Electron Irradiated Effect in Polyurethanes Studied by Positron Annihilation Lifetime Spectroscopy

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Abstract: The intensity variation of positronium as a result of electron irradiation has been studied on polyurethanes (PU) using positron annihilation lifetime spectroscopy (PALS). The PALS measurement was carried out at room temperature with a conventional fast-fast coincidence system. The lifetime spectra were analyzed into four components using melt program to extract the positron parameters such as lifetime and intensity. Due to irradiation a decrease of intensity about 2.7% was observed up to 10kGy. Free volume radius has been calculated for electron irradiated PU. PALS measurement has also been performed to study the effect of temperature variation in the range 30K to 310K. Analysis by melt program on the spectra shows that the fourth lifetime component increases significantly above glass transition temperature.

Keywords: Positron annihilation, positronium lifetime, ortho-positronium, trapped electrons, free volume

Introduction

Many modern techniques have been developed to study the relationships between the molecular and crystal structure of polymers and their physical and chemical properties (Ravat et al., 2001; Cao et al., 1993). A positron injected into a polymer from a radioactive source, after a fast slowing-down requiring some picoseconds at most, becomes thermalized and during diffusion through the medium annihilation between positron and one of the surrounding electrons takes place: the pair disappears with the production of γ rays. Before the last event, the positron can form with an electron, a bound system called positronium (Ps). Ps forms in the two states: ortho- and para-positronium (o-Ps and p-Ps); the triplet and the singlet state of the positron-electron system, respectively (Cao et al., 1998). The intrinsic lifetime of p-Ps is 0.0125 ns, while that of o-Ps is 142 ns in a vacuum. The lifetime of o-Ps in polymers might be shortened to a few (1−5) ns because Ps can be trapped in molecular packing defects, e.g., free volumes, and the positron of o-Ps can annihilate with an electron from the inner wall of the free volume, which is called “pick-off annihilation”. The result is an annihilation spectrum with different components, whose study is a potentially useful to obtain information on the structure of the host medium. In condensed media, 75% of the Ps formed will be o-Ps and 25% will be p-Ps. The probability of Ps formation depends on the physical and chemical properties of the materials.

Using different physical stimuli, like temperature or radiation, information can be obtained on various properties of the investigated solids, such as the annealing properties of extrinsic defects or the glass transition temperature in the case of polymers (Jean, 1990).
PALS enables one to measure the lifetimes and relative abundances or intensities of the various positron state. Both types of parameters are sensitive to the physico-chemical environment of the sites of annihilation. Thus, most generally, it appears that the Ps triplet state (o-Ps) intensity is correlated with the number of free spaces, while its lifetime can be quantitatively correlated with the size of these spaces (Schrader and Jean, 1988).

PUs are the widely used materials and are characterized by the presence of various chemical groups. In this paper we will focus on the change of physical properties of PUs induced by electron irradiation. We investigate the irradiation effects for doses from 5 kGy to 100 kGy using PALS. For the characterization of amorphous polymers, the determination of the free volume plays an important role. Among the techniques which yield information about the free volume, PALS is the most direct one since it allows the detection of free volume holes on an atomic scale. Variation of lifetime with temperature has also been investigated in the present study using the PALS on PU.

PUs are characterized by the presence of urethane (–NHCOO–) groups and other functional groups. The presence of these groups determine the properties of polymers. Generally, the PU studies are based on toluene diisocyanate (TDI) and polyether or polyester diols and a polyfunctional cross linking agent for the extension of the polymer. With these reagents, amorphous polymers are usually obtained.

Materials and Methods

**Instrumentation for PALS:** In this study the PAL spectra of the sample have been determined by detecting the prompt γ ray (1.28 MeV) that accompanies the emission of a positron from the $^{22}$Na radioisotope and the annihilation γ rays (0.511 MeV). A fast-slow coincidence system with a time resolution of 216 ps was used to record all the PAL spectra. The most common positron source employed in the positron annihilation experiment is $^{22}$Na, which decays to $^{22}$Ne with the simultaneous emission of positron and a γ-ray of 1.28 MeV. The positron source was prepared by depositing about 20 μci of aqueous $^{22}$NaCl on a thin aluminum foil of 0.015 μm thick and area of 5×5 mm$^2$ and covering with same foil after drying. The source was sandwiched between two identical samples of about 10×10×1 mm$^3$. About five million events of annihilation being collected in each PALS spectrum.

**Sample Preparation:** In the present study the PU sample produced by the polyaddition reaction of a polyisocyanate with a polyalcohol (polyol) in the presence of a catalyst and other additives. A urethane linkage is produced by reacting an isocyanate group, -N=C=O with a hydroxyl (alcohol) group, -OH. In the present study the PU sample has been obtained by cross linking of 2, 4-Toluene diisocyanate (contains two isocyanate groups) with polytetra myethylene ether glycol (contains two hydroxyl groups).
MOCA, 4,4-methylene-Bis (2-chloroaniline) is a good crosslinking agent for Polyurethane Elastomer. Here it is used as a chain extender. An additive Tris (2-chloroethyl) phosphate (TCEP) has been used as a catalyst.

![4,4-methylene-Bis(2-chloroaniline) (MOCA)](image)

The samples were irradiated by electron beam having the doses of 5, 10, 20, 50, and 100 kGy. The electron irradiations were carried out in air, at about room temperature with a flux: Current: 5.1 mA; Energy: 1.8 MeV; Dose rate: 4.2 kGy/s. The analysis of positron annihilation lifetime spectra were performed using MELT program which is based on the Bayes’ theorem and maximum entropy principle (Shukla et al., 1993, 1997) with no source correction. The entropy weight factors were set to a constant value $10^{-4}$ to $10^{-8}$. In polymers, three lifetime components or more were commonly observed depending on the statistical quality of the measured data. The PALS spectra were analyzed in terms of four components, with lifetime $\tau_i$ and intensities $I_i$. Subscripts $i = 1−4$ are to be ascribed to the singlet Ps state ($\tau_1$: 0.1−0.2 ns) from p-Ps, free positron ($\tau_2$: ~0.4 ns) and triplet states (o-Ps) in the crystalline and amorphous phases ($\tau_3,4$: 1−3 ns), respectively.

**Results**

Before and after irradiations the PAL spectra for PU were automatically decomposed into four lifetime components with melt. Each lifetime corresponds to the average annihilation rate of a positron in different state. The shortest lifetime and intensity components are $\tau_1 = (0.1−0.13)$ ns and $I_1 = (7.6−10)$%, respectively belongs to the annihilation of p-Ps atoms, while the second shortest one, $\tau_2 = (0.351−0.361)$ ns and $I_2 = (66−71)$% arises from the free annihilation of positrons in the polymer matrix. The two longer lifetimes and the corresponding intensities are $\tau_3 = (0.8−1.0)$ ns, $I_3 = (1.7−3.8)$% and $\tau_4 = (2.5−3.6)$ ns, $I_4 = (17.9−20.6)$%, as it is commonly accepted. These are connected with the o-Ps pick off annihilation at open volume holes. In Fig. 1 the variation of lifetimes with irradiation doses has been shown. The holes, connected with $\tau_4$ are located mainly in the amorphous parts of the samples (Dlubek et al., 1998). Most of the authors (e.g. Dlubek et al., 1998, and references therein) consider that the lifetime of the order of 1 ns is due to annihilation of o-Ps trapped at holes in the crystalline regions of the polymers. Several workers have suggested that this may be ascribed to Ps trapped in voids at the crystal-amorphous interface (Balta et al., 1985; Kindle and Reiter, 1987). In any case, due to high degree of imperfection of polymer materials, Ps atoms and positrons should be considered as localized before annihilation.

The variation of $I_1$ and $I_2$ with irradiation doses has been shown in Fig 2. A semiempirical correlation between the free volume hole radius $R$ and the o-Ps lifetime $\tau_4$ has been established (Eldrup et al., 1981 and Tao, 1972) as:

$$\tau_4 = 0.5 \left(1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0}\right)\right)^{-1}$$

where the cavity hosting Ps is assumed to be a spherical void with effective radius R. Such a Ps trap has a spherical potential of radius $R_0$ with an electron layer of thickness: $\Delta R = R_0 - R$ in
which positron annhilates. The $\Delta R = 0.166 \text{ nm}$ has been determined empirically by fitting Eq. (1) to o-Ps annihilation data (Nakanishi and Jean, 1988). For this electron irradiated PU sample free volume ($V = \frac{4}{3}\pi R^3$) has been calculated for those holes belongs to the amorphous region using the value of $\tau_4$ as shown in Fig.3. Free volume just follows the trend of lifetime which implies that there is no expansion of the free volume.

The temperature dependence of PU between 30 K to 310 K has been investigated using PALS technique. A monotonic increase in $\tau_4$ is observed, which is very similar for the various samples (Wang et al., 1998; Uedono et al., 1997; He et al., 2003; Consolati et al., 1998). As shown in Fig.4 two temperature regions are distinguished as $T < 200 \text{ K}$ and $200 < T < 320 \text{ K}$. Below $200 \text{ K}$ there is a moderate increase rate whereas above $200 \text{ K}$ there is a sharp increase rate of $\tau_4$ with temperature.

Discussion
Fig.1 shows that $\tau_4$ is quite constant with doses that means the average sizes of the free volume holes do not change with the irradiation dose. Whereas $\tau_3$ does not show a particular trend with the irradiation dose. The constancy in $\tau_4$ and $\tau_3$ may be explained as follows. Above the glass
transition temperature (240–260) K (Consolati et al., 1998), polymers are rubbery and microstructures in the amorphous region can move easily like bubbles in liquid. The Ps which seeks and digs holes in the amorphous region, expands the hole size like forming bubbles in liquid. Finally the hole sizes become almost constant and depends on the temperature, pressure etc.

Fig. 2 shows the variation of intensity of o-Ps lifetime component \( I_3 \) and \( I_4 \) with electron irradiation dose. The variation of \( I_4 \) with increasing dose shows three different regions. First there is a smooth decrease of \( I_4 \) to about 2.7% up to 10 kGy. From 10 kGy to 20 kGy there is a sharp rise of \( I_4 \) whereas from 20 kGy to 50 kGy it rises more slowly. Above 50 kGy \( I_4 \) becomes almost constant with the doses.

In this case Ps formation is considered to be affected by the two factors: free radical and change of polymer structures induced by cross-linking. A sharp decrease of 2.7% in \( I_4 \) at around 10 kGy was observed in electron irradiated PU is supposed to be mainly due to the radiation induced free radicals. This indicates that PU has a large fraction of amorphous part with a small number of free radicals in the amorphous region. Considering the increase in \( I_4 \) above 10 kGy, it seems that structure changes induced by an irradiation dose of less than about 50 kGy contribute to the increase in \( I_4 \), which may be due to the development of network structures. Hence, the overall decrease in \( I_4 \) between (10-50) kGy is mainly suspected due to free radicals; the structure changes may have a smaller effect on \( I_4 \) than the free radicals in this dose range resulting in a smaller back increase in Ps formation.

The trend of \( \tau_4 \) versus the temperature in the range (30-310) K is shown in Fig.4. The lifetime \( \tau_4 \) undergoes a transition in the range (180-200) K and then increases rapidly with temperature. A linear correlation between \( \tau_4 \) and temperature is observed with a definite slope change at (180–200) K. The glass transition temperature \( T_g \) is conventionally assigned to the onset temperature of micro-Brownian motion of the amorphous main chain. Above \( T_g \), the polymer matrix becomes rubbery and the fractional free volume content of polymer increases dramatically with temperature. The trapped Ps experiences an environment in which the electron density rapidly decreases with increasing temperature. A corresponding sharp rise of o-Ps lifetime with increasing temperature above \( T_g \) is observed. To define more accurately the \( T_g \), a linear least-squares analysis was used to fit two straight line segments to the lifetime versus temperature data, as shown in Fig.4. The intersection of two straight lines above 180 K and below 200 K shows a glass transition temperature of about 190 K.

**Conclusion**

The study of electron irradiation effects on PU by PALS allows us to extract the information that the observed fall in o-Ps intensity in the dose range 0–10 kGy is due to the electron quenching by radical, produced in irradiation. Cross-linking seems to be the more likely explanation to the increase in the Ps yields. The o-Ps lifetime in either crystalline or amorphous phase remains constant with dose variation. The increase of \( \tau_4 \) with temperature is related with the free volume change due to micro-Brownian motion of the amorphous main chain. However further information is still necessary in such system for a better understanding of the relationship between lifetime spectroscopy parameters and various properties of polymeric matrices.

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