

# New Polyimide–Silica Organic–Inorganic Hybrids

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**ABSTRACT:** A series of polyimide–silica hybrid films with silica contents up to 30 wt % were successfully prepared by the sol-gel reaction of tetraethoxysilane in the presence of poly(amic acid) containing pendent hydroxyl groups. The films were yellow and transparent when the silica content was less than 11 wt %. The chemical structure of the films was characterized by Fourier transform infrared spectroscopy, and the morphology of the films was investigated by scanning electronic microscopy and atomic force microscopy. Thermogravimetric analysis, differential scan-

ning calorimetry, and stress–strain tests were used to measure the performance of the films. The results indicate that the glass-transition temperatures and decomposition temperatures of the hybrid films increased with increasing silica content, whereas the tensile strength had a maximum with the variety of silica contents. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2210–2214, 2003

**Key words:** polyimides; silicas; composites; films

## INTRODUCTION

Polyimides (PIs) have been widely used in microelectronic industry because of their outstanding thermal and chemical stabilities, high tensile strength and modulus, and good dielectric properties. However, PIs exhibit relatively higher values of water absorption and coefficients of thermal expansion (about  $5 \times 10^{-5} K^{-1}$ ). Their competitors for microelectronics are ceramics (silica). Ceramics show lower coefficients of thermal expansion (about  $5 \times 10^{-7} K^{-1}$ ) and water absorption,<sup>1</sup> which is very important in electronic applications, for example, in multilayer structures of module chips. So, polyimide–silica organic–inorganic hybrids have been developed to combine the extraordinary properties of both materials.

In the past 3 decades, the sol-gel process has been developed as a method to prepare inorganic metal oxides from organic metal alkoxides under mild conditions. The network forming from the sol-gel process involves the simultaneous hydrolysis and condensation of poly (valent) metal alkoxides to produce a gel.<sup>2</sup> Early in the 1990s, this method was used to prepare PI–SiO<sub>2</sub> hybrids. Nandi et al. made PI–SiO<sub>2</sub> hybrids by mixing solutions of pyromellitic dianhydride (PMDA), oxydianiline (ODA), and silicon tetraalkoxides. These materials became opaque at low weight percentage of silica due to phase separation on a mi-

cro-meter scale.<sup>3</sup> Morikawa et al. reported that when the content of silica was more than 8%, particles bigger than 1  $\mu$  were observed, and the film became opaque.<sup>4</sup> Sysel pointed out that there are only physical interactions between the organic and inorganic phases in common PI–SiO<sub>2</sub> hybrids,<sup>5</sup> but PIs usually have bulky backbone structures, which created less intermingling with silica, so the size distribution of the second phase is not homogeneous over the hybrid film.

Recently, we successfully synthesized a novel diamine, 1,3-bis(4-aminophenoxy)-2-propanol (HAPP), and polyamic acids containing pendent hydroxyl groups, as shown in Scheme 1. PI–silica hybrids were prepared by the sol-gel process from tetraethoxysilane (TEOS) and poly(amic acid) (PAA). The presence of hydroxyl groups improves the compatibility between PI and silica due to the formation of hydrogen bonding.<sup>1</sup> As the condensation reaction of silanol proceeds, the pendent hydroxyl groups may partly crosslink with the silica network and form a strong interconnection between the organic and inorganic phases, so the hybrids show no obvious phase separation down to the nanoscale regime when the silica content is less than 16 wt %.

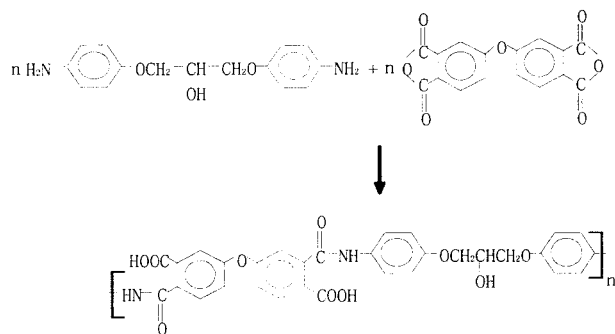
## EXPERIMENTAL

### Materials

Chemical-grade epichlorohydrin, *p*-nitrophenol, and hydrazine monohydrate were used as received without further purification. 3,3',4,4'-Oxydiphthalic dianhydride (ODPA) was dried at 180°C for 6 h before use. ODA and TEOS were obtained from Shanghai Chemical Reagent Co. (Shanghai, China). *N*-Methyl-2-pyr-

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**Scheme 1** Synthesis of PAA with pendent hydroxyl groups.

rolidone (NMP) was obtained from Shanghai Qunli Chemical Co. (Shanghai, China) and was distilled under reduced pressure. Other solvents were purified by common methods.

### Synthesis of 1,3-bis(4-nitrophenoxy)-2-propanol

To a 100-mL three-necked flask equipped with a stirrer and a reflux condenser, 6 g of *p*-nitrophenol and 2 mL of epichlorohydrin were added. After it was stirred for 10 h at reflux temperature, the mixture was filtered. The product was recrystallized in toluene, and a white needle crystal was obtained. The melting transition temperatures were in the range 143.5–114.5°C.

IR: 1503, 1347 ( $-\text{NO}_2$ ), 3517  $\text{cm}^{-1}$  ( $-\text{OH}$ ).  $^1\text{H-NMR}$  ( $\delta$ ): 7.2–8.4 (Ar-H), 4.3 ( $-\text{CH}_2-$ ), 4.4 ( $-\text{CH}-$ ), 4.8 ( $-\text{OH}$ ).  $^{13}\text{C-NMR}$  ( $\delta$ ): 165, 145, 124, 115 (Ar); 72 ( $-\text{CH}_2-$ ); 71 ( $-\text{CH}-$ ).

### Synthesis of HAPP

Dinitro (10 g), ethyl alcohol (110 mL), and palladium on activated carbon (0.11 g) were added to a 100-mL three-necked flask equipped with a stirrer, nitrogen inlet, pressure equalizing addition funnel, and reflux condenser. The mixture was stirred and heated to reflux; then, hydrazine monohydrate (10 mL) was added dropwise via the addition funnel in 2.5 h. The

reaction was maintained for 10 h. After the mixture was filtered to remove the carbon black, a clear solution was obtained and concentrated by rotavapor. A white powder was obtained after recrystallization in the refrigerator. The melting transition temperatures were in the range 113–114°C.

IR: 3386, 3320  $\text{cm}^{-1}$  ( $-\text{NH}_2$ );  $^1\text{H-NMR}$  ( $\delta$ ): 6.5–6.8 (Ar-H), 3.9–4.0 ( $-\text{CH}_2-$ ,  $-\text{CH}-$ ), 4.2 ( $-\text{NH}_2$ ), 4.3 ( $-\text{OH}$ );  $^{13}\text{C-NMR}$  ( $\delta$ ): 149, 140, 117, 115 (Ar); 74 ( $-\text{CH}_2-$ ); 71 ( $-\text{CH}-$ ).

### Preparation of PI-silica hybrids

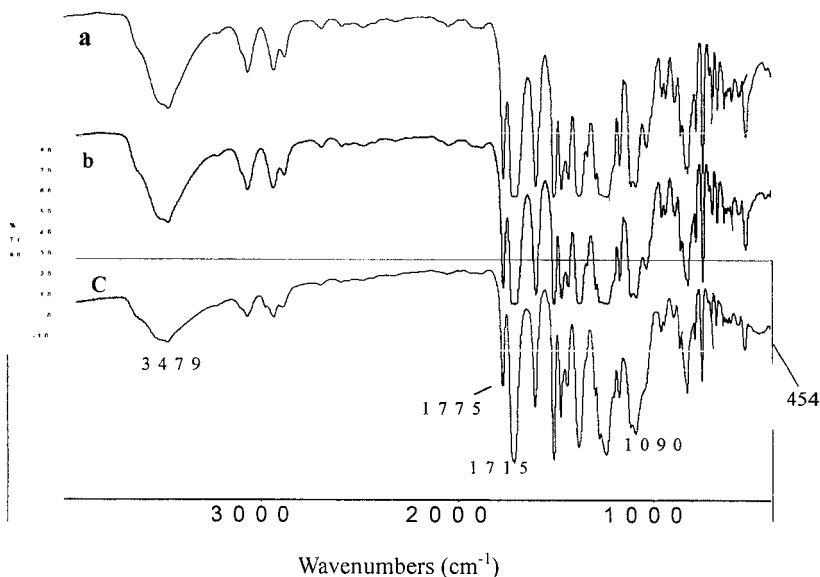
An equimolar amount of ODPA was added to the NMP solution of HAPP (or ODA). The solid content was 10 wt %. The mixture was stirred at 0°C for 10 h to gain a viscous PAA solution. Then, TEOS and water were added. The amount of TEOS was decided by the  $\text{SiO}_2$  content desired in the hybrid. The ratio of water to TEOS was 4. After the addition of TEOS and water, further stirring was needed to recover a homogeneous solution. The transparent solution was spun onto a glass plate and subsequently dried at 100°C for 4 h in the atmosphere. Then, the film was heated for 2 h at 160°C, 2 h at 200°C, and 1 h at 240°C in a nitrogen atmosphere. The formulations for the PI-silica hybrids discussed in this article are shown in Table I.

### Measurements

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of BNPP and HAPP were measured with a Unity INOVA-400 MHz instrument (Varian Corporation, USA). Fourier transform infrared (FTIR) spectra of PI and hybrid films were recorded on a Nicolet 560 FTIR spectrophotometer (USA), and the photomicrographs were taken with an XSJ-1 photomicroscope (Chongqing Optical Instruments Factory, China). The morphology of the cross-section was investigated by scanning electron microscopy (SEM) with a Hitachi X-650 microscope (Japan), operating at 20 KV. Atomic force microscopy (AFM) analysis of the surface of the hybrid film was carried out on a Digital Instruments Nano III atomic force microscope (USA) in air. Thermogravimetric analysis

**TABLE I**  
Silica Contents of PI- $\text{SiO}_2$  Hybrid Materials

Hybrid film	PAA	TEOS (wt %)	$\text{H}_2\text{O}/\text{TEOS}$ (molar ratio)	HCl (wt %)	$\text{SiO}_2$ (wt %)
PI	HAPP-ODPA	0	0	1	0
Hybrid-3	HAPP-ODPA	10	4	1	3
Hybrid-7	HAPP-ODPA	20	4	1	7
Hybrid-11	HAPP-ODPA	30	4	1	11
Hybrid-16	HAPP-ODPA	40	4	1	16
Hybrid-22	HAPP-ODPA	50	6	2	22
Hybrid-30	HAPP-ODPA	60	6	2	30



**Figure 1** FTIR spectra of PI and PI-SiO<sub>2</sub> hybrid films: (a) PI, (b) Hyb-7, and (c) Hyb-30.

(TGA, USA) was performed on a TGA-2950 under air and nitrogen at a heating rate of 10°C/min. The glass-transition temperatures ( $T_g$ 's) of the hybrid films were detected by a TA Instruments DSC2910 machine. The tensile strength of PI-SiO<sub>2</sub> hybrid films was determined on a XLL-50 tester (Instron 4302, UK) at room temperature with a drawing rate of 10 mm/min.

## RESULTS AND DISCUSSION

### FTIR studies of PI and hybrid films

Figure 1 shows the IR spectra of PI with pendent hydroxyl groups [Fig. 1(a)], hybrid-7 [Fig. 1(b)], and hybrid-30 [Fig. 1(c)]. All the three films had the characteristic absorption peaks of imido groups at 1775 cm<sup>-1</sup> (C=O symmetric stretching), 1715 cm<sup>-1</sup> (C=O asymmetric stretching), and 1382 cm<sup>-1</sup> (C-N stretching). Because of the presence of a strong absorption at 1090 cm<sup>-1</sup> from C—O [Fig. 1(a)], the characteristic peak of Si—O stretching vibrations (near 1080 cm<sup>-1</sup>) was not obvious, but we found the band of Si—O bending vibration<sup>5</sup> at 454 cm<sup>-1</sup>, which increased with silica content [Fig. 1(b,c)].

The wide band at 3479 cm<sup>-1</sup> corresponded to the stretching vibration of C—OH. Figure 1(b) is similar to Figure 1(a) because the content of silica was lower in the hybrid-7 film. When we compared the intensity of the band at 3479 cm<sup>-1</sup> in Figure 1(b) with Figure 1(c), we observed that this absorption peak decreased with increasing silica content. It may have been related to the decrease of C—OH concentration because of the condensation between C—OH and silanol.

### Appearance of hybrid films

Different PAAs were synthesized from HAPP-ODPA and ODA-ODPA, and two series of hybrid films were

prepared in the same experimental conditions. The appearances of the films were compared, as shown in Table II. The transparency hybrid-1 was much better than that of hybrid-2 as shown by direct observation. This indicated that the hybrid films with higher silica content and no obvious phase separation could be obtained due to the presence of the pendent hydroxyl groups of PI.

### Photomicroscope analysis

The photomicrographs of PI and the hybrid films are shown in Figure 2. The PI film was highly transparent, as shown in Figure 2(a). When the silica content reached 16% in the hybrid film, the size of inorganic particles increased up to 200–500 nm and resulted in a decrease in the transmittance of the film, as shown in Figure 2(b).

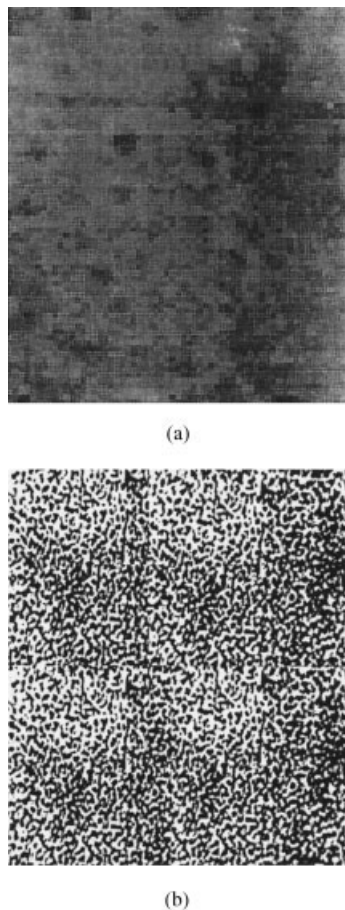
### SEM analysis

The SEM photographs gave us important information on the morphology of the hybrid films. Figure 3 shows the SEM photograph of the cross-section of the hybrid film containing 11 wt % silica. The dispersed silica particles could be seen as white beads with a diameter less than the wavelength of visible light (400–700 nm), which made the hybrid film transparent.

**TABLE II**  
Transparency of the Hybrid Films

Hybrid film	PI type	Silica content (wt %)						
		0	3	7	11	16	22	30
1	HAPP-ODPA	T	T	T	T	Tr	Tr	O
2	ODA-ODPA	T	T	T	O	O	O	O

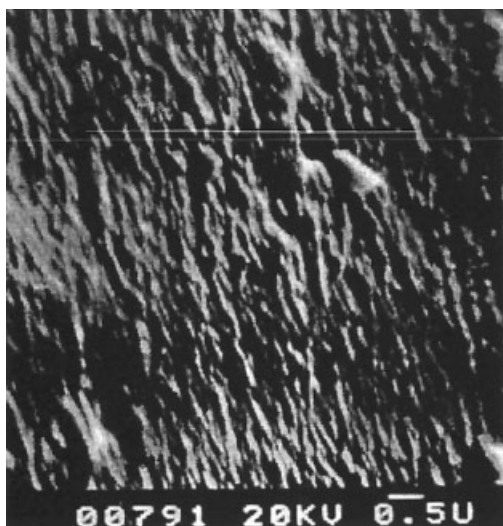
T = transparent; Tr = translucent; O = opaque.



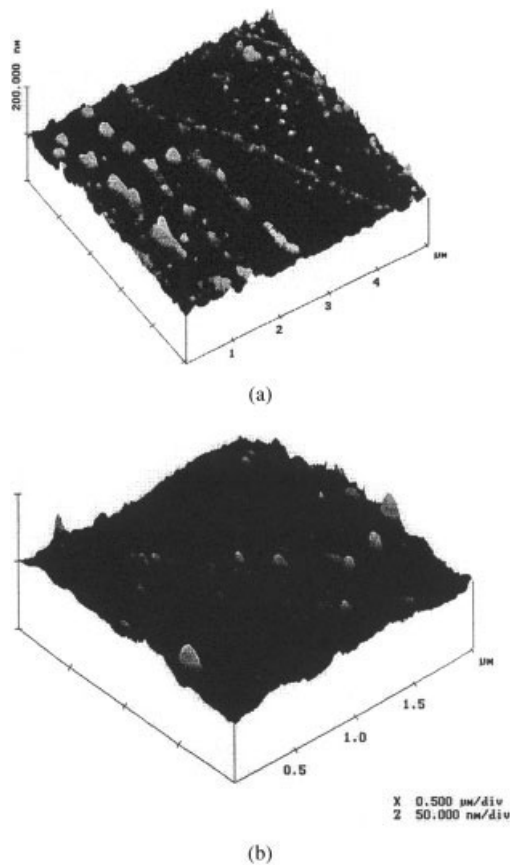
**Figure 2** Photomicrographs (enlarged 1000 times) of PI and the hybrid films: (a) PI (HAPP-ODPA) and (b) PI-SiO<sub>2</sub> (16 wt %).

**AFM analysis**

The micromorphology of the hybrid materials was detected by AFM. The AFM images of the hybrid films



**Figure 3** SEM photograph of the PI-SiO<sub>2</sub> hybrid-11 film.

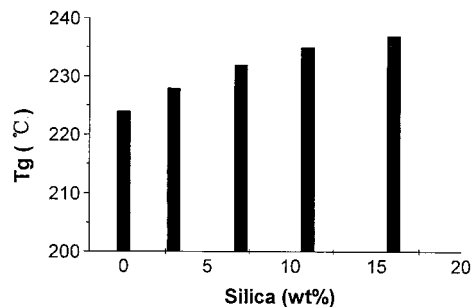


**Figure 4** AFM photographs of PI-SiO<sub>2</sub> hybrid films containing 3 wt % silica: (a) ODA-ODPA and (b) HAPP-ODPA.

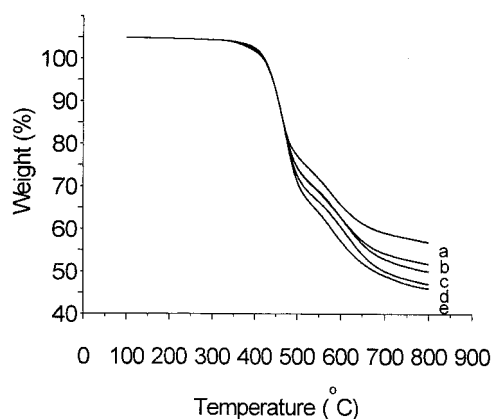
containing 3 wt % silica are shown in Figure 4. The size of the silica particles of HAPP-ODPA hybrid was 20–100 nm, which was much smaller than that of the ODA-ODPA hybrid (100–300 nm).

**T<sub>g</sub> analysis**

The T<sub>g</sub>'s of the hybrid films detected by differential scanning calorimetry (DSC) are shown in Figure 5. The addition of silica resulted in an increase in the hybrid film's T<sub>g</sub>. In these systems, the silica particles



**Figure 5** Effects of silica composition on the T<sub>g</sub> of the hybrids (HAPP-ODPA).



**Figure 6** TGA curves of PI-silica hybrid films (HAPP-ODPA). Silica content: (a) 16, (b) 11, (c) 7, (d) 3, and (e) 0%.

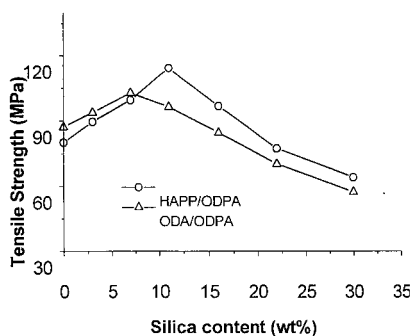
acted as physical crosslink points, which limited the movement of the molecular chain of PI.

### TGA analysis

Figure 6 shows the thermogravimetric curves of the hybrid films with different silica contents. The thermal stability of the PI-silica hybrids increased with increasing silica content. Because the silica network was very stable up to 800°C, the weight loss of the hybrids arose mainly from the decomposition of PI.

### Mechanical properties of the hybrid films

The influence of silica content on the tensile strength is shown in Figure 7. The tensile strength increased with the addition of more silica up to 7 wt % in both systems. Then, a fast reduction of tensile strength was



**Figure 7** Tensile strength of two kinds of hybrid films

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**TABLE III**  
Ultimate Elongation and Modulus of the Hybrid Films (HAPP-ODPA)

	Silica content (%)						
	0	3	7	11	16	22	30
Ultimate elongation (%)	7.4	9.7	12.3	8.5	7.1	5.8	4.0
Modulus (GPa)	1.6	1.8	2.1	2.4	2.5	2.8	3.0

found for hybrid-2 (ODA-ODPA), which was related to the phase separation. It was remarkable to observe a continuous rising of the tensile strength for hybrid-1 (HAPP-ODPA) when 11 wt % silica was added; the tensile strength of the hybrid reached 114 MPa (an increase of about 43%). Up to the introduction of 16% silica, hybrid-1 still maintained a high strength (97 MPa). This effect may have resulted from the strong physical interactions between organic and inorganic phases (e.g., the formation of hydrogen bonding improved the compatibility of PI and SiO<sub>2</sub><sup>1</sup>) and the crosslinking of C—OH and silanol.

The ultimate elongation and modulus of the hybrid films (HAPP-ODPA) are listed in Table III. The elongation reached a maximum at lower silica contents, but the modulus increased rapidly with the addition of silica.

### CONCLUSIONS

PAA with pendent hydroxyl groups were synthesized, and the correspondent PI-silica hybrid materials were prepared via a sol-gel process. Transparent hybrid films with higher silica contents were obtained, for the presence of hydroxyl groups improved the comparability of the two components due to the formation of hydrogen bonds and chemical bonds between the organic and inorganic phases. The tensile strength of PI-SiO<sub>2</sub> (HAPP-ODPA) hybrid films increased with the addition of silica and reached a maximum value when the silica content was up to 11 wt %.

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