Investigation on domain structure of poly(phenylene sulphide) and poly(ether sulphone) blends by solid-state nuclear magnetic resonance methods

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The domain structure of blends of poly(phenylene sulphide) (PPS) and poly(ether sulphone) (PES) has been studied by solid-state nuclear magnetic resonance methods. ^{1}H T_2, T_1 and $T_{1\rho}$ data have been measured and a cross-polarization magic-angle spinning (CP/MAS) technique has been used. The relaxation data indicate that solution-cast blends are partially compatible. When the PPS/PES ratio equals 4/6, the compatibility of the blends is best, PES and amorphous-phase PPS mixing intimately besides the 10% crystalline domain. CP/MAS spectra of ^{13}C and ^{1}H $T_{1\rho}$ data of the blends show that the morphology of PPS crystalline phase has been changed when PPS is solution-cast with PES; the shorter T_2, longer T_1 and $T_{1\rho}$ crystalline phase may correspond to the PPS cold crystalline phase. The domain size of the solution-cast blends with PPS/PES = 4/6 is just at the 0.1 μm scale determined by Goldman–Shen CP/MAS spin-diffusion methods. But the compatibility of mechanical blends is poor; they have the same domain structure as that of the respective homopolymers.

(Keywords: poly(phenylene sulphide); poly(ether sulphone); solid-state nuclear magnetic resonance; domain structure; polymer blends; compatibility; spin diffusion)

INTRODUCTION

Poly(phenylene sulphide) (PPS) is a semicrystalline plastic material with excellent properties, e.g. dimensional stability, good heat, solvent and chemical resistance and excellent adhesion ability. Composites composed of PPS and fibres or other polymeric materials also have many superior properties, and possess applications value[1]. The glass transition temperature of PPS is low ($T_g = 90°C$); however, poly(ether sulphone) (PES) has a high glass transition temperature ($T_g = 225°C$) and good heat resistance properties at both high and low temperatures. It has good mechanical and electrical properties and good resistance to acid and basic organic solvents. In addition PES is amorphous under normal conditions, but will crystallize under certain treatments[2]. Significant improvements will be obtained, especially in impact strength, toughness and ductility, etc., when blending amorphous polymer with a crystalline one[3]. Considering the similar chemical structures and complementary properties of PPS and PES, blends of PPS with PES may have quite good compatibility and superior mechanical properties. To investigate microphase separation, the morphological structure and compatibility of PPS–PES blends is of both theoretical and practical interest.

Published experimental results[1,4] have shown that PPS homopolymer presents as spherulites with about 50% crystallinity. Solution casting blends of PPS and PES will influence the morphology and crystallization behaviour of PPS. Increasing the PES content in the blends is beneficial for PPS to undergo cold crystallization. The continuous phase of the blends changes from PPS to PES when the PES content increases to 60–70% by weight. Solid-state n.m.r. has provided useful information through exploration of the morphological regions of polymer blends by virtue of their characteristic molecular n.m.r. relaxation data and the spin-diffusion coupling between different polymers[5]. It is known that through the mechanism of spin diffusion the component that is highly coupled to the lattice may cause other resonant nuclei in the spin system to relax either totally or partially. A totally efficient coupling will give a single T_1 or $T_{1\rho}$ and partial coupling will cause multicomponent relaxation and give several T_1 or $T_{1\rho}$ values. From the solid-state n.m.r. relaxation data of polymer blends, we can estimate the compatibility of the blends and the domain size of each component. Many 'compatible' blends were studied based on this principle[6–8]. It can be seen that the domain sizes of the amorphous polymer pairs cited in the above references are all within the range of several nanometres to several tens of nanometres. However, crystalline–amorphous polymer blends are usually very heterogeneous on the scale of micrometres, due to their different condensed structures[9]. Scanning electron microscopy (SEM) experimental results show that the domain sizes of PPS–PES blends are larger than n.m.r. T_1 measurement scales (several tens of nanometres)[4], so that not only T_2 but also $T_{1\rho}$ (even T_1) may correspond to the multiphase structure of the blends. It is a great advantage of solid-state n.m.r. methods over others that multi-n.m.r. relaxation data and CP/MAS high-resolution n.m.r. techniques can give resolvable and detailed information. By these methods the partial

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compatibility and domain structure within the blends can be investigated. Efforts have also been made to determine the domain size of the blends by solid-state n.m.r. spin-diffusion methods.

EXPERIMENT

The PPS sample used in the study is uncured poly(phenylene sulphide) $-(C_6H_5-S)_n-$ and PES is poly(phenyl ether sulphone) with the structure $-(O-C_6H_4-SO_2-C_6H_4)_n-$. The PPS–PES mechanical blends were prepared by mixing PPS and PES powders in a high-speed mixer–agitator with alcohol as dispersion agent. The solution used in preparation of PPS–PES solution-cast blends is α-chloronaphthalene/dimethylsulphoxide (1/3)[4].

The PPS–PES samples are of the composition shown in *Table 1*.

Solid-state n.m.r. experiments were carried out on Bruker MSL-300 n.m.r. spectrometer with the proton resonance frequency of 300 MHz and 75 MHz for carbon-13. The pulse sequences used in the experiments and parameters are specified on *Figure 1*.

The T_2, T_1 and $T_{1\rho}$ of proton relaxation data were fitted by the following equations[10]:

$$M = \sum_{i=1}^{n} M_{0i} \exp(-t/T_{2i})^E \qquad (E = 1 \text{ or } 2)$$

$$M = \sum_{i=1}^{n} M_{0i}[1 - 2\exp(-t/T_{1i})]$$

$$M = \sum_{i=1}^{n} M_{0i} \exp(-t/T_{1\rho i})$$

on the Aspect-3000 computer using the SIMFIT program together with the spectrometer. S, I and L are used to denote the short, intermediate and long values of T_2, $T_{1\rho}$ and T_1 multicomponent relaxation times.

RESULTS AND DISCUSSION

Since polymeric chain motion is frozen at room temperature, semicrystalline PPS and amorphous PES have similar ^{1}H T_2 values (about 15 μs); a difference in T_2 values can be observed at high temperature, e.g. 385 K, when the mobility of non-crystalline chains is increased and T_2 becomes longer due to motional narrowing (*Table 2*). The non-exponential free induction decay (FID) of PPS may be decomposed into two components, crystalline and amorphous, the amount of each corresponding to the degree of crystallinity of the sample. The FID of PES is a Gaussian decay. It is worth while to notice that at 385 K solution-cast blends reveal a shorter T_2 term (10 μs) in multicomponent T_2, which is still shorter than the T_2 of crystalline PPS phase, the amount of this phase being about 10% from ^{1}H results. This indicates that the domain structure of the blends is different from that of homo-PPS and homo-PES.

Proton T_1 data of PPS–PES blends at 298 K are shown in *Table 3*. For the micrometre-scale domain size of PPS, the two T_1 components T_{1S} and T_{1L} of PPS may correspond to the amorphous and crystalline regions.

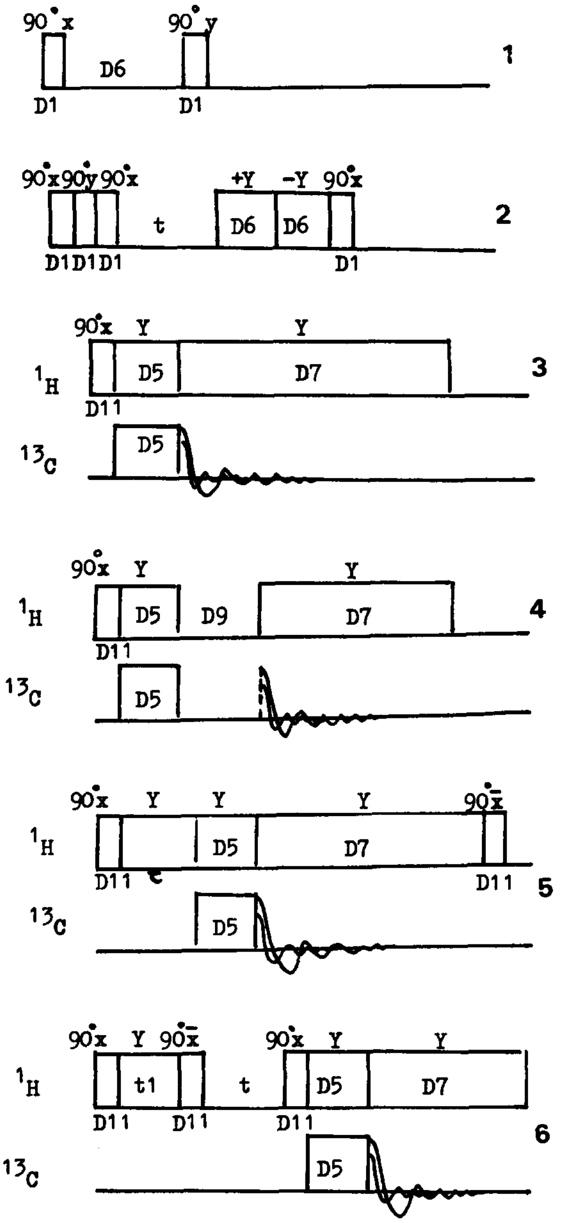


Figure 1 Pulse sequences used in solid-state n.m.r. experiments. (1) Pulse sequence for solid echo: $D_1 = 2\,\mu s$, $D_6 = 8\,\mu s$. (2) Pulse sequence for ^{1}H T_1 measurement: $D_1 = 2\,\mu s$, $D_6 = 8\,\mu s$. (3) Pulse sequence for CP/MAS/DD: $D_{11} = 5\,\mu s$, $D_5 = 3$ ms, $D_7 = 20$ ms, $R_{MAS} = 4.5$ kHz. (4) Pulse sequence for dipole dephase delay: $D_{11} = 5\,\mu s$, $D_5 = 3$ ms, $D_7 = 20$ ms, $D_9 = 45\,\mu s$, $R_{MAS} = 4.5$ kHz. (5) Pulse sequence for ^{1}H $T_{1\rho}$ measurement with CP MAS/DD: $D_{11} = 5\,\mu s$, $D_5 = 3$ ms, $D_7 = 20$ ms, $R_{MAS} = 4.5$ kHz. (6) Pulse sequence for Goldman–Shen spin diffusion CP/MAS/DD: $D_{11} = 5\,\mu s$, $D_5 = 3$ ms, $D_7 = 20$ ms, $t_1 = 20$ ms, $R_{MAS} = 4.5$ kHz

Table 1 PPS–PES samples

Samples[a]	1	2	3	4	5	6	7
PPS/PES (wt%)	90/10	70/30	50/50	40/60	30/70	60/40	40/60
PPS/PES by ^{1}H (%)	90/10	71/29	52/48	42/58	32/68	61/39	42/58

[a] Samples 1 to 5 are solution-cast blends and 6 and 7 are mechanical blends

Table 2 T_2 values (μs) of PPS–PES solution-cast blends for ^1H at 385 K

Sample	T_{2S}	T_{2I}	T_{2L}
PPS	18 (41%)		36 (59%)
PES			24
No. 1	16		33
No. 2	16		25
No. 3	11 (11%)	17	25
No. 4	10 (11%)	18	25
No. 5	10 (12%)	19	24

Table 3 T_1 values (s) of PPS–PES blends for ^1H at 298 K

Sample	T_{1S}	T_{1I}	T_{1L}
PPS		0.95 (51%)	2.1 (49%)
PES	0.76		
No. 1		1.4 (63%)	3.3 (37%)
No. 2	1.1	1.6	4.4 (10%)
No. 3	0.98	1.6	3.6 (10%)
No. 4	0.92	0.93	4.3 (9%)
No. 5	1.1	1.5	4.0 (8%)
No. 6	0.70 (41%)	0.93 (32%)	2.1 (27%)
No. 7	0.65 (58%)	0.98 (23%)	2.0 (19%)

PES has only one T_1, indicating the homogeneous structure at T_1 measurement scales. T_1 data of solution-cast blends and mechanical blends are all non-exponential, which implies that there is no strong spin-diffusion coupling interaction within the whole blending system; the domain sizes are larger than the maximum distance over which spin diffusion is effective in period T_1, less than 50 nm. T_1 signals of PPS–PES mechanical blends are composed of three components; the T_1 values and the contents of different T_1 components correspond wholly to the homo-PES and PPS and their composition. It indicates that the domain structures of mechanical blends are simply the sum of that of homopolymer blend pairs; the domain size is quite large. However, for PPS–PES solution-cast blends, although the non-exponential T_1 decays indicate the heterogeneous structure of the blends, the multicomponent decays do not correspond to that of homo-PES and PPS. In accordance with the shortest T_2 phase found in the T_2 experiment, there is a longer T_1 phase. As PES increases, the T_{1L} values of the blends increase and amount to about 10% by ^1H when the PES content is high. It also implies that the domain structure changes with the influence of PES. The T_1 values give more information: when the proportion of PPS to PES is 4/6, only a single T_1 phase appears besides the longer T_1 phase, which means at that proportion amorphous PPS is compatible with amorphous PES to form a uniform domain. Thus continuous phase inversion of the blends occurs and the interfacial effects are enhanced at this blending proportion. The T_{2S}, and T_{1L} components should correspond to the crystalline region, in agreement with the d.s.c. result[4]. The nature of this region should be studied in detail with solid-state high-resolution n.m.r. methods.

CP/MAS ^{13}C solid-state high-resolution n.m.r. spectra of homo-PPS, homo-PES and their solution-cast blends are shown in *Figure 2*. It is clear that the peak of PPS is composed of narrow and broad parts; the narrow peaks should correspond to crystalline regions and the broad peaks to amorphous PPS. By determination of cross-polarization time (pulse sequence 3 in *Figure 1*) and dipolar dephasing delay (pulse sequence 4 in *Figure 1*)[11] (results shown in *Table 4*), the chemical shift of PPS and PES can be identified (shown in *Table 5*).

Because of the smaller influence of spin diffusion and the large domain size of the blends, $T_{1\rho}$ decays of the blends (*Table 6*) should reflect the domain structure. Four

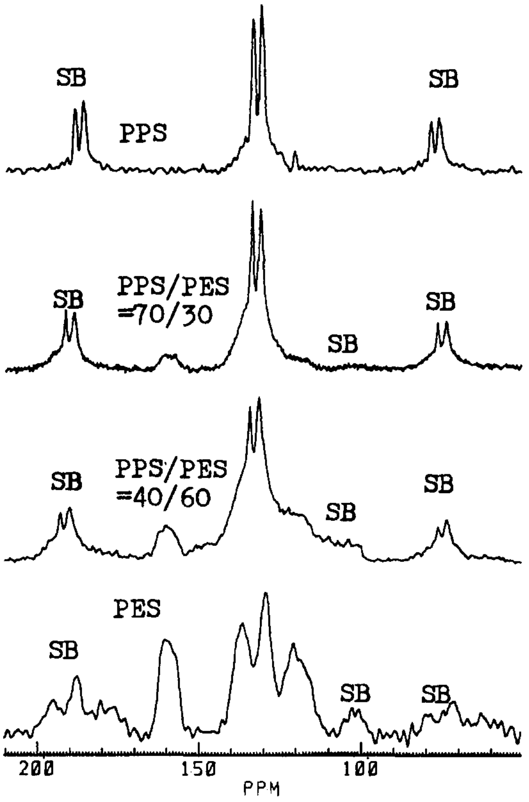


Figure 2 ^{13}C CP/MAS spectra of PPS, PES and PPS–PES solution-cast blends

Table 4 The CP contact time (ms) and dipole dephase delay experiment results[a]

Sample	160 ppm	136 ppm	133 ppm	131 ppm	120 ppm
PES			3.0*	2.0	
PES	1.2*	1.2*		0.6	0.6
No. 4	1.2*		2.0*	0.6	
No. 7	1.2*	1.2*	1.6*	1.2	0.6

[a] After 45 μs dipole dephase delay, the peaks marked by an asterisk (*) still appear

Table 5 Assignment of PPS, PES ^{13}C CP MAS spectra

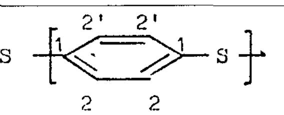
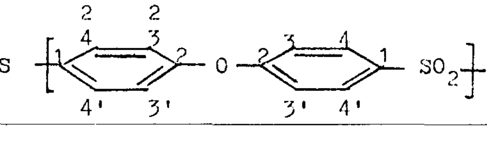
PPS		1 133 ppm 2,2′ 131 ppm
PES		1 160 ppm 2 136 ppm 3,3′ 131 ppm 4,4′ 120 ppm

Table 6 $T_{1\rho}$ values (ms) of PPS–PES blends for ^1H at 298 K

	160 ppm	134 ppm			120 ppm
Sample	$T_{1\rho}$	$T_{1\rho S}$	$T_{1\rho I}$	$T_{1\rho L}$	$T_{1\rho}$
PPS			11 (53%)	224 (47%)	
PES	5.4	5.3			5.1
No. 2	6.6	6.9 (22%)	22 (78%)	267 (10%)	
No. 4	9.0	10	11	321 (10%)	
No. 7	5.1	6.1 (38%)	13 (32%)	256 (30%)	

peaks of PES have identical $T_{1\rho}$ values for the strong spin diffusion within homo-PES, but for the two peaks of PPS, $T_{1\rho}$ decays are non-exponential and may be decomposed into amorphous and crystalline parts. On examining proton $T_{1\rho}$ decays, it is found that the same conclusion can be drawn as we obtained from T_2 and T_1 experiments. The $T_{1\rho}$ peaks at 130–140 ppm also occur with one of extraordinarily long $T_{1\rho}$ other than that of PPS crystalline phase and the value grows longer when the proportion of PES is increased. When PPS/PES = 4/6, the solution-cast blends become more compatible as the amorphous PPS and PES form a uniform domain other than 10% by ^{1}H crystalline regions on the scale of several nanometres.

The peaks of PES at 160 ppm do not overlap with PPS in the blends; it is thought that $T_{1\rho}$ decays of this peak will reflect the nature of PES in the blends. Some authors had suggested that blending PPS with PES may induce crystallization of amorphous PES[4]; if this were so, the $T_{1\rho}$ peak of the blends at 160 ppm would be decomposed into two or more parts with one longer $T_{1\rho}$ over tens of milliseconds. But we found that this is not the case, and there is only one $T_{1\rho}$ with a value near that of PES homopolymer. In the spectra of the blends we also cannot find any clear narrow crystalline component on the 160 ppm peak. These results imply that the crystalline phase in PPS–PES solution-cast blends would be a recrystalline PPS, the domain structure of which has been changed by the influence of solution casting with PES.

We have tried to use a Goldman–Shen spin-diffusion pulse sequence with CP/MAS techniques (*Figure 1*, pulse sequence 6) on the PPS–PES blends. The $T_{1\rho}$ of PPS crystalline phase in the blends differs noticeably from that of the amorphous phase. For PPS/PES = 4/6 solution-cast blends, during the period t_1 (20 ms), the magnetization of the amorphous compatible phase of PPS–PES has relaxed to zero while there is still sufficient magnetization of crystalline phase due to its longer $T_{1\rho}$. During the diffusion time magnetization will diffuse from the PPS crystalline domain to the PPS–PES compatible domain through the magnetic dipolar coupling and it can be visualized from the height of the PES peak at 160 ppm. The process of spin diffusion can be expressed as the following equation[12]:

$$\partial M(\mathbf{r}, t)/\partial t = \nabla D(\mathbf{r}) \nabla M(\mathbf{r}, t) - (T_1)^{-1} M(\mathbf{r}, t)$$

where $D(\mathbf{r})$ is the spin-diffusion coefficient and $\mathbf{r}$ is the position vector. The recovery of the magnetization of compatible domain can be measured and the diffusion rate depends on the domain structure and size. Although much effort has been made to solve the diffusion equation and to fit the theoretical results to the experimental data[13–15], there are in fact still many difficult problems, e.g. the model of domain structure with interfaces, the determination of $D(\mathbf{r})$ and so on. In a system such as PPS–PES blends, which have very large domains compared to the maximum diffusion length in T_1 measurements, the second term in the equation cannot be ignored, which makes the problem more complicated. Here we can only discuss it in a simple way.

Let the recovery factor $R(t) = A(t)/A(t \rightarrow \infty)$, where $A(t)$ is the magnetization of the compatible domain expressed by the peak at 160 ppm of the PPS–PES solution-cast blends during the diffusion time t and $A(t \rightarrow \infty)$ is that of the same peak when equilibrium is recovered. The magnetization contributed by T_1 relaxation is subtracted from the data observed from the Goldman– Shen experiment. Thus an $R(t)$ *versus* t plot can be obtained, and is shown in *Figure 3*.

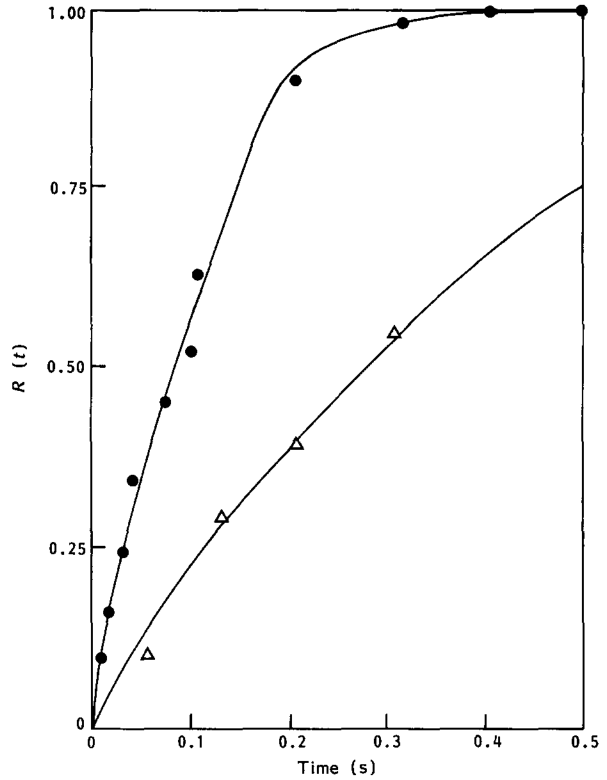


Figure 3 $R(t)$ vs. spin-diffusion time for PPS/PES = 40/60 (●) and PPS/PES = 70/30 (△) solution-cast blends

By the treatment methods of Assink[16] with a three-dimensional spherical model, the domain size of the partially compatible PPS–PES solution-cast blends with proportion 4/6 is of the order of 0.1 μm. Because of the longer magnetization recovery time, the domain size of PPS–PES solution-cast blends is larger. Comparison of regions of homo-PPS crystal of some tens of micrometres in size clearly shows that the domains of PPS crystal decrease drastically when solution-cast with PES. That is in good agreement with the observation of polarized light microscopy, scanning electron microscopy and small-angle light scattering[4].

The physical properties of crystalline–amorphous blends are highly dependent on phase morphology, relative crystallinity and crystallization behaviour of the crystalline components of the blends. It is known that the crystallinity of the crystalline polymer will decrease considerably as the amount of amorphous polymer increases in the miscible or partially miscible blending system, e.g. PVF_2–PMMA[17], PVF_2–PEMA[18] and PPS–PS[19]. As the domain size is large, we can consider the amount of T_{1L} component of the blends to correspond to the crystallinity of PPS in the blends, and the results are shown in *Figure 4*. With an increase of PES content, for mechanical blends the crystallinity only decreases slightly, in agreement with the results of the small domain change seen in SEM[4] and poor compatibility obtained in T_1 experiments. In such a case PES only acts as a diluent. PES is not compatible with PPS.

It is very interesting that, for solution-cast blends, with an increase of PES content the crystallinity decreases quickly (even when the PES content is as low as 30 wt% it is only 14%) then recovers somewhat. It was found

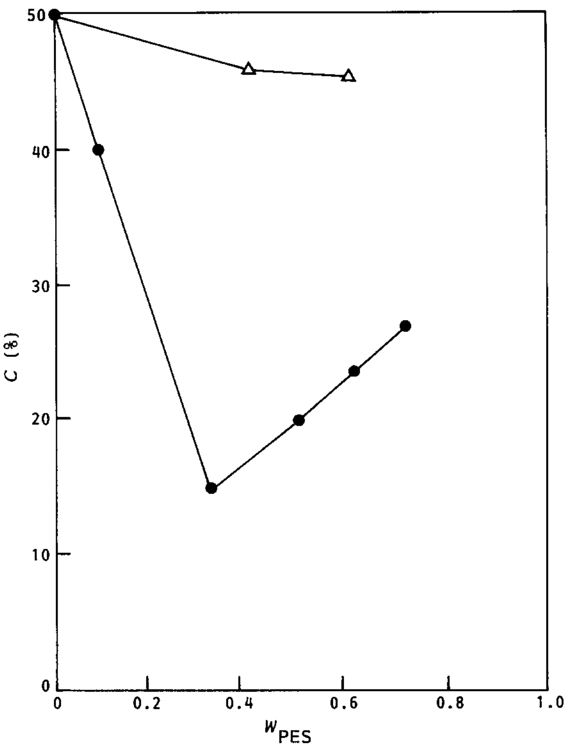


Figure 4 Crystallinity vs. W_{PES} for PPS–PES solution-cast blends (●) and PPS–PES mechanical blends (△)

that with the increase of PES, spherulites of PPS were more and more irregular and formed minute crystallites for which a Maltese cross could not be observed under an orthogonal polarized light field[4]. In the d.s.c. curve[4] there was an exothermic crystallization peak that corresponded to PPS cold crystallization of solution-cast blends. The addition of PES would increase this cold crystallization and the heat given off from cold crystallization reached maximum when PES content was 60–70% by weight. The solid-state n.m.r. experiments indicate that for PPS–PES solution-cast blends, the increase of PES content will destroy the original structure of the PPS crystal and decrease the crystallinity considerably owing to partial compatibility. Then as the PES content increases to a certain amount the cold crystallization of PPS also increases and gives the results we got in *Figure 4*. The phase of shorter T_2 and longer $T_{1\rho}$ and T_1 corresponds to this cold crystallization. When the PES content is low, the PPS crystalline domains in the blends are contributed by both formal and cold crystalline structure; the $T_{1\rho}$ and T_1 of this domain have intermediate values. When PPS/PES = 4/6 the partial compatibility is best, PES can mix intimately and have a great effect on PPS; then the crystal mainly consists of PPS cold crystalline structure with small domains. PES may be considered as a crystalline centre; it may change the morphology of PPS crystal and also decrease the crystalline domain size. The well distributed domain structure and the partial compatibility of the blends are beneficial to the improvement of mechanical properties of the materials.

CONCLUSIONS

PPS–PES mechanical blends are poorly compatible blends with large domain size and the same domain structure of homo-PPS and homo-PES, but solution-cast blends are partially compatible and the crystalline phase of PPS has changed its morphology. The increase of PES content not only destroys the usual domain structure of PPS crystal and decreases its crystallinity, but also promotes the growth of PPS cold crystal, and forms a domain structure of shorter T_2 and longer $T_{1\rho}$ and T_1. When PPS/PES = 4/6, the partial compatibility of the solution-cast blends becomes best. Apart from the cold crystal of PPS the amorphous PPS and PES mix intimately to a compatible phase on the scale of several nanometres, and at the same time the domain size of PPS crystalline domains in the blends decreases noticeably.

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REFERENCES

1 Zeng, H. M. and He, G. R. *Polym. Commun. (China)* 1986, **4** (2), 97
2 Zhou, X. M., Liu, R. R. and Liu, A. M. *Polym. Commun. (China)* 1984, **2** (2), 81
3 Shen, M. and Kawai, H. *AIChE J.* 1978, **24**, 1
4 Zeng, H. M. and Yang, C. 'Interfaces in Polymer, Ceramic, and Matrix Composites', Proc. ICCI-II, 1988, p. 305
5 McBrierty, V. J. and Douglass, D. C. *J. Polym. Sci., Macromol. Rev.* 1981, **16**, 295
6 McBrierty, V. J. and Douglass, D. C. *Macromolecules* 1978, **11**, 1265
7 Alber, B., Jerome, R., Teyssie, P., Smyth, G., Boyle, N. G. and McBrierty, V. J. *Macromolecules* 1985, **18**, 388
8 Zhang, X. Q. and Wang, Y. S. *Chin. J. Polym. Sci.* 1988, **2**, 159
9 Paul, D. R. and Newman, S. 'Polymer Blends', Academic Press, New York, 1978
10 McBrierty, V. J. *Polymer* 1975, **15**, 503
11 Axelson, D. E. and Russell, K. E. *Prog. Polym. Sci.* 1985, **11**, 221
12 Tanaka, H. and Nishi, T. *Phys. Rev. (B)* 1966, **33**(1), 32
13 Cheung, T. T. P. and Gerstein, B. C. *J. Appl. Phys.* 1981, **52**, 5517
14 Packer, K. J., Pope, J. M. and Yeung, R. R. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 589; Krnaright, A. M., Packer, K. J. and Say, B. J. *J. Magn. Reson.* 1986, **69**, 426
15 Chen, Q. and Wang, Y. S. Proc. BCEIA-II, 1987, pp. 1079, 1081
16 Assink, R. A. *Macromolecules* 1978, **11**, 1233
17 Tekely, P., Laupretre, F. and Monnerie, L. *Polymer* 1985, **26**, 1081
18 Li, X., Wang, Y. K. and Yang. Y. *Polym. Commun. (China)* 1987, **5** (1), 75
19 Radhakrishnan, S. and Joshi, S. G. *Eur. Polym. J.* 1987, **23**, 819