

SYNTHESIS AND CHARACTERIZATION OF AMINO FUNCTIONALIZED LADDER-LIKE POLYSILSESQUIOXANES AND THEIR HYBRID FILMS WITH POLYIMIDE*

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Abstract Ladder-like polysilsesquioxanes (LPSQs) with different amino contents have been synthesized by controlling of the dosage of Pd/C catalyst. The concentration and activity of amino groups were investigated by Fourier transform infrared spectroscopy. Polyimide (PI)/LPSQ hybrid films have been prepared by incorporating of the obtained LPSQs with different amino contents into PI matrix, respectively. The interfacial interactions between PI matrix and LPSQ were studied with scanning electron microscopy and X-ray photoelectron spectroscopy, meanwhile the thermal and mechanical properties of the hybrid films were studied using dynamic mechanical analysis and tensile tests. The results indicate that the functionality of LPSQ has great effects on the interfacial interactions and the properties of hybrid films. With the increase of amino content, both the interfacial interactions and the cross-linking density of hybrids enhanced, which results in the decline of surface silicon concentration, increase of Young's modulus and drop of elongation at break. Excessive amino content makes the hybrid films brittle and leads to incomplete imidization.

Keywords: Organic-inorganic; Hybrid; Amino functionalized ladder-like polysilsesquioxane; Polyimide.

INTRODUCTION

Organic-inorganic nanocomposite materials have attracted considerable interest since the properties can be controlled through systematic design of the inorganic (rigidity, thermal stability) and organic (flexibility, light weight, dielectric behavior and processibility) segments^[1]. The incorporation process combines the advantages and overcome the disadvantages of the two phases, but these properties can also lead to phase separation in hybrid composites. *In situ* polymerization is a conventional method of achieving organic-inorganic hybrid composites, which forms the uniform dispersion of soluble nanoparticles in the polymer matrix solution in order to improve the dispersion^[2]. A more effective way to enhance compatibility would be to use inorganic nanofillers with organic groups.

Ladder-like polysilsesquioxanes (LPSQs) possess excellent thermal stability, good mechanical properties and radiation resistance because of the unique double-chained ladder-like structure and high bond energy of Si—O linkage^[3–6]. In double-chained skeletons, a tetravalent silicon atom links to three oxygen atoms and one functional group (R), which can be tailored to be reactive organic group^[7–11]. Furthermore, LPSQs are soluble in common organic solvent, so there are big potentials for LPSQs as nanofiller within polymer matrices to obtain novel composite materials^[12, 13].

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Polyimides (PIs) have emerged as advanced polymer with excellent mechanical properties, good thermal stability and dielectric property^[14–17]. Recently, lots of research has focused on the silicon-containing PI. Incorporation of Si-O bonds such as silica^[18, 19], linear polysiloxane^[20–22] and polyhedral oligomeric silsesquioxane^[23, 24] has been a very effective way to enhance erosion resistance of atomic oxygen, improve adhesive properties and reduce water absorption capacity of PI matrix. These hybrid materials can be widely used in aerospace and microelectronic industries.

The effects of functional groups in LPSQs on the interfacial interactions and the properties of the PI hybrids have been studied using phenyl, nitro and amino functionalized LPSQs, respectively^[25]. In addition to the type of functional groups, the degree of functionality of LPSQ can also be tuned. In this article, LPSQs with different amino contents have been synthesized by controlling of the dosage of Pd/C catalyst in order to investigate the effects of functionality on the interfacial interactions and the properties. The concentration and activity of amino groups in obtained LPSQ were studied by Fourier transform infrared spectroscopy (FT-IR). The interfacial interactions between PI matrix and LPSQ were studied with scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), meanwhile the thermal and mechanical properties of the hybrid films were studied using dynamic mechanical analysis (DMA) and tensile tests.

EXPERIMENTAL

Materials

The poly(nitrophenyl)silsesquioxane (LPNPSQ) used in this study was made in our laboratory. 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. 5 wt% Pd/C and phthalic anhydride (PA) were produced by Sinopharm Chemical Reagent Co., Ltd. and used without purification. *N,N*-dimethylacetamide (DMAc) was purchased from Tianjin Guangfu Chemical Research Institute and used after distillation. Tetrahydrofuran (THF) and 80 wt% diamide hydrate, hexane, ethylacetate and methanol were obtained from Beijing Chemical Works and used as purchased. Deionized water was used for all the aqueous solution preparation.

Instrumentation

FT-IR spectra were collected using a Nexus 670 Fourier transform spectrometer (Nicolet, USA). KBr was used as a nonabsorbent medium. A minimum of 32 scans with a resolution of 4 cm⁻¹ was collected for each sample.

The cross-sectional morphology of the films was obtained on an S-4700 electron microscope (JEOL Ltd., Japan) operating at an accelerating voltage of 20 kV. Samples for SEM observations were prepared by embedding the film in epoxy resin followed by snapping it in liquid nitrogen. These fractured surfaces were coated with *ca.* 5 nm platinum prior to measurements.

XPS measurements were carried out on an ESCALAB 250 spectrometer (Thermo Electron Corporation) with a monochromatic Al K α X-ray source. All the spectra were collected at a takeoff angle of 45°. Surface elemental compositions were calculated from the peak area ratios on the XPS spectra.

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 K min⁻¹ and a frequency of 1 Hz. Rectangular strips up to 5 mm wide and 20 mm long were mounted on a DMA tension clamp, and the test was run with a temperature ramp frequency sweep program.

The mechanical properties (Young's modulus, tensile strength and elongation at break) of the films were evaluated at room temperature by a CMT4104 universal testing machine (Shenzhen SANS Testing Machine Co., Ltd., China) according to GB/T 1040.3-2006. Tests were performed at a tensile rate of 10 mm min⁻¹ with the standard distance of 20 mm, and at least five samples were tested for each datum.

Synthesis of LPSQs with Different Amino Contents

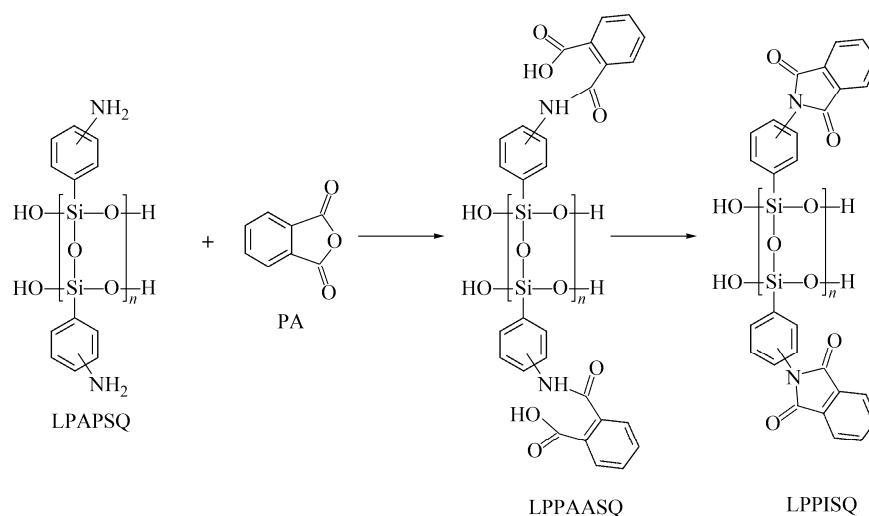
LPAPSQ was synthesized in two steps by nitration of ladder-like polyphenylsilsesquioxane (LPPSQ) in fuming nitric acid to form LPNPSQ, followed by mild reduction. The detailed procedure was described in our early research^[25]. In this paper, the content of amino group in LPSQ was tuned by decreasing the dosage of Pd/C catalyst (Table 1). LPNPSQ was completely altered to LPAPSQ with 368 mg Pd/C catalyst. LPSQ-10 and LPSQ-20 were prepared by reducing the dosage of Pd/C catalyst from 368 mg to 36.8 mg (10%) and 73.6 mg (20%), respectively.

Table 1. The dosage of Pd/C catalyst in reaction procedure

LPSQ	Pd/C (mg)	Functional groups	The degree of reduction
LPNPSQ	–	Nitro groups	–
LPSQ-10	36.8 (10)	Nitro and amino groups	Partially
LPSQ-20	73.6 (20)	Nitro and amino groups	Partially
LPAPSQ	368 (100)	Amino groups	Completely

Synthesis of Poly(phthalimidephenyl)silsesquioxane (LPPISQ)

The LPPISQ was synthesized using a similar procedure of preparation of PI depicted in Scheme 1. LPAPSQ was dissolved in DMAc, followed by adding excessive PA in portions under stirring at room temperature for over 2 h. Then the reaction mixture was precipitated into methanol to obtain the light brown precipitate. This precipitate was collected by filtration, cleaned by deionized water for several times, and then thermally treated at 350°C for 7 h in air atmosphere to yield a light brown powder of LPPISQ.



Scheme 1 Synthesis of LPPISQ

Preparation of PI/LPSQ Hybrid Films

The PI/LPSQ hybrid films were prepared by a conventional procedure^[26]. PMDA/ODA (1.01/1, mol/mol) poly(amic acid) (PAA) solution was synthesized by dissolving ODA in DMAc, followed by adding PMDA in portions under stirring at room temperature for over 1 h to obtain a light yellow viscous solution. A series of amino 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 15 wt%. After casting the PAA/LPSQ mixed solution on a clean glass plate, the wet film needs 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.

RESULTS AND DISCUSSION

Characterization of LPSQs with Different Amino Contents

LPSQs with different contents of amino functional groups were synthesized and their structures were characterized by FT-IR as shown in Fig. 1. A prominent peak located at around 1130 cm^{-1} was assigned to Si—O—Si^[5, 27], which means the polymer skeleton of LPSQ was well preserved during reduction procedure. The two distinct peaks at 1351 and 1531 cm^{-1} (Fig. 1, curves a–c) were assigned to symmetric and asymmetric $\nu(\text{N}=\text{O})$ in nitro group^[12], respectively, and a broad peak around 3351 cm^{-1} characteristic of $\nu(\text{N}-\text{H})$ in amino group^[12] was observed in Fig. 1 (curves b–d). Comparing with the peak intensity of Si—O—Si, the relative intensity of these three peaks can indicate the degree of reduction. The Figure showed that with the increasing amount of catalyst, the characteristic peaks of the nitro group were gradually weakened until it disappeared, while the amino peak became strong. When enough catalyst is given, all nitro groups are reduced to amino in order to produce LPAPSQ. On the contrary, insufficient catalyst will lead to a partial reduction of nitro groups, so amino and nitro groups coexisted in synthetic LPSQ-10 and LPSQ-20. In conclusion, a series of LPSQs with different amino contents can be obtained by controlling the dosage of Pd/C catalyst during the reduction process.

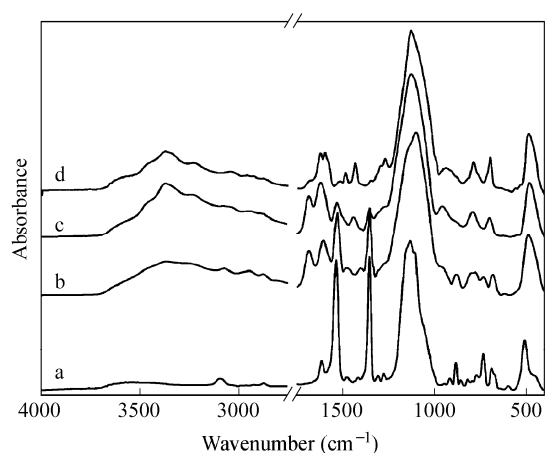


Fig. 1 FT-IR spectra of (a) LPNPSQ, (b) LPSQ-10, (c) LPSQ-20 and (d) LPAPSQ

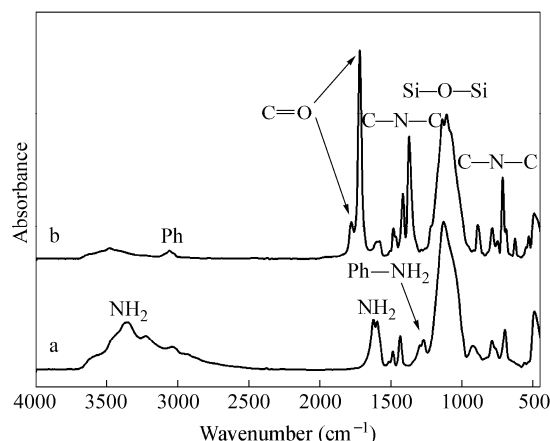


Fig. 2 FT-IR spectra of (a) LPAPSQ and (b) LPPISQ

In order to prove the activity of amino group in LPSQ, thermal imidization reaction of LPAPSQ and PA was attempted on similar conditions of synthesis of PI. FT-IR spectra of LPAPSQ and LPPISQ are shown in Fig. 2. The new peaks of imide group (1780 , 1722 and 1375 cm^{-1}) appeared in FT-IR spectrum of LPPISQ and the characteristic peaks of amino group (3351 , 1623 , 1597 and 1270 cm^{-1}) significantly weaken comparing with those of LPAPSQ^[28]. This suggested that high activity amino group in LPSQ can be easily react with the anhydride. It is also worth to note that there were still some unreacted amino groups in LPPISQ owing to the steric hindrance of PA.

Structure of PI/LPSQ Hybrid Film

After a series of LPSQs with different amino contents (LPSQ-10, LPSQ-20 and LPAPSQ) were synthesized, they were dispersed into PI matrix, respectively, to prepare PI/LPSQ hybrid films in order to investigate the effect of functionality of LPSQ on the interfacial interactions and the properties of the hybrids. Because of the polyfunctional property of LPSQ and its high activity amino groups, LPSQ with amino groups played the role of chemical cross-linking agent in the film. Although the excessive dosage of cross-linking agent will result in brittle hybrid films, a relatively high doping concentration (15 wt%) was chosen in order to highlight the influence of amino content of LPSQ.

The morphology of the fracture surfaces of pure PI and PI/LPSQ-10 hybrid films is shown in Fig. 3. There was no phase separation in the micrograph of PI/LPSQ-10, and the results of PI/LPSQ-20 and PI/LPAPSQ were the same. This excellent dispersion of LPSQ-10 in PI matrix proved the existence of strong interfacial interactions including the physical entanglement networks provided by nitro groups and the chemical cross-linking contributed by amino groups^[25]. There was limited effect of amino group content on microstructure of its hybrid films with PI due to the good compatibility between the two phases.

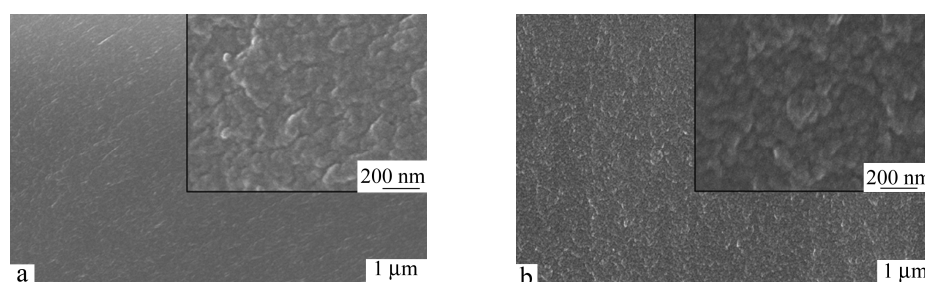


Fig. 3 SEM micrographs of (a) pure PI and (b) PI/LPSQ-10 hybrid films

Table 2. XPS surface composition data for PI/LPSQ with different amino contents

LPSQ	Atom contents (atomic %)			
	C _{1s}	O _{1s}	N _{1s}	Si _{2p}
LPSQ-10	67.7	20.8	3.7	7.8
LPSQ-20	66.4	23.0	5.0	5.7
LPAPSQ	70.4	19.1	4.9	5.6

According to the report, the low surface energy component (Si—O bonds) will tend to migrate to the surface in order to minimize the total free energy of the system, thereby enhancing surface properties^[29]. On the surface of hybrid films, XPS data were collected as shown in Table 2 in order to investigate the enrichment of LPSQ. Normally, the Si/N ratio was used to represent the degree of migration by representing siloxane and polyimide component with Si_{2p} peak and N_{1s} peak, respectively. However, this approach was not entirely suitable for all studies, because LPSQ in this research also contain nitrogen. Thus, the surface silicon concentrations were only used as a rough representation of migration. With the increasing of the amino content in LPSQ, the surface silicon concentration is decreased. This result indicated that LPSQ with more amino groups resulted in high crosslinking density of hybrid, therefore LPSQ was restricted to migrate which led to the decrease of surface silicon concentration. To sum up, the surface properties of PI/LPSQ hybrid films can be controlled by adjusting the amino content of LPSQ.

Properties of PI/LPSQ Hybrid Films

In this paper, DMA was mainly used to investigate the interfacial interaction between the PI matrix and the LPSQ nanofiller. The curves of $\tan\delta$ versus temperature of PI/LPSQ with different amino contents are shown in Fig. 4. The chemical interactions between amino groups in LPSQ and PI are the main reasons to cause these changes in $\tan\delta$ peak. Typically, the reduction in the intensity of $\tan\delta_{\max}$ indicated the decrease of polymer chain mobility^[2, 30]. With the increase of the amino concentration in LPSQ, the $\tan\delta_{\max}$ dropped, which indicated that the movement of PI chains was restricted effectively by cross-linking reaction. According to the literature, rigid inorganic filler with strong interfacial interaction will lead to an increase in the glass transition temperature (T_g)^[30]. However, with the enhancing of crosslinking density, the T_g of hybrids was not increased but decreased which can be explained by the two kinds of chemical interactions between PI and amino group in LPSQ. In addition to reacting with terminal anhydride groups in PAA to form imide groups, the amino groups also can engender hydrogen bond with carboxyl groups in PAA chains and then transform into the amide linkages after thermal treatment. The formation of amide linkages will lead to an incomplete imidization of PI, which causes the decline of T_g .

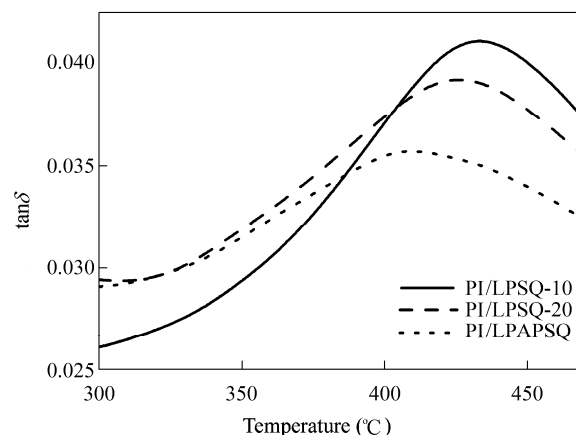


Fig. 4 DMA curves of PI/LPSQ with different amino contents

Table 3. Mechanical properties of PI/LPSQ with different amino contents

Film	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PI	2.0	124	30
PI/LPSQ-10	3.4	109	12
PI/LPSQ-20	3.6	103	10
PI/LPAPSQ	3.6	89	7

Generally, the rigid nanofiller with strong interfacial interaction will enhance the mechanical properties evidently^[31]. The mechanical properties such as Young's modulus, tensile strength and elongation at break of the PI/LPSQ with different amino contents are given in Table 3. Compared to pure PI, the Young's modulus increased while the elongation at break dropped markedly. That is because the addition of rigid LPSQ and the high cross-linking density can restrict the movement of PI and prevent large scale extensions. However, the tensile strength of hybrid films decreased with the increasing of amino content. As mentioned above, a high doping content (15 wt%) was chosen on purpose to highlight the influence of amino content of LPSQ. High concentration of amino group will not only increase incomplete imidization but also heighten the cross-linking density, which result in brittle films sensitive to defects and notches. This problem can be easily solved by reducing the doping content of LPSQ or further controlling cross-linking density in hybrid films. In a word, the mechanical properties of the composites are largely dependent on the content of amino group in LPSQ.

CONCLUSIONS

A series of LPSQs with different amino contents were successfully synthesized by controlling of the dosage of Pd/C catalyst, they were then incorporated in PI matrix, respectively, to prepare PI/LPSQ hybrid films. The functionality of LPSQ has great effects on the interfacial interactions and the properties of hybrid films. The strong chemical interfacial interactions lead to molecularly dispersion of LPSQ in PI. With the increase of amino concentration in LPSQ, the cross-linking density of hybrids was raised and the interfacial interactions were enhanced, thereby the movement of PI and LPSQ was more restricted. As a result, the surface silicon concentration decreased, Young's modulus increased and the elongation at break dropped. However, due to the incomplete imidization, both T_g and tensile strength decreased with the increase of amino content. In brief, by controlling the functionality of LPSQ, the properties of PI/LPSQ composites can be tuned for different application purposes.

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