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Free-Volume Hole Properties of Polymer Blends Probed by Positron Annihilation Spectroscopy: Miscibility

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ABSTRACT: Positron annihilation lifetime (PAL) spectroscopy has been utilized to investigate the free-volume hole properties of two types of polymer blends, a miscible blend of tetramethyl-Bisphenol A polycarbonate (TMPC) and polystyrene (PS) and an immiscible blend of Bisphenol A polycarbonate (PC) and PS. Larger fractional hole volumes are observed in TMPC than in PC in order to form a miscible blend with PS. In miscible blends, the free volume shows a negative deviation due to blending. In immiscible blends, the relationship between the free volume as detected by positronium annihilation and the weight fraction is complicated due to the presence of interfaces. The free-volume hole distribution is additive in miscible blends, while a significant broadening is observed in immiscible blends. The observed negative deviation of the free-volume hole fraction in miscible blends is interpreted in terms of segmental conformation and packing between dissimilar polymers.

Introduction

In the last few decades, it has been realized that many physical and mechanical properties of polymers can be significantly improved by a process of blending.[1] Miscibility and phase-separation phenomena of polymer blends have received significant attention in polymer applications.[2] In order to predict and enhance the material properties of blends, it is important to understand the nature and the underlying factors of blending at the molecular level. One rational approach in this line of research is to investigate the correlation between free-volume and miscibility properties of blending.[3]

There exist many physical probes for characterizing the structures and properties of polymer blends.[1,4] However, only a limited number of probes are available for characterizing free-volume properties due to the very small size and dynamic nature of free volume.[4] In recent years, positron annihilation spectroscopy (PAS) has emerged as a unique and potent probe for characterizing the free-volume properties of polymers.[5] In PAS, one employs the antiparticle of electrons, the positron, as a nuclear probe. Because of its positively charged nature, the positron is repelled by the ion cores and preferentially localized in the atomic-size free-volume holes of a polymeric material. Therefore, the positron and positronium (a bound atom which consists of a positron and an electron) annihilation signals are found to be contributed mainly from the free-volume holes in a polymer.

Currently, PAS has been mainly developed in monitoring the ortho-positronium (o-Ps, a triplet state) annihilation lifetimes (PAL) for polymeric applications. The results for o-Ps lifetime and its probability are related to the free-volume hole size, fraction, and distribution. Free-volume hole sizes, fractions, and distributions in a variety of polymers have been reported using PAL methods. In polymer blends, some PAL results have been reported.[6−9] In this paper, we report a PAL study for two well-known polymer blends, polystyrene (PS)−tetramethyl-Bisphenol A polycarbonate (TMPC) and PS−Bisphenol A polycarbonate (PC). These two blends have similar chemical structures but a distinct difference in compatibility:[10] PS−TMPC is miscible, while PS−PC is not. The purpose of this study is to investigate this difference in terms of their free-volume properties.

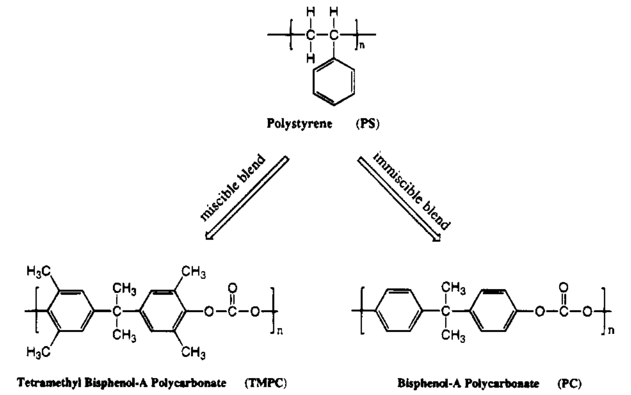

Figure 1. Chemical structures of initial polymers in this study.

Table 1. Physical Properties of Initial Polymers in This Study[a]

polymer	M_w	M_w/M_n	density	T_g(DSC) (°C)	V_f (Å^3)	f_v (%)
PS	105 000	1.06	1.058	102	106 ± 2	5.9 ± 0.1
PC	79 000	3.9	1.200	145	110 ± 2	3.7 ± 0.2
TMPC	67 000	2.6	1.083	196	137 ± 2	5.9 ± 0.1

[a] V_f and f_v are the mean free volume and its fraction from this work. [b] Other parameters were measured as reported in ref 8.

Experiments

Sample Preparation. The initial chemical structures of the polymers under investigation, Bisphenol A polycarbonate (PC), tetramethyl-Bisphenol A polycarbonate (TMPC), and polystyrene (PS), are shown in Figure 1. These materials were supplied by General Electric Co. Physical properties of these polymers are listed in Table 1.

The appropriate weight percents of the polymer blends were prepared by dissolving them in dichloromethane solvents. The

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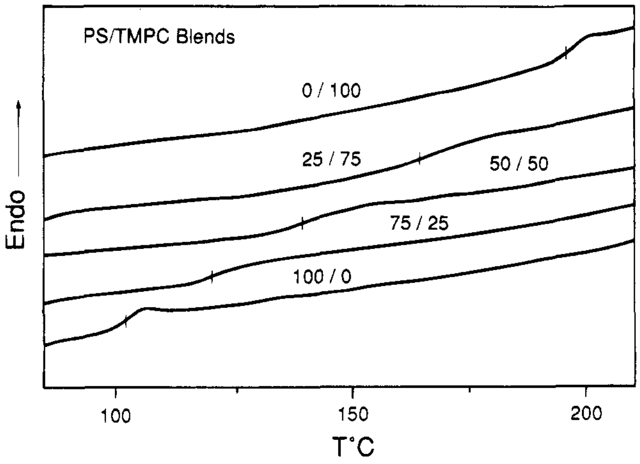

Figure 2. DSC curves for miscible blends of PS–TMPC.

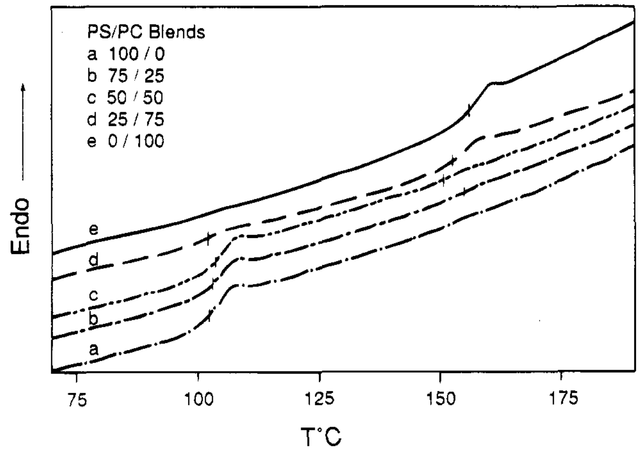

Figure 3. DSC curves for immiscible blends of PS–PC.

mixed polymer solutions were cast in a glass dish and dried at 80 °C in a vacuum oven for several days. The dried films were then annealed above T_gs for 8 h and then used for the positron lifetime experiments.

Miscibility Measurements by DSC. Differential scanning calorimetry (DSC) has been applied to characterize the miscibility of these two types of blends at selected compositions: PS–TMPC and PS–PC. The T_g and ΔC_p values of the neat polymers and the blends were measured using a Perkin-Elmer DSC-7. Samples weighing 7–15 mg were heated at a rate of 10 °C min^{-1}. The samples were scanned from 0 to 230 °C and then fast-quenched to 0 °C for the second run. Figures 2 and 3 show the second run DSC curves for the selected blends. The T_g is defined as the midpoint of the transition from the second run of the DSC measurements. The miscibility of the blends is characterized by the behavior of the T_g. As shown in Figures 2 and 3, PS–TMPC and PS–PC blends show a single T_g and two T_gs, respectively. The results of miscible PS–TMPC and immiscible PS–PC blends are consistent with the existing data.[10,11] The variation of T_g in miscible blends of PS–TMPC follows the predicted values according to the Fox equation:[12] $1/T_g = w_1/T_{g1} + w_2/T_{g2}$, where w_1, T_{g1}, w_2, and T_{g2} are the weight percents and T_g for components 1 and 2, respectively. Detailed descriptions of DSC measurements can be found elsewhere.[13] The Flory–Huggins interaction parameters (χ) between component polymers were reported to be positive ($\approx$0.03) for PS–PC and negative ($\approx$−0.001) for PS–TMPC at selected weight percents.[14,15]

Positron Annihilation Lifetime (PAL) Spectroscopy. The positron annihilation lifetimes of polymer blends were determined by detecting the prompt γ-ray (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from the ^{22}Na radioisotope and the annihilation γ-rays (0.511 MeV). A fast–fast coincidence circuit of a PAL spectrometer with a lifetime resolution of 260 ps as monitored by using a ^{60}Co source was used to record all PAL spectra. Many spectra (between 1×10^6 and 20×10^6 counts) were collected on each sample for a complete data analysis of lifetime distribution. The counting rate was about 200 cps. Detailed descriptions of PAL can be found elsewhere.[16]

Mean Free-Volume Hole Size and Fraction. All of the PAL spectra obtained were analyzed by two methods: (1) finite-term lifetime analysis, and (2) continuous-lifetime analysis. The former analysis employs the PATFIT program,[17] and the later method uses the CONTIN program.[18,19] The finite-term lifetime decomposes a PAL spectrum into two to five terms of negative exponentials. In these polymers, we found that three lifetime results give the best χ^2 (<1.1) and most reasonable standard deviations. The shortest lifetime ($\tau_1 \approx$ 0.12 ns) is the lifetime of p-Ps (singlet Ps), and the intermediate lifetime ($\tau_2 \approx$ 0.40 ns) is the lifetime of the positron. The longest lifetime ($\tau_3 \approx$ 1–3 ns) is due to o-Ps annihilation. In the current PAL method, we employ the results of o-Ps lifetime to obtain the mean free-volume hole radius by the following semiempirical equation:[20]

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \qquad (1)$$

where τ_3 (o-Ps lifetime) and R (hole radius) are expressed in ns and Å, respectively. R_0 equals $R + \Delta R$ where ΔR is the fitted empirical electron layer thickness (=1.66 Å).

The fractional free volume (%) is expressed as an empirically fitted equation as:[21]

$$f_v = AV_f I_3 \qquad (2)$$

where V_f (in Å^3) is the volume of free-volume holes calculated by using the spherical radius (R) of eq 1 from τ_3 (in ns), I_3 (in %) is its intensity, and A is empirically determined to be 0.0018 from the specific volume data.[21]

Free-Volume Hole Distributions. Since the free-volume hole exists in a distribution, the o-Ps lifetime is expressed more correctly as a distribution rather than as discrete values. Hence, we employ the expression of positron lifetime spectra in the form:

$$N(t) = \int_0^\infty \lambda\alpha(\lambda) e^{-\lambda t} d\lambda + B \qquad (3)$$

where λ (the annihilation rate) is the reciprocal of lifetime τ with an annihilation probability–density function $\lambda\alpha$, and B is the background of the spectrum. The computer program CONTIN[18,19] was employed to provide $\lambda\alpha$ vs λ for a PAL spectrum by using the measured reference spectrum in Cu (τ = 122 ps). Following the correlation between τ_3 and the hole radius R (eq 1), considering the difference of o-Ps capture probability in different hole sizes with a linear correction $K(R)$ (=1 + 8R), and using a spherical approximation of free-volume holes, the free-volume probability–density function, V_f(pdf), is expressed as:[22]

$$V_f(\text{pdf}) = -3.32\{\cos[2\pi R/(R + 1.66)] - 1\}\alpha(\lambda)/ \\ \{(R + 1.66)^2 K(R)\, 4\pi R^2\} \qquad (4)$$

The fraction of hole volume between V_f and dV_f is V_f(pdf) dV_f. Detailed descriptions in this regard can be found elsewhere.[22,23]

Results and Discussion

Free-Volume Hole Size and Distributions in Initial Polymers. The PAL spectra in PS, PC, and TMPC were measured at room temperature at total counts between 1×10^6 and 20×10^6. The spectra were stored at an interval of every hour. The stability of the PAL spectra was carefully monitored by observing the shift of time zero (T_0) in the spectra. Any part of the spectra with a T_0 shift exceeding 15 ps was discarded.

Table 2. Positron and Positronium Lifetime Results Obtained by Finite-Term Analysis in Initial Polymers

polymers	$\tau_1{}^a$ (ps)	τ_2 (ps)	τ_3 (ps)	I_2 (%)	I_3 (ps)	R^b (Å)
PS	120 ± 0	398 ± 5	2100 ± 9	48.11 ± 0.31	30.89 ± 0.24	2.94 ± 0.09
PC	120 ± 0	395 ± 5	2154 ± 9	62.53 ± 0.35	18.70 ± 0.22	2.98 ± 0.08
TMPC	120 ± 0	388 ± 5	2426 ± 9	56.98 ± 0.36	23.50 ± 0.22	3.20 ± 0.08

[a] τ_1 was fixed to 120 ps which corresponds to the p-Ps lifetime in the data analysis by using the PATFIT program. [b] $-R$ is the mean free-volume hole radius obtained by using τ_3 according to eq 1.

Only the spectra collected at a stable experimental condition are considered good data and reported here. Table 2 lists the results of three lifetime analyses for the spectra recorded. Both RESOLUTION and POSITRONFIT programs in the PATFIT package[17] were employed for data analysis.

Our PAL results listed in Table 2 are consistent with the existing lifetime results in polystyrene and polycarbonate.[7-9,24,25] The longest lifetime τ_3 is due to o-Ps annihilation. The o-Ps lifetime and intensity I_3 are the parameters which vary as functions of the chemical structure of polymers and the composition of polymers. They are used to evaluate the free-volume hole properties. The results of PAL and hole radii are listed in Table 2. The results of hole volumes and fractions are listed in Table 1.

The hole size results (i.e., R in Table 2) show that PS and PC have about the same size of free-volume holes, while TMPC has a larger size. Typically, the o-Ps lifetime decreases as the molecular weight (M_w) increases up to about 50 000; then it stays unchanged as M_w increases further.[24,25] Since these polymers have a M_w in a range which is expected to have no variation of o-Ps lifetime with respect to M_w, the larger value of τ_3 in TMPC than in PC and PS could be interpreted in terms of molecular structure and its packing in the polymer. Larger values of V_f and f_v in TMPC than in PC can be explained from the substitution effect. Four methyl groups attached to the phenyl group of TMPC (see Figure 1) can create more free spaces in molecular packing of polymer chains than in PC. The steric effect of four additional methyl groups distorts the planar structure of two phenyl groups in TMPC and thus creates more spaces in TPMC than in PC. It can be rationalized that local free-volume hole properties of polymers in blends are very important for local packing and segmental arrangements for the case of blends involving only weak interaction, i.e., the van der Waals types. A larger free volume in TMPC could accommodate the phenyl ring of PS to fit into the space available and to form favorable interactions between PS and TMPC. On the other hand, PC does not have enough free volume with PS, thus making PC-PS an immiscible blend.

Free-Volume Hole Sizes and Distributions in Blends. The results for the lifetime and intensity of o-Ps, τ_3, and I_3 as a function of weight percent of TMPC and PC in PS blends are shown in Figure 4. Free-volume hole radii and fractions are then calculated according to eqs 1 and 2 in a spherical-hole model and are shown in Figure 5.

In Figure 5, we found that the variations of R_f and f_v as a function of weight percent are different between PS−TMPC and lend the following: (1) R_f has a greater negative deviation in PS−TMPC blends than in PS−PC blends; (2) f_v has a negative deviation in PS−TMPC blends, but in PS−PC blends it changes from a negative deviation at low weight percent of PS to a positive deviation at the high percent. Similar but smaller negative deviations in f_v have been reported in a miscible blend of the TMPC−PC system.[8]

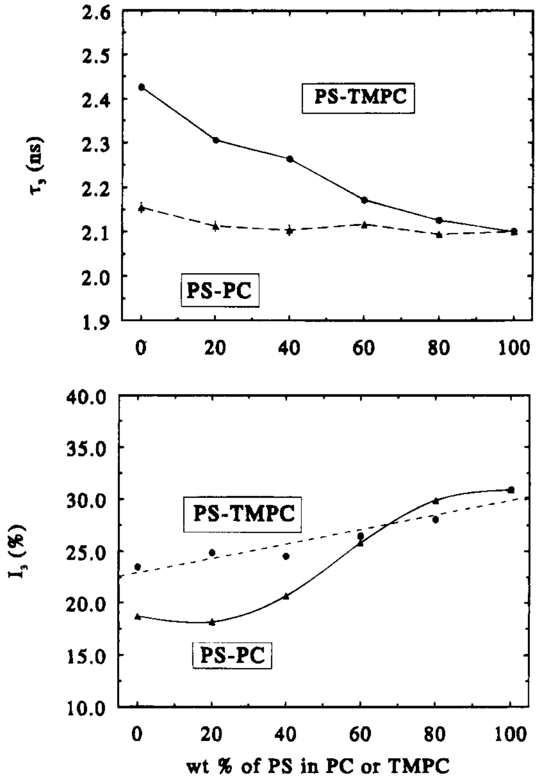

Figure 4. o-Ps lifetimes and intensities of PS−TMPC and PS−PC blends vs wt % of PS.

There exist some free-volume theoretical interpretations concerning blending.[3] It has been suggested that, in miscible blends, the variations of free volume related to blending are due to the interaction between dissimilar chains and the segmental conformation and packing of component polymers for van der Waals type blends.[3] When we consider a simple binary interchain interaction, we express the mean free-volume hole fraction f_v in a blend as:[3]

$$f_v = f_{v1}\Phi_1 + f_{v2}\Phi_2 + \beta f_{v1}f_{v2}\Phi_1\Phi_2 \qquad (5)$$

where f_{v1} and f_{v2} are the free-volume hole fractions in pure polymers 1 and 2 and Φ_1 and Φ_2 are the specific volume fractions (as calculated from density and weight percent data) of component 1 and 2 polymers, respectively. Then β in eq 5 is a parameter that could be related to the interaction between dissimilar chains. The results of β are plotted in Figure 6.

As shown in Figure 6, we observe a contraction of free-volume fraction for the miscible PS−TMPC blend (minimum $\beta = -0.07$) but a complicated variation for the immiscible blend PS−PC; i.e., β varies from −0.21 to +0.04. A similar negative deviation of fractional free volume has also been reported in a miscible TMPC−PC blend with a much smaller β value (minimal at −0.03).[8] In another immiscible polymer blend, PS−PMMA [poly(methyl methacrylate)], we found a complicated variation (+ and −) of f_v similar to the current result in PS−PC. The existing results consistently show

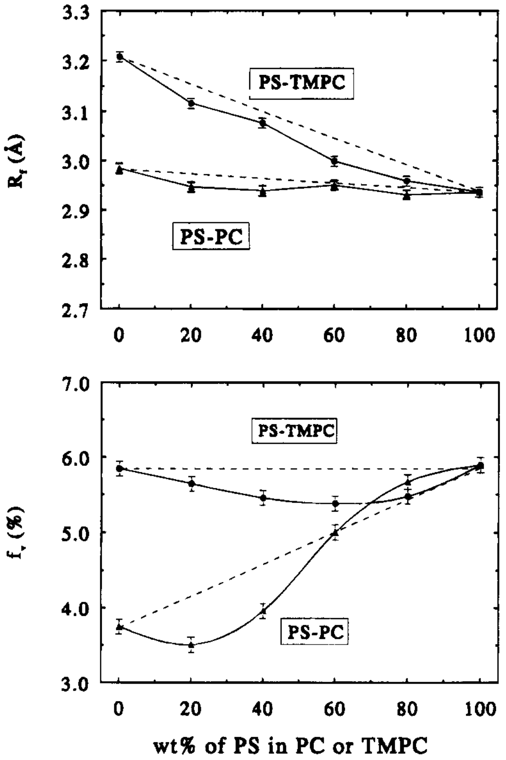

Figure 5. Hole radius and fractions of free volume in PS–TMPC and PS–PC blends vs wt % of PS. Solid lines were drawn through data points for clarity, and dashed lines represent the linear additive relationships.

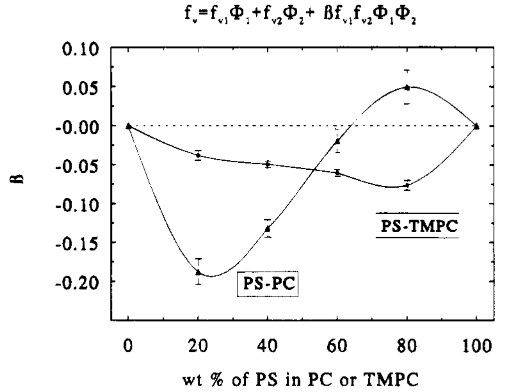

Figure 6. Calculated interaction parameter β (according to eq 5) in PS–TMPC and PS–PC blends vs wt % of PS.

a contraction of free-volume hole size and fraction in miscible blends but a complicated variation in immiscible blends.

The complicated variation of free-volume hole fractions in immiscible blends observed by the PAS technique is a result of the high sensitivity of the o-Ps atom not only to free-volume holes but also to any interfacial spaces, such as those created between boundaries of two phases. The fluctuation of f_v shown in Figure 5 is an indication of the fact that Ps dynamic behavior interferes with the PAL-extractable properties of polymers in separate phases. The free-volume hole properties obtained in these systems can be further interpreted only when we more fully understand Ps behavior in systems involving more than a single phase. This could be pursued by using monoenergetic positrons, which we will be commencing in the near future.

It is interesting to observe that the free-volume fraction is less than the fractional additive of free volumes from two polymer components in miscible blends, as shown in Figures 5 and 6. There are some specific volume data reported in blends:[2,3] many miscible blends show a positive deviation; a few systems show a negative deviation. The results from PAL may not necessarily be the same as those from macroscopic measurements. Since the Ps atom probes the local environment, the free-volume results from PAL should be more appropriate for understanding interactions at the molecular level. In terms of interaction between dissimilar chains, a contraction of free volume may result in a decrease of Gibb's free energy, which is a general criterion for a blend to be miscible. The current results indicate that there might be a correlation between the Flory–Huggins interaction parameter (χ) and the β parameters obtained by PAL. The negative deviation of free volume in miscible blends can be interpreted as a result of favorable interactions of segmental conformation and packing between dissimilar molecules. In PS–TMPC systems, PS segments can easily fall into the large free-volume holes available in TMPC polymers when they are blended. This will result in a reduction of free volume in blends as seen in a larger negative β for all ranges of composition, as shown in Figure 6. For the same reason, PC polymers do not have sufficient free volume for PS to make such a segmental packing to form a miscible blend. A complicated variation of f_v in PS–PC immiscible blends results from the trapping and detrapping of Ps between free-volume holes and interfaces.

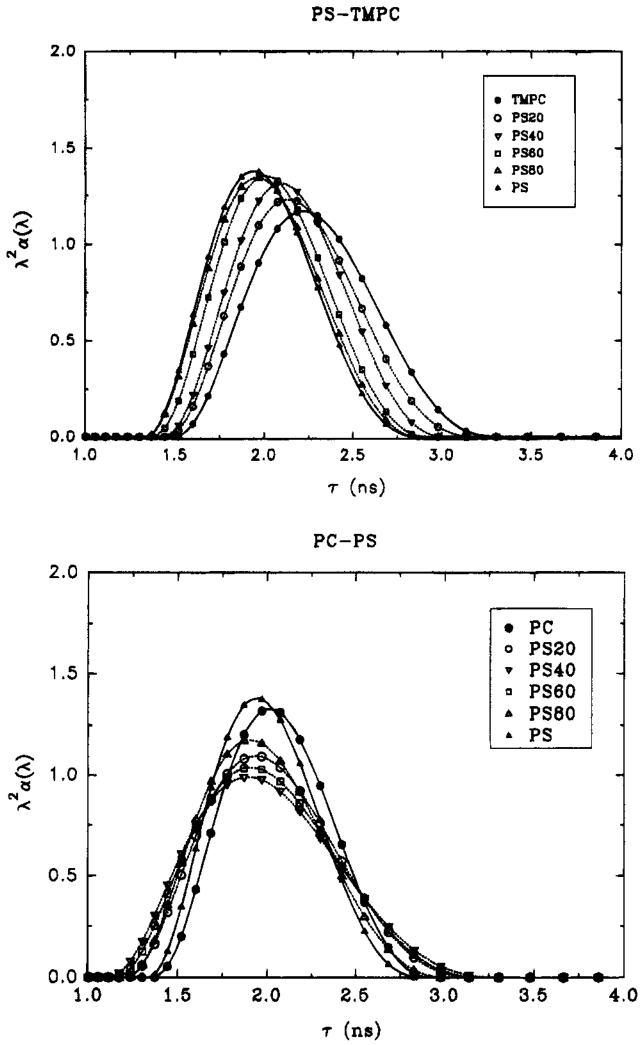

Figure 7. o-Ps lifetime distributions in PS–TMPC and PS–PC blends at different wt % of PS.

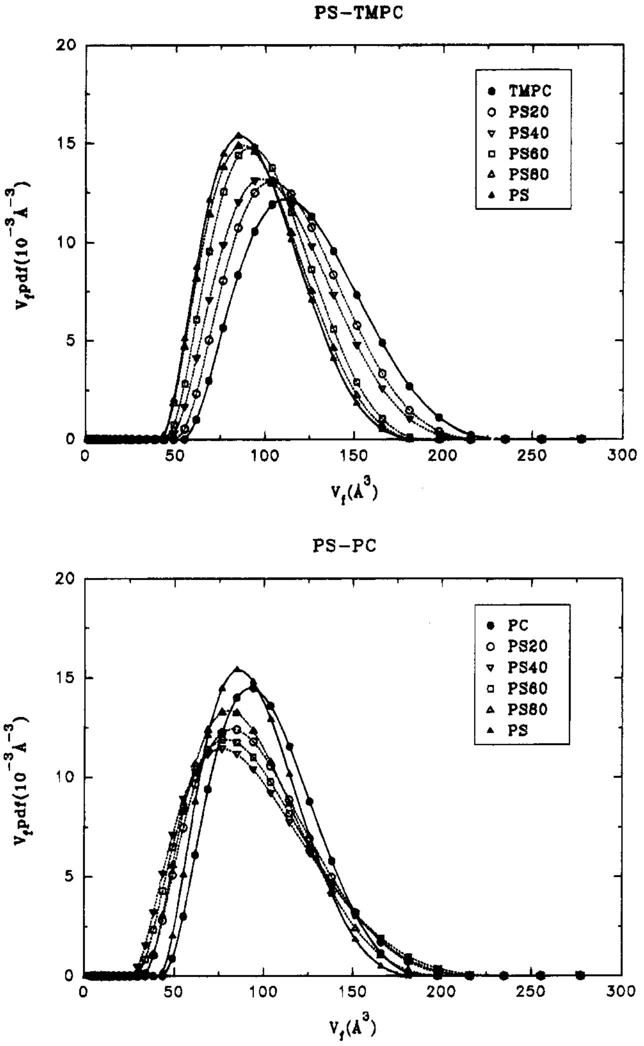

Figure 8. Free-volume hole distributions V_f(pdf)(V_f) of PS–TMPC and PS–PC blends at different wt % of PS. The distributions were calculated according to eq 4 from the data shown in Figure 7. Errors are about the size of the data points. Smooth curves are drawn through the data points for clarity.

The difference in the free volume due to blending between two types can be seen more clearly in the distributions. Figure 7 shows the deconvoluted o-Ps lifetime distributions in both types of blends as a function of composition. Based on the assumption that o-Ps remains in a hole after it is trapped and on the theory developed by us,[22] we convert the o-Ps lifetime distributions into free-volume hole distributions according to eq 4. The results of the free-volume probability density function [V_f(pdf)] are shown in Figure 8. It is worthwhile to mention that the V_f(pdf) results obtained by the current PAL method agree well with the predictions by the existing free-volume theories,[26] despite some questions recently raised about its validity.[27] From the V_f(pdf) results based on our theory, we see the following: (1) a larger difference between the blends and the pure polymers in the distribution of free-volume holes is observed in the immiscible blend (PS–PC) and (2) a monotonical variation of the distribution of free volume is observed in the miscible blend (PS–TMPC). In order to see a more quantitative difference, we have calculated the dispersion of the V_f(pdf) in terms of full-width at half-maximum (fwhm) from the data shown in Figure 8 and plotted the results in Figure 9. As shown in Figure 9, the dispersion of V_f(pdf) for miscible PS–TMPC follows a simple additive relationship, indicated by the dashed line. But for immiscible PS–PC, we observe a significant broadening of V_f(pdf). The maximum broadening occurs at about 50% of the composition with a 20% broadening of the free-volume distribution. In the immiscible blend, the broadening of the free-volume distribution can be attributed to the formation of interfacial regions between incompatible polymers as detected by Ps. Another system of the immiscible blend of PS–PMMA also shows a similar broadening result.

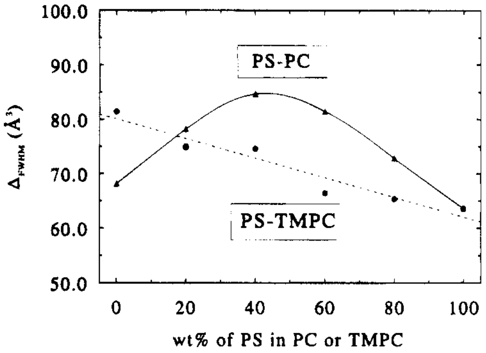

Figure 9. Dispersion of free-volume hole distribution (full-width at half-maximum, fwhm) of PS–TMPC and PS–PC blends vs wt % of PS. The fwhm's were calculated from the data shown in Figure 8. Smooth curves are drawn through the data points for clarity.

Conclusion

We reported a detailed analysis of free-volume hole size, fraction, and distribution in two well-characterized polymer blends: miscible PS–TMPC and immiscible PS–PC. These microscopic volume results as determined by PAL show a negative variation of free-volume holes in miscible blends and fluctuating positive and negative deviations in immiscible blends. We suggest that the contraction of free volume is a result of the segmental conformation and packing of dissimilar polymers which require sufficient free volume to form a miscible blend. The results of no dispersion in the free-volume hole distributions in miscible blends and of large broadening in immiscible blends support this suggestion. PAL is certainly a useful technique to study local segmental motion and packing at the molecular level for miscible blends. For immiscible blends, further studies on Ps dynamics are needed for future applications of PAL to such blends.

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