Polymer 42 (2001) 2901–2905

polymer

www.elsevier.nl/locate/polymer

Free volume changes in physically aged polyethylene by positron annihilation

J. Borek[a], W. Osoba[b,*]

[a]Institute of Chemistry, Silesian University, Katowice 40-006, ul. Szkolna 9, Poland
[b]Institute of Physics, Silesian University, Katowice 40-007, ul. Uniwersytecka 4, Poland

Received 20 June 2000; accepted 11 September 2000

Abstract

Positron lifetime measurements in polyethylene (PE) have been performed. A conventional slow–fast coincidence lifetime spectrometer with plastic scintillators has been used for the lifetime measurements. The investigated samples have been aged in a Xenotest 250T apparatus for different time (from 0 to 3000 h). All the lifetime measurements have been made in air and at room temperature. The degree of the crystallinity and the melting temperatures of the investigated samples have been estimated using the differential scanning calorimetry (DSC) technique. Additional measurements of the hardness (Brinell) have been performed for them. Mean free volumes radii and fractional free volumes have been calculated from the lifetime data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Positron annihilation; Polyethylene; Polymer aging

---

1. Introduction

Positron annihilation spectroscopy is widely used for investigations of different aspects of polymer properties [1–6]. When a positron with a kinetic energy of several keV enters an absorber it quickly reaches thermal energies. The thermalized positron can annihilate with an electron from the absorber or it may form, with the electron, a bound system — positronium (Ps). In amorphous regions of a polymer substance free volumes exist where orthopositronium (o-Ps) may live for several nanoseconds. Positron lifetimes in polymer matter may be perturbed by different factors, for instance: changes in degree of crystallinity [7], blending of polymers [8–11], plasticization of polymers [12–15], and so on. Aging of polymers may also influence positron lifetimes [16–19]. The influence of water absorption and water saturation in polymers on positron lifetimes have also been checked [20–22].

The purpose of this paper is to investigate the influence of the physical aging on the free volumes in polyethylene (PE).

2. Experimental

2.1. A lifetime spectrometer

A conventional slow–fast coincidence spectrometer with plastic scintillators has been used. The time resolution of the spectrometer, approximated by two Gaussian curves, has been determined by analysing the positron lifetimes in Kapton foils. The resolution, defined in this manner, has been characterized by two full widths at half of the maximum (FWHM_i) and two relative percentage intensities (I_i). Typical values of the FWHM are: FWHM_1 about 257 ps and I_1 about 70%; FWHM_2 about 360 ps. The centres of the curves are displaced by about 5 ps. A multichannel analyser with a digitally stabilized peak position has been used during measurements. Positron lifetime spectra have been accumulated to approximately $5–6 \times 10^6$ counts. The measurements have been repeated at least twice for each sample. Parameters values obtained after numerical analyses of the raw lifetime spectra have been reproducible.

2.2. A positron source

Several droplets of a carrier free solution of ^{22}NaCl were deposited and then evaporated on a piece of Kapton foil (8 μm thick). Another piece of the foil was sealed over the first one to form a positron source with activity about 0.2 MBq. This activity has allowed to reach a count rate of 30 cps. During all of the measurements the source was sandwiched between two identical samples of the investigated polymer.

A source correction has been taken into account during numerical evaluations. It has been estimated that about 5%

---

* Corresponding author.

PII: S0032-3861(00)00687-X

Table 1
Melting point, T_m, the degree of the crystallinity, dcr, and hardness (Brinell), h_B, for the aged samples of polyethylene

Aging time (h)	T_m (K)	dcr (%)	h_B (MPa)
0	387 ± 1	51.4 ± 0.1	245 ± 3
200	387 ± 1	51.3 ± 0.1	276 ± 3
400	388 ± 1	53.2 ± 0.1	277 ± 3
600	388 ± 1	48.9 ± 0.1	285 ± 3
800	388 ± 1	49.7 ± 0.1	288 ± 3
1000	388 ± 1	53.1 ± 0.1	293 ± 3
1200	387 ± 1	53.4 ± 0.1	294 ± 3
1400	388 ± 1	50.7 ± 0.1	295 ± 3
1600	387 ± 1	50.6 ± 0.1	296 ± 3
1800	387 ± 1	52.6 ± 0.1	301 ± 3
2000	387 ± 1	51.8 ± 0.1	305 ± 3
2200	387 ± 1	52.9 ± 0.1	294 ± 3
2400	388 ± 1	51.4 ± 0.1	298 ± 3
2600	387 ± 1	49.0 ± 0.1	306 ± 3
2800	389 ± 1	48.7 ± 0.1	304 ± 3
3000	387 ± 1	54.2 ± 0.1	309 ± 3

of the total number of positrons have been annihilated in the source with the following typical lifetimes and intensities: $\tau_1 = 346.1 \pm 1.4$ ps and $I_1 = 91.63 \pm 1.04\%$; $\tau_2 = 580.0 \pm 15.6$ ps. All of the measurements were performed in air and at room temperature.

2.3. Sample preparation

All of the measured samples were made of polyethylene (PE): $(-[CH_2{-}CH_2]_n-)$ produced by Petrochemia Płock (Poland) as a commercial product: polietylen LD-003. Its weight-average molecular weight equals 299,000 and its density is 0.921 g/cm^3 at 298 K. The polymer powder was heated up to 528 K in a mould and then pressed (at about 15 MPa) to form disc-shaped samples about 3 mm thick and 20 mm in diameter. Two such discs were prepared and used as sample for each measurement. A separate pair of samples was prepared for different aging times. To evaluate the degree of the crystallinity (dcr) and the melting points (T_m) of the samples, differential scanning calorimetry (DSC) measurements were performed. A heating rate of 11 K/min (down to 213 K) and 1 K/min (down to 173 K) has been used during the DSC measurements. The mechanical properties of the samples were checked by hardness measurements (Brinell). The results of the DSC and the hardness measurements are presented in Table 1.

It is obvious from these results that T_m and dcr values do not change with the aging time (though dcr values are randomly distributed at 51 ± 3%). In spite of this, the hardness of the samples increases as the aging time rises.

Aging of the samples was performed in a Xenotest 250T apparatus in the temperature range 303–308 K. It is equipped with a power source xenon burner with the filter set $(250 \leq \lambda \leq 450)$ μm. The samples were exposed to cyclic watering (5 min per 30 min cycle). Relative humidity inside a working chamber was 60%, and increased, during watering procedure, up to 95%.

3. Results and discussion

Positron lifetime measurements were performed on the aged PE samples. The spectra were analysed using the package programs PATFIT-88 [23]. These programs have fitted four exponential components to the measured spectra. No constraints on lifetimes and intensities were imposed during numerical calculations, i.e. all the fitting parameters were free.

The shortest (the mean lifetime equal to 125 ps) lived component, τ_1, is usually attributed to p-Ps annihilation. In our case, because of the relatively poor time resolution and no constraints on lifetimes during computer analyses, it might contain not only p-Ps annihilation contribution but also contributions from positronium compounds. This

Table 2
Lifetimes, τ_i, intensities, I_i, and variance values obtained for the aged samples of polyethylene

Aging time (h)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	I_2 (%)	I_3 (%)	I_4 (%)	Variance
0	0.1340 ± 0.0057	0.3378 ± 0.0064	1.0088 ± 0.0698	2.5483 ± 0.0206	52.98 ± 0.72	8.08 ± 0.44	24.19 ± 0.38	1.079 ± 0.053
200	0.2640 ± 0.0097	0.3775 ± 0.0335	0.9998 ± 0.1274	2.5183 ± 0.0145	22.03 ± 4.11	7.72 ± 1.32	21.76 ± 0.38	2.562 ± 0.052
400	0.1558 ± 0.0091	0.3422 ± 0.0077	0.9918 ± 0.0670	2.5768 ± 0.0142	56.13 ± 1.28	8.34 ± 0.55	22.11 ± 0.34	1.249 ± 0.053
600	0.2809 ± 0.0092	0.4682 ± 0.0822	1.0168 ± 0.2281	2.5023 ± 0.0187	21.39 ± 5.21	5.81 ± 2.58	20.48 ± 0.51	2.057 ± 0.052
800	0.1607 ± 0.0088	0.3536 ± 0.0071	1.0490 ± 0.0841	2.5525 ± 0.0164	58.62 ± 1.21	7.09 ± 0.44	21.02 ± 0.40	1.209 ± 0.053
1000	0.2917 ± 0.0098	0.4784 ± 0.1425	0.9205 ± 0.2663	2.4760 ± 0.0167	16.14 ± 4.15	6.19 ± 5.24	20.44 ± 0.43	2.219 ± 0.052
1200	0.1614 ± 0.0101	0.3519 ± 0.0084	0.9552 ± 0.0795	2.5385 ± 0.0137	58.81 ± 1.19	7.45 ± 0.71	21.15 ± 0.31	1.358 ± 0.053
1400	0.2827 ± 0.0099	0.4691 ± 0.0838	1.0021 ± 0.2627	2.4948 ± 0.0192	22.83 ± 5.50	5.36 ± 3.07	19.96 ± 0.50	1.966 ± 0.052
1600	0.1401 ± 0.0095	0.3458 ± 0.0059	0.9854 ± 0.0732	2.5252 ± 0.0166	63.38 ± 0.75	7.72 ± 0.54	19.37 ± 0.36	1.245 ± 0.053
1800	0.2684 ± 0.0441	0.3693 ± 0.0815	0.8297 ± 0.1705	2.4424 ± 0.0136	40.49 ± 35.03	8.93 ± 3.26	18.51 ± 0.28	1.648 ± 0.052
2000	0.2339 ± 0.0163	0.3499 ± 0.0148	0.8576 ± 0.1130	2.3978 ± 0.0116	63.09 ± 2.57	7.49 ± 1.69	18.52 ± 0.23	1.057 ± 0.052
2200	0.2871 ± 0.0184	0.3891 ± 0.0643	0.8639 ± 0.2113	2.4011 ± 0.0164	18.80 ± 8.03	6.57 ± 3.83	17.94 ± 0.36	2.013 ± 0.052
2400	0.3047 ± 0.0083	0.5755 ± 0.6034	0.8107 ± 0.4625	2.4218 ± 0.0183	7.83 ± 9.33	8.25 ± 22.09	18.52 ± 0.43	2.186 ± 0.052
2600	0.2422 ± 0.0256	0.3744 ± 0.0393	0.8337 ± 0.1220	2.3963 ± 0.0144	48.31 ± 12.26	7.20 ± 2.44	17.84 ± 0.30	1.551 ± 0.052
2800	0.3125 ± 0.0139	0.4647 ± 0.3460	0.8586 ± 0.2945	2.4247 ± 0.0195	8.64 ± 6.09	7.63 ± 9.40	17.48 ± 0.44	2.546 ± 0.053
3000	0.2958 ± 0.5876	0.4321 ± 0.2201	0.7857 ± 0.1930	2.3899 ± 0.0165	14.19 ± 8.61	7.97 ± 6.90	16.89 ± 0.34	1.894 ± 0.053

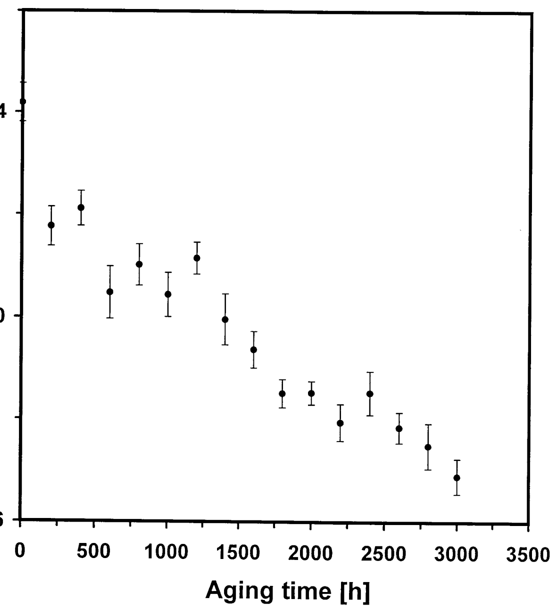

Fig. 1. The longest lived component intensity, I_4, as a function of the aging time.

lengthens our τ_1 values from about 130 to about 310 ps. The intermediate component, τ_2, describes the annihilation of the free positrons but in our case it contains contributions from positron and positronium compounds (340–580 ps). The third component, τ_3, is interpreted as the pick-off annihilation of o-Ps in the crystalline regions of the polymer. Finally, the longest lived component, τ_4, is attributed to the pick-off annihilation of o-Ps in the amorphous regions of the polymer. According to a model proposed by Tao [24] and Eldrup et al. [25], the longest lived component of the positron lifetime spectrum may be correlated with the mean radius of the free volume cavity in the polymer matter. They derived the following equation:

$$\tau_4 = 0.5[1 - R/(R + 0.1656) + 1/(2\pi) \times \sin[2\pi R/(R + 0.1656)]]^{-1} \quad (1)$$

where τ_4 is the o-Ps lifetime expressed in nanoseconds, R is the mean radius of the spherical well expressed in nanometres and 0.1656 nm is an empirical constant.

The results, i.e. lifetimes τ_i, intensities I_i, and the variance values of the fits are listed in Table 2.

These results suggest that there is no correlation between the aging time and τ_i and I_i ($i = 1$–3) values. On the contrary, it seems that τ_4 and I_4 values show decreasing tendency with the aging time. Our aim in this investigation was to find a relation between the aging time of the polymer samples and the mean radius of the free volume cavity and this is the reason that we are mainly interested in the τ_4 and I_4 values. The relative intensity of the longest lived component of the positron lifetimes, I_4, and the mean free volumes of the spherical wells, $V = (4\pi R^3)/3$ (where R values are obtained from Eq. (1)), as the functions of the aging time are presented in Figs. 1 and 2, respectively. Both values decrease gradually with increase of the aging time. Relative percentage changes of I_4, as function of the aging time are much larger than these changes for V. I_4 is assumed to be proportional to the number of the free volume holes because it gives the information on the o-Ps formation probability. On the other hand, the V values estimate the dimensions of the cavities in the amorphous regions of the investigated PE. The o-Ps "atoms" diffuse through such cavities and live there much longer than in crystalline regions of the polymer.

Lifetime measurements of the positron in polymers allow the estimation of the fractional free volume parameter, f. It is defined as

$$f = \frac{V - V_0}{V} = \frac{V_f}{V} \quad (2)$$

where V is the total macroscopic volume of the polymer, V_0 is the volume occupied by molecules and V_f is the free volume of the polymer.

Wang et al. [26] and Kobayashi et al. [17] have proposed a semiempirical equation which may be used to evaluate the fractional free volume f

$$f = A \times I_4 \times V_{sph} \quad (3)$$

where I_4 is the relative intensity of the o-Ps lifetime component, $V_{sph} = 4\pi \times R^3/3$ is the free volume of the single hole (in nm^3, the R value is taken from Eq. (1)), and A is the normalization constant.

Wang et al. [26] have proposed how the A value can be evaluated. It has not been estimated in this work but as it is the constant, the f value must be proportional to the product of the I_4 and V_{sph} values. The results of our f values estimation are presented in Fig. 3.

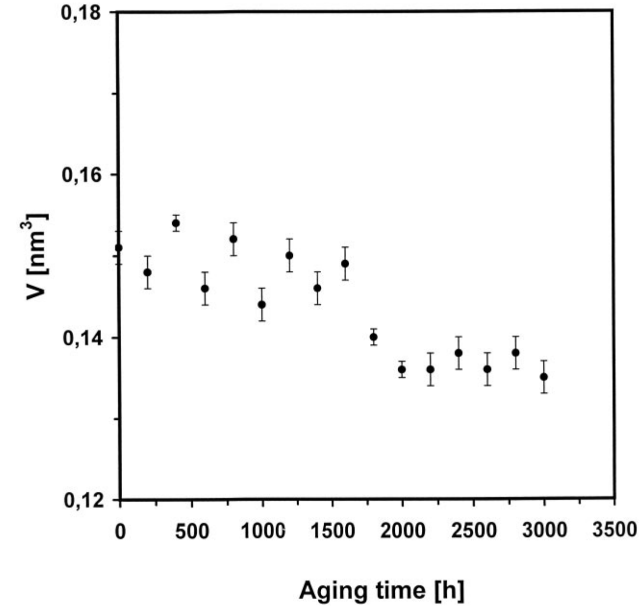

Fig. 2. The mean free volumes of the spherical well, V, versus the aging time.

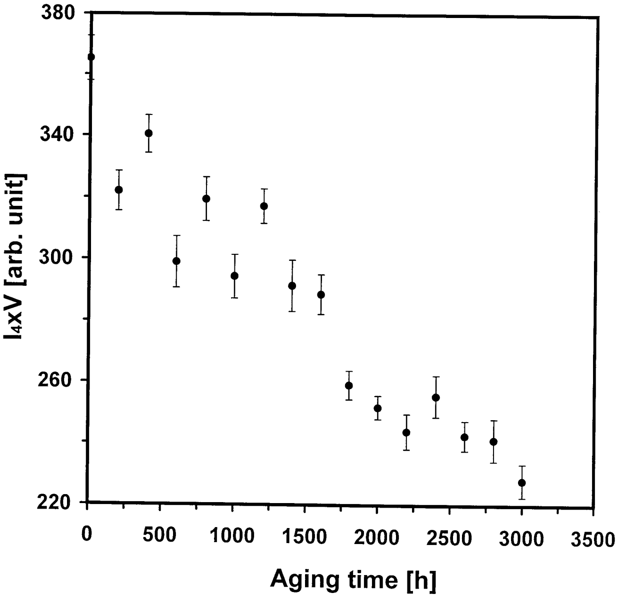

Fig. 3. The $I_4 \times V$ product as a function of the aging time.

It is clear that there is a correlation between the *f* values and the aging time. The *f* values decrease by about 38% taking into account the non-aged sample and that aged for 3000 h. This decrease is a consequence of the decrease in the I_4 and *V* values as functions of the aging time. I_4 drops from 24.2 to 16.9% and similarly *V* drops from 0.151 to 0.135 nm^3 for the "new" (non-aged) sample and the aged (3000 h) one, respectively. Madani et al. [21] observed similar effect of decreasing *f* in epoxy. Kobayashi et al. [17] observed the decrease of *f* as the result of, mostly, the decrease in the intensity of the longest lived component of the positron lifetimes in poly(vinyl acetate). The decrease in the longest lived positron lifetime component was found by Wästlund and Maurer [8] in polymer blends. Kluin et al. [18] also observed the decreasing intensity of this component in bisphenol A polycarbonate as the function of the time aging. It is thought, and generally accepted, that I_4 is proportional to the number density of the free volumes cavities, i.e. it is proportional to o-Ps probability formation. As τ_4 is proportional to the overlap of the positron and electron wavefunction in a free volume cavity it is obvious that τ_4 will be correlated with the dimension of that cavity. The presented results show that both values, I_4 and *V*, decrease as a function of the aging time. The investigated samples were exposed to light and water vapour in the Xenotest 250T apparatus. The relative humidity reached 95% in the working chamber of this apparatus during the sample aging. The observed I_4 decrease might be explained as the reduction of the number of cavities during physical aging of the samples. Crosslinking process, generated by the light in the polymer samples during the aging process in the working chamber of the Xenotest 250T, causes the reduction of the large free volume cavities. The presence of the crosslinking, in our results, is demonstrated by gradual increase of the hardness of the investigated samples with the aging time. This hardness increases from 245 MPa (for the non-aged sample) to 309 MPa (for the sample aged 3000 h). Water molecules diffused into the polymer and could occupy the free space in cavities. This resulted in the diminishing of the free volume cavities dimensions. There was no longer so much free space to allow o-Ps to live so long. The gradual decrease of τ_4 suggests that the mean free volumes become smaller and smaller as the time storage of the samples in the Xenotest 250T is longer and longer. The presented results suggest that we did not observe any plasticization effect of the water molecules on the investigated PE. On the contrary, the decrease of *f* implies that the water molecules act, in this case, as anti-plasticization agents.

4. Conclusions

The results of the investigations of the free volume changes in the PE samples as the function of the aging time are presented in the article. The samples were exposed to light and to the water molecules penetration during the aging process. As a result of these conditions the decrease of *f* was registered. It was caused by the decreases of both I_4 and *V* values. The relative changes of I_4 were much larger (about 30%) than the relative changes of *V* (about 10%). It suggests that the o-Ps probability formation decreases much faster than the decrease of the longest lived component of the positron lifetime.

References

[1] Hautojärvi P, editor. Positrons in solids. Berlin: Springer, 1979.
[2] Stevens JR. Methods of experimental physics, vol. 16A. 1980.
[3] Jean YC, Schrader DM. Positron and positronium chemistry. Amsterdam: Elsevier, 1988.
[4] Ache HJ. Positron and positronium chemistry. Amsterdam: Elsevier, 1988.
[5] Jean YC. Microchem J 1990;42:72.
[6] Mogensen OE. Positron annihilation in chemistry. Berlin: Springer, 1995.
[7] Nakanishi H, Jean YC, Smith EG, Sandreczki TC. J Polym Sci Part B: Polym Phys 1989;27:1419.
[8] Wästlund C, Maurer FHJ. Macromolecules 1997;30:5870.
[9] Li H-L, Ujihira Y, Nanasawa A, Jean YC. Mater Sci Forum 1977;255–257:399.
[10] Olson BG, Srithawatpong R, Peng ZL, McGervey JD, Ishida H, Maier TM, Halasa AF. J Phys: Condens Matter 1998;10:10451.
[11] Nagai Y, Nonaka T, Hasegawa M, Kobayashi Y, Wang CL, Zheng W, Zhang C. Phys Rev B 1999;60(17):11863.
[12] Elwell RJ, Pethrick RA. Eur Polym J 1990;26:853.
[13] Anderson L, Grulke EA, DeLassus PT, Smith PB, Kocher CW, Landes BG. Macromolecules 1995;28:2944.
[14] Borek J, Osoba W. J Polym Sci Part B: Polym Phys 1996;34:1903.
[15] Borek J, Osoba W. J Polym Sci Part B: Polym Phys 1998;36:1839.
[16] Chang G-W, Jamieson AM, Yu Z, McGervey JD. J Appl Polym Sci 1997;63(4):483.
[17] Kobayashi Y, Zheng W, Meyer EF, McGervey JD, Jamieson AM, Simha R. Macromolecules 1989;22:2302.

[18] Kluin JE, Yu Z, Vleeshouwers S, McGervey JD, Jamieson AM, Simha R. Macromolecules 1992;25:5089.

[19] Wästlund C, Maurer FHJ. J Radioanal Nucl Chem Articles 1996;211(1):269.

[20] Domjan A, Ivan B, Suvegh K, Vertes A. J Radioanal Nucl Chem Articles 1996;211(1):219.

[21] Madani MM, Miron RR, Granata RD. J Coat Technol 1997;69(872):45.

[22] Dlubek G, Stolp M, Nagel Ch, Fretwell HM, Alam MA, Radusch H-J. J Phys: Condens Matter 1998;10:10443.

[23] Kirkegaard P, Pedersen NJ, Eldrup M. PATFIT-88, Riso-M-2740, 1989.

[24] Tao SJ. J Chem Phys 1972;56:5499.

[25] Eldrup M, Lightbody D, Sherwood JN. Chem Phys 1981;63:51.

[26] Wang YY, Nakanishi H, Jean YC, Sandreczki T. J Polym Sci Part B: Polym Phys 1990;28:1431.