic (*mm*), heterotactic (*mr*) and syndiotactic (*rr*) triads tacticity in solution[22]. They have also proved that the relative intensities of the three peaks of the methine carbon resonances in CP/MAS spectra showed no contact time dependence over the range 0.05–5 ms, hence the discrepancy between the relative intensities of the three peaks and the triad tacticity is not attributable to the difference in the CP efficiency. Besides, the splitting of the methine carbon resonance cannot be attributed to a difference in conformation[23], since the crystalline part of PVA takes the same zigzag planar conformation regardless of the tacticity[24,25]. Consequently, they considered that the downfield shifts (compared with the ^{13}C spectrum of PVA in solution) of the methine carbon in the solid state were due to strong intramolecular hydrogen bonds (in pure PVA), while the intermolecular hydrogen bonds (in pure PVA) may cause broadening of the linewidth of the resonance to some extent. In addition, they assigned peak 1 to the *mm* triad with two intramolecular hydrogen bonds, peak 2 to the *mm* and *mr* triads with one intramolecular hydrogen bond and peak 3 to the *mm*, *mr* and *rr* triads with no intramolecular hydrogen bond.

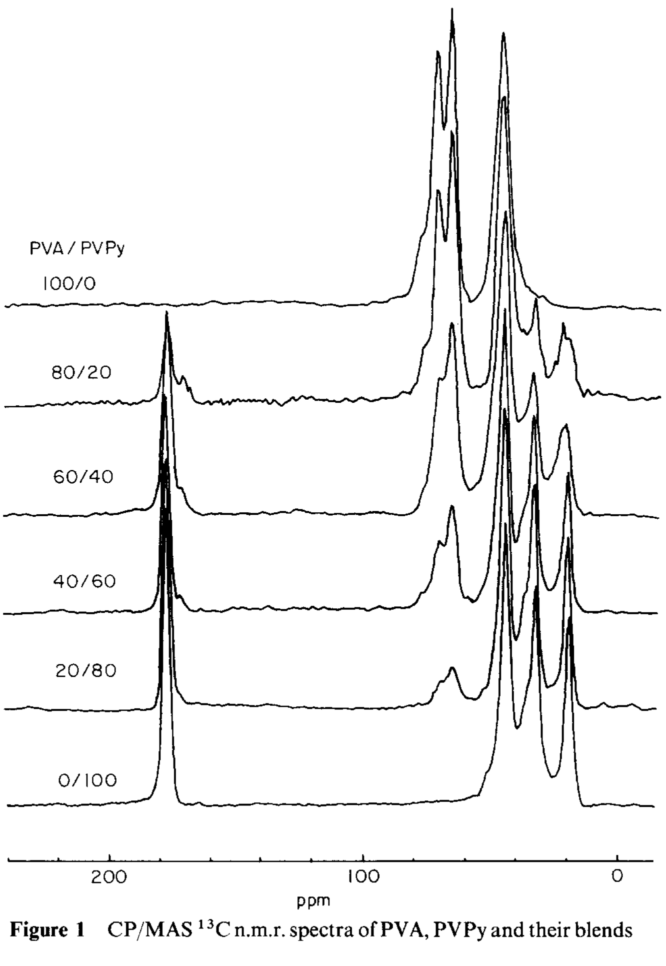

Figure 1 CP/MAS ^{13}C n.m.r. spectra of PVA, PVPy and their blends

The methine carbon resonance of PVA in PVA/PVPy blends is very interesting, where peak 2 of the methine carbon of PVA is markedly weakened with increasing PVPy content. When the PVPy content is >60 wt%, the three peaks of the methine carbon of PVA become very poorly resolved, almost merging into one broad peak. Of the three peaks, peak 2 is the most strongly affected by increase in PVPy content. At the same time, the linewidths of the three peaks are also reduced with increasing PVPy content. Therefore, from the changes in the three peaks of the methine carbon, it may be concluded that the addition of PVPy into PVA severely disrupts the formation of the intra- and intermolecular hydrogen bonds of PVA molecules, the greater the PVPy content the more severe the disruption.

It is interesting that the situation for PVPy is similar to that for PVA. The CP/MAS ^{13}C n.m.r. spectrum of PVPy shows four well resolved peaks. The lowest field peak is assigned to the carbonyl carbon (C=O) resonance. The highest peak is assigned to C_1, C_2 and C_6. The third and fourth peaks in order of decreasing frequency are assigned to C_4 and C_5, respectively. A marked change in the PVPy carbon resonances in blends is that the carbonyl carbon peak is split into two peaks due to addition of PVA, and the intensity of the splitting peak increases with increase in PVA content. We assign the split peak to the peak of the carbonyl carbon which forms intermolecular hydrogen bonds with the hydroxyl group of PVA. At the same time, a finite splitting of the C_4 and C_5 resonances of PVPy in blends can be observed with increasing PVA content. Similarly, the splitting of the C_4 and C_5 resonances is assigned to the methylene carbons which contact with the carbonyl carbon forming intermolecular hydrogen bonds with the hydroxyl groups of PVA.. It is well known that the formation of intermolecular hydrogen bonds often results in a change of chemical shifts of the atoms and groups involved[26]. Data in *Table 1* give further evidence for the formation of intermolecular hydrogen bonds between PVA and PVPy. The PVPy carbon resonances regularly shift to lower magnetic field with increasing PVA content, and the PVA carbon resonances regularly shift to higher magnetic field with increasing PVPy content. Hence, we can conclude that the PVA and PVPy are intimately miscible over the whole composition range of their blends. Also, the intermolecular hydrogen bonds between PVA and PVPy, whose formation is at the expense of the breakage of the inter- and intramolecular hydrogen bonds of PVA, play a critical role in the miscibility of PVA/PVPy blends.

Table 1 Chemical shifts of PVA, PVPy and their blends

Groups	PVA/PVPy				
	0/100	40/60	60/40	80/20	100/0
C=O	176.0	176.4	176.6	176.7	
$CH_{(PVA)}$		67.8	69.2	70.0	70.2
		64.2	64.5	64.7	64.9
$C_{4(PVPy)}$	31.8	32.0	32.1	32.4	
$C_{5(PVPy)}$	18.6	18.8	19.1	21.7	

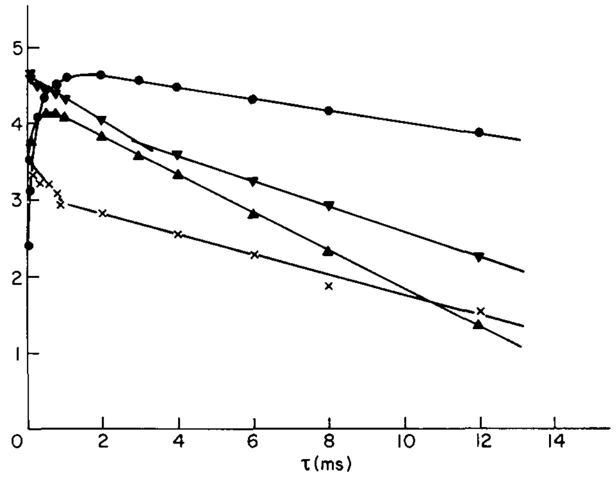

Figure 2 Logarithmic intensity *versus* the proton spin-locking time, τ, for the carbonyl carbon of pure PVPy (●), the methine carbon of pure PVA (▲), the carbonyl carbon of PVPy in 80 PVA/20 PVPy (×) and the methine carbon of PVA in 80 PVA/20 PVPy (▼)

Crystallization behaviour of PVA, PVPy and their blends

Figure 2 shows the variation in signal intensity of PVA, PVPy and PVA/PVPy (80/20) blend as a function of contact time. Significant differences of the spin-relaxation between the two homopolymers and the two polymers in blends can be observed. First, the CP time, T_{CH}, of the carbonyl carbon of pure PVPy, which is $\sim 450\,\mu s$, is larger than that of PVPy in the blend ($\sim 300\,\mu s$). Similarly, the T_{CH} of the methine carbon of pure PVA, which is $\sim 100\,\mu s$, is larger than that ($\sim 50\,\mu s$) of PVA in the blend. Second, spin-lattice relaxations of pure PVA and pure PVPy in the rotating frame are both exponential decays, but spin-lattice relaxation of PVA and PVPy in the blend are all bicomponent decays.

The CP rate of various carbons, $1/T_{CH}$, changes dramatically as a function of the environment of the carbon and the nature and extent of molecular motion[3,27–29]. Generally speaking, more mobile carbon atoms take longer to cross-polarize than less mobile or immobilized carbons, and the greater the number of protons directly attached to a carbon atom, the shorter the CP time of that carbon atom. The markedly increased CP rate of the carbonyl carbon results from the formation of intermolecular hydrogen bonds, which effectively shorten the average distance between PVA and PVPy, and efficiently hampers the motion of PVPy molecules.

A single $T_{1\rho}(H)$ for the homopolymers means that there exists strong dipolar coupling between protons which gives rise to efficient spin diffusion, the rate of which is rapid enough to damp non-equilibrium magnetization in any part of the proton spin system. The non-linear decays of PVA and PVPy in the blend indicate the existence of heterogeneous phases in the blend. For PVA, the coexistence of a PVA crystallite rich phase and an intimately blended phase with PVPy occurs, and for PVPy there exist two kinds of carbonyl carbons simultaneously, one forming a hydrogen bond with the hydroxyl group of PVA and the other not.

Figure 3 illustrates the results of ^{13}C spin-lattice relaxation time measurements by the T_1 CP method[17]. Obviously, the recovery of magnetization is multicomponent whose $T_1(C)$ values fitted by tri-component decays are 60.0, 4.0 and 0.2 s orders, respectively, which are in good agreement with the $T_1(C)$ values of pure PVA determined by Terao *et al.*[21]. Naturally, we can assign the component with $T_1(C)$ of 60.0 s order to the crystalline component, and the components with $T_1(C)$ values of 4.0 and 0.2 s orders to the interfacial and amorphous components, respectively. It is interesting to note that the recovery of magnetization of the methine carbons in blends with different PVPy contents has almost the same shape as that of pure PVA and is tri-component, but their $T_1(C)$ values are slightly different. The tri-component decay of PVA in blends indicates the coexistence of crystalline, interfacial and amorphous phases. Therefore, we may conclude that the addition of PVPy into PVA has a definite effect on the crystallization behaviour of PVA, although PVA in the blends is crystallizable over the whole composition range. This conclusion is supported further by the results of WAXD measurements of the samples[30] and is consistent with the results of *FT*i.r. spectra[2].

Figure 4 shows the d.s.c. curves of the samples and

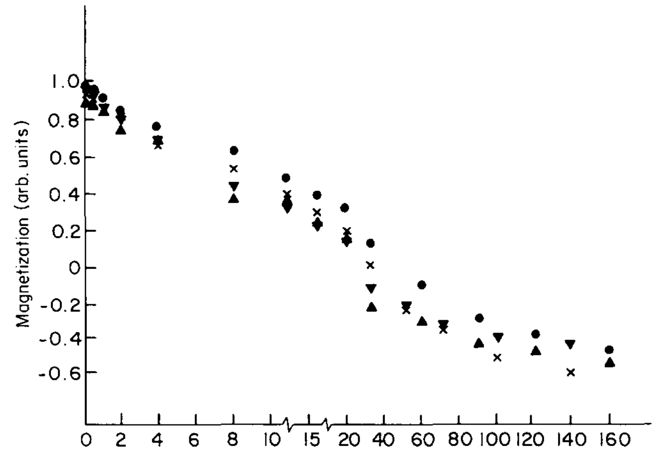

Figure 3 ^{13}C T_1 plots of the methine carbon of pure PVA and PVA in blends by the T_1 CP method: (×) pure PVA; (●) 60 PVA/40 PVPy; (▲) 40 PVA/60 PVPy; (▼) 20 PVA/80 PVPy

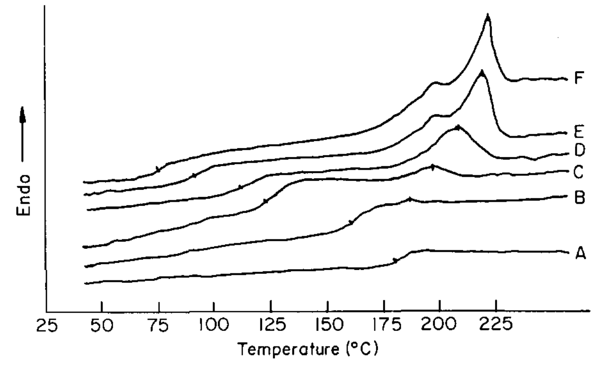

Figure 4 D.s.c. plots of PVA, PVPy and their blends: (A) PVPy; (B) 80 PVPy/20 PVA; (C) 60 PVPy/40 PVA; (D) 40 PVPy/60 PVA; (E) 20 PVPy/80 PVA; (F) PVA

Table 2 Glass transition temperatures (T_g) and melting points (T_m) of PVA, PVPy and their blends

PVA content (wt%)	T_g (°C)	T_m (°C)
100	73.1	218.7
80	92.6	217.4
60	110.6	207.5
40	121.9	196.8
20	158.9	186.3
0	180.0	–

their T_g and T_m values are listed in *Table 2*. The d.s.c. results indicate that there is a single T_g for each blend composition, thus the PVA/PVPy blends are intimately miscible over the whole composition range. The changes of T_m and T_g as a function of PVPy content in the blend indicate that the addition of 20 wt% PVPy into PVA has almost no effect on the crystallinity of PVA, but has a significant effect on the T_g of PVA. This means that PVPy is mainly miscible with PVA in the amorphous phase. The melting point of PVA rather obviously decreases with increasing PVPy content beyond 20 wt% PVPy, and it almost disappears when the PVPy content is up to 80 wt%, due to the sensitivity of d.s.c. However, even then, there still exists a very small excursion on the d.s.c. curve. Its peak temperature is 186.3°C which is higher than the T_g (180.0°C) of pure PVPy. Therefore, it may be attributed to the T_m of imperfect PVA crystallites, which implies that PVA is crystallizable over the whole composition range. According to the melting point equation[31]:

$$T_m = T_m^0\left(1 - \frac{2\sigma_e}{l\Delta h}\right) \qquad (1)$$

the depression of the melting point is related to the lamellar thickness l, fold surface free enthalpy σ_e and the heat of fusion per unit volume Δh. The depression of the melting point of PVA in blends may be due to the formation of intermolecular hydrogen bonds between PVA and PVPy, which hampers the normal folding of PVA chains, enhances the fold surface free enthalpy, and reduces the lamellar thickness of PVA, and hence results in the depression of the melting point of PVA crystallites.

CONCLUSIONS

PVA/PVPy blends are miscible at a molecular level over the whole composition range, but PVPy is mainly miscible with the amorphous phase of PVA. The intermolecular hydrogen bonding between PVA and PVPy plays a critical role in the miscibility of PVA/PVPy blends. Intermolecular hydrogen bonds form between PVA and PVPy whilst parts of the inter- and intramolecular hydrogen bonds of PVA are broken.

The blending of PVPy with PVA has a definite effect on the crystallization behaviour of PVA, but there is still detectable crystallinity of PVA in each blend over the whole composition range. The intermolecular hydrogen bonding between PVA and PVPy to some extent hampers the normal folding of PVA chains, and hence results in depression of the melting point of crystalline PVA.

The results of ^{13}C CP/MAS n.m.r. are almost consistent with those from d.s.c. ^{13}C CP/MAS n.m.r. can give more detailed information about the miscibility of blends than d.s.c. Combining the results of ^{13}C CP/MAS n.m.r. and d.s.c. enables one to understand better the mechanism of miscibility of polymer blends.

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