Polyimide-Silica Hybrid films made from poly(amic acids) containing pendent phenolic hydroxyl group*

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ABSTRACT: A diamine containing phenolic hydroxyl group and its polyamic acids were synthesized. A series of polyimide/silica hybrid films with strong interacton between organic and inorgamic components have been prepared via sol-gel reaction. The morphology of the hybrid films was investigated by scanning electron microscopy and atom force microscopy. The thermal stability and mechanic properties of the films were detected. The results indicated that the introduction of hydroxyl groups remarkably attributed to the improvements of tensile strength.

Keywords: hybrid films; polyimide; silica; morphology; mechanic properties

Introduction

Polyimides (PI) are promising materials for a wide range of application because of their high glass transition temperature, low dielectric constant, excellent mechanical properties and thermal stability. Ceramics (silica) are their competitors for microelectronics. Since 1990, polyimide-silica hybrids have been developed to combine the excellent properties of both organic and inorganic materials.[1,2]

Many research observed that when the content of inorganic component was more than 8%, silica particles with diameters ranging from 1 to 10 micron were detected, which made the films opaque and weakening 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 active group on the side chain of polyimide had positive affection on the interaction between organic and inorganic components.[7] In this paper, 4,4'-diamino-4"-hydroxyltriphenylmethane (DHTM), and polyamic acids containing phenolic hydroxyl groups(PAA-OH) were synthesized. Polyimide-silica hybrid films were prepared by sol-gel process from tetraethoxysilane (TEOS) and PAA-OH. The films were almost transparent when the silica content was up to 16 wt %. The morphology of the hybrid films was investigated by scanning electron microscopy and atom force microscopy. The thermal stability and mechanic properties of the films were detected. It was found that the introduction of phenolic hydroxyl group increases the comparability between organic and inorganic components and improves the tensile strength of the hybrid films.

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Experimental

Materials

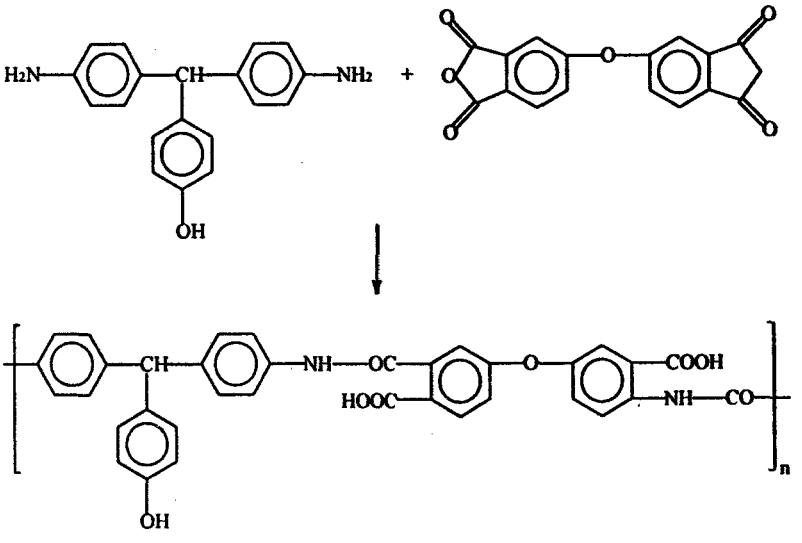
4,4'-diamino-4"-hydroxyltriphenylmethane (DHTM) was synthesized by the method described in literature.[6] 3,3`,4,4`—oxydiphthalic dianhydride(ODPA) was dried at 180℃ for 6 hr before using. Oxydianiline (ODA), tetraethoxysilane (TEOS) were obtained from Shanghai Chemical Reagent Co. N-Methyl-2-pyrrolidone (NMP) was distilled under reduced pressure. Other solvents were purified by common methods.

Preparation of polyimide-silica hybrids

An equimolar amount of ODPA was added to the NMP solution of DHTM (or ODA) in a three neck flack which was cooled with an ice-water base. The solid content was 10 wt %. The mixture was stirred at 0℃ for 10 h to gain a viscous polyamic acid solution as shown in scheme 1. TEOS and water were added and further stirred for 6 h was needed to recover homogeneous solution. The amount of TEOS was calculated 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℃ for 12 h in atmosphere. Then the film was heated in a nitrogen atmosphere for 2 h at 160℃, 2 h at 200℃, 2 h at 260℃, and 0.5 h at 300℃.

Measurements

Fourier transform infrared spectra (FTIR) of PI and hybrid films were recorded on a Nicolet 560 FTIR spectra photometer. The morphology of the cross section was investigated by scanning electron microscopy (SEM) using a Hitachi X-650 operating at 20 KV. Atomic force microscopy (AFM) analysis of the surface of the hybrid film was carried out on a Digital Instruments Nano II atom force microscope in air. The tensile strength of PI-SiO2 hybrid films was determined on a XLL-50 tester at room temperature with a drawing rate of 20 mm/min.



Scheme 1. Synthesis of polyamic acid with pendent phenolic hydroxyl group

Results and Discussion

FTIR analysis of polyimide containing phenolic hydroxyl group

FTIR spectrum (Figure 1) of PI film has been detected to investigate the stability of phenolic hydroxyl groups in the process of polycondensation 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 evidence in Figure 1, revealed the finish of imidization. The wide band at 3484 cm^{-1} is corresponding to the stretching vibration of C—OH, which informed that the phenolic hydroxyl groups was stable in this process.

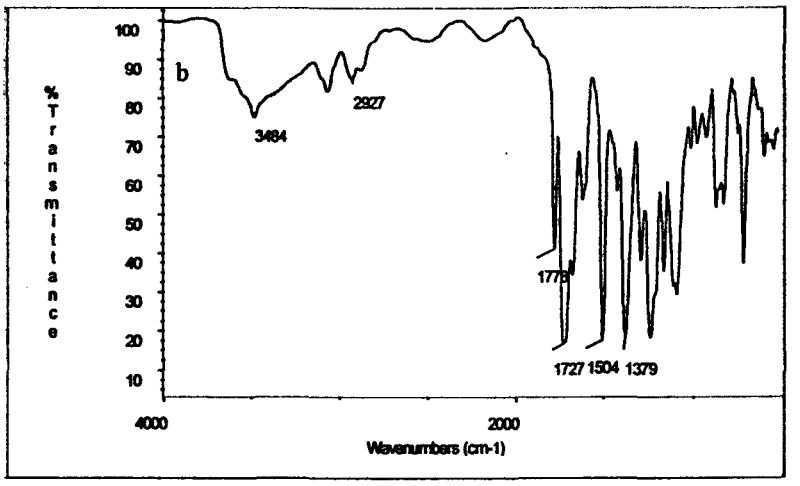


Fig. 1 FTIR spectrum of PI

Appearance of hybrid films

Two series of polyimide-silica hybrid films were prepared from DHTM-ODPA and ODA-ODPA under the same experimental condition. The appearances of the films were compared (Table 1). The hybrid film 2 containing 11 wt % silica becomes opaque. Whereas the films were almost transparent when DHTM was used to replace ODA. This indicates that hybrids with higher silica content, showing no obvious phase separation, can be obtained due to the presence of pendent phenolic hydroxyl group.

Table 1 The Transparency of Hybrid Films *

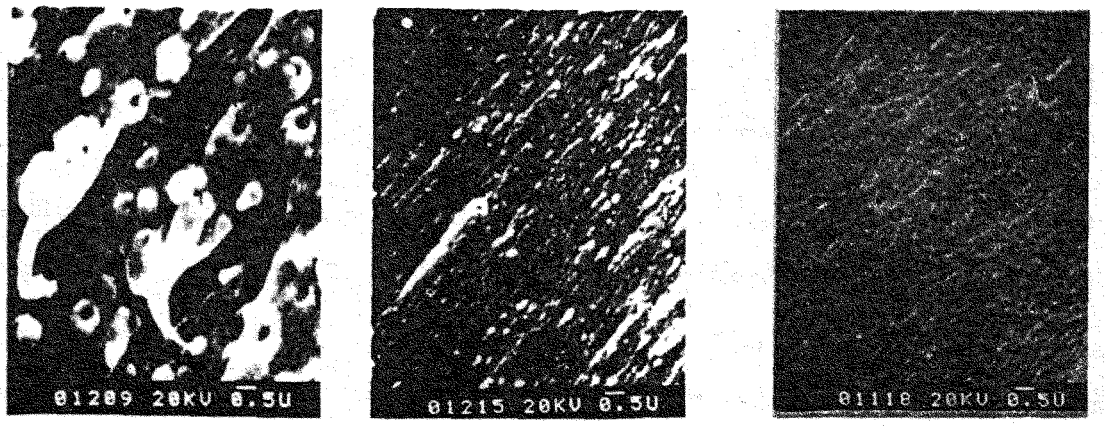
Hybrid films	PI	Silica Content (wt %)						
		0	3	7	11	16	22	30
1	DHTM-ODPA	T	T	T	T	Ta	O	O
2	ODA-ODPA	T	T	T	O	O	O	O

* T - transparent; Ta - almost transparent; O – opaque

SEM analysis

Scanning electron microscopy was used to analysis the morphology structure of the hybrids film. 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 300-500 nm

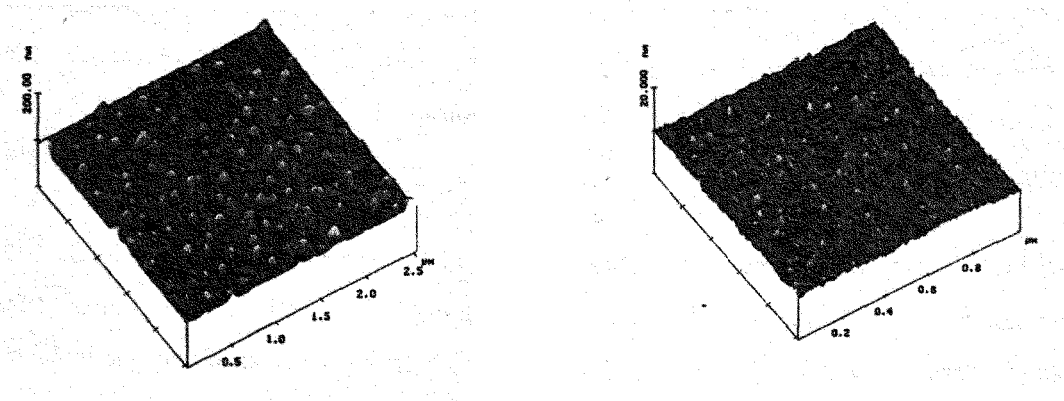
(Figure 2a), which make the hybrid film translucent. When the content of inorganic component SiO_2 is below 11 wt % (Figure 2b and 2c), the diameter of silica is about 100-300 nm, which is less than the wavelength of visible light (400-700 nm), so the hybrid films are clear and transparent.



a b c

Fig. 2 SEM Photograph of （DHTM-ODPA） PI/ SiO_2 hybrid films

Silica (wt %) : a – 16 b – 11 c – 7



a b

Figure 3 AFM Photograph of PI/ SiO2 hybrid films

a—11 wt % silica b—7 wt % silica

To investigate the microstructure of the hybrid materials from three dimensions, the atomic force microscopy (AFM) analysis has been made out. The AFM image of hybrid film containing 11 wt % silica (Figure 3a) reveals that regular silica particles with a diameter of 100-300 nm disperse in polyimide matrix. In Figure 3b, the size of phase separation of the hybrid containing 7 wt % silica is down to nano-scale.

TGA analysis

As showing in the thermogravimetric curves (Figure 4), this polyimide/silica hybrid films have excellent thermal stability. The onset temperature is more than 550℃ and the thermal stability of the hybrids improve with the increasing of silica content.

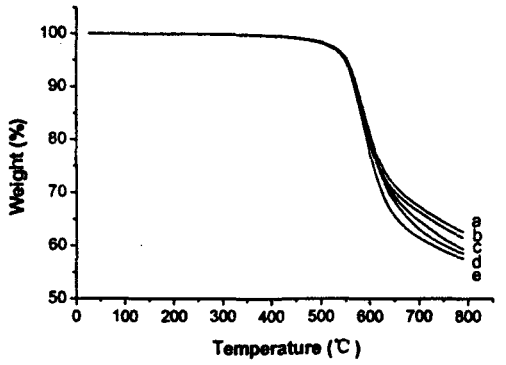


Figure 4 TGA curves of Polyimide/silica hybrid films

Silica content : a - 16%; b - 11%; c - 7%; d - 3%; e - 0%.

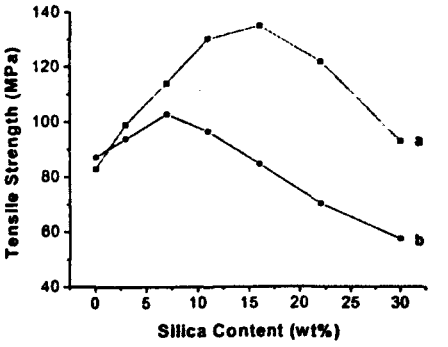


Figure 5 Tensile strength of two kinds of hybrid films

a—DHTM:ODA:ODPA=0.3:0.7:1 b—ODA:ODPA=1:1

Mechanical properties of hybrid films

The introduction of phenolic hydroxyl group into polyimide has significant affect on the mechanical properties of polyimide-silica hybrid materials. As shown in Figure 5, the influence of silica content upon the tensile strength in two systems are different. For common hybrid films prepared from ODA-ODPA, the tensile strength has a maximum (103 MPa) when the silica content is 7 wt % (Figure 5b). After 30% (molar ratio) DHTM was used to replace ODA (Figure 5a), a continuous rising of the tensile strength was observed until 16 wt % of silica was added. The maximum value reached 138 MPa (increased by about 66%). This effect may result from the strong physical interactions between organic and inorganic phases (e.g., the formation of hydrogen bonding improved the compatibility of PI and SiO_2[1]) and also the crosslinking of C—OH and silanol, as we have pointed out previously.[7]

CONCLUTIONS

A novel PI/SiO_2 hybrid material were successfully prepared at the presence of polyamic acids with phenolic hydroxyl group and TEOS in NMP solution. This hybrid film has good thermal stability. At the same time, the transparency and tensile strength are improved, for the introduction of phenolic hydroxyl group increased the comparability between organic and inorganic components.

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