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Positronium formation in PE/EVA polymer blends at low temperatures

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Abstract

Positronium (Ps) formation in a polymer blend system consisting of polar and non-polar components has been investigated. We measured positron lifetime spectra for a series of polymer blends between polyethylene (PE) and ethylene-vinyl acetate (EVA) as functions of temperature ($T = 100$–300 K) and composition (EVA weight content $\Phi = 0$–100%) as well as measurement time ($t = 0$–100 h) at $T =$ 100 and 250 K. The glass transition temperatures for blends, around 227 K as determined by the *ortho*-positronium (*o*-Ps) lifetime τ_3 versus temperature, were invariant, within the experimental error, as a function of EVA concentration. Large variations of the *o*-Ps formation probability I_3 versus temperature and time, observed for pure LDPE and blends with relatively low concentrations of EVA, were interpreted on the basis of the spur reaction model of Ps formation, with reference to the effects of localized electrons and trapping centers produced by positron irradiation. In the blends with higher EVA concentrations, the effects of positron irradiation were appreciably weakened, as the result of positron trapping on the polar acetate group of EVA. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Positronium formation; PE/EVA polymer blends

1. Introduction

Recently there is a growing interest in probing free volume properties in polymers using positron annihilation lifetime spectroscopy (PALS) on the basis that there exists a correlation between the lifetime of *ortho*-positronium (*o*-Ps) and the free volume cavity size [1–5]. In order to quantify the PALS data, efforts are being made to derive a quantitative relation between the *o*-Ps lifetime and cavity radius in terms of a simple square-well potential approximation [6]. There are, however, still some fundamental problems relevant to the formation and annihilation of *o*-Ps in polymers. In this work we investigate the problem of Ps formation using polymer blends of polyethylene (PE) and ethylene-vinyl acetate copolymer (EVA) as a model polymer system consisting of non-polar and polar components.

The understanding of Ps formation in polymers is still incomplete and full of controversy. For example, *o*-Ps intensity (or the *o*-Ps formation probability) had once been assumed to be proportional to the free-volume hole concentration [7]. However, more and more experimental observations have been accumulated, showing that *o*-Ps intensity is influenced by many factors including temperature [2], positron irradiation [2,8], chemical composition [9], additives [10] and electric field [11,12]. So one cannot claim that there exists a one-to-one correlation between the *o*-Ps intensity and the free volume concentration. According to the spur reaction model, Ps is formed by a two step reaction between a positron and one of the electrons liberated from the molecules by the positron itself [13]. An acceptable explanation for the already known *o*-Ps intensity data for polymers is that Ps formation takes place before it is localized in a free volume hole. The spur reaction model has been applied to explain many Ps yield data in liquids and other molecular substances [13,14].

This work is a continuation of our previous studies on Ps formation in polyethylene/ethylene-vinyl acetate (PE/EVA) blends [11,15]. To further explore the Ps formation mechanism in these immiscible polymer blends, we performed PALS measurements versus temperature, time and EVA concentration. It is reported that at low temperatures Ps formation is appreciably increased with increasing positron irradiation time. This effect is sensitively affected by the presence of small amounts of EVA and the importance of efficient positron trapping onto the polar acetate group in blends is emphasized.

2. Experiment and data analysis

The detailed procedure of sample preparation has been

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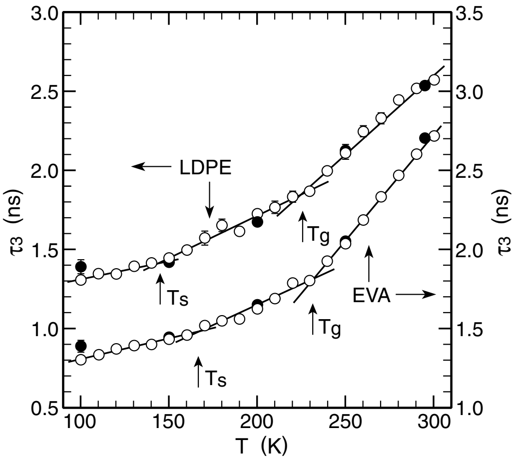

Fig. 1. Variation in *o*-Ps lifetime, τ_3, as a function of temperature for PE and EVA. The full and open circles denote the results for quenched and slowly heated samples, respectively.

described in Ref. [11]. Pure low density polyethylene (LDPE) and EVA as well as three kinds of their polymer blends (EVA weight content $\Phi = 3$, 12 and 60%) were chosen for the PALS study as functions of temperature and time. The vinyl acetate content in pure EVA (random copolymer) was about 14%. Crystallinities and densities of these samples were reported in Ref. [11]. Samples had a thickness of 2 mm.

Positron lifetime measurements were conducted using a conventional fast–fast coincident positron lifetime spectrometer with a time resolution of 310 ps (FWHM). A ^{22}Na source with an activity of about 0.74 MBq (or 20 μCi), deposited on an area of about 10 mm^2 between two 0.8 mg/cm^2 Kapton foils, was sandwiched between two identical pieces of the sample. Each lifetime spectrum contained a total number of counts of 1.2–1.6 million.

The source–sample assembly was mounted on a cryostat and was cooled down to 200 K within about 10 min. Then, the temperature was changed as follows: 200 K $\longrightarrow$ 100 K $\longrightarrow$ 300 K, with intervals of 100 and 10 K for cooling and heating, respectively. After the sample being kept at a given temperature for about 10 min, a lifetime spectrum was accumulated for 4 h.

Another scan was performed by cooling a sample directly from room temperature to $T = 250$ or 100 K. Lifetime spectra were repeatedly recorded as a function of measurement time ($t = 0$–100 h) at one of the above temperatures. To obtain $I_3(T)$ plots under the condition of minimum positron irradiation [2], we also measured the spectra of fresh samples at room temperature (295 ± 2 K), and at 250, 200, 150 and 100 K following a quench from room temperature to one of the target temperatures. Possible effects of light illumination were avoided by performing all measurements in the dark [16].

The resolution function of the spectrometer, assumed to be a sum of three Gaussians, was determined several times from analysis of the lifetime spectra of Kapton using the RESOLUTION program [17], which contain only one lifetime component (about 382–385 ps). Lifetime spectra of LDPE, EVA and blends were decomposed into three or four components using the PATFIT software [17] after a source correction of 7%. Four-component analysis gave somewhat smaller χ^2 values than three-component analysis, but the uncertainties of some resulting parameters were quite large. So we report only the results of three-component analysis in this paper, so that the *o*-Ps yield is given as I_3, the intensity of the longest-lived third component. For the spectra measured at 100 and 250 K, the third lifetimes (τ_3) scattered around 1.36 and 2.09 ns, respectively, without any obvious change as a function of time. To reduce the errors of I_3, all these spectra were analyzed into three components, under the constraint of $\tau_3 = 1.36$ or 2.09 ns.

3. Results

Variations of the *o*-Ps lifetime τ_3 in pure EVA and pure LDPE as a function of temperature are shown in Fig. 1. Qualitatively, the increase of τ_3 with temperature is attributed to the thermal expansion of the free volume, where Ps is localized. For the sake of simplicity, we approximate each $\tau_3(T)$ curve with three straight lines. Thus, relaxation temperatures can be obtained from the inflection points of the two neighboring lines. Using the straight line equation, i.e. $\tau_3(T) = aT + b$, the secondary transition temperature T_s (associated with the crankshaft motion of local segments

Table 1

Secondary transition temperature T_s, glass transition temperature T_g, parameters a and b in the fitting equation $\tau_3(T) = aT + b$ for LDPE, EVA and their blends ($\Phi = 3$, 12 and 60%). The values of a and b are given in units of ns K^{-1} and ns, respectively. The average errors of a and b are 3×10^{-4} ns K^{-1} and 0.08 ns, respectively

	T_s (K)	T_g (K)	$100\ \text{K} \le T \le T_s$		$T_s \le T \le T_g$		$T_g \le T \le 300$ K	
			10^3a	b	10^3a	b	10^3a	b
LDPE	145 ± 47	225 ± 46	2.73	1.03	5.33	0.65	10.26	−0.46
$\Phi = 3\%$	166 ± 34	225 ± 60	1.73	1.17	6.70	0.35	9.90	−0.38
$\Phi = 12\%$	180 ± 34	239 ± 41	2.10	1.14	6.91	0.29	11.16	−0.73
$\Phi = 60\%$	164 ± 30	216 ± 22	1.90	1.14	5.13	0.62	11.22	−0.70
EVA	167 ± 36	232 ± 19	2.48	1.06	5.20	0.61	13.48	−1.32

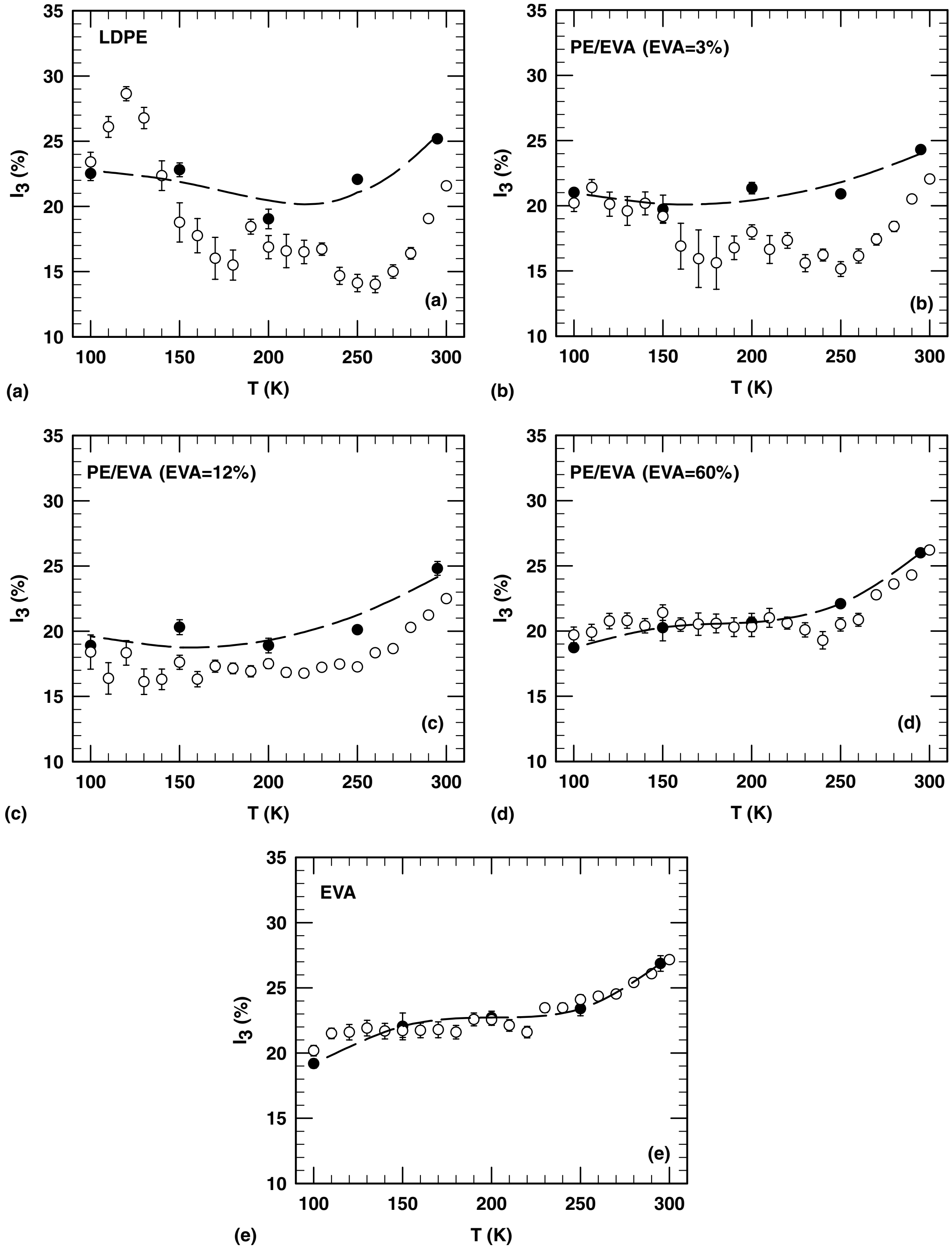

Fig. 2. Variation in *o*-Ps yield, I_3, as a function of temperature for five polymers: (a) LDPE; (b)–(d) blends with $\Phi = 3$, 12 and 60%; and (e) EVA. The full and open circles denote the results for quenched and slowly heated samples, respectively. The dashed lines show tendencies of I_3 for the quenched samples.

[18]) and the glass transition temperature T_g (corresponding to the onset of correlating main-chain segmental motions [19]) were determined by means of the least-squares method. The transition temperatures as well as the values of *a* and *b*, thus deduced, are listed in Table 1. The transition temperatures are in rough agreement with the results by differential scanning calorimetry [20]. However, large errors of 19–60 K for T_s and T_g suggest that PALS may not be so effective in determination of relaxation temperatures, especially for those semicrystalline polymers, in which the transitions occur in wider ranges of temperatures [21]. In Table 1 similar values of *a* and *b* among different

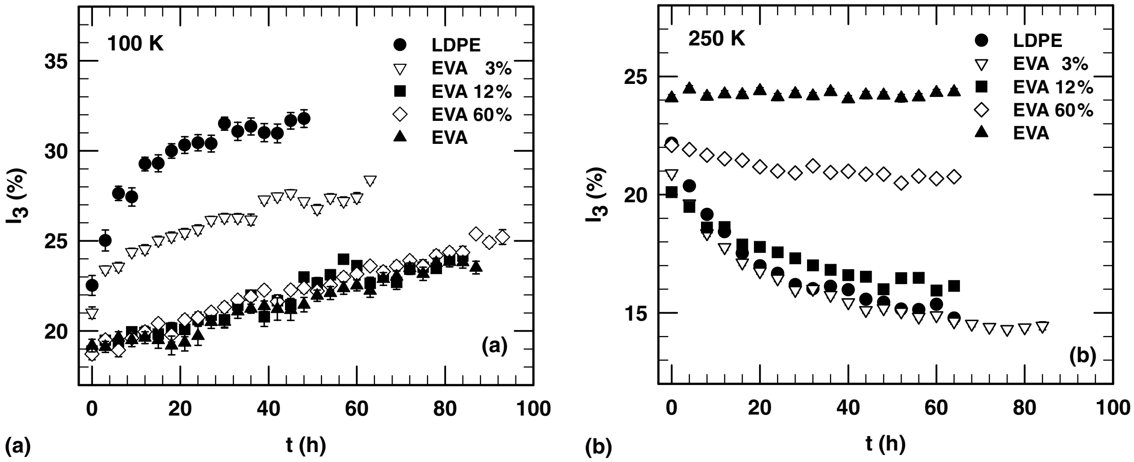

Fig. 3. Variation in *o*-Ps yield, I_3, as a function of elapsed time for five polymers: LDPE, EVA and their blends with EVA contents $\Phi = 3$, 12 and 60% at: (a) $T = 100$ K; and (b) $T = 250$ K.

samples imply that the addition of EVA to LDPE does not change the free volume size significantly [6,11].

Fig. 2 shows variations of the *o*-Ps formation probability I_3 versus temperature. For LDPE, when the temperature is slowly increased from 100 to 300 K, $I_3(T)$ exhibits a peak (of ' ∧ ' shape) at 120 K and two valleys (of 'V' shape) around 180 and 250 K. Similar behaviors were observed for other non-polar polymers as well, e.g. high density polyethylene (HDPE) [22], polystyrene (PS) [23]. The *o*-Ps intensity observed for quenched LDPE varies smoothly with temperature, a remarkably different behavior from that for slowly-heated LDPE. With the increase in EVA content, the difference of I_3 between the data obtained with slowly-heated and quenched samples becomes less obvious (Fig. 2b–e).

The *o*-Ps formation probability I_3 recorded at a fixed temperature is shown as a function of elapsed time t in Fig. 3. At $T = 100$ K, for LDPE and the blend with $\Phi = 3\%$ I_3 increases with time until it saturates at $t > 20$ h and $t > 40$ h, respectively. Note that the saturated I_3 for the blend is significantly smaller than that for LDPE. For blends with larger EVA contents and pure EVA, I_3 rises slowly with t and no saturation is achieved within 90 h. At $T = 250$ K, I_3 undergoes a pronounced decrease with time for LDPE. Similar behaviors were observed for HDPE [8], PS [23] and polycarbonate [24]. The decrease of I_3 becomes less obvious as the EVA concentration is increased, and there is little change in I_3 for pure EVA.

4. Discussion

Since the *o*-Ps intensity I_3 in pure LDPE is, depending on temperature, increased (e.g. at $T = 100$ K) or decreased (e.g. at $T = 250$ K) with time, we cannot attribute the variation of I_3 to the well-known physical aging effect of a glassy polymer, in which the fractional free-volume gradually *decreases* with time [25]. Furthermore, the I_3 behaviors versus temperature and time in LDPE are strongly influenced by the addition of a small amount of EVA ($\Phi = 3$–12%) (Figs. 2 and 3), while the free-volume size (as characterized by τ_3) is not significantly affected by the addition of EVA (Fig. 1). The free volume model, in which *o*-Ps intensity is assumed to be simply proportional to the free volume concentration, cannot convincingly explain why the addition of EVA strongly influences the hole concentration (characterized by I_3) but not free-volume size and τ_3. The spur reaction model [13,14], which allows us to relate the Ps formation process to various radiation chemical effects, can explain, though only qualitatively, the present results as described below.

Let us first consider Ps formation in pure LDPE. At low temperatures in the vicinity of $T = 120$ K, it was shown that electrons generated in LDPE by γ-irradiation are localized in shallow traps, which may exist in the chain-fold regions of the polymer [26,27]. Localized electrons in these shallow traps give rise to broad photon absorption bands in visible and near-infrared regions [26], as well as photoemission through their recombination with parent ions [28]. Similar localized electrons may be produced by positron irradiation as well [29], with their concentration gradually increasing with increasing positron irradiation time. If the localized electrons are uniformly generated in the sample, their concentration may reach such a level that the mutual distance between the nearest pair is about 10 nm after 10 h of positron irradiation with our source of about 0.74 MBq. This value (10 nm) is comparable to the average initial separation of positron–electron pairs in the positron terminal spur in LDPE (about 21 nm) [12], suggesting that the number of electrons, available for Ps formation by

$$e^+ + e^- \rightarrow \mathrm{Ps}, \qquad (1)$$

is significantly increased.

The localized electrons, responsible for the enhanced Ps formation in LDPE at 100–120 K, may disappear as the temperature is increased. It is claimed by Markiewicz and

Fleming that around 120 K the traps are destroyed due to the onset of the short side branch motion of polymer chains [26]. Hence, the contribution of localized electrons to Ps formation is gradually reduced. Between T_s (about 145 K) and 250 K, I_3 values recorded during slow heating are always below the data for quenched samples. This may be attributed to the formation of positron traps due to positron irradiation in slowly heated samples, i.e. chemical traps (free radicals) or physical traps (non-uniform potentials due to enhanced local molecular motions [28]). The positron, which would otherwise combine with an electron to form Ps, may be captured by these traps and Ps formation is suppressed [30]. This explanation is supported by large positron mobility 14–28 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in unirradiated PE [11,31,32] in the sense that because of the high mobility even a low concentration of the traps can have a significant effect on Ps formation. Above 250 K, a sharp rise in *o*-Ps intensity, presumably due to the disappearance of positron traps [33,34], is observed in Fig. 2a. Note that with increasing temperature the data for slowly heated samples approach those for quenched samples.

Here it deserves mentioning that I_3 for LDPE decreases with increasing positron irradiation time at 250 K, which is higher than $T_g \approx 225$ K (Fig. 3b). Further, the data in Fig. 2a suggest that there might be a reduction of I_3 with time even when the temperature is as high as 300 K. This is in qualitative agreement with the results for other semicrystalline polymers, HDPE and polypropylene (PP) [8,35]. For amorphous polymers such as PMMA and PVAc [2], however, positron irradiation does not affect I_3 above T_g. The discrepancy in the behavior of $I_3(t)$ above T_g between semicrystalline and amorphous polymers can be attributed to the presence of the crystalline region in the former polymers. It has been confirmed that in γ-irradiated crystallized polyethylene a high concentration of free radicals are present until the temperature reaches 330 K, about 80 K below the melting point [36]. Furthermore, above T_g part of the amorphous phase in semicrystalline polymers is still glassy due to the restriction of the chain motion imposed by the crystalline region [21]. Therefore, even at temperatures higher than T_g the concentration of positron traps in the crystalline region and some parts of the amorphous region could be high enough to reduce Ps formation. This can explain why the positron irradiation effect on I_3 is observed only for semicrystalline polymers above T_g.

Previously, we compared Ps formation in EVA with that in LDPE by measuring *o*-Ps intensity as a function of external electric field up to 60 kV/cm at room temperature [11]. It was observed that the application of the electric field appreciably decreases Ps formation in LDPE but not in EVA. The observed constancy of I_3 versus electric field in pure EVA indicates that the polar acetate group captures mobile positrons and Ps is formed exclusively from positron–electron pairs with short initial separations (possibly 1 nm or so) [12], which cannot be separated from each other by electric fields as high as 60 kV/cm. It was also observed that the positron mobility is appreciably reduced in EVA in comparison with LDPE [11]. Recently additional evidence for the positron trapping at the polar acetate group of EVA was provided by the coincidence-Doppler broadening technique [15]. Since the thermal vibration energy of polymer segments is too low to effectively detrap the positron from EVA at low temperatures, we can safely assume that the acetate group contained in EVA traps positrons over the whole temperature range of this study. Using this assumption we can explain weaker positron irradiation effects in pure EVA and blends than LDPE at $T = 100$ and 250 K.

At $T = 100$ K, due to the accumulation of localized electrons with time, the number of electrons that are available for Ps formation increases with time. However, because of the positron trapping, the diffusion length and mobility of the positron are considerably decreased in EVA [11] and the effective number of the localized electrons that a mobile positron can pick up to form Ps is reduced in comparison with LDPE. This can explain why the *o*-Ps intensity increases only slightly with time in EVA at 100 K. At 250 K positron irradiation may produce positron traps, which are responsible for the reduction of I_3 in LDPE, where Ps formation occurs from positron–electron pairs with both large and small initial separations [11]. The traps produced by positron irradiation may capture mobile positrons, thereby reducing Ps formation from positron–electron pairs with large initial separation. The concentration of such traps accumulated in EVA after a certain time of positron irradiation may be similar to that in LDPE. However, since Ps formation from mobile positrons is inhibited as a result of fast positron trapping on the polar acetate group of EVA, there is less probability of the positron capture by the traps competing with electron–positron recombination [37]. Hence, the effect of positron irradiation on Ps formation in EVA is much weaker than in LDPE not only at 100 K but also at 250 K.

The *o*-Ps formation probability I_3 versus temperature and time in PE/EVA blends (with EVA weight contents $\Phi = 3$, 12 and 60%) more or less intervenes between PE and EVA (see Fig. 2). However, due to the trapping effect of the positron by EVA, we do not expect that $I_3(T)$ and $I_3(t)$ in blends versus EVA content satisfy the rule of simple additivity [3]. Indeed, the I_3 values in the blends are not the weighted averages of I_3 in the two components. We can understand the results of $I_3(T)$ and $I_3(t)$ on the basis that Ps atoms are formed from positron–electron pairs with both large and small initial separations in LDPE but not in EVA [11]. As shown in Fig. 3, at $T = 100$ K, the $I_3(t)$ curves for the blends with $\Phi = 12$ and 60% coincide well with the curve for EVA, indicating that most Ps atoms are formed from positron–electron pairs with short initial separations. Moreover, at $T = 250$ K there is still a significant irradiation effect on I_3 for the blends with $\Phi = 3$ and 12%, while at $\Phi \geq 60\%$ the positron irradiation effect on $I_3(T)$ is appreciably weakened. All these facts indicate that Ps atoms formed from positron–electron pairs with large initial separations are sensitively affected by positron trapping on the acetate group of EVA.

5. Conclusion

The formation probability of *o*-Ps has been measured in LDPE, EVA and their polymer blends versus temperature and measurement time. The most important result in the present work is that Ps formation in LDPE and some blends was strongly influenced by positron irradiation. Good qualitative correlations were found between the *o*-Ps formation probability and some already known facts concerning electron localization and carrier transport in radiation chemistry. The observed weakening of the positron irradiation effects in PE upon the addition of EVA was related to positron trapping on the polar acetate group of EVA. The complex effects of EVA and positron irradiation on Ps formation revealed that care should be taken when we interpret *o*-Ps lifetime data in terms of the free volume for polymer blends consisting of non-polar and polar components.

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