Local Compositional Fluctuations in PPO/HIPS and PPO/SBS Blends

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SYNOPSIS
Solid-state NMR relaxation has been used to explore the distribution of components in poly(phenylene oxide) (PPO) high impact polystyrene (HIPS) and PPO/poly(styrene-b-butadiene-b-styrene) (SBS) blends. The nuclear relaxation of PPO in the former system is single exponential for all compositions, but the relaxation of PS in the blend is simple exponential only when the PPO content is low but is otherwise nonexponential. The nuclear magnetization decay curves were analyzed in terms of statistical compositional fluctuation at the scale of spin diffusion distances of several nm. Distribution functions for nuclear relaxation and for blend composition have been derived. Extraction of low molecular weight occluded PS from HIPS resulted in blends having reduced homogeneity. Addition of low molecular weight PS enhanced homogeneity in both the PPO/HIPS and PPO/SBS blends.

INTRODUCTION
The usefulness of a polymeric material is determined by its thermal, mechanical, rheological, and impact properties. However, a homopolymer or a copolymer may excel in some yet deficient in other properties. By blending two or more polymers, scientists were able to obtain new materials possessing a balance of a certain set of properties far superior to those of the constituent homopolymers. An outstanding example is the family of Noryl resins of General Electric Plastics. It combines poly(2,6-dimethyl-phenylene oxide) (PPO), and poly(styrene) (PS) to gain both high heat distortion temperature and processability, polybutadiene (PB) or high impact poly(styrene) (HIPS) to dissipate impact energy, and thermoplastic elastomer such as linear triblock poly(styrene-b-butadiene-b-styrene) (SBS) which may act as compatibilizer. The resulting materials of superior impact resistance are industry standards for engineering plastics.

Various techniques had been used to study the PPO/PS blends. Even though PPO and PS are considered to be miscible in all proportions there were observations indicative of microheterogeneity. Solid-state nuclear magnetic resonance (NMR) is capable of discerning the miscibility of blend at nm scale. We have performed measurement of proton spin-lattice relaxation in the rotating frame \( T_1^\text{H} \) on PPO/PS blends for a range of composition and MW; the relaxation was found to be biphasic. This suggests that the blend is heterogeneous in the scale of proton spin-diffusion distance, particularly for specimen either containing high MW PS, or prepared from toluene solution, or thermally annealed.

The purposes of this work are twofold. The first was to extend the NMR measure of microheterogeneity to PPO/HIPS and to PPO/SBS blends. The second was to formulate a theory, based on local compositional fluctuations, to explain the microheterogeneity observed by solid-state NMR.

EXPERIMENTAL
PPO (\( M_n = 23,000 \) and \( M_w/M_n = 1.9 \) from General Electric Plastics) was purified by dissolving in chlo-
roform, precipitated with methanol, and dried in vacuo at 60–70°C for 48 h. HIPS and Kraton B SBS was obtained from General Electric Plastics and Shell, respectively. Monodisperse PS with 9000 (9K) $M_n$ was purchased from Pressure Chemicals.

Direct polarization solid $^1$H-NMR showed that the HIPS from GE contains PS (96 wt \%, 92.3 mol \%) and PB (4.0 wt \%, 7.7 mol \%), the former was present as both occluded and grafted PS. HIPS was extracted with acetone using Soxhlet apparatus. The extract contains only low MW PS (designated as a-PS, $M_n = 10,000$, $M_w/M_n = 1.9$). This extracted material is referred to as e-HIPS.

Blend samples were prepared by dissolving the polymers in chloroform, cast on a clean aluminum surface at room temperature in air, allowed to stand for one day, dried in vacuum at 60°C for 2 days, and pulverized into powder with a Spex freezer-mill.

Solid state NMR spectra were obtained on an IBM AF 200 spectrometer. With $^1$H observed at 50.3 MHz. The operating conditions and pulse sequences were described elsewhere. \(^{22}\) $^1$C-NMR intensity was measured as a function of contact (spin-lock) time; $T_{1\rho}(H)$ was obtained from the slope of the semilog plot.

RESULTS AND DISCUSSION

PPO/HIPS

The DSC curves of PPO/HIPS blends of several compositions are shown in Figure 1. Only one $T_g$ was observed, the values of which increases monotonically with the increase of amount of PPO in the blend. This is the behavior of a compatible mixture.

A homogeneous polymeric material is characterized by single-valued $T_{1\rho}(H)$. The spins can exchange energy with each other through flip-flop diffusion process which eliminates differences in their spin temperature. \(^{22-26}\) For a well-dispersed blend of different polymers, the protons will relax with a single rate as long as the average separation between protons is smaller than the random diffusion distance of the spin during its excited life-time. Otherwise, complicated distribution of spin-lattice relaxation rates is expected.

The $T_{1\rho}(H)$ decay for PPO monitored by the carbon nuclear magnetization of the methyl resonance at 16 ppm was single exponential \(^{20}\) with a time constant of 20 ms. Similarly, single exponential decay ($T_{1\rho}(H) = 6 \pm 0.3$ ms) was observed with the methylene carbon resonance at 40 ppm of PS. The non-rigid PB carbons in the HIPS were not cross polarized and thus not observed. Therefore, the nuclear magnetic relaxations of the PPO and the PS components in the PPO/HIPS blend can be followed separately by the 16 ppm and 40 ppm peaks, respectively. On the other hand, the decay of $^{13}$C magnetization of PS in HIPS is nonexponential. This indicates that the various kinds of PS (i.e., PS occluded in or grafted to PB) or PS in the rigid phase, are not well mixed at a scale of spin-diffusion distance. Consequently, their different relaxation times were not averaged by the spin-diffusion process.

Three PPO/HIPS blends were prepared; their compositions are: (A) 75 PPO/25 HIPS, (B) 50 PPO/50 HIPS, and (C) 25 PPO/75 HIPS. Figure 2 gives the semilogarithmic plots of $^{13}$C intensity versus spin-lock time for these blends. The experimental error was estimated from the signal to noise and is represented by the error bar. The relaxations of the PPO components in all three specimens are simple exponential. This means that the distribution of PPO are uniform in these materials. If there is any fluctuations in PPO composition, they are averaged by proton spin-diffusions. The $T_{1\rho}(H)$ values are summarized in Table I. Blends A and B have nonexponential relaxation rates for the PS resonance. This was as expected because the relaxation of HIPS itself is biphasic (vide supra). The nonexponential decay data was analyzed in terms of two exponential processes; the time constants are given in Table I (however, see below for the theoretical treatment). The fraction of $^{13}$C nuclear magnetization which decays by the fast and slow processes are given in parentheses next to the relaxation times.
Figure 2. Plots of logarithmic $^{13}$C intensity versus spin lock time for PPO/HIPS blends: (a) PPO (75/25); (b) PS (75/25); (c) PPO (50/50); (d) PS (50/50); (f) PPO (25/75); (g) PS (25/75).

Figure 3. Plots of logarithmic $^{13}$C intensity versus spin lock time for PPO/e-HIPS blends: (a) PPO (75/25); (b) PS (75/25); (c) PPO (50/50); (d) PS (50/50); (e) PPO (25/75); (f) PS (25/75).

These fraction values may or may not have quantitative significance depending on whether the differently relaxing nuclei have comparable or dissimilar cross-polarization efficiencies.

Blend C differs from the other two in that the PS relaxes single exponentially. Furthermore, the $T_{1\rho}(H)$ values are the same for both PS and PPO. This suggests that the relaxation rates of various PS and of the PPO are averaged by spin-diffusion in this homogeneous blend.

**PPO/e-HIPS Blends**

Blend samples were prepared from PPO and HIPS which had been extracted with acetone: (D) 75 PPO/25 e-HIPS; (E) 50 PPO/50 e-HIPS; (F) 25 PPO/75 e-HIPS; their relaxation behaviors are described in Figure 3. Both the PPO component and the PS component relax nonexponentially, which is significantly different from that of PPO/HIPS blends. The latter contains the low molecular weight a-PS and the former does not. This results suggests that the 10,000 $M_n$ PS does affect the molecular relaxation in well-dispersed blends.

<table>
<thead>
<tr>
<th>Blend wt %</th>
<th>$T_{1\rho}(H)$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>PS</td>
</tr>
<tr>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
</tr>
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</table>

The presence of a-PS appreciably influences the nuclear relaxations in blends rich in PPO in two ways. First, the PPO components in blends D and E relaxed nonexponentially whereas relaxations were simple exponential in blends A and B. Second, the PS components in the PPO/e-HIPS have much longer relaxation times than the corresponding PPO/HIPS blends. Both the PPO and the PS in these samples are microheterogeneous. The behavior suggests that the low MW a-PS helps to homogenize the PPO. This possible explanation was investigated by two kinds of experiments.

In the first experiments, the e-HIPS was reconstituted by adding back the a-PS. Blends were prepared with this reconstituted HIPS (r-HIPS). The NMR relaxation behaviors of the 25 PPO/75 r-HIPS and 50 PPO/50 r-HIPS blends were indistinguishable from the respective C and B specimens. However, the 75 PPO/25 r-HIPS sample exhibited noticeably longer relaxation times than sample A. Apparently, reconstitution can improve homogeneity of blends comprising of 25 and 50% PPO, but it was not very effective in the case of the blend with 75% PPO.

In the second experiments various amounts of monodispersed PS (9K) were added to e-HIPS and blended with PPO. Figure 4 shows the magnetization decay plots for such blends containing 50% PPO. There is a clearly discernible trend of progressive approach toward simple exponential decay as the PS (9K) content in the blend increases. However, a substantial amount of the PS (9K) [i.e., 50 wt % of 45:5 mixture of PS(9K)]; e-HIPS, is required to render the blend with PPO homogeneous. Therefore, the PS (9K) is less effective than the a-PS in elim-
minating microheterogeneity. Even though \( \alpha \)-PS has \( M_M \) of 10K close to the monodisperse PS (9K), the former contains PS chains of both higher and lower MW which may be responsible for its apparently better efficacy as compatibilizer.

**PPO/SBS Blends**

Figure 5 shows the logarithmic intensity versus spin-lock time plots for various PPO/SBS blends. Both polymer components decayed biphasically in the 75 PPO/25 SBS and 50 PPO/50 SBS blends showing that the terminal poly(styrene) blocks are not free to mix like homopoly(styrene) blocks. The same conclusion\(^1\)\(^2\) was also drawn from observed broadening of thermal transitions in PPO/SBS blends. However, the 25 PPO/75 SBS blend exhibits single exponential decay for both components, indicating that in this case the blend is uniform at spin-diffusion scale. Fifty-fifty PPO/SBS blend exhibits non-exponential NMR decay. The addition of PS(9K) also had the effect of compatibilization (Fig. 6) as it did for the PPO/HIPS case (vide supra).

**A Statistical Theory of Compositional Fluctuation for Microheterogeneity**

The above discussion of the microheterogeneity of PPO/HIPS and PPO/SBS blends is of qualitative nature which employs only exponential versus non-exponential magnetization decay as the criterion. In this section we present a quantitative analysis of the data based on the local fluctuation of blend composition.

In solid NMR, the dipolar–dipolar interactions causes mutual flip-flop of proton spins. This process is referred to as spin-diffusion; it can be described by a diffusion equation,

\[
\frac{\delta P}{\delta t} = D (\delta^2 P / \delta x^2)
\]

where \( P \) is the proton magnetization and \( D \) is the diffusion coefficient. The maximum mean square diffusion distance \( \langle L^2 \rangle \) in time \( t \) is,

\[
\langle L^2 \rangle = 6Dt
\]
For a random walk diffusion,
\[ D = v_0 \langle I_0^2 \rangle \]  
(3)

where \( \langle I_0^2 \rangle \) is the mean square distance of each step and \( v_0 \) is the frequency which for NMR is \( T_2^{-1} \). Therefore,
\[ \langle L^2 \rangle = t \langle I_0^2 \rangle / T_2 \]  
(4)

In the \( T_1 \) experiments, \( t \) is of order of msec, and \( \langle L^2 \rangle^{1/2} \) is several nm. Note that in the laboratory 
frame experiment, \( t \) is about 100 times longer so \( \langle L^2 \rangle^{1/2} \) is about 10 times greater.

When the domain size is small compared with \( \langle L^2 \rangle^{1/2} \) or the spin-diffusion rate is faster than the relaxation rate, a single average decay constant is observed:
\[ T_{1p}(H)_{ob} = M_A / T_{1p}^A(H) + M_B / T_{1p}^B(H) \]  
(5)

here \( T_{1p}^A(H) \) and \( T_{1p}^B(H) \) are the decay constants of polymers \( A \) and \( B \) in the blend; their values may be the same as or different from the values for these processes in the neat homopolymers depending upon whether blending affects molecular interactions or not. The values of \( T_{1p}^A(H) \) and \( T_{1p}^B(H) \) can be determined by measuring \( T_{1p}(H) \) for each blend component at several compositions. \( T_{1p}(H) \) is the relaxation time for the \( i \)-th domain in the blend of composition \( M \),
\[ T_{1p}^i(H) = f(M_i) \]  
(6)

Then \( T_{1p}^A(H) \) and \( T_{1p}^B(H) \) are the extrapolated values for 100% of polymers \( A \) and \( B \), respectively. The decay of the carbon magnetization \( (S) \) for the pulse sequence used in the present experiment may be described as,
\[ \frac{dS}{dt} = S_0 \exp(-t/T_{1p}(H)) - \frac{S}{T_C(H)} \]  
(7)

where \( S_0 \) is the maximum carbon magnetization, \( t \) is the spin-lock time, \( T_{1p}(C) \) is the carbon spin-lattice relaxation times in the rotating frame, and \( T_C(H) \) is the Hartmann-Hahn cross-polarization time constant. The solution for eq. (7) is,
\[ S = \frac{S_0 \exp(-t/T_{1p}(H))}{T_{1p}(H)} \]  
(8)

In our experiments, \( T_{1p}(C) \gg T_C \); \( T_{1p}(H) \gg T_C \) and \( t \gg T_C \), so eq. (8) may be simplified to,
\[ S = S_0 \exp[-t/T_{1p}(H)] \]  
(9)

For a multirelaxation system, the decay of the magnetization is a sum over all the \( i \)-species with different \( T_{1p}(H) \):
\[ S(t) = \sum_{i=1}^{4} S_0 \exp[-t/T_{1p}(H)] \]  
(10)

For continuous \( S(T_{1p}) \),
\[ S(t) = \int S(T_{1p}) \exp[-t/T_{1p}(H)] dT_{1p} \]  
(11)

Our objective is to find the distribution function from the experimental \( S(t) \) data. To do this we used a multipol modified Gaussian function as a starting distribution function:
\[ F(T_{1p}) = \sum_{i=1}^{4} f_i(T_{1p}) \]  
(12)

\[ f_i = A_i \exp\left(-\frac{(T_{1p} - T_{1p}^i)^2}{2(\Delta T_{1p}^i)^2}\right) \]  
(13)

The physical meaning of \( F(T_{1p}) \) is the probability of finding a particular component with relaxation \( T_{1p} \) in the system, and \( T_{1p}^i \) is the most probable relaxation time for phase \( i \) and \( \Delta T_{1p}^i \) is the relaxation time distribution width of phase \( i \). Substitution of eq. (5) into eq. (12) leads to a distribution function of the relaxation times for the blend averaged over the \( \langle L^2 \rangle^{1/2} \) domain size.

Corresponding to \( F(T_{1p}) \) is a distribution function of composition for the blend,
\[ F(M) = \sum f(M) \]  
(14)

Figure 7 shows the parameters in eq. (13). The average composition within the spin-diffusion domain is given by:
\[ M(T) = \int_{\min}^{T} F(T_{1p}) M dT_{1p} \]  
(15)

The dependence of compositional fluctuation at segmental length is obtained by plotting \( M(T) \) versus \( T \).

Though PPO/PS and PPO/HIPS blends exhibit single \( T_e \), their solid state NMR relaxation is often
non-exponential. The decay data of a typical experiment was analyzed by the above program. Figure 8 shows the agreement between experimental data and calculated results for the 25 PPO/75 HIPS blend, and Figure 9 gives the distribution of $T_{1s}(H)$ for this blend. If we assume that the $T_{1s}(H)$ of each polymer is the same as that of neat homopolymer, then the linearity relation is,

$$T_{1s}(H)^{-1} = M_{PPO}/34.7 + M_{HIPS}/4.7$$

(16)

From this relation we can obtain a distribution function for molar compositions of PPO in Figure 10.

The concept of distribution of composition represents a statistically random segmental mixing. The probability of finding a particular average composition within a microdomain of spin-diffusion dimension in the blend is given by this distribution function. It shows two peaks implying that the blend system can be approximated by two-phases containing 35 and 67% of PPO corresponding to the two maxima in Figure 10. The results also showed that the HIPS rich phase has broader distribution of composition than the regions richer in PPO. A nonvanishing probability of pure HIPS composition is seen in Figure 10 suggesting that there are microdomains containing only HIPS.

When we observe microdomains in a polymeric blend by solid NMR we are observing them through the spin diffusion. Assuming spin diffusion rate is constant throughout the specimen, then $T_{1s}(H)$ is the time scale for spin diffusion. Spin diffusion will traverse various microdomain size for various $T_{1s}(H)$. We can plot the $M_i$ vs. $T_{1s}(H)$ according to eq. (6) as shown in Figure 11. It is evident that if $T_{1s}(H)$ is short enough, then only pure HIPS is seen by spin diffusion. As $T_{1s}(H)$ increases the probability of finding HIPS in the spin diffusion range rapidly decreases. When the $T_{1s}(H)$ becomes longer than 12 ms, the composition reaches a constant one of 45 PPO/55 HIPS. This implies that any technique which samples regions much greater than this critical spin diffusion range for this system, i.e., DSC measurement of $T_g$, cannot give any in-

![Figure 7](image7.png)

**Figure 7.** Parameters for the distribution function in eq. (13).

![Figure 8](image8.png)

**Figure 8.** Experimental magnetization decay of PS carbon resonance in 25 PPO/75 HIPS blend, the dotted line is the theoretical results.

![Figure 9](image9.png)

**Figure 9.** Distribution of $T_{1s}(H)$ obtained in Fig. 8.

![Figure 10](image10.png)

**Figure 10.** Distribution of mol % of PPO in the 25 PPO/75 HIPS blend.
Figure 11. Compositional fluctuation of PS in the 25 PPO/75 HIPS blend as a function of spin-diffusion distance.

formation about the inhomogeneity in blend compositions.

CONCLUSIONS

Solid-state NMR relaxation of PPO/HIPS blends showed single magnetization decay for the PPO protons but the process is nonexponential for the HIPS protons. Removal of 10K MW α-PS from the HIPS causes biphasic relaxation for PPO; indicating the α-PS is acting as a compatibilizer. Similar study made on PPO/SBS blends gave analogous results. The nonexponential relaxation was attributed to microheterogeneity in blend composition. A statistical theory of compositional fluctuation was derived. From the distribution function for $T_1(\delta)$ obtained a distribution function for local composition. The analysis showed that NMR relaxation in the rotating frame is a powerful technique to observe microheterogeneity in domain size governed by spin diffusion distance of order of nm.

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REFERENCES AND NOTES


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