

Optical Degradation of Polydimethylsiloxane Under 150 keV Proton Exposure

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ABSTRACT: The optical degradation of polydimethylsiloxane (PDMS) was investigated under exposure of 150 keV protons to reveal the damage behavior of organic silicone in space. The exposure was performed in a ground-based simulation for space protons. The experimental results show that the optical degradation mainly occurs in the visible region. With increasing proton fluence, the absorption band shifts toward longer wavelengths (red-shift) and the solar absorptance α_s ascends. The analysis of Fourier transform infrared spectroscopy indicates that under the exposure, the degradation of the PDMS occurs to form hexamethylcyclotrisiloxane, the amount of which

increases with increasing the proton fluence. This could cause an increase in delocalization degree of the σ electrons, resulting in the red-shift of absorption bands. Also, the energy for valence electrons to be excited decreases and the $n \rightarrow \pi^*$ jump is intensified, increasing the probability of optical absorption. As a result, the solar absorptance α_s of the PDMS increases under exposure of 150 keV protons. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 4060–4064, 2008

Key words: proton exposure; organic silicone; optical degradation; Fourier transform infrared spectroscopy

INTRODUCTION

The organic silicone such as polydimethylsiloxane (PDMS) is often used as a binder in thermal control coatings for spacecraft, because it possesses outstanding properties such as the good electric isolation performance, the resistance to heat and aging, and the weather fastness.^{1–3} The service behavior of thermal control coatings is an important factor to influence the lifetime and reliability of spacecraft. Under the effects of space environment such as the solar electromagnetic radiation and the energetic charged particles (protons and electrons) exposure, the optical properties of thermal control coatings will be degraded. In the Earth radiation belts, a large amount of protons with <200 keV exists, which cause the damage to thermal control coatings. It is of significance to examine the damage behavior of the organic silicone caused by the <200 keV protons.

PDMS has a unique structure, in which the main chain is composed of Si—O bonds and the d- π bonds can be formed between the Si and O atoms. It is known that the silicon atom possesses with empty 3d-orbit and the oxygen atom has lone pair electrons. When the lone pair electrons in the 2p-orbit of oxygen atom occupy the empty 3d-orbit of Si atom,

the d-orbit will overlapped with the p-orbit to form π -bond. Such a π -bond is referred to as the d- π bond, which is beneficial to improve the bond strengths, increasing the stability of polymers. To date, a little work has been conducted on the optical degradation of the PDMS under proton exposure. Previous investigations were primarily involved with the evolution in mechanical properties and thermal stability of organic silicone.^{4–8} It was believed that the damage mechanism in the silicone resin caused by <200 keV protons irradiation might be changed with increasing the proton fluence. When the fluence is less than 10^{14} cm^{-2} , the cross-linking effect dominates, whereas the degradation effect does under the fluence larger than 10^{14} cm^{-2} . With increasing proton fluence, the mechanical properties first increase and then decrease, such as the hardness, the tensile strengths, and the storage modulus at low temperatures. Also, the glass transition temperature (T_g) changes with increasing the proton fluence. It was found that the transmittance in the wavelength range of 200–1000 nm decreases with increasing the energy and fluence of protons for the silicone resin. Although the evolution in transmittance of the silicone resin was examined, the micro-mechanism for such a change was not given. In addition, the change in the reflective spectrum of the silicone resin caused by <200 keV protons has not been reported.

The aim of this study was to reveal the micromechanism of optical degradation in the organic silicone caused by <200 keV protons. Fourier transform

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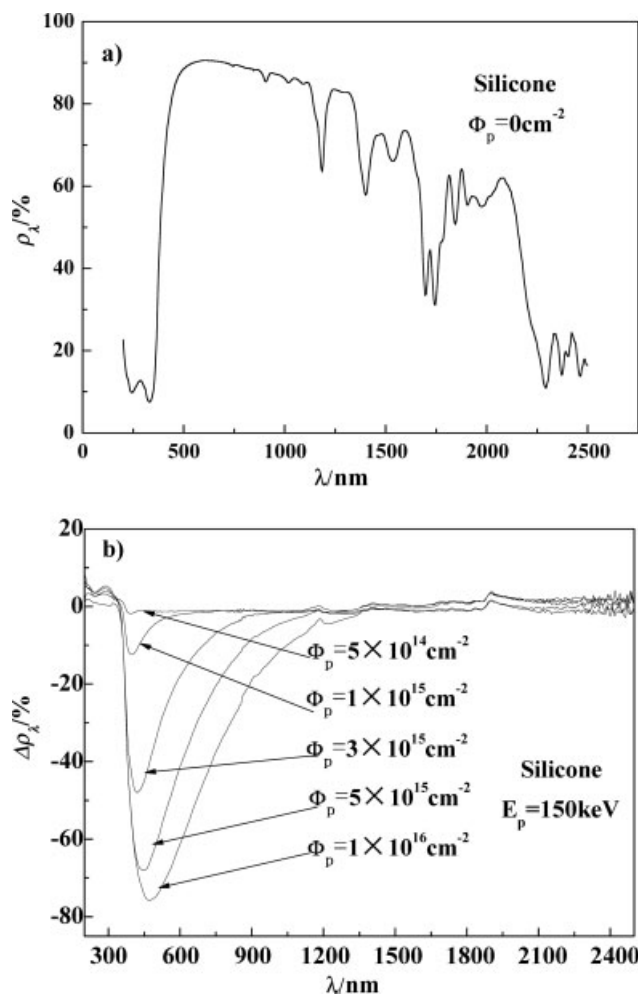


Figure 1 The pristine reflective spectrum (a) and the change in spectral reflectance $\Delta\rho_\lambda$ versus proton fluence (b) for PDMS.

infrared spectroscopy (FTIR) was used to examine the change in microstructure of the organic silicone. The results could help to understand the service behavior of thermal control coatings such as the ZnO/silicone white paint in space.

EXPERIMENTAL

PDMS was chosen as the testing material for the organic silicone. The samples were 20 mm in diameter and 3 mm in thickness. The silicone resin was cured at ambient temperature, and hydroxy was used for the dead-end polymerization. After curing, the PDMS film is white in color.

The proton irradiation was performed in a simulator for the space proton radiation. The simulator was made by Harbin Institute of Technology in Harbin in 2000, China. The type is SCRM/HIT. The proton energy was chosen as 150 keV, and the flux as $5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$. The proton fluence was changed from $5 \times 10^{14} \text{ cm}^{-2}$ to $1 \times 10^{16} \text{ cm}^{-2}$. The sample

holder is placed in a vacuum chamber. The vacuum was 10^{-4} Pa , and the sample temperature was kept at $298 \pm 5^\circ\text{K}$.

The reflective spectra were measured using a Lambda 950-type photometer produced by American Perkin-Elmer (Foster, U.S.A.). The measurements were performed immediately after the irradiation. FTIR was conducted using a VECTOR22 type spectrometer produced by Bruker (Karlsruhe, Germany). The resolution was 4 cm^{-1} and the scale ranged from 400 to 4000 cm^{-1} .

RESULTS AND DISCUSSION

Change in optical properties

Figure 1 shows the pristine reflective spectrum (a) and the change in spectral reflectance $\Delta\rho_\lambda$ as a function of proton fluence (b) for the PDMS. It is indicated that the optical degradation mainly occurs in the visible region after the 150-keV proton irradiation. With increasing the proton fluence, the intensity of the absorption band increases and the spectral reflectance of samples decreases. The absorption band shifts to longer wavelengths (red shift) and widens due to the proton irradiation.

The solar absorptance α_s is an important parameter to characterize thermal control coatings and can be obtained according to the following equation⁹:

$$\alpha_s = 1 - R_s = 1 - \sum_i^n \rho_\lambda / n$$

where R_s is the solar reflectance; ρ_λ is the spectral reflectance; and n is chosen as 24. Table I shows the change in solar absorptance $\Delta\alpha_s$ as a function of proton fluence for the PDMS samples. The $\Delta\alpha_s$ increases with increasing the fluence.

Change in surface morphology

The change in surface morphology of samples after the proton exposure is shown in Figure 2. It is noticed that after the exposure, mosaic cracks are formed and the cracks become deeper with increasing proton fluence. Also, the surface color of samples

TABLE I
The Change in Solar Absorptance $\Delta\alpha_s$ Versus Proton Fluence for PDMS

Proton energy (keV)	Flux ($\text{cm}^{-2} \text{ s}^{-1}$)	Fluence (cm^{-2})	$\Delta\alpha_s$
150	5×10^{11}	5×10^{14}	0.006
		1×10^{15}	0.025
		3×10^{15}	0.139
		5×10^{15}	0.252
		1×10^{16}	0.353

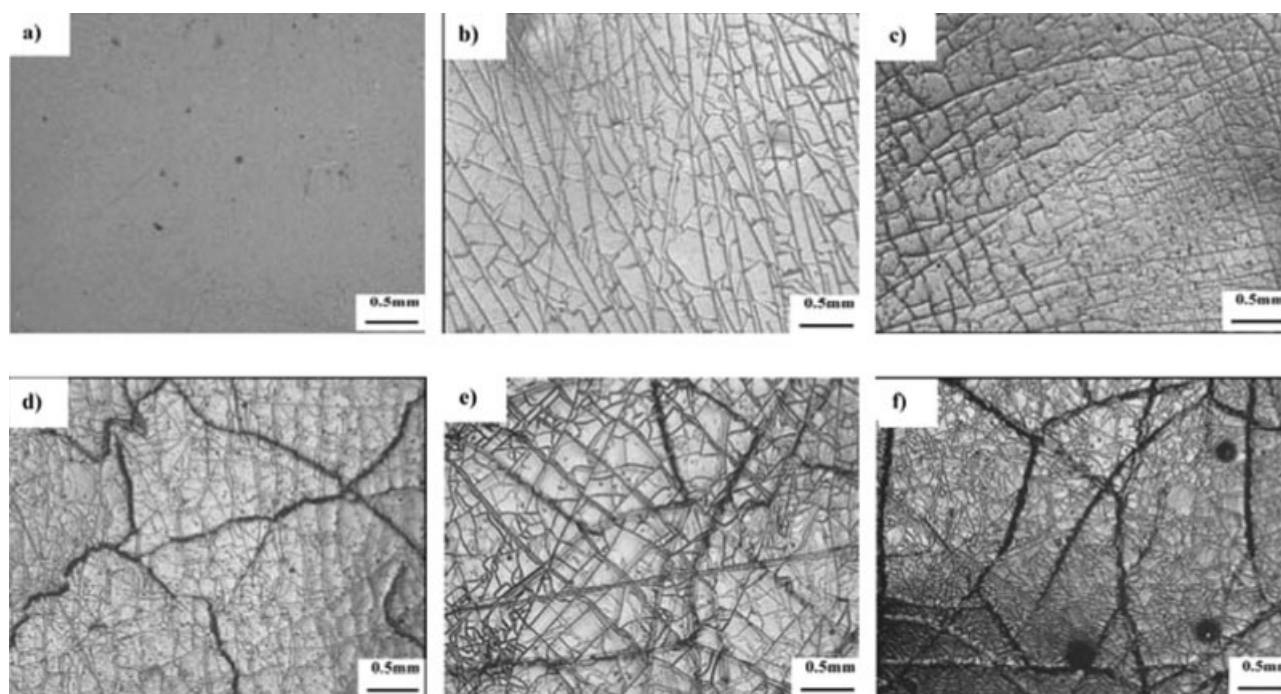


Figure 2 Change in surface morphology of samples with increasing proton fluence: (a) 0 cm^{-2} , (b) $5 \times 10^{14} \text{ cm}^{-2}$, (c) $1 \times 10^{15} \text{ cm}^{-2}$, (d) $3 \times 10^{15} \text{ cm}^{-2}$, (e) $5 \times 10^{15} \text{ cm}^{-2}$, (f) $1 \times 10^{16} \text{ cm}^{-2}$.

deepens obviously after the irradiation from the light-yellow to the dark-yellow.

FTIR analysis

Figure 3 shows the change in FTIR spectra before and after proton exposure for the PDMS. Five absorption bands exist in the pristine FTIR spectrum, which are located at 2962, 1261, 1084, 1018, and 796 cm^{-1} , respectively. It is believed that the absorption

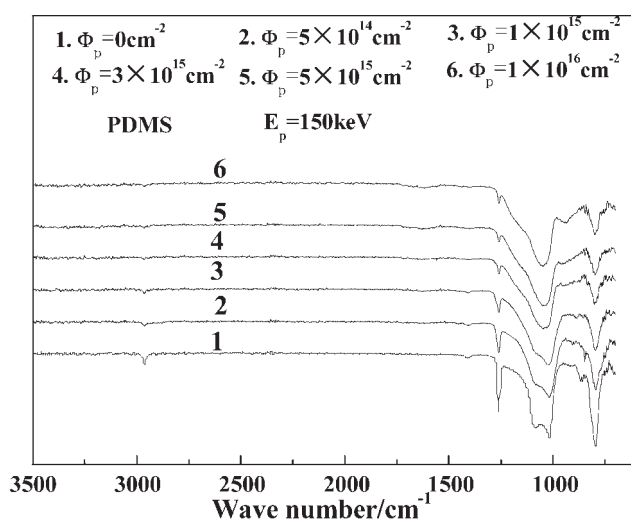


Figure 3 FTIR spectra for polydimethylsiloxane irradiated by 150 keV protons for various fluences.

band at 2962 cm^{-1} originates from the tensile vibration of C—H bonds, the band at 1261 cm^{-1} from the symmetrically deformed vibration of CH_3 groups in Si— CH_3 bonds, the bands at 1084 and 1018 cm^{-1} from the Si—O stretching vibration of the Si—O—Si structure, and the band at 796 cm^{-1} from the stretching vibration of Si—C bonds.^{10–13}

Except for the bands originating from the Si—O stretching vibration, the location and profile of the other absorption bands change a little after the proton irradiation, but the area gradually reduces with increasing the proton fluence. When the proton fluence is larger than $3 \times 10^{15} \text{ cm}^{-2}$, a new absorption band at 942 cm^{-1} gradually appears. This new band might be related to the Si—OH absorption one, and needs to be further studied. The decrease in the area of the absorption bands implies that scission of bonds occurs during the proton irradiation. The variation in the amount of each functional group in the PDMS irradiated by the protons can be characterized by the relative change of the corresponding absorption band area $\Delta A/A_0$ in the FTIR spectra, where A_0 is the related absorption band area in the pristine FTIR spectrum. Figure 4 shows the $\Delta A/A_0$ as a function of proton fluence for the C—H, Si—C, Si—O—Si, and Si— CH_3 groups. It is shown that $\Delta A/A_0$ decreases with increasing proton fluence for the four functional groups. This phenomenon can be attributed to the bond scission caused by the proton irradiation, which leads to the decrease in relative amount of the above functional groups. An analysis

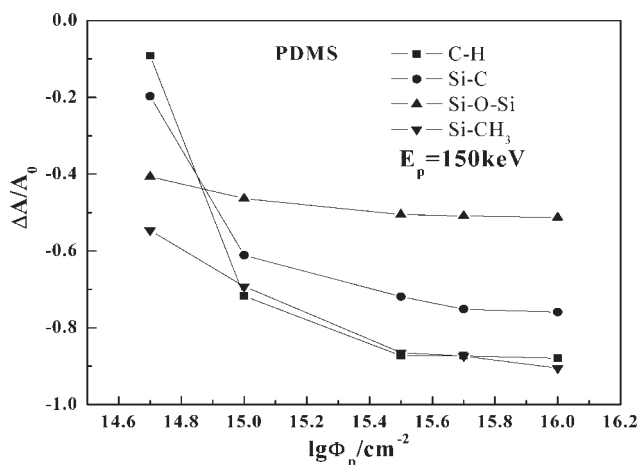


Figure 4 The relative change of absorption band area in FTIR spectra $\Delta A/A_0$ versus proton fluence for various functional groups.

on photodissociation of PDMS in terms of *ab initio* molecular dynamics demonstrates that the H in the CH₃ groups is most easily knocked off, leading to the scission of C—H bonds and the formation of the H and the Si—CH₃ radicals.¹⁴ Also, the C—Si bonds could be broken forming the methyl radicals as well as the main chain radicals. This analysis is in agreement with the above testing result.

It is also found in Figure 3 that the profile of the absorption bands related to Si—O—Si stretching vibration changes during the proton irradiation, from the double bands to a single one. Before the irradiation, the two bands appear at 1084 and 1018 cm⁻¹, respectively. With increasing proton fluence, the band at 1084 cm⁻¹ tends to disappear, whereas the band at 1018 cm⁻¹ widens gradually. This phenomenon has not been reported in references. It could be related to the Si—O—Si bond scission due to proton irradiation, resulting in shortening the Si—O—Si chain length and formation of hexamethylcyclotrisiloxane (D₃). It is demonstrated that the pyrolysis product in vacuum of the straight chain PDMS is the cyclotrisiloxane.¹⁵ The activation energy for the main chain of PDMS to be pyrolyzed in vacuum is 40 kcal/mol. Under the pyrolysis, the uncoupled electrons of O atoms in the PDMS chains can be coordinated with 3d-vacant orbitals of the neighboring Si atoms, and the Si—O—Si bonds

might be broken. As a result, the cyclotrisiloxane (D₃) is formed, as shown in Figure 5. In reference 16, it is pointed out that the Si—O—Si absorption band in D₃ structure is a single one appearing at 1020 cm⁻¹ due to the Si—O stretching vibration. Therefore, the change in profile from double bands to a single one for Si—O stretching vibration bands of the Si—O—Si structure in Figure 3 could be related to the formation of D₃ structure due to the proton exposure. The profile of the absorption band at 1018 cm⁻¹ tends to widen with increasing proton fluence, illustrating that the amount of the D₃ structure increases during the proton exposure.

Discussion

The change in color of PDMS samples can be attributed to the jump of valence electrons after absorbing photons of a given wavelength. In the unsaturated hydrocarbon molecules containing impure atoms such as N, S, and O, the uncoupled electrons in the *p*-orbit of impure atoms are referred to as the *n* electrons, which are ready to be excited into the antibonding orbitals with the lowest energy (namely, the *n*→*π** electron jump). It is believed that the *n*→*π** jump is a primary reason for the coloration of polymers.¹⁷ The *σ*-electrons (bonding electrons for a single bond) are usually localized, but are apt to be delocalized in PDMS. In the Si—O—Si main chain of PDMS, the Si atoms have low negativity and 3d-vacant orbitals, and the *d*-orbitals of Si atoms and the *p*-orbitals of O atoms overlap, providing an opportunity for the *σ*-electrons to be delocalized. The delocalization of *σ*-electrons is beneficial to decrease the energy of *π** orbit and thus the energy levels of excitation, which would help to produce the *n*→*π** jump. As demonstrated earlier, the cyclotrisiloxane structure are formed in the PDMS samples due to proton exposure and increases with increasing proton fluence. Since the delocalization degree of cyclotrisiloxane is higher than the straight chain siloxane and increases with increasing proton fluence, the required energy for the valence electrons to be excited decreases after the irradiation. On the one hand, this could lead to the red-shift of absorption bands; on the other hand, the *n*→*π** jump might be enhanced, increasing the probability of photo-

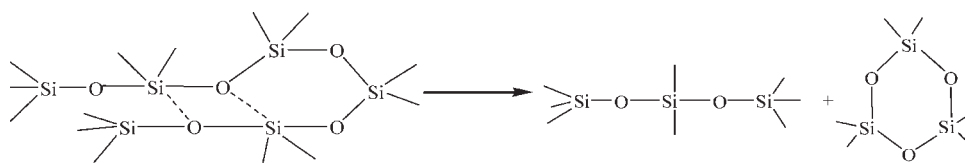


Figure 5 The change in structure of PDMS under proton irradiation.

absorption. Consequently, the optical degradation in the PDMS occurs under the proton exposure.

CONCLUSIONS

The organic silicone such as PDMS is often used as the binder in thermal control coatings on spacecraft. It is of significance to investigate the optical degradation of the organic silicone caused by <200 keV protons that exist in a large amount in the Earth radiation belts. It is demonstrated that with increasing the proton fluence, the solar absorptance α_s of PDMS increases, and the optical degradation mainly occurs in the visible region. The change in the FTIR spectra shows that under the proton irradiation, the PDMS is degraded and cyclotrisiloxane (D_3 structure) can be formed. The formation of the D_3 structure could result in an increase of delocalization degree for the σ -electrons and decrease in the required energy to excite valence electrons. As a result, the red-shift of absorption bands occurs and the $n \rightarrow \pi^*$ jump is enhanced, leading to the increase in photoabsorption probability and thus the optical degradation in the organic silicone.

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