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Study on Damage Effects of Methyl Silicone Rubber Induced by Proton Radiation

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The damage behaviors of methyl silicone rubber induced by radiation of protons with 150-keV energy were studied. The surface morphology, tensile strength, Shaw hardness, cross-linking density, and glass temperature were evaluated. Positron annihilation lifetime spectroscopy and infrared attenuated total reflection analysis were carried out to reveal the damage mechanism of the rubber. The results show that the tensile strength, Shaw hardness, cross-linking density, and glass temperature of the silicone rubber increase and then decrease with increasing radiation fluence. Analysis indicated that all of the annihilation span τ_3 and the intensity I_3 of the longest lifetime positrons spouses, as well as the free volume V_f, decreased with increasing radiation fluence, under lower radiation fluences, and then increased slowly after the fluence 10^{15} cm^{-2}. The proton radiation would mainly induce cross-linking reactions in the silicon rubber when the fluence is lower, whereas degradation becomes dominant as the fluence increases.

Nomenclature

I_3 = annihilation intensity of the longest lifetime positron spouses
R = radius of free volumes
T_g = glass temperature
V_f = ratio of free volumes before and after radiation
V_0 = free volumes before radiation
τ_3 = annihilation span of the longest lifetime positron spouses
Φ = radiation fluence of protons

Introduction

THE silicone rubber has been applied widely in spacecraft as binders and sealant for its excellent characteristics of electric isolation, the performance at low and elevated temperatures, and the resistance to ozone and radiations. However, the long-term radiation of protons and electrons in space environment can induce microstructure changes and property degradation of the silicone rubber or even affect the spacecraft reliability and lifetime.[1,2]

Recently the positron annihilation lifetime spectroscopy (PALS) was applied to study the structure of polymers.[3,4] Positrons are either in free state or bounded by the electrons in molecules, forming positron spouses. The positrons in both the states tend to reside in the regions of low electron density such as the free volumes. As the annihilation lifetime is inversely proportional to electron density, some information on free volumes in polymers can be obtained from the PALS analysis. Generally, it is believed that the annihilation span τ_3 of the positron spouses with the longest lifetime is related to the size of free volumes and the intensity I_3 of such positron spouses to the amount of free volumes.[3–5] The relations between the longest annihilation span τ_3 of positron spouses and the radius R of free volumes in the polymers can be expressed by the following equation[5]:

$$\tau_3 = [2(1 - R/R_0 + 0.159 \sin 2\pi R/R_0)]^{-1} \quad (1)$$

where $R_0 = R + \Delta R$ and $\Delta R = 1.656$ Å for polymers. The ratio of free volumes V_f before and after radiation can be calculated by the following formula:

$$V_f = 4/3\pi R^3 I_3/V_0 \quad (2)$$

In this paper, the PALS method was employed to investigate the effect of proton radiation on the microstructure of a space-grade silicone rubber. Meanwhile, mechanical properties, cross-linked density, and glass transition temperature of the silicon rubber were also measured after the proton radiation.

Experimental

In this study, the silicone rubber with the molecular mass of 68,000 was used as the experimental material, which was treated in vacuum, and then incorporated with 2∼3wt.% Si and 3∼5%wt.% $Bu_2Sn(OCOC_{11}H_{23})_2$. After mixing homogeneously, the material was degassed for several minutes in vacuum, poured into a tetrafluoroethylene mould, and then vulcanized at room temperature. The main properties of the silicone rubber are listed here: the rubber is condensation cured, is yellow, has a hardness of 60.0–64.2 A, has a tensile strength of 5.0–5.3 MPa, and has a mass loss of 0.9–1.1%. The rubber specimens were radiated by protons with energy 150 keV. The beam current density was 0.1 μA/cm^2, and the radiation fluence was in the range of 10^{14}∼5×10^{16} cm^{-2}.

The specimens for PALS analysis were 2 mm thick, and their surface area was 1 cm^2. The ^{22}Na positron source was sealed with Kapton film and clamped between two specimens, and its intensity was 1 μCi. A BaF_2 probe with the sensitivity 260 Ps (which was calibrated by Co-60) was applied to measure the positron annihilation span. The experiment was performed at room temperature and lasted for about 1.5 h to reach more than 10^6 accumulated counts. Each specimen was tested three times. The Positronfit-Extended program was applied for the PALS analysis.[5]

The structure of the specimen surface layer was examined by means of infrared attenuated total reflection spectroscopy using an IR 100 FTIR Fourier transformed-infrared spectrometer. The dynamic mechanics analysis (DMA) was applied to study the influence of proton radiation on the glass temperature T_g of silicone rubber. The experiment was carried out using a Rheolograph solid dynamic viscidity-spring instrument. The heating rate is 5 K/min. The cross-linking density was measured according to the procedure given in the Ref. 6. The Shaw hardness and tensile properties were tested at room temperature.

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Results and Discussion

Changes in Surface Morphology and Tensile Strength

Figure 1 shows the changes in surface morphology of the silicone rubber after the proton radiation for various radiation fluences. It was found that with increasing the proton fluence the surface color became deeper gradually and surface cracks formed. The crack number increased with radiation fluence. Table 1 and Fig. 2 show the changes in Shaw hardness and tensile strength with the proton fluence, respectively. Both the tensile strength and Shaw hardness increase first and then decrease with increasing radiation fluence.

Changes in the Cross-Linking Density and Glass Temperature

Figure 3 indicates that with increasing the radiation fluence the cross-linking density of the rubber increases and then gradually levels off. The DMA analysis, as shown in Fig. 4, indicated that the glass temperature of silicone rubber T_g shifted to high temperatures with increasing the radiation fluence and then dropped gradually after the radiation fluence 10^{15} cm^{-2}. The results imply that the proton radiation under lower fluence would mainly result in cross linking of macromolecules in the silicon rubber. Increasing the cross-linking points would lead to decreasing the quantity of dissolved rubber and increasing the cross-linking density. Thus, the molecular chain movement could be restrained, and the glass temperature T_g, as well as the tensile strength and Shaw hardness, was increased. However, after the radiation fluence more than 10^{15} cm^{-2}, the T_g, tensile strength, and Shaw hardness were decreased, implying that the effect of degradation would dominate over the cross linking.

Table 1 Influence of proton fluence on the surface hardness of silicon rubber

Fluence, cm^{-2}	Shaw hardness, A
0	68.4
10^{14}	70.3
5×10^{14}	72.6
10^{15}	74.5
5×10^{15}	68.2
10^{16}	69.4
5×10^{16}	65.4

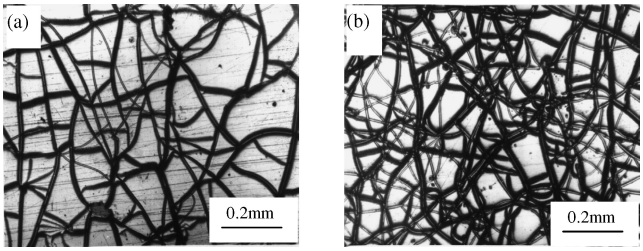

Fig. 1 Change in surface morphology of the silicone rubber after proton radiation for various fluences: a) $\Phi = 10^{15}$ cm^{-2} and b) $\Phi = 10^{16}$ cm^{-2}.

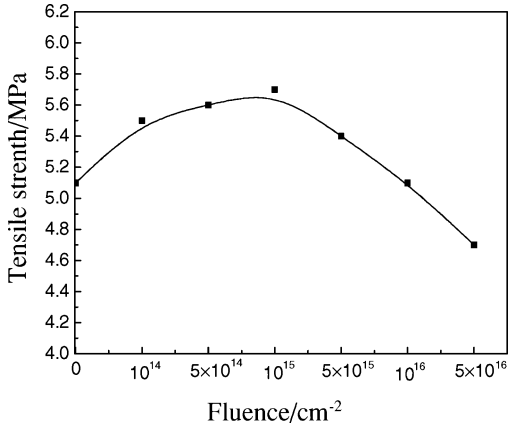

Fig. 2 Tensile strength of the silicone rubber as a function of proton fluence.

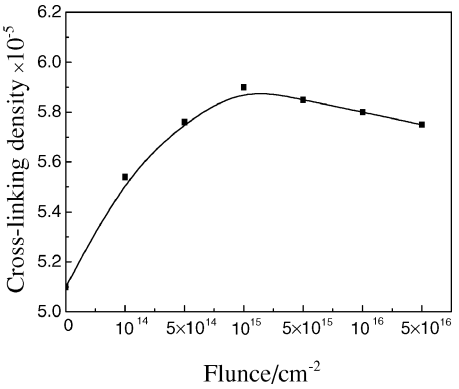

Fig. 3 Cross-linking density of rubber vs proton fluence.

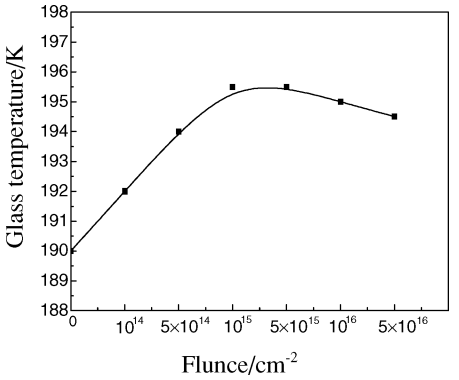

Fig. 4 Glass temperature of the silicone rubber vs proton fluence.

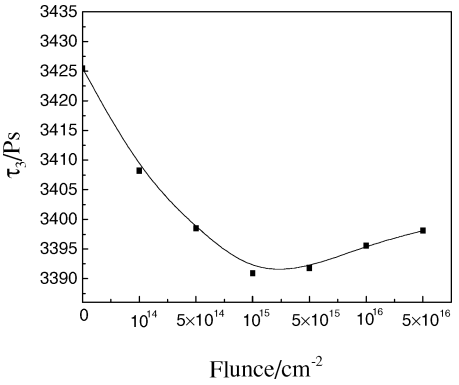

Fig. 5 Annihilation span τ_3 of the positron spouses with longest lifetime in the silicone rubber vs proton fluence.

Changes in PALS Characteristics

Figures 5 and 6 present the relation between PALS characteristics of the silicone rubber and radiation fluence. Obviously, the annihilation span τ_3 and relevant intensity I_3 decrease with increasing the radiation fluence at lower fluences and then gradually level off after the radiation fluence is more than 10^{15} cm^{-2}. Figure 7 shows a similar trend for the relation between the V_f and the fluence.

The PALS results are in accordance with the analyses of cross-linking density and DMA. Intrinsically, the free volumes in polymers result from the randomly arranged thermofluctuation of molecular chains. At lower fluences, the proton radiation would an induce increase in the cross-linked points and the polymerization degree, leading to a decrease in free volumes. Therefore, the annihilation span τ_3 of the positron spouses becomes shorter, as shown by the PALS results. And, the I_3 of PALS and the quantity of relevant free volumes would decrease with increasing the numbers of cross-linked points. But after increasing the radiation fluence to a certain degree, the radiated degradation in the rubber becomes dominant and

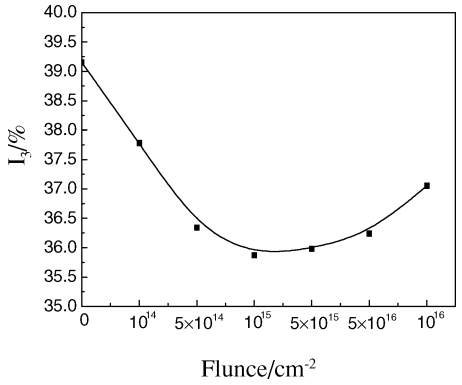

Fig. 6 Intensity I_3 of the positron spouses with the longest lifetime in silicone rubber vs proton fluence.

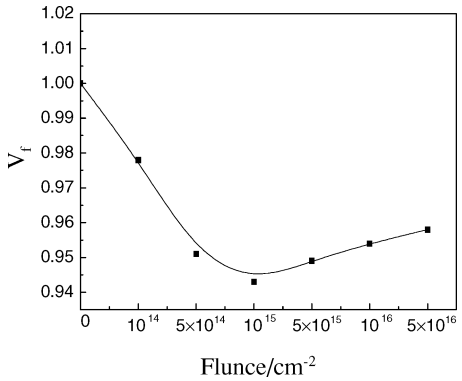

Fig. 7 Free volume fraction V_f in the silicone rubber vs proton fluence.

shows a reversal effect on the free volumes. Therefore, an increasing trend of the τ_3, I_3, and V_f was observed with the radiation fluence more than 10^{15} cm^{-2}.

Analyses of Infrared Spectra

The infrared spectra of the silicone rubber before and after proton radiation are shown in Fig. 8. No new peaks appeared, and all of the peak positions did not change for the radiated rubber compared to the original one. However, the relative intensity of the peaks was changed in the spectra after the proton radiation. The wave numbers at 800 and 1259 cm^{-1} were assigned to $-CH_3$ group peaks, and the overlapping peak around the 800 cm^{-1} was assumed to originate from the vibration absorption of C−H bonds. The absorption peaks at 2962 and 2900 cm^{-1} were caused by the C−H extensive vibrations, and the 1070 cm^{-1} peak was caused by the Si−O stretching vibration of the Si−O−Si structure.

Generally the relative change of absorbency in the infrared spectra accounts for the relative content of the corresponding valence bonds or radicals. Figure 9 shows the changes in infrared absorbency change of the Si−O bonds and $-CH_3$ radicals in the silicone rubber as a function of radiation fluence. The content of Si−O bonds increases gradually at lower radiation fluences, suggesting that the cross-linking effect for Si−O bonds is predominant. In contrast, the number of Si−O bonds tends to decrease in the range of higher proton fluence, indicating that radiation degradation is the dominant mechanism. However, the $-CH_3$ content decreases with increasing the radiation fluence in the whole range.

It is known that in polymers there are two types of molecular chain movement, including the displacement of main chains and the movement of chain segments. The cross linking of polymers results from the interconnection of free radicals formed in the macromolecules. The probability of the cross-linking process depends on the chain flexibility and the free radical amont. Owing to the excellent flexibility of the molecules in the silicone rubber and the free radicals generated in the initial radiation stages, cross links would occur. During proton radiation, the density of cross-linked networks increases so as to result in higher steric hindrance to the aiterconnection of free radicals. Therefore, with increasing the radiation fluence, the cross-linking probability decreases, and the degradation effect becomes a controlling factor. The degradation mainly results from chain scission.

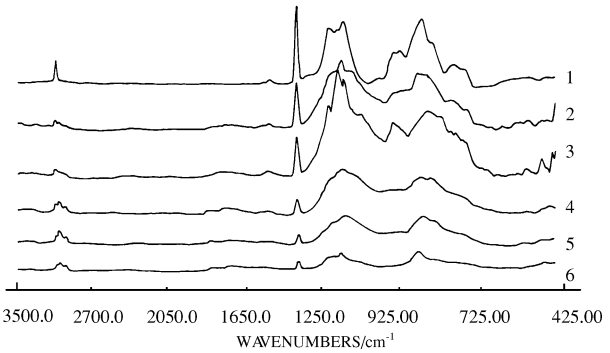

Fig. 8 Infrared spectra before and after the radiations for various of fluences: 1, no proton radiation; 2, $\Phi = 5 \times 10^{14}$ cm^{-2}; 3, $\Phi = 10^{15}$ cm^{-2}; 4, $\Phi = 5 \times 10^{15}$ cm^{-2}; 5, $\Phi = 10^{16}$ cm^{-2}; and 6, $\Phi = 5 \times 10^{16}$ cm^{-2}.

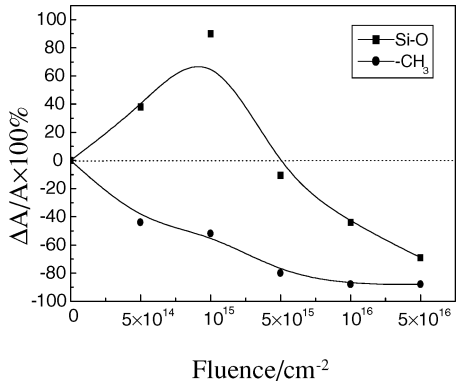

Fig. 9 Changes in infrared absorbency of silicone rubber as a function of proton fluence.

Conclusions

The tensile strength, Shaw hardness, cross-linking density, and glass temperature of the silicone rubber increase first and then decrease with increasing the proton fluence. PALS analysis indicated that all of the annihilation span τ_3 and the intensity I_3 of the longest lifetime positrons spouses, as well as the free volume V_f, decreased with increasing the radiation fluence, under lower radiation fluences, and then increased slowly after the fluence 10^{15} cm^{-2}. The proton radiation would mainly induce cross-linking reactions in the silicon rubber when the fluence is lower, whereas degradation becomes dominant as the fluence increases.

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