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## Atomic oxygen erosion resistance of polysiloxane/POSS hybrid coatings on Kapton

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### Abstract

Polysiloxane/POSS hybrid coatings were deposited on Kapton substrate by copolymerizing epoxy-modified polysiloxane resin with trisilanolphenyl-silsesquioxane (POSS) and their atomic oxygen (AO) erosion resistance was tested in a ground-based AO simulator. The surface morphologies and structures of the exposed and unexposed hybrid coatings were analyzed by scanning electronic microscopy and X-ray photoelectron spectroscopy. The results indicate that the polysiloxane/POSS hybrid films are capable of providing protection against AO attack. Unlike the polysiloxane coating, no crack was observed in the hybrid coatings during AO exposure. The results of XPS analysis indicated that a continuous high-quality protective SiO<sub>2</sub> surface layer was formed on the polysiloxane/POSS hybrid coatings after the AO exposure. It can prevent further degradation of the underlying polymer with increased exposure to the AO flux and provide high-quality erosion protection for these materials. The erosion yield of the polysiloxane/POSS hybrid coatings decreased by a factor of more than two orders of magnitude compared with that of the polyimide film, reduced to 0.4% of Kapton film.

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## 1. Introduction

Atomic oxygen is the most abundant elements in the low earth orbit (LEO) space environment. LEO atomic oxygen possesses sufficient energy to break most organic polymer bonds and sufficient flux to cause oxidative erosion of polymers, developing a light-diffusing needlelike surface (Buczala et al., 2006). This change of the surface texture might decrease the optical reflectance and increase solar absorptance. Moreover, AO attacks degrade polymers' mechanical properties. Crack initiations can be produced easily on the needlelike surface (Shimamura et al., 2009). These degradations might cause a significant failure of spacecraft systems: its thermal, optical, or structural design. Therefore, ground simulation tests are mandatory techniques for space programs in terms of the degradation assessment of space polymer materials.

Since atomic oxygen-induced erosion phenomena in low Earth orbit (LEO) were recognized, much effort for the development of atomic oxygen-resistant material has been carried out for more than two decades. Numerous schemes are available to mitigate the AO damage to polymers and polymer matrix composites in the LEO environment (Miyazaki et al., 2010). Researchers found that inorganic metallic oxide coatings have excellent AO resistance, such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (Banks et al., 2005). However, it is very different to make a defect-free AO protective layer in a big surface, and the oxidation erosion of the underlying polymer can occur at pinhole and scratch defects through undercutting erosion (Dworak et al., 20065). In contrast, the AO erosion yields of organic coatings are one or two orders of magnitude higher than that of inorganic coatings (Brunsvold et al., 2007). Thus, organic/inorganic hybrid coatings are proposed as potential protective coatings due to their unique combination of the merits of organic and inorganic coatings. This research focused on the development of new surface modification method to protect polymeric substrates against AO attack. Previous work showed that POSS-containing polyimides have significantly lower erosion yields compared to polyimide. The nanometer-sized structure of POSS, with its large surface area, has led AO-irradiated samples to form a  $\text{SiO}_2$  passivation layer, which protects the underlying polymer from further AO attack (Brunsvold et al., 2007).

In this study, Hybrid inorganic/organic polymers have been prepared by copolymerizing an epoxy-polysiloxane with a TriSilanolPhenyl-silsesquioxane (POSS). The erosion resistance of the polysiloxane/POSS (20 wt pct) coating was investigated by exposure tests of AO beam in a ground-based simulation facility. After exposure to AO flux, the physics and chemistry properties of the samples surface were analyzed.

## 2. Experimental

Epoxy-modified polysiloxane resin from Anshan city special resin limited company was employed as an organic component. TriSilanolPhenyl-silsesquioxane (TSP-POSS, purchased from American Hybrid Plastics Company) was used as inorganic constituents. Tetrahydrofuran (THF,  $\text{C}_4\text{H}_8\text{O}$ ) were used as the organic solvents. All materials were used as received.

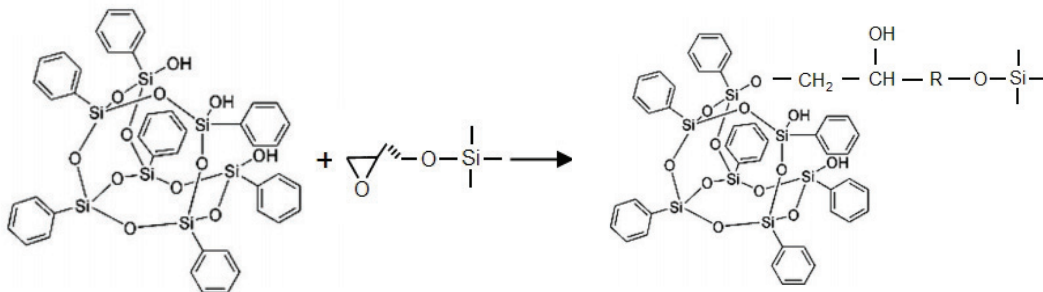


Fig. 1. eaction scheme of epoxy modified polysiloxane/POSS hybrid thin films.

The procedure for sample preparation is described as follows. The appropriate amounts of polysiloxane resin were dissolved in THF. This solution was denoted as solution *A*. The appropriate amount of TSP-POSS was dissolved in THF and stirred (solution *B*). Solutions *A* and *B* were mixed in a flask and immediately refluxed and stirred in a water bath at 80 °C for 4 h. The clear solution was then cooled to 25 °C with ice water. The clear solution was dipping-coated on a precleaned glass or Kapton substrate with dimensions of 1 cm × 1 cm. Then, the coated films were allowed to dry under the ambient conditions for 24 h and further in a furnace at 60 °C for 2 h, at 100 °C for 2 h and at 220 °C for 2 h. The thickness of the coating was about 1 μm. The detailed reaction scheme and molecular structure of the polysiloxane/POSS hybrid films are shown in Fig. 1.

The ground-based tests of atomic oxygen erosion were carried out in the facility established in our lab. In this facility, a 2.45 GHz microwave source with a power of 100 W was launched into the circular cavity to generate electron cyclotron resonance (ECR) oxygen plasma. The oxygen ions moved to a negatively biased Mo plate under the electric force and the confining of a symmetrical magnetic mirror field, and then they were neutralized and reflected to form the AO beam. Details about this facility and AO parameters calibration have been reported in our previous work (Duo et al., 2004). The AO flux at the sample position was calibrated using a pure Kapton film, which is a current accepted method for determining atomic oxygen flux. The incident oxygen atoms were controlled to energy of about 5 eV by adjusting the bias on Mo plate. In this study, the AO with beam density of  $2 \times 10^{16}/\text{cm}^2 \cdot \text{s}$  and energy of 5 eV can be obtained in the facility. During the exposure, a vacuum level of  $\sim 10^{-3}$  Pa was maintained. When the test period was about 10 h, the AO fluence was about  $7.2 \times 10^{20}$  atoms/cm<sup>2</sup>.

### 3. Results and discussion

#### 3.1 AO erosion kinetics

AO effect experiment of polyimide and polysiloxane/POSS samples were conducted in the AO ground simulator. The erosion kinetics of these samples was determined gravimetrically by weighing the samples on an analytical balance. Fig. 2 shows AO erosion kinetics of polyimide, polysiloxane and polysiloxane/POSS (20 wt%) hybrid films during the exposure for 10 hours in AO ground simulation facility. As shown in Fig. 2, the mass of the polyimide sample decreased continually, the mass loss was 3.3 mg/cm<sup>2</sup> under the test conditions. The erosion of the polyimide sample appeared to increase linearly with the fluence. However, hybrid films have not apparent mass change. According to these measurements, polysiloxane/POSS (20 wt%) hybrid films possessed minimum AO erosion rate.

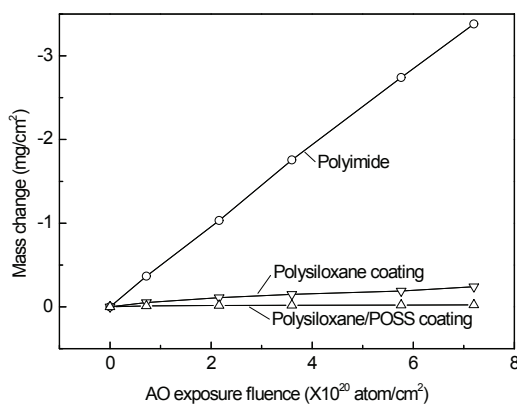


Fig.2. Mass changes of polyimide, polysiloxane, polysiloxane/20 wt%-POSS hybrid coating under AO exposure conditions.

Based on the above erosion kinetics, the erosion yield of the polysiloxane/POSS hybrid coating can be determined through the following equation:

$$R_e = \frac{\Delta m}{\rho A t f} \quad (1)$$

Where  $R_e$  is the erosion rate ( $\text{cm}^3/\text{atom}$ ),  $\Delta m$  is the mass loss of the sample (g),  $\rho$  is the density of the sample ( $\text{g}/\text{cm}^3$ ),  $A$  is the exposed area of the sample ( $\text{cm}^2$ ),  $t$  is the exposed time (s) and  $f$  is the AO flux ( $\text{atoms}/(\text{cm}^2 \text{ s})$ ). The erosion rate of the polysiloxane and polysiloxane/POSS hybrid coatings derived from these experiments is  $2.1 \times 10^{-25}$  and  $1.3 \times 10^{-26} \text{ cm}^3/\text{atom}$ , respectively. The AO resistance of the polysiloxane/POSS hybrid coatings is two orders of magnitude lower than that of the pristine polyimide ( $3.0 \times 10^{-24} \text{ cm}^3/\text{atom}$ ). The incorporation of POSS into the chemical structure of a polysiloxane resin clearly leads to a hybrid material that is largely resistance to atomic oxygen attack.

### 3.2 Surface morphology

SEM photographs of the surfaces of the polysiloxane and the polysiloxane/ (20 wt.%) POSS hybrid coatings, after exposure to the 5 eV AO beam are displayed in Fig. 3. The surfaces of both the polysiloxane and polysiloxane/POSS hybrid coatings are smooth, compact and crackless before AO exposure. After AO exposure, the polysiloxane coating due to the resultant conversion to silicon dioxide occurred to crack by shrinking (Fig. 3(a)); however, the polysiloxane/POSS (20 wt%) hybrid coating showed an intact surface with obvious appearance of homogeneous distribution of POSS nanoparticles (Fig. 3(b)), surface shrinkage or cracks were not found. The incorporation of POSS can alleviate and release stress (Liu et al., 2009) which were generated during the polysiloxane coating was exposed in AO beams, thereby it can be inhibiting the cracking of the coating. Hence the polysiloxane/POSS hybrid films are capable of providing protection against AO attack.

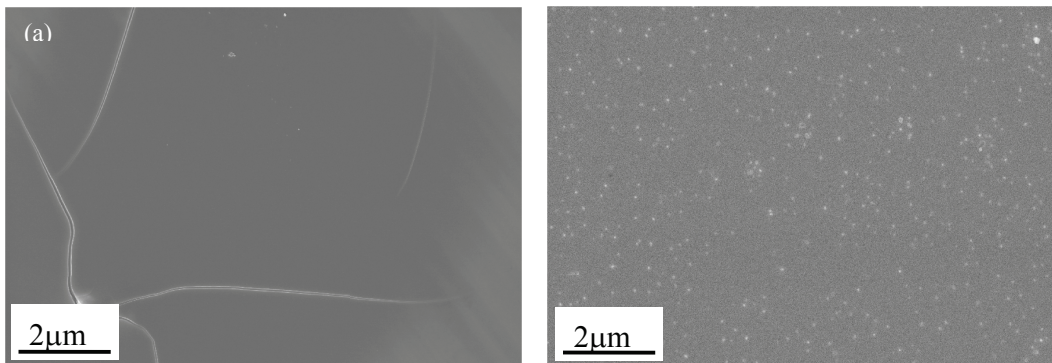


Fig.3. SEM photograph of (a) the pristine polysiloxane and (b) the polysiloxane/POSS (20 wt.%) hybrid coating after the AO exposure.

### 3.3 Surface compositional and structural change

The elemental composition of the 15 wt% POSS polyimide samples was determined by XPS survey spectra obtained before and after exposure to the AO equivalent fluence. The surface elemental composition (at%) is summarized in table 1. The carbon atomic concentration decreased drastically from 69.6 at% to 15.3 at% after exposure, while the oxygen atomic concentration increased apparently from 16.8 at% to 57.1 at%. The O-to-Si atomic ratio is 1.23 for the sample before AO exposure; it is increased to 2.07 after the 10 h AO exposure. The data indicate that the AO irradiation the surface of the coating mainly to silicon oxide with residues of hydrocarbons.

Table.1. Surface composition obtained by XPS analysis for the polysiloxane/POSS (20 wt%) coating before and after AO exposure

Conditions	C(at%)	O(at%)	Si(at%)	O/Si
Unexposed	69.6	16.8	13.6	1.23
AO	15.3	57.1	27.6	2.07

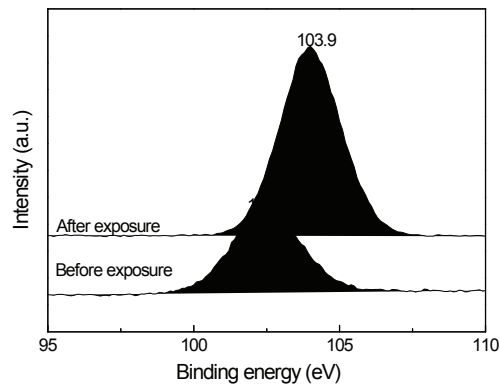


Fig.4. High-resolution XPS spectra of Si 2p of the polysiloxane/POSS hybrid coating before and after AO exposure.

High-resolution XPS spectra of Si 2p peaks obtained from the polysiloxane/20 wt% POSS surface before and after AO exposure are shown in Figs. 4. The peaks in Si 2p spectra for the hybrid coatings shifted from 102.3 eV to 103.9 eV after exposure to AO. This binding energy shift indicates oxidation of the silicon into a passivation layer in the form of SiO<sub>2</sub> (Beamson et al., 1992). That is to say, SiO<sub>2</sub> formed on the surface of the hybrid film during AO exposure. The formation of the silica layer could provide a protective barrier on the surface preventing further degradation of the polymer during extended exposure to atomic oxygen.

#### 4. 4. Conclusions

In this work, the polysiloxane/POSS hybrid coatings have been prepared on Kapton substrate by copolymerizing epoxy-modified polysiloxane resin with trisilanolphenyl-silsesquioxane (POSS). The erosion resistance of polysiloxane/POSS (20 wt%) hybrid coating was investigated by AO exposure tests in a ground-based simulation facility. The erosion of the polyimide sample appeared to increase linearly with the fluence. However, hybrid films have not apparent mass change. The erosion yield of the coated Kapton decreases to  $1.3 \times 10^{-26}$  cm<sup>3</sup>/atom, two orders of magnitude less than the value of  $3.0 \times 10^{-24}$  cm<sup>3</sup>/atom of pristine Kapton. The analysis through XPS indicates that a passive inorganic SiO<sub>2</sub> layer was formed on the surface of POSS/PDMS hybrid coatings during the AO exposure, which can prevent the further erosion of underlying materials.

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