

Synthesis and Characterization of Nanocomposite of Polyimide–Silica Hybrid from Nonaqueous Sol–Gel Process

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Received 11 May 1999; accepted 19 May 1999

ABSTRACT: Polyimide–silica (PI–SiO₂) hybrids with a nanostructure was obtained using the nonaqueous sol–gel process by polycondensation of phenyltriethoxysilane in a polyamic acid solution. Self-catalyzed hydrolysis of phenyl-substituted akoxysilane and modification on the polyimide structure are applied and result in highly compatible PI–SiO₂ hybrids. Transparent PI–SiO₂ with a high silica content of about 45% was thus obtained. The prepared PI–SiO₂ films were characterized by infrared spectrometry, ²⁹Si-NMR, thermogravimetric analysis, differential scanning calorimetry, and scanning electron microscopy. These characterizations showed the silica influence on the properties of the hybrid. The thermal expansion coefficient of the PI–SiO₂ and the temperature correlation were also established for probing the potential for application.
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Key words: nanocomposite; polyimide; silica; sol–gel process

INTRODUCTION

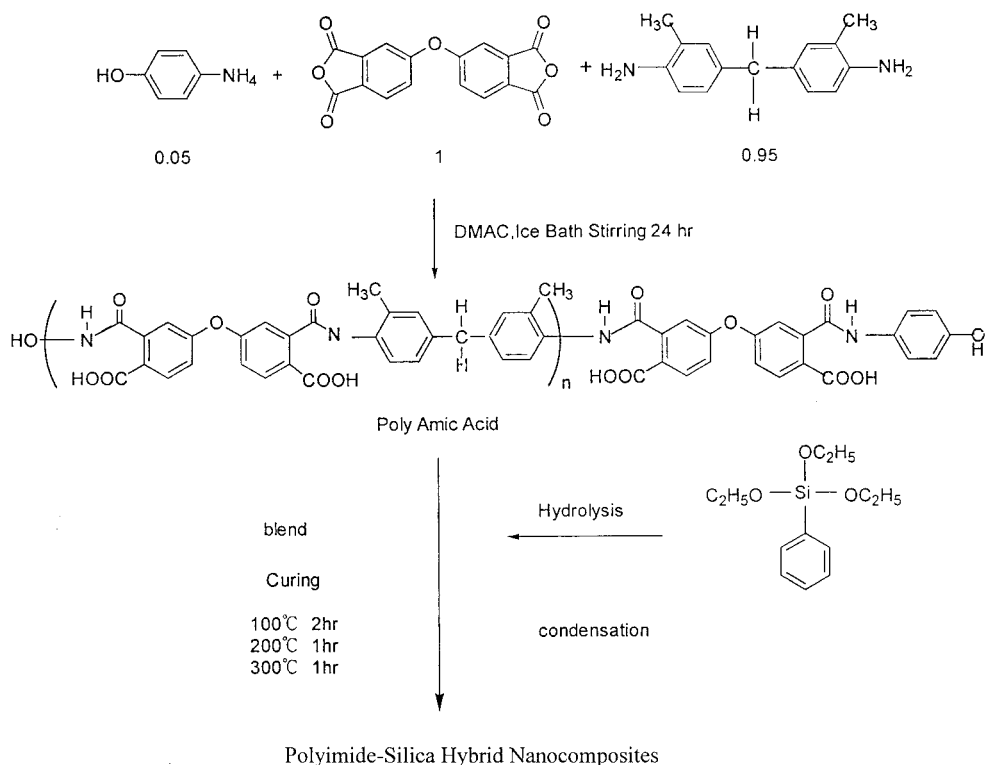
Generally, crystalline ceramic oxides and oxide glasses are prepared by treating raw materials at a temperature above 1000°C. Since some disadvantages are associated with the high-temperature reactions, low-temperature techniques for the preparation of crystalline and glassy oxide have been widely investigated.^{1,2} Specifically, the sol–gel technique has generated a great deal of interest among the low-temperature processes. This process involves room-temperature reactions of metal–alkoxides in a liquid solution to form amorphous porous gels. The gels are then dried and heat-treated to give crystalline or glassy oxide.² The classic example is the reaction of tetraethoxysilane (TEOS) to give silica glass. Recently, the sol–gel reactions were applied to the preparation of organic–inorganic hybrid materials, which synergistically combine the best properties

of organic materials with the excellent properties of inorganic glass.^{3–14} Therefore, a new class of high-performance polymeric materials was developed. Furthermore, further improvement of the mechanical properties of the organic–inorganic composites, as well as some other new features, can be gained by bringing the dispersion of the reinforced inorganic materials/organic materials to a molecular level.¹⁵ This type of molecular composite, that is, nanocomposites, has thus received much attention in investigations.^{15–17}

Many polymers have been used in the above sol–gel process for preparing organic–inorganic hybrids. Among these polymers, polyimides are of particular interest,^{18–26} since they have gained commercial importance due to their reliable high-temperature stability, good mechanical strength, and excellent chemical resistance. However, the compatibility between polyimide and silica in the obtained polyimide–inorganic hybrids is not as good as expected. Most of the reported polyimide–silica hybrids became opaque with a silica content of about 10%. In addition, the silica in the polyimide–silica hybrid material was observed as in-

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Journal of Applied Polymer Science, Vol. 76, 1609–1618 (2000)
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Scheme 1 Synthesis of polyimide-silica hybrid nanocomposites.

dividual particles with diameters of 2–10 μm using a scanning electron microscope (SEM). Since the morphology of two-phase systems is known to have an effect on the mechanical and dynamic mechanical properties of polymer hybrids, in subsequent experiments, attempts were made to improve the compatibility between polyimides and silica.^{21,22,27} Remarkable improvements in the mechanical properties and in reducing the particle size of silica from a micrometer to a nanometer scale were observed. However, several drawbacks, such as using uncommon silica precursors, demanding stoichiometric amounts of water, and employing a poor solvent of polyamic acid, are brought about with the aforementioned systems.

In the present study, a novel system for preparing polyimide-silica hybrids with silica particles at a nanometer scale was established. Several special techniques, such as the nonaqueous sol-gel process, employing organically substituted phenoxy silanes, and modification of the chemical structure of polyimide, are applied to result in the hybrid polyimide-silica nanocomposites. The prepared polyimide-silica films are observed to be transparent, while containing a high silica content of 45%.

EXPERIMENTAL

Materials

Phenyltriethoxysilane (PTEOS) from Tokyo Kasei Organics Chemicals (TCI) was used as received. 4,4'-Oxydipthalic anhydride (ODA), 4,4'-diamino-3,3'-dimethyldiphenylmethane (DDDM), and 4-aminophenol (APN) were from TCI and were purified by sublimation prior to use. *N,N'*-Dimethylacetamide (DMAc) and tetrahydrofuran (THF) from the Tedia Chemical Co. (Fairfield, OH, USA) were distilled under reduced pressure prior to use.

Measurement

IR spectra were recorded with a Perkin-Elmer 842 FTIR-5000 spectrophotometer. ²⁹Si-NMR analysis was performed with a Bruker DSX-400WB solid NMR spectrophotometer with polydimethylsilane as an external standard. Differential scanning calorimetry (DSC) thermograms were recorded with a Seiko 5200 DSC. Thermogravimetric analysis (TGA) was performed with a Seiko Exstar 6000 thermogravimeter. A scanning elec-

Table I Compositions for Synthesis of Polyimide-Silica Hybrid Nanocomposites

Code		PAAOH/PTEOS (Weight Ratio)
Before Curing	After Curing	
PAASi-0	PISi-0	1/0
PAASi-5	PISi-5	0.95/0.05
PAASi-15	PISi-15	0.85/0.15
PAASi-25	PISi-25	0.75/0.25
PAASi-35	PISi-35	0.65/0.35
PAASi-45	PISi-45	0.55/0.45
PAASi-55	PISi-55	0.45/0.55
PAASi-100	PISi-100	0/1

tron micrograph (SEM) was obtained from a Hitachi S-2300 SEM. Thermal mechanical analysis (TMA) was performed with a thermal analyzer TMA-2100.

Procedure for Typical Sol-Gel Reaction

First, polyamic acid was prepared from ODA, DDM, and APN in DMAc as described in the literature²⁰⁻²³ (Scheme 1). The obtained polyamic acid was then purified by reprecipitation from a methanol/water (1:1 by volume) solution to give slight yellow powder product for use in the polyimide synthesis.

Polyimide-silica hybrids were prepared from various compositions based on PTEOS and the obtained powder polyamic acid by reacting in a flask with THF as a solvent. The mixture was then stirred for about 24 h until the reaction solution became homogeneous. The film was prepared by casting the solution on aluminum foil. After being dried at 80°C for 24 h, the film was then heated at 100°C for 2 h, 200°C for 1 h, and 300°C for another 1 h under air.

RESULTS AND DISCUSSION

The synthesis route of the polyimide-silica hybrid is depicted in Scheme 1. Since polyimide is not soluble in organic solvents, the sol-gel reaction was carried out in a solution of polyamic acid.²⁰⁻²³ Generally, the sol-gel reaction requires water to hydrolyze TEOS.²⁰⁻²⁷ However, the existence of water might induce the hydrolysis of polyamic acid, reducing the molecular weight of the polyamic acid, that is, the following formed polyimide.

Therefore, a nonaqueous sol-gel process, that is, an acid-catalysis system of the sol-gel reaction, was performed in our present work to avoid the hydrolysis degradation of polyamic acid during reaction. The reactive scheme of the nonaqueous sol-gel process has been proposed as follows:^{28,29}

Metathesis



Esterification



Hydrolysis

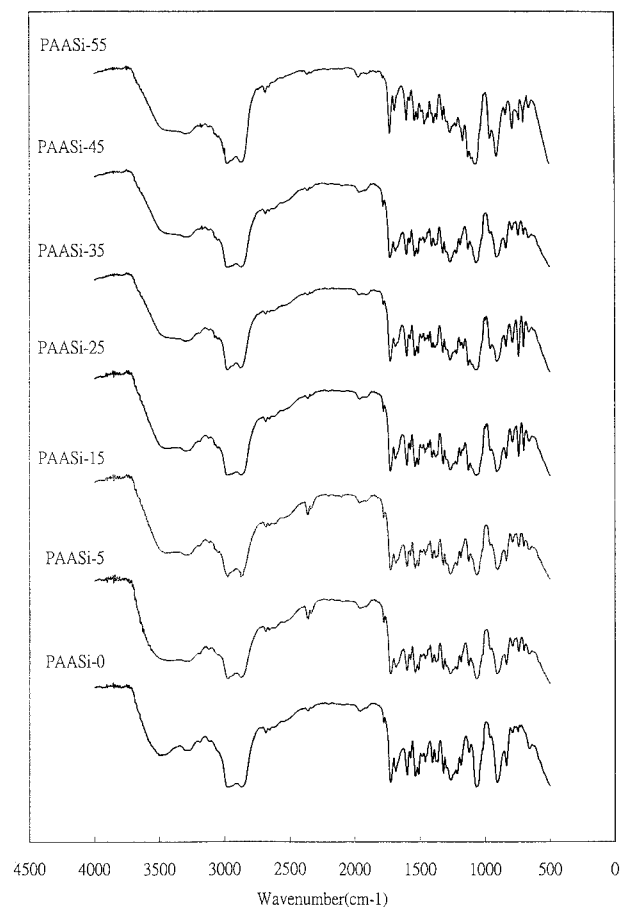


Figure 1 IR spectra of the polyimide-silica hybrid nanocomposites.

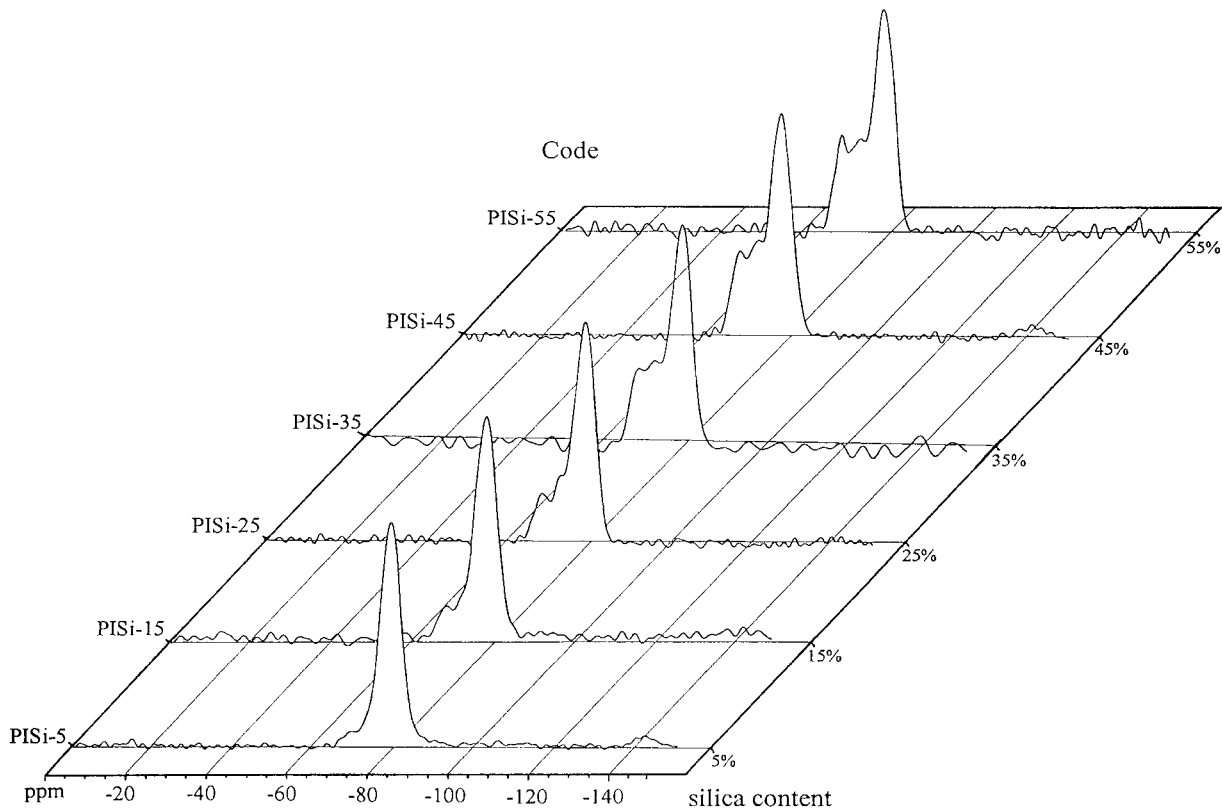


Figure 2 ^{29}Si spectra of the polyimide-silica hybrid nanocomposites.

Condensation



Therefore, this reactive system possesses several advantages relative to the aqueous sol-gel process. The network formation is very fast, tending to avoid or minimize phase separation of the organic polyimide. Additionally, the extremely small pore sizes associated with the silica gel may lead to a greater level of efficiency of entraining polyimide chains in the pores of the inorganic silica network. Furthermore, an acid-catalysis sol-gel reaction provides relatively fast hydroly-

sis and a slow condensation reaction. The slow condensation reaction implies slow formation of the silica network, therefore providing a favorable environment for polyimide chains being able to penetrate in the silica networks. Polyimide-silica hybrids prepared from the above mechanism would thus increase the silica contents in the hybrid, promote the compatibility of polyimide and silica, and, consequently, bring about some benefits in improving their physical and mechanical properties, which can be seen in this elsewhere in this article.

The compositions of the obtained polyimide-silica hybrids are collected in Table I. *p*-Aminophenol, used as an end-capping reagent, as well as methyl-substituted diamine are utilized for obtaining a much more organosoluble polyimide. The increase of solubility of polyimide is expected to avoid or minimize the occurrence of phase separation of polyimide during the period of solvent removal (condensation reaction stage) and, therefore, provide optically transparent materials with enhanced properties. Moreover, the phenoxy-sub-

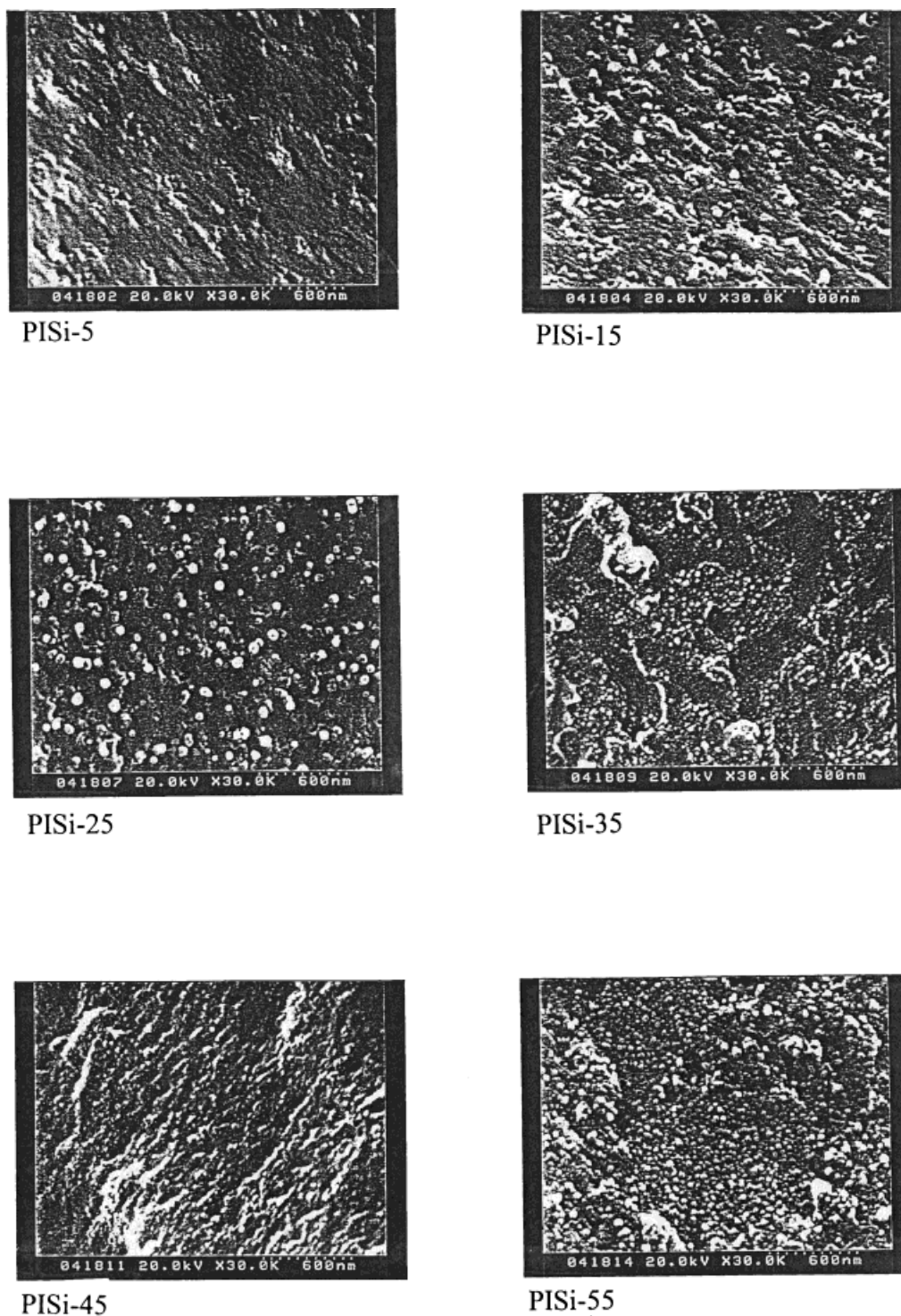
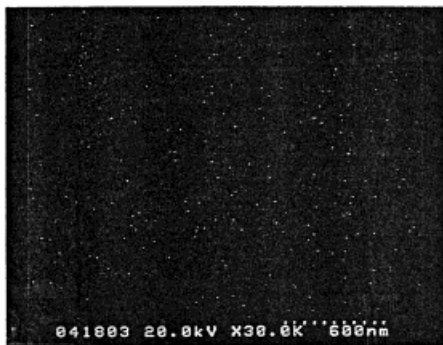


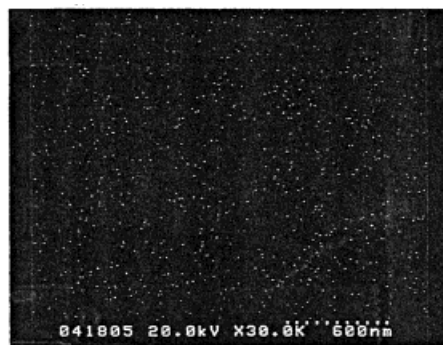
Figure 3 SEM photographs of the polyimide-silica hybrid nanocomposites.

stituted silane, PTEOS, is utilized to replace TEOS. This replacement would introduce phenyl groups into the final formed silica network, to

increase the compatibility between the organic polyimide and the inorganic silica network.²⁰ All the above-mentioned efforts indeed bring effec-



PISi-5



PISi-15



PISi-25



PISi-35



PISi-45



PISi-55

Figure 4 Si-mapping photographs of the polyimide–silica hybrid nanocomposites.

Table II Thermal Properties of the Polyimide-Silica Hybrid Nanocomposites

Samples	Thermal Stability from TGA (°C)					
	In N ₂		In Air		T _g (°C)	
	T _d ^a	R _c ^b	T _d ^a	R _c ^b	DSC	TMA
PISi-0	444	21.4	435	0.6	259	269
PISi-5	451	26.5	445	4.7	276	280
PISi-15	456	28.3	451	7.5	293	300
PISi-25	459	30.5	457	10.3	301	305
PISi-35	467	33.9	463	14.5	321	328
PISi-45	475	39.8	471	19.7	330	339
PISi-55	493	44.7	477	24.8	340	343

^a Temperature at 5% weight loss.

^b Char residuals at 900°C.

tive improvement to the compatibility of polyimide and silica, since the resulting polyimide-silica hybrids are transparent while containing a high silica content of 45%.

The chemical structure of the formed polyimides was examined using IR spectroscopy. Figure 1 shows the IR spectra of a polyamic acid/PTEOS mixture before and after imidization. The conversion of polyamic acid to polyimide could be elucidated by the decreasing of the carboxylic acid absorption at 3400 cm⁻¹ and amide carbonyl absorption at 1650 cm⁻¹ and by the appearance of imide carbonyl absorption at 1720 and 1780 cm⁻¹. Moreover, the appearance of absorptions at 1100 and 830 cm⁻¹ meant the formation of silicon-oxygen bonds, that is, the silica network. The silica network is further characterized by ²⁹Si-NMR (Fig. 2). Three major absorption peaks are observed for the polyimide-silica hybrids and are assigned to the corresponding absorptions of dihydroxy-substituted silica [$-\text{O}-\text{Si}(\text{OH})_2$, -78.2 ppm], monohydroxy-substituted silica [$-\text{O}-\text{Si}(\text{OH})$, -72.3 ppm], and nonhydroxy-substituted silica ($-\text{O}-\text{Si}-\text{O}-$, -68.9 ppm), respectively. This suggests that the formation of a silica-oxygen network structure like silica glass was incomplete.^{20,23} However, the proportion of formed nonhydroxy-substituted silica was observed to increase with increased PTMOS contents.²⁰ This implies that increasing the silicon content of the polyimide-silica hybrid can favor the formation of the silica-glass structure, therefore providing a more complete polyimide-silica hybrid structure. Increasing the silica content of the hybrids certainly results in the formation of opaque materials.²⁰⁻²⁴ The remarkable improve-

ment in increasing the silicon contents for the formation of transparent polyimide-silica hybrids was achieved in this study. The following discussion on the SEM experiment will show the remarkable results:

The SEM results gave important information on the morphology of the hybrid materials. The SEM photographs of the fracture surface of the polyimide-silica hybrid films containing various silicon contents are illustrated in Figure 3. The dispersed silica particles having a diameter of

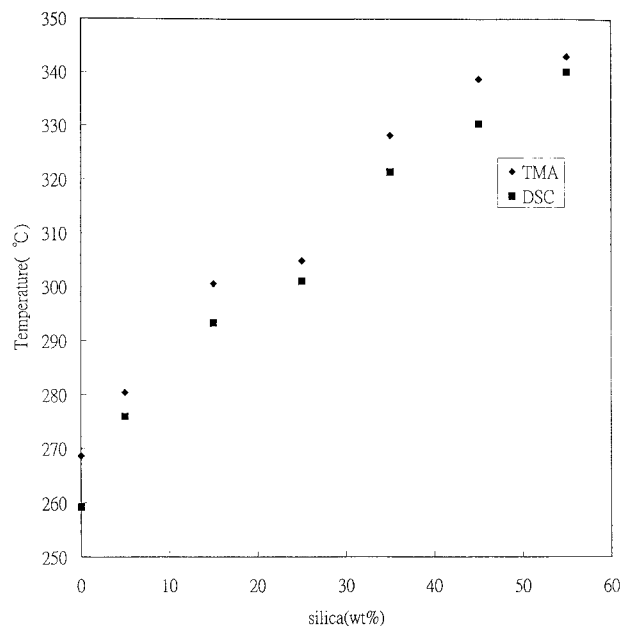


Figure 5 Correlation of the glass transition temperatures of the polyimide-silica hybrid nanocomposites on their silica contents.

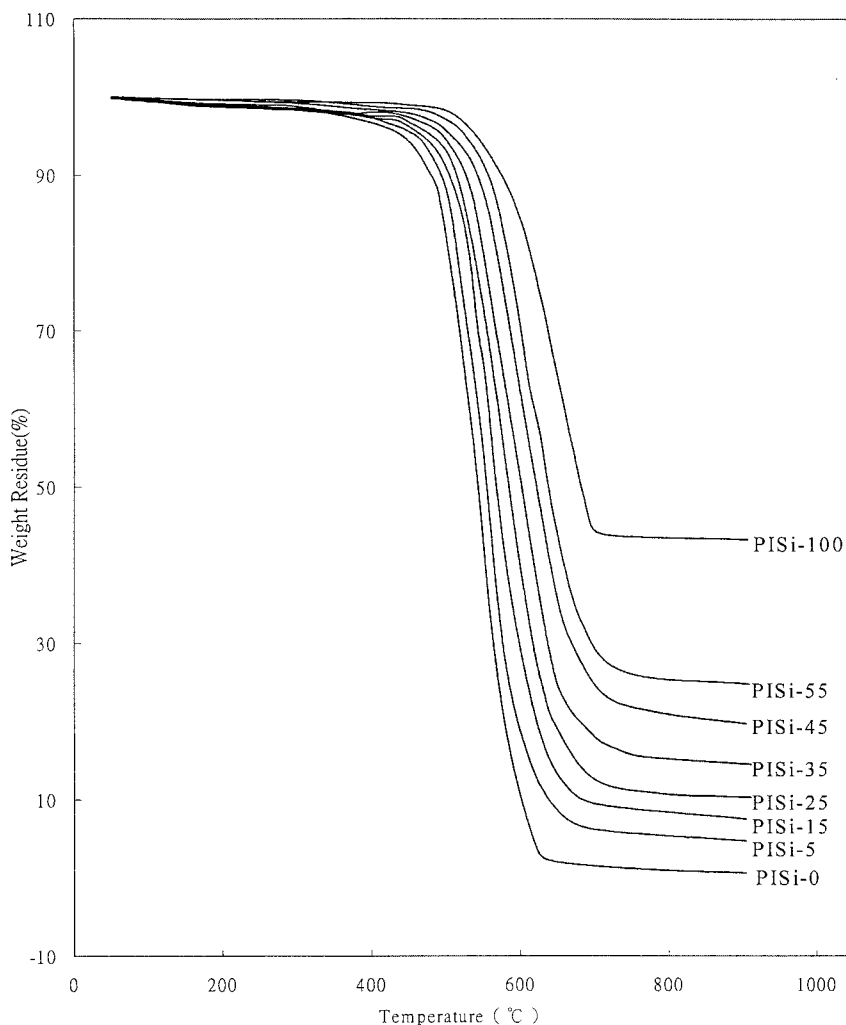


Figure 6 TGA thermograms of the polyimide-silica hybrid nanocomposites in air.

less than 50 nm were observed as white beads. In spite of the particle size increasing with increasing silica content, all the obtained polyimide-silica hybrids are demonstrated to form a nanoscale composite structure. The EDAX corresponding silicon distribution maps of the hybrids are shown in Figure 4. Homogeneous distribution of silicon on the surface of the fracture sections is observed for all the polyimide-silica hybrids.

The glass transition temperatures (T_g 's) of the obtained polyimide-silica hybrids determined by both DSC and TMA are collected in Table II. The relationship between the T_g and the silica content is also shown in Figure 5. The T_g 's of the polyimide-silica hybrids increase with increasing silica content. It is noteworthy that, even when a small amount of 5% silicon is introduced into the hybrid, the T_g of the hybrid is notably enhanced.

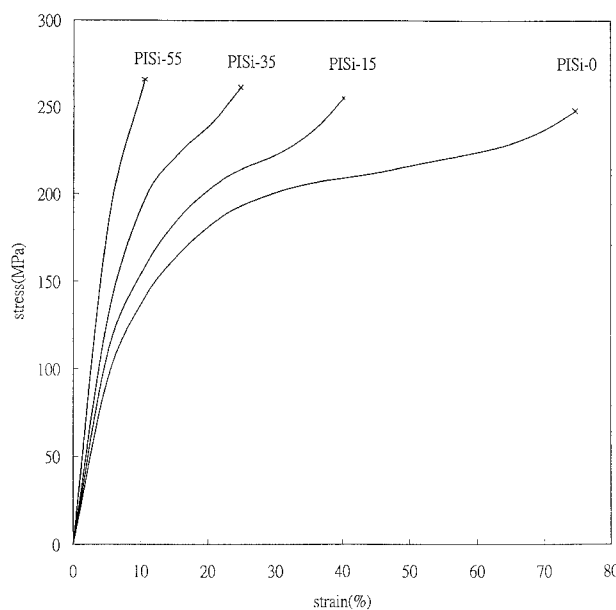
The T_g of polyimide-silica hybrids being decreased by a small content of silica, coming from the plasticizing effect of low molecule weight silica, was reported.²⁰ In the present study, however, the plasticizing effect was not observed. On the other hand, the formation of a silica network limits the chain motion of the polyimide. Therefore, the high T_g of the polymer hybrid was observed. The thermal stability of the polyimide-silica hybrids was investigated by TGA (Fig. 6). The results are summarized in Table II. The decomposition temperature of the hybrids steadily increase with increasing silica content. Since the formed silica network exhibits good thermal stability even at 800°C, the weight loss of the hybrids is coming mainly from the decomposition of the polyimide. The nonchemically bonding silica did not show efficient enhancement in increasing the thermal stability of the polyimide.

Table III TEC of the Polyimide–Silica Hybrid Nanocomposites

Sample	TEC ($\alpha \times 10^6$)		
	50–150°C	150–250°C	250–300°C
PISi-0	55.8	43.6	33.1
PISi-5	48.5	41.7	31.7
PISi-15	46.4	32	29.1
PISi-25	33.5	27.4	22.5
PISi-35	27.6	21.5	19.7
PISi-45	25.3	18.7	15.7
PISi-55	20.8	17.6	13.3

The thermal expansion coefficients (TECs, α) of the polyimide–silica hybrids were measured for probing their potential for application in electronic and aerospace fields. The correlation of the TECs of the hybrids and temperatures was established (Table III). Incorporating silica into polyimide reduces its TEC. Furthermore, by tailoring the silica content, the TEC of the polyimide–silica hybrid could be adjusted to a practicable range.

Moreover, introducing silica into the polyimide by the sol–gel process gives well-dispersed particles in the polymer matrix. This would give the advantage of achieving reinforcement of the hybrid materials. Typical stress–strain curves for the hybrid materials are shown in Figure 7. The

**Figure 7** Stress–strain curves of the polyimide–silica hybrid nanocomposites.**Table IV** Measured Modulus of the Polyimide–Silica Hybrid Nanocomposites

Sample	Ultimate Strength ^a (MPa)	Ultimate Elongation ^b (MPa)	Modulus ^c (MPa)
PISi-0	248	74.8	1830
PISi-15	255	40.2	2119
PISi-35	261	24.9	2504
PISi-55	266	15.6	3526

^a Stress at break.

^b Elongation at break.

^c Initial slope of the stress–strain curve.

samples with silica reinforcement have lower strength but a higher initial modulus (Table IV). This is consistent with the results of earlier studies.^{20,23} It is especially noteworthy that a very high modulus of 3526 MPa is seen for PISi-55. The reinforcement of the silica particles in the polyimide–silica hybrid materials is thus demonstrated.

CONCLUSIONS

In conclusion, a nanocomposite based on a polyimide–silica hybrid was successfully obtained by the sol–gel process with several modified techniques in our investigation for enhancing the compatibility of polyimide and silica. The morphology of the resulting polyimide–silica hybrid films was controlled by the compositions of imidization and the sol–gel reactions. Studies on the thermal properties and the TEC reveal the utilization potential of this type of hybrid. Furthermore, very high stress moduli were obtained for these polyimide–silica hybrid materials. This demonstrates that the well-dispersed particles of silica in the hybrid indeed reinforce these hybrid materials.

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