Pergamon

0014-3057(95)00050-X

Eur. Polym. J. Vol. 31, No. 10, pp. 1019–1020, 1995
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0014-3057/95 $9.50 + 0.00

SHORT COMMUNICATION

INFLUENCE OF HIGH PRESSURE ANNEALING ON FREE VOLUME IN POLYCARBONATE STUDIED BY POSITRON ANNIHILATION

F. SZŐCS,[1]* O. ŠAUŠA,[2] K. KRIŠTIAKOVÁ,[2] J. KRIŠTIAK[2] and M. KLIMOVÁ[1]

[1]Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava and [2]Institute of Physics, Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic

(Received 17 May 1994; accepted in final form 7 June 1994)

Abstract—The method of positron annihilation was used to study changes of free volume in polycarbonate. Annealing at 180°C and pressure 800 MPa causes significant changes of free volume (~23%) compared to nonannealed polycarbonate. The free volume compressibility was estimated to be $\sim 3.10^{-5}$ MPa^{-1}. The distribution of free volume has changed. This work discusses the influence of free volume on molecular dynamics and the transportation mechanism of free radical decay.

INTRODUCTION

Free volume and its distribution are closely connected to a molecular movements of segments of main polymer chains. In fact only such types of molecular motions can be realized for which there is enough free volume in the vicinity of chain segments. To understand the impact of the mechanism of molecular motions one needs information about the size and distribution of free volumes. The processes of physical ageing, fatigue of polymers, formation and decay of free radicals are closely connected with changes of free volumes. The method of positron annihilation permits determination of free volume as well as a free volume distribution curve connected with the polymer structure and properties. The method is based on the fact that the lifetime τ of the bound state of injected positron and electron, positronium atom Ps, depends on the spherical free volume radius R, in which there is Ps. The relation between τ and R is determined by a semiempirical formula [1]

$$\tau = 0.5[1 - R/(R + 1.656) + 0.159 \sin(R/(R + 1.656))]^{-1}$$

where τ is given in nsec and R in Å.

This work determines changes of free volumes initiated by external high pressure on polycarbonate in the solid state and discusses the influence of free volume on the molecular dynamics of macromolecular segments.

EXPERIMENTAL

The measurements were performed with samples of polycarbonate, PC Makrolon 3100 (Bayer, Germany) of a cylindrical shape with a 5 mm diameter and 10 mm length with the following characteristics: $M_n = 3.2 \times 10^4$, $\rho = 1.2$ g cm^{-3} and $T_g = 150$°C.

The polymer samples were annealed for 10 min in pressure equipment described in detail elsewhere [2] at a temperature of 180°C and under pressures of 50 and 800 MPa. At the given pressures the sample was cooled to 25°C during 30 min. The shape of the untreated sample was plate-like with a thickness of 2 mm. The samples were measured at room temperature and under 0.1 MPa pressure during all the measurements.

The lifetime measurements have been performed using a standard lifetime spectrometer with plastic scintillators coupled to Philips XP 2020 photomultipliers. Ortec 583 discriminators were used for selecting the energy and providing timing signals to a time–amplitude converter. The time resolution (FWHM) of prompt spectra was about 320 psec.

The positron source ^{22}NaCl was deposited in an envelope of Kapton foils (8 μm thick). It was then sandwiched in between two identical pieces of the samples. A model independent estimate of the instrument resolution function was obtained from the decay curve of ^{207}Bi isotope with a single lifetime of 182 psec.

In the analysis the Gregory–Provencher's program CONTIN [3] and the PATFIT-88 program [4] were employed. The CONTIN provides the positron annihilation rate probability density function $\alpha(1/\tau)$ using a Laplace transform of experimental data. Only that part $\alpha(1/\tau)$ describing the distribution of rates for the Ps species has been considered in the derivation of the corresponding free volume probability density distribution (PDF) for the hole radius $f(R)$ or the hole volume $g(V)$, respectively. The details of the procedure are given in [5]. The standard PATFIT-88 package provides mean values of the lifetime τ and its intensities, I.

RESULTS AND DISCUSSION

Results of three component analysis of the lifetime are listed in Table 1. Figure 1 shows the dependence of the relative probability $f(R)$ to find a hole with a radius R in the samples annealed under the pressures of 50 and 800 MPa as well as for untreated samples. Fig. 2 displays the distributions of free volumes $g(V)$ calculated from the $f(R)$ distribution for all three kinds of samples.

The results of the paper [6] and the data from Table 1 permit the calculation of the fractional free volume f, which

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*To whom all correspondence should be addressed.

Table 1. Results of positron lifetimes in polycarbonate. All results were from least-squares fit using PATFIT-88 program [4]. All lifetimes are in picoseconds, and all intensities are in percentages

Sample	τ_1	τ_2	τ_3	I_1	I_2	I_3
Untreated	203.2 ± 5.9	507 ± 12	2141 ± 10	36 ± 2	35 ± 2	29 ± 1
Pressed 50 MPa	223.5 ± 1.3	566 ± 18	2007 ± 9	75 ± 1	11 ± 1	14 ± 1
Pressed 800 MPa	206.3 ± 3.9	443 ± 33	1991 ± 20	71 ± 3	18 ± 3	11 ± 1

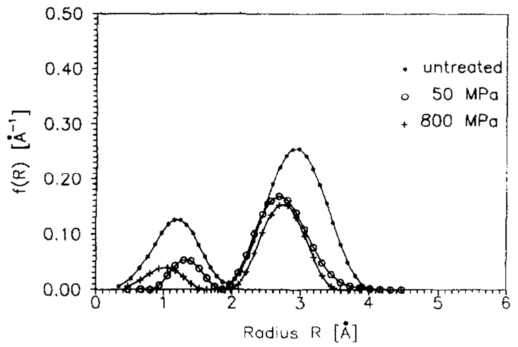

Fig. 1. Hole radius distribution function $f(R)$ for untreated polycarbonate and treated sample under pressures of 50 and 800 MPa, respectively.

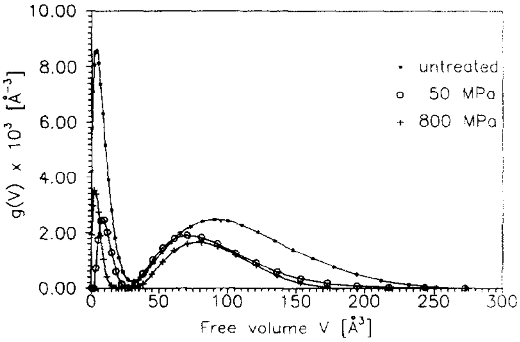

Fig. 2. Distribution of free volume $g(V)$ for untreated polycarbonate and treated sample under pressures of 50 and 800 MPa, respectively.

is equal to 10.8 and 8.3% in the case of untreated and 800 MPa samples, respectively. From this, the free volume compressibility β as defined by $\beta = -(\Delta f/\Delta P)_T$, is estimated to be 3.10^{-5} MPa^{-1}. It should be noted that this compressibility value is related to the compressibility of the free volume where Ps is created and excludes the compressibility of the occupied volume as well as the free volume with a very small value of R.

From Figs 1 and 2 we can see two kinds of free volumes. The first one with a maximum around the radius of 1.4 Å had smaller intensity (probability to appear) in comparison with the second one. This has a maximum of the $f(R)$ distribution around $R \sim 2.8$ Å. If the sample is annealed under pressure, the values of the maximum radii are diminished and the distribution curves are compressed. The shifting and the compression of the distribution are also observed for the first kind of free volume. In this case we see a different behaviour of $f(R)$ at different pressures. The impact of high pressure is a reduction of free volumes from 102 to 78 Å^3. Free volumes of ~ 7 Å^3 are almost unchanged.

The influence of high pressure on the dynamics of molecular motions in polycarbonate was monitored by an ESR method by measurement of the rate of macroradical decay in γ-irradiated polycarbonate for a temperature range of 90–200°C and pressure range of 0.1–800 MPa [2]. A kinetic study of macroradical decay in amorphous polymers at high pressure provided information about slowing down of free radical decay as a result of diminution of free volume [7]. Pressed polymer does not facilitate molecular motions of polymer chains requiring over-critical free volume. As a result the free-radical centre motion, of the macroradical decay is slowed down. Work [2] showed the dependence of the rate constant of polycarbonate macroradicals decay in detail. It is obvious from the results that the rate constant of free radical decay in polycarbonate at 180°C falls with increasing pressure up to 600 MPa. In the region of high pressures, that is 600–800 MPa, one can follow saturation and further pressure increase has only a slight impact on the value of the rate constant of free radical decay.

Long physical ageing of amorphous polycarbonate causes slowing down of free radical transport as a result of reduction of free volume [8]. During ageing, there are similar changes of volumes as the ones followed in polycarbonate annealed at 50 and 800 MPa.

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