Local Free Volume in Ethylene−Vinyl Acetate Copolymers: A Positron Lifetime Study

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ABSTRACT: We report on the local free-volume properties in a series of commercial ethylene−vinyl acetate (EVA) copolymers ranging from PE to PVA, obtained via positron lifetime spectroscopy. The samples were characterized by DMA (dynamic mechanical analysis), DSC (differential scanning calorimetry), WAXS (wide-angle x-ray scattering), and density measurements. For the analysis of the lifetime spectra, the routines MELT (maximum entropy for lifetime analysis) and LIFSPECFIT were used. Three or four lifetimes are resolved, depending on the composition of the specimen. The longest lifetime is attributed to *o*-Ps (positronium) annihilation from free-volume holes of the amorphous phase and is used to estimate the mean volume, v, of these holes. By using crystallinity data (DSC, WAXS), the specific volume of the amorphous phase V_a is estimated from the experimental total specific volume. By assuming a linear superposition of the specific bulk volumes V_b of PE (polyethylene) and PVA (polyvinyl acetate), the fractional (free) hole volume $h = (V_a - V_b)/V_a$ in EVA (ethylene−vinyl acetate) copolymers is estimated. We find that v and h remain constant for VA contents between 0 and ~45% and decrease thereafter linearly down to the values for PVA. This behavior correlates well with the nonclassical (constant) behavior of T_β (DMA) and T_g (DSC), which is attributed to a correlation between the crystallinity and the chemical and physical structure of the amorphous phase. For higher concentrations of VA, T_β and T_g increase linearly with increasing VA content. From the relation $N = h/v$, a number density of holes of $N = 0.67 \pm 0.05$ nm^{-3} was estimated, which does not change with composition of EVA copolymers.

Introduction

The free-volume concept is central in the interpretation of many properties of polymeric materials.[1−3] It was introduced to explain the molecular motion and physical behavior of glassy and liquid states. Its implementation as a quantitative measure of the structural disorder in polymers is, however, a challenging problem. Several investigations have explored the possibility of employing spectroscopic techniques to directly probe the free volume in polymeric materials.[4] Positron annihilation lifetime spectroscopy has been developed as probably the most successful technique for studying local free volumes.[5−9]

Positrons emitted from radioactive sources such as ^{22}Na into the polymeric matrix become thermalized and may annihilate with an electron or form positronium (Ps), a hydrogen-like bound state.[10] Although *para*-positronium (*p*-Ps) decays quickly via self-annihilation, the long-lived species *ortho*-positronium (*o*-Ps) undergoes pick-off annihilation during collision with molecules. *o*-Ps preferentially annihilates from regions of low atomic density (i.e., a "hole"). The pick-off lifetime is strongly sensitive to the local free volumes of typical dimensions between 0.3 and 1 nm.[5−8]

Here, we study the free volume characteristics in a series of commercial copolymers containing different concentrations of ethylene $-CH_2-CH_2-$ and vinyl acetate $-CH_2-CH(OCOCH_3)-$ units. The ethylene−vinyl acetate (EVA) copolymers are of commercial importance, but due to their multiphase character, the relationships between their structural, physical, and thermal properties are not yet clearly established.[11−15] Positron lifetime spectra of high statistical precision are analyzed using both the discrete-term analysis (routine LIFSPECFIT[16]) and the routine MELT (maximum entropy for lifetime analysis[17]), which assumes a continuous lifetime distribution. From the lifetime parameters, we assess the size of free-volume holes in the amorphous phase and discuss their properties in relation to the glass transition temperature and the specific volume of the amorphous phase. To aid the interpretation of our results, we also characterized the polymers using differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), dynamic mechanical analysis (DMA), and measurements of the mass density ρ.

Experimental Section

Polymers. The EVA copolymers under investigation were commercial products obtained from different companies. EVA copolymers with 3, 5, and 18 wt % vinyl acetate (Lupolen series) were supplied by BASF and one with 24 wt % (Miravithen D24) by Leuna AG. All other products (40, 50, 60, 70, and 80 wt % vinyl acetate, Levapren series) came from Bayer AG. As boundary systems, low-density polyethylene provided by the Buna Company (also previously investigated by our group[18]) and polyvinyl acetate (PVA) made by Hoechst (all Germany) were studied.

Polymer Characterization. For DSC measurements, a heat flux calorimeter DSC 820 (Mettler-Toledo) calibrated with indium and zinc was used. The experiments were performed in the temperature range from 150 to 410 K at a scan rate of 10 K/min. The degree of crystallinity of EVA copolymers was calculated from $X_{cr} = \Delta H/\Delta H_0$, where ΔH is the measured melting enthalpy of EVA copolymers and ΔH_0 is equilibrium

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melting enthalpy of a pure crystal of PE and is taken to be equal to 293 J/g.[19] The glass-transition temperature T_g was estimated as the midpoint of the corresponding stage in the exothermic heat flow curves.

The WAXS investigations were carried out on a diffractometer URD 6 (Freiberger Präzisionsmechanik) (see Androsch et al.[20] for more details). Scattering patterns were obtained with Ni-filtered Cu Kα radiation in reflection mode detected by a scintillation counter. From the scattering diagram, the crystallinity X_{cr} was determined as a ratio of the (integrated) crystalline intensity to the total intensity of the diffraction peak, $X_{cr} = I_{cr}/(I_{cr} + I_{am})$, using the method of Hermans and Weidinger.[21] In the analysis, we assumed a multiple Gaussian intensity distribution for the crystalline peaks and a single Gaussian for the scattering intensity from the amorphous phase. Effects due to thermal vibrations, lattice imperfections, and wavelength-dependent Compton scattering[22] were assumed to be negligible. Further, we interpreted the data in terms of a simple two-phase model (PE crystals, EVA amorphous phase: see below) and ignored the possible occurrence of a third, interfacial phase.[23] The crystallinities estimated from DSC and WAXS experiments under these assumptions, therefore, are not absolute quantities. However, their values are of sufficient accuracy for the purpose of comparison in this work.

DMA investigations were performed on a system MARK IIIE, supplied by Rheometric Scientific. The measurements were carried out in tensile mode at a frequency of 1 cycle/s and constant heating rate of 2 K/min. The temperature was varied between 170 and 400 K. The β-transition temperature T_β was determined as the maximum of the tan δ peak of the β-process.[13]

The density ρ of the polymers at 25 °C was determined by a flotation method using mixtures of methanol and water for $\rho < 1$ and solutions of $CaCl_2$ in water for $\rho > 1$ as the flotation media. For each of the various copolymers, several samples were measured in order to ascertain that they were free of voids.

Positron Lifetime Experiments. The positron lifetime experiments were carried out at room temperature using a fast−fast coincidence system[10] with a time resolution of 235 ps (full width at half-maximum, fwhm, of a Gaussian resolution function) and a channel width of 12.6 ps. The specimens were platelets of 8 × 8 mm^2 in area and 1.5 mm in thickness. For each experiment, two identical samples were sandwiched around a 1×10^6 Bq positron source (^{22}Na), prepared by evaporating carrier-free ^{22}NaCl solution on a Kapton foil of 8 μm thickness. Well-annealed aluminum platelets ($\tau_{Al} = 162$ ps) were studied as a reference material for estimating the resolution fwhm and the positron source correction. Thirty-five measurements, each lasting 1200 s, were performed for each of the specimens. In a preliminary inspection, the time-zero of each 1200 s spectrum was determined. The counts of those spectra where the time-zero did not differ by more than 1 channel were summed to give the total spectrum, in each case, containing $\sim 25 \times 10^6$ coincidence counts. For the final analysis, the counts in four consecutive channels were summed to improve statistical accuracy.

Lifetime Spectra Analysis. The positron lifetime spectrum is conventionally described by a sum of discrete exponentials,[10]

$$s(t) = \sum_i (I_i/\tau_i) \exp[(-t/\tau_i)] \tag{1}$$

each with a characteristic positron lifetime of τ_i with a relative intensity of I_i ($\sum_i I_i = 1$). If the real positron lifetime values are assumed to consist of a wider continuous distribution rather than the discrete nature considered above, the lifetime spectrum may be described by a continuous decay of the following form:

$$s(t) = \int_0^\infty (1/\tau) I(\tau) \exp(-t/\tau)\, d\tau \tag{2}$$

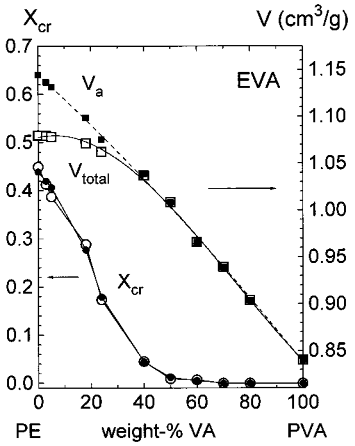

Figure 1. Specific volume of the amorphous phase, V_a (filled squares), as a function of the VA content in EVA copolymers. V_a was estimated from the total specific volume V_{total} (empty squares) using the crystallinity X_{cr} estimated from the average of DSC (filled circles) and WAXS data (open circles).

where $\int_0^\infty I(\tau)\, d\tau = 1$. The observed spectrum may then be expressed by

$$y(t) = R(t) \otimes (N_t s(t) + B) \tag{3}$$

where ⊗ denotes a convolution of the decay integral with the resolution function $R(t)$ (a Gaussian) and B and N_t are the background and the total counts in the spectrum, respectively.

For the discrete-term analysis, we used the routine LIFSPECFIT.[16] In this routine, the model function (eq 1) together with eq 3 is least-squares fitted to the experimental data points. From the fit, the characteristic lifetimes τ_i and their intensities I_i are obtained. The routine MELT[17] inverts the lifetime spectrum into a continuous lifetime distribution $I(\tau)$ (eq 2) using a quantified maximum entropy method. The details on the choice of parameters used in this analysis are to be found in previous papers.[24] For comparison, analysis of the continuous lifetime distributions were also carried out with the standard routine CONTIN-PALS2.[25] Although, the results from CONTIN are almost the same as those obtained via MELT, due to the greater sensitivity of the MELT program to closely spaced lifetime distributions,[24] we shall only discuss the results from the MELT analysis.

Results

Polymer Characterization. The crystallinities X_{cr} obtained from DSC and WAXS investigations of the EVA copolymers are plotted in Figure 1 as a function of the VA comonomer content. The estimates from DSC and WAXS investigations agree very well with each other. In pure LDPE, the crystallinity amounts to ∼45%. It decreases approximately linearly with increasing content of vinyl acetate comonomer and disappears between 40 and 50% VA. These results also agree well with those published in the literature.[11−14]

The density of the copolymers varied from $\rho = 0.9263$ ($\pm$ 0.0005) g/cm^3 for pure LDPE to 1.189 g/cm^3 in PVA, in agreement with the literature.[26−28] This corresponds to a variation in the specific volume from $V = 1/\rho = 1.0796$ ($\pm$0.0005) to 0.8410 cm^3/g (Figure 1). We take the crystallinity estimated from the average of DSC and WAXS data as mass crystallinity, X_m, and use this to calculate the specific volume of the amorphous phase, V_a, from the total specific volume V via[27]

$$V_a = (V - X_m V_c)/(1 - X_m) \tag{4}$$

In these calculations, we assumed that the specific

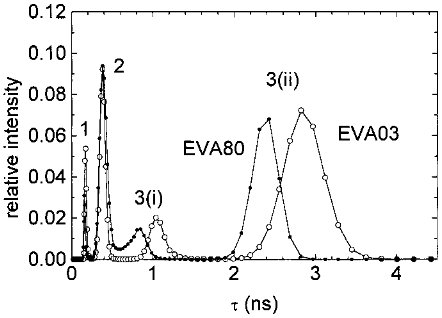

Figure 2. Positron lifetime intensity distribution $I(\tau)$ analyzed with the MELT routine from the lifetime spectra of EVA03 and EVA80.

volume of the crystalline phase in EVA copolymers is identical to that of pure PE, $V_c = 1/\rho_c = 1$ cm^3/g (see below). However, the X-ray diffraction peaks of the (200) and (110) crystalline lattice planes showed small variations from which an increase in the specific volume V_c by approximately 3% between pure PE and EVA copolymer with 24% VA can be estimated. Because this increase practically does not affect the values of V_a, it was ignored in estimation. The results of our estimated V_a, as well as the total specific volume, $V = V_{\text{total}}$, are plotted in Figure 1. Our estimated value for the specific volume for PE, $V_a = 1.145$ cm^3/g, is slightly smaller than the commonly accepted value[26−28] of $1/\rho_a = 1/0.855 = 1.170$ cm^3/g. The experimental data for the total specific volume V fit a polynomial curve of third degree (Figure 1),

$$V\,(\text{cm}^3/\text{g}) = 1.0775 + 6.6377 \times 10^{-4}c - 5.5218 \times 10^{-5}c^2 + 2.4783 \times 10^{-7}c^3 \quad (5)$$

with a correlation coefficient of $r^2 = 0.9984$, where c is the VA content (by weight percent). A parabolic curve is sufficient to fit the data well for the specific volume of the amorphous phase,

$$V_a\,(\text{cm}^3/\text{g}) = 1.1445 - 2.6037 \times 10^{-3}c - 4.6753 \times 10^{-6}c^2 \quad (6)$$

The correlation coefficient of the fit was $r^2 = 0.9988$.

The relaxation temperature, T_β, estimated from our DMA experiments is plotted in Figure 5 (see next section) together with T_g and hole characteristics obtained from positron data. T_β stays constant at approximately 250 K until a VA content of 60% is reached. At higher concentrations, it increases linearly to the value of 312 K for PVA, in agreement with the literature.[13,14] It was found that the trace of the first DSC heating run contained up to three exothermic peaks. However, the middle peak disappeared in the second heating run. The higher temperature peak is attributed to crystal melting. Its maximum decreases from 381 K in EVA03 to 323 K in EVA40, with the peak disappearing for higher VA contents. A lower exothermic step, resolved for VA contents of 18% and more, can be attributed to the glass transition as sensed in DSC experiments.[11−15] Its midpoint temperature, (T_g) is lower than T_β by 5−15 K but behaves otherwise like T_β (Figure 5).

Positron Lifetime Parameters in EVA Copolymers. Figure 2 shows examples of the lifetime distributions $I(\tau)$ obtained from the MELT analysis of the lifetime spectra for EVA03 and EVA80. The lifetime distribution exhibits four well-separated peaks. The characteristic lifetime, τ_i, of each peak is calculated from its mass center, and its intensity, I_i, is calculated from the relative area below the corresponding peak. The two lower peaks have mass centers at $\tau_1 = 160$ ps and $\tau_2 = 380$ ps. These lifetimes are well-known and arise from *p*-Ps self-annihilation and free positron (not Ps) annihilation.[10]

The third ($\tau_{3(\text{I})} \approx 1$ ns) and fourth ($\tau_{3(\text{II})} \approx 2-3$ ns) lifetime peaks must be attributed to *o*-Ps annihilation. In a vacuum, *o*-Ps lives 142 ns and decays via emission of three γ-photons.[10] In matter, the so-called pick-off annihilation occurs, in which the positron of the Ps annihilates with an electron of opposite spin compared to its bound partner, during a collision with a molecule. The results are the emission of two 0.51 MeV γ-photons rather than three and a much reduced *o*-Ps lifetime depending on the frequency of collisions. In the presence of a sufficient concentration of small cavities in the sample, the Ps density is largely confined within these open volumes, and their extent is reflected in the *o*-Ps pick-off lifetimes being in the nanosecond range. From this, it follows that the *o*-Ps lifetimes respond to material properties (hole size,[5,7,8] packing density[6]), whereas the *p*-Ps and the free positron annihilation do not or only weakly respond.

The third lifetime $\tau_{3(\text{I})}$ appearing in LDPE is attributed (according to our previous work[18]) to *o*-Ps annihilation in the crystalline phase of the semicrystalline polymers. Our DSC and WAXS measurements for ethylene copolymers containing more than ∼45% VA comonomer do not show a detectable crystalline fraction. Nevertheless, we observe the third lifetime, although reduced in lifetime and intensity, even in these EVA copolymers. It is difficult to interpret the appearance of two different *o*-Ps states in single-phase amorphous polymers. One could envisage a bimodal hole size distribution in EVA copolymers. One type of hole may occur near ethylene sites (or ethylene-enriched regions) and the second type, due to the bulky $OCOCH_3$ groups, at vinyl acetate sites. *o*-Ps lifetimes of 1.8 and 2.0 ns were determined at the glass-transition temperature for LDPE[18] ($T_g = 195$ K) and PVA[29,30] ($T_g = 305$ K). The lower *o*-Ps lifetime of $\tau_{3(\text{I})} \approx 1$ ns, however, appears too small to be attributed to holes in an amorphous phase. In PE of different crystallinity, we observed *o*-Ps lifetimes at room temperature between 2.5 and 2.9 ns, attributed to the amorphous phase. In a previous paper,[24] we have argued in detail that a single but broad *o*-Ps lifetime distribution may also lead to a two-peak structure observed in the *o*-Ps distribution analyzed via MELT (and via CONTIN). These analysis routines are not able to reproduce very broad (fwhm of about 1 ns) lifetime distributions but deliver two artificial subpeaks. From this, it follows that it is not entirely clear whether the lower *o*-Ps lifetime $\tau_{3(\text{I})}$ has a physical relevance or is an artifact of the spectrum analysis.

In the following, we compare the results obtained via the MELT routine with those from LIFSPECFIT, assuming four and three discrete lifetime terms. The lifetime parameters for EVA copolymers estimated via MELT (filled circles) are plotted in Figure 3. τ_1 and τ_2 exhibit a slight increase from 150 to 160 ps and from 360 to 400 ps, whereas $\tau_{3(\text{I})}$ fluctuates between 800 and 1000 ps. The intensities of these lifetimes show a random fluctuation in the range $I_1 = 10-16\%$, $I_2 = 41-52\%$, and $I_{3(\text{I})} = 9-14\%$. The longer *o*-Ps lifetime $\tau_{3(\text{II})}$

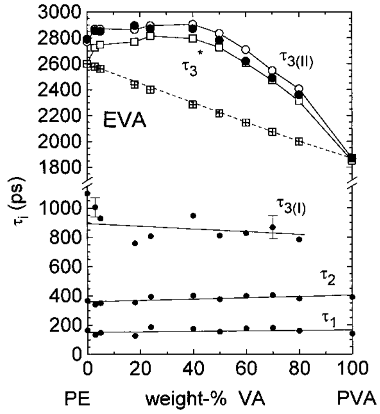

Figure 3. Characteristic positron lifetimes τ_i in ethylene–vinyl acetate copolymers as a function of the content of vinyl acetate. Filled circles: mass centers τ_1, τ_2, $\tau_{3(I)}$ and $\tau_{3(II)}$ of the four peaks in the lifetime distribution obtained from MELT. Empty circles: $\tau_{3(II)}$ obtained from the unconstrained four discrete-term analysis (LIFSPECFIT). Empty squares: τ_3* obtained from the unconstrained three discrete-term analysis. Cross-centered squares: τ_3* obtained from the analysis of simulated spectra for the copolymers, synthesized (see text) from the spectra for the individual constituents. If not indicated, the statistical error of the data is not larger than the size of the data points.

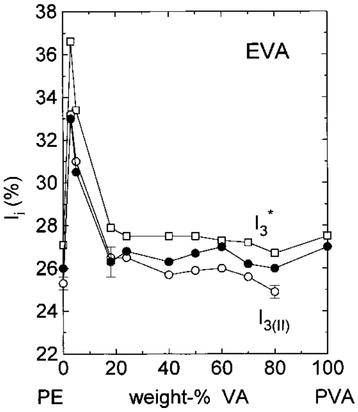

Figure 4. Intensities I_i of various *o*-Ps lifetime components. Filled circles: intensity $I_{3(II)}$ of the fourth peak in the MELT lifetime distribution. Empty circles: $I_{3(II)}$ obtained from a four-component LIFSPECFIT analysis. Empty squares: I_3* obtained from a three-component LIFSPECFIT analysis.

shows an increase from 2780 to 2870 ps when going from LDPE to EVA03. Between EVA03 and EVA40, $\tau_{3(II)}$ stays at this level followed by a distinct decrease. The intensity $I_{3(II)}$ has a small but very pronounced maximum around EVA03 and EVA 05 but is almost constant above a VA concentration of 18% (Figure 4).The longer of the *o*-Ps lifetimes, $\tau_{3(II)}$, obtained from the four-discrete term analysis (LIFSPECFIT), is shown in Figure 3 as open circles. From the three-discrete term analysis (denoted by *), we obtained the parameters τ_1* = 185–230 ps, τ_2* = 430–500 ps, I_1* = 25–37%, and I_2* = 35–50%. The single *o*-Ps lifetime τ_3* (open squares in Figure 3) is smaller than that of $\tau_{3(II)}$ by 100–200 ps, but otherwise behaves like $\tau_{3(II)}$. In correlation to this, I_3* is larger than $I_{3(II)}$, but their relative difference remain roughly constant throughout the composition range of the polymers (Figure 4). Our τ_3* values agree with the results of Kobayashi et al.,[31] who estimated τ_3* = 2580 ps for pure PE and τ_3* = 2680 ps for EVA copolymer with 14% vinyl acetate comonomer. In PVA, only three lifetime components, i.e., one *o*-Ps lifetime $\tau_{3(II)} = \tau_3$*, was observed. τ_3* is somewhat larger than the results published by Kobayashi et al.[29] and Wang et al.[30]

The cross-centered squares in Figure 3 represent τ_3* lifetimes obtained from the analysis of synthesized spectra for the copolymers constructed by superposition of the experimental pure PE and PVA spectra weighted with their concentration in the corresponding copolymer. τ_3* of these simulated spectra varies almost linearly with the composition of EVA. This is in sharp contrast to the behavior of the measured *o*-Ps lifetimes, which shows that, as expected, the copolymer cannot be considered as a simple linear superposition of the boundary systems.

As can be observed in Figure 3, the mass center of the longer of the two *o*-Ps MELT peaks is within the error limits identical to the $\tau_{3(II)}$ of the discrete-term analysis in the range between PE and EVA40. Above EVA40, it corresponds more to τ_3*. This behavior is due to the decreasing intensity of the lower (~1 ns) *o*-Ps peak in the MELT lifetime distribution with increasing content of vinyl acetate.

Discussion

Estimation of the Mean Hole Volume *v*. The size of the open spaces seen by the *o*-Ps probe may be described either via a packing coefficient or as a mean local hole size. The first model provides a good description of the *o*-Ps pick-off annihilation in molecular crystals. Lightbody et al.[6] established a linear dependence of the *o*-Ps pick-off lifetime τ_{po} on the crystal packing coefficient *C* in hydrocarbon molecular crystals. This allows the derivation of a packing coefficient from the measured τ_{po} for comparison with those obtained from crystallographic data. The van der Waals volume of the CH_2 group is 0.017 nm^3 (Bondi;[33] see also the tabulated values collected by van Krevelen[34]). Crystalline PE has an orthorhombic unit cell with parameters $a = 0.740$ nm, $b = 0.494$ nm, and $c = 0.255$ nm at 300 K.[26] From this, a total volume per CH_2 group at room temperature of $(a \times b \times c)/4 = 0.0233$ nm^3 follows. This is equivalent to a packing coefficient of $C = 0.017/0.0233 = 0.73$. From the third lifetime in the EVA copolymers, $\tau_{3(I)} = 0.8$–1.1 ns, packing coefficients of 0.71–0.75 are derived using the data of Lightbody et al.[6] The close proximity of this experimental packing coefficient with the theoretical value may support the idea that $\tau_{3(I)}$ reflects the *o*-Ps pick-off annihilation in crystallites of semicrystalline EVA copolymers. As mentioned previously, the nature of this lifetime in EVA with higher content of vinyl acetate (no crystallinity according to WAXS data) is not entirely clear.

The concept of local holes is more suitable for the description of the *o*-Ps pick-off annihilation in amorphous materials. This simple model assumes that the Ps annihilates from an infinite square well potential where the Ps wave function has a finite penetration depth δr into the material surrounding the potential well. If the radius of the square well is *r*, it follows from elementary quantum mechanics that the observed *o*-Ps pick off lifetime can be related to the radius of the hole (same size as the potential well) as

$$\tau_{po} = 0.5 \text{ ns}\left[1 - \frac{r}{r+\delta r} + \frac{1}{2\pi}\sin\left(\frac{2\pi r}{r+\delta r}\right)\right]^{-1} \quad (7)$$

The prefactor of 0.5 ns is the spin-averaged Ps annihila-

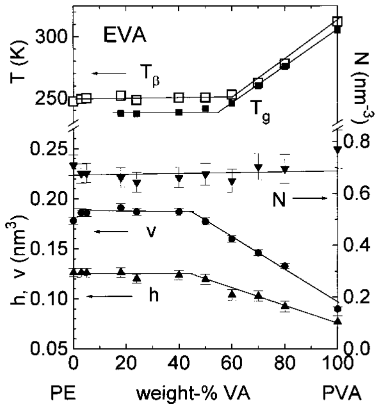

Figure 5. The mean volume v of holes estimated from positron experiments and the fractional hole volume $h = (V_a - V_b)/V_a$ estimated from the specific volume of the amorphous phase, V_a, assuming a linear superposition of the specific bulk volumes V_b of PE and PVA in EVA copolymers. The number density of holes was estimated via $N = h/v$. The temperatures of the β transition, T_β (DMA), and of the glass transition, T_g (DSC) are also shown.

tion lifetime, while $\delta r = 0.166$ nm is obtained by fitting eq 7 to observed *o*-Ps lifetimes of known mean hole radii in porous materials.[5,7,8]

Comparison of the Behavior of the Hole Volume *v* and of the Fractional Free Volume *h*. The mean volume of holes, v, and the fractional hole volume, h, are shown in Figure 5 for EVA copolymers as a function of the VA comonomer content. h was estimated in the following way. As in previous papers of our group,[18,35] we assume that the specific volume of an amorphous polymer, V_a, is a composition of the volume formed by the holes, V_h, and a hypothetical (equilibrium) volume that we call bulk volume V_b. Hence, $V_a = V_b + V_h$ (see earlier refs[2,33-37]). In semicrystalline polymers, the specific bulk volume may approximated by the specific volume of the crystalline phase,[34] $V_b = V_c = 1/\rho_c$. It represents the most dense packing of a given polymer consisting of the van der Waals volume and the interstitial free volume. The hole volume, V_h, then represents an excess free volume that appears to be due to the structural disorder in the amorphous polymer. We assume that the bulk volume of the EVA copolymers may be linearly composed of the bulk volumes of the constituent systems, $V_b = (1 - c)V_b^{PE} + cV_b^{PVA}$, where c is the VA content of the copolymer. We assume $V_b^{PE} = V_c^{PE} = 1$ cm^3/g. We estimated V_b^{PVA} in the following way. The fractional hole volume h may be deduced from P−V−T data using the statistical mechanical theory of Simha and Somcynsky.[2] From the P−V−T data of PVA, a fractional free volume at room temperature of $h = 0.077$ was estimated by McKinney and Simha.[38] From $V_b^{PVA} = V_a^{PVA}(1 - h)$ and $V_a^{PVA} = 0.841$ cm^3/g (Figure 1), a bulk volume of $V_b^{PVA} = 0.7847$ cm^3/g follows. With these data one can now calculate the fractional hole (or free) volume via

$$h = (V_a - V_b)/V_a = \{V_a - [(1 - c)\,V_b^{PE} + c\,V_b^{PVA}]\}/V_a \quad (8)$$

In Figure 5, we observe a slight increase in the mean hole volume v from 0.178 (±0.003) nm^3 in pure PE to 0.186 (±0.003) nm^3 in EVA copolymer with 3% VA comonomer. This variation may be attributed to the appearance of the bulky $OCOCH_3$ groups in the amorphous phase of EVA copolymers. The mean hole volume stays constant at $v = 0.186$ nm^3 up to a content of approximately 45% VA comonomer. Subsequently, v decreases linearly to a value of 0.105 nm^3, which is slightly larger than that found by Kobayashi et al.[29] at room temperature ($v = 0.093$ nm^3). Similar to mean hole volume v, the fractional free volume h in EVA copolymers remains constant at $h = 0.125$ in the range between 0 and approximately 45% VA. After that, it decreases linearly to the value of $h = 0.077$ assumed to be valid for PVA.

The number density of holes, N, may be estimated from the relation

$$N = h/v \quad (9)$$

In EVA copolymers (Figure 5), the N values are scattered in a narrow range around a mean value of $N = 0.67$ (±0.05) nm^{-3}. This value agrees with $N = 0.73$ nm^{-3} estimated in a previous paper[18] for our LDPE from thermal expansion experiments. Our value for PVA, $N = 0.77$ nm^{-3}, is somewhat smaller than $N = 0.84$ nm^{-3} estimated by Kobayashi et al.[29] The constant behavior of the number density of holes indicates that in EVA copolymers the variation in the fractional hole volume h is almost exclusively determined by the variation in the mean hole volume v. This interesting conclusion was also drawn previously by us for a completely amorphous copolymer system.[35]

Comparison of the Behavior of the Hole Volume *v* and of the Transition Temperatures T_β and T_g. In Figure 5, we have also plotted the β-transition temperature T_β (DMA) and the glass-transition temperature T_g (DSC). It is observed that v and h vary in opposite sense to T_β and T_g. The behavior of v may be understood by taking into account the following: (1) the difference between measurement temperature ($T_{meas} = 298$ K) and the relevant transition temperatures, $T_{meas} - T_g$ and $T_{meas} - T_\beta$; (2) a possible change of the hole size at the glass-transition temperature, $v_g = v(T_g)$; and (3) a possible change of the slope dv/dT of the coefficient of thermal expansion of the hole volume, $\alpha_h = dv/v_g dT$. Between VA contents of 0 and ∼60%, the transition temperatures T_β and T_g stay constant although the VA comonomer concentration increases.

In branched PE, three peaks are known to appear in the mechanical damping curves denoted as α (353 K), β (258 K), and γ (168 K) relaxation. The β relaxation is usually attributed to the effect of branch points in the amorphous phase of PE (see Brydson[39] and references given therein). The constant behavior of T_β in EVA copolymers with low and medium VA concentrations shows that acetate groups have apparently the same effect as branch points in PE. If the β transition of completely amorphous copolymers is extrapolated back from the value at high acetate concentrations to that for pure polyethylene, a value of 163 K is obtained. This temperature is somewhat lower than the glass-transition temperature estimated from the hole volume v versus T dependence for LDPE,[18] $T_g = 195$ K. The extrapolated value for the β transition is nearly identical with that for the γ transition, which is associated with the movement of three or four methylene groups (the crankshaft mechanism, for example[40]). Thus, the γ transition is associated with movements of the normal hydrocarbon backbone, whereas the β transition is associated with polymer segments containing both straight-chain hydrocarbon groups as one comomoner and some other group, such as branched hydrocarbons or acetate groups, as the other comonomer. From this, it follows that T_β as detected in DMA experiments can be expected to be closely related to the glass-transition temperature T_g observed in DSC experiments. In fact, T_g is slightly smaller than T_β but behaves otherwise similarly.

The dependence of hole volume v on the concentration of VA comonomer correlates well with that of T_β and T_g with the only exception that v starts to deviate from a constant at a somewhat lower VA content than those of T_β and T_g. The observed correlation between v and T_β or T_g may indicate that all of these values are related to the presence of the vinyl acetate comonomer units in the amorphous phase of EVA copolymers. The nonclassical behavior of the transition temperatures T_β and T_g in EVA copolymers is discussed in the literature in terms of correlation between crystallinity and chemical and physical structure of the amorphous phase.[11−15] Due to the bulky character of the acetate groups, it is expected that vinyl acetate units are not able to participate in the crystalline lattice. That is to say that, in a simple two-phase model, the crystalline phase in the EVA copolymers results from the pure polyethylene co-units. The slight decrease in the Bragg diffraction angle and an increase of the width of the crystalline peaks that we observed between 0 and 24% VA may indicate a decreasing size or increasing distortion of crystallites.[41] Due to the incorporation of only ethylene units in the crystalline phase, the vinyl acetate comonomer content in the amorphous phase is larger than that given by the nominal copolymer composition. Thus, the variation of the ratio of the vinyl acetate to ethylene concentration in the amorphous phase is smaller than the ratio of the total concentrations. Depending on the amount of crystalline phase present, the points representing the parameters of the amorphous phase will be shifted along the composition axis in order to account for the higher VA content. However, this shift cannot explain the observed invariability of the parameter values in the copolymer composition region where the crystalline phase is present and the sudden change in their behavior when the VA content exceeds 50% and the crystalline phase disappears. We offer the following explanation of this phenomenon.

Pure low-density polyethylene contains mainly short branches that are distributed randomly along the chain backbone and are responsible for its low crystallinity. The crystalline phase consists of sufficiently long unbranched chain segments; the branched parts of the chains are rejected into the amorphous phase. The copolymerization with VA results in a random insertion into an already branched polyethylene backbone of vinyl acetate branches that are also rejected from the crystalline phase. The increasing content of VA in the copolymer decreases its crystallinity and increases the amount of the amorphous phase. However, the *total* concentration of short branches in the amorphous phase irrespective of their origin (vinyl acetate branches from the VA comonomer together with the alkyl branches inherent in the PE) remains constant until the crystalline phase is consumed by the increasing content of VA units in the copolymer. From this point, the system consists of a single amorphous phase, and the branch concentration in the amorphous phase increases linearly with the increasing concentration of the VA comonomer. Consequently, this linear increase in branch concentration in the amorphous phase is responsible for the linear change of the T_β, T_g, h, and v parameters, and it shows that the effect of the vinyl acetate and the short alkane branches on the free-volume properties of the EVA copolymer is similar. Further phenomena such as the restricted motion of chain segments imposed by the adjacent crystallites, loops, and entanglements in the chain topology and the coexistence of different (PE and EVA) amorphous phases are discussed in the literature in this context.[11−15]

Above a comonomer concentration of ~60% vinyl acetate, the transition temperatures T_β and T_g show a classical behavior; i.e., they increase linearly with composition of the completely amorphous, random copolymer (Figure 5). The behavior is in good correlation with the mean hole volume, which decreases in this range linearly with the value of PVA. This behavior again correlates very well with the behavior of T_g and T_β: the smaller the separation between the temperature of measurement and the glass-transition, $T_{meas} - T_g$ ($T_{meas} - T_\beta$), the smaller the size of the free-volume holes. The relatively small hole volume in PVA correlates with the high temperature of the β transition and with the glass-transition temperature of $T_g = 312$ K estimated from DSC and from positron experiments (305 K).[29,30]

The *o*-Ps intensity $I_{3(II)}$ (and I_3*) is almost the same in the EVA copolymers (Figure 4) with the exception of EVA03 and EVA05. Obviously, the Ps yield in PE is approximately the same as that in PVA and remains relatively unchanged when forming the EVA copolymers. The pronounced increase of $I_{3(II)}$ (and I_3*) for EVA03 and EVA05 is surprising. The reason for this rise is not clear at present and will not be discussed further in this paper. An unexpected behavior of the *o*-Ps intensity I_3* was also observed by Kobayashi et al.[31] in blends of PE and EVA14 and discussed in terms of the spur model of Ps formation.

Conclusions

(1) In positron lifetime spectra of ethylene-vinyl acetate (EVA) copolymers, four different lifetimes appear when analyzed with the routine MELT that assumes continuous lifetime distributions. The longest lifetime, $\tau_{3(II)} = 2-3$ ns, is attributed to *o*-Ps annihilation from free-volume holes in the amorphous phase of the polymers. The nature of a medium lifetime time, $\tau_{3(I)} \approx 1$ ns, is not entirely clear. It could be due either to *o*-Ps annihilation from crystalline or more densely packed regions of the material or appear as an artifact of the spectrum analysis. By assuming three lifetimes in a discrete-term (LIFSPECFIT) fit, the analyzed *o*-Ps lifetime τ_3* is smaller than $\tau_{3(II)}$ by only ~5%.

(2) In EVA copolymers with 3−45 wt % vinyl acetate, the hole volume v is constant at 0.190 nm^3. This behavior of the hole size correlates well with the nonclassical behavior of the transition temperatures T_β and T_g. It is attributed to the constant *total* short branch (VA groups and alkyl branches together) concentration in the amorphous phase of the copolymer. Above this composition range, where only amorphous phase exists, the concentration of the short branches increases linearly with the VA content. This is reflected in the linear decrease of the hole volume down to 0.105 nm^3 for the pure PVA and the linear increase of T_β and T_g.

(3) By using crystallinity data obtained with DSC and WAXS, the specific volume of the amorphous phase V_a

may be estimated from the experimental total specific volume. By assuming a linear superposition of the specific bulk volumes of PE and PVA in the EVA copolymers, the fractional (free) hole volume $h = (V_a - V_b)/V_a$ may be estimated. The values of h stays constant at 0.125 for VA contents between 0 and ~45% and decreases afterward linearly down to 0.077 for PVA. From the relation $N = h/v$, a number density of holes of $N = (0.67 \pm 0.05)$ nm^{-3} was estimated, which does not change with the VA content in EVA copolymers.

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