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Effects of composition and external electric field on positronium formation in a polymer blend system

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Positron lifetime measurements were carried out for polymer blends between polyethylene and ethylene vinyl acetate copolymer (E/VA) over the entire concentration range. The intensity I_3 of the longest-lived component due to the annihilation of *ortho*-positronium (o-Ps) exhibited a complex behavior as a function of E/VA concentration. The addition of up to 12% E/VA to polyethylene decreased the intensity from 28.2 to 25.8 %. Further addition of E/VA, somewhat surprisingly, resulted in an enhancement of positronium (Ps) formation that continued until I_3 reached a value of 29.7% for pure E/VA. The effect of E/VA on Ps formation was found to be strongly influenced by the application of an external electric field. For example, the o-Ps intensity recorded at a field of 50 kV/cm monotonously increased from 18.8% to 29.6% with increasing E/VA concentration. These results are discussed on the basis of the spur reaction model of Ps formation. [S0163-1829(98)00134-9]

I. INTRODUCTION

After injection into a condensed matter, some of the positrons combine with an electron to form the bound state, positronium (Ps). Because of two possible spin orientations of the two particles there are two substrates in Ps, singlet *para*-positronium (p-Ps) and triplet *ortho*-positronium (o-Ps). In vacuum, p-Ps annihilates into two γ rays with a lifetime of 125 ps, whereas o-Ps decays into three γ rays with a much longer lifetime of 142 ns. In condensed medium, however, the o-Ps lifetime is shortened to a few ns or less, because the positron in o-Ps undergoes two-photon annihilation with one of the bound electrons with opposite spin. This process is called pickoff annihilation.[1–4]

The lifetime spectrum of positrons annihilating in polymers usually contains three exponentially decaying components. The longest-lived component with a lifetime τ_3 and the corresponding relative intensity I_3 is attributed to the pickoff annihilation of o-Ps localized in a nm size hole. In 1981, an empirical equation relating the pickoff annihilation lifetime to the Ps cavity size was introduced by Eldrup, Lightbody, and Sherwood[5] and it became possible to quantify the cavity size in various materials.[6] The Ps cavity volume deduced from this empirical equation was found to be well correlated with the diffusion coefficients of argon, nitrogen, and oxygen in various polymers,[7] demonstrating the usefulness of Ps as a probe to study free volume in polymers.

Although the pickoff annihilation lifetime has been successfully correlated to the amount of free volume present in polymers, its intensity is affected by many factors including the free volume. Nakanishi *et al.*[8] studied Ps formation in semicrystalline poly(aryl-ether-ether-ketone) with different crystallinities and observed that the lower the crystallinity is the higher the o-Ps intensity is. They interpreted the result by assuming that the free volume suitable for Ps formation is present only in the amorphous region of the polymer. Meanwhile, according to the spur reaction model,[9] Ps is formed by a two-step reaction between a positron and one of the electrons, released from the polymer molecules by the positron at an earlier time. This process must compete with other spur processes and Ps formation is influenced by such processes as electron-ion recombination, positron and electron scavenging, trapping, positron and electron escaping from the spur, etc. The spur model has been successfully applied to explain many experimental results for molecular liquids.[4,10] The effects of additives,[11,12] electric fields[13,14] and irradiation[15–17] on Ps formation have been studied for a number polymers and well explained by the same model.[4]

This paper concerns formation and annihilation of Ps in a complex system of polymer blends between polyethylene and ethylene vinyl acetate copolymer (E/VA). Positron lifetime measurements were carried out over the entire composition range of the blends. The aim of the research was to find out how the Ps formation in semicrystalline and nonpolar polyethylene is affected by the addition of polar E/VA and further clarify the factors which influence Ps formation in polymers.

II. EXPERIMENT

Polyethylene (low-density polyethylene) and E/VA (random copolymer) were purchased from UBE Industries, Ltd. and Beijing Organic Chemical Factory, respectively. The melt-flow index of polyethylene was 0.25 g/10 min and that of E/VA was 2.0 g/10 min. The vinyl acetate content of the copolymer was about 14%. Polyethylene and E/VA were mixed at 130–140 °C with a roller and then pressed into sheets with a thickness of about 2 mm at 140 °C using a liquid press machine. Densities and dielectric constants of the blends thus prepared are listed in Table I, whereas the crystallinity determined by x-ray diffraction is plotted versus

TABLE I. Densities and dielectric constants of the blends between polyethylene and ethylene vinyl acetate copolymer (E/VA). The vinyl acetate content of E/VA is about 14%.

E/VA concentration (wt. %)	Density (g/cm^3)[a]	Dielectric constant[b]
0	0.924	2.32
3	0.923	2.33
6	0.924	2.32
9	0.925	2.32
12	0.925	2.33
15	0.926	2.32
18	0.926	2.42
21	0.927	2.44
24	0.927	2.37
36	0.929	2.57
48	0.930	2.56
60	0.932	2.70
72	0.933	2.75
84	0.935	2.79
100	0.937	2.88

[a] Determined with a water/ethanol density column at 25 °C.

[b] Determined by the impedance bridge method at a frequency of 1 kHz.

E/VA concentration in Fig. 1. Miscibility of the blends was studied by differential scanning calorimetry (DSC) with a heating rate of 5 °C/min.

Positron lifetime spectra were recorded with a fast-fast coincidence system by determining the time interval between the detection of a 1.27 MeV γ ray from the nuclear decay of the ^{22}Na source and the detection of one of 0.511 MeV annihilation photons. The time resolution of the lifetime spectrometer was 290 ps full width at half maximum. A 0.37 MBq ^{22}Na source sealed between two Kapton foils with a thickness of 7.5 μm was sandwiched between two identical samples. The lifetime spectra were decomposed into three exponential components by the POSITRONFIT EXTENDED program.[18] The longest-lived component with the lifetime τ_3 and the intensity I_3 was easily attributed to the pickoff annihilation of o-Ps atoms. Correction was made for the positrons annihilating in the source material. All the measurements were carried out at room temperature.

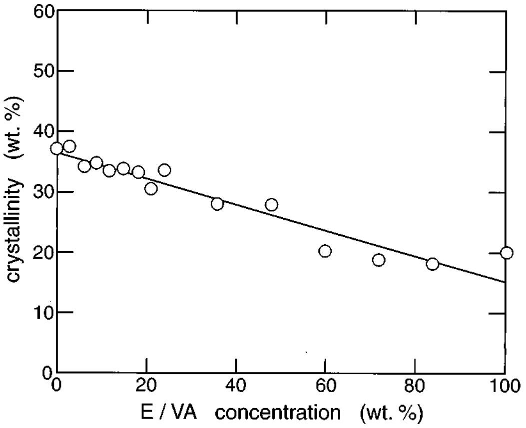

FIG. 1. Plot of crystallinity versus E/VA concentration for the blends between polyethylene and ethylene vinyl acetate copolymer (E/VA). The crystallinities were determined on the basis of the relative intensity of the (110) and (200) reflections in the x-ray-diffraction data.

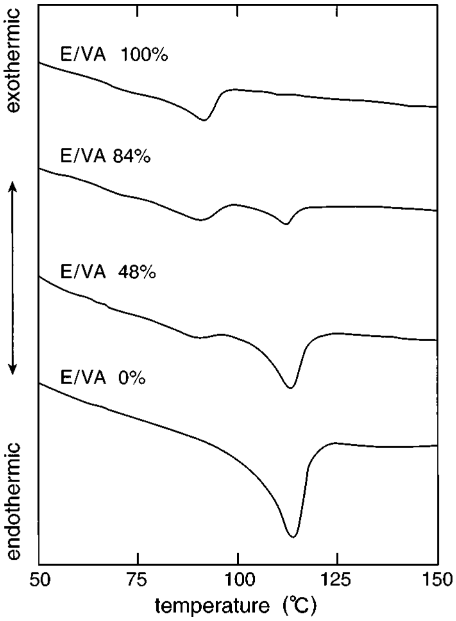

FIG. 2. Differential scanning calorimetric analysis of the blends containing 0, 48, 84, and 100 % E/VA. The data were obtained with a heating rate of 5 °C/min.

III. RESULTS

Figure 2 shows the DSC data for the samples with the E/VA contents of 0, 48, 84, and 100 %. The blend samples containing 48 and 84 % of E/VA clearly exhibit two endothermic peaks at about 115 and 90 °C, which are due to the melting of polyethylene and E/VA crystals, respectively. The two melting peaks are observed for most of the blend samples studied and the intensity of the peak at 90 °C is linearly increased, whereas that at 115 °C is linearly decreased with increasing E/VA concentration, revealing the immiscible nature of the blends over the entire concentration range.

The variation of the o-Ps lifetime τ_3 in polyethylene upon the addition of E/VA is shown in Fig. 3. The lifetime increases, though slightly, with increasing E/VA concentration, suggesting that the Ps cavity becomes larger as the E/VA concentration is increased. Following Tao,[19] Eldrup, Lightbody, and Sherwood[5] approximated the Ps cavity as a spherical potential well with radius R_0. The potential has an infinitely high wall and there is an electron layer with thickness ΔR on the wall surface. By further assuming that the Ps lifetime in the case of no free volume is 0.5 ns, these authors derived the relation between the o-Ps pickoff annihilation lifetime and the Ps cavity radius R:

$$\tau_3 = 0.5(\mathrm{ns})\{1-(R/R_0)+0.159\sin(2\pi R/R_0)\}^{-1}. \quad (1)$$

Here $R=R_0-\Delta R$ is the cavity radius and $V_c=(4\pi/3)R^3$ is the cavity volume. The value of ΔR was somewhat arbitrarily chosen to be 0.166 nm by Nakanishi, Wang, and Jean.[20] In view of the complex nature of Ps annihilation in polymers this simple model should not be taken too

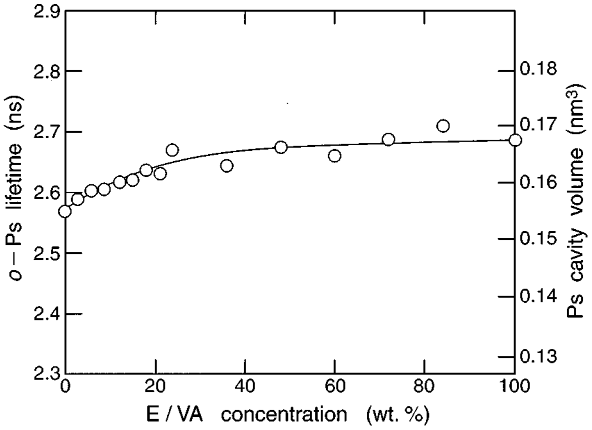

FIG. 3. Variation of o-Ps lifetime τ_3 and calculated Ps cavity volume as a function of E/VA concentration. The error range of each point is smaller than the plotting symbol.

seriously,[5] but the use of Eq. (1) with $\Delta R = 0.166$ nm can reproduce known hole volumes in zeolites and other substances.[20] The same choice of ΔR gives hole volumes shown on the right-hand scale in Fig. 3. The deduced cavity volume is ranged from 0.154 to 0.166 nm^3 and it seems that the increase of the cavity volume with increase in E/VA concentration is rather small.

In contrast to the variation of the lifetime, the o-Ps intensity I_3 exhibits a complex behavior as a function of E/VA concentration (Fig. 4). The addition of up to 12% E/VA to polyethylene decreases the intensity from 28.2 to 25.8%. Further addition of E/VA, quite interestingly, results in an enhancement of Ps formation that continues until I_3 reaches a value of 29.7% for pure E/VA. One can see in Fig. 1 that the crystallinity of the blend monotonously decreases with increasing E/VA concentration. Therefore the complex variation of the Ps formation, in particular the reduction of I_3 at low E/VA concentrations, cannot be related to the change of the crystallinity alone, and further consideration is required.

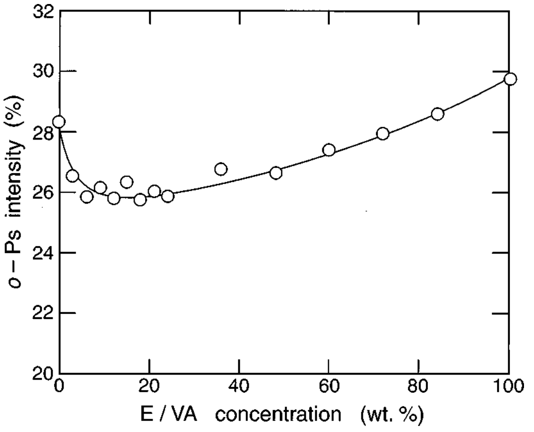

FIG. 4. Variation of o-Ps intensity I_3 as a function of E/VA concentration. The error range of each point is smaller than the plotting symbol.

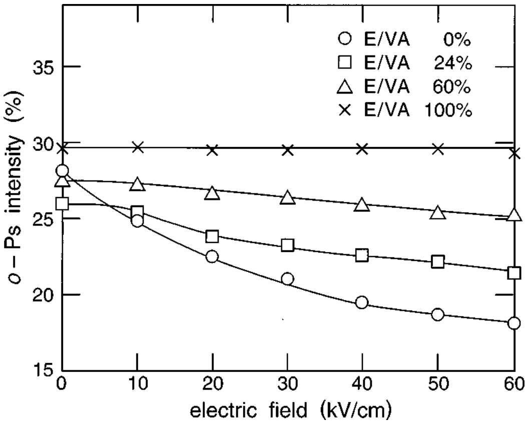

FIG. 5. Electric-field dependence of I_3 for the samples with the E/VA contents of 0, 24, 60, and 100 %. Note that there is a crossover point around 10 kV/cm for the sample containing 24% E/VA.

The simplest version of the spur model assumes that Ps formation occurs after both the positron and electron are completely thermalized. The probability P of a thermalized electron-positron pair with initial separation r recombining together to form Ps is given as

$$P = 1 - \exp(-r_c/r), \tag{2}$$

where r_c is the Onsager radius, expressed as $r_c = e^2/(4\pi\epsilon\epsilon_0 kT)$.[14,21,22] Here e is the electronic charge, ϵ is the relative dielectric constant of the medium, ϵ_0 is the dielectric constant in vacuum, k is the Boltzmann constant, and T is the absolute temperature. The addition of E/VA to polyethylene increases the dielectric constant (Table I), which according to Eq. (2) should result in a reduction of Ps formation. This expectation is in qualitative agreement with our result at low E/VA concentrations, suggesting that positron spur processes may have something to do with the complex variation of I_3.

To further explore the positron spur processes in our blends between polyethylene and E/VA, o-Ps yields were measured, for all the samples, as a function of external electric field. The samples were clamped between two silver electrodes to which static electric fields up to several tens of kV/cm were applied. In order to avoid possible effects of positron irradiation,[15,17] the source was moved after each 2 h run to a new position so that a lifetime spectrum of a fresh part of the samples could be recorded.[16] Some results are shown in Fig. 5. The application of an electric field to polyethylene considerably decreases the Ps yield; the o-Ps intensity at 60 kV/cm (18.2%) is lower by 10% than that at 0 kV/cm (28.2%). The electric-field effect in reducing Ps formation becomes increasingly weaker as the E/VA concentration is increased. For example, the reduction in I_3 for the sample containing 60% E/VA upon the application of 60 kV/cm is only 2% and there is no noticeable change in I_3 as a function of electric field for pure E/VA.

In Fig. 6 is shown the comparison of the concentration dependence of I_3 observed at the field of 50 kV/cm with that at 0 kV/cm. Because of the stronger electric-field effect at lower E/VA concentrations, there is no minimum in the data at 50 kV/cm, and the o-Ps intensity increases monotonously from 18.8 to 29.6 % with increasing E/VA concentration.

IV. DISCUSSION

Based on the data in Fig. 6, it is possible to distinguish two contributions, one being sensitive and the other being insensitive to the electric fields up to 50 kV/cm, to the over-

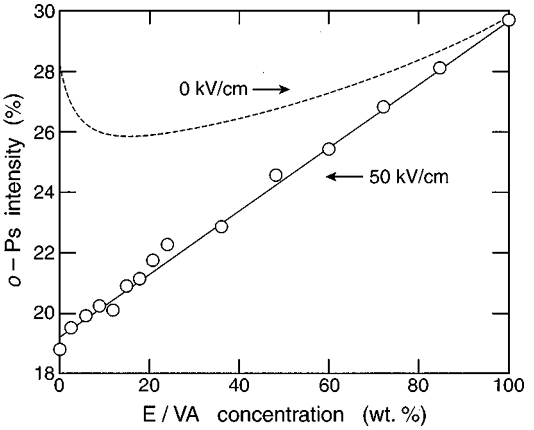

FIG. 6. Comparison of the concentration dependence of I_3 at 50 kV/cm with that at 0 kV/cm. Note that the o-Ps intensity recorded at 50 kV/cm increases linearly with increasing E/VA concentration.

all Ps formation in the blends between polyethylene and E/VA. Variation of the field-sensitive contribution derived as the difference of the data between 0 and 50 kV/cm is shown in Fig. 7. It is seen from Figs. 6 and 7 that with increasing E/VA concentration the former field-dependent contribution decreases, whereas the latter contribution, insensitive to the fields as high as 50 kV/cm, increases. The complex variation of the o-Ps intensity in Fig. 4 is, thus, found to be due to a combined effect of two contributions which behave quite differently as a function of E/VA concentration.

The field-dependent Ps formation is supposed to be associated with recombination of electron-positron pairs with large initial separation in the positron spur. Because of weak Coulomb interaction between the two particles, they are easily separated from each other by an electric field. At low fields only a small fraction of the pairs can be separated and the Ps formation is slightly reduced from that at zero field. With increasing the field strength, more and more pairs are separated and the Ps formation is further reduced. It should be mentioned that the strong electric-field effect on Ps formation has been observed for nonpolar polymers such as polyethylene and polypropylene with high positron mobility.[23–26]

At first sight, it seems that the reduction of the field-dependent contribution with increasing E/VA concentration in Fig. 7 can be ascribed to the reduction of the Onsager radius as the result of the increased dielectric constant in Eq. (2). However, one can easily confirm that the rather small increase (about 24%) in dielectric constant is not sufficient to account for the rapid decline of the field-dependent component, for whatever r value in the reasonable range. Furthermore, the electric-field dependence of the blend containing 24% E/VA in Fig. 5 is not straightforward and cannot be explained in terms of the simple Onsager theory.

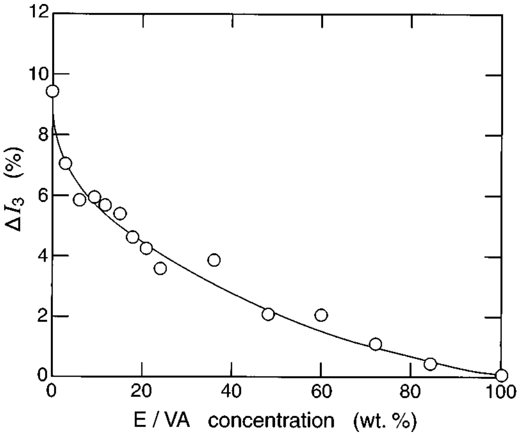

FIG. 7. Variation of the amount of o-Ps reduced by the electric field of 50 kV/cm (ΔI_3) as a function of E/VA concentration.

TABLE II. Positron mobilities in some of the samples.

E/VA concentration (wt. %)	Positron mobility (cm^2/Vs)
0	14±2
3	6±2
6	4±2
15	1±2
100	0±2

The electric-field dependence of the 24% E/VA sample is similar in shape to our previous results for γ-irradiated polyethylene and polypropylene,[16] suggesting that positron trapping by E/VA plays an important role. In order to confirm the presence of the trapping effect, overall positron mobilities were measured for some of the blend samples by observing the Doppler shift of the annihilation γ ray as a function of external electric field.[26] Results are listed in Table II. It is seen that the positron mobility is drastically reduced by the addition of a small amount of E/VA. As only minor structural changes are expected at such low E/VA concentrations, the rapid decline of the positron mobility can only be explained by immobilization of an increasing fraction of positrons at traps. In view of the very low positron mobilities in oxygen-containing polymers,[23] it is likely that the polar acetate group of E/VA captures mobile positrons, thereby increasing the number of the positrons that annihilate in the trapped state.

According to Tachiya,[27] the recombination probability P of an electron-positron pair in the presence of both an electric field and a positron trapping center is written as

$$P = 1 - \exp(-r_c/r)\{1 + (F^2 + \mu^2)^{1/2}\}. \tag{3}$$

The factors F and μ account for the effect of the electric field and that of the trapping, respectively. F is directly proportional to the field strength E

$$F = eEr_c/2kT, \tag{4}$$

whereas μ is proportional to the square root of the trap concentration C

$$\mu = (\kappa C/D)^{1/2}/r_c. \tag{5}$$

Here κ is the trapping rate constant and D is the diffusion coefficient. Equation (3) predicts that as far as $\mu \gg F$, P is independent of field strength, but at sufficiently high fields the trapping effect becomes negligible and P decreases with increasing field strength. This prediction is in qualitative agreement with the behavior of our sample containing 24% E/VA in Fig. 5, where the o-Ps yield stays nearly constant up to 10 kV/cm, beyond which it decreases. Since the factor μ is supposed to become larger with increasing E/VA concentration, Tachiya's equation can also explain the rapid decline of the field-dependent component in Fig. 7.

The fact that Tachiya's equation can nicely explain the results of the field dependence (see Figs. 5 and 7) signifies that the positron traps are rather well dispersed and the average domain size of the E/VA phase in most of the blends is smaller than the spur size characterized by the Onsager radius (19–24 nm). If the domain size exceeded the spur size, one should observe a superposition of the E/VA and polyethylene signals in Fig. 5 rather than the curve with the crossover for the 24% E/VA concentration.

Returning to the data in Fig. 6, the enhancement of the field-insensitive contribution (recorded at 50 kV/cm) with increase in the amount of E/VA may be related to the reduced crystallinity of the blend. We believe that this component is associated with electron-positron pairs with short initial separation r. The factor $\exp(-r_c/r)$ in Tachiya's equation should be small for such pairs and the recombination probability P is not much affected by the electric field or the positron trapping. This may be the reason why this component depends mainly on the crystallinity. Thus, a simple correlation between the crystallinity and the o-Ps intensity is expected only when the Ps formation occurs through thermalized electron-positron pairs with short initial separation.

So far, we have assumed that the o-Ps yields observed for the blends between polyethylene and E/VA can be separated into two components, one being sensitive and the other being insensitive to the electric fields as high as 50 kV/cm. The former component is related to Ps atoms formed from electron-positron pairs with large initial separation in the positron spur, whereas the latter component is related to those from pairs with short separation. However, the separation of the electron-positron pairs into only two components is obviously an oversimplification and some generalization will be required. In order to further develop the ideas presented in this paper, it is necessary to consider the distribution of the initial separation of the electron-positron pairs in the spur. The fact that even at a field of 50 kV/cm there is some electric-field dependence of I_3 for most of the samples in Fig. 5 suggests that such generalization may be necessary. It might be possible to extract the distribution of the initial separation of electron-positron pairs in polymers by precise measurements of the o-Ps yields as a function of the external electric field.

V. CONCLUSION

The addition of polar E/VA to polyethylene has two different effects on Ps formation. At low concentrations the o-Ps intensity is decreased, but at high concentrations it is increased by the addition of E/VA. The reduction of the o-Ps yield at low concentrations is due to the trapping of mobile positrons, which would otherwise combine with an electron to form Ps in the positron spur. On the other hand, the increased Ps formation at high E/VA concentrations may be ascribed to the reduction of the crystallinity. By assuming appropriate distributions in the initial separation of the electron-positron pairs in the spur, both of the effects can be rationalized within the framework of the spur reaction model, though this does not necessarily mean that it is the only mechanism of Ps formation. Finally it should be pointed out that the simple correlation between the crystallinity and the o-Ps intensity is expected only under certain conditions.

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