

Influence of low temperature on the free volume in polyethylene by positron annihilation

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Abstract. Positron lifetime measurements were performed as a function of temperature in thermo-shrunk, modified polyethylene. Mean volume of free volume cavities in the investigated polymer was estimated from the results of the measurements. This mean volume turned out to be a smooth function of temperature (from room temperature to 8.5 K). The effect of trapping of free electrons, produced during positron irradiation, was observed at lowered temperature.

Key words: positron annihilation • polymers • free volume

Introduction

Positron annihilation spectroscopy turned out to be a very useful method for investigation of different aspects of polymer properties [8, 11]. The results of the positron lifetime measurements for thermo-shrunk, modified polyethylene as a function of low temperature are presented in this paper. Temperature influences strongly the fate of positrons in polymers [7]. This work is a continuation of our former investigations [3, 4].

Experimental

A conventional, slow-fast coincidence spectrometer with plastic scintillators was used for lifetime measurements. The measurements were performed as a function of low temperature. The time resolution function of the spectrometer, approximated by two Gaussian curves, was determined by analysing the positron lifetimes in Kapton foils. Typical values of the full widths at half maximum (FWHM_i) were: $\text{FWHM}_1 = 294.5$ ps, ($I_1 = 93.86\%$) and $\text{FWHM}_2 = 586.9$ ps. Positron lifetime spectra were accumulated to approximately 1×10^6 counts. A positron source (^{22}Na , about $0.8 \div 0.9$ MBq) was sealed between two Kapton foils (about $8 \mu\text{m}$ thick). The measurements were performed in the dark, in vacuum ($10^{-8} \div 10^{-9}$ mbar at low temperature, and $10^{-4} \div 10^{-5}$ mbar, at room temperature). One spectrum was acquired about 12 h. A closed cycle helium refrigerator system was used to keep the sample at fixed temperature. A digital, microprocessor controlled measurement and control unit was used to regulate the temperature of the sample. It allowed to keep the temperature of the sample constant, within

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± 0.030 K. The measurements started at about 300 K, and then the sample was cooled down to 8.5 K and later on it was heated up again to 300 K. The measurements were carried out at 20 K spaced intervals (from 300 K to 200 K for the cooling cycle and from 190 K to 300 K for the heating one). The measurements performed in the temperature ranges from 200 K to 8.5 K (during cooling cycle) and then from 8.5 K to 190 K (in the heating one) were carried out at 40 K steps. The sample was kept at the newly chosen temperature for 40 to 50 min and afterwards the new measurement started.

The sample was made of 1.3 mm thick sheet of thermo-shrunken polyethylene, from the Institute of Nuclear Chemistry and Technology, Warsaw (Poland). This sheet was made of granules (their density was: 0.933–0.939 g/cm³) of Lupolen 2012D and schwarz 413 (manufactured by BASF) by melting the granules. In the course of production process, the polyethylene sheet was lengthened (40% elongation) at elevated temperature. The sheet was a commercial product. This was the reason that the producer refused to reveal details concerning properties of this product. The thermo-shrunken polyethylene shrinks enormously at about 600 K, this is why it is used, for instance, for electric cables insulation. In was thought, it would be interesting to check changes of its free volume, as a function of temperature by the annihilation method.

Four disc-shaped pieces (about 12 mm in diameter) were cut down from the polymer sheet and the positron source was sandwiched between them (two discs on each side of the source). The sample did not undergo any additional thermal treatment before the measurements.

Results and discussion

The positron lifetime spectra, measured as the function of temperature in the range from about 300 K to 8.5 K, were analysed using the package programs [10]. Three exponentially decaying components were fitted to the measured raw spectra. The lifetime of the second component, τ_2 , was fixed. Taking into account former measurements, the value $\tau_2 = 380$ ps was taken for this fixed lifetime. The source correction was taken into account during numerical evaluations. Separate measurements on Kapton foils were performed for evaluation of this correction.

There is no correlation between temperature and the shortest lifetime component values τ_1 and its relative intensity I_1 . Similarly, there is no correlation between temperature and I_2 values. In spite of this, it is thought that τ_3 and I_3 present such correlation. The dependence of the τ_3 values vs. temperature is presented in Fig. 1 and the dependence of I_3 vs. temperature is shown in Fig. 2.

According to the model proposed by Tao [14] and Eldrup *et al.* [5], the longest lived component of the positron lifetime spectrum may be correlated with the mean radius of the spherical, free volume cavity in the polymer matter. They proposed an equation, in the case when the third component of the positron lifetime spectrum is the longest one:

$$(1) \quad \tau_3 = 0.5 \left\{ 1 - \frac{R}{R + 0.1656} + \frac{1}{(2\pi) \cdot \sin[2\pi R / (R + 0.1656)]} \right\}^{-1}$$

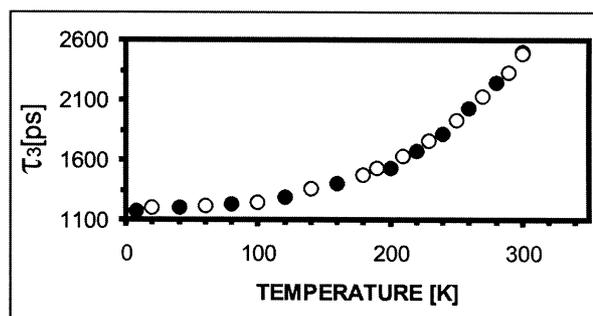


Fig. 1. The τ_3 values vs. temperature: ● – cooling cycle; ○ – heating cycle.

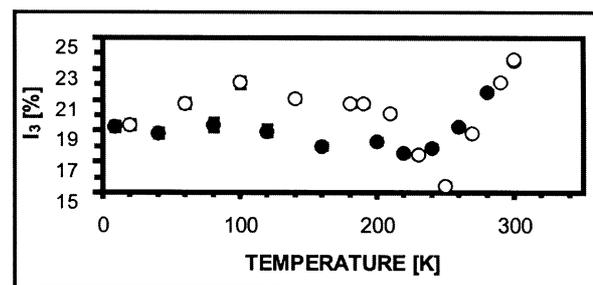


Fig. 2. The I_3 values vs. temperature: ● – cooling cycle; ○ – heating cycle.

where: τ_3 is the *ortho*-positronium (*o*-Ps) lifetime expressed in nanoseconds, R is the mean radius of the spherical well (with an infinite potential barrier) expressed in nm and 0.1656 nm is an empirical constant.

In the presented results the τ_3 values changed from (2.494 ± 0.006) ns at about 300 K to (1.198 ± 0.010) ns at about 8.5 K.

Free volume cavities V vs. temperature are shown in Fig. 3. This volume was calculated as the volume of a sphere, where R is taken from Eq. (1).

The V value decreases gradually with decreasing temperature, in the cooling cycle and increases in the heating one. It seems that there is no thermal hysteresis in the presented results. On the contrary, it seems that there is no simple correlation between the relative intensity of the longest lived component of the positron lifetimes I_3 and temperature. The I_3 values as a function of temperature are presented in Fig. 2. It is absolutely clear that the experimental points in the heating cycle do not follow the results observed in the cooling cycle. Going down from room temperature to lower ones, I_3 decreases (to approximately 220 K) and then it starts to gradually increase. Finally, the I_3 value, starts to decrease (in the heating cycle) for temperatures higher than about 120 K.

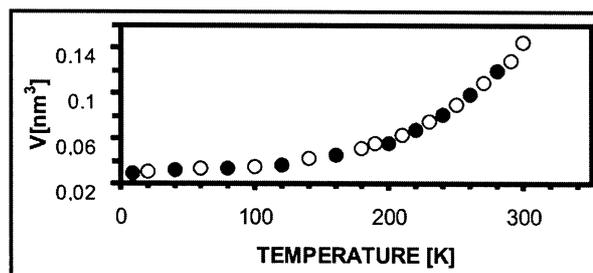


Fig. 3. The values of the free volume cavities V vs. temperature: ● – cooling cycle; ○ – heating cycle. Error bars are smaller than dot dimensions.

Many authors observed for different polymers, qualitatively similar behaviour of the I_3 values vs. temperature [6, 12, 15] (in the case of the papers [6, 15] their data in the dark, as the presented experiment was carried out in the dark, as well).

The relative intensity of the longest-lived component I_3 vs. temperature is more complex. It is well known and generally accepted, in a framework of the spur model of positron annihilation, that a large number of free electrons is produced in the investigated sample (irradiated by positrons during measurements). When a positron with a kinetic energy of several keV enters an absorber it quickly thermalizes. It loses its energy mainly by excitation and ionization of atoms and molecules of the absorber. The electrons released in this process might be trapped in shallow traps, [9]. According to Ref. [7], free volume cavities may play a role of such traps in the polymer sample. During positron lifetime measurements in polymers, the number of electrons trapped in those traps increases, especially at low temperature. Those electrons are detrapped at higher temperature. If it is so, the increasing number of the trapped electrons will cause an increase of the positronium formation probability. It might result in the larger I_3 values, during the heating cycle, from 8.5 K to about 120 K. For higher temperature, I_3 starts to drop as a result of detrapping of the electrons. Figure 2 shows these changes pretty well. Characteristic minimum of the I_3 curve at about 250 K, in the heating cycle, was observed also in polyethylene [12, 13] and in polyethylene-co-vinyl acetate [1]. In Ref. [13], authors explained the existence of this minimum taking into account the temperature caused contraction of the sample and freezing of local motions of polymers chains.

From Fig. 2, one can find out that I_3 rises gradually with temperature from about 200 K to 8.5 K (in the cooling cycle) and it still rises, in the heating cycle, from 8.5 K to about 120 K. It seems that I_3 rises with the elapsed time of the measurements (or with the time when the sample was kept at temperature below 180 K). The I_3 values start to decrease after about 120 h of the measurement. After that time of the measurement the temperature of the sample reached about 120 K (in the heating cycle). Though the temperature of the measurement between 200 K, in the cooling cycle, and 120 K, in the heating one, was not constant, it was obviously low. It was decided to check out the tendency of changes of the I_3 values with the elapsed time of the measurement. This attempt is presented in Fig. 4. The time values, as an independent variable, were estimated taking into account the elapsed time of the measurements. The time started to run in Fig. 4 when the temperature of the investigated sample was established at 200 K (in the cooling cycle) and it ran till the end of the measurements. It seems that I_3 rises with time of the measurements (or with keeping the sample in temperature below 180 K). I_3 starts to decrease after about 120 h of the measurements. After this time of the measurements, the temperature of the sample reached about 120 K (in the heating cycle). The observed changes of the I_3 values, with elapsed time of the measurement, confirm the already mentioned mechanism of the formation of the electron traps in polymers at low temperature. The beginning of the decrease in the

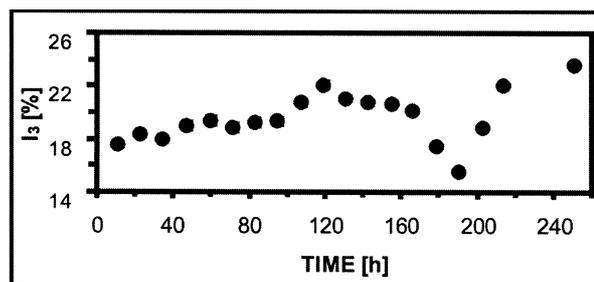


Fig. 4. The I_3 values vs. the elapsed time of the measurement.

I_3 values at about 120 K, in the heating cycle, might be explained as the result of detrapping of the electrons from their shallow traps, due to molecular motion of the polymer molecules, what results in decreasing of the o -Ps formation probability. Quite a similar behaviour of the relative intensity of the longest-lived component I_3 , at low temperature, was observed in Refs. [2, 6] (the data for the measurements in the dark).

Conclusions

The results of the positron lifetime measurements in thermo-shrunk, modified polyethylene as a function of temperature (below room temperature) are presented. At low temperature, the effect of trapping of the free electrons produced during positron irradiation was observed. Trapping of those electrons in free volume cavities increases the o -Ps formation probability. For the temperature higher than about 120 K, in the heating cycle, those electrons are detrapped and the relative intensity of the longest-lived positron lifetime component I_3 decreases. This decrease might be explained by the motion of molecules of the polymer chains. The values of the free volume cavities V seem to be the smooth function of temperature. This volume changes gradually: first, it decreases with decreasing temperature and then it increases with increasing temperature. No thermal hysteresis was noticed in the evaluated values of the free volume cavities V in the performed experiments.

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