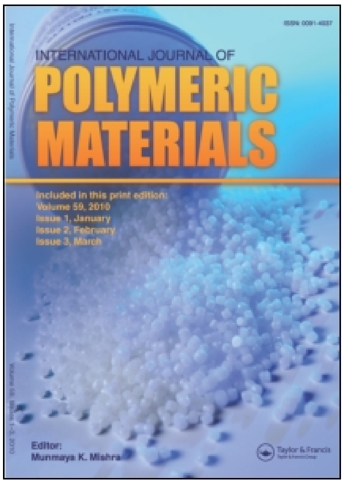

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Studies of Deformed Poly(Methyl Methacrylate) Using Positron Annihilation Lifetime Spectroscopy

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Structural rearrangements in glassy PMMA on polymer plastic deformation and recovery of residual plastic deformation in glassy state were studied by positron annihilation lifetime spectroscopy. Uniaxial compression was shown to be accompanied by a decrease in concentration of free volume microregions in disordered polymer regions, which were characterized by low packing density. Recovery of residual deformation at elevated temperatures but below glass transition point T_g proceeds without any noticeable changes in fractional content of free volume both in disordered and ordered polymer regions. The advantages of positron annihilation lifetime spectroscopy for studying microstructure and structural rearrangements in polymers were discussed.

Keywords: PMMA; positron annihilation; deformation; relaxation; structure

INTRODUCTION

In recent years, many publications concerning studying elementary free volumes in polymer materials by positron annihilation lifetime spectroscopy appeared [1–6]. The advantages of this method are related not only to estimation of a certain correlation between anni- hilation characteristics and intensity of external field but also to providing a quantitative description of polymer microstructure. This approach necessitates development of the proper mathematical apparatus and specific physical models such as the model of entrapment of positron and positronium by defects proposed by Brandt even in 70s [7, 8], speculations concerning preferential localization of positrons in ordered polymer regions and positronium (electron-positron system) in disordered regions, the corresponding kinetic equations [1], finding two positronium components in lifetime spectra of positron annihilation (lifetime of one of the components is higher than 10 nsec), and calculations of mean radius of defect from lifetime characteristics [9, 10]. Computer program CONTIN was advanced to obtain a continuous distribution of defects in polymer material from positron annihilation lifetime spectra [4].

In this work, positron annihilation lifetime technique was used to study evolution of elementary free volumes during plastic deformation of glassy PMMA and subsequent strain recovery. Note that this method has been already used to study temperature transitions in PMMA in a temperature region from 73 to 523 K as well as polymer microstructure [6].

EXPERIMENTAL

We studied commercial PMMA prepared by bulk polymerization ($M_\eta = 1.5 \times 10^6$). Before testing the cylindrical samples of PMMA (height 5 mm, diameter 5 mm) were annealed at glass transition temperature (393 K) for 1 h and then cooled to room temperature (293 K) with a cooling rate of 2 K/min.

Polymer deformation was carried out by uniaxial compression using an UTS-10 testing machine (Germany) at 293 K with a strain rate of 0.1 mm/min (2%/min) to a strain of 30 %. Then, the samples were unloaded with the same rate. Residual plastic deformation $\varepsilon_{\mathrm{res}}$ was estimated as $\varepsilon_{\mathrm{res}} = (h_o - h_{\mathrm{def}})/h_o$, where h_o-initial height of the sample, h_{def}- the height of deformed sample.

After unloading, polymer samples were allowed to relax in a free state at 333 and 363 K. Recovery of residual deformation was studied by measuring the changes in height of the test samples until a constant value of $h_{\mathrm{rel}\,\infty}$. Residual plastic deformation after relaxation was estimated as $\varepsilon_{\mathrm{res}}^{\mathrm{rel}} = (h_o - h_{\mathrm{rel}\,\infty})/h_o$. The results are summarized in Table I.

TABLE I Deformation Characteristics of PMMA Samples

Sample	h_0, mm	h_{def}, mm	$\varepsilon_{res}, \%$	T_{rel}, K	$h_{rel,} mm$	$\varepsilon^{rel}_{res}, \%$
A	Initial polymer sample with a given prehistory					
B	5.0	4.2	16.5			
C	5.2	4.3	17.3	333	4.6	11.5
D	4.9	4.0	18.4	363	4.4	10.2

Lifetime spectra of positron annihilation (lifetime and intensity) were obtained at 293 K using an ORTEC spectrometer with a resolution function of 225 ps. Contribution to positron annihilation from ^{22}NaCl source in nickel foil did not exceed 20% and was accounted for by calculating program. Annihilation characteristics τ_i and I_i as calculated by computer program POSITRONFIT [11] are presented in Table II.

Variations in fractional content and dimensions of free volume microregions induced by compression and following relaxation of PMMA samples 333 and 363 K were calculated according to a procedure described in [1,6,9]. In this case, local free volumes with positron (component with lifetime τ_2 and intensity I_2) and positronium (component τ_3 and I_3 as well as components τ_4 and I_4 in the case of four-component resolution) were presented as a three-dimensional potential well with a finite depth, and entrapment by defect was described by the corresponding kinetic equations assuming preferential localization of positrons in the polymer regions with increased packing density and of positronium in the regions with reduced packing density.

TABLE II Characteristics of positron annihilation lifetime spectra of PMMA samples

Sample	τ_1, ns	$I_1, \%$	τ_2, ns	$I_2, \%$	τ_3, ns	$I_3, \%$
A	0.242 ±0.012	45.0 ±5.0	0.514 ±0.039	32.2 ±4.7	1.93 ±0.03	22.8 ±0.7
B	0.205 ±0.015	50.3 ±8.1	0.416 ±0.043	32.0 ±7.7	1.86 ±0.04	17.7 ±0.6
C	0.227 ±0.015	48.0 ±7.0	0.457 ±0.045	31.7 ±6.9	1.85 ±0.04	20.3 ±0.7
D	0.215 ±0.011	53.0 ±6.0	0.469 ±0.043	28.9 ±5.1	1.91 ±0.04	18.1 ±0.6

Table III shows the data on the rate of free positron annihilation λ_f, concentration N_+, and effective dimensions R_+ of free volume regions in ordered structural regions of PMMA, which are characterized by higher packing density as well as the corresponding values of N_{Ps} and R_{Ps} for disordered structural regions with lower packing density.

RESULTS AND DISCUSSION

As was mentioned earlier, the number of defects N_+ and N_{Ps} is approximated by the corresponding intensities of spectral components I_2 and I_3, and effective radii R_+ and R_{Ps} are characterized by lifetimes τ_2 and τ_3. Quantitative relationships of these parameters [1] also involve the rate of free positron annihilation and the fraction of positrons involved in a positronium for a given polymer Q. Mobility of positron and positronium determined by the corresponding diffusion coefficients D_+ and D_{Ps} is also taken into account. In the case of PMMA, they are equal to 0.1–1 and 10^{-4} cm^2/s, respectively [1,7,8]. When modern equipment with high resolution is used, an exact determination of Q presents substantial difficulties because of a variety of annihilation processes involved. When spectral resolution of singlet positronium and annihilation of non-localized positrons is not allowed, and annihilation of triplet positronium before its localization is not prevented (they contribute to the shortest-lived component I_1), then an exact determination of Q is impossible. However, for PMMA samples, $Q > 4I_3/3$, and in the case of initial sample, this is equal to 32%. Evidently, no changes in fraction of positrons involved in positronium are induced by compression, but formation of positronium is prevented by elimination of free microvolumes. Hence, Q is assumed to be equal to 40 %, and this value is similar to that used in [12, 13] for PE.

TABLE III Structural parameters of PMMA samples calculated from positron annihilation lifetime spectra

Sample	λ_f, s^{-1}	$R_+, 10^{-8} cm$	$N_+ 10^{16} cm^{-3}$	$R_{Ps}, 10^{-8} cm$	$N_{Ps}, 10^{19} cm^{-3}$
A	2.46	3.4	0.7	4.1	1.46
B	3.11	3.4	1.0	4.5	0.66
C	2.67	3.4	0.6	4.2	0.76
D	2.97	3.6	0.9	4.4	0.67

Table III shows that on polymer deformation slight changes in N_+ (approximately from 0.7×10^{16} to 1.0×10^{16} cm^{-3}) lie within anticipated experimental error (20%). At the same time, a two-fold decrease in N_{Ps} is observed: from 1.5×10^{19} to 0.7×10^{19} cm^{-3}. This evidence allows one to suggest that deformation of PMMA (transition from sample A to sample B) is accompanied by decrease in fractional free volume in disordered polymer regions, and the net decrease in free volume is accomplished via decrease in fractional content (concentration) of free volume regions (N_{Ps}, Table III) not via changes in dimensions of these regions (R_{Ps}, Table III).

Recovery of residual plastic deformation in PMMA at elevated temperatures in glassy state (transition from sample B to samples C and D) proceeds without any noticeable changes in concentration and dimensions of free volume microregions both in ordered (N_+, R_+) and disordered (N_{Ps}, R_{Ps}) polymer regions (Table III).

However, the dimensions of free volume microoregions in loosely packed PMMA regions, as estimated from effective radius R_{Ps}, are equal to 0.3–0.4 nm^3 for all samples studied. By order of magnitude, this value coincides with activation volume of relaxation segmental transition (0.8–1.0 nm^3) and with the volume of statistic segment of PMMA (0.9 nm^3) [14]. This fact may serve as a supporting evidence that recovery of residual plastic deformation in PMMA at $T < T_g$ proceeds via segmental motion in disordered polymer regions.

Hence, positron annihilation lifetime spectroscopy provides a reliable means for studying polymer microstructure as well as structural transformation in polymer, in particular in PMMA, induced by deformation.

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