Polyimide–Silica Hybrid Films Made from Polyamic Acids Containing Phenolic Hydroxyl Groups

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ABSTRACT: A diamine and polyamic acid containing phenolic hydroxyl group was synthesized. A series of polyimide/silica hybrid films with strong interacton between organic and inorgamic components was prepared via sol–gel reaction. The morphology of the hybrid films was investigated by scanning electron microscopy and atomic force microscopy. The thermal stability and mechanical properties of the films were detected. The results indicated that the introduction of phenolic hydroxyl groups remarkably attributed to the improvement of tensile strength. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1198–1202, 2004

Key words: hybrid films; polyimide; silica; morphology; mechanical properties

INTRODUCTION

Polyimides (PI) are promising materials used for a wide range of applications because of their high glass transition temperature, good heat resistance, low dielectric constant, and excellent mechanical properties. Since the 1990s, polyimide–silica hybrids have been developed to combine the excellent properties of both organic and inorganic materials.[1,2]

Much research observed that when the content of inorganic component was more than 8%, silica particles with diameters ranging from 1 to 10 μm were detected, which made the films opaque and weakened the mechanic properties of the hybrids.[3,4] Sysel pointed out that there are only physical interactions between the organic and inorganic phases in common PI–SiO_2 hybrids,[5] so the size distribution of the second phase was not homogeneous over the hybrid film.

In the work carried out previously, we found that the introduction of pendent hydroxyl groups on the backbond of polyimide had positive affection on the interaction between organic and inorganic components.[6] In this article, 4,4′-diamino-4″-hydroxyltriphenylmethane (DHTM) and its polyamic acids containing phenolic hydroxyl groups were synthesized. New polyimide–silica hybrid films were prepared by sol–gel process from tetraethoxysilane (TEOS) and polyamic acid (PAA). The films were still transparent when the silica content was up to 16 wt %. The morphology of the hybrid films was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The thermal stability and mechanic properties of the films were detected. It was found that the introduction of phenolic hydroxyl groups increases the compatibility between organic and inorganic components and improves the tensile strength of the hybrid films.

EXPERIMENTAL

Materials

4-Hydroxybenzaldehyde (Shanghai Shuang xi Aroma Auxiliary Plant, Shanghai, China) and 36% HCl were used as received without further purification. Aniline (Chengdu Kelong Chemical Reagent Co., Chengdu, China) was distilled with reflux condenser. 3,3′,4,4′-Oxydiphthalic dianhydride (ODPA) (Shanghai Research Institute of Synthetic Resin, Shanghai, China) was dried at 180°C for 6 h before using. Oxydianiline (ODA) and TEOS were obtained from Shanghai Chemical Reagent Co. (Shanghai, China). *N*-Methyl-2-pyrrolidone (NMP), obtained from Shanghai Qunli Chemical Co. (Shanghai, China), was distilled under reduced pressure. Other solvents were purified by common methods.

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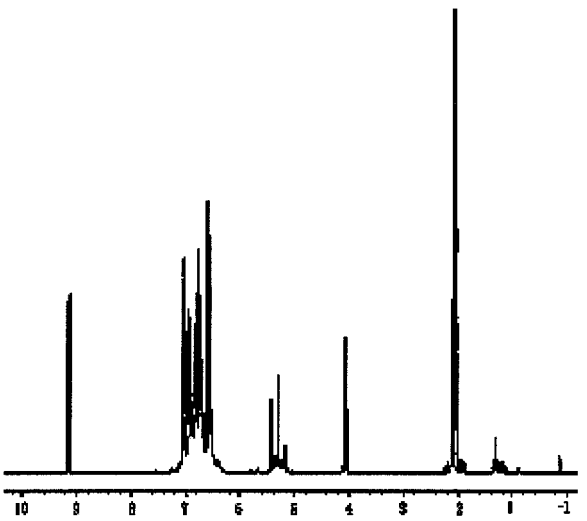


Figure 1 ^{1}H-NMR spectrum of DHTM.

Synthesis of 4,4′-diamino-4″-hydroxyltriphenylmethane

To a 250-ml three-necked flask equipped with reflux condenser and nitrogen inlet, 12.1 g (0.1 mol) 4-hydroxybenzaldehyde, 40 mol fresh distilled aniline, and 0.0108 g aniline hydrochloride were added. The reaction mixture was purged with nitrogen, then maintained under a nitrogen atmosphere with stirring, and introduced to an oil bath at 125°C. The temperature was increased to 150°C and heating was continued for 4 h. After the reaction mixture was cooled, the excess aniline was removed under reduced pressure at 110°C. Nine percent HCl was added to the mixture until the homogenous solution formed; then the solution was adjusted with triethylamine up to pH 9. To remove all remaining aniline, the solid phase was washed with diethyl ether and then washed with water by the same method. The resulting DHTM was dissolved throughly in ethanol and then precipitiated in water; a fuchsia-colored crystal was obtained. The melting temperature of DHTM was 203–204°C.

IR of DHTM: 3380 (—OH, —NH_2), 2913 (CH), 1617, 1510 (—C_6H_4—), 1248 (Ar—OH). ^{1}H-NMR of DHTM (δ): 6.5–7.1 (Ar–H), 5.2–5.4 (—CH—), 4.0–4.1 (—NH_2), 9.2 (—OH) (Figs. 1 and 2).

Preparation of polyimide–silica hybrids

An equimolar amount of ODPA was added to the NMP solution of DHTM (or ODA), which was cooled with an ice-water base. The solid content of the solution was 10 wt %. The mixture was stirred at 0°C for 10 h to get a viscous polyamic acid solution as shown in Scheme 1. TEOS and water were added and further stirring for 6 h was needed to recover a homogeneous solution. The amount of TEOS was decided by the SiO_2 content desired in the hybrid. The ratio of water to TEOS was 4. The transparent solution was spun onto a glass plate and subsequently dried at 80°C for 12 h in atmosphere. Then the film was heated in a nitrogen atmosphere for 2 h at 160°C, 2 h at 200°C, 2 h at 260°C, and 0.5 h at 300°C.

Measurements

Fourier transform infrared spectra (FTIR) of PI and hybrid films were recorded on a Nicolet 560 FTIR spectrophotometer. The morphology of the cross section was investigated by (SEM) by using a Hitachi X-650 operating at 20 kV. AFM analysis to the surface of the hybrid films was carried out on a Digital Instruments Nano II atomic force microscope in air. The tensile strength of PI–SiO_2 hybrid films was determined on a XLL-50 tester at room temperature with a drawing rate of 20 mm/min.

RESULTS AND DISCUSSION

FTIR analysis of polyimide containing phenolic hydroxyl group

FTIR spectrum (Fig. 3) of PI film was detected to investigate the stability of phenolic hydroxyl groups in the process of condensation and imidization. The characteristic absorption peaks of imido groups at 1778 cm^{-1} (C═O symmetric stretching), 1727 cm^{-1} (C═O asymmetric stretching), and 1379 cm^{-1} (C—N stretching) are evident, revealing a perfect imidization. The wide band at 3484 cm^{-1} is correspondent to the stretching vibration of C—OH, which means that the phenolic hydroxyl groups was stable in this process.

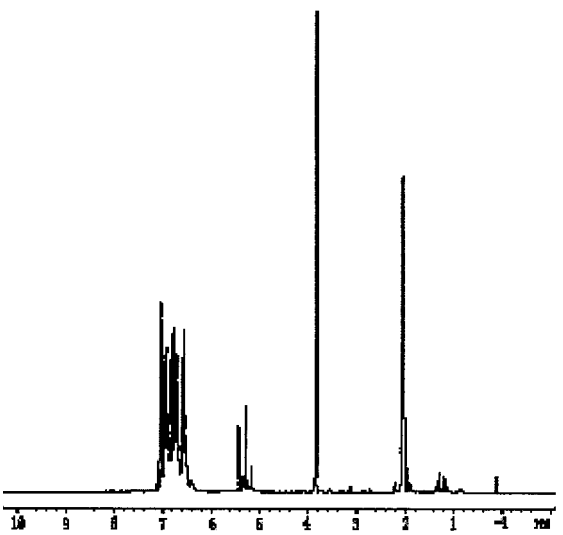
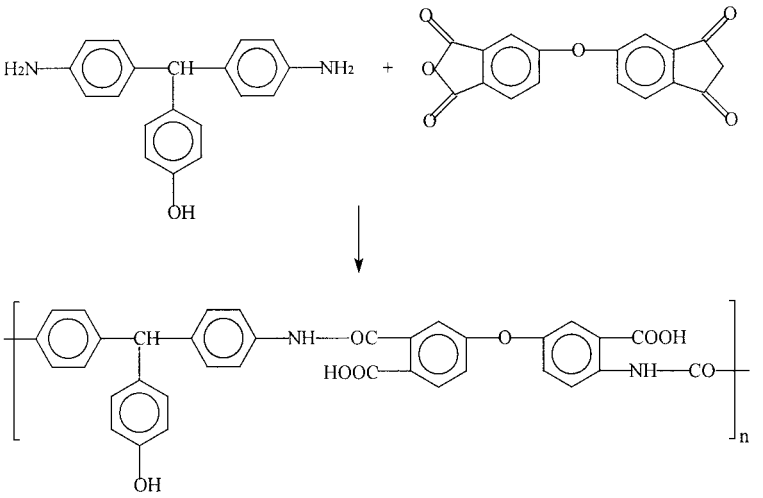


Figure 2 ^{1}H-NMR spectrum of DHTM (+D_2O).



Scheme 1 Synthesis of polyamic acid with phenolic hydroxyl group.

Appearance of hybrid films

Two series of polyimide-silica hybrid films were prepared from DHTM–ODPA and ODA–ODPA with the same experimental conditions. The appearances of the films were compared (Table I). Hybrid film 2 containing 11 wt % silica becomes opaque, whereas the film containing 22 wt % silica is almost transparent when DHTM is used to replace ODA. This indicates that PI–SiO_2 hybrids with higher silica contents showing no obvious phase separation can be obtained because of the presence of phenolic hydroxyl groups.

SEM analysis

SEM was used to analyze the morphology of the hybrids. Figure 2 shows the SEM photograph of the fracture surface of the hybrid films containing 7–16 wt % silica. The silica particles in the hybrid containing 16 wt % silica have a size distribution ranging from 300 to 500 nm [Fig. 4(a)], which makes the hybrid film translucent. When the content of inorganic component is below 11 wt % [Fig. 4(b,c)], the diameter of silica is about 100–300 nm, which is less than the wavelength of visible light (400–700 nm); so, the hybrid films are clear and transparent.

AFM analysis

To investigate the microstructures of the hybrid materials from three dimensions, the AFM analysis was made out. The AFM image of hybrid film containing 11 wt % silica [Fig. 5(a)] reveals that regular silica particles with a diameter of 100–300 nm disperse in polyimide matrix. In Figure 5(b), the size of phase

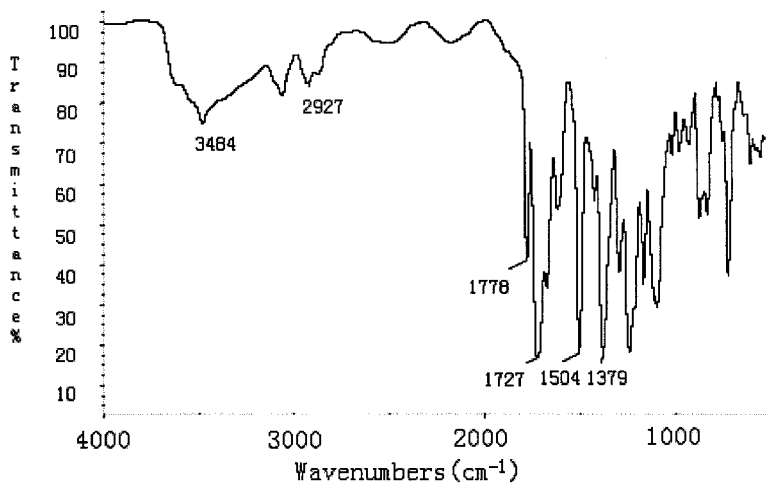


Figure 3 FTIR spectrum of PI.

TABLE I
The Transparency of Hybrid Films[a]

Hybrid films	PI composition	Silica content (wt %)						
		0	3	7	11	16	22	30
1	DHTM-ODPA	T	T	T	T	Ta	Ta	O
2	ODA-ODPA	T	T	T	Ta	O	O	O

[a] T, transparent; Ta, almost transparent; O, opaque.

separation of the hybrid containing 7 wt % silica is down to nanoscale.

TGA analysis

As shown in the thermogravimetric curves (Fig. 6), this polyimide–silica hybrid film has excellent thermal stability. The onset temperature is more than 550°C and the thermal stability of the hybrids is improved with increasing silica contents.

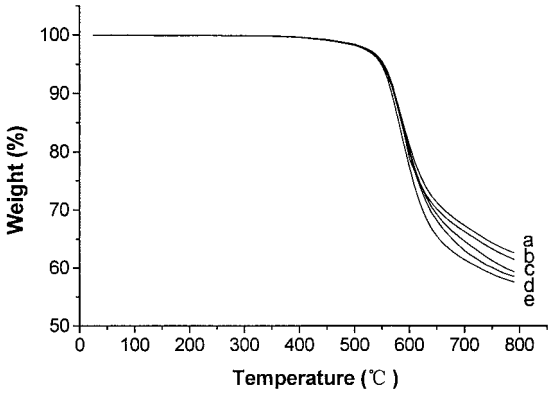


Figure 6 TGA curves of polyimide–silica hybrid films. Silica contents: a, 16%; b, 11%; c, 7%; d, 3%; e, 0%.

Glass transition temperature (T_g)

The T_g's of the hybrid films detected by differential scanning calorimetry (DSC) are shown in Fig. 7. The addition of silica results T_g of the hybrid films increased. In these systems, the silica particles act as some physical crosslinking points, which limited the movement of the molecular chain of PI.

Mechanical properties of hybrid films

The introduction of phenolic hydroxyl groups into polyimide has a significant effect on the mechanical

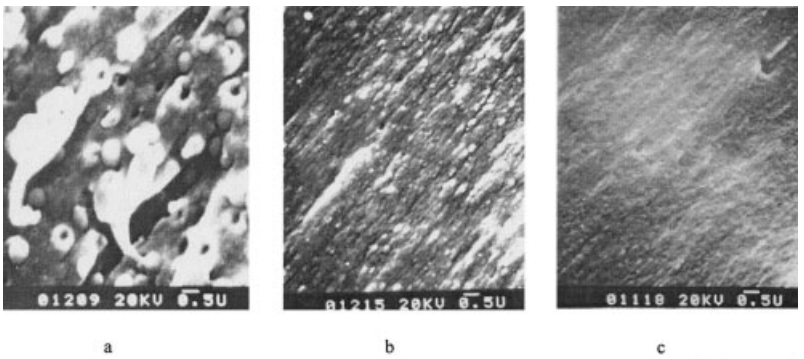


Figure 4 SEM photograph of (DHTM–ODPA) PI–SiO_2 hybrid films. Silica (wt %): a, 16; b, 11; c, 7.

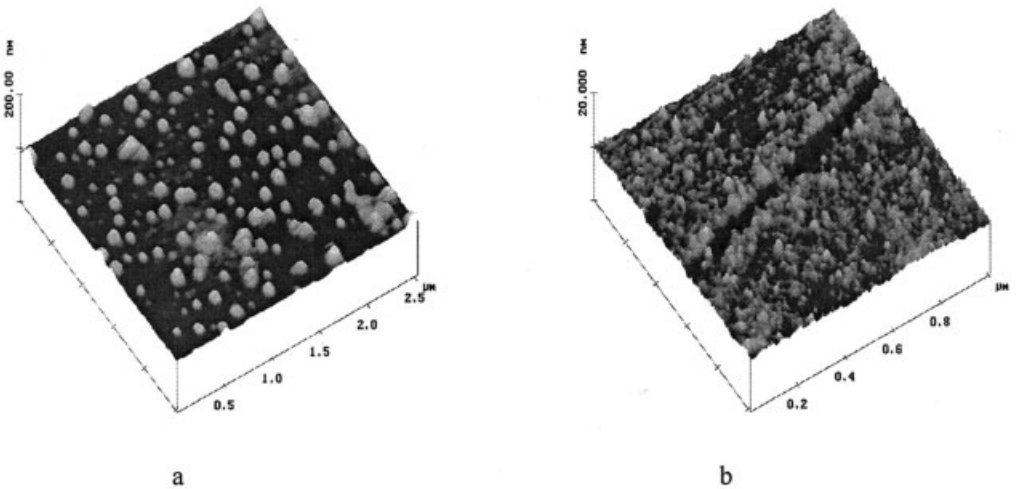


Figure 5 AFM photograph of PI/SiO_2 hybrid films. (a) 11 wt % silica; (b) 7 wt % silica.

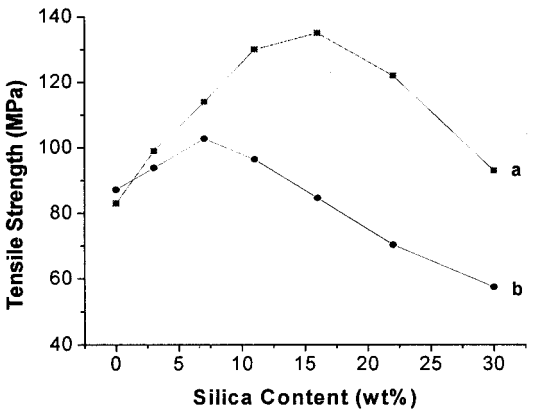


Figure 8 Tensile strength of two kinds of hybrid films. a, DHTM : ODA : ODPA = 0.3 : 0.7 : 1; b, ODA : ODPA = 1 : 1.

properties of polyimide–silica hybrid materials. As shown in Figure 8, the influence of silica contents upon the tensile strength in two systems are different. For common hybrid films prepared from ODA–ODPA, the tensile strength has a maximum value (103 MPa) when the silica content is 7 wt % [Fig. 8(b)]. After 30 mol % DHTM are used to replace ODA [Fig. 8(a)], a continuous rising of the tensile strength is observed until 16 wt % of silica is added. The maximum strength reachs 138 MPa, increased by about 66%. This effect may result from the stronger physical interactions between organic and inorganic phases; in other words, the formation of hydrogen bonding improved the compatibility of PI and SiO_2[1] and the crosslinking of C—OH and silanol, as we have pointed out previously.[6]

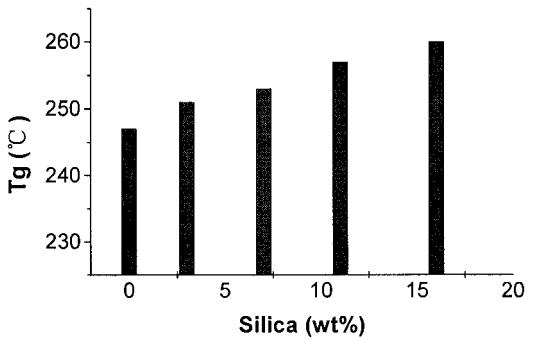


Figure 7 Effects of silica composition on the T_g of the hybrids from DHTM.

CONCLUSION

A novel PI–SiO_2 hybrid material was successfully prepared at the presence of PAA with phenolic hydroxyl groups and TEOS in NMP solution. The hybrid film containing 16 wt % silica is almost transparent and has good thermal stability and improved tensile strength because the introduction of phenolic hydroxyl group increased the compatibility between organic and inorganic components.

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