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Synergistic Effect of Protons and Electrons on Radiation Damage of Silicone Rubber

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Methyl silicone rubber has been used as a binding material in spacecraft. The synergistic effect of protons and electrons on radiation damage of methyl silicone rubber was investigated using a ground-based simulator for space radiation environment. The energy of protons and electrons was chosen as 180 keV and the fluence 10^{16} cm^{-2}. The experiment results showed that discharged patterns and aged cracks appeared on the surface of the irradiated silicone rubber. The tensile strength and electrical insulation properties were degraded, and the mass loss rate increased after the combined irradiation of protons and electrons. The influence on the properties of the silicon rubber induced by the combined irradiation was greater than that induced by the separate irradiation of protons or electrons. The synergistic effect of protons and electrons did not show additivity. According to the infrared spectra, degradation effect of the silicone rubber occurred after the combined irradiation, which was similar to that caused by the separate irradiation. The degradation effect was responsible for the decrease of mechanical properties and the increase of mass loss rate. Electron-spin-resonance analysis indicated that the free radicals formed by the breakage of molecular chains because of the combined irradiation were the primary cause of the change in electrical properties.

Nomenclature

K_{add} = additivity coefficient
$tg\delta$ = loss angle tangent
ΔP_p = property change caused by proton radiation
$\Delta P_{(p+e)}$ = property change caused by combined radiation of protons and electrons
ΔP_t = property change caused by electron radiation
ε = dielecttic coefficient
ρ_v = volume resistivity
σ_f = tensile fracture strength
Φ = radiation fluence

Introduction

AS a spacecraft flies in orbit, the complicated space environment will be experienced. Depending on the orbit, the spacecraft will experience the various space environment factors separately, sequentially, and simultaneously. Whether there is an additivity for the impact on material properties induced by combined the space environment is an uncertain problem. In recent years, the silicon rubber was widely applied to spacecraft for its excellent properties such as electrical insulation and the resistance to high and low temperatures, coronae, water and moisture, chemical attack, atmospheric aging, ozone, and radiations. It used as a binder between the cover glass and solar cells as well as between the cells and baseplate. Also, the silicon rubber can be used as the sealant in spacecrafts. Under the charged particle radiations in space environment, the silicon rubber would be aged, resulting in degradation of properties, which directly influences the reliability and lifetime of spacecraft.[1–3] The previous work showed that the radiation of protons and electrons led to mass loss ratios, the outgassing, and the changes of microstructure.[4–10] In this paper, the effect of combined radiation of protons and electrons on the methyl silicone rubber was investigated. The following formula is introduced to discussed the additivity for the combined radiation effect of protons and electrons on the silicone rubber:

$$K_{\mathrm{add}} = \frac{\Delta P_{(p+1)}}{\Delta P_p + \Delta P_t} \tag{1}$$

From the preceding formula, it can be deduced that there is an additivity for the influence of the combined radiation on material property when $K_{\mathrm{add}} = 1$, whereas the additivity does not exit when $K_{\mathrm{add}} \neq 1$.

Experiment

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 2–3 wt.% $Si(OEt)_4$ 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 irradiation experiment was done in equipment that can simultaneously and separately simulate the radiations of electrons and protons with 30–200 keV under high vacuum and heat-sink environment. A special monopole radio-frequency mass spectrometer was mounted in the sample chamber used to monitor the material outgass in the irradiation process. In the test, the energy of protons and electrons was chosen as 180 keV, the irradiation fluence of protons and electrons was 10^{16} cm^{-2}, the vacuum of sample chamber was 10^{-5} Pa, and the surface temperatures of irradiatied samples were controlled at $10 \pm 5^{\circ}$C by the cold screen with liquid nitrogen.

The sample surface morphology was observed by using an OLYMPUS BH2-UMA type light microscope. Tensile test was carried at room temperature, and the tension speed 0.24 mm/min was chosen. The sample size was shown in Fig. 1.

The samples were deposited with aluminum in vacuum for measuring the volume resistivity ρ_v, the dielectic coefficient ε, and the

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loss angle tangent $tg\delta$. The ρ_v was measured using a ZC-36 type megger with a frequency of 60 Hz, and the steady-state values were chosen after pressurization for 1 min. The tests for ε and $tg\delta$ were conducted using the TR-10C transformer bridge. The sample dimension was 100×50 mm, and the thickness about 100 μm.

After the irradiation of protons, the samples were preserved at low temperatures and then analyzed by a JES-FE3AX type electron spin resonance spectrometer made by JEOL, Japan. The following parameters were chosen: the scanning width was 500 G; the scanning velocity, 30 s; the magnification, 4000; the time constant, 0.03; the experimental temperature, 20°C; the microwave frequency, 9.435 GHz; and the central magnetic field, 3365 G. The sample dimension was $20 \times 4 \times 4$ mm.

Results and Discussion

Surface Morphology

Figure 2a shows that the sample surface is smooth and flawless. After proton irradiation, the surface color of the silicon rubber deepened, and the aging cracks appeared, as shown in Fig. 2b. Our previous work demonstrated that the aging degradation of the silicon rubber surface occurred under the protons' irradiation with 180 keV for 10^{16} cm^{-2} (Refs. 9 and 10). After the electrons irradiation, the surface color of the silicon rubber was also deepened, and the arborescent discharge stripes appeared on the surface of silicon rubber, as seen in Fig. 2c. The measuring for the surface potential showed that the silicon rubber surface was charged to 1–2 kV under the electron irradiation. It is believed that the discharge is a main mode of surface damage under the electron irradiation. After the combined irradiation, the surface color of the silicon rubber was deepened further, and the aging cracks and more arborescent discharge stripes were observed at the same time, as shown in Fig. 2d. There is a combined feature of the surface damage modes for the two-type charged particle irradiation after the combined radiation.

Mass Loss and Tensile Strength

Table 1 indicates that the mass-loss ratios of silicon rubber are 1.28, 1.06, and 2.99% after the electron, proton, and combined irradiation, respectively. The mass loss ratio of silicon rubber induced by the combined irradiation is the greatest; the second by the proton irradiation and the lowest by the electron irradiation. However, the additivity does not exist because $K_{add} = 1.28$. The in situ mass-spectrometric analysis showed that the micromolecule gaseous products such as H_2 (m/z:2.1, 1.1) and CH_4(m/z:16.2, 15.2, 14.2) were formed during the proton, electron, and combined irradiations. Also, the gaseous product CH_3SiOCH_3(m/z:73.3, 57.3) was found during both the proton and the combined irradiations, as shown in Fig. 3. This could be attributed to the protons participating in the destruction of macromolecular chains of silicon rubber.[10]

Table 1 indicates that the change in tensile fracture strength of silicon rubber is 8.69, 7.25, and 20.1% after the electron, the proton, and the combined irradiation, respectively. The change in tensile fracture strength of silicon rubber induced by the combined irradiation is larger than those for the independent irradiations of protons and electrons. However, the additivity does not exist because $K_{add} = 1.26$. The aging cracks and arborescent discharge stripes might be primarily responsible for the decrease of tensile fracture strength.

Electrical Properties

Table 2 shows the changes in volume resistivity ρ_v, dielectric coefficient ε, and dielectric loss tangent $tg\delta$ for the silicon rubber after the proton, the electron, and the combined irradiation. After the irradiation, the ρ_v decreases, while the ε and $tg\delta$ increase. Usually, with increasing the molecular dipole moment, the ε and $tg\delta$ increase. On the one hand, the appearance of free radicals after the irradiation would enhance the dipole polarization. On the other hand, the radiations could induce the degradation of macrochains of the silicon rubber, decreasing the intermolecular forces. As a result, the orientation of polar groups becomes easy. Both of the preceding factors might contribute to the increase of the ε and $tg\delta$. The change in the electrical properties of silicon rubber induced by the combined irradiation is much greater than the independent irradiations. Also,

Table 1 Change in mass-loss ratios and tensile fracture strength under different irradiation conditions

Irradiation condition	m, g	$\Delta m/m$, %	σ_f, MPa	$\Delta\sigma_f/\sigma_f$, %
Before irradiation	5.745	——	4.83	——
After protons irradiation	5.660	1.28	4.41	8.69
After electrons irradiation	5.684	1.06	4.48	7.25
After combined irradiation	5.573	2.99	3.86	20.1
K_{add}	——	1.28	——	1.26

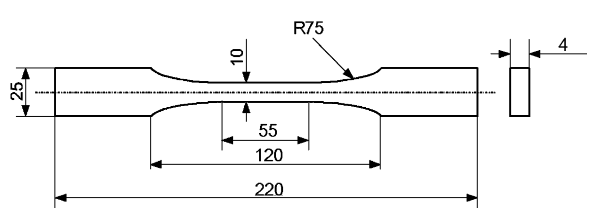

Fig. 1 Sample size for tensile test (millimeters).

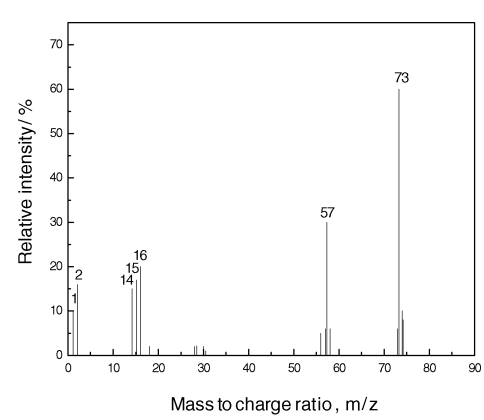

Fig. 3 Mass spectrum of atmosphere in the sample chamber during combined irradiation of protons and electrons for silicone rubber.

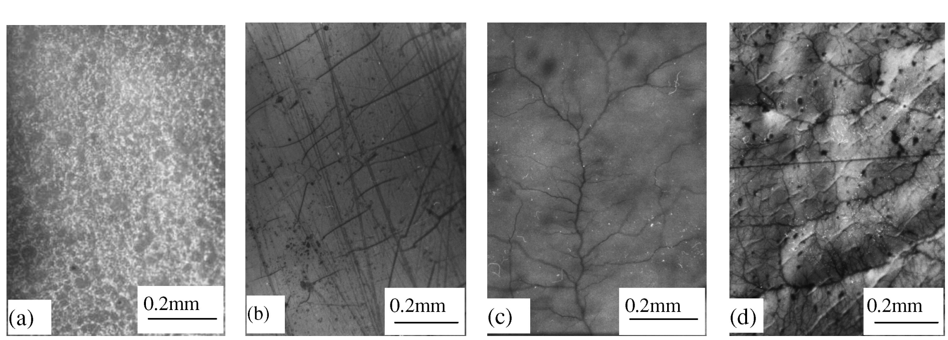

Fig. 2 Change in surface morphology of silicone rubber before and after irradiation: a) before irradiation, b) $\Phi_p = 10^{16}$ cm^{-2}, c) $\Phi_e = 10^{16}$ cm^{-2}, and d) $\Phi_{e+p} = 10^{16}$ cm^{-2}.

Table 2 Changes in electrical properties of silicon rubber under different irradiation conditions

Irradiation condition	$\rho_v \times 10^{-13}$, Ω cm	$\Delta\rho_v/\rho_v$, %	ε	$\Delta\varepsilon/\varepsilon$, %	$tg\delta \times 10^3$	$\Delta tg\delta/tg\delta$, %
Before irradiation	1.54	——	3.13	——	3.53	——
After proton irradiation	1.44	6.49	3.21	2.56	3.74	5.94
After electron irradiation	1.42	7.79	3.46	10.54	3.71	5.10
After combined irradiation	1.17	24.0	3.77	20.44	4.06	15.01
K_{add}	——	1.68	——	1.56	——	1.36

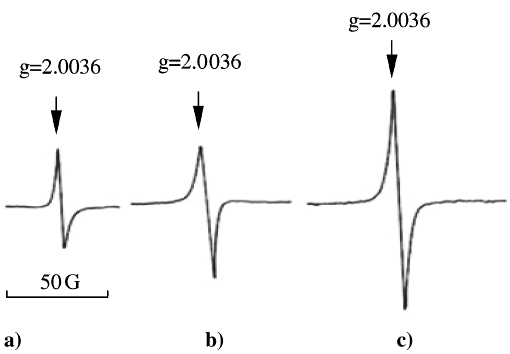

Fig. 4 ESR spectra for silicone rubber after the proton, electron, and combined irradiation: a) $\Phi_p = 10^{16}$ cm^{-2}, b) $\Phi_e = 10^{16}$ cm^{-2}, and c) $\Phi_{e+p} = 10^{16}$ cm^{-2}.

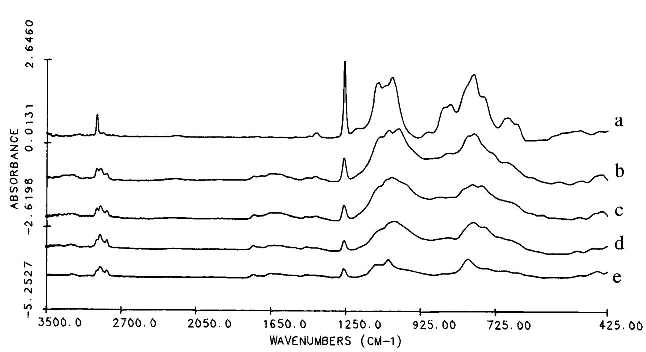

Fig. 5 Changes in infrared spectrum of silicon rubber before and after the proton, electron, and combined irradiation: a) before irradiation, b) $\Phi_p = 10^{16}$ cm^{-2}, c) $\Phi_e = 10^{16}$ cm^{-2}, d) $\Phi_{e+p} = 10^{16}$ cm^{-2}, and e) $\Phi_{e+p} = 2 \times 10^{16}$ cm^{-2}.

there is not an additivity for the change in the ρ_v, ε, and $tg\delta$. The K_{add} values are 1.68, 1.56, and 1.36, respectively.

Electron Spin Resonance Spectra Analysis

Figure 4 presents the electron spin resonance spectra for silicon rubber after the proton, the electron, and the combined irradiation. In the figure, the g value was equal to 2.0036, which represents the overlapped peak for the free radicals of ⩸Si• and ⩸SiO• (Ref. 11). The fourfold split peak for the $CH_3\cdot$ and the from ternary split one for the ⩸$SiCH_2$• do not appear in the figure because the attenuation rates of these free radicals are more quick. Some macrochains of the silicon rubber could break down as a result of radiation. After the irradiation, these free radicals attenuate automatically. Figure 5 shows that the peak for the combined irradiation is the highest, implying that the concentration of survival free radicals is much larger than those of the independent irradiations. Therefore, the decrease of the ρ_V value is the most obvious.

Infrared Spectrum Analysis

The changes in the infrared spectrum of methyl silicone rubber before and after the proton, the electron, and the combined irradiation are shown in Fig. 5. Although no new peaks appear, the relative intensity of the peaks changes after the proton irradiation. The peaks at the wave numbers of 800 and 1259 cm^{-1} originate from the vibration of CH_3 groups, and the overlapped peaks around the 800 cm^{-1} might be related to the nonplanan vibration absorption of C-H bonds. The absorption peaks at 2962 and 2900 cm^{-1} are caused by the stretch vibration of C-H bonds, and the 1070 cm^{-1} absorption peak was caused by the Si-O stretching vibration in the Si-O-Si structure.[12] As seen in the figure, the height of all of the peaks decreases after the proton, the electrons, and the combined irradiation, showing that the degradation occurs for both the macromolecule main chain Si-O bonds and the lateral chains. Moreover, the decreasing extent for all of the peaks is larger for the combined irradiation, indicating that the combined one would lead to more severe degradation effect on the methyl silicone rubber.

Conclusions

The preceding results show that after the combined irradiation of protons and electrons the changes in the surface morphology and outgassing products for the silicon rubber show a combined feature of the two independent radiation effects. The changes of tensile strength, mass-loss ratio, and electrical properties are not possessed of an additivity. The combined irradiation results in a more severe degradation effect on the methyl silicon rubber, which is primarily responsible for the decrease in mechanical properties and the increase in mass-loss ratios. Under the combined irradiation, breaking molecular chain and the formation of free radicals are induced, because the scissors of molecular chains contributes to the decrease in the electrical properties of the methyl silicon rubber.

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