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Surface modification of POSS–polyimide hybrid films by atomic oxygen using ECR plasma

Shuwang Duo [a,*], Huan Ke [a], Tingzhi Liu [a], Mimi Song [a], Meishuan Li [b]

[a] *Jiangxi Key Laboratory of Surface Engineering, Jiangxi Science & Technology Normal University, Nanchang 330013, China*
[b] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China*

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ABSTRACT

A novel polyimide (PI) hybrid nanocomposite containing polyhedral oligomeric silsesquioxane (POSS) had been prepared by copolymerization of trisilanolphenyl-POSS, 4,4′-oxydianiline (ODA), and pyromellitic dianhydride (PMDA). The atomic oxygen (AO) resistance of these PI/POSS hybrid films was tested in the ground-based AO simulation facility. Exposed and unexposed surfaces were characterized by SEM and XPS. The SEM images showed that the surface of the 20 wt.% PI/POSS became much less rough than that of the pristine PI. Mass measurements of the samples showed that the erosion yield of the PI/POSS (20 wt.%) hybrid film was 1.2×10^{-25} cm^3/atom, and reduced to 4.3% of that of the PI film. The XPS data indicated that the carbon content of the near-surface region was decreased from 66.0 to 7.0 at.% after AO exposure. The ratio of oxygen and silicon concentrations in the near-surface region increased to 2.08 after AO exposure. The nanometer-sized structure of POSS, with its large surface area, had led AO-irradiated samples to form a SiO_2 passivation layer, which protected the underlying polymer from further AO attack. The incorporation of POSS into the PI could dramatically improve the AO resistance of PI films in low earth orbit environment.

1. Introduction

Spacecraft operating in low Earth orbit (LEO) at altitudes ranging from 200 to 700 km are exposed to an extremely harsh environment. The degrading environment in LEO includes atomic oxygen (AO), ultraviolet (UV) and ionizing radiation, thermal cycling, and orbital debris [1]. The predominant environmental species in LEO responsible for the spacecraft materials degradation is AO. The effect of AO on spacecraft material degradation has been studied on space-exposed materials and in the AO simulation facilities. Due to AO interactions with the space materials, polymers in particular suffer rapid erosion, chemical and structural modification, and surface roughening. This might lead to irreversible degradation of optical, thermal, electrical and mechanical properties [2–4].

Polyimides (PIs) such as Kapton® are well-known for their excellent mechanical properties, high temperature durability, and controlled structures and have been widely used in spacecraft external surfaces as thermal blankets, in solar arrays, and space inflatable structures. Numerous efforts have been made to protect PIs from AO, mainly by the use of protective layers. PI surfaces coated SiO_2 or Al_2O_3 have been shown to exhibit good atomic oxygen erosion resistance [5,6], however, inherent or debris-induced defects in the coating will permit AO penetration and undercut the underlying polymer substrate [7]. Developing materials which can sustain such erosion and still function under the harsh conditions of the LEO environment is therefore needed.

Hybrid nanocomposites are the materials whose structural components are mixed at a nanometer scale. Organic–inorganic hybrid nanocomposite materials are regarded as a new generation of high-performance materials since they combine the advantages of inorganic materials (rigidity, high stability) and organic polymers (flexibility, dielectric properties, ductility, processibility). Due to their dispersed nanometer sizes, nanoparticles can easily serve as bridges between the molecules in polymer matrix. Many research groups [8,9] have endeavored to synthesize nanocomposites, and it has been found that, in comparison with macroscopic composites made of the same component phases, these nanocomposites have immense potential because they possess enhanced mechanical, thermal, optical, and anti-oxidative properties. To improve the AO resistance of PIs, POSS cage structures with various functionalities recently attract much attention among materials scientists. For example, POSS and silica inorganic particles have been used to achieve simultaneous enhancements in the thermomechanical and AO resistant properties of the final PI-based nanocomposites [10,11]. Therefore, the trend of increasing in synthesizing new

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* Corresponding author. Tel.: +86 791 88537923 (office), mobile: +86 13517099545; fax: +86 791 83831266.
E-mail address: swduo@126.com (S. Duo).

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functional group-terminated POSS and their use as nanoscale building block for preparing PI/POSS hybrids with controlled mechanical and AO resistant properties is still of crucial interest to the burgeoning field of coatings, optics, and thermal blankets.

In this paper, we describe the preparation and properties of PI/POSS nanocomposites. The nanocomposites were prepared using trisilanolphenyl-silsesquioxane with units of radius 1.3 nm including rigid silica core and three silanol groups. It is found that the AO resistance of the PI/POSS nanocomposites is significantly improved in comparison with that of pure PI.

2. Experimental

TriSilanolPhenyl-silsesquioxane(TSP-POSS) purchased from American Hybrid Plastics Company. *N*,*N*-methyl-2-pyrrolidone (NMP, analytical reagent grade) was obtained from Sigma–Aldrich. Pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) from Aldrich were refluxed with an excess amount of acetic anhydride and tetrahydrofuran, respectively. POSS-OH was dried in vacuum oven at 40 °C for 1 day before use. Other chemicals were used as received unless mentioned.

The PMDA-ODA PI/POSS-OH hybrids were prepared with the following steps: according to Fig. 1, various weight percentages of POSS-OH were added into the flask that contained predetermined amount of PAA solution with inert atmosphere at room temperature. At first, the POSS-OH particles were dispersed in NMP by a ultrasonic nano dispersion equipment (VCY-1500, 1.5 kW, 20 kHz, Shanghai Yanyong Ultrasonic Equipment Co., Ltd) for 1.5 h and then to make homogeneous mixing by a magnetic stirrer (50 °C, DF-101Z, 2000 r/min, Zhengzhou Great Wall Instrument Co., Ltd). POSS-OH was added into PAA solution very carefully when prior added part had completely dissolved in the PAA solution. The solution was then stirred continuously for few hours, yielding a viscous PAA/POSS-OH solution. Again the mixture was continued for mixing for several hours. The PI/POSS-OH thin film was obtained by casting the solution on glass substrate. Thermal imidization were used for converting PAA to the cured PI and its nanocomposite films. The curing of the pre-mixed solution is based on a process developed by proposed by Junchao Huang [12]. The imidization temperature was maintained from 70 to 300 °C (at 70 °C for 4 h, 90 °C for 2 h, 120 °C for 2 h, 200 °C for 2 h, and 300 °C for 2 h), in order to completely removed the solvent and fully imidized. Finally, resulting films were peeled off after imidization from the glass substrates as self-standing nanocomposite films. Similar protocol was used for fabricating pure PI film.

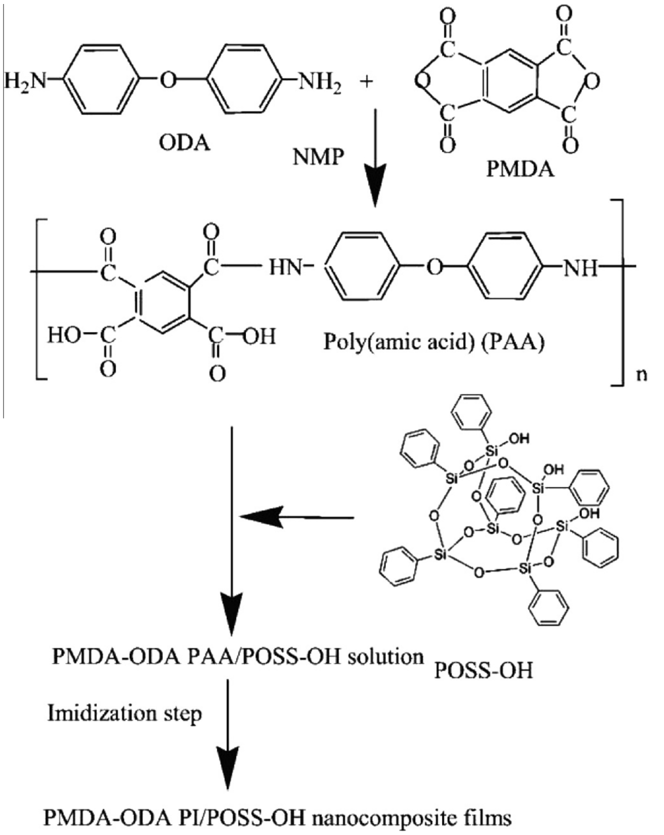

Fig. 1. Reaction sequence and procedure for preparation of the POSS-OH/PI hybrid films.

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, 100 W microwave source was launched into the circular cavity to generate electron cyclotron resonance (ECR) oxygen plasma. The molybdenum neutral target is placed via a supporter at the center of the magnetic mirror field. Our designed mirror field configuration showed in the Fig. 2. 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 described elsewhere [13]. The incident oxygen atoms were controlled to energy of about 5 eV by adjusting the bias on Mo plate. AO equivalent fluence measurements were conducted based on 25 μm thick Kapton-HN film (DuPont, Inc.) mass loss, assuming an erosion yield of 3 × 10^{-24} cm^3/O-atom [2]. During the exposure, a vacuum level of $\sim 10^{-3}$ Pa was maintained. The space equivalent AO flux at the sample's position was 2 × 10^{16}/cm^2 s. When the test period was about 10 h, the AO fluence was about 7.2 × 10^{20} atoms/cm^2.

The mass change of sample was measured before and after exposure to AO using a Sartorius BP211-D analytical balance accurate to ±0.01 mg. Samples are outgassed in 10^{-3} Pa vacuum for 2 h prior to exposure, and then weighed. This procedure eliminates most of mass loss raised by the outgassing effect.

The surface morphologies of samples before and after exposure were observed by scanning electron microscopy (SEM, Zeiss Sigma, Germany). The surfaces of the polymer samples were sputtered with a 10 nm thick gold film before viewing in order to prevent charging. The change of chemical composition and structure due to the surface reactions after exposure to AO flux was determined by X-ray photoelectron spectrometer (XPS, ESCALAB 250) and Fou-

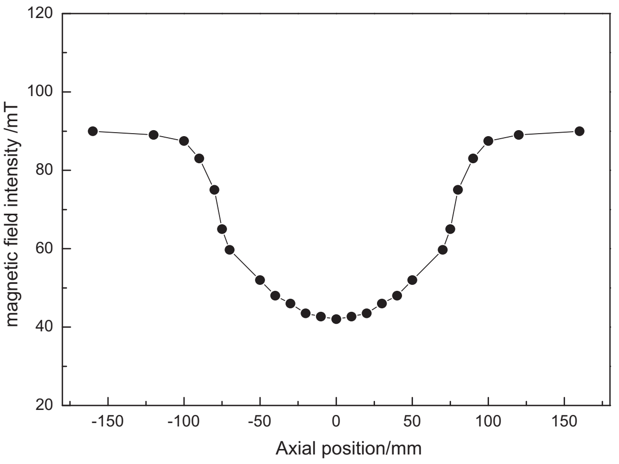

Fig. 2. Configuration of our designed magnetic mirror fields.