

Characterization of the Free Volume in High-Impact Polystyrene/Polypropylene and High-Impact Polystyrene/High-Density Polyethylene Blends Probed by Positron Annihilation Spectroscopy

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ABSTRACT: The free-volume properties of high-impact polystyrene (HIPS)/polypropylene (PP) and HIPS/high-density polyethylene (HDPE) blends were investigated by means of positron annihilation lifetime spectroscopy (PALS). The measured results show that the free-volume holes in the semicrystalline polymers, such as PP and HDPE, were not large enough to accommodate the branched chains and the end groups of the macromolecular chains in HIPS to produce favorable interactions between the semicrystalline polymers and the HIPS polymer in these blends; thus immiscible blends were formed. The weak interaction between

two dissimilar polymer molecules only took place in the regions between two amorphous phases. In addition, the observed negative deviations of the longest lifetime intensity and the free-volume fraction were attributed to the influence of the interfacial polarization during PALS measurement. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1507–1514, 2003

Key words: polystyrene; poly(propylene) (PP); polyethylene (PE); blends

INTRODUCTION

In recent years, the positron annihilation technique has been recognized as a useful method for studying the free-volume properties of polymer materials.^{1–3} The lifetime spectra collected from positron experiments are composed of a number of exponentially decaying functions attributed to the annihilation of positrons from different states in the polymer.⁴ Two short components in lifetime spectra are considered to be the combination of para positronium and “free” positron annihilation and are independent of the free volume in polymers. The longest component [the lifetime (τ_3) and the corresponding intensity (I_3)] is usually ascribed to the ortho positronium (*o*-Ps) pickoff annihilation. The *o*-Ps prefers to annihilate in the regions of low atomic density.⁵ τ_3 and I_3 exhibit correlations to the size and numerical concentration of free-

volume holes in the amorphous region of polymers. The average radius (R) of free-volume holes on a quantum mechanical model developed by Tao⁶ and Eldrup⁷ were proposed as follows:

$$1/\tau_3 = 2\{1 - R/(R + 0.1656) + \sin[2\pi R/(R + 0.1656)]/2\pi\} \quad (1)$$

The apparent free-volume fraction (f_{app}) is generally defined by the following equation:^{8,9}

$$f_{\text{app}} = V_f I_3 \quad (2)$$

where V_f is the hole volume and is equal to $\frac{4}{3}(\pi R^3)$ and R is obtained from eq. (1). f_{app} is not generally considered to express the absolute value of the free-volume fraction, but the basic variation in the free-volume fraction can be considered.

In early studies, researchers mainly concentrated on studying the free-volume properties of miscible blends, and little attention was paid to immiscible blends.¹⁰ High-impact polystyrene (HIPS), polypropylene (PP), and high-density polyethylene (HDPE) are important mechanical and electrical materials. The

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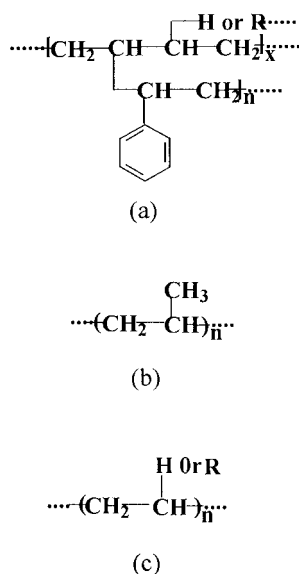


Figure 1 Simple sketches of the chemical structures of (a) HIPS, (b) PP, and (c) HDPE.

elemental backbones of macromolecular chains in these polymers are C—C bonds. Because of the different structures of lateral groups and condensed states, each polymer itself has a clear character. The mixture of different characteristic polymers usually results in an obvious change in the properties of the polymers. However, a study on the behavior of free volume in the two-component blends will help us to understand the interaction between the different macromolecular chains and the relationship between the microstructure and the properties of blends. In this article, we describe the variation of the free-volume properties in HIPS–PP and HIPS–HDPE blends studied by means of positron annihilation spectroscopy. These experimental materials were prepared by the mechanical mixture of different weight percentages of HIPS with PP and HDPE under same temperature and pressure, respectively. The free-volume properties had obvious effects on the miscibility of the two different polymer components. Our purpose was to develop a greater understanding of correlation between the free-volume properties and the miscibility in these blends.

EXPERIMENTAL

The HIPS (styrene/butadiene = 91.5:8.5 w/w, error = ± 0.5), PP, and HDPE for this experiment were purchased from Lanzhou Chemical Industry. Their chemical structure are depicted schematically in Figure 1. The densities and molecular weights were 1.0332 g/cm^3 and 25×10^4 in HIPS, 0.9071 g/cm^3 and 25×10^4 in PP, and 0.9524 g/cm^3 and 20×10^4 in HDPE, respectively. The content of stereoregular polymer in PP was more than 96%. The degree of branching in HDPE was 3.

The samples of two-component blends were made by two courses. First, two kinds of polymers were evenly mixed in a high-speed mixer for 5 min and were then melted, stirred, and pressed into granular blends in a squeezing machine (made in a Japanese modern machine). The operative conditions of the machine were as follows: temperature = $165\text{--}190^\circ\text{C}$ and rotational velocity = 80 rpm. Second, the granular blend was melted and then pressed into a film (5 mm) in a 50t press vulcanizer (First Rubber Machine Factory, Shanghai, China). The operative conditions were as follows: pressure = 10 MPa, temperature = $170 \pm 5^\circ\text{C}$, time = 13 ± 1 min.

Positron annihilation lifetime spectroscopy (PALS) was measured with an EG&ORTEC fast-fast lifetime spectrometer (Tennessee) with a FWHM191Ps for a ^{60}Co prompt peak of 1.18 Mequiv and a 1.33 Mequiv γ ray. A 6×10^5 Bq positron source (^{22}Na) was deposited in a piece of Kapton ($3 \mu\text{m}$), which was sandwiched between two films of the same sample material; these were placed in a sample chamber together. All PALS measurements were performed at room temperature ($20 \pm 0.5^\circ\text{C}$; moistness = 60%). Every spectrum contained about 10^6 counts. The resulting spectra were consistently modeled with a three-component fit with the computer program PATFIT-88.¹¹

A Rigaku D/Max-2400 diffractometer (Tokyo, Japan) was used for the diffraction experiments of the blends. The operative condition were as follows: Cu $K\alpha$ monochromator, voltage = 36 kV, electronic current = 60 mA, scan speed = $10^\circ/\text{min}$ 2θ , slit and diverged slit (DS)/scattered slit (SS) = 1° and received slit (RS) = 0.3 mm. The degree of crystallinity for the blends was calculated with a computer program with the peak separation in the diffractometer.

The densities of the blends were measured at 20°C (temperature error $\pm 0.1^\circ\text{C}$) with a capillary pycnometer (50 mL). The immersion liquid was distilled water. Samples of about 1 g that did not contain visible bubbles or pores were examined. The accuracy of the measurement was estimated to be $\pm 0.2\%$.

The tensile tests were measured by the state standard (standard of People's Republic of China GB1040-92). The experimental conditions were as follows: temperature = 23°C and moistness = 50%.

RESULTS AND DISCUSSION

Figure 2(a,b) depicts the variation in density and specific volume as a function of HIPS content in the HIPS–PP and HIPS–HDPE blends. The curves showed that the density presented a linear increase with increasing HIPS content, and accordingly, the specific volume decreased.

Figure 3 shows the curves of o -Ps τ_3 as a function of HIPS content in the blends. The R values of the free-volume holes in these blends were calculated from τ_3

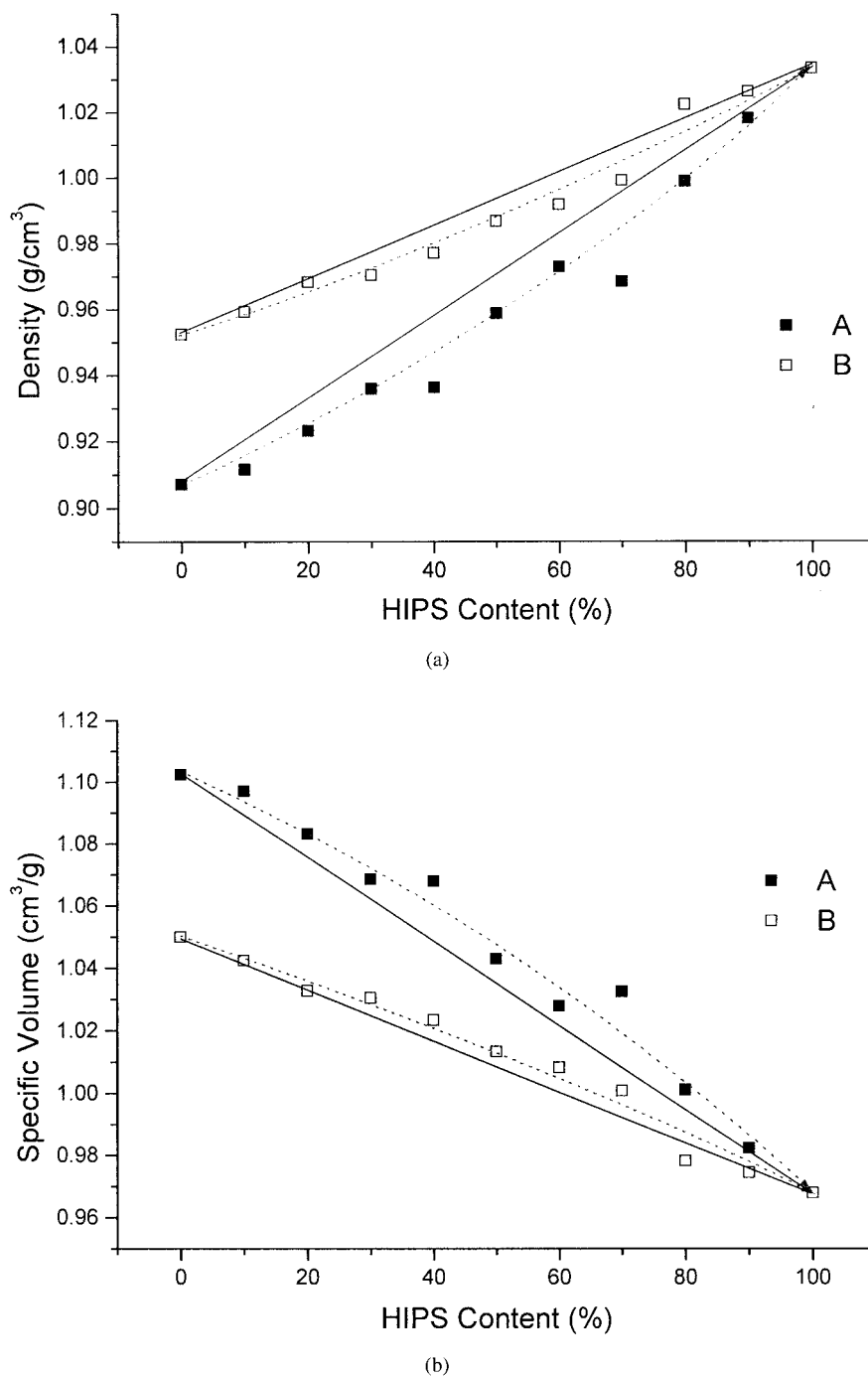


Figure 2 (a) Density and (b) specific volume as a function of HIPS content in the (A) HIPS-PP and (B) HIPS-HDPE blends. The dashed lines are drawn through data points, and the solid lines represent the linear additive relationships.

with eq. (1). The results (Fig. 4) show that the order of R values in the pure polymer was HDPE > PP > HIPS. It is well known that HIPS is an amorphous polymer, and PP and HDPE are semicrystalline polymers. o -Ps annihilation mainly takes place in the amorphous regions of polymers. The order indicated that the average sizes of the free-volume holes of the amorphous regions in the two semicrystalline polymers were larger than that in HIPS. The long branched

chains in HDPE also played an important role for a larger HDPE R compared to the PP R . The small volume of the lateral methyl group in PP was an advantage to the fit into available space and decreased the free-volume hole size. However, as also shown in Figure 4, R decreased with increasing HIPS content, and the variation of R was in proportion to the weight percentage of HIPS in the blends. The experimental phenomena made it clear that only weak interactions ex-

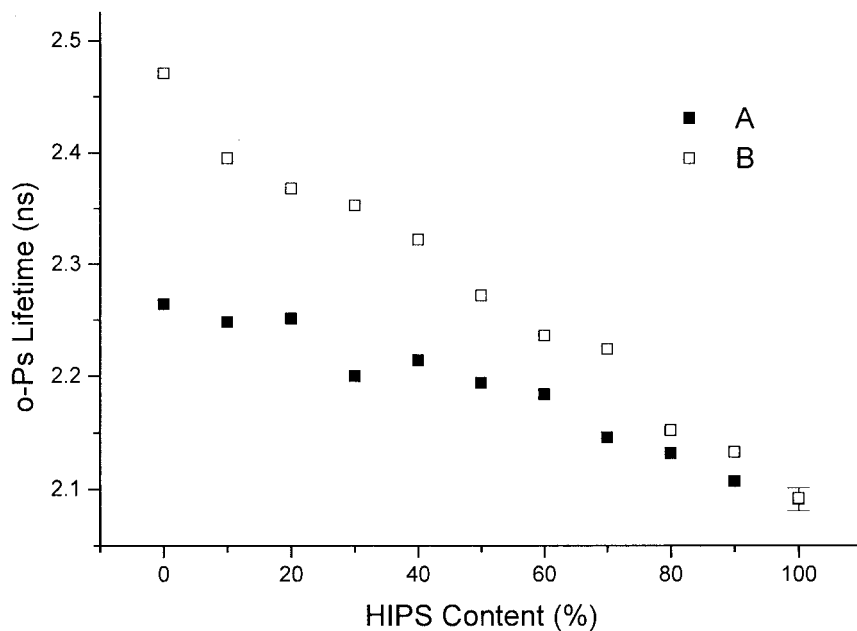


Figure 3 *o*-Ps τ_3 as a function of HIPS content in the (A) HIPS-PP and (B) HIPS-HDPE blends.

isted between the two different polymeric molecules in the blends. To further explore the behavior of HDPE and PP in the blends, we also performed X-ray crystallinity diffraction experiments on the pure polymers and blends. Curves of the degree of crystallinity as a function of HIPS content in the blends are shown in Figure 5. Figure 5 shows that the crystal content in the blends linearly decreased with increasing content of the amorphous polymer HIPS and that the crystallinities in the blends were in a direct ratio to the content

of the semicrystalline polymers. The results indicate that amorphous HIPS addition to PP and HDPE did not influence the crystal formation of pure HDPE and PP in the blends. These experimental phenomena were in close correlation with the free-volume properties in the blends. 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 interactions, that is, Van der Waals types.¹⁰ Branched

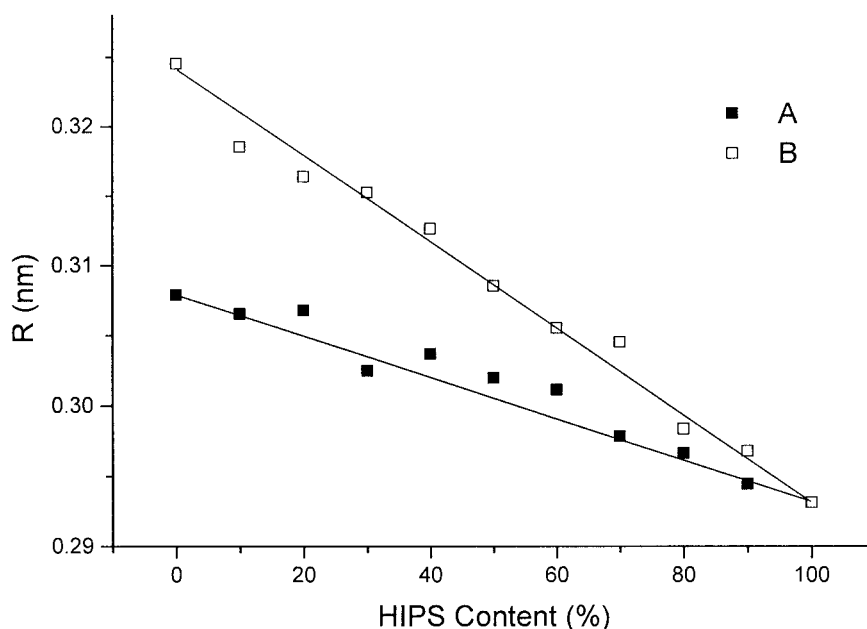


Figure 4 R of the free-volume hole as a function of HIPS content in the (A) HIPS-PP and (B) HIPS-HDPE blends. The solid lines represent the linear additive relationships.

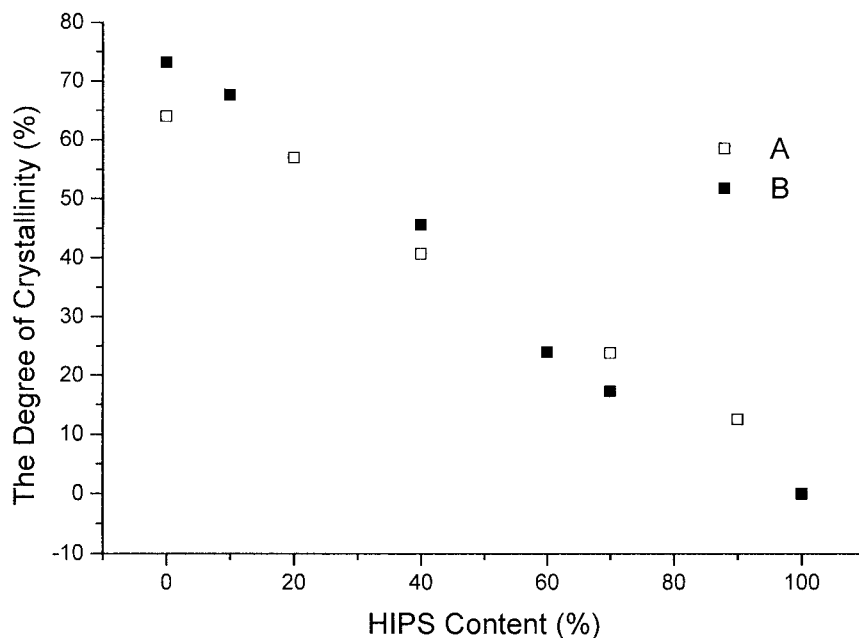


Figure 5 Degree of crystallinity as a function of HIPS content in the (A) HIPS–PP and (B) HIPS–HDPE blends.

chains, such as phenyl in HIPS, cannot effectively fit into the free-volume holes of HDPE and PP in the blends. In other words, the amorphous regions in HDPE and PP did not have enough large free-volume holes to hold the branched chains in HIPS, thus making HIPS–HDPE and HIPS–PP immiscible blends. There were interfaces existing between HIPS and HDPE or PP. The combination of HIPS and HDPE or PP in the blends only depended on the weak interaction, such as Van der Waals types, between the different polymers. Moreover, the interactions mainly took place in the regions between the two amorphous phases where the local packing of component polymers could produce and form a loose condensed structure. This was in agreement with our experiments on the mechanical properties for these polymers (Table I), where the tensile strength sharply decreased from 38.46 (HDPE) to 24.14 [HIPS (10%)–HDPE (90%)] and from 40.10 (PP) to 33.07 [MPa; HIPS (10%)–PP (90%)] with the content of HIPS increasing from 0 to 10% in the blends, respectively. When the materials were pulled, the defects in the regions between the two phases caused the rupture of the blend materials.

I_3 is generally considered an important parameter connecting the free-volume concentration. As shown in Figure 6, the order of I_3 in pure polymers was HIPS

> PP > HDPE, and I_3 increased with increasing HIPS content. Compared to the HDPE and PP polymers, the largest I_3 in HIPS was likely mainly a result of a smaller average free-volume hole size and a higher free-volume hole concentration.

f_{app} was calculated with eq. (2). The variations of f_{app} as a function of HIPS content are plotted in Figure 7. Interestingly, when the content of HIPS in the HIPS–PP blends exceeded 40%, the f_{app} values in the HIPS–PP blends were less than the free volume fraction of HIPS–PP blends ($f_{HIPS-PP}$) from two pure polymer components and that f_{app} in the HIPS–HDPE blends kept basically consistent with the free volume fraction of HIPS–HDPE blends ($f_{HIPS-HDPE}$), except the f_{app} of the HIPS content, which was 30 and 60% in the blends. The negative deviations of the measured f_{app} in some blends seemed to be a result of the favorable interaction of segmental conformation and packing between dissimilar molecules, which caused a contraction of free volume when the two components were blended. However, Figure 2(b) shows that the specific volumes of these blends had approximately positive deviations. The mixture of two different polymers increased the free-volume fraction in the blends. The results in Figure 2(b) are contrary to the negative

TABLE I
Tensile Strength of the Blends (Mpa)

	HIPS content (%)										
	0	10	20	30	40	50	60	70	80	90	100
HIPS–PP	40.10	33.07	27.47	27.08	20.30	22.65	19.72	17.75	20.82	18.91	24.52
HIPS–HDPE	38.46	24.14	21.36	21.42	21.24	14.92	16.67	22.54	24.20	21.21	24.52

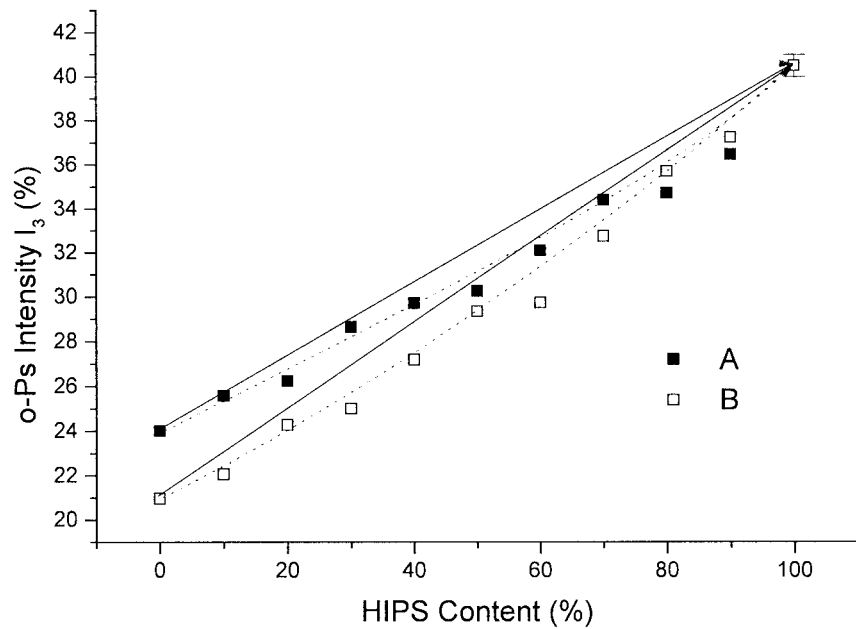


Figure 6 *o*-Ps I_3 as a function of HIPS content in the (A) HIPS-PP and (B) HIPS-HDPE blends. The dashed lines are drawn through data points, and the solid lines represent the linear additive relationships.

deviations of f_{app} described in Figure 7. The negative deviations were probably a result of competition between the two following factors:

1. Because of the immiscibility between the two different polymers, some new free-volume holes formed in the regions between the two phases. In addition, the size of these new holes was proba-

bly larger than the average free-volume size in the two pure polymers.

2. The two behaviors in the blends would be beneficial to positrons to increase the *o*-Ps pickoff annihilation and result in a increase in the measured f_{app} . As discussed previously, with regard to the immiscible blends, each polymer component itself could form a phase in the blend, thus

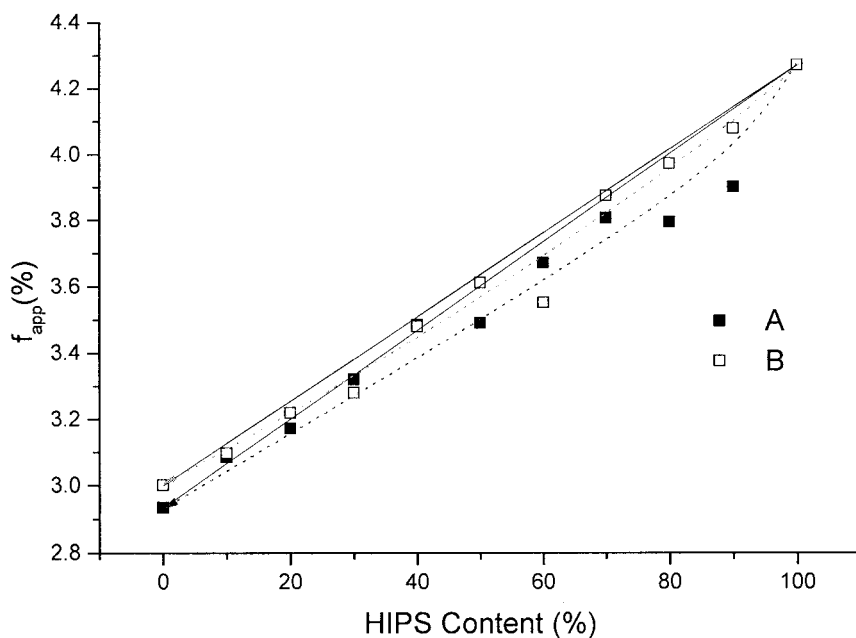


Figure 7 f_{app} as a function of HIPS content in the (A) HIPS-PP and (B) HIPS-HDPE blends. The dashed lines are drawn through data points, and the solid lines represent the linear additive relationships.

producing many interfaces between the two different polymer components. HIPS, HDPE, and PP were all nonpolar polymers, but the molecular polarity in the HIPS polymer was different than in HDPE and PP. The dielectric constants were 3.15 in HIPS, 2.82 in HDPE, and 2.4 in PP.¹² It is well known that dielectric constant is closely related to medium polarization and molecular polarity¹³ and that the interfacial polarization in polymers can generally lead to an increase in the dielectric constant.¹⁴ In our experimental system, the weak interactions in the regions between the two phases under the influence of the electric field that was built during PALS measurement^{15–18} caused a change in the electronic cloud distribution and led to the formation of an impermanent dipole moment in the molecules. The local dipole played the same role as polar groups and had a higher probability to trap the positrons that would otherwise combine with a spur electron to form a positronium or to combine with free electrons appearing in the positron spur by its electron affinity.¹⁶ The results brought about a decrease in the probability of positronium formation and in I_3 value. This was in agreement with the results in Figure 6, where I_3 had a negative deviation compared to the fractional additive of I_3 from the two polymer components in blends. In addition, in our other experiments,¹² we found that the dielectric constant of HIPS–PP blends sharply increased from 2.4 to 2.93 with the addition of 10% HIPS in the PP polymers. The increase in the dielectric constant indicated the formation of interfacial polarization in the regions between the two amorphous phases. The inference about the influence of the interfacial polarization on measured I_3 was also supported by an earlier experiment of Mogensen¹⁹ and our other experiments,¹² where it was found that variations of the measured I_3 had a good relationship with the dielectric constants of polymers.

Consequently, we suggest that the interfacial polarization in the blends resulted in a decrease in the measured I_3 and was responsible for the negative deviation of f_{app} . The influence of interfacial polarization on f_{app} was contrary to factor 1. Therefore, we considered the influence of factor 2 on f_{app} to be larger than that of factor 1, where f_{app} produced a negative deviation. This was probably the main reason why the measured f_{app} of some blends showed negative deviations. Moreover, the negative deviations of f_{app} in HIPS (30%)–HDPE (70%) and HIPS (60%)–HDPE (30%) blends were probably related to the immiscibility between the two polymer components. When the two components were mixed at a ratio of 30 and 60% HIPS in the blends, there were more phase interfaces

in the two blends than in the other HIPS–HDPE blends. The interfacial polarization in the two blends played an important role for the negative deviations of f_{app} . Detailed work still needs to be done.

In addition, some free-volume theoretical interpretation concerning blending has been proposed in earlier articles.^{20,21} For example, Liu et al.¹⁰ considered a sample binary interchain interaction and expressed f_{app} in a blend as following:

$$f_{\text{app}} = f_{\text{app}(1)}\Phi_{(1)} + f_{\text{app}(2)}\Phi_{(2)} + \beta f_{\text{app}(1)}\Phi_{(1)}f_{\text{app}(2)}\Phi_{(2)} \quad (3)$$

where $f_{\text{app}(1)}$ and $f_{\text{app}(2)}$ are the free-volume hole fractions in the pure polymers 1 and 2; $\Phi_{(1)}$ and $\Phi_{(2)}$ are the specific volume fractions (as calculated from density and weight percentage data) of the component 1 and 2 polymers, respectively; and β is a parameter that can be relative to the interaction between dissimilar molecules. The β results for two kinds of blends are plotted in Figure 8.

As shown in Figure 8, the β values showed a negative deviation in the HIPS–PP blends and a negative deviation at low contents of HIPS to a positive deviation at high contents in HIPS–HDPE blends. In the early experiments of Liu et al.,¹⁰ where they thought the negative deviation of β was the miscible blends, such as polystyrene (PS)–tetramethyl bisphenol A polycarbonate blends, and that a complicated variation of β (+ and –) similar to these results in HIPS–HDPE blends was the immiscible blends, such as PS–poly(methyl methacrylate)¹⁰ and PS–bisphenol A polycarbonate blends.¹⁰ As discussed previously, in the Experimental Section, the interfacial polarization played an important role in the variations of measured f_{app} and I_3 in our system. Therefore, the β could not represent the real variation of the interaction between dissimilar molecules. In other words, the results further reveal the positrons due to the high sensitivity not only annihilated in the free-volume holes and any interfacial spaces¹⁰ but also were trapped by polar groups and local dipoles. The different variations of β in immiscible HIPS–PP and HIPS–HDPE blends also further showed that the measured o -Ps I_3 was not always appropriate to evaluate the f_{app} and β with eqs. (2) and (3).

CONCLUSIONS

In this article, we reported the results of PALS measurement on HIPS–HDPE and HIPS–PP blends. The results show that the amorphous regions in the semicrystalline polymers HDPE and PP had larger average sizes of free-volume holes than the amorphous polymer HIPS, and the sizes of free-volume holes in HDPE and PP were not large enough to accommodate the lateral chains in HIPS, thereby producing immiscibility between the two polymer components. In addition,

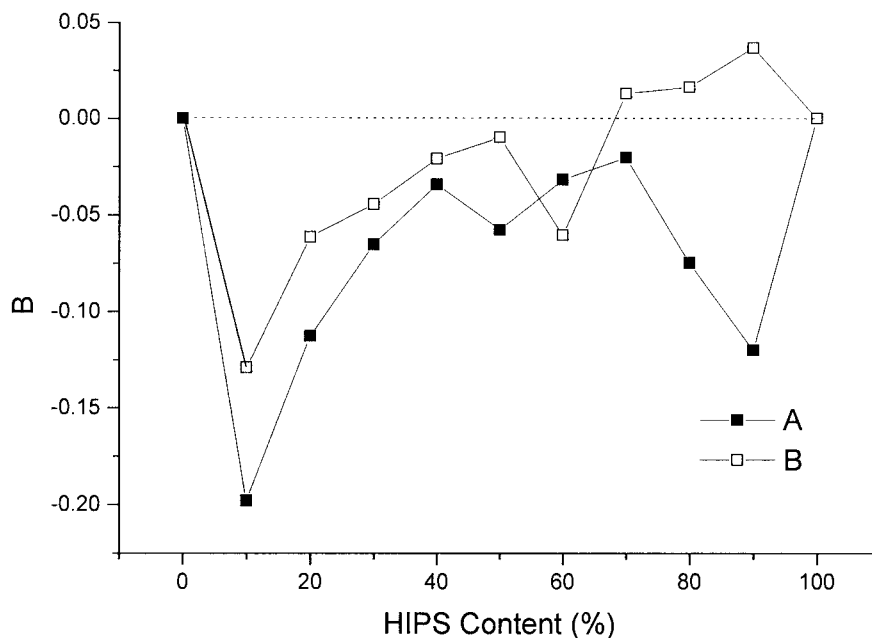


Figure 8 β as a function of HIPS content in the (A) HIPS-PP and (B) HIPS-HDPE blends. β was calculated with eq. (3).

the interfacial polarization caused a decrease in o -Ps I_3 . The negative deviation of f_{app} in the experimental blends was mainly attributed to the negative deviation of I_3 . In other words, the variation of free volume in the blends was not responsible for the negative deviation of f_{app} . The interfacial polarization between two amorphous phases during PALS measurement played an important role in the negative deviation of measured f_{app} .

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