



Comprehensive study of positronium formation in polymer blends between polyethylene and ethylene-vinylacetate copolymer

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Abstract

The intensity I_3 of *ortho*-positronium (*o*-Ps) in a polymer blend system consisting of polyethylene (PE) and ethylene-vinylacetate (EVA, random copolymer with a vinylacetate content of about 14%) was measured as functions of EVA weight content ($\Phi = 0$ –100%), electric field ($E = 0$ –60 kV/cm), positron irradiation time ($t = 0$ –200 h) and temperature ($T = 100$ –300 K). It was found that the addition of small amounts of EVA to PE significantly alters the electric field, positron irradiation time and temperature dependence of I_3 . Positron trapping on polar EVA is suggested to be responsible for the sensitive effects of EVA. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Positronium formation; PE/EVA polymer blends

1. Introduction

Positrons implanted into molecular substances such as polymers may capture an electron to form positronium (Ps). The *ortho*-positronium (*o*-Ps) formation probability is influenced by many factors such as temperature (see a review by Mogensen, 1995), positron irradiation (Welander and Maurer, 1992; Wang et al., 1998a) and the electric field (Brandt and Wilkenfeld, 1975; Bisi et al., 1983; Kobayashi et al., 1997). According to the spur reaction model (Mogensen, 1995), Ps is formed by a two-step reaction between a positron and one of the electrons liberated from the molecules by the positron itself. The previously known *o*-Ps intensity

data for polymers suggest that the formation of Ps may take place prior to its localization in a free volume hole (Hirata et al., 1997).

In this paper, by summarizing the experimental results on Ps formation in polyethylene/ethylene-vinyl acetate (PE/EVA) blends versus electric field (Kobayashi et al., 1998), temperature, time and EVA concentration, we emphasize the importance of radiation chemical processes in Ps formation.

2. Experiments

Pure low density polyethylene (LDPE) and EVA as well as their blends (PE/EVA) with EVA weight contents of $\Phi = 3, 12, 60\%$ were studied by positron annihilation lifetime spectroscopy (PALS) as functions of temperature and time. The vinyl acetate content in

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pure EVA (random copolymer) was about 14%. Densities and crystallinities of these samples are summarized in Table 1. The ^{22}Na source, deposited on an area of about 10mm^2 between two 0.8 mg cm^{-2} Kapton foils, had an activity of about 0.74 MBq. The resolution of the fast–fast coincidence lifetime spectrometer was 310 ps (FWHM).

The source–sample assembly was first cooled down to 200 K within about 10 min. Then, the temperature was changed in the order: 200 K \rightarrow 100 K \rightarrow 300 K, with intervals of 100 K for cooling (cooling rate $q_c \approx -4\text{ K/min}$) and 10 K for heating (heating rate $q_h \approx 0.04\text{ K/min}$). After the sample was kept at a given temperature for about 10 min, a lifetime spectrum was recorded for 4 h. Time dependence of the lifetime spectra was measured by cooling a sample directly from room temperature to $T = 250$ or 100 K, after which the data were repeatedly recorded as a function of time at one of the above temperatures. To obtain $I_3(T)$ plots under the condition of minimum positron irradiation (Wang et al., 1998a), the spectra of fresh samples were collected at room temperature ($295 \pm 2\text{ K}$), and at 150 K, following a quench from room temperature.

Lifetime spectra were decomposed into three components plus a 7% source component using the PATFIT software (Kirkegaard et al., 1989), with variances (χ^2) ranging between 0.96 and 1.16. 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, regardless of EVA concentration. To reduce the errors of I_3 , all these spectra were analyzed under the constraint of $\tau_3 = 1.36$ or 2.09 ns.

3. Results

Temperature dependence of the *o*-Ps lifetime τ_3 in all the samples was characterized by two transition

Table 1
Densities, crystallinities at room temperature and *o*-Ps yields (I_3) for the samples right after a quench from room temperature to $T = 100\text{ K}$

EVA content	Density ^a (g/cm^3)	Crystallinity ^a (%)	I_3 at 100 K (%)
$\Phi = 0\%$	0.924	36.9	22.5 ± 0.6
$\Phi = 3\%$	0.923	37.6	21.0 ± 0.3
$\Phi = 12\%$	0.925	33.3	18.9 ± 0.2
$\Phi = 60\%$	0.932	20.4	18.7 ± 0.3
$\Phi = 100\%$	0.937	20.4	19.2 ± 0.4

^a From Kobayashi et al. (1998).

temperatures, T_s (145–166 K) and T_g (216–239 K), associated with secondary and glass transitions, respectively. Approximating the $\tau_3(T)$ curves by three straight lines, the transition temperatures were determined. Both T_s and T_g were almost invariant as a function of EVA composition.

Fig. 1 shows variations of the *o*-Ps intensity (I_3) versus temperature and EVA composition. For LDPE, when the temperature was slowly increased from 100 to 300 K, $I_3(T)$ exhibited one peak and two valleys. The *o*-Ps intensity observed for quenched LDPE varied smoothly with temperature, a remarkably different behavior from the case of slow heating. With the increase in EVA content, the difference of I_3 between the slowly-heated and quenched samples became less obvious (Fig. 1). The *o*-Ps intensity I_3 recorded at a fixed temperature is shown in Fig. 2. At 100 K, for LDPE and the blend with 3% EVA, I_3 first increased with time and then became saturated. For the blends with larger EVA contents and pure EVA, I_3 rose slowly with t . At $T = 250\text{ K}$, I_3 showed a pronounced decrease with time for LDPE. The decrease in I_3 became less obvious as the EVA concentration was increased, and there was little change in I_3 for pure EVA. During all these isothermal measurements, the *o*-Ps lifetime was unchanged.

Numerical values of I_3 for samples quenched to 100 K are listed in Table 1. The addition of up to 12% EVA reduces the *o*-Ps intensity I_3 from 22.5% to 18.9%, which is not significantly affected by further addition of EVA. As the crystallinity of the blend gradually decreases with increasing EVA concentration, the reduction of I_3 cannot be simply correlated to the change in crystallinity, in contrast to the observation for poly(aryl-ether-ether-ketone) (PEEK) at room temperature (Nakanishi et al., 1989).

4. Discussion

The variation of I_3 with temperature and time in LDPE is strongly influenced by the addition of small amounts of EVA ($\Phi = 3\text{--}12\%$) and that as a function of EVA concentration cannot be simply related to the change in crystallinity. We interpret the present results with reference to various radiation chemical effects caused by positron irradiation.

Previous pulse radiolysis experiments for LDPE showed that, at low temperatures in the vicinity of $T = 120\text{ K}$, electrons generated by irradiation are localized in shallow traps (Markiewicz et al., 1986; Szadkowska-Niese et al., 1992). We expect that their concentration gradually increases with positron irradiation time. Provided that the localized electrons are uniformly generated in the sample, their concentration may reach such a level that their mutual distance is in the order of 10

nm after 10 h of positron irradiation. This value of 10 nm is comparable to the average initial inter-particle separation of the positron–electron pairs in the positron terminal spur in LDPE (about 21 nm) (Wang, et al., 1998b). So the number of electrons available for Ps formation increases, and I_3 is enhanced with t and T at 100–120 K.

The localized electrons may disappear as the temperature is increased. It is claimed by Markiewicz and Fleming (1986) that around 120 K the traps begin to be destroyed due to the onset of the short side branch motion of the polymer chains. Hence, the contribution

of the localized electrons in Ps formation is gradually reduced. The I_3 values recorded, between T_s about 145 and 250 K, during slow heating are always below the data for the quenched samples. This may be attributed to free radicals produced by the decay of the localized electrons. Above 250 K, it is seen from Fig. 1 that there is a sharp rise in the *o*-Ps intensity (I_3) with temperature, and this may be ascribed to the disappearance of the free radicals (Kovarskii et al., 1989).

The *o*-Ps intensities in blends were measured as a function of external electric field up to 60 kV/cm at room temperature (Kobayashi et al., 1998). An ap-

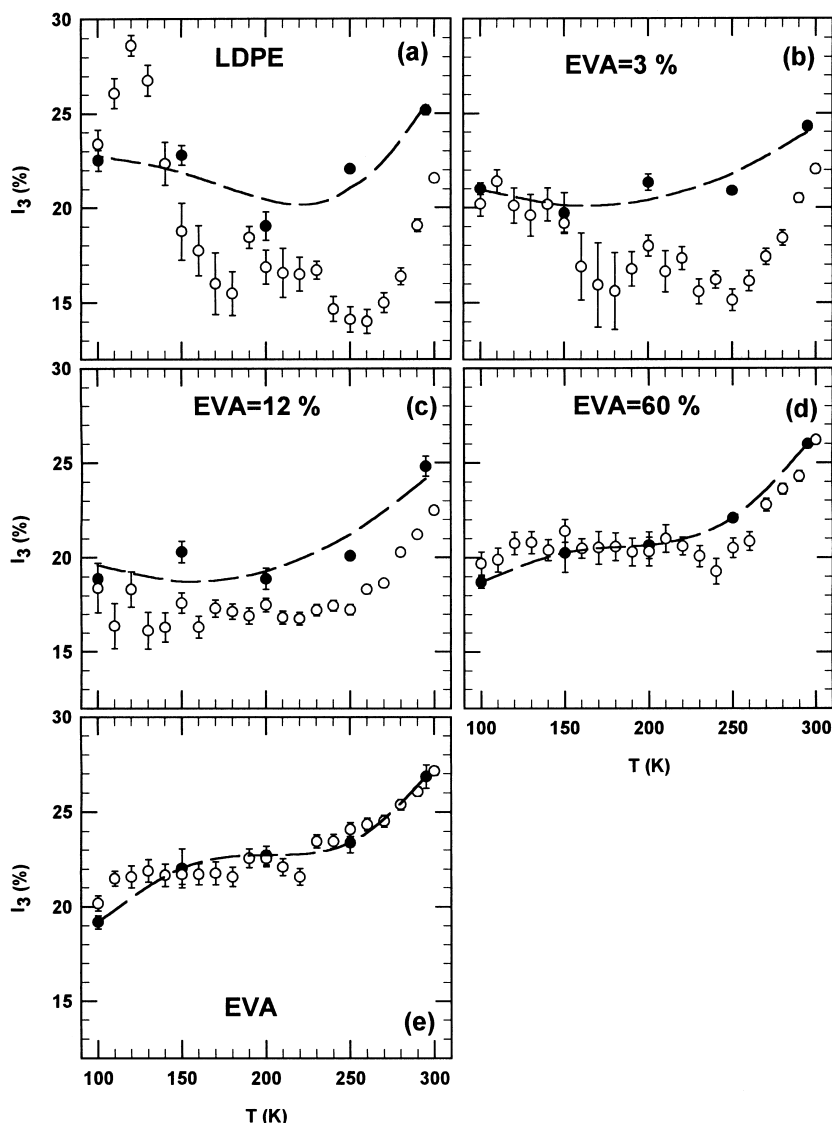


Fig. 1. Variation of the *o*-Ps yield, I_3 , as a function of temperature for five polymers: (a) LDPE, (b)–(d) blends with $\Phi = 3, 12$ and 60%, (e) EVA. The full and open circles denote the results for the quenched and slowly heated samples, respectively. The dashed lines show tendencies for the quenched samples.

preciable decrease in Ps formation in LDPE was found; but the constancy of I_3 versus electric field in pure EVA indicates that the polar acetate group captures mobile positrons and Ps is formed almost exclusively from the positron–electron pair with short initial separation of the two particles (possibly around 1 nm) (Wang et al., 1998b), 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 (Kobayashi et al., 1998). Since the thermal vibration energy of the polymer segments is too low to effectively detrapp the positron from EVA at low temperatures, we can safely assume that EVA traps positrons in the whole temperature range of this study. Using this assumption we can explain the weaker positron irradiation effects in the pure EVA and the blends than LDPE at $T = 100$ and 250 K.

At $T = 100$ K, due to the positron trapping, the number of localized electrons the positron can pick up to form Ps in EVA is reduced in comparison with

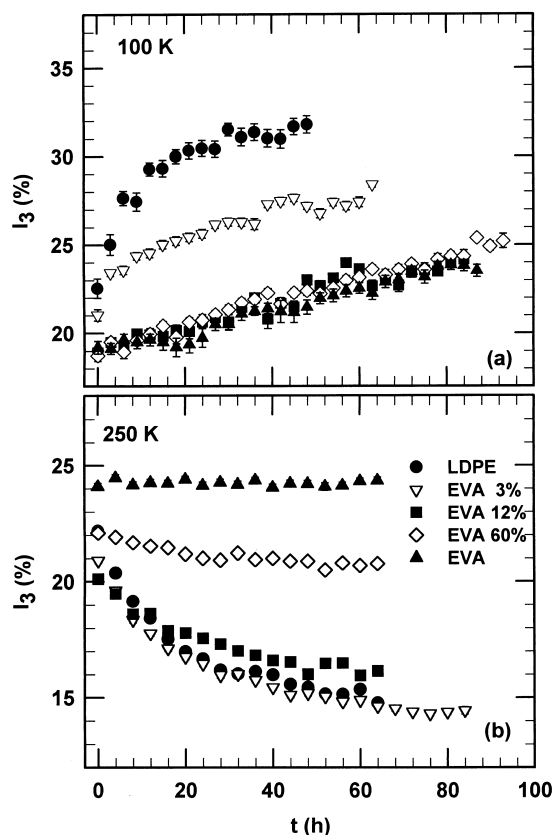


Fig. 2. Variation of the *o*-Ps yield, I_3 , as a function of elapsed time for five polymers: LDPE, EVA and their blends with EVA contents $\Phi = 3, 12$ and 60% at: (a) $T = 100$ K; (b) $T = 250$ K.

LDPE. So the *o*-Ps intensity (I_3) increases only slightly with time in EVA at 100 K. At 250 K, positron irradiation produces free radicals, which may be responsible for the reduction of I_3 in LDPE, where Ps formation occurs from positron–electron pairs with both large and short inter-particle separations (Kobayashi et al., 1998). The radicals produced by positron irradiation may capture mobile positrons, thereby reducing Ps formation from the pairs with large initial separation. The concentration of the radicals 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, there is less probability of the latter being captured by the radicals competing with electron–positron recombination in EVA. Hence, the effects of positron irradiation on Ps formation in EVA are much weaker at 250 K.

The observed $I_3(T)$ and $I_3(t)$ in blends can be understood on the basis that Ps atoms are formed from the positron–electron pairs with both large and short inter-particle separations in LDPE, but not in EVA. As shown in Fig. 2, when $T = 100$ K, the $I_3(t)$ curves for the blends with $\Phi = 12$ and 60% well coincide with the curve for EVA, indicating that most of the Ps atoms are formed from the positron–electron pairs with short initial separation. Moreover, at $T = 250$ K a significant irradiation effect on I_3 exists in the blends with $\Phi = 3$ and 12%, while at $\Phi \geq 60\%$ the irradiation effect on $I_3(T)$ is appreciably weakened. All these facts indicate that Ps atoms formed from the pairs with large initial separation are sensitively affected by positron trapping on the acetate group of EVA.

Acknowledgements

We thank the Science and Technology Agency (STA) and the Agency of Industrial Science and Technology (AIST) for financial supports.

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