Preparation of a New Polyimide-Silica Organic-Inorganic Hybrids*

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Introduction

Polyimides(PI) have been widely used in microelectronic industries because of their outstanding thermal and chemical stability, high tensile strength and modulus, and good dieletric properties. However , PI exhibit relatively high values of water asorption and coefficients of thermal expansion (about $5\times10^{-5}K^{-1}$) [1]. Their competition for microelectronics are ceramics (silica). Ceramics show a lower values of coefficient of thermal expasion(about $5\times10^{-7}K^{-1}$) and water asorption , which is very important in electronic applications, for example, in multi-layer structrue of module chips. So polyimide-silica Organic-Inorganic hybrids have been developed to combine the extraordinary properties of both materials.

In the past three decades, the sol-gel process is a method to prepare inorganic metal oxides under mild conditions from organic metal alkoxides. The network forming reaction of the sol-gel process involves the simultaneous hydrolysis and condensation of poly(valent) metal alkoxides to produce the gel[2]. Early in 1990s, this method was used in preparing PI-SiO_2 hybrids. Nandi[3] produced PI-SiO_2 hybrids by mixing solutions of PMDA,ODA and silcon tetraalkoxides. This material become opaque at low weight percentage of silica due to phase separation on the micrometer scale. Morikawa et al[4] reported that when the content of silica was more than 8%, particles bigger than 1 micron were observed and the film become opaque. Sysel[5] pointed out that common PI-SiO_2 hybrids relied only on physical interactions between the organic and inorganic phases, but polyimides usually have bulky backbone structures which creating less intermingling with silica, so size distribution of the second phase was not homogeneous over the hybrid film.

We have successfully synthesized a novel diamine, 1,3-bis(4-aminophenoxy)-2-propanol (HAPP), and polyamic acids (HAPP-ODPA) containing pendent hydroxyl group, as shown in Scheme 1. Polyimide-silica hybrids were prepared by sol-gel peocess from tetraethoxysilane (TEOS) and PAA. The presence of hydroxyl group will increase the compatibility between PI and silica due to the formation of hydrogen bonding. At the same time , as the condensation reaction of silanol proceed, the pendent hydroxyl group may partly crosslink with the silica network and form a strong interconnection between organic and inorganic phases, so the hybrids show no obvious phase seperation down to the nanoscale regime when silica content less than 20%.

Experimental

Materials

Epichlorohydrin , p-nitrophenol and hydrizine monohydrate were used as received without further

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purification. 3,3`,4,4`—oxydiphthalic dianhydride(ODPA) was dried at 180℃ for 6 hr before using. Oxydianiline(ODA) and 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.

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

In a 100 ml three neck flask equipped with a stirrer and a reflux condenser, 6g p-Nitrophenol and 2ml Epichlorohydrin were added. After stirring for 10h at reflux temperature, the mixture was filtered. The product was recrystalized in toluene and a white needle crystal was gained.

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

Dinitro (10g), ethyl alcohol (110ml) and palladium on activated carbon (0.11g) were added in a 100ml three neck flask equipped with a stirrer, nitrogen inlet, pressure equalizing addition funnel and reflux condenser. The mixture was stirred and heated to reflux, hydrizine monohydrate (10ml) was added dropwise via the addition funnel in 2.5 h. The reaction was maintained for 10h. 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 crystalized in refrigerator.

Preparation of polyimide-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℃ for 10 h to gain a viscous poly(amic acid) solution. Then TEOS and water were added. The amount of TEOS was decided by the 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 homogeneous solution.

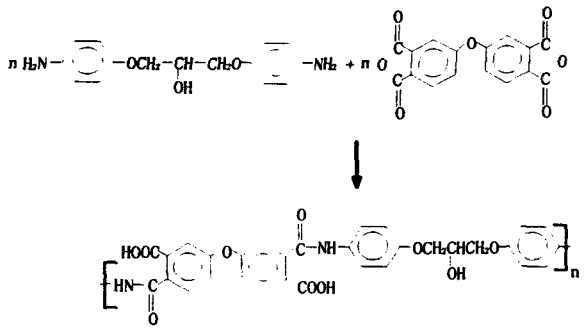
The transparent solution was spun onto a glass plate and subsequently dried at 100℃ for 4 h in atmosphere. Then the film was heated for 2 h at 160℃, 2 h at 200℃ and 1 h at 240℃in a nitrogen atmosphere. Formulations for polyimide–silica hybrids disscussed in this paper are shown in table 1.

Table 1 Silica Content of Polyimide-SiO_2 Hybrid Materials

Hybrid Films	PAA	TMOS (wt%)	H_2O/TMOS (mol ratio)	HCl (wt%)	SiO_2 (wt%)
PI	HAPP-ODPA	0	0	0	0
Hybrid-3	HAPP-ODPA	10	4	0	3
Hybrid-7	HAPP-ODPA	20	4	0	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

Measurements

Fourier transform infrared spectra of PI and hybrid films were recorded on a Nicolet 560 FTIR spectra photometer, and the photomicrograph were taken with a XSJ-1 photomicroscope. The thermogravimetry analysis (TGA) was performed on a TGA-2950 under air and nitrogen at a heating rate of 10℃/min. The tensile strength of PI-SiO2 hybrid films were 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 hydroxyl group

Results and Discussion

The structure characteristics of dinitro and diamine

The melting point of 1,3-bis(4-nitrophenoxy)-2-propanol is 143.5-144.5℃. From FTIR spectra, the two strong bands at 1503 and 1347cm^{-1} are the streching of NO_2. The band at 3517cm^{-1} is assigned to OH group. For the diamine, its m.p. is 113-114℃. The IR spectrum shows that the two bands around 3386 and 3320 cm^{-1} are coresponded to NH_2 group. The other bands are alike to dinitro.

Preparation of the PI-SiO_2 hydrid films

The effect of water and apueous hydrochloric acid on the speed of silica network formation and the hydrolysis of polyamic acid were investigated. In agreement with the reults of other reports[1-2], we find an acceleration of the hydrolysis of TEOS when hydochloric acid was added. At the same time, the viscosity of polyamic acid solution was lowered.

We aslo observed that there were particles produced and phase separated solutions formed when the system containing hydrochloric acid was heated to 80℃ for 8 h, and resulted in opaque films and decrease of tensele strength. Otherwise comparable solutions containing distilled water formed transparent solutions at room tempreture. This was probably due to the fact that the presence of HCl accelerated the crosslinking of TEOS, resulting in big silica particles, and the decomposation of PAA at this temperature. So the concentration of hydrochliric acid and the reaction temperature are very important to prepare high performance hybrid films.

FTIR studies of PI and hybrid films

Figure 1 shows the IR spectra of PI (curve a), Hybrid-7(curve b) and Hybrid-30(curve c). The three films all have the characteristic absorption peaks of imide groups at 1775 cm^{-1} (C=O symmetric stretching), 1715 cm^{-1} (C=O asymmetric stretching) and 1382 cm^{-1}(C—N stretching). Because of the presence of a strong absorption at 1090 cm^{-1} due to C-O (a), the charateristic peak of Si-O stretching vibrations (near 1080 cm^{-1}) is not obvious, but we can find the band of Si-O bending vibration[5] at 454 cm^{-1}, which increases with silica content (b,c).

The wide band at 3479 cm^{-1} is coresponding to the stretching vibration of C—OH. Curve b are is similar to curve a, because the content of silica is low in Hyb-7 film. Comparing the intensity of the band at 3479 cm^{-1} in curve b with curve c, it was observed that this absorption peak decreased with the increasing of silica content. It may be related to the decrease of the C—OH concentration because of the condensation between C—OH and silanol.

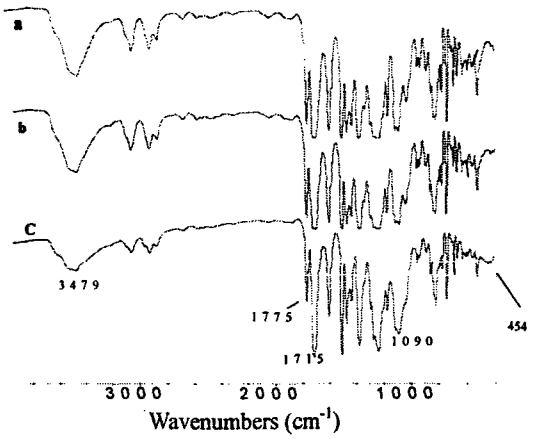


Figure 1 FTIR spectra of PI and PI-SiO_2 hybrid films

a — PI, b — Hyb-7, c — Hyb-30

Appearance of hybrid films

Different polyamic acids were synthesised from HAPP-ODPA and ODA-ODPA, and two series of hybrid materials were prepared with the same experimental conditions. The appearance of the films were compared, as shown in table 2. It is evident that the transparency of hybrid 1 is much better than hybrid 2. This indicates that hybrids with higher silica content , at the same time showing no obvious phase seperation , can be obtained due to the presence of pendent hydroxyl group.

Table 2 the Transparency of Hybrid Films

Hybrids	PI	Silica Content (wt %)						
		0	3	7	11	16	22	30
1	HAPP-ODPA	Trans-parent	Trans-parent	Trans-parent	Trans-Parent	Almost trans-parent	clouded	Opaque
2	ODA-ODPA	Trans-parent	Trans-parent	clouded	Opaque	Opaque	Opaque	Opaque

Photomicroscope Analysis

The photomicrographs of PI and Hybrid films are shown in Figure 2. Pure PI film is highly transparent. It can be seen from Figure 2 (b), the diameter of silca is much smaller than the wavelength of visible light (400-700 nm) making the hybrid film transparent. the size of inorganic particles increased up to 100-500 nm, resulting in the decrease of transmittance of the film when the silica content reaches 16%, as shown in Figure 2 (c) .

Mechanical properties of hybrid films

The influence of silica content upon the tensile strength is shown in Figure 3. The tensile strength increases with the increase of the silica content up to 7 wt % in both system. Then the fast reduction of tensile strength is found for hybrid 2 (ODA-ODPA) related to the phase separation. It is remarkable to observe a continious increasing of the tensile strength for hybrid 1 (HAPP-ODPA) when 11 wt % of silica is introduced, and the increasing value of tensile strength reach 31% (22 MPa). When 16% silica was added , hybrid 1 still maintain a high value of strength (74 MPa). This effect may result from the strong physical interactions between organic and inorganic phases (e.g., the formation of hydrogen bonding increased the compatibility of PI and SiO_2) and the crosslinking of C—OH and silanol.

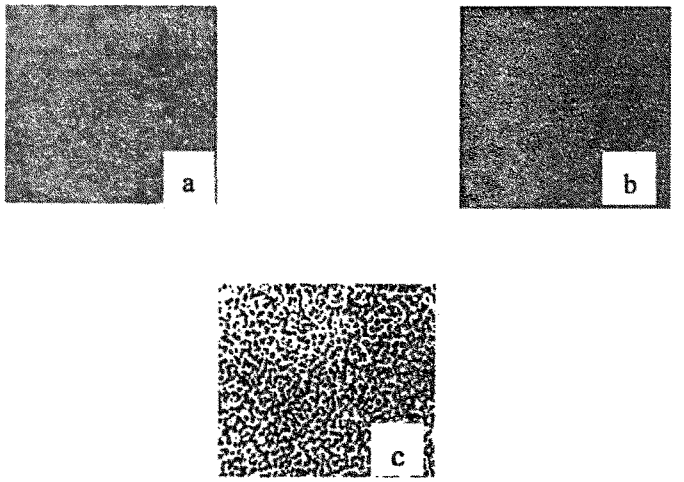


Figure 2 Photomicrographs (enlarged 1000 times) of PI and hybrid films

a:PI(HAPP-ODPA) b: PI/SiO_2(7wt%) c: PI/SiO_2(16wt%)

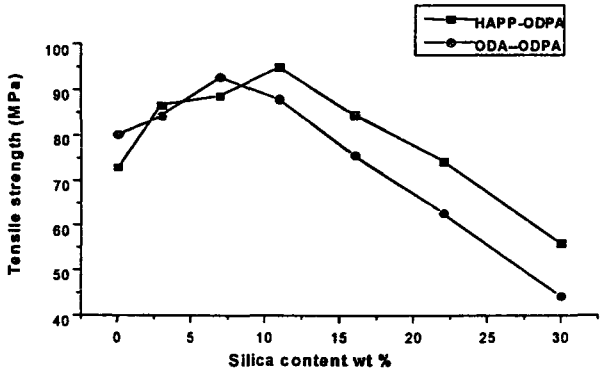


Figure 3 Tensile strength of two kinds of hybrid films

CONCLUTIONS

1. Polyamic acid with pendent hydroxyl group has been synthsised and polyimide-silica hybrid materials were prepared via sol-gel process.
2. Transparent hybrid films with higher silica content were obtained, for the presence of hydroxyl group increased the comparibility of two components due to hydrogen bonding and chemical bond between organic and inorganic phases was probably formed.
3. The tensile strength of (HAPP-ODPA)PI-SiO_2 hybrid films increases with the increase of silica content and reach a maximum value when the silica content is up to 11 wt %.

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