

Strategy for avoiding the gelation of polyimide derived from octa (amino phenyl) polyhedral silsesquioxane

Chunbo Wang(王春博), Xiaogang Zhao, Hongwei Zhou*(周宏伟)
Jilin University(吉林大学)

Abstract A series of POSS polyimide films derived from OAPS were synthesized by facile polymerization method. Mole ratio of amine to anhydride groups was controlled at 1:1, but the polymerization process without gelation. Inherent viscosity (η_{inh}) of PAA was in the range of 0.41-0.77 dL/g, which increased as the loading of OAPS increased. They exhibited a combination of desirable properties such as good thermal stability ($T_g > 240^\circ\text{C}$, $T_{d5\%} > 500^\circ\text{C}$), excellent mechanical strength (> 119 MPa), and outstanding AO resistance properties. When the loading of OAPS was 5.1 wt%, the mass loss was 60.2% than that of Kapton after 1.03×10^{20} AO/cm² fluence. These results suggest that incorporating OAPS into the polyimide backbones by adding an additional constituent, low-cost phthalic anhydride (PA) to avoiding gelation was feasible. The low-cost POSS polyimide is desirable candidate to replace the widely used Kapton polyimide on spacecrafts functioning in LEO environment.

1. INTRODUCTION

Polyimides, in particular Kapton and Uplix, are extensive application on spacecrafts in multilayer insulation blankets, and flexible substrates for lightweight, high-power solar arrays. Nevertheless, this kind of hydrocarbon-based polymers is severely corroded in the harsh atomic environment of low earth orbit (LEO) and shortens the working life on the spacecrafts. The primary mechanism for degrading organic polymer materials has been proverbially studied is oxidation by atomic oxygen, which can quickly erode hydrocarbon-based polymers and convert to carbon monoxide, carbon dioxide and other gaseous components within short time, days to months, during exposure in LEO. Currently, many efforts has been devoted to devise and prepare, even manufacture the organic polymers which can resist atomic oxygen to be applied for protecting spacecrafts running in LEO from AO destroying, and at last, improving the lifetime of spacecrafts.

In order to endow traditional polyimide with outstanding anti-AO property, several promising methods including introducing silicon element into polymers by copolymerization, polymer blend or organic-inorganic hybrid technology has been developed up to now. During AO exposure, a new passivation layer can be formed in situ on the topmost surface of polymer membranes to protect the underlying polymer materials from AO erosion. Polyhedral oligomeric silsesquioxane (POSS) frameworks consist of a 3D inorganic cage structure, with the Si/O ratio of 2:3 and typical dimensions of *ca.* 1.5 nm, surrounded by tailorable organic groups. POSS with functional groups often was adopted as silicon-containing components to form organic-inorganic polyimides, which can exhibit excellent space survivability and also possessed good thermal and mechanical properties when exposed to AO environment to some extent.

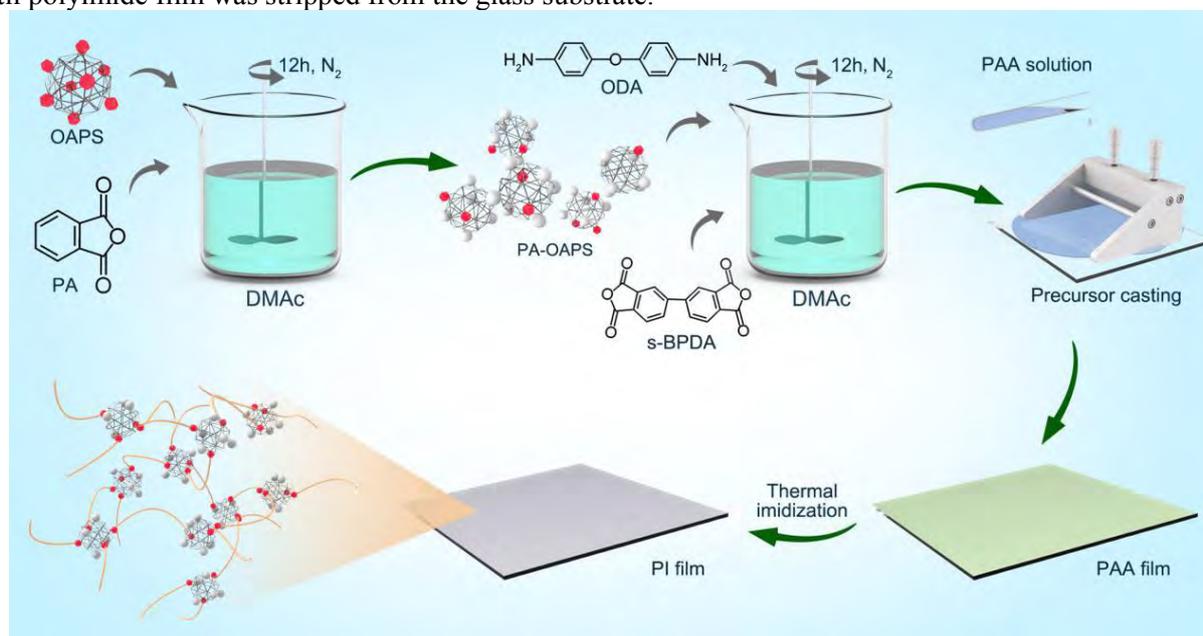
Comparing with POSS including two amine groups, octa (amino phenyl) polyhedral silsesquioxane (OAPS) is easier to produce with relatively low cost and high productivity.²⁸ Incorporated POSS into the main chain of the polyimide backbone by copolymerizing OAPS with polyimide precursors is typical three dimensional polycondensation, so avoiding the gelation is crucial factor to prepare POSS polyimide. Song et al, prepare POSS polyimide with outstanding AO resistant by copolymerizing OAPS with polyimide precursors, and excess dianhydride monomer was used for the polymerization to avoid gelation according to Flory gelation theory.²⁹ In practice, the process of preparation of polyimide based on OAPS is difficult to handle, and excess dianhydride monomer increases final cost. Hence, developing a facile method to produce this kind of polyimide with low cost is desired.

In this paper, our groups introduce an additional constituent, low-cost phthalic anhydride (PA) to the system of OAPS and polyimide precursors and control polycondensation sequence to avoid gelation during the process of preparing POSS polyimide by copolymerizing OAPS with polyimide precursors.

2. POSS POLYIMIDES SYNTHESIS

The synthesis of polyimide with 1.2 wt% OAPS addition is used as an example to illustrate the general synthetic route. Firstly, 0.1111 g PA (0.75 mmol) was added to a solution of 0.1442 g OAPS (0.125 mmol) in 1.5 g DMAc. The mixture was stirred at room temperature in nitrogen for 12 h to form the precursors with residual amino groups (PA-OAPS). The final solid content of PA-OAPS was 15 wt% in DMAc. Secondly,

7.1637 g s-BPDA (24.348 mmol) was added to a solution of 4.8504 g ODA (24.223 mmol) in 68.1 g DMAc. Subsequently, all the PA-OAPS precursors added. The mixture was stirred at room temperature in nitrogen for 12 h to produce the viscous PAA. Whereafter PAA solution was cast onto glass plate, followed by a preheating program (40°C/2h, 60°C/2h, 80°C/2h, 100°C/2h, 120°C/1h) and the imidization procedure under vacuum (200°C/1h, 250°C/1h, and 300°C/1h). At last, the glass plate was immersed into deionized water until polyimide film was stripped from the glass substrate.



Scheme 1. The preparation process of POSS polyimide films.

3. RESULTS AND DISCUSSIONS

3.1. Preparation of POSS polyimides

A series of POSS polyimide films were synthesized. PA was initially reacted with OAPS forming PA-OAPS precursors with residual amino groups. The average number of residual amino groups (f) in every PA-OAPS precursor was $8 - N_B / N_A$ (N_A is the mole number of OAPS; N_B represents the mole number of PA). f can be adjusted by the mole ratio of PA with OAPS. Then the residual amino groups were facilitated to react with ODA and s-BPDA. Mole ratio of amine to anhydride groups was controlled at 1:1. However, PA-OAPS precursors reacted with ODA and s-BPDA to produce PAA is typical $A_2 + A_f + B_2$ reaction. For avoiding gelation, the average number of residual amino groups in every PA-OAPS precursor was

determined as two ($f=2$) according to Flory gelation theory: $P_c = \frac{1}{[1 + \rho(f-2)]^{1/2}}$. Hence, mole ratio of

PA to OAPS was kept at 6: 1 to prepare PA-OAPS precursors. Experimental results show the viscous PAA can successfully obtain according to above-mentioned conclusion, and easy to repeat (See Figure 1 (c) and (d)), and PAA without PA formed gelation (See Figure 1 (a) and (b)). The mass percentages of OAPS in polyimides were ranged from 1.2% to 5.1% by calculation and listed in **Table 1**. Meanwhile, the OAPS contents in polyimides were estimated to be from 1.3 wt% to 5.7 wt% decided by the weight residuals at 800°C in air, which was well in agreement with the calculated OAPS contents.

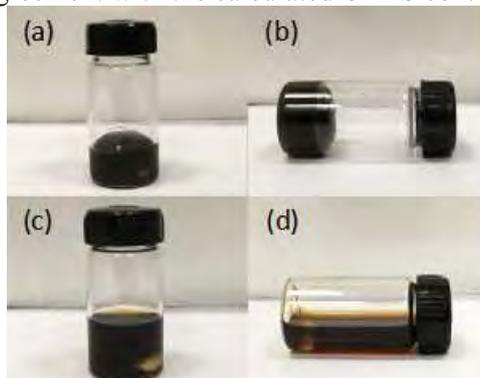


Figure 1. PAA without PA: (a) and (b); PAA after adding PA: (c) and (d) at the solid content of 10 wt% in DMAc (OAPS: 5.1 wt%).

3.2 Thermal properties of POSS PI

To perfectly evaluate the thermal properties of POSS polyimide films, DSC, TGA, DMA measurements were carried out, and the results listed in Table 1. Glass transition temperatures (T_g) of the resulted polyimides were in the range of 273-255°C and 268-244°C, as displayed by DSC and DMA, respectively. $T_{d5\%}$ and $T_{d10\%}$ were in the range of 577-506°C and 595-540°C, respectively.

Table 1 Thermal properties of the resulted polyimide films

Sample codes	OAPS contents (%)		DSC (°C)	TGA (°C)		DMA (°C)	η_{inh} Of PAA (dL/g)
	Calc.	Exp.	T_g	$T_{d5\%}$	$T_{d10\%}$	T_g	
	1	0	0	273	577	595	
2	1.2	1.3	267	522	559	266	0.59
3	2.4	3	266	508	544	256	0.61
4	3.7	4.2	256	507	541	245	0.71
5	5.1	5.7	255	506	540	244	0.77

3.3 Mechanical properties of POSS PI

To investigate the influence of OAPS incorporation on the mechanical properties of the resulted polyimide films, and tensile strength, tensile modulus and elongation at break were measured according to ASTM D882-88. The results were summarized in Table 2. Obvious enhancement in tensile strength and tensile modulus and slight decrease in elongation at break of 1.2 wt% OAPS PI film in comparison with the pure one (142 MPa vs. 124 MPa, 3.3 GPa vs. 2.9 GPa, and 16.0% vs. 11.9%). From 1.2 wt% to 5.1 wt%, tensile strength, elongation at break and the tensile modulus of OAPS PI films present a gradually decreasing trend.

Table 2 Mechanical and morphological properties of the resulted polyimides

Samples	Tensile properties		
	T_S (MPa)	E_B (%)	T_M (GPa)
0 wt% OAPS-PI	124	16.0	2.9
1.2 wt% OAPS-PI	142	11.9	3.3
2.4 wt% OAPS-PI	130	7.6	3.1
3.7 wt% OAPS-PI	127	6.7	3.1
5.1 wt% OAPS-PI	119	5.8	3.2

3.4 Mass loss of POSS polyimide films

The mass losses of POSS polyimide films were listed in Figure 8. The mass loss of POSS polyimide was decreased dramatically with increasing the OAPS loading. The OAPS addition was only 5.1 wt%, the mass loss of POSS polyimide films was 60.2% than that of Kapton. These results revealed that POSS polyimide films prepared by adding PA to the system of OAPS, ODA and s-BPDA were not deteriorated the anti-AO property.

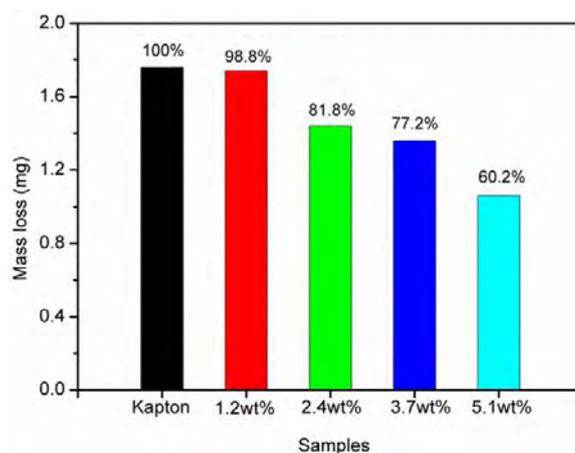


Figure 8. Mass loss of the resulted polyimide films.

4. CONCLUSION

In this work, POSS polyimides were synthesized via introducing an additional constituent, low-cost phthalic anhydride (PA), to the system of OAPS and polyimide precursors and control polycondensation sequence to avoid gelation during the process of preparing POSS polyimide by copolymerizing OAPS with polyimide precursors. They exhibited a combination of desirable properties such as good thermal stability, excellent mechanical strength, and outstanding AO resistance properties.

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