



# Improved space survivability of polyhedral oligomeric silsesquioxane (POSS) polyimides fabricated via novel POSS-diamine



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## ABSTRACT

Polyhedral oligomeric silsesquioxane (POSS) surrounded by two amine groups, namely POSS-diamine, was prepared via hydrolytic co-condensation. POSS polyimide hybrid membranes were subsequently fabricated by co-polymerizing POSS-diamine with imide monomers. Hybrid membranes exhibit significantly improved space survivability. A hybrid membrane with 29.7 wt% POSS loading shows the best atomic oxygen (AO) resistance with the lowest erosion yield of  $0.9 \times 10^{-25} \text{ cm}^3 \cdot \text{atom}^{-1}$ . The enhancement in AO resistance is attributed to the formation of a  $\text{SiO}_2$  passivating layer on the membrane surface upon AO exposure. POSS polyimides with desirable AO survivability may find wide usage in aerospace.

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## 1. Introduction

Materials, not only metals but also polymer composites, tend to corrode or degrade in almost every atmospheric condition [1–8]. To speak of, a large portion of high-performance polymeric materials, in particular aromatic polyimides, are extensively used in man-made satellites. However, those hydrocarbon-based polyimides are subject to severe degradation when exposed to atomic oxygen (AO), ultraviolet (UV) and vacuum-ultraviolet (VUV) radiation and thermal cycles, which are present in the low earth orbit (LEO) [9,10]. Among which, AO is ubiquitous in LEO and strong enough to induce organic bond cleavage due to its strong oxidation and considerable translational energy of approximately 4.5–5.0 eV [11–13]. Consequently, most of the organic polymers onboard spacecraft are oxidized and eroded and then generate free radicals and give rise to reactions that finally result in chain scission and/or cross-linking or even releasing volatile gases, which can cause significant reduction in physical, mechanical and optical properties of polymers [9,10].

A variety of promising methods focusing on physically and chemically tailoring the molecular structure of polyimides to improve oxidation resistance of polyimides, including polymer blending [14,15], copolymerization [16–18], organic–inorganic hybrid technology [9,19] and coating technology [20], have been

attempted during past several years. The synthesis of fluorinated polyimides has been one such approach [21–23], for fluorinated polyimides often exhibit good resistance to AO attack. However, remarkable increases in the erosion yield (mass loss) is typically observed when such polyimides are exposed simultaneously to AO and UV radiation [21,22]. In addition, poor mechanical properties and high monomer costs also restrict its wide use.

A second approach is introducing phosphorus into polyimide molecular backbones to fabricate phosphorus-containing polyimides by copolycondensation [16–18,24–26]. A substantial reduction in the AO erosion yield has been obtained, and the resulting polyimides demonstrated a combination of admirable properties. In this approach, however, the resulting membranes were relatively brittle and exhibited poor fracture toughness [18], which cannot meet the space requirements, either.

Strategies to making polyimides with high space survivability that access AO erosion yield below 1% that of pristine polyimide typically introduce silicon to improve the AO resistance [9,19,27,28]. Among a few examples of silicon-containing polyimides, those derived from polyhedral oligomeric silsesquioxane (POSS) are the most thoroughly investigated representatives of this new class of materials [9,19], owing to its potential applications in various areas and the ease with several functional groups can be attached on POSS vertex [9,29–37]. As reported by Gonzalez [38] and Minton [9,19], POSS polyimides are likely to form a  $\text{SiO}_2$  passivating layer upon AO exposure, and thus prevents AO from eroding the bulk matrix, thereby increasing AO resistance. It is another noticeable problem that the previously reported work typically involving POSS

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monomer looks specifically at bifunctional POSS-diamines, which are relatively expensive and difficult to synthesize [9,19,39]. For instance, in the approach of Minton's group [9,19], such expensive chemical reagents as octa-cyclopentyl POSS, (aminopropyl)-heptaisobutyl POSS, *N-p*-Lithiophenyl-*N*-1,1,4,4,-tetramethyldisilylazacyclopentane, *n*-BuLi etc. were typically employed and the whole preparation process was relatively complicated and difficult to operate, which is adverse to mass production and hence compromise wide use of POSS polyimides and should be rationally solved for practical application. In contrast, octa-functional POSS, such as octa-(aminopropyl or aminophenyl)silsesquioxane (OAPS), is relatively easy to manufacture and not that expensive in comparison to POSS-diamine [29,33,40], but it is difficult to get all of the amine groups reacted and hence one could not make polymers with well-defined structures. Additionally, insoluble polyamic acid (PAA) gels usually form [41], and thus hybrid membranes could not be obtained or only membrane fragments were acquired due to extreme brittleness [42].

We wonder whether, in another approach, POSS-diamine can be synthesized and incorporated into polyimide molecular backbones to fabricate POSS polyimides inherently withstanding the "ambitious" AO attack through a versatile method without significantly sacrificing the other properties. Previously, we have reported that covalently tethering amine-functionalized hyperbranched polysiloxanes (HBPSis) into polyimide molecular skeletons results in organic-inorganic HBPSi polyimides with good thermal stability and outstanding AO resistance [43]. Here, we adopt phenyltriethoxysilane and  $\gamma$ -aminopropyltriethoxysilane to directly synthesize newly developed POSS-diamine via moderate hydrolytic co-condensation reactions. Finally, POSS polyimides could be easily obtained by copolymerizing POSS-diamine with other imide monomers in a polar aprotic solvent and subsequent thermal imidization. This copolymerization approach provides a facile method to design a variety of polyimide nanocomposites with tunable AO resistance and mechanical properties by varying POSS addition. Polyimide matrix maintains the advantage of both high thermal and mechanical strength while POSS molecule imparts excellent AO resistance to the resulting nanocomposites.

In the present study, the AO resistance of POSS polyimides was investigated by exposing its surface to various AO fluences, and the protection/oxidation mechanism was established. Several surface analytical techniques were herein adopted to reveal the relationship between the erosion yields of resulting POSS polyimides and their structures. Curve-fitting models were also used to predict the service life of POSS polyimide in the simulated AO environment. These evaluations may contribute to providing some effective viewpoints to the degradation behaviour and protection mechanism of POSS polyimides in AO environment.

## 2. Experimental

### 2.1. Materials

Phenyltriethoxysilane (PTES) and  $\gamma$ -aminopropyltriethoxysilane (APS) were purchased from Nanjing Chengong silicon co., Ltd (Nanjing, China) and used as received. Tetraethylammonium hydroxide (TEAOH, 25 wt% in aqueous solution), absolute ethanol, 4,4'-diaminodiphenyl ether (ODA) and pyromellitic dianhydride (PMDA) were provided by Sinopharm Chemical Reagent Co., Ltd (Beijing, China). ODA and PMDA were purified by vacuum sublimation prior to use while the other reagents were used as received. *N,N*-Dimethylacetamide (DMAc) was purchased from Tianjin Fuyu Fine Chemicals Co. Ltd (Tianjin, China) and freshly distilled under reduced pressure over phosphorus pentoxide and stored over 4 Å molecular sieves prior to use.

### 2.2. General characterization

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra of POSS-diamine were recorded on a BRUKER AVANCE-300 spectrometer in DMSO- $d_6$  at room temperature. Chemical shifts were referenced to tetramethylsilane.  $^{29}\text{Si}$  NMR spectrum of POSS-diamine was acquired on a Bruker Avance 500 spectrometer (Bruker BioSpin, Switzerland) operating at 50.7 MHz in DMSO- $d_6$ . Elemental analysis of POSS-diamine was run in a Heraeus VarioEL-III CHN elemental analyzer (Germany). The molecular weight of POSS-diamine was measured with gel permeation chromatography (GPC) by using tetrahydrofuran (THF) as eluent solvent. Polystyrene standards were used for calibration of the GPC. Amino content was acquired by acid-base back titration using phenolphthalein as indicator. The purity (wt%) of POSS-diamine was estimated based on its amino content. Fourier transform infrared spectroscopy (FT-IR) measurements were conducted on a FT-IR spectrophotometer (BRUKER TENSOR 27). The FT-IR spectrum of POSS-diamine was obtained by using thin KBr disk as the sample holder, while FT-IR spectra of polyimide films were collected by using an attenuated total reflectance (ATR) instrument. Thermal gravimetric analyses (TGA) of POSS-diamine and polyimide membranes were carried out on a TGA/DSC 1 synchronous thermal analyzer at a heating rate of 10 °C/min under air and/or nitrogen atmosphere from room temperature to 1000 °C. The isothermal TGA of polyimide membranes were conducted under nitrogen atmosphere aging at two different temperatures (400 °C and 500 °C) for 10 h. The *d*-spacing within POSS-diamine molecule and resulting membranes was determined by wide angle X-ray diffraction (WAXD) by using a Shimadzu XRD-700 (Shimadzu, Japan) X-ray diffractometer (40 kV, 40 mA) with a copper target at a scanning rate of 4°/min and calculated from the scattering angle ( $2\theta$ ) according to Bragg's equation:

$$n\lambda = 2d \sin \theta \quad (1)$$

The storage modulus  $E'$  and internal loss factors  $\tan \delta$  of polyimide membranes were determined on a Mettler Toledo DMA/SDTA861e instrument. The cast membranes were cut into 6 × 30 mm rectangular samples for dynamic mechanical thermal analysis (DMA). All polyimide samples were subjected to the temperature scan mode at a programmed heating rate of 10 °C/min at a frequency of 1 Hz from room temperature to 450 °C in a tensile mode. The glass transition temperatures ( $T_g$ s) of resulting membranes are regarded as the peak temperature in the  $\tan \delta$  curves. Thermo-mechanical analysis (TMA) was performed on a TMA/SDTA 840 device at a heating rate of 5 °C/min. The coefficients of thermal expansion (CTE) of the membranes were measured in the temperature range of 75–150 °C. Mechanical properties of polyimide membranes were measured with a universal testing machine (UTM) according to GB13022-91 at a drawing rate of 10 mm/min at ambient temperature on strips approximately 40–45  $\mu\text{m}$  thick and 15 mm wide with a 60 mm gauge length. An average of at least seven individual determinations was used. UV-vis transmittance and absorbance of the resulting membranes was measured by using a U-3010UV-VIS spectrophotometer and the wavelength ranged from 200 to 800 nm. Membrane thickness was measured with a thickness gauge, and densities were obtained by liquid suspension method with a mixture of toluene and tetrachloromethane at 25 °C. Inherent viscosities ( $\eta_{\text{inh}}$ ) were obtained on 0.5% (w/v) polyamic acid (PAA) solutions in freshly distilled *N,N*-dimethylacetamide (DMAc) at 25 °C with an Ubbelohde viscometer. Presented  $\eta_{\text{inh}}$  values are the average of at least nine individual tests of each sample.

### 2.3. AO exposure testing

Ground-based AO exposure measurements were performed with a combined space effect testing facility (CSETF) equipped with

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