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Compatibility of Soluble Polyimide/Silica Hybrids Induced by a Coupling Agent

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In this paper, a new type of soluble polyimide/silica (PI/SiO_2) hybrid was prepared by the sol−gel process. The coupling agent γ-glycidyloxypropyltrimethoxysilane (GOTMS) was chosen to enhance the compatibility between the polyimide (PI) and silica (SiO_2). Furthermore, the effects of the coupling agent on the morphologies and properties of the PI/SiO_2 hybrids were investigated using UV−vis and FTIR spectroscopies and SEM. The densities and solubilities of the PI/SiO_2 hybrids were also measured. The results show that the size of the silica particle was markedly reduced by the introduction of the coupling agent, which made the PI/SiO_2 hybrid films become transparent. The solubility of the PI/SiO_2 hybrid was also improved by the coupling agent. In addition, all of these effects became even more pronounced with increased amounts of the coupling agent. The thermal properties of the compatibilized PI/SiO_2 hybrids were investigated by DSC and TGA. Moreover, their mechanical properties were also characterized. The results showed that the glass transition temperatures (T_g) of the hybrids were higher than those of their counterparts without the coupling agent. The thermal stability was lowered by the addition of the coupling agent, but it was still higher than that of the pure polyimide. The compatibility of the two components was effectively improved by the coupling agent; this resulted in the markedly improved mechanical properties.

Introduction

Organic/inorganic nanocomposites have become an effective source of advanced materials as they usually exhibit unique properties that traditional composites and conventional materials do not have. They combine the advantages of the inorganic material (rigidity, high thermal stability) and the organic polymer (flexibility, dielectric, ductility, and processability).[1−19] Moreover, they usually also contain special properties of nanoparticles that can be developed, leading to materials with improved properties for electrical, optical, structural, electrooptical, nonlinear-optical, or related applications.

Because of their excellent properties, aromatic polyimides have been considered as suitable polymer matrix materials for preparing advanced hybrid composites that have potential applications in the microelectronics and aircraft industries since the first report of Nandi et al.[20] Additionally, silica is viewed as an important inorganic component in hybrid composites for the improvement of thermal and mechanical properties.[20] Therefore, polyimide/silica hybrid composites have attracted particular interest.

A simple method for obtaining organic−inorganic hybrids is mixing an organic polymer with a silicon alkoxide such as tetraethoxysilane (TEOS), followed by a sol−gel reaction involving the hydrolysis and polycondensation of TEOS. In this case, the incompatibility of the two components of the polyimide/silica (PI/SiO_2) hybrids makes the dispersion of the inorganic SiO_2 particles into the polyimide matrix difficult. This is obviously not a favorable factor in the preparation of

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transparent free-standing PI/SiO_2 hybrid films owing to phase separation, especially at high silica contents. Furthermore, the morphology and interfacial properties of the separated two phases will not lead to composites with excellent properties.[21−23] Therefore, it is important to improve the compatibility between the two phases for the preparation of organic−inorganic hybrids with good properties. In this work, a coupling agent, γ-glycidyloxypropyltrimethoxysilane (GOTMS), was chosen to improve this compatibility and thereby improve the mechanical properties of the hybrid materials.

Although several papers on the structure and properties of polyimide/silica hybrid composites have been published,[7,9,24−27] they are generally concerned with insoluble polyimides. In our laboratory, a new kind of organo-soluble polyimide has been synthesized that has potential applications in microelectronics for its excellent photo-etching properties.[28] In this paper, this kind of organo-soluble polyimide was chosen as the polymer matrix, and a new series of soluble polyimide/silica hybrids was prepared by the sol−gel process with a coupling agent. Furthermore, the effects of the coupling agent on the size of the SiO_2 particles, the distribution of particle size, and the properties of the PI/SiO_2 hybrids were also studied.

Experimental Section

Materials. Benzophenone 3,3′,4,4′-tetracarboxylic dianhydride (BTDA) was prepared from benzophenone 3,3′,4,4′-tetracarboxylic acid (an industrial product, purchased from Beijing Tar Chemicals Company, Beijing, China) by refluxing with an excess amount of acetic anhydride. 4,4′-Diamino-3,3′-dimethyldiphenyl methane (MMDA) was prepared from *o*-methyl aniline and formalin.[28] Tetraethoxysilane (TEOS, chemical reagent grade, purchased from Beijing Chemicals Company, Beijing, China) was used as received. *N*-Methyl-2-pyrrolidone (NMP, analytical reagent grade, purchased from Shanghai Reagent Company, Shanghai, China) was dried over molecular sieves (5 Å) before use. γ-Glycidyloxypropyltrimethoxysilane (GOTMS, analytical reagent grade, purchased from Nanjing Shuguang Chemicals Company, Nanjing, China) was used directly without purification. Other reagents were used as received.

Preparation of the PI/SiO_2 Hybrids. PI/SiO_2 hybrids were prepared by the sol−gel process depicted in Figure 1. An equimolar amount of BTDA was added to a MMDA/NMP solution (solid content, 10 wt %). The mixture was kept at room temperature for 16 h, and a viscous polyamic acid (PAA) solution was obtained. To this PAA solution, a mixture of TEOS with distilled water (4/1 based on TEOS moles) and acetic acid (to keep the pH value at 4) were added. The mixture was then stirred at room temperature for 6 h to give a transparent solution. The solution was cast on a glass substrate and thermally treated at 80 °C for 12h, 120 °C for 4h, 200 °C for 2h, and 270 °C for 2h. The thickness of the imidized films was about 50 μm. The films were removed from the glass substrates with the aid of deionized water and dried for several hours at 100 °C in a vacuum oven. The recipe for the PI/SiO_2 hybrid samples is listed in Table 1.

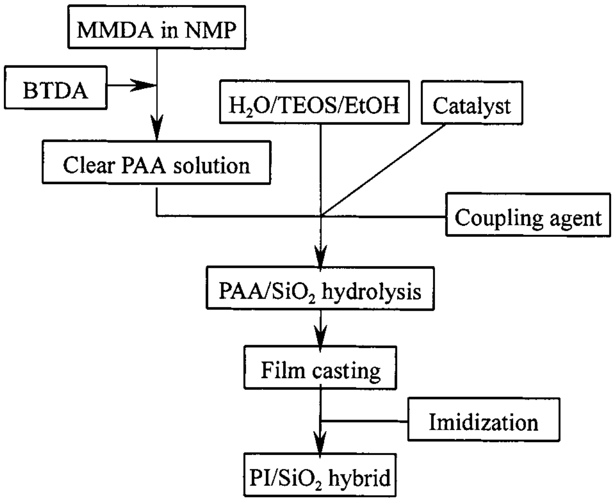

Figure 1. Preparation procedure of polyimide/silica hybrids.

Table 1. Preparation Recipe for the PI/SiO_2 Hybrids

run	silica[a] (wt %)	GOTMS/TEOS (mole ratio)	remarks[b]
b0	0	0	T
b1	5	0	T
b2	10	0	T
b3	20	0	O
b4	30	0	O
b5	40	0	O
b6	10	1/10	T
b7	20	1/10	T
b8	30	1/10	O
b9	20	1/4	T
b10	20	1/7	T
b7	20	1/10	T
b11	20	1/15	O
b3	20	0	O

[a] Silica contents were calculated theoretically. [b] T, transparent; O, opaque.

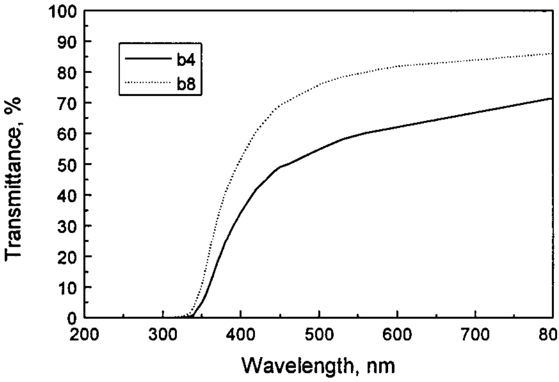

Figure 2. Effect of coupling agent on the UV−vis spectra of the PI/SiO_2 hybrid films (SiO_2 = 30 wt %).

Instrumentation. FTIR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer with KBr pellets. UV−vis spectra were measured on a Perkin-Elmer Lambda 20 UV−vis spectrophotometer. The morphologies of the fracture surfaces of the hybrid materials were observed with a JSM-6300 scanning electronic microscope (SEM). An epoxy block with the embedded PI/SiO_2 hybrids was cut to form a triangular block face for microtoming. The ultrathin sections (100 nm or less) were microtomed from the epoxy block at room temperature using a LKB2088 ultramicrotome. The transmis-

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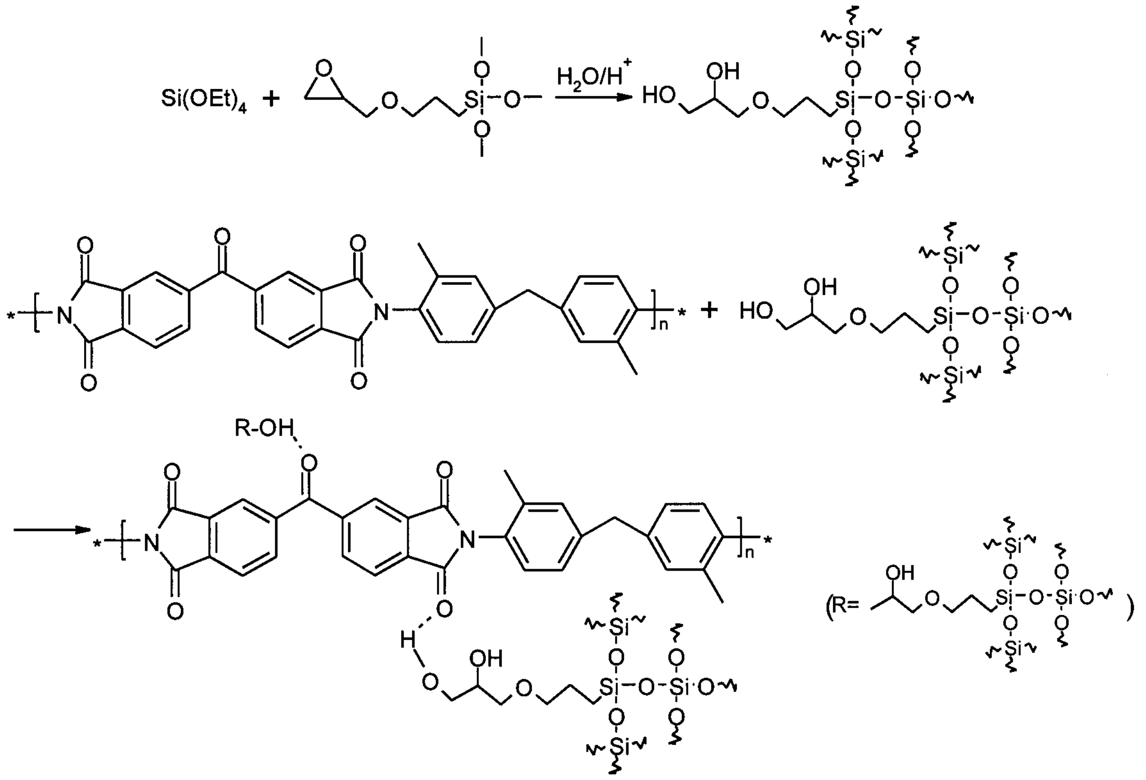
Scheme 1. Reaction Mechanism of Coupling Agent



sion electron microscopic (TEM) investigations were performed on a Philip CM120 TEM operating at an acceleration voltage of 80 kV. The thermal properties were characterized by DSC and TGA analyses, which were performed on a Perkin-Elmer Pyris 1 DSC and a Perkin-Elmer TGA 7 instrument, respectively, at a heating rate of 20/min under nitrogen atmosphere. The temperature range for the TGA measurements was from 50 to 900 °C. The solubilities of PI and the PI/SiO$_2$ hybrids in various organic solvents at room temperature were also measured. The linear coefficients of thermal expansion (CTEs) of the PI and PI/SiO$_2$ hybrids were measured on a Perkin-Elmer TMS-2 thermal mechanical analyzer. The heating rate was 10 °C/min. The densities of the samples were measured according to China State Standard GB 1033-70. The mechanical properties of the PI and PI/SiO$_2$ hybrid films were recorded on an Instron-8500 universal tester at room temperature at a drawing rate of 5 mm/min.

Results and Discussion

Optical Behavior of the PI/SiO$_2$ Hybrids. The appearances of the PI/SiO$_2$ hybrid films with different PI/SiO$_2$ contents and different amounts of coupling agent (GOTMS) are listed in Table 1. It can be seen that the transparency of the PI/SiO$_2$ hybrid films is improved by the coupling agent. A hybrid film will become translucent when the silica content is more than 10 wt % without GOTMS. However, this critical point is moved to 20 wt % by the addition of GOTMS. Figure 2 shows the effect of GOTMS on the UV−vis spectra of the PI/SiO$_2$ hybrid films. The transparency of the PI/SiO$_2$ hybrid films is greatly improved by GOTMS. This reveals that the transparency of the PI/SiO$_2$ hybrid films can be increased by the addition of the coupling agent. This is because GOTMS hydrolyzes to form silanol groups that can polycondense with the hydrolysis product of TEOS. Moreover, the other end of GOTMS hydrolyzes to form hydroxyl groups that can form hydrogen bonds with the carbonyl groups in polyimide, leading to increased compatibility with polyimide (see Scheme 1). These two factors lead to a reduction of the average particle size and good dispersion of the SiO$_2$ particles in the polyimide matrix.

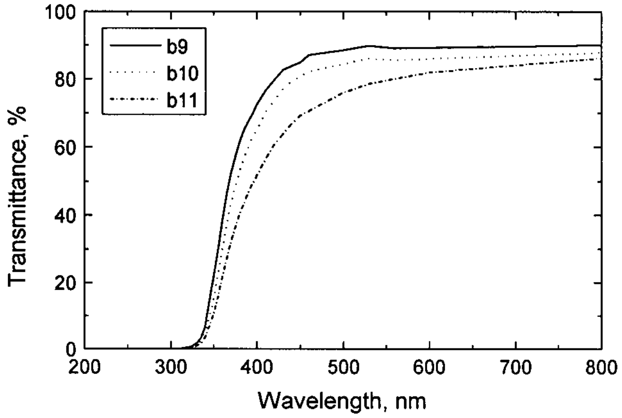


Figure 3. Effect of coupling agent content on the UV−vis spectra of the PI/SiO$_2$ hybrid films.

As shown in Figure 3, the transparency of the PI/SiO$_2$ hybrid films increases with the amount of coupling agent. This might result from the improved compatibility between the two components of PI and SiO$_2$ with increasing amount of coupling agent, which leads to smaller-sized SiO$_2$ particles and better dispersion in PI. From Figure 3, it can also be observed that the effect of the coupling agent reaches a constant level when the content is sufficiently large.

Effects of GOTMS on the Structure of the PI/SiO$_2$ Hybrids. To investigate the morphology of the PI/SiO$_2$ hybrids, the PI/SiO$_2$ hybrid films were quenched in liquid nitrogen and then broken to obtain fracture surfaces. The thin sections of the fracture surfaces were

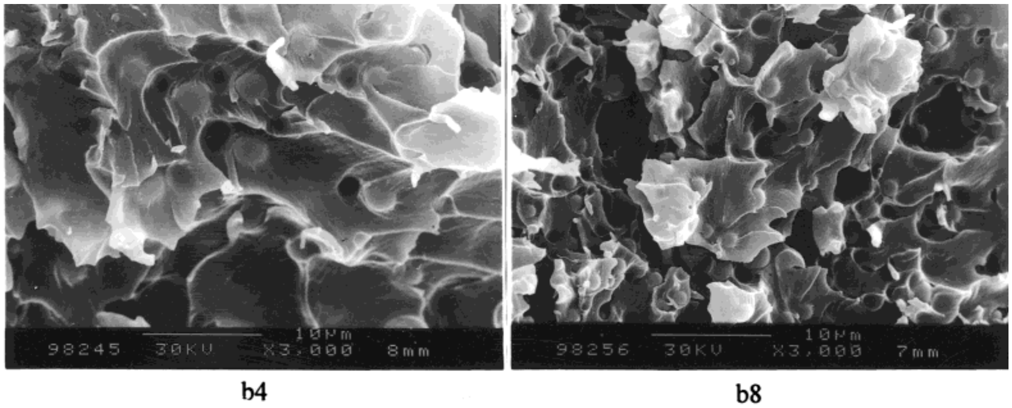


Figure 4. SEM photographs of the PI/SiO$_2$ hybrids (SiO$_2$ 30 wt %) (b4, without coupling agent; b8, with GOTMS/TEOS = 0.10).

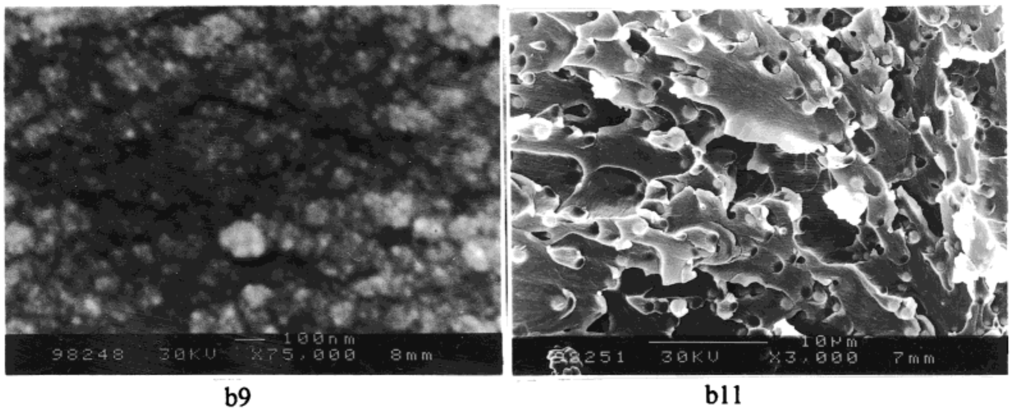


Figure 5. SEM photographs of the PI/SiO$_2$ hybrids (SiO$_2$ 20 wt %) with different contents of GOTMS (b9, GOTMS/TEOS = 1/4; b11, GOTMS/TEOS = 1/15).

cut and mounted on an aluminum stub using a conductive (silver) paint and were sputter coated with gold before fractographic examination. Figure 4 shows the SEM photographs of the fracture surfaces of PI/SiO$_2$ hybrid samples with 30 wt % silica both without and with GOTMS. The silica particle size of hybrid b4 (without GOTMS) is about 1.3−2.5 μm, whereas that of hybrid b8 (with GOTMS) is about 0.9−1.5 μm. By comparison of the two samples (b4 and b8), it can be observed that the SiO$_2$ particle size in the hybrids decreases markedly with the addition of GOTMS. It can also be observed that the dispersion of the SiO$_2$ particles in the hybrids becomes more even, narrower in size distribution, and less aggregated with the addition of GOTMS. Figure 5 shows the SEM photographs of the fracture surfaces of PI/SiO$_2$ hybrid samples (20 wt % silica) with different amounts of GOTMS. It can be observed that the compatibility between the two phases of PI and SiO$_2$ is greatly improved with increasing amounts of GOTMS. Accordingly, this results in the reduced particle size (b11, 0.75−1.2 μm; b9, 30−40 nm) and good dispersion of SiO$_2$ in the hybrid materials.

The morphological structure of the hybrids was also studied by TEM (Figure 6), and the results were consistent with the SEM results. TEM revealed that the use of the coupling agent effectively reduced the silica particle size in the hybrids. The silica particle size in the sample with 30 wt % silica (b4) was in the range of 1.2−2.4 μm, with an average of 1.9 μm. With the use of the coupling agent (sample b8), the particle size was reduced to 0.8−1.8 μm, with an average of 1.2 μm. We also found that the silica particle size was smaller for samples with lower silica contents. The hybrid containing 20 wt % silica (b11) had silica particles with size ranging from 0.8 to 1.3 μm with the use of the coupling agent. The average particle size was 0.9 μm.

FTIR Characterization of the PI/SiO$_2$ Hybrids. Figure 7 shows the FTIR spectra of two PI/SiO$_2$ hybrids (a, hybrid with 20 wt % silica; b, hybrid with 20 wt % silica and GOTMS). The characteristic absorption bands of the imide groups near 1775, 1772, 1377, 1119, and 721 cm^{-1} were observed in the FTIR spectra of the cured samples. The characteristic absorption of the amide carbonyl at 1650 cm^{-1} did not appear in the spectra, meaning that the imidization reaction was complete. This also revealed that GOTMS had no noticeable effect on the thermal imidization process of polyamic acid. The characteristic absorption bands of the hydrolysis product of TEOS were also observed. The spectrum showed absorption bands due to O−H bond stretching at 3480 cm^{-1} and Si−OH bond stretching at 882 cm^{-1}, as well as typical absorption bands for Si−O−Si network vibrations at 1130 and 823 cm^{-1}.[20,29] The characteristic absorption band of Si−O−Si asymmetric stretching (1130 cm^{-1}) became stronger and moved to higher wavenumber (1180 cm^{-1}) with the addition of the coupling agent, indicating a more “condensed” silica network (which can be confirmed by specific volume measurements).

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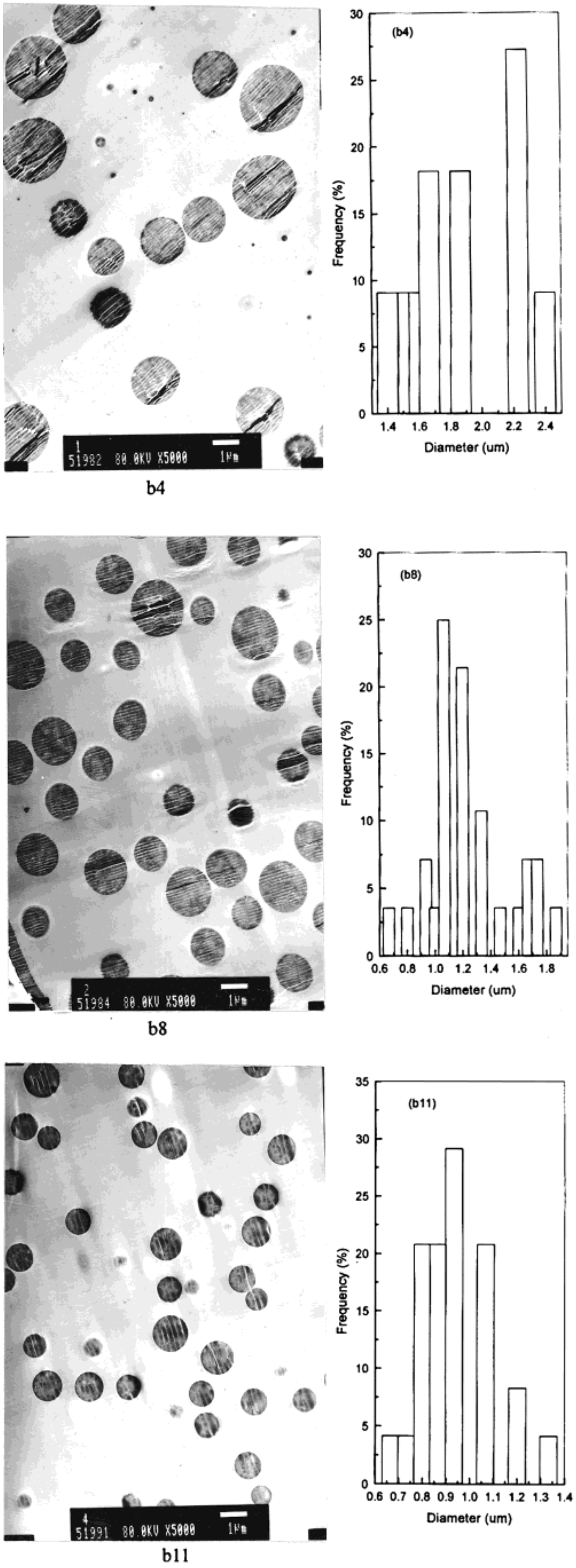

Figure 6. TEM photographs of the PI/SiO_2 hybrids (b4, 30 wt % SiO_2 without coupling agent; b8, 30 wt % SiO_2 with GOTMS/TEOS = 0.10; b11, 20 wt % SiO_2 with GOTMS/TEOS = 1/15).

Specific Volume of the PI/SiO_2 Hybrids. The influence of the SiO_2 content on the density of the hybrids is shown in Figure 8. It can be seen that the density of the hybrids with the coupling agent increases linearly with the content of SiO_2, similarly to its counterpart without coupling agent. The specific volume of silica estimated by extrapolation of the curve is 0.53 cm^3/g, which is smaller than its counterpart (0.60 cm^3/g) without coupling agent. However, this value is still greater than that of typical silica glass (0.45 cm^3/g). This means that the addition of coupling agent improves the compatibility of the SiO_2 and PI phases and thus results in a more "compact" hybrid structure. Figure 9 shows that the density of the PI/SiO_2 hybrids increases with the amount of coupling agent. This also serves as proof that the coupling agent has effectively improved the compatibility between the two phases of the PI/SiO_2 hybrids. This result can be attributed to the following two reasons. First, the coupling agent strengthens the interaction between the organic polymer matrix and the inorganic mineral and results in a more compact hybrid structure with less porosity. Second, the coupling agent reduces the size of the silica particles and greatly increases the interfacial area at the same silica content level. Furthermore, a reduced silica particle size, to some extent, means an increased cross-linking density. Additionally, the reduced size of the SiO_2 particles is apt to form a more compact silica network. All of these effects lead to higher density values for the PI/SiO_2 hybrids with coupling agent than for their counterparts.

Solubility of the PI/SiO_2 Hybrids. Because of the high aromaticity of the BTDA moiety, conventional polyimides based on BTDA 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 BTDA. The incorporation of the two methyl groups on the diamine moiety leads to an increase in the free volume and a resultant decrease of the molecular packing. The steric hindrance from the methyl groups might also lead to a distortion of the conjugation of the polyimide backbones. For these reasons, the polyimide based on BTDA and MMDA is organo-soluble.[28]

It is known that the solubility of a hybrid is mainly determined by the dispersion behavior of inorganic particles. Fortunately, all of the above results show that the addition of coupling agent greatly improves the dispersion behavior of the silica in the polyimide matrix. Thus, the effect of coupling agent on the solubility of the PI/SiO_2 hybrids was also investigated. Solubility data for the PI/SiO_2 hybrids are presented in Table 2. It can be observed that only when the silica content is less than 5 wt % is a hybrid without coupling agent soluble in aprotic polar solvents. This must be attributed to the fact that, when the silica content is low, the SiO_2 particle size is small and does not affect the solubility of the PI/SiO_2 hybrid. However, at high contents of silica, large SiO_2 particles form. These larger particles restrict the movement of the polyimide molecules and result in poor solubility of the PI/SiO_2 hybrids. The solubility is increased by the decreased size and lower aggregation of the SiO_2 particles resulting from the addition of the coupling agent.

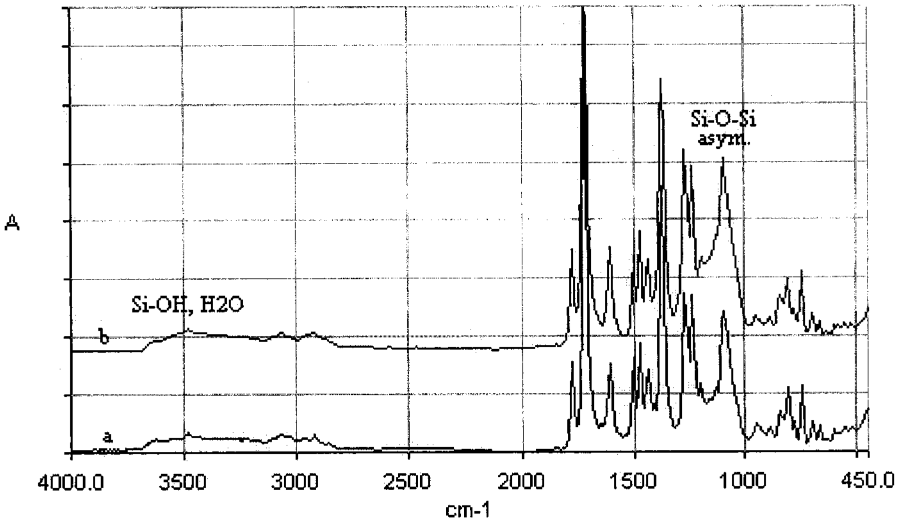

Figure 7. FTIR spectra of the PI/ SiO_2 hybrids (20 wt % SiO_2) (a, without coupling agent; b, with GOTMS/TEOS = 0.10).

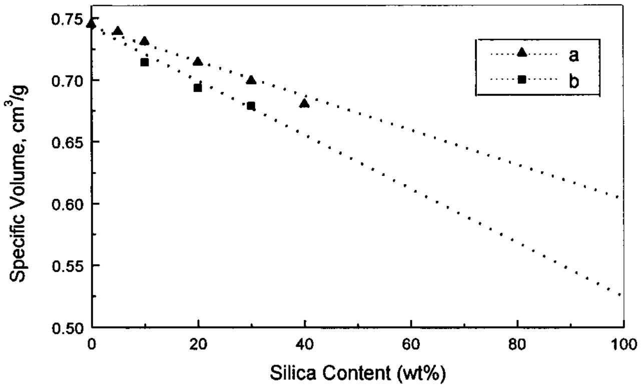

Figure 8. Specific volume of the PI/SiO_2 hybrid films a, without coupling agent; b, with GOTMS/TEOS = 0.10).

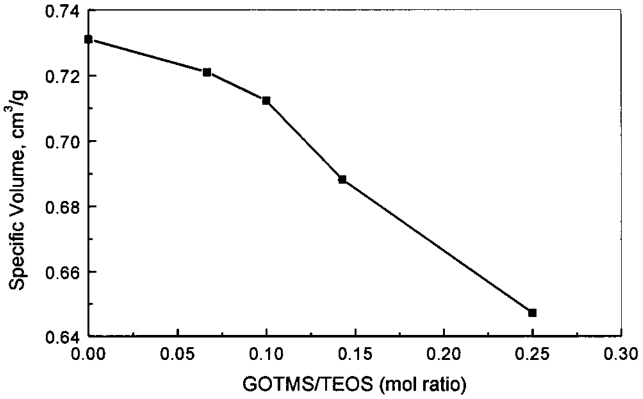

Figure 9. Effect of coupling agent on the specific volume of the PI/SiO_2 hybrid films (20 wt % SiO_2).

Thermal Properties of the PI/SiO_2 Hybrids. Figure 10 shows the DSC traces of the PI/SiO_2 hybrids with identical GOTMS/TEOS molar ratios (1/10) but different SiO_2 contents. The glass transition temperatures (T_g) obtained are listed in Table 3. The thermal decomposition temperatures (T_d) determined by TGA and the coefficients of thermal expansion (CTEs) of the hybrid samples are also listed in Table 3. It can be seen that the T_g of the hybrids increases with increasing content of silica. The hybrid films with coupling agent exhibit higher T_g's and much lower CTEs than their counterparts. These phenomena can be explained as follows: First, the coupling agent strengthens the interaction between the organic polymer matrix and the inorganic mineral particles, which causes an increased restricting strength of SiO_2 on the PI molecules. Second, the coupling agent reduces the size of the SiO_2 particles and thereby greatly increases the interfacial area at a given silica content. Furthermore, the reduced size of the SiO_2 particles, to some extent, results in an increase in the cross-linking density. All of these effects lead to higher T_g and lower CTE values for the PI/SiO_2 hybrids with coupling agent than for their counterparts. From Table 3, it can also be seen that the hybrids exhibit higher thermal stabilities than the corresponding PI.

Table 2. Solubility of the PI/SiO_2 Hybrids (at 25 °C)[a]

	b2	b3	b4	b11	b10	b9
SiO_2, wt %	5	10	20	20	20	20
GOTMS/TEOS	0	0	0	1/15	1/7	1/4
NMP	+	±	−	±	±	+
DMAc	+	±	−	±	±	+
DMF	+	±	−	±	±	+
DMSO	+	±	−	±	±	+

[a] Notes: +, soluble; ±, partly soluble; −, insoluble.

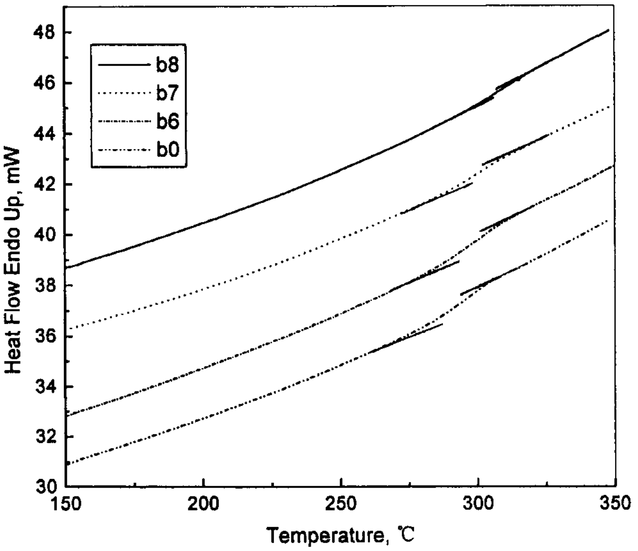

Figure 10. DSC traces of the PI/SiO_2 hybrid films at a heating rate of 20 °C min^{-1} in N_2.

Table 3. Effects of Coupling Agent on the Thermal Properties of the PI/SiO$_2$ Hybrids

run	SiO$_2$[a] (wt %)	GOTMS/TEOS	T_d[b] (°C)	CTE ($\times 10^{-5}$ K^{-1})	T_g[c] (°C)
b0	0	0	561	5.41	289
b2	10	0	581	4.86	294
b3	20	0	588	3.45	301
b4	30	0	600		310
b6	10	1/10	572	2.53	298
b7	20	1/10	576		309
b8	30	1/10	592		316

[a] Calculated silica contents in hybrid films. [b] T_d determined by TGA in N$_2$, on-set. [c] T_g determined by DSC.

Table 4. Effects of Coupling Agent on the Mechanical Properties of the PI/SiO$_2$ Hybrids

	without coupling agent			with coupling agent[a]		
SiO$_2$ (wt %)	M (GPa)	T_b (MPa)	ϵ_b (%)	M (GPa)	T_b (MPa)	ϵ_b (%)
0	2.09	59.4	6.1			
5	2.18	116.4	7.9	2.74	105.1	3.6
10	2.46	122	12.3	2.85	135.6	6.5
20	2.78	105.3	9.7	3.08	143.4	7.9
30	3.54	45.5	3.5	3.38	74.7	2.9
40				3.49	51.9	1.8

[a] GOTMS/TEOS (mole ratio) = 1/10.

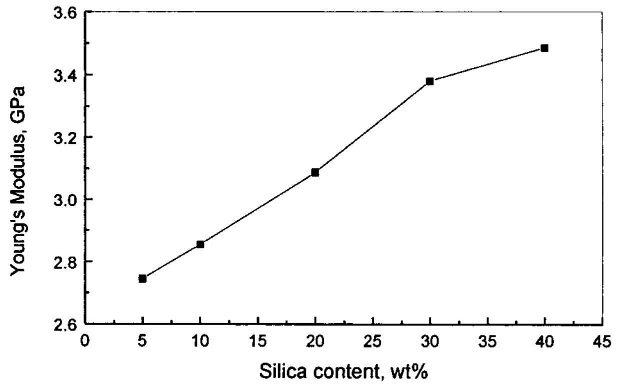

Figure 11. Correlation between Young's modulus of the PI/SiO$_2$ hybrids and silica content (with GOTMS/TEOS = 0.10).

It can also be seen that the thermal decomposition temperature (T_d) of a hybrid increases with its silica content. The thermal stabilities of the hybrids with coupling agent are slightly lower than those of their counterparts without coupling agent because of the alkyl chains of GOTMS, but they are still higher than that of the corresponding PI.

Mechanical Properties of the PI/SiO$_2$ Hybrids. The influence of the silica content on the mechanical properties of the hybrids is shown in Table 4 and Figures 11–13. From Figure 11, it can be observed that the Young's moduli (E) of the hybrid films increase linearly with the silica content. It can be seen in Figures 12 and 13 that, when the silica content is less than 20 wt %, both the tensile strength (σ_b) and the elongation at break (ϵ_b) increase with increasing silica content. When the silica content exceeds 20 wt %, both the tensile strength and the elongation at break decrease. These phenomena might be distinctive features of a nanometer composite. However, this critical point is only 10 wt % for PI/SiO$_2$ hybrids without coupling agent.

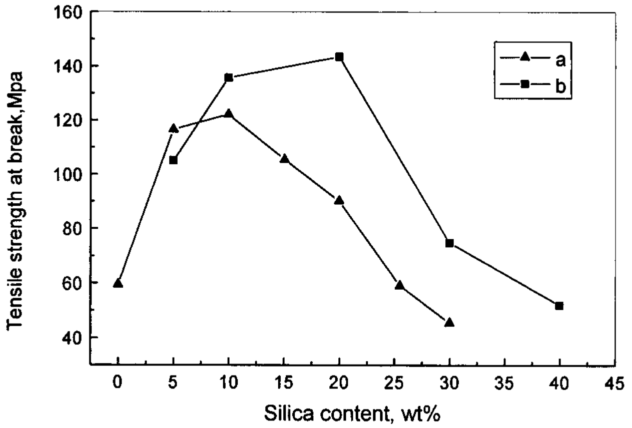

Figure 12. Effect of coupling agent on the tensile strength at break of the PI/SiO$_2$ films (a, without coupling agent; b, with GOTMS/TEOS = 0.10).

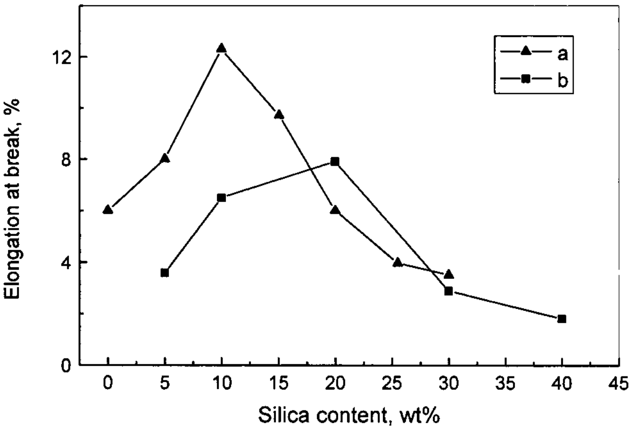

Figure 13. Effect of coupling agent on the elongation at break of the PI/SiO$_2$ films (a, without coupling agent; b, with GOTMS/TEOS = 0.10).

Most of the moduli and tensile strengths are higher in the hybrids containing coupling agent than in their counterparts without coupling agent. This effect can be attributed to the improved interaction between the PI matrix and the silica resulting from the reduced size of the SiO$_2$ particles and to the chemical bonds introduced by the coupling agent. In contrast, the elongations at break (ϵ_b) of the hybrids decrease dramatically with the addition of coupling agent. This can be explained by an increased cross-linking density resulting from the reduced particle size.

Conclusion

The compatibility between the two phases of PI/SiO$_2$ hybrids was greatly improved by the addition of the coupling agent GOTMS. The size of the silica particles in the PI/SiO$_2$ hybrids was markedly reduced by GOTMS. Therefore, the properties of the PI/SiO$_2$ hybrids were greatly improved. That is to say, the addition of GOTMS can provide PI/SiO$_2$ hybrids with improved mechanical properties, decreased thermal expansion coefficients, retentions of the solubility of the polyimide matrix, and high optical transparencies.

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