Positron Annihilation Lifetime *in situ* Study of Deformed Polyolefin Elastomers

K. Krzemień, J. Kansy and J.E. Frąckowiak

Institute of Material Science, University of Silesia

Bankowa 12, 40-007 Katowice, Poland

The positron annihilation lifetime spectroscopy was used to investigate the free volume hole size of ethylene octane copolymers as a function of deformation in the range from 0 to 110% in steps of 10%. For each degree of deformation a series of 5–6 positron annihilation lifetime spectra was collected *in situ*. All spectra of a given series were analysed simultaneously. They were resolved into three exponential components, of lifetimes parameters τ_i and intensities I_i. The variations of τ_3 reflect three deformation regions, the elastic range, strain softening range, and plastic region.

PACS numbers: 78.70.Bj, 71.60.+z, 61.41.+e

1. Introduction

The positron annihilation lifetime spectroscopy (PALS) is one of the most important methods that provides unique information about the properties of sub-nanometer size local free volumes in polymers. In these materials a part of positron injected from radioactive source may annihilate from a positronium (Ps) state, a bound state of a positron and an electron. Ps has two spin states, a short-lived singlet state (*para*-Ps, p-Ps) with a lifetime of about 125 ps in vacuum, and a long-lived triplet state (*ortho*-Ps, o-Ps) with a lifetime of about 142 ns in vacuum. However, the lifetimes of o-Ps in polymers is shortened to a few nanoseconds because Ps can trap in free volumes, and the positron of o-Ps can annihilate with a surrounding electron from molecule. The positron annihilation lifetime spectrum of polymers usually contains at least three exponential components, attributed to annihilation of p-Ps, free positrons and o-Ps, respectively. The most important component is third component related to o-Ps. The lifetime parameter τ_3 of this component is related to the mean size of local free volume cavity [1, 2]. This relation was used by us to study the variations of size of free volume cavities as

a function of sample unidirectional deformation. It was determined that both the o-Ps lifetime τ_3 as well as its intensity I_3 depend on the deformation degree of sample [3–6]. However, according to the recent point of view I_3 depends on many factors [7] so its interpretation is not straightforward. Therefore we base in our interpretation on the variations of τ_3.

2. Experimental

2.1. Materials

The materials under investigation were four different types of ethylene octane copolymer (commercial name — engage), all supplied by DuPont Dow Elastomers. The general formula of engage type polymer is given by

$$-[CH_2-CH_2]_n-[CH_2-CH-(CH_2)_5-CH_3]_m- \qquad (1)$$
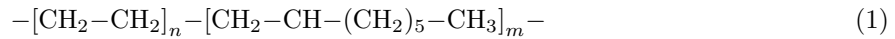
These types of polymers beside an amorphous phase include a few percent of crystal lamellar phase. There are typical and most important properties of engage in Table.

TABLE

Typical properties of engage polymers.

	Engage 8150	Engage 8200	Engage 8400	Engage 8003
Density [g/cm^3]	0.868	0.870	0.870	0.885
Crystallinity [%]	≈ 16.4			
Comonomer content [%]	39	38	40	30
Ultimate elongation [%]	780	> 1000	> 1000	670
Hardness in Shore scale	75	75	72	86
Glass transition temperature [°C]	–56	–56	–57	–86

2.2. PALS Experiment

The PALS experiment was carried out at room temperature using a fast-fast coincidence system with a time resolution of 219 ps (FWHM) monitored by using ^{60}Co source. In our experiment two identical samples were sandwiched around 5 μCi sodium chloride radioactive source ^{22}Na, which was prepared by the evaporate ^{22}NaCl solution on a kapton foil. The measurements were performed in the deformation range 0 and 110% in steps of 10%. For each degree of deformation a series of 5–6 PALS spectra was collected *in situ*. Each lifetime spectrum contained *ca.* 2.5×10^6 counts. In this way, the total statistics of the spectra making up a series was not less than 10^7 counts.

2.3. Computer analysis

The computer analysis was performed with the LT v9 program [8]. Each spectrum was resolved into three exponential components, of lifetimes parameters τ_i and intensities I_i ($i = 1\ldots3$). The whole series of spectra related to the same deformation of sample ($\varepsilon = $ const) was analyzed simultaneously. The model parameters τ_i and I_i were assumed common to all spectra making up a given series. The contribution from the annihilation in the source ($I = 11.2\%$, $\tau = 0.386$ ns) and instrumental resolution were taken into account during the analysis.

3. Result and discussion

From the measured spectra the third component parameters I_3 and τ_3 were determined. The values of τ_3 were used to determining of the mean radius (R) of free volume cavities from the Tao–Eldrup formula [1, 2]:

$$\tau_{o-\mathrm{Ps}} = 0.5 \left[1 - \frac{R}{R + R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + R_0} \right) \right]^{-1}, \qquad (2)$$

where R — the mean radius hole, $R_0 = 1.65$ Å.

Figures 1 and 2 show the variation of I_3 and R, respectively, as a function of the degree of deformation (ε) for each investigated polymer. Both those parameters are sensitive to the changes of ε. However, as it was already mentioned, I_3 depends on many different factors i.e. the Ps formation processes inside the spur [9], crystallinity of polymer [10], the degree of cross-links, the condition of polymerization [7] so our discussion of results will base exclusively on the measured values of τ_3. It is clearly seen that for higher content of comonomer the size of the
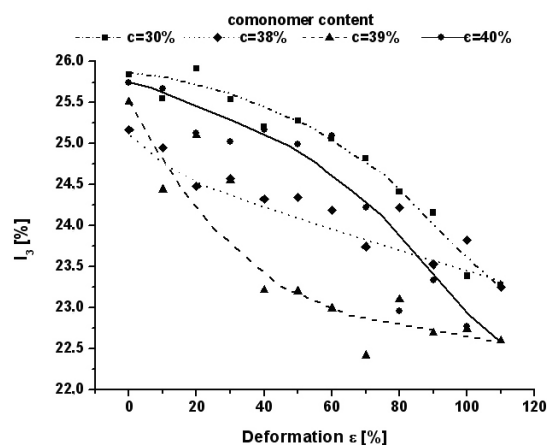

Fig. 1. The variation of intensity (I_3) as a function of deformation (ε) in ethylene octane copolymer of different comonomer content (c).
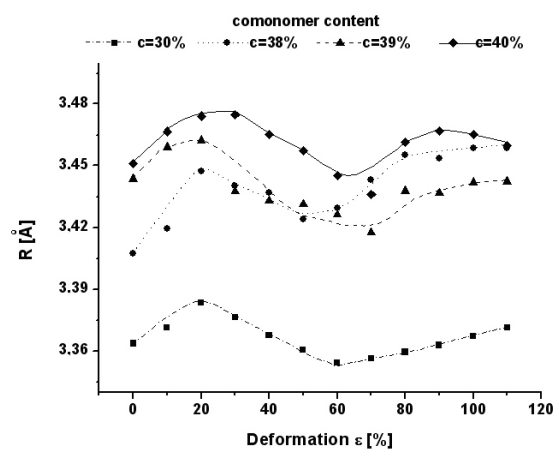
Fig. 2. The variation of free volume hole radius (R) (calculated from the Tao–Eldrup formula [3, 4]) as a function of deformation (ε) in ethylene octane copolymer of different comonomer content (c).

free volume cavities tends to bigger values. As the free volume holes are sensitive to the packing irregularities of segments as well as the amount of chains ends and free radicals [3] the hole concentration and the sizes of the free volume cavities should change during the deformation process.

The results showed in Fig. 2 reflect the three regions of stress–strain function $\sigma = \sigma(\varepsilon)$:

1) In the elastic region $(0 < \varepsilon < 20)\%$, where deformation of polymer is reversible the small deformation in the amorphous region is mainly caused by the displacement of bound lengths and rotation on bounds angles. In this region R slightly increases due to a small separation of segments [4] caused by the deformation.

2) Under a larger stress, in the strain-softening range $(20 < \varepsilon < 70)\%$, the segments tend to align and have more ordered arrangement, which reduces the effective hole size because of the more extended shapes of the holes.

3) In the plastic region $(70 < \varepsilon < 110)\%$ the degree of orientation reaches a saturation level. Chains can be ruptured owing to high stress, hence chains ends and free radicals are produced. This leads to increase in the free volume dimension [5], which is observed in increase in R.

4. Conclusions

PALS is a sensitive method to the comonomer content and to changes in microstructure of polymers caused by deformation of sample. It allows estimate quantitatively the dependence between the degree of deformation ε and the mean

radius R of free volume cavities. The obtained $R = f(\varepsilon)$ curves are strictly correlated with the different deformation regions in the $\sigma = \sigma(\varepsilon)$ dependence.

References

[1] S.T. Tao, *J. Chem. Phys.* **56**, 5499 (1972).

[2] N. Eldrup, D. Lightbody, J.N. Sherwood, *Chem. Phys.* **63**, 51 (1981).

[3] J.D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York 1980.

[4] E.E. Abdel Hady, *Polymer Degradation and Stability* **80**, 363 (2003).

[5] C.L. Wang, B. Wang, S.Q. Li, S.J. Wang, *J. Phys., Condens. Matter* **5**, 7515 (1993).

[6] S.J. Wang, C.L. Wang, B. Wang, *J. Radioanal. Nucl. Chem.* **210**, 407 (1996).

[7] T. Suzuki, T. Hayashi, Y. Ito, *Mater. Res. Innovation* **4**, 273 (2001).

[8] J. Kansy, *Nucl. Instrum. Methods Phys. Res. A* **374**, 235 (1996).

[9] Y. Ito, T. Suzuki, *Radiat. Phys. Chem.* **66**, 343 (2003).

[10] J. Serna, J.Ch. Abbe, G. Duplatre, *Phys. Status Solidi A* **115**, 389 (1989).