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Relationship between free volume and mechanical properties of polyurethane irradiated by gamma rays

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Abstract Polyurethane was irradiated at various gamma radiation doses up to 1,000 kGy at room temperature in nitrogen. Positron annihilation lifetime spectroscopy, tensile test and dynamic mechanical analysis were used to find the relationship between free volume and mechanical properties. An increase of the free volume fraction in soft segments (SS) and a decrease of the free volume fraction in hard segments (HS) during gamma radiation was observed and analyzed. The results showed that HS in polyurethane had the excellent resistance to gamma radiation, whereas SS had a tendency to degrade. The reason for the decrease of the strain at break and the ultimate tensile strength was analyzed, which showed the changes in the mechanical properties of polyurethane irradiated by gamma rays were mainly determined by the changes of free volume in SS. If the resistance properties of polyurethanes exposed to radiations need to be improved, SS should be paid more attention to.

Keywords Polyurethane · Free volume · Positron annihilation lifetime spectroscopy · Gamma ray

Introduction

Polyurethane adhesives have been widely used in the areas of aerospace and nuclear energy for their good thermal stability, excellent resistance to radiations and wonderful adhesive properties for almost any solid materials. In such applications, polyurethane adhesives are exposed to various radiations, and some performances, especially mechanical properties will change, which could affect the security of the related systems.

Gamma radiation effects on polyurethane have been reported in some references [1–8]. Bukanoval and Degtyareva [5, 6] investigated polyester polyurethanes consisting of toluene diisocyanate (TDI), dimethy biphenyl diisocyanate or hexamethylene diisocyanate. Their results showed that the main radiation effect on polyurethane was degradation leading to the decrease of tensile strength and elongation with increasing the radiation dose from 50 to 500 kGy. Ozdemir et al. [7] investigated the mechanical properties of poly(carbonate urethane) irradiated by gamma ray. It was concluded that the degradation mechanism at a high radiation dose was the possible reason for the decrease in the toughness of poly(carbonate urethane). Katarzyna Gorna and Sylwester Gogolewski [8] irradiated the polyurethanes with varying hydrophilic-to-hydrophobic content ratios at a dose of 25 kGy, and observed that polyurethane underwent significant degradation resulting in the reduction of tensile strength and modulus.

According to the above researchers' results, they all have claimed that degradation resulting in the reduction of mechanical properties. However, the answers for how the

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degradation happens and how the degradation reduces the mechanical properties are not described there.

Polymers irradiated by radiations usually undergo two fundamental processes: degradation and cross-linking [3, 9]. Both the two processes have an important influence on polymer mechanical properties for mechanical properties are decided by micro-structures. Degradation usually results in the break in the polymer molecular chains, leading to the production of the new free volume. Cross-linking can form new bonds between polymer molecules and make the molecules closer to each other, which could increase the interaction between polymer chains and therefore reduce the free volume [10]. PALS is a powerful method for the characterization of free volume [11].

Positron in the polymer will either annihilate directly with an electron or forms a bound state called positronium (Ps) in free volume. Ortho-positronium (*o*-Ps) as a kind of Ps has an intrinsic lifetime 142 ns in vacuum. In polymers, *o*-Ps will have a 'pick-off' reaction with an anti-parallel spin electron from the wall of free volume, form para-positronium (*p*-Ps) and annihilate rapidly. Hence, the lifetime of *o*-Ps reduces to several nanoseconds. The *o*-Ps lifetime mirrors sensitively the electron density in the nearest surrounding the Ps and the size of free volume where *o*-Ps is localized [10].

The *o*-Ps annihilated results can be used to calculate the free volume fraction f using the following Eq (1) [10].

$$f = C \times I \times V_{sph} \tag{1}$$

where C is a constant, I is the intensity of *o*-Ps annihilation from PALS results, and $V_{sph} = 4\pi/3 \times R^3$ is the average free volume of a single hole. R as the average free volume radius can be obtained from the following semi-empirical Eq. (2).

$$\tau = 0.5\left(1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\frac{2\pi R}{R + \Delta R}\right)^{-1} \tag{2}$$

where *o*-Ps pick-off lifetime τ is expressed in ns, and R in nm. ΔR is an empirical constant 0.1656 nm.

In this study, in order to study the relationship between free volume and mechanical properties, physical structure was studied by PALS.

Experimental

Materials

Polyurethane was synthesized by two components (A and B) of Tie Mao 101 adhesive from Shanghai Xinguang Chemical Co., Ltd. located at No. 588 Huating Xiangzhu Road, Jiading District, Shanghai, China. Component A contains polyethyleneglycol adipate, and B with a concentration of 11–13 % –NCO groups was the modified toluene diisocyanate (TDI) by trimethylolpropane (TMP). Tie Mao 101 adhesive is usually used with a mass ratio of A:B = 10:1–5. In this experiment, component A was mixed with B uniformly with a mass ratio of A:B = 10:4 by stirring with a glass rod in a glass beaker. Then the glass beaker was transferred to a vacuum oven to remove the gas bubbles. After that 113 g of the mixture was transferred to a polyethylene cup. Then, the weighed mixture was poured onto a horizontal flat glass slice with a size of 200 mm × 200 mm which was environed by the glue strip and kept the upside of the strip at least 5 mm higher than the glass surface. After 7 days' solidification, a vacuum oven was used to get rid of the remaining solvents (ethyl acetate and acetone) for a month at 30 °C. Finally, the solidified polyurethane was peeled off from the glass slice and was cut into different sizes for the tests of PALS, DMA and mechanical properties.

Gamma radiation

^{60}Co source was used to irradiate the samples at various doses up to 1,000 kGy at an approximate dose rate of 5 kGy/h at room temperature at Institute of Nuclear Physics and Chemistry located at No. 64 Mianshan Road, Mianyang, Sichuan Province, China. The samples were placed in the special glass ampoules. Then, the high temperature acetylene flame was used to seal the mouth of the glass ampoules on the top. After that, the ampoule was vacuumed to get rid of the air and filled with 50 kPa inert gas (pure N_2, 99.99 %) from the branch pipe in the side. Finally, the ampoules were sealed by the acetylene flame.

Measurements

PALS were carried out using a fast-slow spectrometer with a time resolution of 194 ps full width at half maximum at room temperature. This lifetime spectrometer employed two BaF_2 detectors. The positron source ^{22}NaCl was sandwiched by two specimens with a size of 10 mm × 10 mm × (1 ± 0.1) mm. In order to get a better statistical analysis, the collection of $\sim 2\times10^6$ counts was allowed. The acquired lifetime spectra were resolved into four lifetime components (τ_1, τ_2, τ_3, τ_4) by a computer program named LT9 [12]. The source component 382 ps (13 %) was used for source correction.

Dynamic properties were measured using DMA Q800 in single cantilever bending mode. The samples with a size of 20 mm × 10 mm × (1 ± 0.1) mm were subjected to a sinusoidal displacement of 10 μm at the temperature range from −60 to 230 °C with a heating rate of 5 °C/min and a frequency of 1 Hz.

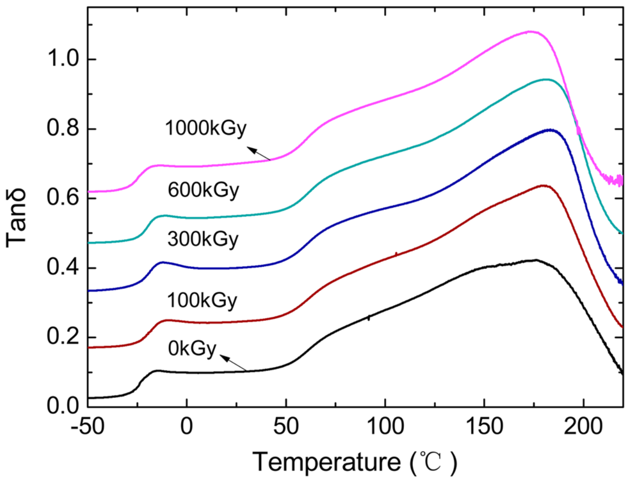

Fig. 1 DMA spectra of polyurethanes irradiated at various dose

Tensile properties of the specimens were carried out at room temperature. The polyurethane was cut out in a dumbbell shape with dimensions of 5 mm (neck) × 1 mm(thickness) × 75(length). Tensile strength and the elongation at break were measured at a cross-head speed of 50 mm/min. All the given values were the averages of three measurements for each condition.

Results and discussion

DMA and PALS results

The loss tangent (tan δ) versus temperature curves for the irradiated and un-irradiated polyurethanes are shown in Fig. 1. No obvious changes are observed at different radiation doses. Three transition regions throughout the whole heating range: A (−25–0 °C), B (40–100 °C), C (140–200 °C) are observed. Polyurethane usually possesses a segmented structure: HS are formed by a diisocyanate and a chain extender whereas SS are composed of a polyol, polyether or polyester [13]. A and B are the glass transition temperature ranges of SS and HS, respectively, and C is the viscous flow temperature range [14]. The two glass transitions observed in DMA results shows that the polyurethane we used has two phases structure.

For the crystalline polymer, it usually has two phases structure: crystalline region and amorphous region, and the free volumes of these two phases are different. The crystalline region usually has a smaller free volume than the amorphous region. Thus, the crystalline polymer is commonly analyzed with four components results in PALS [10]. The two longer components are due to the pick-off annihilation of o-Ps in crystalline region and amorphous region. Polyurethane also has the two phases: HS and SS. It is certain that HS has the smaller free volume than SS for the strong interaction (high polarity and the hydrogen bonding) between urethane linkages in HS. Therefore, the polyurethane lifetime spectra are analyzed into four components in our experiment. Actually, the PALS results of polyurethane with four components have been reported in some references [15, 16]. Consolati et al. [15] discussed some correlations among macroscopic features of some cross-linked fluorinated polyether-urethanes and their free volume properties as probed by PALS. They observed that PALS was sensitive to the phase separation, the spectra were analyzed into four components and τ_3 corresponds to the Ps state which was associated to the urethane phase. Ferrerira Marques and his partners [16] studied urethane/urea membranes by PALS, two types of free volume with different sizes had been identified, probably corresponding to two separate domains of SS and HS.

The PALS results are shown in Table 1. The shortest component τ_1 (120–150 ps) with intensity I_1, is due to the annihilation of *p*-Ps [10]. The second shortest component τ_2 (300–335 ps) with intensity I_2, is attributed to the annihilation of free positrons and positrons trapped in various vacancies and interfaces [10]. The two longest components τ_3 (0.8–1.15 ns) and τ_4 (2.08–2.28 ns), are the results of *o*-Ps annihilation in the free volume of HS and SS respectively.

Changes in the free volume of SS

The lifetime τ_4 and intensity I_4 of the longest component are shown in Fig. 2. The lifetime τ_4 which mirrors the size of free volume decreases a little with increasing the dose. I_4 increases gradually. The intensity of the long component is assumed to be proportional to the number of the free volume for it gives the information on the *o*-Ps formation probability. Thus, there are more and more free volumes produced in SS, whereas the average free volume size seems to become smaller and smaller.

Lifetime measurements allow the estimation of the free volume fraction f_4 from Eqs (1) and (2). Here, C is a constant. f_4 value must be proportional to the product of V_{sph} and I_4. The results of f_4 values estimation are presented in Fig. 3. It shows that f_4 is dose dependent. f_4 increases with increasing the dose. These results reveal the degradation effects in SS in polyurethane, which is corresponding to our former 2D-TG studies that SS in polyurethane have a tendency to degrade [17]. When the backbone chains are broken by gamma rays, new free volumes are produced at the break position, which is helpful to increase the number of free volume. The reason why τ_4 decreases might be that many smaller new free volumes will be produced when polyurethane is irradiated by gamma rays and these new produced smaller free

Table 1 PALS results of poly-ester urethane irradiated at different radiation dose

Dose (kGy)	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)	Variance
0	0.1489	23.54	0.3328	48.16	1.140	14.70	2.262	13.59	0.9549
100	0.1280	17.10	0.3020	52.10	0.943	14.68	2.150	16.11	1.0218
300	0.1232	16.88	0.3039	53.24	0.984	14.25	2.151	15.62	1.0123
600	0.1340	18.10	0.3056	50.20	0.849	14.37	2.096	17.35	1.0583
1,000	0.1275	16.19	0.3133	53.69	0.953	13.40	2.129	16.71	0.9782

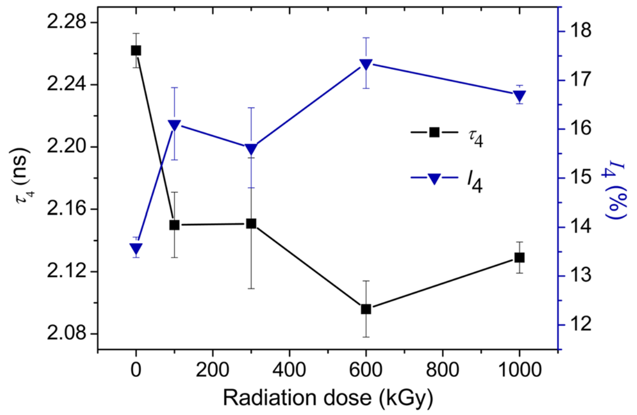

Fig. 2 The lifetime and intensity of the longest component as a function of radiation dose

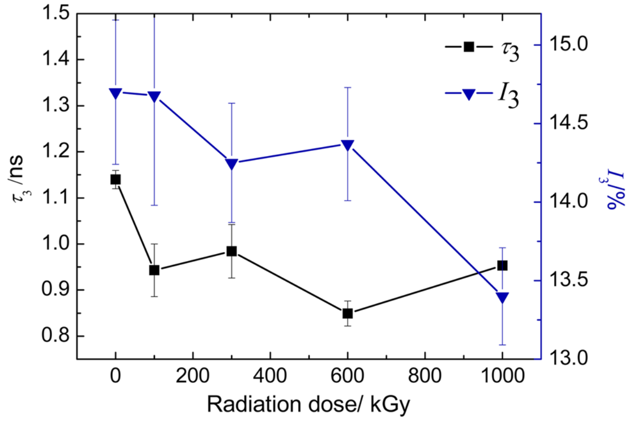

Fig. 4 The lifetime and intensity of the second longest component as a function of radiation dose

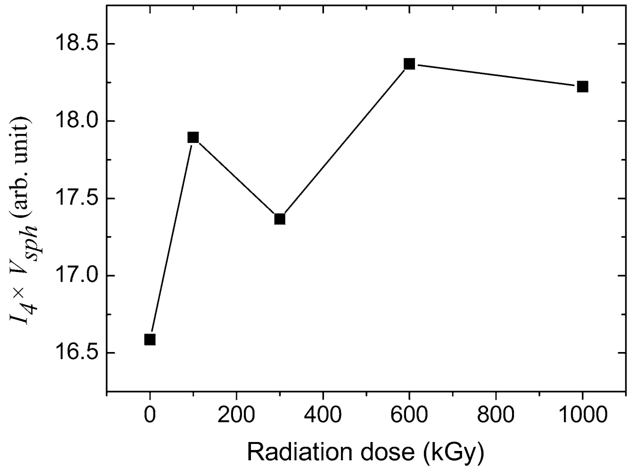

Fig. 3 The $I_4 \times V_{sph}$ product as a function of the radiation dose

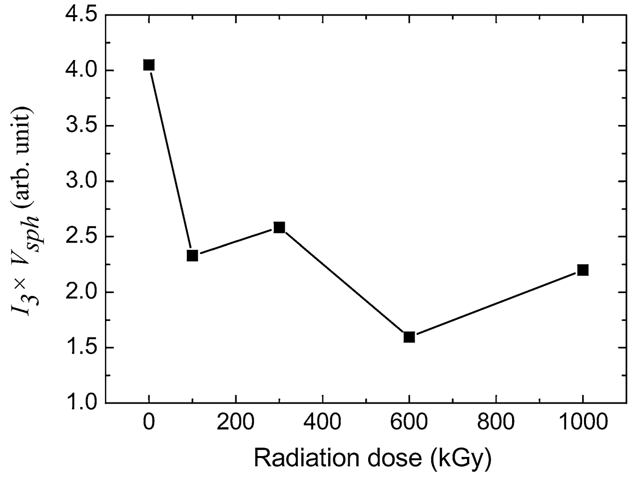

Fig. 5 The $I_3 \times V_{sph}$ product as a function of the radiation dose

volumes averaging with the primary free volume causes the mean size of free volume to decrease.

Changes in the free volume of HS

The positron annihilation lifetime τ_3 and intensity I_3 are shown in Fig. 4. τ_3 has a tendency to decrease with increasing the radiation dose, which indicates that the mean size of free volume becomes smaller and smaller. The decrease of I_3 reveals that the number of the free volume decreases. Figure 5 shows the changes in the free volume fraction f_3 in HS. It is observed that f_3 decreases gradually with increasing the radiation dose. Such results reveal that no degradation effects are observed in HS during gamma radiation. Phenyl ring with conjugated structure possesses wonderful resistance to radiations because the absorbed energy can diffuse to the whole ring avoiding the energy concentration in one bond. There are plenty of phenyl rings in HS, which could be helpful in resisting the radiations.

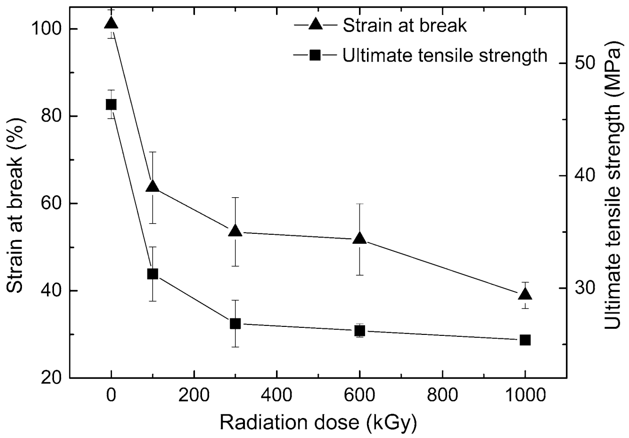

Fig. 6 Changes in strain at break and ultimate tensile strength as a function of radiation dose

Isocyanate (–NCO) in the polyurethane adhesive is usually remanent to keep the adhint ability. We have reported that the content of isocyanate groups would be reduced through the chemical reactions when the polyurethane experiences gamma radiation [17]. Maybe, isocyanate groups have some chemical reactions, produce new chemical bonds occupying free volumes and result in the decrease of free volume fraction in HS.

Changes in mechanical properties

The results of tensile test are shown in Fig. 6. Both the strain at break and the ultimate tensile strength decrease gradually, and when radiation dose exceeds 300 kGy they decrease much more slowly. It means that the polyurethane irradiated by gamma ray is more easily to be broken.

Several references have claimed that degradation resulting in the reduction of mechanical properties. Surely, polymer degradation will increase the chain ends, produce new free volume and reduce the interaction between molecules. The mechanical results we observe also reveal the degradation effect is present. PALS results have illustrated that the free volume fraction in SS increases with increasing the radiation dose, whereas in HS decreases. That's to say, SS have the tendency to degrade whereas HS not when polyurethane is irradiated by gamma ray. Therefore, the decrease of the strain at break and the ultimate tensile strength is most likely due to the more and more produced free volume in SS.

Conclusions

Free volume of polyurethane has been studied by PALS, and four components were obtained. The two longest components τ_3 (0.8–1.15 ns) and τ_4 (2.08–2.28 ns) were analyzed. The free volume fraction in HS reduced gradually with increasing the dose. The increase of the free volume fraction in SS showed the degradation in SS, which was the reason why the strain at break and ultimate tensile strength reduced. Therefore, the changes in the mechanical properties of polyurethane adhesive irradiated by gamma radiation are mainly determined by the properties of SS.

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