POSITRON ANNIHILATION STUDIES OF GAMMA IRRADIATION EFFECTS ON UV-CURED POLYMERS BASED ON ACRYLATE OLIGOMERS

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Positron annihilation lifetime spectroscopy is applied to the study of gamma irradiation effect on polymers based on the acrylate oligomers. The gamma irradiation of Co^{60} was carried out in air, with a flux of 20 Gy s^{-1}. The measurements were made on specimens with different absorbed dose in the range 10-100 kGy. The longest lifetime, τ_3, in three-component analyses of the spectra was associated with the pick-off annihilation of ortopositronium trapped in voids. After irradiation changes in the lifetimes are observed. The intensity of the longest-lived component, I_3, increases in comparison with the as-received sample. These results are discussed on the basis of free volume model.

INTRODUCTION

Positron annihilation is a useful technique to investigate characteristic of materials. Positrons injected in substances lose their energy through elastic collisions and finally annihilate with electrons through several processes. In polymers positrons can pick up an electron from substance and form a neutral particle called positronium (Ps). However the lifetime of ortho-positronium (o-Ps) (140 ns in vacuum) is long, and positron in o-Ps have good chance to pick up an electron from the surrounding medium and annihilates much faster. This process is called pick-off annihilation.

The lifetime spectrum of positrons annihilating in polymers usually contains three exponentially decaying components. The lifetimes τ_1 and τ_2 are associated to annihilation of positrons not forming bound states, but localised into regions characterised by different electron densities; τ_1 contains also annihilation from para-Ps. The longest-lived component with a lifetime τ_3 is attributed to the annihilation of o-Ps localised in a nm size hole. The positronium formation probability and lifetime are extremely sensitive to electron density surrounding Ps. The o-Ps localises in the space between and along chains and at chain ends (free volume holes), and the lifetime gives indication of the mean radii of these holes. The free volume model, express that Ps can only form in those free spaces of the lattice having a size superior to some critical

value. Furthermore, a very successful semi-empirical equation has been established relating the o-Ps lifetime to the size of the free volume hole in which it annihilates, thus τ_3 corresponds to a spherical space with a radius R, according to the following equation [1]:

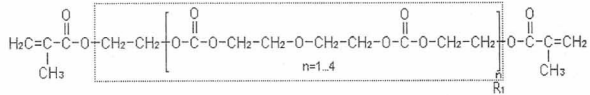
$$\tau_3(ns) = 0.5\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1}, \quad (1)$$

where ΔR=0.166 nm is the fitted empirical electron layer thickness. It is considered too that the o-Ps intensity I_3 reflects the probability of formation of o-Ps atoms, is proportional to the hole concentration [2].
The study of the radiation changes occuring in the structure of materials as well as in their electrical, mechanical and optical properties are of utmost importance to material science. The aim of this paper was to understand the changes induced by gamma irradiation in microscopic structure of a sample of polymers based on the acrylate oligomers, using Ps as a probe.

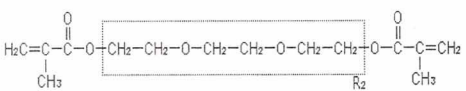
EXPERIMENTAL

Positron lifetime studies were performed in the UV-cured composition based on the acrylate oligomers The sample denoted as D-1 content 88.8% OCM-2, 10% TGM-3 and it has been chosen for current investigations.

OCM-2



TGM-3



Isobutyl-benzoin ether as a photoinitiatior was used The details concerning sample preparations have already been reported [3].
The gamma irradiation was carried out in air using a ^{60}Co source with a flux, at the sample position, of 20 Gy s^{-1}. The measurements were made on specimens with different absorbed dose in the range 10÷100 kGy.
Measurements of positron lifetimes were curried out with an ORTEC spectrometer of resolution FWHM of about 270 ps. A Na^{22} isotope with 7.4×10^5 Bq activity was used as the positron source. The source was

placed between two identical samples, forming a „sandwich" system. The PAL spectra were measured at room temperature.

RESULTS AND DISCUSSION

The positron annihilation lifetime spectra have been analysed into discrete components using the program LT [4] with a three-component model.
According to the common interpretation we attribute the longest component to o-Ps decay. As the o-Ps component is relevant to the free-volume properties, and it is markely sensitive to the microstructure changes; so in this paper, our main attention is paid to the changes in τ_3 and in I_3 with dose γ-irradiation (10-100 kGy). The lifetimes τ_3 of o-Ps and the intensities I_3 versus γ-irradiation dose are shown in Fig.1 and Fig.2.

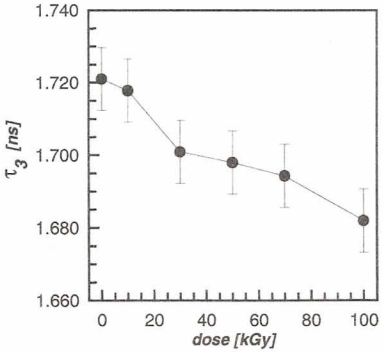


Fig.1. The o-Ps pick-off lifetime τ_3 (related to the average free volume hole radius) as a function of γ-irradiation dose

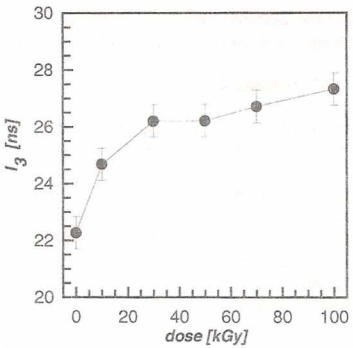


Fig.2. The o-Ps pick-off intensity I_3 (related to the average free volume concentration) as a function of γ-irradiation dose

These figures show that both τ_3 and I_3 are affected by the irradiation. In the dose range the intensity of o-Ps, I_3 increases from about 22% for as-received sample to about 27% for sample irradiated with dose 100 kGy. The lifetime o-Ps τ_3 exhibits decreasing with an increasing dose from about 1.721 (as-received sample) to 1.682 ns (at dose 100 kGy). The mean volume of the free-volume holes (assuming spherical geometry), $V_f = 4\pi/3R^3$, where is R calculated according Eq.(1) are presented in the Table 1.

Table 1. Variation of mean free volume V_f. with dose γ-irradiation

Dose [kGy]	$V_f \times 10^{-30}$ [m^3]
0	71,77±0,51
10	71,50±0,51
30	70,06±0,51
50	69,80±0,51
70	69,46±0,51
100	68,44±0,51

The free volumes are estimated to decrease from about 0.072 nm^3 to 0.068 nm^3. The increase in I_3, which is associated with an increase in the number of free volume holes imply the creation of new free-volume

holes. On the other hand, from a positron annihilation lifetime spectrum analysed into discrete components, it is possible to draw conclusions only on the mean size of the holes. An decrease of of mean volume of the holes, and therefore of τ_3, must be correlated to an increase in hole concentration, owing to the increase of the number of smaller volume holes. This suggests that the decrease of the mean value of the volume can be mainly due to the decrease of larger hole volumes rather than an effective decrease of the volume and that the existing free volumes are divided into smaller parts.

CONCLUSION

Positron lifetime spectroscopy was used to study irradiated polymers. It can give detailed information on the changes of free volume of the sample. The most likely explanation for decrease in τ_3 and simultaneously increase in I_3 is change in the free volume caused by the formation of new bonds or "crosslinking".

ACKNOWLEDGMENT

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