

# synthesis and Properties of Polyimide/Ladder-like Polysilsesquioxane Hybrid Films

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**Abstract:** Novel polyimide (PI) hybrid films containing ladder-like polysilsesquioxane (LPSQ) with phenyl, nitrophenyl and aminophenyl functional group, respectively, have been prepared by casting the mixed solution of polyamic acid (PAA) and LPSQ in N,N-dimethylacetamide (DMAc) and then thermal treating the precursor films in air atmosphere. The surface properties, thermal and mechanical properties of the hybrid films were investigated. The results show that the interfacial interaction between PI and functional groups of LPSQ has great effect on the properties of the hybrid films. The hydrophobicity of the hybrid films decreased as the interfacial interaction became stronger, but still higher than that of the bare PI film due to the surface migration ability of LPSQ. The glass transition temperature and modulus significantly enhanced with increasing the interfacial interaction, while the excellent performance of PI film was preserved.

**Key words:** Polyimide, Ladder-like polysilsesquioxane, Interfacial interaction

## 1. Introduction

High performance polyimides (PIs) have received wide attention due to their outstanding characteristics, such as excellent mechanical properties, good thermal stability, chemically stable against oxidation and low dielectric constants. Furthermore, PI composites have also shown very encouraging properties, for example, the incorporation of silica ( $\text{SiO}_2$ ) particles in PI has been shown to be an effective approach to enhance the mechanical properties and reduce the dielectric constants.<sup>[1]</sup> Also, the compounding of polysiloxane and PI improved the adhesive properties and decreased the water absorption.<sup>[2-3]</sup> A series of PI hybrids based on several types of polyhedral oligomeric silsesquioxane (POSS) have been produced and investigated recently. Comparing with pure PI, the cross-linked composites possess lower coefficient of thermal expansion (CET) and higher glass transition temperature ( $T_g$ ).<sup>[4-5]</sup> These promising properties of PI composites can be widely used in microelectronic and aerospace industries.

In composites, the enhancement of properties depends largely on the shape and distribution of the nanofiller in the polymer matrix and the interphase between them.<sup>[6]</sup> Comparing with  $\text{SiO}_2$ , LPSQs have functional R groups which enable either strong physical or covalent interactions with bulk polymer, and the average functionality is controllable. Moreover, LPSQs possess enhanced mechanical properties and thermal stability, in addition to those properties of usual polysiloxane. Unlike fixed-sized cubic POSS, the length of rigid-rod LPSQ can be adjusted according to the requirement. Therefore, it is hoped that PI can provide all the advanced properties which mentioned above after modification with LPSQs. There has been no reported on this area and these hybrids may be more suitable for industrial applications.

In this paper, a series of polyimide/ladder-like polysilsesquioxane (PI/LPSQ) hybrid films have been prepared by dispersion of LPSQs with different functional groups into PI matrix, respectively. The interfacial interactions between PI matrix and LPSQ were investigated with scanning electron microscopy (SEM). Then the properties of the hybrid films were studied using water contact angle, dynamic mechanical analysis (DMA) and tensile tests. The study described the effect of different functional groups in LPSQs on the interfacial interactions with PI matrix and the properties of the composites.

## 2. Experimental

### 2.1. Materials

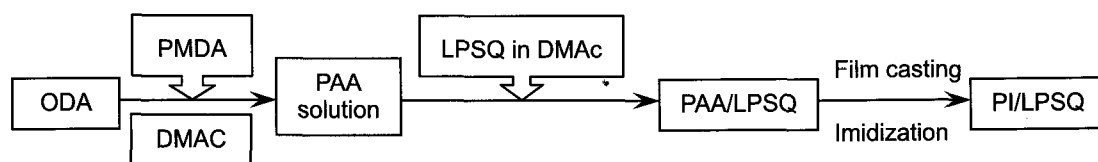
The monomers Pyromellitic dianhydride (PMDA) and 4, 4'-Oxidianiline (4, 4'-ODA) were obtained from Shanghai Research Institute of Synthetic Resins. PMDA was purified by sublimation, and ODA was recrystallized from ethyl acetate prior to use. Dimethylacetamide (DMAc) was purchased from Tianjin Guangfu Chemical Research Institute and used after distillation. Ladder-like polyphenylsilsesquioxane (LPSQ), poly(nitrophenyl)silsesquioxane (LPNPSQ) and poly(aminophenyl)silsesquioxane (LPAPSQ) were self prepared.

### 2.2 Instrumentation

SEM images of the fractured surface of films were obtained on an S-4700 (JEOL Ltd., Japan) operated at 20 kV. The water contact angle values were measured on a Dataphysics OCA20 contact-angle system at ambient temperature. Water droplets were dropped carefully onto the coating films and the contact angle value was obtained by measuring eight different positions of the same sample. Thermal mechanical behaviors of pure PI and PI/LPSQ hybrids were characterized using a Q800 DMA system (TA Instruments, USA) at a heating rate of 5 °C/min and a frequency of 1 Hz. The mechanical properties of films were evaluated by a CMT4104 universal testing machine (Shenzhen SANS Testing Machine Co., Ltd., China) according to GB/T 1040.3-2006 at a drawing rate of 10 mm/min at room temperature.

### 2.3 Preparation of PI/LPSQ hybrid films

The PI/LPSQ hybrid films were prepared by a conventional procedure depicted in scheme 1. Before the formation of composites, the PMDA/ODA (1.01/1, mol/mol) poly(amic acid) (PAA) solution was synthesized by dissolving the diamine in DMAc, followed by adding the dianhydride in portions under stirring at room temperature for over 1 h, after which a light yellow viscous solution was obtained. A series of functional LPSQ solutions (1 g LPSQ/10 ml DMAc) were added into PAA solution, respectively, and stirred for another 2 h. The solid content of PAA and LPSQ in DMAc is 10 wt% and the doping content of LPSQ in PI/LPSQ hybrid films is 10 wt%. After casting the PAA/LPSQ mixed solution on a clean glass plate, the wet film need to be held at ambient atmosphere, most of the solvent was evaporated and damp-dry film was produced. The precursor film was thermally treated to 300 °C over 2 h, heated to 350 °C over 0.5 h, and hold for about 7 h in air atmosphere in order to achieve imidization. The final film was removed from the glass plate by boiled in deionized water and dried in a vacuum oven.



Scheme 1. Preparation flow chart of PI/LPSQ hybrid films

## 3. Results and discussion

A series of PI/LPSQ hybrid films have been prepared in order to combine the excellent properties of the two components. Firstly, the PAA terminated with anhydride groups was obtained by adding a small excess amount (1% mole) of PMDA. Then LPSQ solution in DMAc was blended into PAA solution to get the PAA/LPSQ mixture. The mixed solution was uniform and limpid, because all LPSQs and PAA can be easily dissolved in DMAc. Since all LPSQs were terminated with silanol groups, the hydrogen bonds between the carboxyl groups in PAA chains and the terminal silanol groups in LPSQs can exist in all three PAA/LPSQ mixtures. The nitro groups in LPNPSQ provided extra hydrogen bonds with the amide groups in PAA chains and improved the miscibility of LPSQ with PAA. There are two kinds of interactions between PAA and amino groups in LPAPSQ. One is the hydrogen bond between the carboxyl groups in PAA chains and the amino groups in LPAPSQ which will transform into the amide linkages after thermal treatment. Another is the amide bond between PAA and LPAPSQ, which is formed by the chemical reaction of the amino groups in LPAPSQ with the terminal anhydride groups in PAA, and converted into imide group during the imidization process. In theory, there will be three types of interfacial interactions between PI and LPSQ due to the differences of bonding in PAA/LPSQ solutions. The bonding strength of these interfacial interactions is discussed in following research.

### 3.1 Scanning electron microscopy

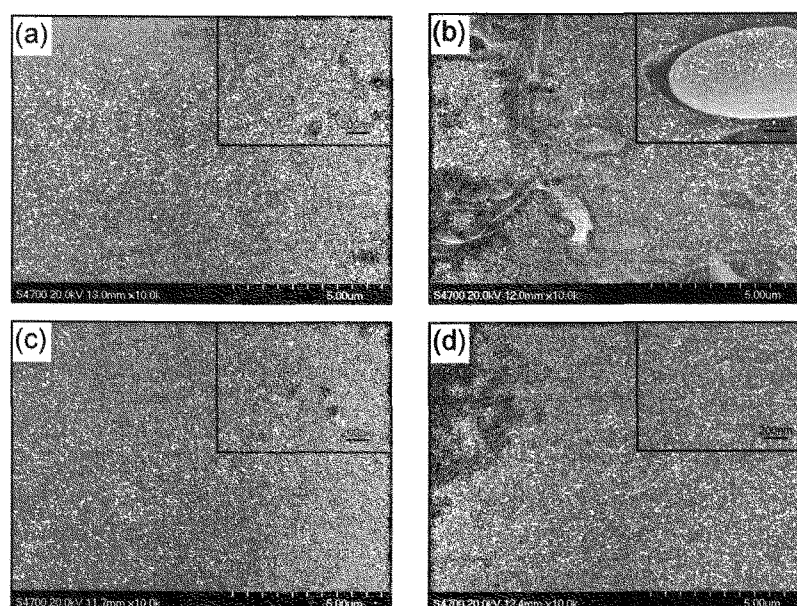


Fig. 1. SEM micrographs of (a) pure PI, (b) PI/LPPSQ, (c) PI/LPNPSQ, and (d) PI/LPAPSQ hybrid films





The morphology of the fracture surfaces of pure PI and its LPSQ-containing hybrid films was probed with SEM. Micrographs of the pure PI, PI/LPPSQ, PI/LPNPSQ and PI/LPAPSQ hybrid films are shown in Figure 1(a-d), respectively. The PI/LPPSQ micrograph (Figure 1(b)) shows obvious phase separation with the micron-sized LPPSQ particles due to poor phase compatibility. The high magnification micrograph of PI/LPNPSQ fracture surface (Figure 1(c)) shows several nanoparticles with the average diameter in the range of 20-40 nm, which implied the existence of the relatively strong interfacial interactions in PI/LPNPSQ. No phase separation was observed in the high magnification morphology image of PI/LPAPSQ as shown in Figure 1(d), which suggested the molecularly dispersion of LPAPSQ in PI. The better dispersion of LPAPSQ than LPNPSQ is attributed to the covalent interactions that are stronger than hydrogen bonds. In short, The SEM study suggested that the nitro and amino functional groups in LPSQs enhanced the

dispersion and interfacial interactions in hybrids.

### 3.2 Water contact angles

The hydrophobicity of hybrid films should increase with the great surface silicon concentration due to the low surface energy of Si-O bonds.<sup>错误! 未找到引用源。</sup> Water contact angles were measured to investigate the wetting state of pure PI and its hybrid films, and the results are given in Table 1. The contact angle increased from 80° to 97° after blending LPPSQ into PI suggested the surface migration of LPPSQ. However, the wetting states of PI/LPNPSQ and PI/LPAPSQ were not appreciably affected after LPSQ blending into PI matrix. This can be explained by the hydrophilicity of nitro and amino functional groups and also confirmed the strong interactions between PI and LPNPSQ/LPAPSQ. It was therefore concluded that poor interactions between PI and LPPSQ were beneficial to improve hydrophobicity of hybrid films, whereas the wetting state of PI/LPNPSQ and PI/LPAPSQ films was retained owing to the strong interactions.

Table 1. Water contact angles and images of pure PI and its hybrid films

Films	PI	PI/LPPSQ	PI/LPNPSQ	PI/LPAPSQ
Images of water contact angle				
Water contact angles (°)	80	97	80	79

### 3.3 Dynamic mechanical properties

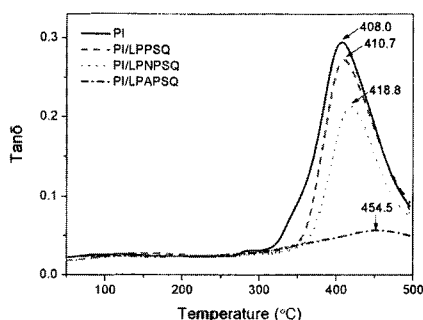


Fig. 2. DMA curves of the pure PI and PI/LPSQ hybrid films

DMA was used to investigate the thermomechanical properties of pure PI and the composite films. The curves of  $\tan\delta$  versus the temperature of pure PI and the composite films are shown in Figure 2. In comparison with pure PI, the tiny changes in  $T_g$  and  $\tan\delta_{\max}$  of PI/LPPSQ can be explained by the weak hydrogen bonds between PI and terminal silanol groups in LPPSQ. By contrast, the physical interactions in PI/LPNPSQ film which limiting the motion of PI chains leads to an enhancement of  $T_g$  and a decline of  $\tan\delta_{\max}$ . Compared to pure PI, the increase in  $T_g$  of PI/LPAPSQ hybrid film is nearly 50 °C implying the improvement of rigidity of copolymer and the movement restriction of molecular chains. In brief, the results of DMA is identical with the SEM observations, which suggest the physical interactions in PI/LPNPSQ are stronger than that in PI/LPPSQ but weaker than chemical cross-links in PI/LPAPSQ and the uniform distribution of LPAPSQ into the PI matrix can heighten the thermomechanical properties efficiently.

### 3.4 Mechanical properties

The mechanical properties such as Young's modulus, tensile strength and elongation at break of the pure

PI and its composites with LPSQs were given in Table 2. Compared with pure PI film, the modulus and tensile strength of PI/LPPSQ both decreased slightly owing to the poor compatibility, and the elongation at break increased by 7% because the phase separation that decreased the forces in inter-chain of PI is beneficial to the locomotion of PI chains. Also, the relatively strong physical interactions PI/LPNPSQ result in higher Young's modulus, better tensile strength and lower elongation at break in comparison with pure PI. Based on above conclusions, PI/LPAPSQ should possess the best mechanical properties among all the films due to the tight chemical cross-links in composite. However, the tensile strength of PI/LPAPSQ is slightly lower than that of PI/LPNPSQ, because this hybrid film was relatively brittle as a result of high cross-linking density and became more sensitive to defects and notches. These problems can be solved by reducing the cross-linking density in hybrid films such as reducing the number of amino groups in LPAPSQ.

Table 2. Atom contents of PI/LPSQ hybrid films

Films	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PI	1940	123	29
PI/LPPSQ	1922	115	36
PI/LPNPSQ	2300	131	26
PI/LPAPSQ	2743	128	13

#### 4. Conclusions

In this paper, PI/LPSQ hybrid films were prepared by blending LPSQ solution with PAA in DMAc. The resulting composites showed different properties owing to the great effect of the functional groups in LPSQs on the interfacial interactions. The hydrogen bonds between PI and LPPSQ were too weak to prevent phase separation so the hydrophilicity increased and the mechanical properties dropped. The relatively strong physical interactions in PI/LPNPSQ hybrid film resulted in the enhancement of compatibility,  $T_g$  and mechanical properties. The  $T_g$  and modulus of PI/LPAPSQ composite increased significantly owing to the tight chemical cross-links and molecularly dispersion, while the material became brittle due to the high cross-linking density. In future research, we will discuss the effect of different content of amino groups in LPAPSQ on the interfacial interactions with PI matrix and the properties of the hybrids.

#### 5. Acknowledgements

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