On the Analysis of Positron Annihilation Lifetime Spectroscopy Data in Semicrystalline Miscible Polymer Blend Systems

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SYNOPSIS

A free volume probing technique, positron annihilation lifetime spectroscopy (PALS) is used to characterize miscible blends of amorphous polycarbonate with a semicrystalline copolyester at room temperature. The paper describes the analysis required to use the PALS technique to probe the amorphous regions in which the miscibility of the blends occurs. Analysis of the raw PALS data in this system involves taking account of the influence of crystallinity on the PALS results. The results demonstrate that the PALS technique is able to discriminate between free volume in the amorphous regions of as-molded and annealed samples. This difference in free volume between samples of differing thermal history is assigned to the influence of polymer crystals on the stress state of the miscible amorphous regions. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Positron annihilation lifetime spectroscopy (PALS) has been used for many years to study vacancy-type defects in crystalline metals, ceramics, and semi-conductors. The analog of the vacancy-type defect in metals is "free volume" in polymers. Free volume has many definitions in the polymer literature. The sites probed by PALS are both static and dynamic free volume. The density fluctuations in polymers, which can be measured by X-ray scattering[1] and modeled by molecular dynamics,[2] can be considered dynamic free volume. Static free volume, as defined for this work, is similar to the holes defined by Glasstone, Laidler, and Eyring,[3] which are those necessary for the flow of solids. This flow is realized at T_g or during yield by the cooperative motion of large scale units of the main chain. At temperatures less than T_g, these holes are "frozen-in" as interstitial free volume.

If the frequency of the density fluctuation is slower than the positron or orthoPositronium (oPs)

annihilation frequency ($\sim 10^{10}$ s^{-1}) then the positron effectively "sees" the free volume, both dynamic and static, and can detect molecular relaxations. PALS has been used previously as a free volume probe to detect T_g and sub-T_g relaxations,[4-6] both of which occur at frequencies less than 10^9 Hz under normal experimental conditions.[7] The proportion of static to dynamic free volume is dependent on the temperature of measurement. Interstitial static free volume which allows chain slippage such as that during yield (flow of polymer chains under stress)[3] also has been detected by the PALS probe.[8-10] The use of PALS as a sensitive "free volume" probe in polymers has been reviewed by a number of authors.[11-14]

The PALS technique involves emission of positrons (antiparticles of electrons) from a decaying radioactive source such as ^{22}Na and penetration of these positrons into the polymer. Various states of the positron exist in polymers but the state of interest in this work is orthoPositronium (oPs). The semistable oPs atom consists of a positron bound to an electron of parallel spin. oPs has a long lifetime with its decay dependent on annihilation with another electron ("pickoff") from the surrounding environment. The oPs tends to localize in free volume sites due to reduced electron density in these

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holes. The annihilation rate (inverse lifetime) is a function of the probability of overlap of the oPs wavefunction and the wavefunction of an electron at the cavity wall of the free volume site.[15] The larger the free volume site, the smaller the probability of overlap and the oPs lifetime increases. Thus, according to the model proposed by Brandt et al.,[15] the oPs lifetime reflects free volume site size. In this model the free volume sites are distributed throughout the solid with increased concentration at chain ends and lower concentration in crystalline regions.[15]

The positron decay spectra are made up of a series of lifetimes attributable to a number of positron annihilation mechanisms. The longest lived component lifetime, τ_3, is due to oPs pickoff annihilation. The oPs lifetime, τ_3, for polymers is usually in the range 1 to 3 ns, which reflects free volume radii of approximately 2 to 6 Å. The intensity parameter, I_3, associated with this oPs pickoff, is a percentage of the positrons annihilating by the pickoff mechanism and, thus, is related to the concentration of the free volume sites.

It has been postulated that oPs pickoff occurs only in amorphous regions;[13,16] therefore, if semicrystalline polymers are investigated, it is necessary to validate this assumption and to carefully analyze the data to ensure correct qualitative and quantitative interpretation. The importance of noting the intrinsic factors such as morphology, which may affect oPs annihilations, was recognized by Stevens[14] over a decade ago when he stated, "it is . . . important that the percentage of crystallinity for crystalline polymers be known. . . . If, in the future, this information and information on sample preparation do not accompany (PALS) results reported in the literature then the contribution that those results make to the advancement of knowledge in this field will be minimal."

A burgeoning academic and industrial area of polymer research is the area of polymer blends. In blend research, questions of miscibility, density, interfacial adhesion, interfacial tension, and the like have become important. Many of these properties, and miscibility in particular, are likely to be related to free volume, and PALS should prove a valuable method for nondestructively probing these systems.[17-20] For example, greater than weighted mean values of density and viscosity of blends compared to the constituent homopolymers are explained in terms of free volume and specific interactions.[21] Polymer/polymer solubility has also been modelled using a free volume approach[22] with recent molecular dynamic simulations of miscible polymer sys-

tems predicting a "squeezing out" of free volume as miscibility occurs.[23]

In a miscible system in which one of the components is semicrystalline, the problem of interpretation of free volume behavior from PALS data becomes complex due to the multiphase nature of the blends. The miscibility refers to molecular associations on a nanometer scale between one amorphous polymer component and the amorphous phase of the semicrystalline component. The crystalline region consists of crystallites composed purely of the semicrystalline component. However, the amount of crystallinity, the dimensions of the crystallites, and their melting point are all dependent on thermodynamic and kinetic aspects of the crystallization process that depend on the overall blend concentration and thermal history.[24] Indeed, melting point depression is an important experimental procedure for determining χ, the Flory-Huggins interaction parameter.[24]

One potentially important use of PALS is in the determination of the relationship between free volume and miscibility in the amorphous region. As such, an attempt to take account of the effects of crystallinity on PALS measurement of free volume can be made through careful data analysis. Because most miscible blends tend to contain at least one component that is semicrystalline, such considerations are important in PALS research and have not yet been addressed in the literature.

In this work a method is developed to account for the oPs annihilations associated with crystalline regions and the annihilations in the amorphous miscible regions. Subtraction of the oPs annihilations associated with the crystalline regions from the total oPs annihilations should allow the remaining effects to be assigned to interactions in the miscible amorphous phase. This is not to say that the presence of crystals does not still influence the state of the amorphous phase. Indeed, by removing the contribution from annihilations associated with the crystallites, more meaningful interpretation of the effect of crystallinity on the amorphous regions is made possible.

Following the development of the analysis method, its application to a miscible, semicrystalline polyester blend of polycarbonate and ThermX is demonstrated. This copolyester system is known to be miscible at all concentrations,[25] and the ThermX crystalline phase (and, hence, the total blend) can be annealed to different levels of crystallinity.

The molecular understanding of miscibility gained from correlation of PALS and other free vol-

ume-related properties will not be discussed in any detail in this paper. These topics will be discussed in conjunction with more experimental evidence in a forthcoming paper.[26] The present work is intended to highlight issues involved with analysis of PALS blend data and to demonstrate the effect of such analysis on the raw PALS data.

METHOD OF DATA ANALYSIS

It is assumed that the blend consists of two polymers (A and B) which represent a miscible blend system. If A is an amorphous polymer and B is semicrystalline, then miscibility implies mixing on a molecular scale between the chains of A and those of the amorphous B phase. The crystalline phase is crystals of pure homopolymer B. The crystalline fraction of B will be dependent on two factors: (a) the total relative concentration of the A and B phases and (b) the thermal history of the blend; this latter point requires further clarification. If a blend sample of a given total composition is quenched, it will have a particular blend crystallinity. Annealing of the sample below the blend melting point of B may result in a greater degree of crystallinity. Correspondingly, the concentration of B in the miscible amorphous region will be inversely proportional to the degree of crystallinity.

In order to examine the free volume of the miscible amorphous phase by PALS experiments it is necessary to present the data as functions of the fraction of A or B in the amorphous region, rather than total relative concentrations in the blend. Conceivably then, two blends with differing total compositions but which have been judiciously annealed could have the same fractional content of B in the amorphous region. This compositional factor is in addition to having to take into account the annihilations associated with the crystalline region.

Define the overall weight fraction of component A as **a** and of component B as **b**. Using this terminology, **a** and **b** are called the "total" concentrations of A and B. This definition differentiates them from, for example, the concentration of the amorphous component of A or B or the amount of B that is crystalline.

The fractional degree of crystallinity of the total blend is X_{blend} (consisting of crystals of B). Thus, for example, $X_{blend} = 1$ implies that the total blend is crystalline and, hence, must consist only of component B ($b = 1$, $a = 0$). Such a degree of crystallinity can be determined for a given blend compo-

sition from differential scanning calorimetry (DSC) using the following equation:

$$X_{blend} = \frac{\Delta H_{blend}}{\Delta H_B^\infty} \qquad (1)$$

where ΔH_{blend} is the energy to melt the crystals present in a blend in Joules per gram of polymer blend and ΔH_B^∞ is the heat of fusion of 100% crystalline B, also in J/g.

The concentration of amorphous phase A in the total blend is **a** (because it is noncrystalline), and the amorphous weight fraction of phase B in the total blend is **c** where

$$c = b - X_{blend} \qquad (2)$$

While **a**, **b**, and **c** are weight or mass fractions of A, B, and amorphous B, respectively, of the total blend, it is possible to determine the concentration of phases A and B *in the miscible amorphous region*. Using eq. (2), define M_a as the mass fraction of A in the miscible amorphous region:

$$M_a = \frac{aM}{aM + cM} = \frac{a}{a + c}$$
$$= \frac{a}{a + b - X_{blend}} = \frac{a}{1 - X_{blend}} \qquad (3)$$

where M is the total mass of material under consideration. In a similar manner, define M_b as the mass fraction of B in the miscible amorphous region:

$$M_b = \frac{cM}{aM + cM} = \frac{b - X_{blend}}{1 - X_{blend}} \qquad (4)$$

As expected, $M_a =$ **a** and $M_b =$ **b** only when $X_{blend} = 0$, and the blend is totally amorphous, as, for example, when rapidly quenched from the molten state. Equations similar to eq. (3) and eq. (4) have been derived previously.[27]

In order to determine the relative concentration, I_3^{am}, of free volume cavities in the miscible amorphous region, the effect of the crystalline zones must be taken into account. Previous work in a semicrystalline polymer PEEK (poly aryl ether ether ketone), with PALS has shown that I_3 in homopolymers is a function of percent crystallinity.[16] In that work[16] and other work,[28] the dependence of I_3 on crystallinity was linear, and I_3 was found to extrapolate graphically to zero at 100% crystallinity. The decrease of I_3 with increasing crystallinity is

expected because less of the material is amorphous and, thus, contains fewer free volume sites for oPs pickoff. Indeed, linearity of I_3 with degree of crystallinity and extrapolation to zero have been used as evidence to assert that oPs pickoff sites exist only in amorphous regions.[13,16] However, other work in other systems is less conclusive,[29-34] with some work showing a decrease in I_3 with percent crystallinity, although not to zero at 100% crystallinity.[29,30] Due to a lack of clear PALS experiments on a range of semicrystalline polymers, each annealed to differing levels of crystallinity, it is unclear if I_3 of a polymer crystal equals zero. It may be that free volume cavities available for oPs localization and pickoff are associated with crystallites (such as defects within the crystal or disorder at the crystal/amorphous interfaces).

Describing the most general case, it can be assumed that there is a contribution to I_3 from the amorphous and crystalline regions and thus:

$$I_3^{\text{exp}} = (1 - X_{\text{blend}})I_3^{\text{am}} + X_{\text{blend}}I_3^{\text{cryst}} \qquad (5)$$

where I_3^{exp} is the experimentally determined I_3, I_3^{am} represents the I_3 of amorphous miscible regions (polymers A and B) and I_3^{cryst} is the I_3 of fully crystalline polymer B. I_3^{cryst} can be obtained by extrapolation to 100% crystallinity of an I_3^{exp} vs. percent crystallinity plot of homopolymer B. An extrapolation would normally be necessary because no polymer ever shows experimentally 100% crystallinity when solidified from the melt or annealed, and, thus, I_3^{cryst} could never be directly determined.

Rearranging eq. (5) leads to:

$$I_3^{\text{am}} = \frac{I_3^{\text{exp}} - X_{\text{blend}}I_3^{\text{cryst}}}{1 - X_{\text{blend}}} \quad \text{if} \quad I_3^{\text{cryst}} \geq 0 \qquad (6)$$

Okamoto et al.[35] recently have corrected their I_3 data for crystallinity in a range of semicrystalline polymers using the assumption that oPs annihilates in amorphous regions only (i.e., $I_3^{\text{cryst}} = 0$). Using this assumption, their equation is similar to eq. (6), with I_3^{cryst} equal to zero.

A similar consideration regarding the contribution from amorphous and crystalline regions arises with calculation of τ_3 of the miscible amorphous phase. If there were no free volume cavities for oPs pickoff in the crystallites, then τ_3^{am} (the τ_3 of the amorphous phase) would be equal to the experimental τ_3^{exp}, regardless of crystallinity. It should be noted, however, that even if there were no free volume cavities associated with crystals, I_3^{am} still would

not equal I_3^{exp} because I_3 is concentration of free volume in the total volume of material probed (both crystalline and amorphous regions). The difference in treatment of τ_3 and I_3 data with respect to the amount of crystallinity arises from the concept that τ_3 reflects the mean size of free volume sites probed and is not a strict function of the total number of these sites in the volume probed. For I_3, however, regardless of the amounts of amorphous or crystalline material in the volume probed, the positron is assumed to probe the same volume. Thus, I_3 is a function of (proportional to) the number of sites in the volume probed and, if there were no free volume cavities associated with crystals, would be expected to decrease with an increasing amount of crystallinity in the volume probed.

Thus, the equations for τ_3^{am} need to be split into two cases. In the case of a semicrystalline system in which τ_3^{cryst} is not zero:

$$\tau_3^{\text{exp}} = (1 - X_{\text{blend}})\tau_3^{\text{am}}$$
$$+ X_{\text{blend}}\tau_3^{\text{cryst}} \text{ for } \tau_3^{\text{cryst}} > 0 \qquad (7)$$

which can be rearranged to give:

$$\tau_3^{\text{am}} = \frac{\tau_3^{\text{exp}} - X_{\text{blend}}\tau_3^{\text{cryst}}}{1 - X_{\text{blend}}} \text{ for } \tau_3^{\text{cryst}} > 0 \qquad (8)$$

and in the case of a semicrystalline system with τ_3^{cryst} equal to zero:

$$\tau_3^{\text{am}} = \tau_3^{\text{exp}} \text{ for } \tau_3^{\text{cryst}} = 0 \qquad (9)$$

For a fully amorphous blend system, the same equation as (9) clearly applies. τ_3^{cryst} is obtained in a similar manner as I_3^{cryst} (i.e., by linearly extrapolating τ_3^{exp} vs. percent crystallinity to 100% crystallinity). In calculating τ_3^{cryst} and I_3^{cryst}, a nonlinear dependence of either parameter with degree of crystallinity can be allowed for by substituting empirical, nonlinear terms in eqs. (5) and (7).

As with I_3 vs. percent crystallinity, little has been reported in the literature on the dependence of τ_3 and crystallinity, and that which has been reported is contrasting.[16,28-34] Serna et al.[31] found that the longest lived (oPs) component lifetime increased with decreasing crystallinity in polyethylene. Nakanishi et al.[16] found that τ_3 remained constant as a function of crystallinity in PEEK as did Lind et al.[33] in polypropylene. The constant τ_3 result in PEEK, in addition to the result that I_3^{cryst} extrapolated to zero at 100% crystallinity (mentioned earlier), was interpreted to mean that there were no τ_3-sized oPs

free volume cavities in the crystalline region of the system.[16] While this is more than likely, there is a possibility that similar τ_3-sized holes exist in both the amorphous and crystalline phases and, thus, annealing to increase crystallinity would not influence the value of τ_3.

It is claimed that the longest lived (oPs) component is affected by degree of crystallinity, either due to a crystalline contribution to free volume or due to physical constraints imposed by crystals; this claim will be discussed further during the presentation of results. The experimental and results sections of this paper demonstrate the application of the above equations to aid in the analysis of the effects of crystallinity on free volume in the amorphous regions of a semicrystalline blend.

EXPERIMENTAL

Materials

Blends of polycarbonate (Lexan 141, GE Plastics) and a random copolyester (ThermX, Eastman Kodak) have been reported to be miscible at all concentrations (single, intermediate T_g),[25] and these were the materials used in this study. The polycarbonate is a bisphenol-A, medium molecular weight polycarbonate material with a T_g of 148°C and is usually noncrystalline. ThermX is a copolyester made by random polymerization of terephthalic acid and cyclohexanedimethanol with a small amount of isophthalic acid. It is semicrystalline with a T_g of 89°C and a melting point of 287°C. Samples were studied in the as-molded state and after annealing in air at 155°C for 3 h (annealed state).

Experimental Techniques

Blends of the two materials were prepared with relative concentrations of 0, 20, 40, 60, 80, and 100%

by weight ThermX in a temperature range of 280–300°C. Samples were blended in a single screw extruder that was part of an injection molder that was used to produce coupons. These coupons (7.5 cm × 5 cm × 2 mm) were quenched by injection into a chilled mold.[36]

Given that both materials are polyesters, there is a possibility of chemical transesterification,[37,38] and, thus, all blends were mixed with 0.3% of a proprietary GE Plastics transesterificiation inhibitor. Both Fourier transform infrared spectrometry and solubility tests[36] indicated that negligible transesterification had occurred.

The samples were analyzed using differential scanning calorimetry (Perkin Elmer DSC7 at 10°C min^{-1}) and dynamic mechanical analysis (Perkin Elmer DMA7 at a frequency of 1 Hz and scan rate of 2°C min^{-1} in a modified three-point-bend mode) in order to determine their glass transition and crystalline properties.

The PALS measurements were made using an automated, thermally stabilized (22 ± 0.5°C), EG&G Ortec fast-fast coincidence system with a ^{22}Na resolution of 250 ps. A 2 mm diameter spot source of 35 μCi was sandwiched between two 0.0001 inch thick titanium foils. Ten spectra of 30,000 peak counts were collected for each set of samples (two identical samples sandwich the source foils). The error bars are population standard deviations of these results. The spectra did not change as a function of sample contact time with the source. All data were collected at 22°C on 2 mm thick injection molded coupons and analyzed using the PFPOSFIT program.[39] The size of the holes corresponding to τ_3 are of the order of 30 to 900 Å^3, and the energy range of the positron "injected" in the solid (approx. 50 keV to 600 keV) corresponds to a penetration depth of a few hundred microns. The size of the free volume sites existing within the volume probed are averaged by the PFPOSFIT program, yielding τ_3 re-

Table I   DSC Thermal Properties of ThermX/Polycarbonate Blends for As-Moulded and Annealed (3 Hours at 155°C)

Total Weight % ThermX	T_m (°C) (ThermX Crystals)	% Crystallinity (±1%) As-moulded Blend	% Crystallinity (±1%) Annealed Blend
0	—	0	0
20	274	3.1	2.7
40	278	1.3	15.8
60	283	4.7	22.8
80	283	7.3	26.9
100	287	10.0	31.0

lated to a mean free volume site size. The number of annihilations taking place in free volume sites, I_3, is related to the number of free volume sites in the volume probed.

RESULTS AND DISCUSSION

Single glass transitions, intermediate to those of the two homopolymers, were determined by a combination of DSC and DMA techniques, indicating that the blends could be classed as miscible. DSC also yielded information on the melting and crystalline nature of the blends, and the results are presented in Table I. Note that it is the percent crystallinity *of the blends* in the as-molded and annealed states that is presented. Percent crystallinity of the blends increased on annealing in all samples except the 20% ThermX sample. Annealing the as-molded samples allows the observation of crystallinity effects on PALS parameters (τ_3, I_3) in samples that are of the

Figure 2 Experimental oPs pickoff lifetime, τ_3^{exp}, vs. total percent ThermX concentration. The filled circles represent as-molded samples and the open circles represent annealed samples.

Figure 1 Experimental oPs pickoff intensity, I_3^{exp}, versus total percent ThermX in the polycarbonate/ThermX blend. The filled circles represent as-molded samples and the open circles represent annealed specimens (3 h at 155°C).
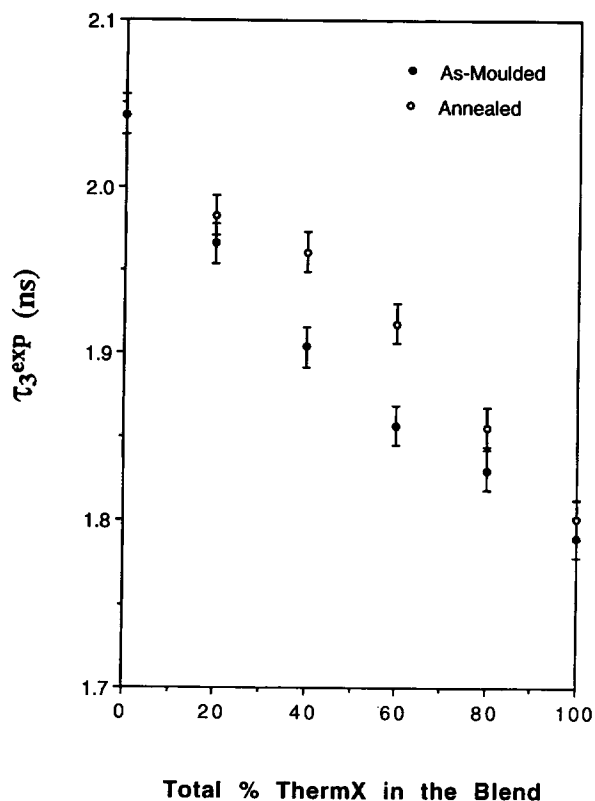
same overall blend composition but different crystalline (and amorphous) fractions. The annealing temperature is above the T_g of both components (and, hence, physical aging[40] of the materials will not occur), and is below the required temperatures for transesterification,[41] which occurs mainly in the molten state.

PALS measurements were performed on the materials at room temperature and analyzed using PFPOSFIT to obtain τ_3^{exp} and I_3^{exp}. In order to demonstrate the application of the PALS analysis described earlier to the polycarbonate/ThermX blend system, the raw uncorrected data for I_3^{exp} (Fig. 1) and τ_3^{exp} (Fig. 2) for total concentrations of ThermX (i.e., as a function of variable b, using the nomenclature from the analysis section of this paper) are presented. Two sets of points are shown in both Figures 1 and 2.

A number of observations can be made from Figures 1 and 2. In both the as-molded and annealed samples, the values of I_3^{exp} and τ_3^{exp} vary approximately monotonically as a function of total percent

ThermX blend composition. I_3^{exp} decreases with increased crystallinity on annealing in all blend samples and also in the ThermX homopolymer. Conversely, the τ_3^{exp} values increase for all annealed blend samples as compared to as-molded values and remain constant for the ThermX homopolymers. The ThermX homopolymer sample crystallinity increases from 10% to 31% with τ_3^{exp} remaining constant. The I_3^{exp} and τ_3^{exp} values for polycarbonate remain constant on annealing, and no crystallinity is induced in the polycarbonate. The variation of the PALS parameters as functions of composition at room temperature is nontrivial because it could be expected that most glassy polymers show similar values of free volume fraction well below T_g. This value of fractional free volume is usually quoted as 0.025.[42] These results indicate that PALS is very likely to be a useful technique in the study of blend systems, even at temperatures greater than 100°C below T_g.

It should be clear from the previous discussion that the degree of crystallinity of the blend must be determined in order to allow unambiguous presentation of the PALS data. Samples with the same total blend composition show quite different values of τ_3^{exp} and I_3^{exp}, dependent on the degree of crystallinity. It is the intention of the analysis described in this work to assist in the explanation of these variations.

The first aspect of the analysis section concerns the presentation of the data in terms of the composition of the amorphous region using eqs. (3) and (4). The miscible amorphous region is the region of interest in this work. Experimental variables that relate to properties of the amorphous region (such as glass transition, density of the amorphous region, and, to a large degree, the PALS parameters τ_3 and I_3) should be presented in terms of the concentration of components in the *amorphous region* as compared to the *total* blend composition. For example, a blend of total ThermX composition of 60% has a composition of 58% ThermX in the amorphous phase [due to the 4.6% crystallinity of the blend (see Table I)]. When the same sample is annealed to 22.8% blend crystallinity, the composition of ThermX is 48.2% in the amorphous phase (although the total composition of ThermX in the blend remains constant at 60%).

The effect of the composition correction can be seen in the data presented in Figure 3 (I_3^{exp}) and Figure 4 (τ_3^{exp}), plotted as functions of percent ThermX in the amorphous region ($M_b \times 100$). The variables for annealed samples (in which crystallinity increased) are shifted noticeably to the left of
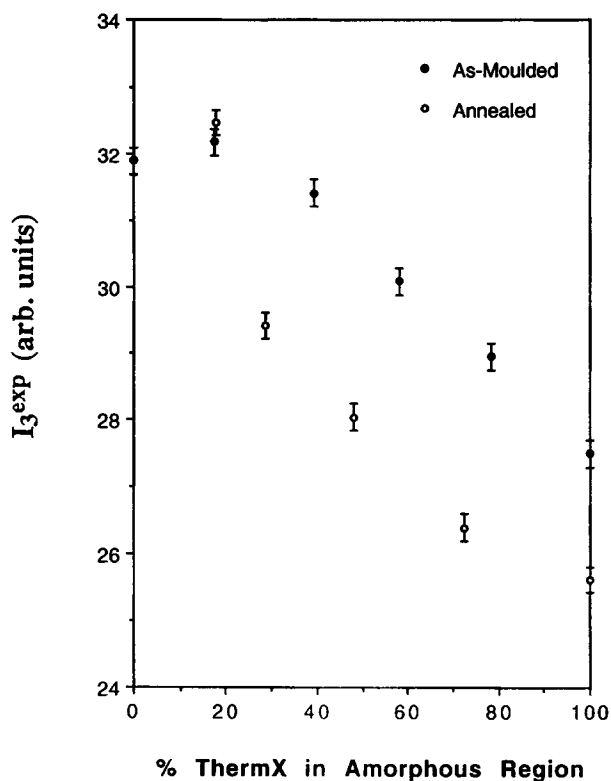

Figure 3 I_3^{exp} vs. percent ThermX in the amorphous phase. The filled circles represent as-molded samples, and the open circles represent annealed samples.

the values for the as-molded samples of identical total blend concentration due to the lower levels of ThermX in the amorphous regions of the annealed samples.

It should be noted that on annealing samples to increase crystallinity, ThermX chains from the amorphous region are removed and incorporated in the crystallites. Thus, ThermX-depleted zones will exist near crystal/amorphous interfaces and a comparatively richer ThermX amorphous phase will exist in between the dispersed crystals. Given the large even spread of crystals in the macroscopic volume probed by the positron technique (ca. 1 mm³) these ThermX-rich and ThermX-depleted amorphous regions are averaged.

The other aspect of analysis involves a correction causing a vertical shift in the data. This correction relates to the plotting of τ_3^{am} and I_3^{am}, because these are the variables of interest in the amorphous miscible region. The analysis involves use of eqs. (6), (8), or (9) (as appropriate) and the evaluation of I_3^{cryst} and τ_3^{cryst} (the value of the PALS parameters attributed to the crystalline phase). The approximation is made that these values in the blend are

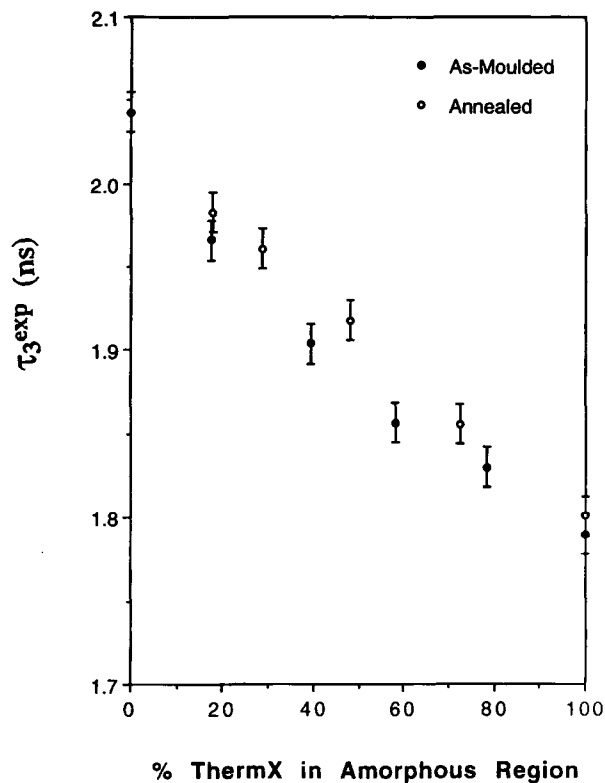**Figure 4** τ_3^{exp} vs. percent ThermX in the amorphous phase. The filled circles represent as-molded samples, and the open circles represent annealed samples.

the same as I_3^{exp} and τ_3^{exp} of 100% crystalline ThermX homopolymer obtained by graphical extrapolation, as the crystals in the blend are solely ThermX. It is recognized that many polymers are often less than 50% crystalline, which leads to the need for quite a substantial extrapolation; however, if the dependence of I_3^{exp} on crystallinity can be measured in the homopolymer over the same range of crystallinity as is present in the blends, then the use of the extrapolation is justified.

Consider first the determination of I_3^{am} using eq. (6). Previous workers have demonstrated a linear dependency between the PALS I_3^{exp} parameter and percent crystallinity.[16,28,30] Nakanishi et al.[16] measured I_3 in samples of PEEK with crystallinities ranging from 1% to 28% and from extrapolation from that range to 100% crystallinity deduced that $I_3^{cryst} = 0$ (i.e., that all free volume sites measured by oPs pickoff were associated only with the amorphous regions in the PEEK homopolymer). If that is the case, eq. (6) becomes substantially simplified.

Figure 5 shows the relationship between I_3^{exp} and percent crystallinity of the ThermX homopolymer. In this study, the maximum amount of crystallinity

induced in ThermX by annealing was 33%. Barnum et al.[41] found that in order to induce crystallinities much higher than 30% in ThermX, samples must be held at temperatures in excess of 250°C (well above the 155°C annealing temperature used in the present study). High annealing temperatures were avoided in this work due to a desire to prevent transesterification.

ThermX homopolymer crystallinity is in the range of 10 to 33%, as shown in Figure 5. A line of best fit is extrapolated from this range to 100% crystallinity ($I_3^{cryst} = 19.7$ for 100% crystalline ThermX), and 19.7 is the value of I_3^{cryst} used in eq. (6). It must be stressed that there are two assumptions made in the use of this extrapolated I_3^{cryst}: (a) that the dependency continues to be linear beyond 33%; (b) that I_3^{cryst} of a totally crystalline material (if it were experimentally possible) is the same as I_3^{cryst} of the crystalline phase in semicrystalline material. The uncertainty associated with the second assumption (b) is minimized by the extrapolation of I_3^{exp} data for a semicrystalline material [assumption (a)]. Extrapolating from 33% to 100% crystallinity means that free volume associated with the crystals (defects within the crystal and free volume
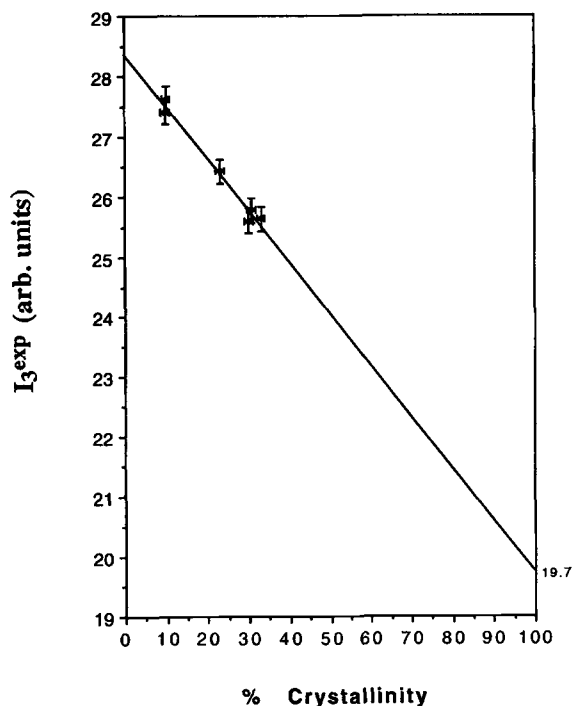

Figure 5 I_3^{exp} vs. percent crystallinity of the ThermX homopolymer (increased crystallinity induced by annealing). A line of best fit shown (correlation coefficient = 0.984) and extrapolated to 100% crystallinity.

associated with the crystal/amorphous interface) is included in the extrapolated I_3^{cryst} at 100% crystallinity. If it were possible to produce a 100% crystalline material by extended annealing or solution precipitation and, thus, produce samples without the interfacial free volume associated with crystalline/amophous phase boundaries, I_3^{cryst} for this 100% crystalline material would be rather less experimentally representative than the value of I_3^{cryst} obtained from extrapolation of a series of semicrystalline materials of varying crystallinity. In addition, the analysis is used in the present work to correct blend data with crystallinities in the range from 1% to 31% based on homopolymer data with crystallinities ranging from 10% to 33%. As mentioned previously, the assumption of linear dependency of I_3^{exp} on crystallinity beyond 33% is inconsequential as long as the values of I_3^{exp} are accurately modeled over the range of interest.

The values of I_3^{am} vs. percent ThermX in the amorphous phase can be seen in Figure 6 and compared with values of I_3^{exp} in Figure 3. The error bars

Figure 7 τ_3^{exp} vs. percent crystallinity of the ThermX homopolymer. A line of best fit is drawn through the data points.

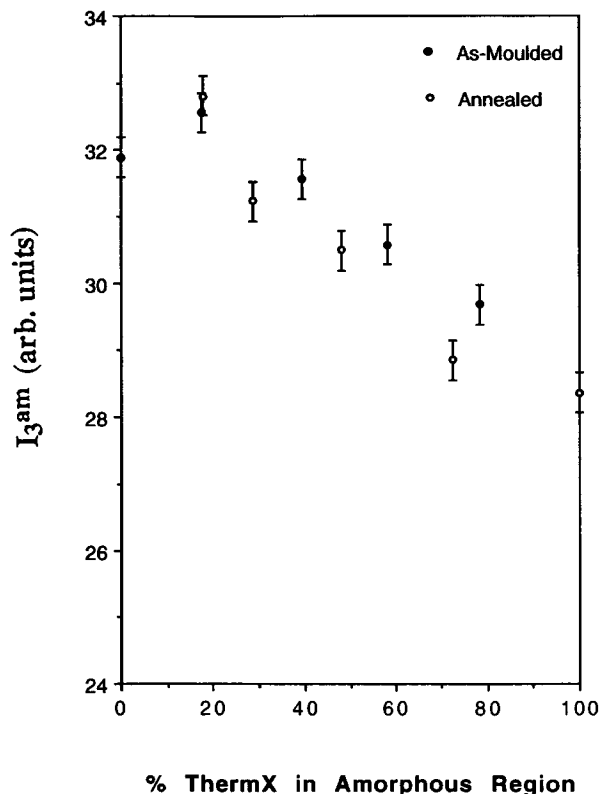**% ThermX in Amorphous Region**

Figure 6 oPs intensity in the amorphous regions, I_3^{am} vs. percent ThermX in the amorphous phase. The filled circles represent as-molded samples, and the open circles represent annealed samples.
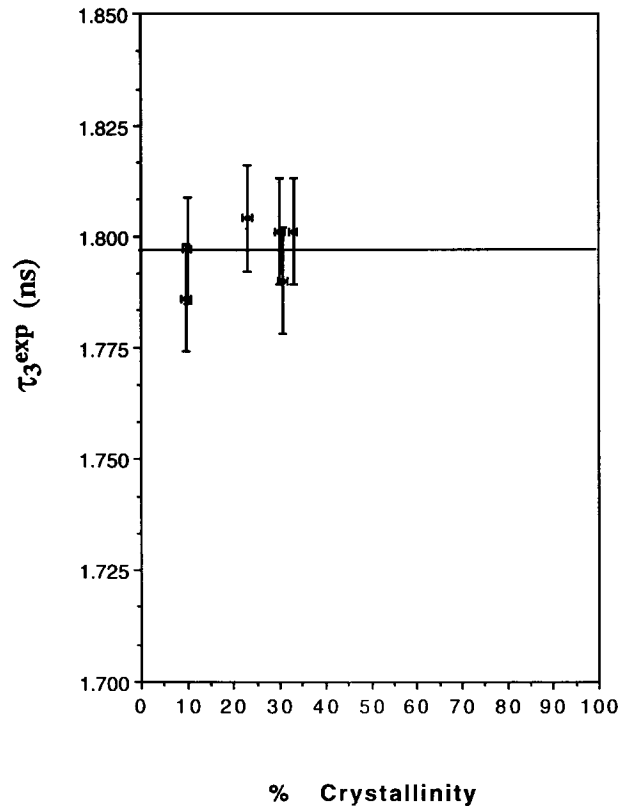
in Figure 3 are population standard deviations, whereas those in Figure 6 also include the error associated with the measurement of crystallinity. The result of the analysis as applied to the I_3^{exp} data is most noticeable in the annealed samples where I_3^{am} is greater than I_3^{exp}. The as-molded and annealed sample I_3^{am} values lie in distinct curves, with the relative concentration of free volume sites being less in the case of the annealed samples.

Determination of τ_3^{am} [eq. (8) or eq. (9)] also requires knowledge of τ_3^{cryst}. A previous study by Nakanishi et al.[16] assumed that because I_3^{exp} extrapolates to zero for 100% crystallinity that there is no free volume associated with the crystalline phase and, hence, τ_3^{cryst} is not a meaningful number. Although not explicitly determined by Filip'ev et al.[28] their data also indicate that I_3 approximately extrapolates to zero at 100% crystallinity in polyethylene. In the present work, however, I_3^{exp} extrapolated to 100% crystallinity is nonzero ($I_3^{cryst} = 19.7$), implying oPs pickoff annihilations (and a meaningful value of τ_3^{cryst}) are associated with the crystallites. Likewise, other workers[29,30] have also implied that
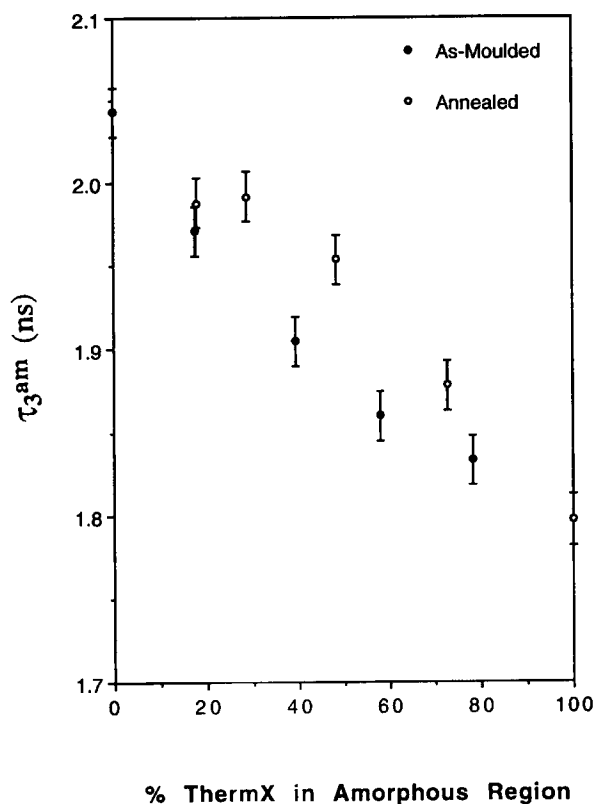
Figure 8 oPs pickoff lifetime in the amorphous regions, τ_3^{am}, vs. percent ThermX in the amorphous phase. The filled circles represent as-molded samples, and the open circles represent annealed samples.

I_3^{cryst} was nonzero in semicrystalline polymer systems.

Figure 7 shows values of τ_3^{exp} as a function of crystallinity for ThermX homopolymer. It can be seen that although there is free volume in the crystalline zones, it does not affect the τ_3^{exp}, which is an average of the free volume size in the amorphous and crystalline zones. Figure 7 indicates that the size of free volume cavities associated with crystals is of a similar magnitude to that of the amorphous region and is invariant to the degree of crystallinity. Thus, a value of τ_3^{cryst} of approximately 1.8 can be assigned and τ_3^{am} determined and plotted as a function of ThermX concentration in the amorphous phase using eq. (8) (see Fig. 8). Comparison of the data in Figure 8 and Figure 4 shows that the τ_3^{am} values for the annealed material are shifted to significantly higher values by the analysis. Figure 8 shows that the τ_3^{am} values of the annealed material are greater for a given amorphous composition than those of the as-molded samples.

As with the determination of I_3^{cryst}, there are assumptions associated with the determination and

use of τ_3^{cryst}. The free volume associated with a crystal relates to the amorphous zone of the crystal interface (folded ends and dangling amorphous chains), as well as possible defects within the crystal, and using the parameter τ_3^{cryst} determined from the ThermX homopolymer may not be totally relevant in a blend with polycarbonate, because the interface of the ThermX crystals will be a molecular mix of polycarbonate/ThermX chains. However, this approximation is probably not too bad in this system, which is a blend of two polyesters. Indeed, in any miscible blend system, the fact that the two materials are miscible means that blend intermolecular interactions and conformations at the crystalline interface between the two materials may be similar to the interfacial effects which occur within the semicrystalline homopolymer.

Use of the analysis method corrects for two effects of crystallinity on PALS (τ_3, I_3) data. The effects which the data correction removes are (a) the relative number of free volume sites associated with the amorphous miscible region is a function of the amount of crystallinity in the volume probed by the positrons, and (b) the free volume associated with defects in the crystals and at the crystalline amorphous/interface contributes to the PALS parameters. Thus, use of the analysis method means that the changes in τ_3^{am} and I_3^{am} values on annealing are not attributable to either (a) or (b). The analysis method allows the effect of the crystalline phase *on* the miscible amorphous regions to be observed. It appears that increasing the crystallinity of the blends increases the mean free volume cavity size and decreases the relative free volume concentration in the amorphous miscible region. This change in free volume distribution could be due to constraint imposed *by* the crystallites. This aspect is discussed further in another publication.[26]

Investigations using free volume techniques such as that presented in this work potentially broaden the depth of understanding of the mechanisms of polymer chain misciblity on the molecular level. In addition to the need for strong interactions, some similarity of molecular shape and conformity between the chains (their ability to pack closely), is likely to be an important component determining miscibility and, indeed, this dependence has been demonstrated by computer-aided molecular modelling approaches[43] to miscible blends.

An interpretation of the data is presented in an accompanying publication.[26] Briefly summarizing this interpretation, it is postulated that chain packing and chain mobility are influenced by the nature of local stresses induced by crystallinity. The free

volume distribution is affected by annealing due to the increased constraint of the crystalline phase on the amorphous region of the miscible polycarbonate/ ThermX system. The fact that these differences in free volume are observable well below the glass transition region indicates that room temperature mechanical properties such as modulus and fracture toughness may be influenced by altering free volume and, consequently, molecular mobility. The classical WLF concept that free volume for a glassy system is frozen at 2.5% well below T_g is shown to be overly simplistic in this system. It should be noted that the analysis developed in this paper for semicrystalline blends can be applied to semicrystalline homopolymers.[44]

CONCLUSIONS

This paper has demonstrated the use of positron annihilation lifetime spectroscopy (PALS) for probing the free volume of the miscible glassy state in semicrystalline blends. A method of analysis has been suggested to determine the PALS parameters (τ_3^{am}, I_3^{am}) related to the free volume in the miscible amorphous region of the blend. This analysis involves presentation of the PALS data in terms of amorphous composition and attempts to remove the contribution from annihilations associated with the crystalline region. After having attempted to remove these crystallinity effects, it was found that the free volume (τ_3^{am}, I_3^{am}) of the miscible region in the glassy phase was dependent on composition and was sensitive to the degree of crystallinity, presumably due to physical constraint of the crystallites on the miscible amorphous phase.

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