Preparation and Properties of Organosoluble Polyimide/ Silica Hybrid Materials by Sol–Gel Process

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ABSTRACT: Organosoluble polyimide/silica hybrid materials were prepared using the sol-gel process. The organosoluble polyimide was based on pyromellitic anhydride (PMDA) and 4,4'-diamino-3,3'-dimethyldiphenylmethane (MMDA). The silica particle size in the hybrid is increased from 100–200 nm for the hybrid containing 5 wt % silica to 1–2 μ m for the hybrid containing 20 wt % silica. The strength and the toughness of the hybrids are improved simultaneously when the silica content is below 10 wt %. As the silica content is increased, the glass transition temperature (T_g) of the hybrids is increased slightly. The thermal stability of the hybrids is improved obviously and their coefficients of thermal expansion are reduced. The hybrids are soluble in strong polar aprotic organic solvents when the silica content is below 5 wt %. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2977–2984, 1999

Key words: hybrid; polyimide; silica; organosoluble; sol-gel process

INTRODUCTION

Recently, the preparation of inorganic/organic hybrids has been intensively studied by combining the sol–gel reaction of compounds such as silicates and metallic organic compounds with polymerization reactions. A wide range of inorganic/ organic hybrids could be prepared by the appropriate selection of the raw materials and the preparative approaches to achieve various properties to meet the requirements of different applications.^{1–9}

Polyimide is a type of organic polymer material characterized by its outstanding thermal stability.¹⁰⁻¹² It also possesses excellent mechanical and electrical properties and has been widely applied in microelectronic industries for packaging, insulation spacing in large-scale integrated circuits (LSIC), and passivative protection, etc. To meet the rapid improvements in microelectronics technology, materials with higher thermal stability and higher mechanical and electrical properties, especially lower thermal expansion coefficient and low dielectric constant, are desired.

Because of the high bond energy of the Si—O bond, SiO₂ has extremely high thermal stability. SiO_2 also possesses the lowest thermal expansion coefficient of known materials. The preparation of polyimide/silica hybrids by the sol-gel process has attracted attention from various research groups in an attempt to improve their mechanical

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Scheme 1 Preparation of PI/silica hybrids via sol-gel process.

properties and thermal stability and to reduce their thermal expansion coefficient. $^{\rm 13-23}$

Most of the studies on polyimide/silica hybrids have used conventional aromatic polyimides. These polyimides, however, are neither soluble nor fusible because of the high rigidity of the molecular chains and the strong intermolecular interactions. The hybrids based on these polyimides are, consequently, neither soluble nor fusible. This low processability may cause difficulties in the fabrication of microelectronic devices. In this article, a rigid-rod organosoluble polyimide is used in an attempt to obtain organosoluble polyimide/silica hybrids. The preparation, characterization, and properties of the hybrids are reported.

EXPERIMENTAL

Materials

Pyromellitic anhydride (PMDA, industrial product) was purchased from Shanghai Tar Chemical Co. (Shanghai, China) and recrystallized from acetic anhydride before use. 4,4'-Diamino-3,3'-dimethyl diphenyl methane (MMDA) was prepared by the reaction of o-methyl aniline and formalin.²⁴ Tetraethoxysilane (TEOS, chemical reagent grade) was purchased from Beijing Chemicals Co. (Beijing, China) and used as received. N-Methyl-2-pyrrolidone (NMP), N,N,-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), and dimethyl sulfone (DMSO) (all analytical reagent grade) were purchased from Shanghai Reagent Co. (Shanghai, China) and dried over molecular sieves before use. Common reagents such as ethanol (anhydrous) and acetic acid (all analytical reagent grade) were used without further purification.

Preparation of Organosoluble Polyimide/Silica Hybrids

An equimolar amount of PMDA particles was added to an MMDA/NMP solution. (The solid content was 15 wt %.) The mixture was kept at 0°C for 16 h to obtain a viscous poly(amic acid) (PAA) solution. To this PAA solution, a mixture of TEOS, distilled water, and acetic acid (as the

Run	PAA ^a (g)	TEOS (mL)	$R^{ m b}$	$\begin{array}{c} H_2O\\(mL) \end{array}$	$Catalyst^{c}$	Silica Content ^d (wt %)	Remark ^e	Sample Name
1	10	0	_		_	0	Т	PI
2	10	0.21	1:4	0.10	5.0	5.0	Т	PI/silica-5
3	10	0.44	1:4	0.14	5.0	10.0	Т	PI/silica-10
4	10	0.99	1:4	0.32	5.0	20.0	Tr	PI/silica-20
5	10	1.64	1:4	0.57	5.0	30.0	0	PI/silica-30

Table I Recipe of Preparation of PI/Silica Hybrids

 $^{\rm a}$ 10 wt % NMP solution.

 ${}^{\rm b}R = [{\rm TEOS}]/[{\rm H}_2{\rm O}].$

^c Weight percentage of acetic acid based on the amount of water added.

^d Calculated silica contents in hybrid films.

^e T, transparent; Tr, translucent; O, opaque.



Figure 1 FTIR spectra of (A) PAA/silica-30 hybrid and (B) PI/silica-30 hybrid.

catalyst to adjust the pH value of the system) was added. The mixture was then stirred at room temperature for 6 h and a transparent solution was obtained. The resultant solution was cast onto a glass substrate and subsequently thermally treated at 80°C for 12 h, 170°C for 4 h, 220°C for 2 h, and 270°C for 2 h to obtain PI/silica hybrids. The preparation of PI/silica hybrids is described in Scheme 1 and Table I.

Structural Analysis and Property Measurement of PI/Silica Hybrids

Infrared spectra of PAA/silica and PI/silica hybrid films were recorded on a Bruker ISF112V FT-IR spectrophotometer. X-ray photoelectron spectra (XPS) were recorded on an NP-1 X-ray photoelectron spectrometer (manufactured by Changchun Scientific Instruments Co.). The density of the hybrids was measured using a density gradient tube at 25°C. Thermal gravimetric analysis (TGA) was conducted on a Perkin–Elmer TGA 7 thermal analyzer with a heating rate of 20°C/min. Dynamic thermal analysis curves were recorded on a Perkin–Elmer DMA 7 thermal analyzer with a heating rate of 10°C/min. The thermal expansion coefficient (TEC) of the PI/silica hybrid films was measured on a Perkin–Elmer TMS-2 thermal mechanical analyzer with a heating rate of 10°C/



Binding energy (eV)

Figure 2 Binding energy of PI/silica-5 hybrid films: (1) before imidization; (2) after imidization.



Figure 3 SEM photograph of PI/silica-10 hybrid film.

min. The stress-strain curves of the PI/silica hybrid films were recorded on an Instron-8500 universal tester at room temperature with a drawing rate of 5 mm/min. Scanning electronic microscope (SEM) photographs of the cross section of PI/silica hybrid films were taken on a Hitachi S-530 scanning electronic microscope. The solubility of the PI/silica hybrid films in organic solvents at room temperature was also measured.

RESULTS AND DISCUSSION

Infrared Spectra

Figure 1 shows the IR spectra of PAA/silica and PI/silica hybrid (containing 30 wt % silica) films. The presence of absorption bands, characteristic of Si—OH (814 cm⁻¹), Si—O— C_2H_5 (963 cm⁻¹), and linear Si—O—Si (1073 cm⁻¹) groups in the spectrum of the PAA/silica hybrid, indicates that TEOS partially undergoes the hydrolysis-condensation process before imidization of the polyimide. In addition, unhydrolyzed and partially hydrolyzed TEOS also exist. The absorption band at 1719 cm^{-1} is the characteristic band of the amide groups in PAA. The broad absorption band at about 3200 cm^{-1} is from the —COOH and —NH groups in PAA.¹⁰ After the thermal treatment, PAA is converted to polyimide. This is confirmed by the observation of the characteristic absorption bands of C=O stretching in imide groups at 1778 and 1725 cm^{-1} and the characteristic absorption band of C—N stretching in imide groups at 1378 $\rm cm^{-1}$.¹⁰ The observation of the absorption bands at 1111 cm⁻¹ (Si-O-Si network) and 850 cm^{-1} (Si-O-Si, symmetrical) and the disap-



Figure 4 Relationship between silica content and density of the hybrid.

pearance of the 963 cm⁻¹ band clearly indicate that most of the TEOS has been converted to the inorganic phase composed of the Si—O—Si linkages. All these results indicate that the Si—O—Si network structure is formed during the thermal treatment process, leading to the imidization of polyimide.

XPS Analysis

Figure 2 shows the XPS spectra of the hybrids before and after the imidization process. The binding energies of Si_{2p} and O_{1s} before the imidization process were found to be 101.8 and 531.0 eV, respectively. They represent the binding energy of the intermediates of the hydrolysis-condensation reaction of TEOS. In the thermal imidization process, the high temperature accelerates the hydrolysis-condensation reaction and the formation of the Si—O—Si-based inorganic



Figure 5 Relationship between silica content and thermal expansion coefficient of PI/silica hybrid films.



Figure 6 TGA curves of PI/silica hybrid films.

phase. In this phase, the binding energies of Si_{2p} and O_{1s} are changed to 103.9 and 532.6 eV, respectively.

SEM Analysis

An SEM photograph of the PI/silica-10 hybrid film is shown in Figure 3. The size of the silica particles in PI/silica-5 is 100–200 nm. As the silica content is increased to 10 and 20 wt %, the particle size is increased to 200-450 nm and 1-2 μ m, respectively. The increase in the silica particle size is caused by the increased aggregation tendency when the silica content is increased.

Density of the Hybrids

The relationship between the silica content and the density of the hybrid is shown in Figure 4. A basically linear relationship is observed between the silica content and the density of the hybrid. When the straight line is extrapolated to a silica content of 100 wt %, a density of 1.66 g/cm³ is obtained. This datum is clearly smaller than is the density of the SiO₂ glass (2.22 g/cm³). This may result from several factors: The conversion from TEOS to SiO₂ may not be 100%. The surface of SiO₂ may absorb —OH groups. The sol–gel conversion may generate a large amount of microvoids. These voids can be observed in the SEM photographs (cf. Fig. 3).

Thermal Expansion Coefficient (TEC) of the Hybrids

Figure 5 is the relationship between the silica content and the TEC of the hybrid. It is observed that the introduction of silica reduces the TEC effectively. The introduction of 5, 10, 20, and 30 wt % leads to the decrease of the TEC of the hybrid from 3.6×10^{-5} to 2.6×10^{-5} , 2.3×10^{-5} , 2.0×10^{-5} , and 1.8×10^{-5} K⁻¹, respectively. This decrease in the TEC clearly results from the low TEC of SiO₂. It is also observed that the rate of the decreases as the silica content is increased. The introduction of the first 5 wt % silica leads to a 28% decrease in TEC while the intro-

Table II Thermal Properties of Polyimide/Silica Hybrid Films

Sample	PI	PI/Silica-5	PI/Silica-10	PI/Silica-20	PI/Silica-30
$ \frac{T_d^{a} (^{\circ}C)}{T_g^{b} (^{\circ}C)} $	$556\\351$	565 352	574 356	582 371	591

^a Initial thermal decomposition temperature (onset temperature) determined by TGA in N₂.

^b Determined by DMA.



Figure 7 DMA curves of PI/silica hybrid films.

duction of the second 5 wt % silica leads to a 8% decrease. This may be caused by the aggregation of the silica particles, which leads to the increase of the size of the particles and, consequently, the decrease of the phase surface area.

Thermal Stability of the Hybrids

The TGA curves of PI and PI/silica hybrids are shown in Figure 6. The initial thermal decomposition temperatures (T_d , onset temperature) are listed in Table II. It is observed that the T_d of the PI is 556°C. When 5 wt % of silica is introduced (PI/silica-5), the T_d is increased by 9°C to 565°C.



Figure 8 Relationship between the Young's modulus and silica content.

The T_d is further increased as the silica content is increased. The increase in the thermal stability could be attributed to the high thermal stability of silica and the existence of the strong interaction between the silica particles and the PI matrix. This strong interaction may make the silica particles act as crosslink points. As the number of the crosslink points increases, the movement of PI is limited.

Glass Transition Temperature of the Hybrids

The glass transition temperatures (T_g) of PI and the PI/silica hybrids obtained from their DMA curves (Fig. 7) are listed in Table II. The polyimide has a T_g of 351°C. The T_g of a hybrid increases with increase of the silica content. The increase in the T_g may result from the existence of the strong interactions between the silica particles and the PI matrix. These strong interactions limit the movement of the polyimide molecules.

Mechanical Properties of the Hybrids

The influence of the silica content upon the Young's modulus is shown in Figure 8. The Young's modulus of the hybrid exhibits a linear increase with increase of the silica content. The influence of the silica content upon the tensile strength (failure) and the elongation at break are shown in Figure 9. It is remarkable to observe that both the tensile strength and the elongation at break increase with increase of the silica con-



Figure 9 Influence of silica content upon the tensile strength and elongation at break of PI/silica hybrid films.

tent up to a silica content of 10 wt %. The tensile strength is increased by about 33% while the elongation at break is increased by about 66% when 10 wt % of silica is introduced. These strengthening and toughening effects may result from the strong interfacial interactions between PI molecules and silica particles, which lead to the formation of the physical crosslinking. The strength and the toughness of the hybrid are, of course, dependent upon the density of the crosslink. In an appropriate range of the crosslink density, the crosslinking could exhibit both the strengthening and toughening effects. It is widely believed that the toughening effects in a rubbermodified plastics system result from the formation of the voids (or cavitation) in rubber particles under the stress.²⁵⁻²⁷ The strengthening and toughening effects in this silica/PI system, how-

Table III Solubility of PAA/Silica and PI/Silica Hybrids (25°C)

Silica	P.	AA/Sil	ica	PI/Silica			
(wt %)	0	5	20	0	5	10	20
NMP	+	+	+	+	+	+-	_
DMAc	+	+	+	+	+	+-	
DMF	+	+	+	+	+	+-	_
DMSO	+	+	+	+	+	+-	

+, soluble; +-, partially soluble; -, insoluble.

ever, are very unlikely to be the result of the formation of the voids in the silica particles under stress because the Si—O bonds in the silica particles seem to be too strong to be broken prior to the failure of the hybrids.

Solubility of the Hybrids

Because of the high aromaticity and rigidity of the pyromellitic dianhydride moiety, the conventional polyimides based on PMDA are neither soluble nor fusible and are difficult to process. In this study, 4,4'-diamino-3,3'-dimethyldiphenylmethane (MMDA) was used to prepare polyimide with PMDA. The incorporation of the two substituent methyl groups leads to increase in the free volume and decrease of the molecular packing. The steric hindrance from the methyl groups may also lead to distortion of the conjugation of the polyimide backbones. For the above reasons, polyimide based on PMDA and MMDA is organosoluble.²⁴

The solubility of PAA/silica (before thermal treatment) and PI/silica hybrids (after thermal treatment) are listed in Table III. The PAA/silica hybrids exhibit good solubility even with high silica content. It is, of course, caused by the high flexibility of the PAA molecules. As PAA is converted to PI through a thermal imidization process, the rigidity of the molecules is much increased. Meanwhile, physical crosslinking is formed between polyimides and silica particles. The increased rigidity and the formation of crosslinking may both contribute to an obvious decrease in the solubility. PI/silica hybrids are not soluble in the aprotic polar organic solvents studied when the silica content is above 10 wt %. However, when the silica content is 5 wt %, the hybrid exhibits good solubility. This solubility is caused by the small silica particle size. Furthermore, the existence of the silica particles may also reduce the interaction between the PI molecules. As the silica particle size is increased, the insolubility of the silica particles leads to the insolubility of the hybrids.

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