Structure dependence of gamma ray irradiation effects on polyurethane and epoxy resin studied by PAL technique

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Abstract

Positron annihilation lifetime (PAL) technique has been employed to study the microstructural changes of polyurethane (PU), EUXIT 101 and epoxy risen (EP), EUXIT 60 by Gamma-ray irradiation with the dose range (95.76 - 957.6) kGy. The size of the free volume hole and their fraction in PU and EP were determined from ortho-positronium lifetime component and its intensity in the measured lifetime spectra. The results show that the irradiation causes significant changes in the free volume hole size (V_h) and the fractional free volume (F_h), and thereby the microstructure of PU and EP. The results indicate that the γ-dose increases the crystallinity in the amorphous regions of PU and increase the cross-linking of EP.

دراسة تأثير اشعة كاما على البنية التركيبية لبولي يوراثين وراتنج الايبوكس باستخدام تقنية عمر فناء البوزترون

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الخلاصة

استخدمت تقانة عمر فناء البوزترون لدراسة التغيرات في البنية المجهرية الناتجة من تعرض البولي يوراثين (EUXIT 101) و راتنج الايبوكسي (EUXIT 60) الى جرع من اشعة كاما ضمن المدى (95.76-957.6) كيلوكري. تم حساب حجم الفجوات الحرة و نسبة الفجوات الحرة في البولي يوراثين والايبوكسي من خلال مركبة عمر البوزترونيوم وشدته في طيف عمرالفناء.

بينت النتائج بان معدل الاشعاع يسبب تغيرات بليغة في مقدار حجم الفجوات الحرة و نسبة الفجوات الحرة، وبالتالي التغيرات في البنية المجهرية.

تظهر النتائج انه بزيادة جرع اشعة كاما يزداد تبلور مادة البولي يوراثين ويزداد تشابك اواصر الايبوكسي.

Introduction

The studies of microstructure like free-volume properties at a molecular and atomic scale can provide a basic understanding of the mechanical and physical properties of polymers [1].

In PAL technique, one employs the positron emitted from a radioactive source as a probe to monitor the lifetime of the positron and positronium (Ps) (a bound atom consists of an electron and a positron) annihilation in the material under study [2].

The positron and positronium atoms entering the polymer can be trapped in open spaces like holes, voids or cavities. The corresponding annihilation 0.511MeV photons come from these open spaces. Positrons produced by the radioactive isotope [22]Na are commonly used. The Ps atom formed can be in a singlet state para-positronium (p-Ps) or triplet state

ortho-Positronium (o-Ps), with mean lifetime in free spaces of 0.125 ns and 140 ns, respectively [3].

In condensed medium, the mean lifetime of o-Ps is reduced to a few nanoseconds due to its interaction with surrounding molecules of the medium [4]. So the results for o-Ps lifetime and its probability are related to free-volume hole size (V_h), fraction free-volume (F_h) and free-volume distribution. The relation between the mean radius of free-volume hole size and the o-Ps lifetime τ_{o-Ps} was found according to the semi-empirical formula [5]:

$$\tau_{o-Ps} = 0.5\left[1 - R/R_0 + 0.159\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} ns \quad (1)$$

where: R is the radius of the hole size and given by $R = R_0 + \Delta R$,
R_0 is the radius of the spherical well potential,
ΔR is the electron layer thickness.
The free-volume — hole size (V_h) is:

$$V_h = \frac{4}{3}\pi R^3 \quad (2)$$

The fractional free-volume (the ratio of free-volume to the total volume) was found according to fitted empirical formula as [6]:
$$F_h = AV_h I_{o-Ps} \quad (3)$$

where A is a constant, its value between 1 and 2 for polymers and I_{o-Ps} is the intensity of τ_{o-Ps} .

PAL is widely used for investigation different aspects of polymer properties[7]. Positron and positronium lifetime in polymer materials may be affected by different factors such as change in degree of crystallinity, blending of polymer, temperature and irradiation of polymer [8-11]. The present paper is prepared to study the effect of Gamma irradiation on the microstructure of Polyurethane (PU), EUXIT 101 and Epoxy Resin (EP) EUXIT 60 (Swiss Chem.), and to find a correlation between the irradiation dose and the changes in V_h and F_h values.

Experimental details and data analysis

The investigated PU and EP were irradiated at room temperature to energetic Gamma ray, using ^{60}Co, which emits mono-energetic 1.17 and 1.33MeV, and has a half-life of 5.3 years. The dose rate was 0.57kGy/h. The samples were irradiated within the dose range (95.76 - 957.6) kGy. The positron lifetime measurements were performed using a fast-slow coincidence system Fig. 1, with time resolution of 420±20 ps (FWHM). The positron source activity was 1.54μCi. The positron lifetime spectra were analyzed using PFPOSFIT program [12]. The free volume hole size, and the fractional free volume were calculated using Eqs.(1, 2 and 3) respectively.
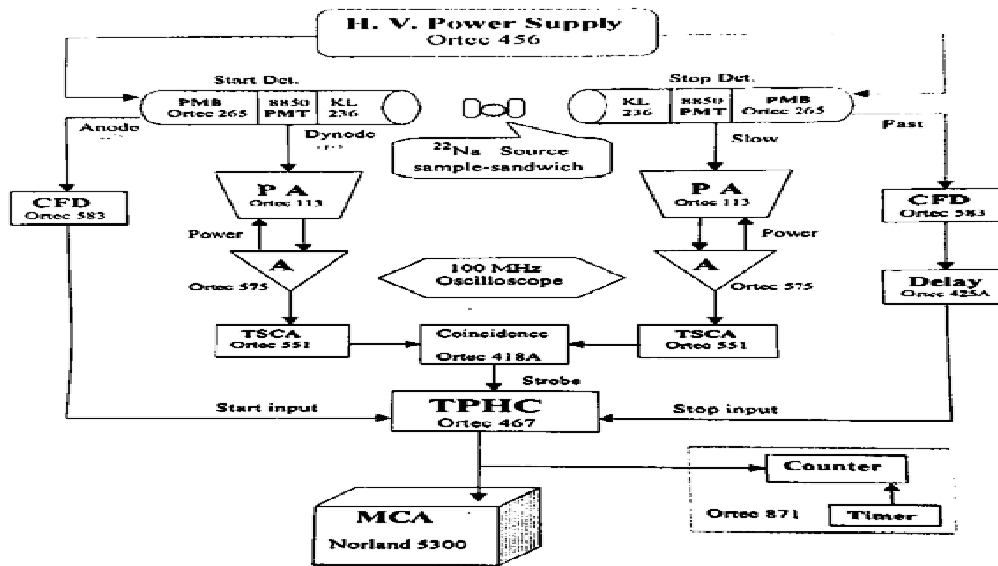
Fig. 1: A schematic diagram of the typical fast-slow coincidence circuit.

Results and discussion

The final analysis results for PU lifetime measurements ofthe spectra recorded different Gamma irradiation doses are displayed in Table 1.

Table 1: The Lifetime parameters of PU as a function of γ-dose.

Dose (kGy)	I_{o-Ps} (%)	τ_{o-Ps} (ns)	V_h (nm^3)	F_h (%)
0.0	8.111±0.250	2.241±0.034	0.121±0.0061	1.745
95.76	7.918±0.195	2.188±0.035	0.115±0.0068	1.674
191.52	7.895±0.290	2.146±0.033	0.114±0.0062	1.617
287.28	7.789±0.192	2.120±0.032	0.108±0.0099	1. 492
383.04	7.738±0.189	2.123±0.031	0.109±0.0082	1.506
478.80	7.641±0.190	2.087±0.043	0.105±0.0059	1.416
574.56	7.484±0.177	2.079±0.052	0.104±0.0072	1.411
670.32	7.526±0.193	2.057±0.022	0.102±0.0072	1.388
766.08	7.412±0.174	2.017±0.031	0.098±0.0058	1.316
861.84	7.427±0.189	1.982±0.029	0.095±0.0094	1.234
957.60	7.269±0.169	1.977±0.050	0.096±0.0053	1.261

The free-volume hole size and the fractional free volume hole sizewere plotted as a function of gamma dose in Figs. 2 and 3 respectively.
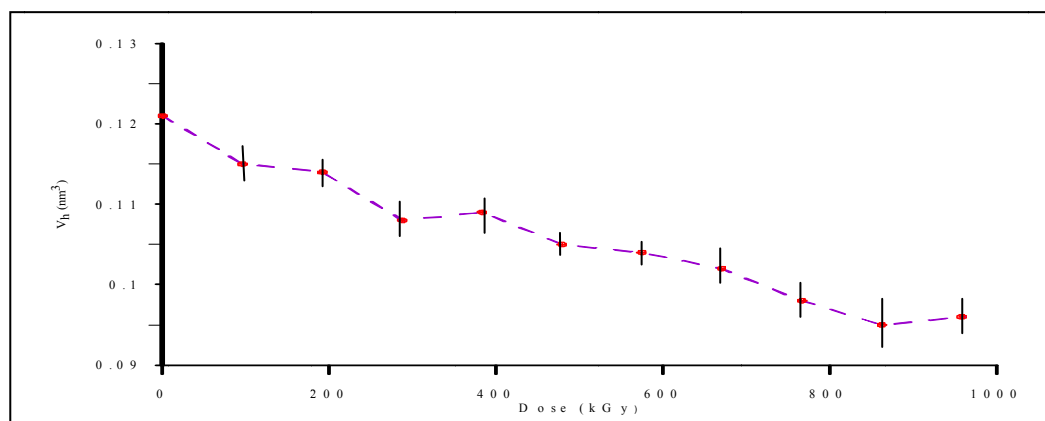

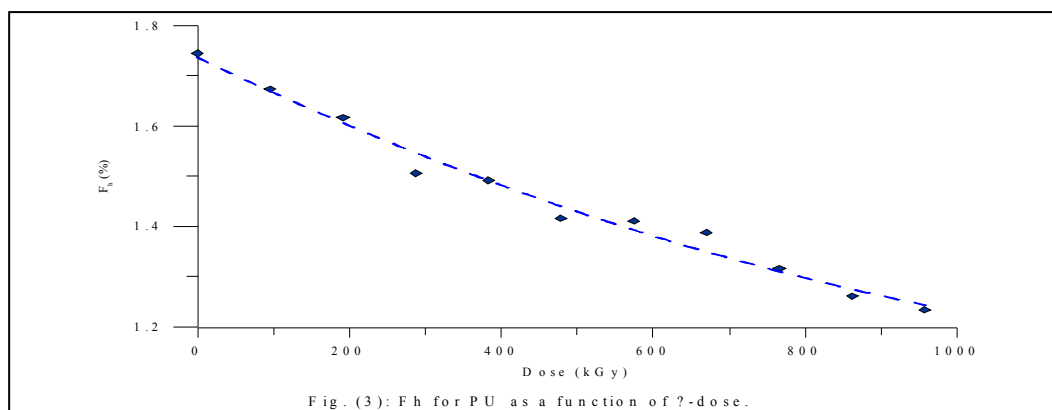*Fig. 2: V_h for PU as a function of γ-dose.*

Fig. 3: Fh for PU as a function of γ-dose.

The fitting line in Fig. 3 represents the third-order of polynomial fit.

$$F_h = a_0 + a_1X + a_2X^2 + a_3X^3$$

where X is the gamma-dose obtained for PU, and (a_0, a_1, a_2 and a_3) are coefficients.

The V_h and F_h values for un-irradiated PU samples were found to be 0.121 nm^3 and 1.745%, respectively. It is clear that V_h and F_h values decrease with increasing Gamma dose up to a total dose of 383.04kGy. An increment of 12.58% and 13.23% are noticed in V_h and F_h values, respectively. The results suggest that γ-ray induces degradation of PU chains, resulting in an increase of both the free-volume hole size and their density. As shown in Figs. 2 and 3, V_h and F_h values, decrease gradually with increasing dose up to a total γ-dose of 861.84kGy, where their maximum decrement are reduced to 20.93% and 18.3% respectively. This result from decreasing $\tau_{o\text{-}Ps}$ with increasing γ-dose up to a final value of 1.977ns, which is only 11.86%, a less than its initial value, as displayed in Table 1. So as that, the value of $I_{o\text{-}Ps}$ decreases gradually with increasing dose, until it reaches a minimum value at 957.60kGy.

This result indicates that the cross-linkingrate of PUbecomes amaximum at that dose. These results indicate thatthe γ-dose increases the crystallinity in the amorphous regions of PU, resulting in the reduction of degradation effect rate, thereby reducing both of the intermolecular spaces, and their number density.

Increasing crystallinity in the amorphous sites reduces the free-volume hole size, and their number density (the regions where Ps atoms form and annihilate). The reduction of V_h and F_h is due to a combined effect of free radicals (induced as a result of γ-irradiation) and increasing crystallinity.

The positron and positronium lifetime spectra for un-irradiated and γ-irradiated EP samples were measured and analyzed using three lifetime components. The results are displayed in Table 2. The free volume hole size V_h size and the fractional free volume hole size F_h, were plotted as a function of γ-dose in Figs. 4 and 5 respectively. The values of V_h and F_h for un-irradiated samples are 0.113 nm^3 and 1.711%, respectively. The initial γ-dose in induces a percentage reduction of V_h and F_h values, indicating that γ-dose results in increasing of cross-linking of EP, and at the same time increasing, the number density of intermolecular spaces available for Ps formation, suggesting the predominant of crystallinity of EP chains due to γ-irradiation.

Table 2: The Lifetime parameters of EP as a function of γ-dose.

Dose (kGy)	I_{o-Ps} (%)	τ_{o-Ps} (ns)	V_h (nm^3)	F_h (%)
0.0	8.415±0.560	2.172±0.034	0.113±0.0065	1.711
95.76	8.568±0.295	2.157±0.035	0.109±0.0068	1.651
191.52	8.441±0.207	2.136±0.030	0.107±0.0046	1.547
287.28	7.993±0.330	2.118±0.032	0.106±0.0042	1.497
383.04	7.873±0.189	2.103±0.033	0.105±0.0079	1.484
478.80	7.764±0.120	2.077±0.043	0.104±0.0092	1.447
574.56	7.717±0.170	2.054±0.055	0.099±0.0039	1.401
670.32	7.626±0.193	1.988±0.042	0.094±0.0064	1.279
766.08	7.572±0.184	1.968±0.031	0.092±0.0058	1.258
861.84	7.497±0.189	1.942±0.029	0.091±0.0046	1.217
957.60	7.429±0.199	1.977±0.050	0.096±0.0098	1.261

As the γ-dose increases up to a total dose of 861.84kGy, V_h and F_h values decrease gradually with increasing γ-dose to reach their minimum values. The total γ-dose induces percent reductions of 20.88% in V_h and 31.12% in F_h values. The reduction in V_h and F_h values is due to an increase of cross-linking and crystallinity in the amorphous regions of EP, as a resultant effect of γ-ray and the reaction of the reactive free radicals. The increasing of EP cross-linking with γ-dose led to reduce both of, the intermolecular spaces, and their number density.
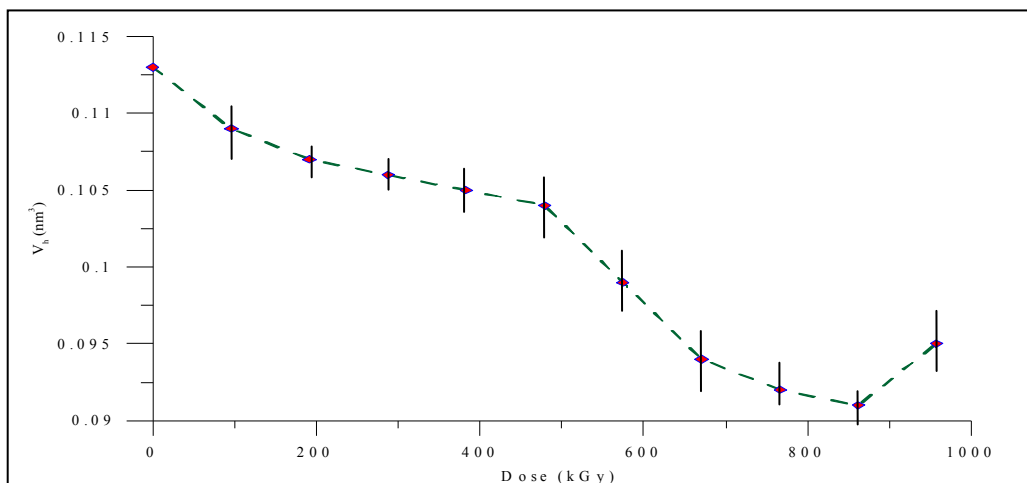

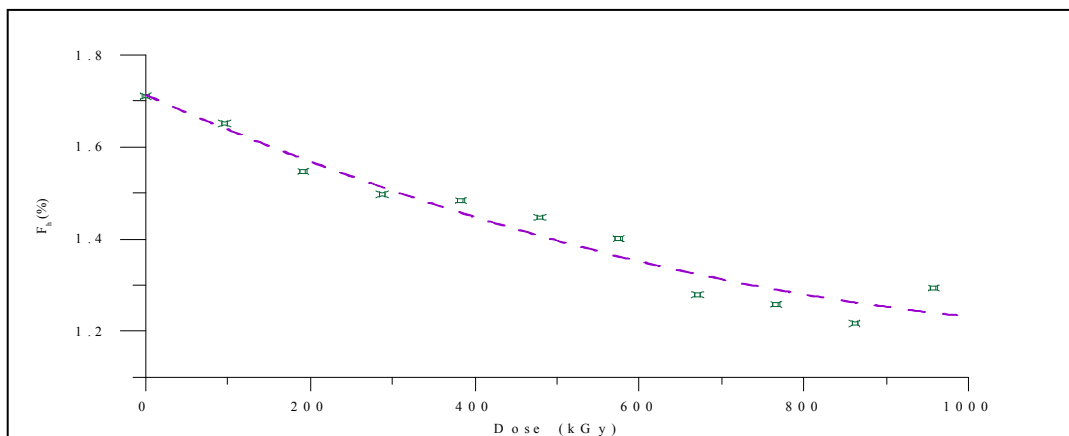***Fig. 4: Vh for EP as a function of γ-dose.***

Fig. 5: Fh for EP as a function of γ-dose.

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A fitting curve was obtained also for the investigated EP as shown in Fig. 5 the free-volume hole fraction as a function of γ-dose. The fitting curve in Fig. 5 also represents the third-order polynomial fit.

These results indicate that, the increases of crystallinity in the amorphous regions of EP, resulting in reduction of degradation effect rate, thereby increasing of V_h and F_h indicates that the intermolecular spaces in EP structure becomes larger due to the effects of γ-dose without altering their number density, which refers as an increase of τ_{o-Ps} value with constant Ps formation probability, I_{o-Ps}. These results reinforced and agree with the idea of, "high γ-irradiation makes radial distribution of EP bonds between molecules in the polymeric chain. Thus, the sample will become more brittle" [13-15].

Ps formation and annihilation is strongly affected by many factors such as three dimensional polymer structure, chemical structure, crystallinity and free radicals. Where γ-irradiation, produce free radicals in EP, as a results of interaction of γ-ray with polymer chain in different chemical reaction, such as recrystallization, cross-linking and degradation.

These results are supported by the idea of depending the free-volume on the amount of hardness, since the decrease of free-volume brings the decrease of possible volume for plastic, deformation results in the increase of hardness [10,16]. Increasing the hardness of the material is due to reduction of free-volume because of increase cross-linking that takes place in the amorphous regions in EP.

Conclusions

Comparing the results of the γ-irradiation effects on PU and EP

microstructure the following remarks are concluded:

1. The value of V_h for un irradiated samples equal to (0.121and 0.113) nm^3 for PU and EP, respectively. Which means' that, EP is more hardness than PU, because of, the high elasticity of PU. Thus, The increases of crystallinity in the amorphous regions of EP, resulting in reduction of V_h, than PU free-volume hole size.

2. Corresponding to V_h, also τ_{o-Ps} , values show that for un irradiated samples equal to (2.241and 2.172) ns for PU and EP, respectively. The increment of PU value, due increasing Ps formation hole size.

3. The final γ-irradiation value of τ_{o-Ps}, have the same value for PU and EP, thereby, increasing crosslinking with increasing γ-dose for PU is greater than EP sample. And so PU is more radiation effects than EP sample.

The present results give evidence, that PAL technique can be sensitively employed as a microprobe to monitor the chemical microstructure changes of the polymer under study. Present work has studied the effects of γ-irradiation, thereby determining the specific dose to be used to enhance or degrade a physical property of the studied polymer.

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