

Dynamic Study of Free Volume Properties in Polyethylene/Styrene Butadiene Rubber Blends by Positron Annihilation Lifetime Method

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Received 16 December 2008; accepted 13 January 2009

DOI 10.1002/app.30311

Published online 7 May 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Positronium (Ps) formation in low and high-density polyethylene (LDPE and HDPE) and styrene butadiene rubber (SBR), as well as in their blends (LDPE/SBR: 50/50 and HDPE/SBR: 50/50) has been investigated by positron annihilation lifetime (PAL) measurements as a function of low temperature (100–300 K). The glass transition temperature (T_g) for the initial polymers and their blends are determined by ortho-positronium (o-Ps) lifetime, τ_3 versus temperature as well as by differential scanning calorimetry (DSC) measurements. The temperature dependence of nanoscale free volume size shows similar trend for all the investigated samples indicating an abrupt change at T_g , which is found to be higher for SBR sample characterized by its high chain mobility. In addition, The T_g values deduced from PAL measurements are compared

with the corresponding data deduced from DSC. The variation of o-Ps formation probability I_3 versus temperature for polyethylene and their blends were interpreted in the frame work of spur reaction model of Ps formation. On the other hand, the lifetime coefficient below and above T_g is found to be one order of magnitude larger than the linear expansion coefficient. This constitutes evidence that Ps is only probing free volumes. The results obtained from change in free volume–hole distribution with temperature reflect both thermal expansion and increase in free volume–hole size with the rise in temperature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3228–3235, 2009

Key words: blends; differential scanning calorimeter; glass transition; polyethylene (PE); rubber

INTRODUCTION

In polymers, it is known that there are several secondary relaxation processes involving localized motion of side groups or short segments that persist even at low temperature. The onset of molecular motion of these segments arguably alters the free volume.¹ It is therefore interesting to examine the temperature behavior of free volume size and its concentration in polymers. At present, positron annihilation lifetime spectroscopy (PALS) becomes a powerful tool for the microstructural characterization of condensed matter.²

After entering a condensed matter, an energetic positron (e^+) is slowed down to thermal energy. At the end of the track, e^+ either annihilates directly with an electron or forms an intermediate state, a positronium atom (Ps). Ps is a hydrogen-like state and corresponds to the mutual spin orientations (antiparallel and parallel) of the consisting particles exists in two states called para-positronium (p-Ps) and ortho-positronium (o-Ps). The intrinsic lifetimes

of p-Ps and o-Ps in a vacuum are 0.125 ns and 142 ns, respectively. In polymers, the Ps is localized in a free volume hole, and the positron of o-Ps annihilates in some nanoseconds with an electron from the surrounding media (the so-called pick-off process)³. In pick-off annihilation, the positron in the o-Ps annihilates with an electron of opposite spin during collisions with molecules. The result is the emission of two 0.511 MeV electromagnetic photons rather than three and with significantly reduced o-Ps lifetime of $\tau_3 = \tau_{o-Ps} = 0.5\text{--}5$ ns. The Ps has been noted as a unique indicator of nanoholes (free volumes) in polymers. The o-Ps lifetime, τ_3 is related to the size of free volume holes. On the other hand, the o-Ps relative intensity I_3 being a measure of o-Ps formation probability is supposed to be proportional to the free volume–hole density. As a result, the PALS enables the study of free volume in polymers on a time scale for molecular motions slower than one nanosecond and the hole dimension greater as ~ 2 Å.⁴ Recently, PALS has been used to determine the free volume in multiblock polyamide-6/poly-(isoprene) copolymers synthesized via activated anionic bulk copolymerization.⁵

Miscibility of polymer blends that depends largely on the specific interactions between polymers has received significant attention in the polymer

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application.^{6,7} PALS is sensitive to small changes in free volume in polymer and polymer blends resulting from temperature changes and composition changes. Many studies about polymer blends by PAL were done to investigate correlation between miscibility and free volume properties.^{8–11} Some other studies were done to reveal the temperature dependence of free volume parameters in polymer or polymer blends.^{12–15} It proved that PAL method is a powerful tool to study glass transition and phase behavior of polymer blends.

The objects of our study are blends of pure low-density polyethylene (LDPE) and styrene butadiene rubber (SBR), LDPE/SBR, as well as of pure high-density polyethylene (HDPE) and SBR, HDPE/SBR. The processing of samples was described by Mohamed et al.⁶ Some of mechanical properties and miscibility of polymer blends are reported in the same article by calculating the heat of mixing as well as by using dielectric method. Our previous study¹⁰ confirmed the miscibility of the polymer blends with different concentration using PALS. In this work, the two blends with compositions polyethylene (PE)/SBR: 50/50 were studied using two experimental techniques; the differential scanning calorimetry (DSC) and PAL. The PAL measurements are reported for the two-system blends to investigate the changes in free volume size and concentration, as well as its probability distribution as a function of temperature.

EXPERIMENTAL

Materials

The investigated materials were supplied by Petrochemical Department Petroleum Research Institute, Nasr City, Cairo, Egypt. The virgin LDPE and HDPE have densities of 0.94 and 0.95 g/cm³ at 23°C, respectively. The nonpolar SBR (butadiene styrene copolymer with a styrene content of 23.5%). Peroxide (1, 3-bis (isopropyl) butyl benzene peroxide) on calcium carbonate; trade name Perkadox 14/40; molecular weight 338 was used in this work.

The melt mixing was carried out in a Brabander Plasticorder at 130°C and a rotor speed of 30 rpm. The mixing was continued for 5 min and then the peroxide was added to the mix on a laboratory two-roll mill (470 mm diameter; 300 mm working distance). The speed of the slow roll was 24 rev/min with a gear ratio of 1 : 1.4. The compounded blends were left overnight before vulcanization.

The vulcanization was carried out in a heated platen press under pressure of about 40 kg/cm² and a temperature of 172 ± 1°C. Details about the investigated materials were described earlier.⁶

LDPE, HDPE, and SBR and their blends, LDPE/SBR, and HDPE/SBR with weight percentage 50/50

were chosen for PAL and DSC measurements as a function of low temperatures from 100 to 300 K.

Differential scanning calorimetry (DSC) measurements

DSC has been applied for measuring the T_g values of the initial polymers and their blends, LDPE/SBR: 50/50 and HDPE/SBR: 50/50. DSC Seiko instrument EXSTAR 6000 connected to liquid nitrogen is used. Each sample was cooled from room temperature (RT) to -70°C at a rate of 10°C/min.

Positron annihilation lifetime measurements

Lifetime measurements were carried out by detecting the coincidences between the prompt γ -ray (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from ²²Na radioisotope and the annihilation electromagnetic ray (0.511 MeV) inside the material using a conventional fast-fast coincident lifetime spectrometer. A 30 μ Ci of ²²NaCl positron source, held between 7- μ m thick Kapton foils, was sandwiched between two identical pieces of each sample. The time resolution of the system is found to be 266 ps (FWHM). The source-sample assembly was fixed on the cooling finger of a closed cycle Helium cryostat (air cooled compressor model 8200). The cold head (model 22) of this cooling system includes design features optimized specifically for the positron annihilation measurements. The sample was cooled indirectly, using static helium exchange gas inside the sample chamber. This cooling system provides a sample temperature range of less than 10–300 K. The temperatures were controlled by a Lakeshore temperature controller (model 321), which could maintain the temperature of the samples to within 0.1 K. In model 321, the temperature was monitored by a silicon diode sensor positioned very close to the sample cell. The polymer sample is cooled down to a selected low temperature (lower than RT), and then the positron lifetime spectrum is recorded at a given temperature.

Positron lifetime spectra were accumulated to approximately one million counts. The analysis of PAL spectra were performed by the program PAT-FIT¹⁶ using two Gaussian resolution function and decomposed into three lifetime components. The shortest lifetime components, $\tau_1 = 0.125$ ns and I_1 (%) belongs to the annihilation of p-Ps atoms and its intensity, these decay via self annihilation and have no or only weak interaction with the environment. The intermediate component, $\tau_2 = 0.3$ – 0.39 ns and its intensity I_2 is mainly due to the positrons trapped in the defects present in the crystalline regions or trapped in the crystalline-amorphous interface regions. The longest-lived component, $\tau_3 =$

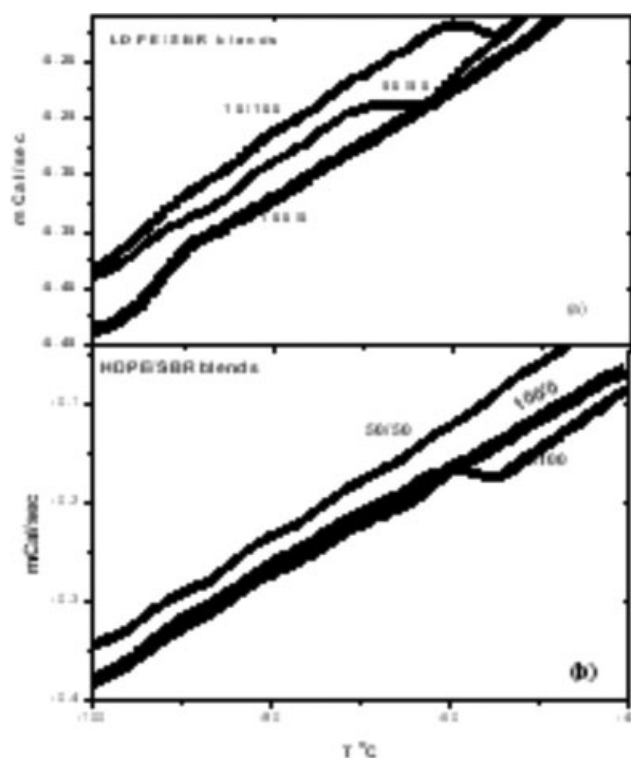


Figure 1 DSC thermogram for LDPE/SBR blends (a) and for HDPE/SBR blends (b).

1.3–2.7 ns and $I_3 = 11$ –35% is attributed to the o-Ps atoms in free volumes of amorphous regions of polymer via the pick-off annihilation.

According to the free volume model^{17,18} for positronium formation, the longest-lived component of the positron lifetime spectra, τ_3 and the correspondent o-Ps intensity, I_3 may be correlated with the mean radius and the relative number of the free volume cavity in the polymer material, respectively. According to this model, τ_3 should increase with increasing volume of the voids, and I_3 should increase with increasing number of the voids. In the free volume model, the o-Ps is confined in the spherical potential well and the lifetime of this species τ_3 is directly related to the free volume radius (R). Assuming that the annihilation rate of the o-Ps inside the electron layer of width ΔR at the internal

surface of V_f is 2 ns^{-1} , the size of the V_f can be estimated through the following equation:

$$(\tau_3)^{-1} = 2 \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right] \text{ns}^{-1} \quad (1)$$

And $V_f = 4\pi R^3/3$; R is the radius of voids in which the o-Ps survives, and $\Delta R = R_0 - R = 0.1656 \text{ nm}$.

Because the free volume hole are likely a distribution, the o-Ps lifetime is expressed as a distribution rather than as a discrete values. Computer program LT 9.0¹⁹ is used to allow log normal distribution of the long lifetime of annihilation rate $\lambda_3 = 1/\tau_3$. This was used to provide the free volume probability density function $V(pdf)$ versus free volume size V . Detailed descriptions in this regard can be found elsewhere.²⁰

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC) results

Figure 1(a,b) shows the DSC thermograms for LDPE/SBR: 50/50 and HDPE/SBR: 50/50 blends as well as their initial polymers. The determination of T_g using DSC technique may be not obvious, particularly for systems in which the crystalline phase is present.¹² T_g of HDPE/SBR: 50/50 blend is not as clear as that of LDPE/SBR: 50/50 blend, it means that the T_g in HDPE/SBR: 50/50 blend is obviously weakened by the high crystallinity of HDPE, which was found to be 87% for HDPE and 60% for LDPE.⁶ Apparently for HDPE, the micro-Brownian motion of large segments of the molecules in the amorphous regions is partly restricted by the microcrystalline regions around and the transitions occur in wider ranges of temperature. The T_g values of the initial polymers as well as of the polymer blends are deduced from DSC analysis and listed in Table I. The results showed single T_g for each blend indicating a single phase system, confirming miscibility between the two polymers.

TABLE I
Parameters a and b in Fitting Equation $\tau_3(T) = aT + b$, Glass Transition Temperatures Obtained from PALS and DSC measurements, and Differential Lifetimes Below and Above T_g for the Investigated Samples

Sample	$100 \text{ K} \leq T \leq T_g$		$T_g \leq T \leq 300 \text{ K}$		T_g PALS (K)	T_g DSC (K)	$\gamma_1 T < T_g$ (10^{-3} K^{-1})	$\gamma_2 T > T_g$ (10^{-3} K^{-1})
	$10^3 a$ (ns K ⁻¹)	b (ns)	$10^3 a$ (ns K ⁻¹)	b (ns)				
SBR	2.7	1.12	10.37	0.44	211 ± 0.5	218	1.729 ± 0.02	6.295 ± 0.04
LDPE	3.44	1.07	5.07	0.79	175 ± 0.5	180	2.183 ± 0.08	2.684 ± 0.03
HDPE	1.87	1.13	5.98	0.49	153 ± 0.5	164	1.353 ± 0.06	3.350 ± 0.03
LDPE/SBR	1.93	1.34	7.9	0.18	200 ± 0.5	210	1.168 ± 0.03	3.854 ± 0.06
HDPE/SBR	2.64	1.31	3.59	1.15	160 ± 0.5	173	1.586 ± 0.06	1.853 ± 0.03

The average errors of a and b are $5 \times 10^{-4} \text{ ns K}^{-1}$ and 0.07 ns, respectively.

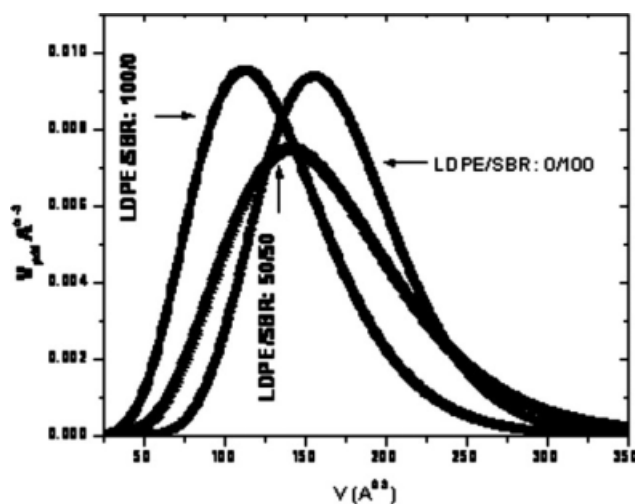


Figure 2 Variation of free volume size distribution in LDPE/SBR blends.

Free volume–hole distribution in initial polymers and their blends

Because of the heterogeneity of local molecular structure in a polymer and the existence of different positron states, it has been proposed that the experimental lifetime spectrum should contain an integral of continuous decay functions. The results of the free volume probability density function, $V(pdf)$ for LDPE/SBR: 50/50 as well as HDPE/SBR: 50/50 and their initial polymers at RT are shown in Figures 2 and 3, respectively. From the figures, it is observed that free volume distribution of the cavities related to the free spaces inter- and intramolecular chains for LDPE/SBR: 50/50 and HDPE/SBR: 50/50 blends are Gaussian-like distribution lies in between those of the initial polymers, which confirm the miscibility of the two polymer blends in the molecular level. In addition, SBR has a larger distribution peak value of free volume than PE indicating the more elastic chain. This is due to the presence of 3π electrons in the benzene ring which create more spaces and increase free volume and its concentration in rubber. The free volume in SBR could accommodate the PE to fit into the spaces available and form an interaction between them making the blend miscible. This could be attributed to that PE behaves as the fiber-forming phase while SBR behaves as the matrix.¹⁰

One can observe from Figure 2 that in LDPE/SBR: 50/50 blends the free volume size distribution is wider and has lower probability distribution function than the initial polymers. The free volumes are aggregates near chain ends when the elastic chains of SBR interact to the free volumes due to LDPE and there is less free the movements of longer back bone chain in the polymer blends. Similar results are obtained by Hong-Ling et al.,²¹ when they studied the temperature dependence of polystyrene-polyph-

nylene ether blends. On the other hand, the distribution in the HDPE/SBR: 50/50 blend is narrower and shifted to a lower free volume value (keeping the profile of the distribution or FWHM) than that in LDPE/SBR: 50/50 blend. This shift may be due to the increase in the degree of crystallinity. This increase in crystallinity of HDPE restricts the motion of large segments of the molecules in the amorphous regions leading to decrease the free volume values. The similarity in free volume size distribution of HDPE/SBR: 50/50 blend to that of initial polymers (Fig. 3) suggests that the movement of most of elastic chains of SBR is controlled so as not to disturb the chain ends of HDPE due to its high crystallinity.

Change of the size and concentration of free volume with temperature

The variations of free volume parameters, o-Ps lifetime τ_3 , and its intensity I_3 in LDPE, LDPE/SBR: 50/50, and SBR as well as HDPE, HDPE/SBR: 50/50, and HDPE as a function of temperature are shown in Figures 4–7. The shape of τ_3 temperature dependence is similar for the two blends and their initial polymers although for HDPE it is shifted to lower temperature and saturates at lower lifetimes due to its higher crystallinity. It is observed from the figures that τ_3 and I_3 are found to strongly influence by changing of temperature. The o-Ps atoms localized in amorphous regions, will most probably reside in free volumes. Thermal expansion of free volumes will be present due to the increase in temperature which in turn leading to an increase in o-Ps lifetime, τ_3 . From the onset of the abrupt change in τ_3 showing an inflection points have been observed at 175, 200, and 211 K for LDPE, LDPE/SBR: 50/50, and SBR, as well as at 153, 160, and 211 K for HDPE, HDPE/SBR: 50/50, and SBR, respectively, which

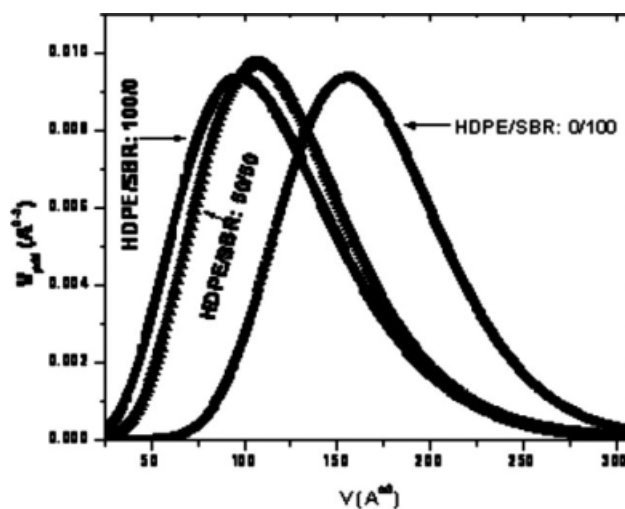


Figure 3 Variation of free volume size distribution in HDPE/SBR blends.

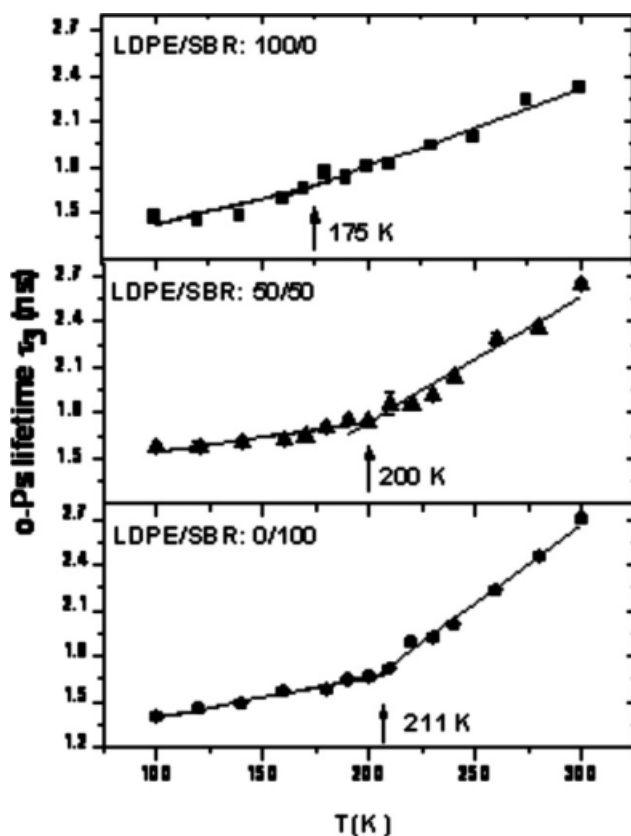


Figure 4 Variation of τ_3 as a function of temperature in LDPE/SBR blends. The smooth lines through the data points represent least square fits of linear functions to the experimental data points. The point at which the two straight line segments intersect marks T_g .

attributed to the phase change occurring at $T = T_g$. It is certain that the values of T_g increase with the increase of SBR content and that each blend has only one T_g lies in between the two initial polymers, so it is further proved that the two blends are miscible in molecular level.

Two distinct variations of τ_3 with temperature is observed, a weaker variation below T_g and a stronger variation above T_g , as well as a steepest change in τ_3 with respect to temperature occur near T_g . For simplicity we approximate each $\tau_3(T)$ curve with two straight lines. Thus, relaxation temperatures can be obtained from the inflection points of the two neighboring lines. Using the straight line equation $\tau_3(T) = aT + b$, the glass transition temperature, T_g (corresponding to the onset of correlating main-chain segmental motions) were determined by means of the least-squares method. T_g values and the values of a and b both below and above T_g , thus deduced for all samples are listed in Table I. From the table, the dissimilar values of a and b among different samples imply that the addition of SBR to PE changes the free volume size significantly. In addition, positive slopes are obtained through the tem-

perature range (100–300 K) indicating thermal expansion of free volume size in initial polymers and in polymer blends. Similar results are obtained in measuring lifetime spectra for series of polymer blends between PE and ethylene-vinyl acetate as a function of temperature and composition.¹²

Below T_g , the side-chain motion begins and this is the region of preglass transition in polymers.²² The motion is mainly on a single chain segment leading to rotation of small parts of the molecules containing several carbon-carbon links. This motion is possible even below T_g . When the temperature increases above T_g , the long chain segments and molecules all participate in the motion owing to thermal activation and the matrix becomes rubbery. This will consequently be result in an increase in the size and concentration of free volume.

The intensity, I_3 is proportional to the number of places suitable for o-Ps atoms and depends on the Ps formation probability. One can notice from Figures 5 and 7 that there are onset temperatures at T_g for all samples. There are large variations in I_3 along the whole range of temperature for PE and their blends, which are obviously observed in HDPE due to its higher crystallinity. I_3 shows an increase at low temperature below T_g (from 100 to 150 K for LDPE and from 100 to 120 K for HDPE), whereas a reduction in I_3 below and above T_g and then a rapid

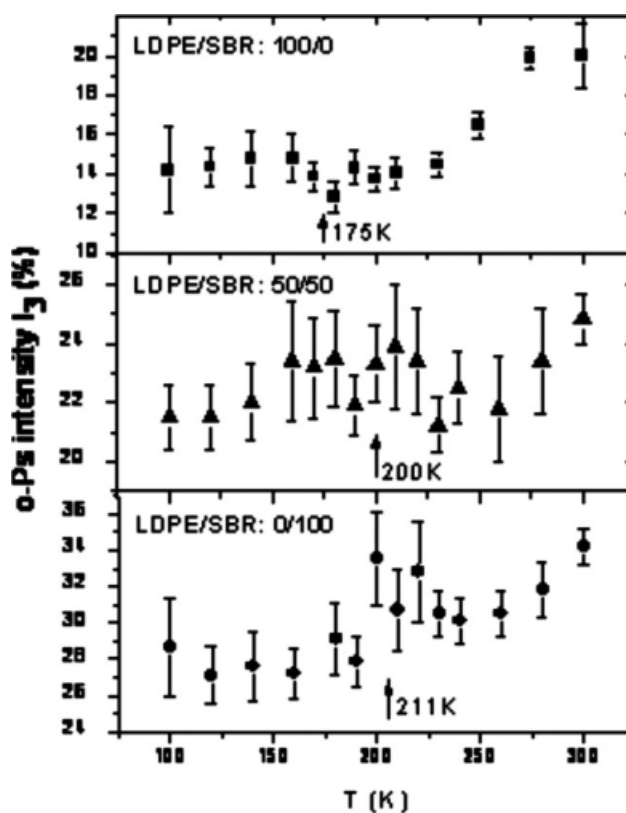


Figure 5 Variation of I_3 as a function of temperature in LDPE/SBR blends.

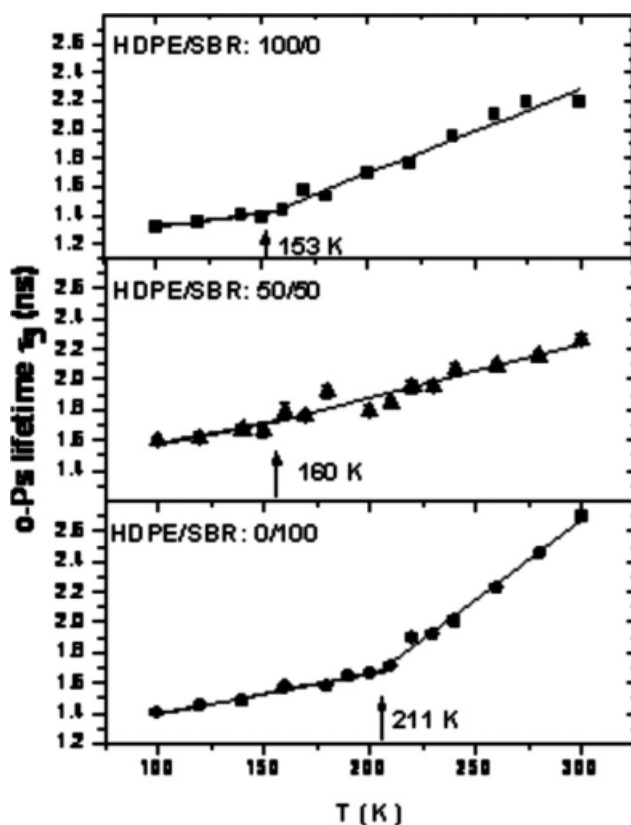


Figure 6 Variation of τ_3 as a function of temperature in HDPE/SBR blends. The smooth lines through the data points represent least square fits of linear functions to the experimental data points. The point at which the two straight line segments intersect marks T_g .

increase is observed above $T = 240$ K for all samples. Similar behavior of I_3 with temperature was observed before in LDPE.¹² These results can be interpreted in the frame work of spur reaction model.²³ According to this model, the Ps formation process is correlated to various radiation chemical effects. At low temperatures, it was shown that electrons generated in polymers by γ -irradiation are localized in shallow traps, which may exist in the chain-fold regions of the polymers.²⁴ Similar localized electrons may be produced by positron irradiation with their concentration gradually increasing with increasing positron irradiation time.²⁵ As a result, the number of electrons available for Ps formation is increased. These localized electrons are responsible for the enhanced Ps formation leading to an increase in I_3 during the low-temperature range (100–150 K for LDPE and 100–120 K for HDPE). As the temperature is increased, the localized electrons may disappeared due to the onset of the short side branch motion of polymer chains,²⁴ leading to a reduction in I_3 below T_g (at $T = 170$ K for LDPE and at $T = 140$ K for HDPE).

The saturation of I_3 in LDPE through the temperature range $T = 180$ – 230 K may be attributed to the

formation of positron traps due to positron irradiation resulting from the enhanced local molecular motion. The positron that would otherwise combine with an electron to form Ps may be captured by these traps and Ps formation is suppressed.²⁶

On the other hand, the valley of I_3 observed in HDPE at $T = 240$ (above T_g) can be attributed to the presence of crystalline region in the semicrystalline HDPE polymer. It has been confirmed that in γ -irradiated crystallized PE a high concentration of free radicals are present until the temperature reaches 330 K about 80 K below the melting point.²⁷ 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. 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.

With further increase in temperature a significant jump in I_3 at $T > 240$ K for all samples due to the increase in probability of o-Ps formation, where the thermal expansion above T_g has introduced new free volume voids. The observed weakening of the positron irradiation effects in PE upon the addition of SBR in blends is related to the positron trapping on the spaces created by three π electrons in the

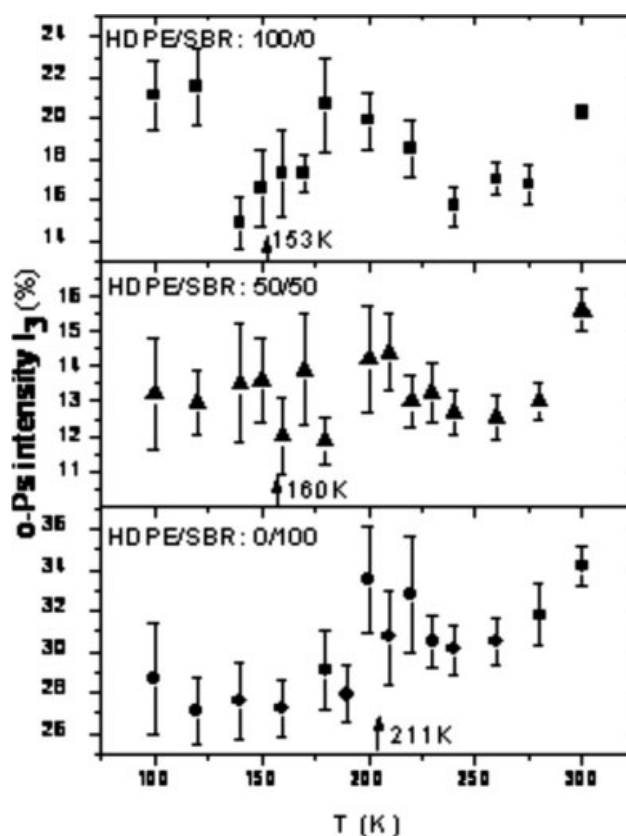


Figure 7 Variation of I_3 as a function of temperature in HDPE/SBR blends.

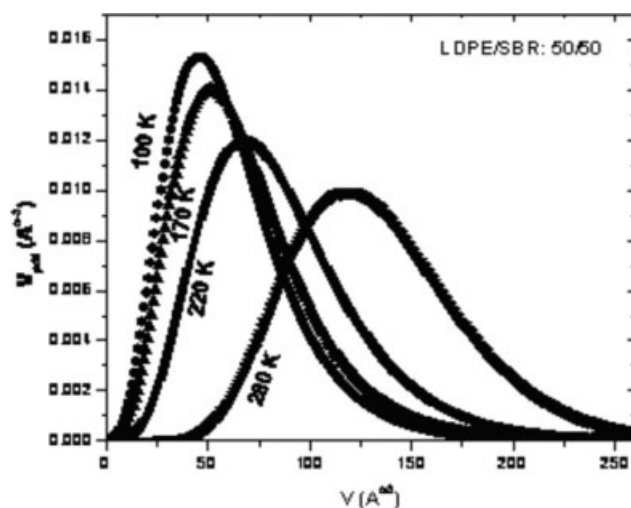


Figure 8 Variation of free volume size distribution as a function of temperature in LDPE/SBR: 50/50 blend.

benzene ring in SBR. However, for amorphous polymers such as SBR, positron irradiation does not affect I_3 . On the other hand, it observed the values of I_3 in HDPE/SBR: 50/50 blend is reduced by about 15% than the values in LDPE/SBR: 50/50 blend through the whole range of temperature. This decrease is due to the higher crystallinity of HDPE in the blend, which hinders the o-Ps formation probability in the blend.¹⁰

Table I lists a comparison of the values of T_g obtained from DSC and PAL measurements. We notice that T_g obtained by PAL is found to be a few degrees (from 5 to 13°C) less than that obtained by DSC. This is due to the duration of measurement by PAL takes hours or even a day, whereas the DSC analysis takes significantly less time (few minutes). This difference in time will affect the molecular structure of polymers leading to the relaxation of molecular chains. This effect is similar to a sub- T_g annealing occurring during the performance of the PAL experiment. The second effect may be due to the trapping of Ps atoms in voids, which possess kinetic energy, causing local heating of Ps on the surfaces of these voids.²² Ps possesses 6.8 eV of binding energy and a size of 1.06 Å³. When Ps is localized in a hole at atomic size of a few Å³, its dynamic motion may disturb the local electronic properties by raising the local temperature above the bulk temperature. This is commonly called a local heating effect, which may lead to a lower T_g than the actual T_g of the bulk.

To analyze transition points more clearly, we deduced the differential lifetime with respect to temperature for all samples, $\gamma = \frac{d\tau_3}{dT} / \tau_3$, where τ_3 is the mean lifetime between two adjacent temperatures. Values of γ both above and below T_g for all samples are listed in Table I. We found that the expansion coefficient of free volume represented by the coeffi-

cient γ is found to be of the order 10^{-3} K^{-1} , which is one order of magnitude larger than the thermal linear expansion coefficient of polymers α_f , which are known to be of the order of 10^{-4} K^{-1} .²⁸ This is a strong evidence of Ps trapping in free volume sites. From the table, it is interesting to observe a decrease of γ in the Glassy state but an increase of γ in the rubbery state.

Change of free volume–hole distribution with temperature

The free volume distributions for the LDPE/SBR: 50/50 and HDPE/SBR: 50/50 blends obtained on the basis of probability density function of the o-Ps lifetime are given at four temperatures (100, 170, 220, and 280 K) and shown in Figures 8 and 9, respectively. One can observe from the figures that the higher the temperature, the bigger free volume values, that is the value peak of distribution shifts toward higher value, and the distribution becomes extremely broad. Similar broadening of the distributions and systematic shift of the position of the maximum of distributions toward higher free volume values with rising temperature are observed also in the initial polymers (LDPE, HDPE, and SBR). These results reflect both the thermal expansion and the increase in the mean squared fluctuations in free volume size with the rise in temperature. Similar results are obtained by Deowska et al.²⁹ when they examined semicrystalline polyamide/acrylic rubber blend. Also, the results obtained by Hong-Ling et al.²¹ showed that the size distribution of free volume for polystyrene-polyphenylene ether blends shift to the bigger side, keeping the profile of the distribution by the elevation of temperature. Our experimental results reveal that the mean free volume–hole size and the free volume–hole size distribution

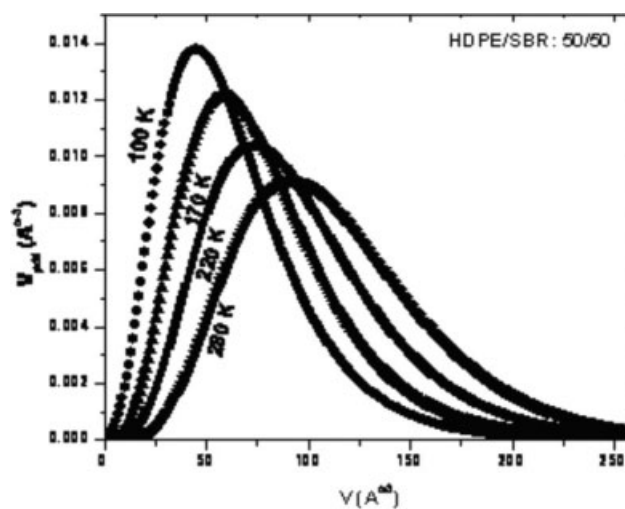


Figure 9 Variation of free volume size distribution as a function of temperature in HDPE/SBR: 50/50 blend.

are changed even if the initial polymers and their blends are in their Glassy state.

CONCLUSIONS

- From the effect of temperature on free volume properties in LDPE, HDPE, SBR, and their blends one can conclude that:
- Significant increase of o-Ps lifetime τ_3 with temperature is observed by PAL technique in the range from 100 to 300 K indicating expansion of nanoscale free volume size in the initial samples and their blends.
- Both PAL and DSC results for the blends showed one clear glass transition temperature of a single phase system confirmed the miscibility.
- The values of T_g deduced from PAL are found to be smaller than the ones determined by DSC by about 4%. This could be attributed to the time duration of the two techniques and to the heating effect of Ps on void surfaces.
- The higher crystallinity of HDPE leads to Ps inhibition results in shifting free volume probability distribution to smaller values and reducing in free volume concentration by about 15% in HDPE/SBR: 50/50 blend than that in LDPE/SBR: 50/50 blend.
- o-Ps formation probability I_3 for PE and their blends were interpreted in the frame work of spur reaction model of Ps formation according to the effects of localized electrons and trapping centers produced by positron irradiation.
- The differential lifetime γ for all samples is found to be one order of magnitude higher than the thermal linear expansion coefficient α_f . This is strong evidence that Ps is only probing free volume.
- A thermal expansion and an increase free volume size distribution are obtained with increasing in temperature in all samples.

The authors thank D. M. Mohamed (Petrochemical Department, Petroleum Research Institute, Nasr City, Cairo, Egypt) for the preparation of blends.

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