Synthesis and Properties of Atomic-oxygen Resistant POSS-Polyimide Aerogels

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Abstract

We report the synthesis of novel POSS-polyimide aerogels (POSS-PIA) by gelling poly(amic acid) (PAA) solutions of 3,3’,4,4’-biphenyltetracarboxylic dianhydride (BPDA), 2,2’-dimethylbenzidine (DMBZ)/N-[(hepta-isobutylPOSS)propyl]-3,5-diaminobenzamide (SC-POSS), and octa(amino-phenyl)-silsesquioxane (OAPS). The gels were chemically imidized and dried using supercritical CO_2 extraction. The effects of mole percent of SC-POSS diamine in place of DMBZ on the density, porosity, shrinkage, surface area, mechanical properties, and resistance to atomic oxygen of the POSS-PIA are discussed. POSS-PIAs with low density (0.13-0.07g/cm^3), high porosity (63.9-92.1%), high surface area (393.3-651.1m^2/g), Young’s modulus (1.1-9.2MPa) were produced in this study. Upon exposure to AO at ambient temperature, POSS-PIA-30 erode significantly less than POSS-PIA-0 or Kapton H (76% or 64% less).

Introduction

Polyimide (PI) aerogels are novel materials with three-dimensional open networks. Due to their many desirable properties, such as enhanced thermal stability, low density, excellent flexibility compared with SiO_2 aerogels, high porosity, high specific surface area, and low thermal conductivity, PI aerogels have widely application requirements in various space and aerospace. These may include thermal insulation for extravehicular activity (EVA) suit for planetary surface missions, inflatable habitat structures, inflatable aerodynamic decelerators for entry, descent and landing operation, and cryotank insulation for advance space propulsion systems [1]. However, organic materials exposed to the low Earth orbit (LEO) envionment typically erode away. Many studies have documented how polymers that can with stand decades of exposure on Earth are quickly eroded and converted to carbon dioxide and other gaseous materials within days to months during exposure in LEO. The main mechanism for destroying organic hydrocarbon materials is oxidation by atomic oxygen (AO), which can be more than 90% of the neutral component of the residual atmosphere at altitudes of 300~700km [2]. Organic materials are not chemically stable in LEO and must be protected. Polymers are typically protected by the application of coating, such as SiOx, which is resistant to degradation in the presence of atomic oxygen. Unfortunately, microscopic scratches, dust particles or other imperfections in the substrate surface can result in defects in the protective coating. These coating defects can provide pathways for AO attack and undercutting erosion of the substrate can occur [3]. A Promising approach toward the production of LEO survivable polymer is to incorporate Polyhedral Oligomeric Silsesquioxanes (POSS) into the polymeric chains. Previous research work showed that the self-passivation of POSS-containing polyimides have significantly lower erosion yields than Kapton

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which is used extensively in spacecraft thermal blanket, solar arrays, and space inflatable structures, since AO irradiation results in formation of SiO_2 passivation layer which protect the underlying polymer from further AO attack [4].

In this study, we report a series of side chain POSS-polyimide aerogels (POSS-PIA) as shown in Scheme 1, which were prepared using 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 2,2'-dimethylbenzidine (DMBZ) / N-[(hepta-isobutylPOSS)propyl]-3,5-diaminobenzamide (SC-POSS), and octa(aminophenyl)silsesquioxane (OAPS). OAPS is used to form a cross-linked poly(amic acid) by reacting with the terminal anhydride groups of oligomers made from BPDA and DMBZ/SC-POSS. The oligomers are formulated with repeat units as shown in scheme 1. BPDA and DMBZ are typical monomers used in polyimide matrix resins for high temperature applications. SC-POSS was subsequently copolymerized to form POSS-polyimide aerogels. As will be discussed in the following, POSS-polyimide aerogels, relative to 0% SC-POSS polyimide aerogel, display effects on glass transition temperature, thermal conductivity, porosity, pole size, AO resistance, and mechanical properties.

Experimental Section

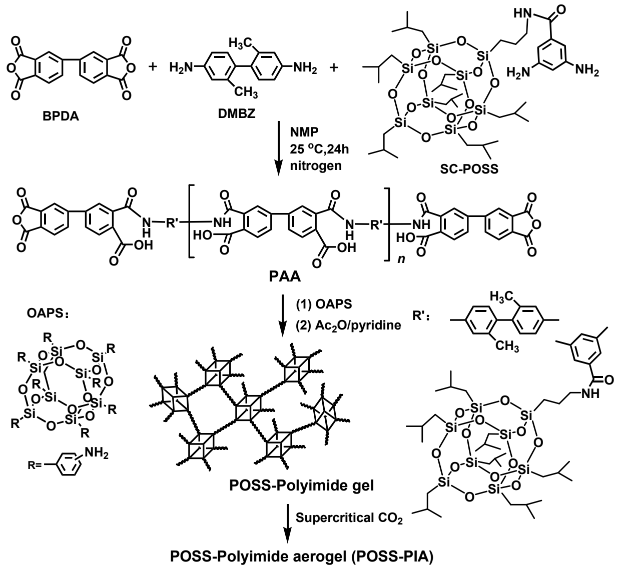
Materials. 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) were purchased from TCI (Tokyo, Japan) and dried in vacuum at 180 °C overnight prior to use, 2,2'-dimethylbenzidine (DMBZ) were purchased from Changzhou Yangguang (Changzhou, China) and used as received. N-[(hepta-isobutylPOSS)propyl]-3,5-diaminobenzamide (SC-POSS) and octa(aminophenyl)-silsesquioxane (OAPS) were synthesized according to literatures[2]. Solvent including *N*-Methyl-2-pyrrolidinone (NMP), acetic acid, acetic anhydride, pyridine, and ethanol were all purchased from Beijing Yili Fine Chemicals, China. NMP was purified by vacuum distillation over CaH_2 prior to use. The other commercially available reagents were used without further purification.

Characterization. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum was obtained on a Bruker Tensor-27 FT-IR spectrometer. Field emission scanning electron microscopy (FE-SEM) was obtained on a Hitachi S-4800 microscope. POSS-PIA surface area (σ) and pore size distribution were measured by nitrogen adsorption and desorption at 77K using a Micrometics ASAP 2000 surface areas and porosity analyzer. Before testing, the POSS-PIA sample was outgassed at 80 °C for 10h in vacuum. The surface area was calculated by Branuaer-Emmet-Teller (BET) method and pore size distribution was calculated by Barret-Joyner-Halenda (BJH) method. The bulky density (ρ_b) and skeletal density (ρ_s) were measured by mercury intrusion porosimetry using a Micrometics Auto Pore IV9520 porosimeter. The percent porosity was calculated as: porosity(%)= $(1-\rho_b/\rho_s)\times 100$. The thermogravimetric *analyses (TGA) were* recorded on a TA-Q50 thermal analysis system at a heating rate of 20 °C/min in nitrogen. Thermal mechanical analyses (TMA) were performed on a TA-Q400 analyzer over 50-400 °C at a heating rate of 5 °C/min in nitrogen. The compression properties of the PI aerogels were measured on an Instron 5567 according to the ASTM Standard D 695-10. The Young's modulus was determined as the initial linear portion of the slope of the stress-strain curve.

Synthesis of POSS-polyimide aerogels (POSS-PIA). A typical experimental procedure is as follows. To a three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a cold water bath was charged with DMBZ/SC-POSS and newly-distilled NMP at 10-15 °C. After stirring for 20 min, a clear diamine solution was obtained. Then, BPDA was added in one batch and an additional volume of NMP was added to wash the residual dianhydride. The cold water bath was removed after 2 h. The mixture was stirred at room temperature for 12 h to yield a colorless and transparent poly(amic acid) (PAA) solution. To the solution, OAPS was added and the reaction mixture was stirred at room temperature for another 12 h to afford a pale-yellow PAA solution. Acetic anhydride and pyridine were then added to the PAA solution. After stirring at room temperature for 30 min, the solution was poured into pre-prepared molds. The solution gelled within 2 h and aged for 24 h in the molds. Then, the gels were continuously immerged into a solution of 75% NMP in ethanol for 24 h, then a 25% NMP in ethanol for 24 h, and finally a 100% ethanol for 24 h. The obtained wet gels were then dried in a supercritical CO_2 autoclave at the condition of 45 °C under 15 MPa for three cycles lasting 6 h.

Results and Discussion

Poly(amic acid) oligomers were formulated in NMP using a ratio of total diamine to BPDA of *n* to (*n*+1), where *n*, the number of repeat units in the polyimide backbone between cross-link, was formulated only 30. This provides oligomers terminated with anhydride, as shown in Scheme 1. All aerogels were produced using a concentration of 5 w/w% total polymer in solution. The mole percent of SC-POSS diamine in place of DMBZ ranges from 0 to 30% in this study as shown in Table 1. The poly(amic acid)s were chemically imidized using acetic anhydride and pyridine. Aerogels were produced by drying the wet gels using supercritical drying. Table 1 shows the formations and detail properties of POSS-PIA.



Scheme 1 Synthesis of POSS-PIA with SC-POSS/DMBZ, BPDA, and cross-linked by OAPS

Table 1 The experimental design and properties of POSS-PIA

POSS-PIA	SC-POSS %	Bulky Density *g/cm³*	Skeletal Density *g/cm³*	Porosity %	Shrinkage %	Pore Size *nm*	Surface area *m²/g*	Thermal conductivity *mW/(m·K)*
POSS-PIA-0	0	0.13	1.25	89.6	16.2	17.1	425.5	32.2
POSS-PIA-10	10	0.09	0.44	79.5	14.7	100.3	402.5	30.4
POSS-PIA-15	15	0.08	0.22	63.9	15.6	93.1	651.1	29.9
POSS-PIA-20	20	0.08	0.30	73.8	13.5	90.4	467.4	28.9
POSS-PIA-25	25	0.08	0.98	92.1	14.8	122.4	393.3	29.6
POSS-PIA-30	30	0.07	0.82	91.6	15.3	88.6	403.1	29.4

Compression tests were performed on all aerogels in this study. Young's modulus of aerogel was measured as the initial slope of the stresss strain curves. Generally in aerogels, the modulus decreases as density decreases. As seen from Table1 and Table 2, as mole percent of SC-POSS diamine in place of DMBZ increases, both density and modulus decreases. This is due to the bulky side-chain POSS group which affects the arrangement between the molecular chains.

Table 2 Compression properties of POSS-PIA

POSS-PIA	Compressive Strength, MPa (@10% Compressive stress)	Young's Modulus, MPa
POSS-PIA-0	0.60	9.2
POSS-PIA-10	0.21	3.7
POSS-PIA-15	0.16	1.7
POSS-PIA-20	0.14	1.5
POSS-PIA-25	0.11	1.5
POSS-PIA-30	0.09	1.1

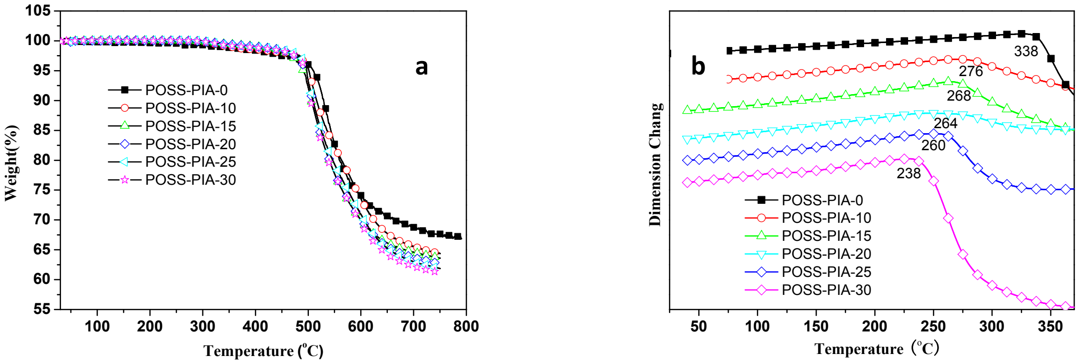


Figure 1 TGA curves (a) and TMA curves (b) of POSS-PIA

Thermal properties of the POSS-PIA were evaluated by thermogravimetric analyses (TGA) and thermal mechanical (TMA) measurements. The TGA measurements of POSS-PIA were performed in nitrogen from 50 to 750°C and the results are shown in Figure 1. As shown in figure 1,it can be observed that the POSS-PIA showed good thermal stability up to 470 °C. The smooth plots around 300 °C indicated the complete remove of residual NMP solvent by the supercritical drying procedure and the complete imidization in system. The 5% weight loss temperature are above 490°C and the residual weight ratio (char yield) of POSS-PIA at 750 °C is 60% in nitrogen, indicating good thermal stability of the POSS-PIA. The dimensional changes of aerogel at elevated temperatures were investigated by TMA measurements, as depicted in Figure 1. The aerogel showed expansion behavior after the occurrence of glass transition. The glass transition temperature decreases as the mole percent of SC-POSS diamine increases. This is due to SC-POSS diamine with the bulky side-chain POSS group, which has more flexible molecular structure than DMBZ diamine.

Figure 2 illustrates the dependence of mass loss of POSS-PIA on the AO fluence. The x-axis represents AO fluence, the y-axis, the mass loss from the initial value, which is divided by exposed surface area. Kapton H was selected as the AO monitoring sample. Ground AO irradiation testing was conducted to calibrate the atomic-oxygen fluence. We conducted irradiation test at Beihang University. As shown in Figure 2, the mass loss decrease dramatically in surface erosion as the mole percent of SC-POSS diamine increases. In other word, erosion rate decrease with increasing POSS content. AO irradiation results in formation of SiO_2 passivation layer which protect the underlying polymer from further AO attack. POSS-PIA-30 erode significantly less than POSS-PIA-0 or Kapton H (76% or 64%

less) with a total fluence of $5.69\mathrm{X}10^{20}$ O atoms/cm^2, indicating good AO resistance of the POSS-PIA.

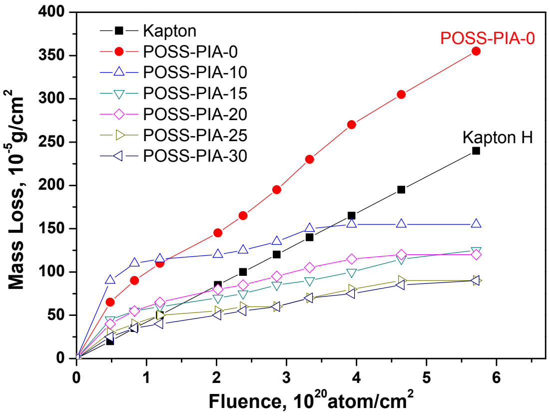


Figure 2 Mass loss plots of POSS-PIA by AO exposure

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