

DAMAGE OF SILICONE RUBBER INDUCED BY PROTON IRRADIATION

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Abstract In this paper, the damage to methyl silicone rubber induced by irradiation with protons of 150 keV energy was studied. The surface morphology, tensile strength, Shore hardness, cross-linking density and glass transition temperature were examined. Positron annihilation lifetime spectrum analysis (PALS) was performed to reveal the damage mechanisms of the rubber. The results showed that tensile strength and Shore hardness of the rubber increased first and then decreased with increasing irradiation fluence. The PALS characteristics τ_3 and I_3 , as well as the free volume V_f , decreased with increasing irradiation fluence up to 10^{15} cm^{-2} , and then increased slowly. It indicates that proton irradiation causes a decrease of free volume in the methyl silicone rubber when the fluence is less than 10^{15} cm^{-2} , while the free volume increases when the fluence is greater than 10^{15} cm^{-2} . The results on cross-linking density indicate that the cross-linking induced by proton irradiation is dominant at smaller proton fluences, increasing the tensile strength and Shore hardness of the rubber, while the degradation of rubber dominates at greater fluence, leading to a decrease of tensile strength and Shore hardness.

Keywords Silicone rubber, Proton irradiation, Tensile strength, Positron annihilation lifetime spectrum, Free volume

INTRODUCTION

In recent years, silicone rubber has been applied widely in spacecraft as binders for solar cells and the sealant for air-locked modules, *etc.*, for its fine electric insulation and excellent resistance to low temperatures and irradiation. However, long-term irradiation of charged particles (protons and electrons) in the space environment may induce microstructure changes and property deterioration of the silicone rubber, or even affect the spacecraft's lifetime^[1, 2].

Recently, PALS (positron annihilation lifetime spectrum) analysis was applied to reveal the changes in polymer structures^[3, 4]. Positrons are in the free state or bound by molecules to form positron spouses. Both states tend to reside in the fields with low electron density such as free volumes. As the annihilation lifetime of the longest lifespan positron spouses is inversely proportional to electron density, one can obtain some information on the free-volumes of polymers from PALS analysis. Generally, in PALS, the characteristic parameter τ_3 of the longest lifespan positron spouses is related to the size of free volumes, and the intensity I_3 to the number of free volumes^[3]. In this paper, PALS analysis was employed to investigate the effect of proton irradiation on the microstructures of space-grade KH-L-Y silicone rubber. Meanwhile, mechanical properties and cross-linking density of the silicon rubber were also measured after the proton irradiation.

EXPERIMENTAL

108 samples of methyl silicone rubber cured at room temperature were used in this study; they were treated in a vacuum chamber followed by addition of 8 wt% $\text{Bu}_2\text{Sn}(\text{OCOC}_{11}\text{H}_{23})_2$. After mixed homogeneously, the materials were degassed for several minutes. The main properties of the silicone rubber are listed in Table 1.

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Table 1. Main properties of the experimental silicone rubber

Type	Color	Hardness (A)	Tensile strength (Mpa)	Mass loss (%)
Condensate cured	Yellow	≥ 60	≥ 5	≤ 1.1

The irradiation of experimental samples was performed in a specially designed accelerator, which can simulate irradiation with protons and electrops of energy less than 200 keV in space, independently or simultaneously. In this work the energy of protons was chosen at 150 keV, and the irradiation fluence at $10^{14} \text{--} 5 \times 10^{16} \text{ cm}^{-2}$.

The specimens for PALS measurement were 2 mm thick with a surface area of 1 cm². The ²²Na positron source, with an intensity of 1 μCi, was sealed with Kapton film and clamped between two specimens. A BaF₂ probe with differentiated ration 260 Ps (that was calibrated by Co-60) was applied to measure the positron annihilation lifetime. The experiment was performed at room temperature and lasted for about 1.5 h to reach more than 10⁶ accumulated counts. Each specimen was tested three times. The positron annihilation lifetime spectrum could be explained according to the method described in literature^[2]. The applied program for the analysis of PALS was Positronfit-Extended^[4].

Dynamic mechanics analysis (DMA) was applied to study the influence of proton irradiation on the glass transition temperature (*T_g*) of the silicone rubbers. The experiment was carried out in a Rheograph solid dynamic viscosity-spring instrument made in Japan, and the heating rate was 5 K/min.

The process of measuring the cross-linking intensity was as follows. The sample weighed as *W*₁ was put in 30 mL toluene for some time at 298 K. Once the samples was taken out, the solvent on the surface was absorbed off quickly with filter paper. The above procedure was repeated, until the sample reached an equilibrium swelling state. The equilibrium sample was weighed as *W*₂. Afterwards, the solvent absorbed in the equilibrium sample was removed by heating at 353–363 K, and the sample was weighed as *W*₃. The difference between *W*₃ and *W*₁ was quantified as the dissolved rubber. According to the formula below, the cross-linking density *V_c* could be calculated^[5]:

$$V_c = [\ln(1 - V_2) + V_2 + 0.456V_2^2]/106.27(V_2^{1/3} - 0.5V_2)$$

where *V*₂ is the volume percent of polymer in the swelling-equilibrium sample, which can be calculated from *W*₁, *W*₂ and the sample density.

The surface morphology of the specimens was observed using an Olympus BH2-UMA optical microscope. Hardness was measured in a LX-A type Shore hardness-tester. The Shore hardness was calculated according to the equation: *F_A* = 549 + 75.12*H_A*^[6], where *F_A*(mN) is the force loaded on specimens, and *H_A* the Shore hardness. According to Chinese Material Testing Standards GB/T2568, tensile tests were performed using a MTS system. Figure 1 shows the tensile specimen dimensions.

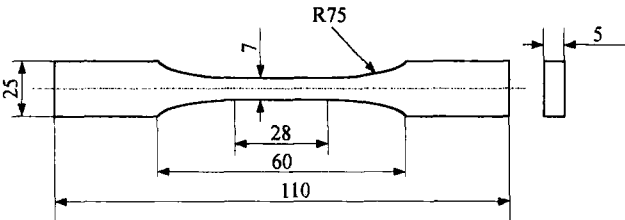


Fig. 1 Sketch of the tensile specimen
Units are in mm.

RESULTS AND DISCUSSION

Influence of Proton Irradiation on Surface Morphology and Properties

The change in surface morphology of the silicone rubber after proton irradiation is shown in Fig. 2. It is seen that after the irradiation, mosaic cracks were formed, and the crack number increased with increasing the irradiation

fluence. Also, the color of the silicone rubber gradually became deeper with increasing fluence.

Table 2 and Fig. 3 show that the Shore hardness and tensile strength of the silicone rubber increase first and then decrease with increasing irradiation fluence.

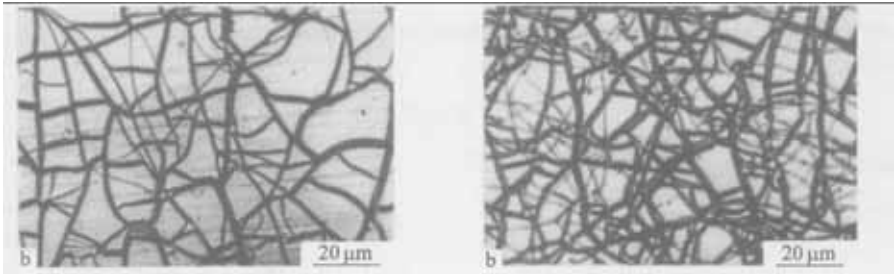


Fig. 2 Change in surface morphology of the silicone rubber with increasing proton fluence (a) $\Phi = 10^{15} \text{ cm}^{-2}$, (b) $\Phi = 10^{16} \text{ cm}^{-2}$

Table 2. Influence of irradiation fluence on Shore hardness of the silicone rubber

Fluence (cm^{-2})	0	10^{14}	5×10^{14}	10^{15}	5×10^{15}	10^{16}	2×10^{16}
Shore hardness (A)	68	70	72	74	68	69	65

Influence of Proton Irradiation on Cross-linking Density and Glass Transition Temperature

During the irradiation of silicone rubber with protons, there were two irradiation-induced effects, namely cross-linking and degradation of the silicone rubber, and their influence could be related to the irradiation fluence. Figure 4 shows that with the increasing of irradiating fluence, cross-linking density of the rubber increase and then decrease slowly. Similarly, the glass transition temperature T_g of the silicone rubber shifts to higher temperatures with increasing irradiation fluence, and decreases gradually after the fluence becomes higher than 10^{15} cm^{-2} , as shown in Fig. 5. The above results imply that the irradiation at lower proton fluence will result mainly in cross-linking of the silicone rubber molecules. Increasing the cross-linking points may reduce the quantity of dissolved rubber, and thus increase the cross-linking density. As a result, the molecular chain movement would be restrained, resulting in an increase of T_g , tensile strength and Shore hardness. However, after the irradiation with protons at more than 10^{15} cm^{-2} fluence, the decrease of T_g , tensile strength and Shore hardness imply that another irradiation-induced effect, namely degradation, would come into play.

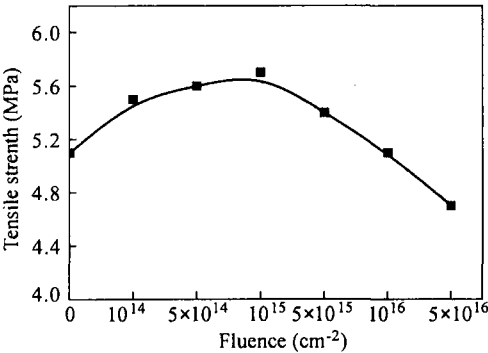


Fig. 3 Tensile strength of the silicone rubber as a function of proton irradiation fluence

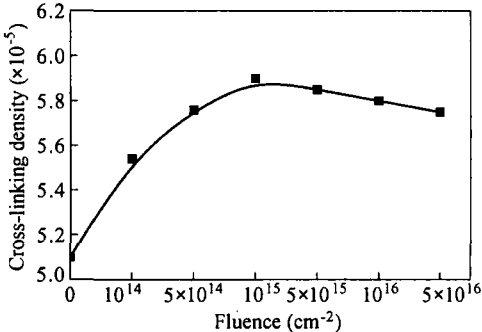


Fig. 4 Cross-linking density of the silicone rubber versus proton irradiation fluence

Influence of Proton Irradiation on the PALS Characteristics

Generally, in the positron annihilation lifetime spectrum, the characteristic parameter τ_3 is related to the size of free volumes, and the intensity I_3 to the free volume quantity in the polymers. The relationship between τ_3 and the

radius R of free volumes is given as follows^[3, 4].

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

where the units of τ_3 and R are nanoseconds and Angstroms, respectively; the parameter $R_0 = R + \Delta R$, and ΔR is 0.166 nm for polymers. The fraction of the free volumes in the rubber after irradiation can be calculated by the following formula:

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

Where V_0 is the volume of non-irradiated specimens.

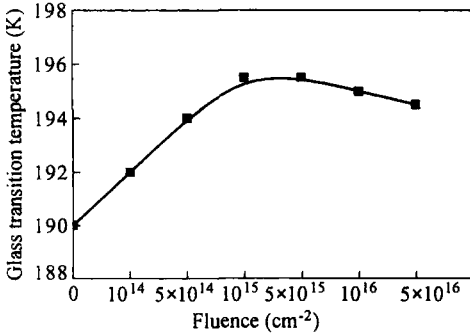


Fig. 5 Glass transition temperature of the silicone rubber versus proton irradiation fluence

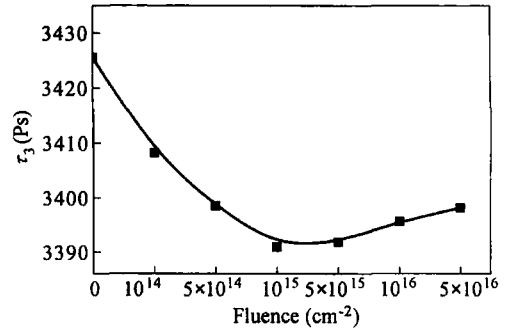


Fig. 6 The τ_3 values in PALS of the silicone rubber versus proton irradiation fluence

Figures 6 and 7 showed the relationships of the characteristics τ_3 and I_3 with irradiation fluence, respectively. Obviously, both the τ_3 and I_3 decreased with increasing irradiation fluence and increased after reaching a fluence of 10^{15} cm^{-2} . Figure 8 showed the similar relationship between the calculated V_f and the irradiation fluence.

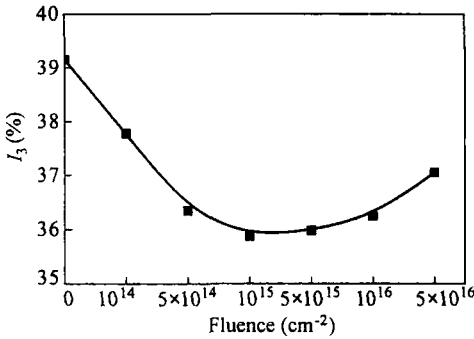


Fig. 7 The intensity I_3 in PALS of the silicone rubber versus proton irradiation fluence

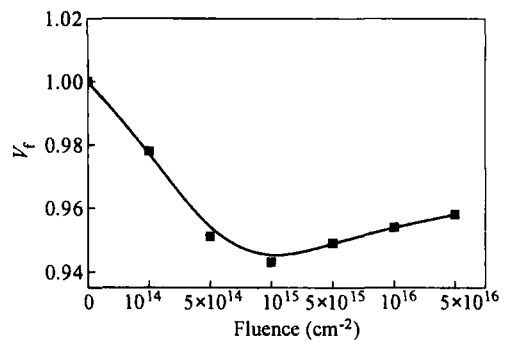


Fig. 8 The free volume fraction V_f in the silicone rubber versus proton irradiation fluence

The above PALS analysis results are in accordance with those for the cross-linking density and the T_g . Intrinsically, the free volumes in a polymer can be related to the random arrangement of molecular chains due to fluctuation of temperature. In the early stages of irradiation, the protons can increase the cross-linking points and the polymerization degree, leading to a reduction of the free volumes. Therefore, the annihilation lifetime τ_3 becomes shorter, as shown in Fig. 6. Meanwhile the intensity I_3 and the quantity of free volumes would decrease with increasing numbers of cross-linking points (Figs. 7 and 8). But after increasing the irradiation fluence to a certain degree, the irradiation-induced degradation in the rubber might become dominant and show a reverse effect on the free volumes. Thus the increase of τ_3 , I and V_f were observed on increasing the irradiation fluence

beyond 10^{15} cm^{-2} , and due to the competition between cross-linking and degradation in the silicone rubber, the increasing tendency was very slow.

CONCLUSIONS

The tensile strength, Shore hardness, cross-linking density and glass transition temperature of the silicone rubber increased first and then decreased with increasing irradiation fluence of protons. The PALS characteristics including τ_3 , I_3 and V_f for the silicone rubber decreased distinctly with increasing irradiation fluence up to 10^{15} cm^{-2} , and then increased gradually. The cross-linking induced by proton irradiation was dominant at smaller proton fluences, increasing the tensile strength and Shore hardness of the rubber, while the degradation of the rubber dominated at greater fluences, leading to decreasing tensile strength and Shore hardness.

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