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Estimating the fractional free volume parameter in polyethylene by the positron annihilation method

Abstract

Positron annihilation lifetime measurements were performed on samples made of commercially available polyethylene (PE) (Lupolen 2012D, schwarz 413, made by BASF). The samples were isothermally annealed at different temperatures (50^0 C, 60^0 C, 100^0 C, 150^0 C and 200^0 C). A conventional slow-fast coincidence spectrometer with plastic scintillators was used. All of the measurements were performed in air at room temperature. The longest-lived component of the positron lifetime spectrum and its relative intensity were used to estimate the fractional free volume of the samples investigated.

Key words: *positron annihilation, polymers, free volume*

1. Introduction

When a positron with a kinetic energy of several keV (for instance one from a radioactive source) enters an absorber it quickly achieves thermal energies. The thermalised positron can annihilate with an electron from the absorber, or it may form together with the electron a bound system - the 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 [1], blending of polymers [2], plasticisation of polymers [3], aging of polymers [4] and so on. The aim of this paper was to investigate the influence of isothermal annealing on the free volume changes in thermo-shrunken PE.

2. Experimental

A conventional slow-fast coincidence spectrometer with plastic scintillators was used. The time resolution of the spectrometer, approximated by two Gaussian curves, was determined by analysing the measurements of the positron lifetimes in Kapton foils. Typical values of the full widths at half of the maximum ($FWHM_i$) were $FWHM_1$, about 292 ps and I_1, about 80%; $FWHM_2$, about 370 ps. Positron lifetime spectra were accumulated to approximately (1.6-2.5)×10^6 counts. A positron source (about 0.2 MBq) was sealed between two Kapton foils (8 μm thick). The source correction was taken into account during numerical evaluations. All the measurements were performed in air at room temperature. The measurements were repeated at least twice for each sample. The values of the parameters obtained after numerical analyses of the raw lifetime spectra were reproducible.

All of the samples measured were made of PE produced by Instytut Chemii i Techniki Jądrowej, Warszawa (Poland). This Institute used granules of Lupolen 2012D and schwarz 413 (made by BASF) for production of the sheets. The density of the granules was 0.933-0.939 g/cm^3. The samples (9 mm in diameter) were cut down from a 1.3 mm-thick sheet. The positron source was sandwiched between two pairs of such discs. Three different types of samples were used for the investigations. The samples of the first type were cut down from the sheet of PE without any modification during the technological process (they are described in the paper as the 'as-produced' samples). The samples of the second type were prepared from the sheet of PE irradiated by electrons during the production process, they are described in the article as the 'irradiated' samples. Finally, the third types were made of the 'orientated' PE sheet (i.e. the sheet was lengthened in the course of production process at elevated temperature). This type of sample is described in the article as the 'orientated' samples. The samples were isothermally annealed at different temperatures (50^0 C, 60^0 C, 100^0 C, 150^0 C and 200^0 C) before the measurements, in an oven in air. Annealing at higher temperatures caused the samples to melt. The samples were annealed for 5 min and 300 min. The samples kept at room temperature (23^0 C), without any further annealing, were used as reference.

3. Results

The positron lifetime spectra were analysed using the PATFIT-88 package programs [5]. This package fitted four exponential components to the measured spectra. No constraints on lifetimes and intensities were imposed during the numerical calculations. In the case of the four-component analyses, the shortest-lived component (with a mean lifetime equal to 125 ps), τ_1 , is usually attributed to parapositronium (p-Ps) annihilation. The intermediate component (with a mean lifetime of about 0.3-0.5 ns), τ_2, describes the annihilation of the free positrons. The third component (with a mean lifetime of about 1 ns), τ_3 is interpreted as the pick-off annihilation of o-Ps in the crystalline regions of the polymer. Finally, the longest-lived component (with a mean lifetime of 1.5 ns and above), 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 [6] and Eldrup et al. [7], 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:

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

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

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

$$f = (V - V_0)/V = V_f/V \quad (2)$$

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.

Table 1. Results of the lifetime measurements for the samples annealed for 5 min.

Annealing temp.[^{0} C]	As prepared samples		Irradiated samples		Orientated samples	
	τ_4 [ps]	I_4 [%]	τ_4 [p]	I_4 [%]	τ_4 [ps]	I_4 [%]
23	2587±20	21.9±0.5	2540±20	19.9±0.4	2609±20	21.6±0.5
50	2552±38	20.4±1.2	2524±14	21.0±0.2	2507±11	21.4±0.2
60	2593±24	20.1±0.5	2570±17	19.9±0.4	2578±16	19.6±0.4
100	2616±22	21.1±0.5	2543±20	21.2±0.5	2628±18	22.1±0.4
150	2620±21	21.7±0.5	2564±28	21.8±0.8	2648±20	21.8±0.5
200	2615±20	21.7±0.5	2590±22	22.3±0.6	2648±15	21.2±0.3

Table 2. Results of the lifetime measurements for the samples annealed for 5 h.

Annealing temp. [^{0} C]	As prepared samples		Irradiated samples		Orientated samples	
	τ_4 [ps]	I_4 [%]	τ_4 [ps]	I_4 [%]	τ_4 [ps]	I_4 [%]
23	2587±20	21.9±0.5	2540±20	19.9±0.4	2609±20	21.6±0.5
50	2526±11	22.1±0.5	2592±19	19.1±0.1	2540±12	21.2±0.2
60	2555±16	22.2±0.4	2531±18	21.1±0.4	2585±17	20.8±0.4
100	2654±29	20.6±0.7	2535±16	22.4±0.4	2626±20	22.0±0.5
150	2590±23	21.4±0.6	2573±20	22.4±0.5	2611±25	21.4±0.6
200	2596±21	21.9±0.5	2573±18	20.1±0.4	2541±21	18.7±0.4

Wang et al. [8] and Kobayashi et al. [9] have proposed a semi-empirical 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.

The A value was not measured in this work, but as it is the constant, the f value must be proportional to the product ($I_4 \times V_{sph}$). The results of our measurements are presented in Table 1 and Table 2. Only the lifetimes and the intensities of the longest-lived component of the positron lifetime spectrum have been noted because they were used to calculate the f values. In this manner we have shortened the paper significantly.

It is apparent that the variations of these values are not large. It seems that the annealing of the samples within these temperature ranges does not produce great changes in the structure of the samples. In Fig. 1 and Fig. 2 the f values, calculated according to Eq.(3), are presented.

It is clear that for the samples annealed for 5 min, the f values increase only for the irradiated samples. It seems that this increase may be explained mainly as the result of the increase in the I_4 value (Table 1). During the production process, in the irradiated samples, macromolecule bonds are cut which might result in the creation of the new free-volume sites in the course of annealing. The experimental points for the as-prepared and orientated samples are randomly distributed. In the case of the samples annealed for 5 h, the situation is different. The f values for the irradiated and orientated samples increase until the annealing temperature equals 150^0 C, and then they start to decrease. The effect of the decrease of the f values is especially large for the orientated samples. For the lower annealing temperatures, the f values for these samples increase, but again at 150^0 C they start to decrease. It is thought that this decrease is mainly caused by the decrease in the I_4 values (Table 2). This fact may be explained by taking into account the production process of the PE sheets. During this process the polymer chains were strongly stretched, especially in the case of the orientated samples. The free volume spaces were created where o-Ps might live for much longer than in the non-orientated samples. When the samples were heated at temperatures of 100^0 C and above for 5 h, the polymer chains shrank and the f values decreased. In spite of this, the f values for the as-prepared samples do not show such clear behaviour.

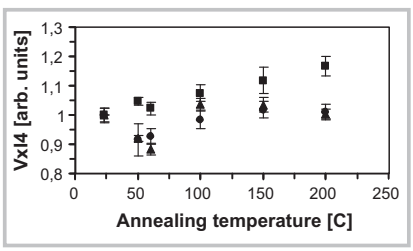

Figure 1. F values vs annealing temperature for the samples annealed for 5 min (■ - the irradiated samples, ◆ - the orientated samples, ● - the as prepared samples).

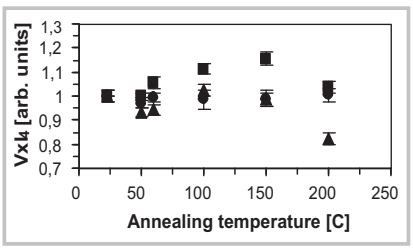

Figure 2. F values vs annealing temperature for the samples annealed for 5 h (■ - the irradiated samples, ◆ - the orientated samples, ● - the as-prepared samples).

4. Conclusion

Three different kinds of PE samples were investigated by positron annihilation. For some of the samples, a correlation was observed between thermal treatment of the samples and their fractional free volume parameter, f. For the irradiated samples, annealed for 5 min, the f values increased with the temperature. It seems that this behaviour may be explained as the result of the irradiation process of the samples. In the case of the irradiated and orientated samples, annealed for 5 h, the decrease of the f values may be explained by taking into account the production process of the PE sheets. Further investigation are needed to understand this phenomena better.

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