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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).

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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).

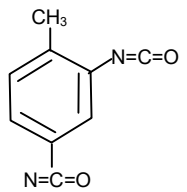
PUs are the widely used materials and are characterized by the presence of various chemical groups. In this paper we will focus on the change of physical properties of PUs induced by electron irradiation. We investigate the irradiation effects for doses from 5 kGy to 100 kGy using PALS. For the characterization 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.

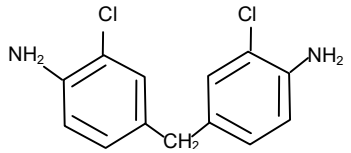
Sample Preparation: In the present study the PU sample produced by the polyaddition reaction of a polyisocyanate with a polyalcohol (polyol) in the presence of a catalyst and other additives. A urethane linkage is produced by reacting an isocyanate group, -N=C=O with a hydroxyl (alcohol) group, -OH. In the present study the PU sample has been obtained by cross linking of 2, 4-Toluene diisocyanate (contains two isocyanate groups) with polytetra mythylene ether glycol (contains two hydroxyl groups).



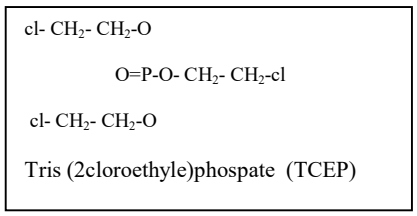
2, 4 Toluene diisocyanate

HO-CH_2- CH_2- CH_2-O-H
Polytetra mythylene ether glycol

MOCA, 4,4-methylene-Bis (2-cloroaniline) 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-cloroaniline) (MOCA)



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 $1e^{-4}$ to $1e^{-8}$. 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 τ_i and intensities I_i. Subscripts i = 1−4 are to be ascribed to the singlet Ps state (τ_1: 0.1−0.2 ns) from p-Ps, free positron (τ_2: ~0.4 ns) and triplet states (o-Ps) in the crystalline and amorphous phases (lifetime $\tau_{3,4}$: 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 τ_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, τ_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 τ_3 = (0.8-1.0) ns, I_3 = (1.7−3.8)% and τ_4 ~2.5 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 τ_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_3 and I_4 with irradiation doses has been shown in Fig 2. A semiempirical correlation between the free volume hole radius R and the o-Ps lifetime τ_4 has been established (Eldrup *et al.,* 1981 and Tao, 1972) as:

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

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 annihilates. The ΔR = 0.166 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 ($V = 4/3\pi R^3$) has been calculated for those holes belongs to the amorphous region using the value of τ_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 τ_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 K and 200 <T < 320 K. Below 200 K there is a moderate increase rate whereas above 200 K there is a sharp increase rate of τ_4 with temperature.

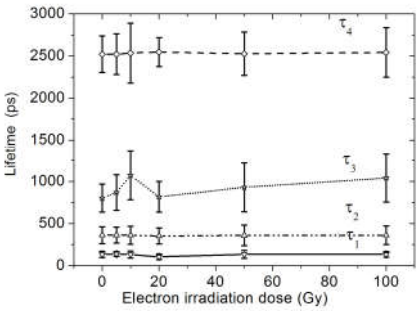


Fig.1. The variation of o-Ps lifetime τ_1, τ_2, τ_3, τ_4 for PU as a function of electron irradiation dose

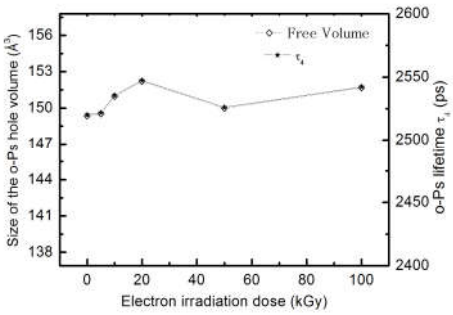


Fig. 3. The variation of free volume V as a function of electron irradiation dose in PU

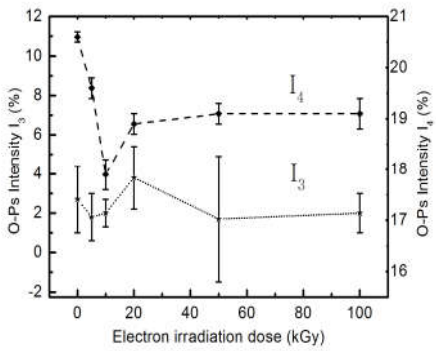


Fig.2 . The variation of o-Ps intensity I_3 and I_4 for PU as a function of electron irradiation dose

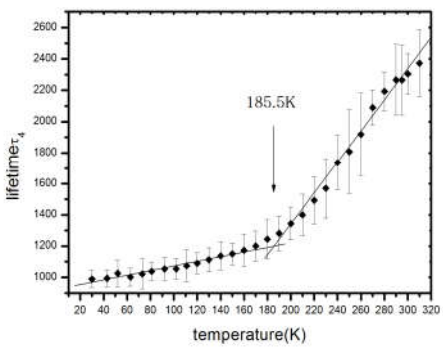


Fig. 4. The variation of o-Ps lifetime τ_4 as a function of temperature T in PU

Discussion

Fig.1 shows that τ_4 is quite constant with doses that means the average sizes of the free volume holes do not change with the irradiation dose. Whereas τ_3 does not show a particular trend with the irradiation dose. The constancy in τ_4 and τ_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 τ_4 versus the temperature in the range (30-310) K is shown in Fig.4. The lifetime τ_4 undergoes a transition in the range (180-200) K and then increases rapidly with temperature. A linear correlation between τ_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 τ_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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References

Balta Calleja, F.J., Serna, J., Vicenta, J. and Segovia, M.A. 1985. Structural implications on positron lifetimes in lamellar polyethylene with chain defects. *Journal of Applied Physics* 58: 253-259

Cao, H., Zhang, R., Yuan, J.P., Huang, C.M., Jean, Y.C., Suzuki, R., Ohdaria, T. and Nielsen, B. 1998. Free volume hole model for positronium formation in polymers: surface studies. *Journal of Physics Condensed Matter* 10: 10429-10442

Cao, N., Pegoraro, M., Biachi, F., Landro, L.D. and Zanderighi, L. 1993. Gas transport properties of polycarbonate-polyurethane membranes. *Journal of Applied Polymer Science* 48: 1831-1842

Consolati, G., Kansy, J., Pegoraro, M., Quasso, F. and Zanderighi, L.1998. Positron annihilation study of free volume in cross-linked amorphous polyurethanes through the glass transition temperature. *Polymer* 15 39: 3491-3498

Dlubek, G., Saarinen, K. and Fretwell, H.M. 1998. The temperature dependence of the local free volume in polyethylene and polytetrafluoroethylene. *Journal of Polymer Science: part B: Polymer Physics* 36: 1513-1528

Eldrup, M., Lightbody, D. and Sherwood, J.M. 1981. The temperature dependence of positron lifetimes in solid pivailic acid. *Chemical Physics* 63: 51-58

He, C., Suzuki, T., Shantarovich, V.P., Ma, L., Matsuo, M., Kondo, K. and Ito, Y. 2003. Positronium formation in low density polyethylene. *Physics Letters A* 313: 223-230

Jean, Y.C. 1990. Positron annihilation spectroscopy for chemical analysis: a novel probe for microstructural analysis of polymers. *Microchemical Journal* 42: 72-102

Kindle, P. and Reiter, G. 1987. Investigations on the low temperature transitions and time effects of branched polyethylene by the positron lifetime technique. *Physica Status Solidi A* 104: 707-713

Nakanishi, N. and Jean, Y.C. 1988. Positron and positronium chemistry. In: Schrader, D.M. and Jean, Y.C. (eds) *Positron Positronium Chemistry, Studies in Physical and Theoretical Chemistry*. Elsiever, Amsterdam

Ravat, B., Grivet, M., Grohens, Y. and Chambaudet, A. 2001. Electron irradiation of polyesterurethane: study of chemical and structural modifications using FTIR, UV spectroscopy and GPC. *Radiation Measurements* 34: 31-36

Schrader, D.M. and Jean, Y.C. (eds) 1988. *Positron Positronium Chemistry, Studies in Physical and Theoretical Chemistry*. Elsiever, Amsterdam

Shukla, A., Peter, M. and Hoffmann, L. 1993. Analysis of positron lifetime spectra using quantified maximum entropy and a general linear filter. *Nuclear Instrumentents & Methods in Physics Research A* 335: 310-317

Shukla, A., Hoffmann, L., Manuel, A.A. and Peter, M. 1997. MELT 4.0 a program for positron lifetime analysis. Presented in *11th International Conference on Positron Annihilation (ICPA-11)*, Kansas City, Missouri, USA, May 25-30

Tao, S.J. 1972. Positronium annihilation in molecular substances. The *Journal of Chemical Physics* 56: 5499-5510

Uedono, A., Kawano, T., Tanigawa, S., Ban, M., Kyoto, M. and Uozumi, T. 1997. Transition and relaxation processes of polyethylene, polypropylene, and polystyrene studied by positron annihilation. *Journal of Polymer Science. B: Polymer Physics* 35: 1601-1609

Wang, C.L., Hirade, T. and Maurer, F.H.J. 1998. Free-volume distribution and positronium formation in amorphous polymers: temperature and positron-irradiation-time dependence. *The Journal of Chemical Physics* 11 108: 4654-4661