

Preparation and Properties of Polyimide/Silica Hybrid Composites Based on Polymer-Modified Colloidal Silica

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Received 2 March 2005; revised 2 July 2005; accepted 8 August 2005

DOI 10.1002/app.22896

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A new type of polyimide/silica (PI/SiO₂) hybrid composite films was prepared by blending polymer-modified colloidal silica with the semiflexible polyimide. Polyimide was solution-imidized at higher temperature than the glass transition temperature (T_g) using 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-diaminodiphenyl ether (ODA). The morphological observation on the prepared hybrid films by scanning electron micros-

copy (SEM) pointed to the existence of miscible organic-inorganic phase, which resulted in improved mechanical properties compared with pure PI. The incorporation of the silica structures in the PI matrix also increased both T_g and thermal stability of the resulting films. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2053–2061, 2006

Key words: polyimides; silicas; composites

INTRODUCTION

Organic-inorganic hybrid composites have been recognized as a new class of advanced materials because they combine the advantages of inorganic material (rigidity, high thermal stability) and organic polymer (flexibility, dielectric, ductility, and processability).^{1–7} Among the polymers used as matrix materials for the high-performance composites, aromatic polyimides (PIs) have attracted much interest because of their potential applications in the electronic and aerospace industries due to their outstanding dielectric and mechanical properties at elevated temperatures.^{8,9} Additionally, the incorporation of silica (SiO₂) has been proved very effective in enhancing the mechanical and thermal properties of PI.

Several studies have been carried out on the preparation of polyimide/silica (PI/SiO₂) with high-performance, mostly based on the sol-gel method.^{10–16} However, the main concern here is to obtain significant improvements in the interfacial adhesion between polymer matrix and inorganic filler phases by suppressing the phase separation involved. Recently, chemical surface-modification of inorganic fine particles has been employed to improve dispersibility and compatibility in organic phase, thus providing an al-

ternative route for preparing organic-inorganic hybrid composites.^{17–19} In this regard, we reported on the preparation of a new type of PI/SiO₂ composites based on polymer-modified silica gel, using poly(maleic anhydride-co-styrene) [P(MA-ST)] as a grafted polymer.²⁰

In the present study, another attempt to prepare PI/SiO₂ composite films based on colloidal silica particles of 80 nm size, modified with PMMA has been made to ensure better dispersion stability of particles within the polymer matrix due to the possibility of incorporation of PMMA to PI chains via transesterification. Thus, PI/SiO₂ hybrid composites of different silica content were obtained by blending polymer-modified silica with poly(amic acid) (PAA) from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-diaminodiphenyl ether (ODA) in *N*-methyl-2-pyrrolidinone (NMP). The resulting hybrid films were characterized with regard to morphology, thermal stability, and mechanical properties.

EXPERIMENTAL

Materials

Monodispersed colloidal silica in ethanol, containing 20 wt % SiO₂ of 80 nm diameter, was obtained from Catalysts and Chemical Co. Ltd. (Tokyo, Japan). The monomers used to synthesize PI samples were BPDA and ODA. They were obtained from Aldrich Chemicals (Milwaukee, WI) and were used as received. Anhydrous NMP from Lancaster was dehydrated with

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Contract grant sponsor: Korea Science and Engineering Foundation; contract grant number: R01-2003-000-11612-0.

TABLE I
Sample List of Pure PI and PI/SiO₂ Hybrid Composites

| Sample | BPDA (5 mmol) | ODA (5 mmol) | PAA ^a (5 mmol) | PMMA/SiO ₂ ^b (wt %) | SiO ₂ ^c (wt %) |
|--------|------------------|-----------------|------------------------------|--|---|
| PI | 1.47 | 1 | 2.47 | 0 | 0 |
| PI-2.5 | 1.47 | 1 | 2.47 | 2.5 | 2.2 |
| PI-5.0 | 1.47 | 1 | 2.47 | 5.0 | 4.4 |
| PI-7.5 | 1.47 | 1 | 2.47 | 7.5 | 6.6 |
| PI-10 | 1.47 | 1 | 2.47 | 10 | 8.9 |
| PI-20 | 1.47 | 1 | 2.47 | 20 | 18 |
| PI-30 | 1.47 | 1 | 2.47 | 30 | 27 |

^a 10.7 wt % solution in NMP.

^b Calculated polymer-modified silica content (wt %) in the hybrid films assuming that complete imidization of PAA was made.

^c Calculated from the constant A.P., i.e., 134 mg g⁻¹ SiO₂.

molecular sieves. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were purchased from Aldrich Chemicals and were stored in nitrogen. Methyl methacrylate (MMA) from Aldrich Chemicals was purified by distillation before use. 3-Mercaptopropyltrimethoxysilane was purchased from Aldrich Chemicals.

Preparation of polymer silane, PMMA-Si(OMe)₃

To prepare trimethoxysilyl-terminated poly(methyl methacrylate), PMMA-Si(OMe)₃, used as a coupling agent for the synthesis of polymer-modified silica (PMMA/SiO₂), THF solution (17.78 g) containing MMA (18.72 g), 3-mercaptopropyltrimethoxysilane (41.56 mg) and 2,2'-azobis(isobutyronitrile) (40 mg) was stirred under refluxing for 6 h at 60°C. The solution was poured into diethyl ether to precipitate a crude polymer. Precipitation from acetone solution with diethyl ether and drying under vacuum gave 16 g of PMMA-Si(OMe)₃ with the number-average molecular weight (*M_n*) of 8000 as measured by gel permeation chromatography (GPC).

Preparation of polymer-modified silica, PMMA/SiO₂

Colloidal silica (40 cm³) was added to a mixture of 4 g PMMA-Si(OMe)₃ in 277.44 g 1,2-dimethoxyethane and 21.34 g THF. The suspension was stirred at 90°C and 277.44 g solvent was removed by azeotropic distillation. Then, the mixture was gently stirred under refluxing at 75°C for 12 h to obtain the polymer-modified silica. The polymer-modified silica was separated from unreacted polymer by centrifugation in acetone and dried under vacuum, giving the yield of 7 g. The attached polymer (A.P.), defined as the amount of polymer bound on silica per unit gram of SiO₂, was determined by weight loss (mg) during temperature elevation from 100°C to 800°C, after having the

sample at 100°C for 30 min, according to previous studies.¹⁹

Preparation of polyimide/silica hybrid films

The PAA, a precursor molecule to PI, was synthesized by the reaction of the dianhydride (BPDA) and diamine (ODA) in NMP as follows: into a 250-mL flask equipped with nitrogen inlet and mechanical stirrer, ODA (5 mmol, 1 g) and NMP (10.28 g) were placed and the mixture was stirred until a clear solution resulted. An equimolar amount of solid BPDA (5 mmol, 1.47 g) was added in one batch to the ODA solution and the wall of the flask was washed with 10.28 g of NMP. The reaction mixture was stirred for 12 h at ambient temperature to give a transparent yellow viscous solution of 10.72 wt % of PAA. PAA solutions prepared from the higher concentrations than 15 wt % were found to be too viscous to get homogeneous blends with the polymer-modified silica.

Consecutively, the required ratios of silica composites (PMMA/SiO₂) in NMP were blended with PAA in NMP. The blends were stirred for 24 h and subjected to ultrasonic irradiation for 30 min to achieve complete dispersion of silica composites into PAA. The blends were then cast on glass plates, dried in an electric furnace at 70°C for 6 h, cured at 100 and 200°C for 1 h each, and postcured at 300°C for 30 min under nitrogen, as fixed on the substrates, to obtain yellow colored translucent films. The transparency of the resulting films was reduced with the increase of silica content probably due to the aggregation effect. Furthermore, we prepared the PI/SiO₂ films (PI-U-5) using 5 wt % unmodified silica as counter sample. The PI/SiO₂ hybrid films prepared were denoted as PI, PI-2.5, PI-5.0, PI-7.5, PI-10, PI-20, and PI-30, where the number indicates the weight percent of polymer-modified silica, PMMA/SiO₂, in the hybrid films, as calculated by assuming that complete imidization of PAA was carried out (Table I).

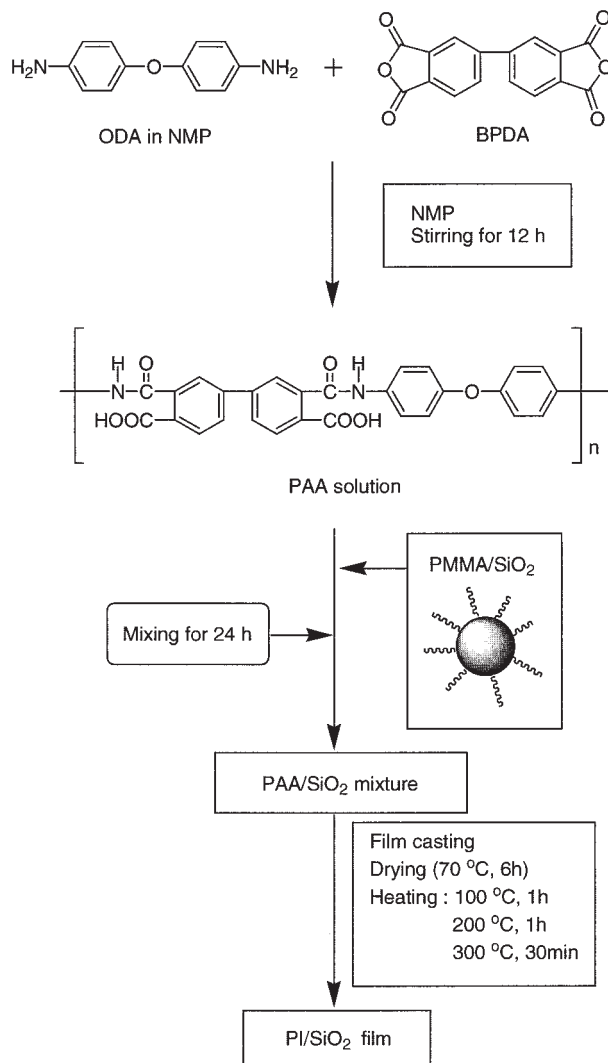
Characterization

The inherent viscosity (η_{inh}) of PAA was determined at a concentration of 0.5 g/dL in NMP at 30°C by an Ubbelohde viscometer. ²⁹Si cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were recorded using a 7-mm rotor probe on a Bruker Advance 300. The chemical shifts were given with reference to tetramethylsilane (TMS). Infrared (IR) spectra were recorded in the range of 4000–400 cm⁻¹ on a JASCO-FT/IR-460. The M_n of the polymer was determined by GPC on TSK gel 3000H with a THF eluant, based on calibration with polystyrene (PS) standard. The scanning electron microscopy (SEM) study was carried out with a Hitachi S-4200, focusing on the surface of hybrid films. Thermogravimetric analyses (TGA) studies on the samples were performed using TA instrument Q50 at a heating rate of 20°C/min under a nitrogen purge. Differential scanning calorimetry (DSC, TA instrument Q100) measurement was conducted on pure PI and hybrid films from 25 to 450°C under a nitrogen purge, at a heating rate of 10°C/min. The sample weight was in the range of 5–6 mg. The thermograms shown in this paper were the results of the second run. The (thermal) glass transition temperature (T_g) by DSC was taken as the middle point of the heat flow versus temperature curve at the transition interval. The ratio of the loss-to-storage modulus, $\tan \delta$, characterizing dynamic thermal motions of PI and hybrid materials was obtained with Rheometrics dynamic analyzer (RDA) at a heating rate of 5°C/min and a frequency of 1 Hz. The (dynamic) T_g by RDA was identified with the maximum of the $\tan \delta$ versus temperature curve. Mechanical (tensile) properties of the hybrid films were measured using a Tinius Olsen universal testing machine (UTM) at an extension rate of 2 mm/min. Small dumb-bell specimens with waist dimensions of 20 × 10 mm² were used for the tensile tests and the thickness of the samples was in the range of 0.08–0.10 mm. The mechanical properties of each sample were determined from an average of at least three tests. When the silica content was more than 10 wt %, no phase separation was observed during the reaction, but the resulting films were too fragile to be characterized for UTM and RDA studies.

RESULTS AND DISCUSSION

Sample preparation

The synthetic scheme for the PI/SiO₂ hybrid composites is shown in Scheme 1. The polymer-modified silica was synthesized by the reaction of trimethoxysilyl-terminated PMMA with the surface hydroxyl group of colloidal silica particles. The reaction using the alkoxysilane will give a stable covalent bonding via the siloxane bond on silica. Thus, if it is possible to opti-



Scheme 1 Preparation of PI/SiO₂ hybrid composites.

mize the reaction conditions in the coupling to prevent the particle aggregation, the coupling reaction using polymer silane would be available for the modification of inorganic colloidal particles. The polymer silane can be easily synthesized by the radical polymerization in the presence of 3-mercaptopropyl-trimethoxysilane. In this modification, azeotropic removal of methanol and water produced during the reaction gave an effective attachment of the grafted polymer. The polymer-modified silica thus prepared would be expected to provide the stability in dispersion media and the favored interaction between organic and inorganic phases. The PI precursor, PAA, was synthesized by the condensation reaction of the dianhydride (BPDA) and diamine (ODA) in NMP at 10.72 wt % solid concentration. The inherent viscosity (η_{inh}) of PAA solution was 0.51 dL/g, which is considered to be of sufficiently proper molecular weight for preparation of homogeneous PAA/SiO₂ solution. The temperature range for imidization was between 250 and

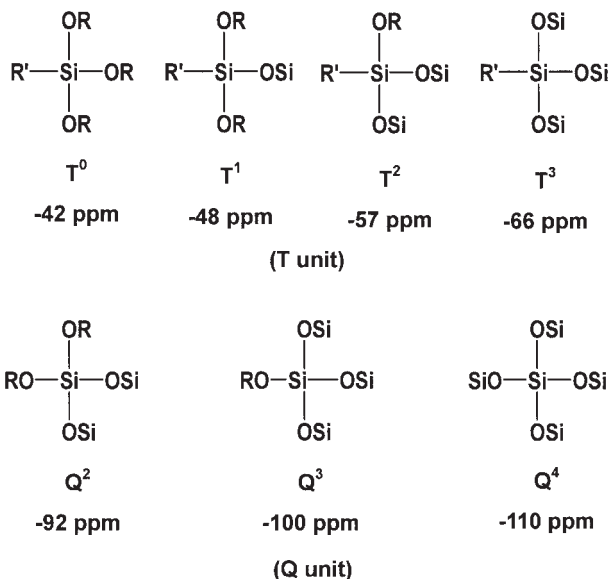


Figure 1 Key to the structural features detected by ^{29}Si CP/MAS NMR.

300°C, which is nearly identical to that for the condensation reaction and the loss of solvent.

The PI/SiO₂ hybrid films were successfully prepared using the polymer-modified silica for the purpose of improving the affinity of silica for the PI matrix. The resulting films containing less than 10 wt % silica were quite homogeneous and had a very fine dispersion state of silica particles within the PI matrix, which may lead to enhanced physical properties of hybrid materials.

Analysis of chemical structure

The ^{29}Si CP/MAS NMR spectra are expected to provide valuable information on the chemical structures of polymer silane, PMMA-Si(OMe)₃, and polymer-modified silica, PMMA/SiO₂. The nomenclature of T^i and Q^i is taken from Glaser et al.²¹ T^i and Q^i denote, respectively, species that have one and no organic side group, where i refers to the number of —O—Si groups bounded to the silicon atom of interest.^{22,23} Figure 1 provides a key to the nomenclature and the chemical shift regions associated with chemical structures used in the present study, to interpret the ^{29}Si CP/MAS NMR spectra of hybrids.

As shown in Figure 2, the major peak characterizing the polymer silane was observed at -42 ppm (T^0 structure unit) because of the specified type of silane silicon of PMMA—Si(OMe)₃. The spectrum of polymer-modified silica resulting from the condensation reaction of the surface hydroxyl group of silica with a polymer silane shows the expected peaks in the Q and T unit regions (Fig. 3). The peak at -48 ppm indicates T^1 structure unit and the other peak at -58 ppm

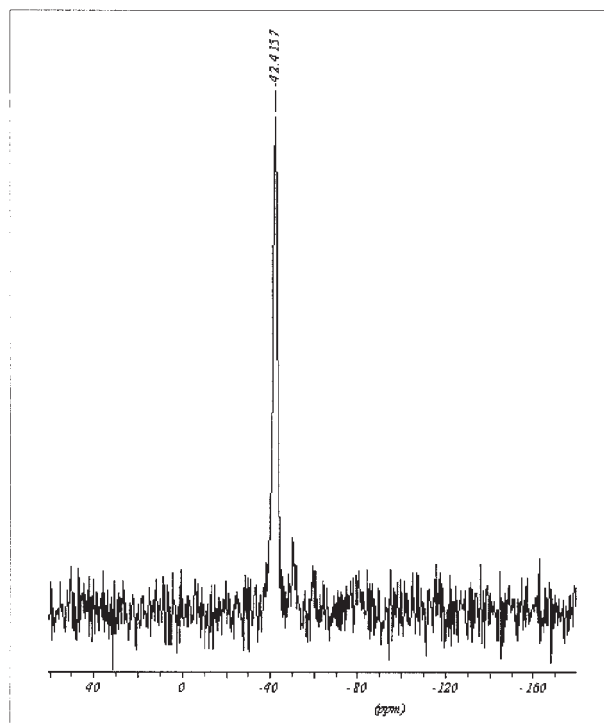


Figure 2 ^{29}Si CP/MAS NMR spectrum of polymer silane, PMMA-Si(OMe)₃.

corresponds to T^2 structure unit. These T^1 and T^2 resonances reveal that a covalent bonding is formed between PMMA and the silica surface to give the

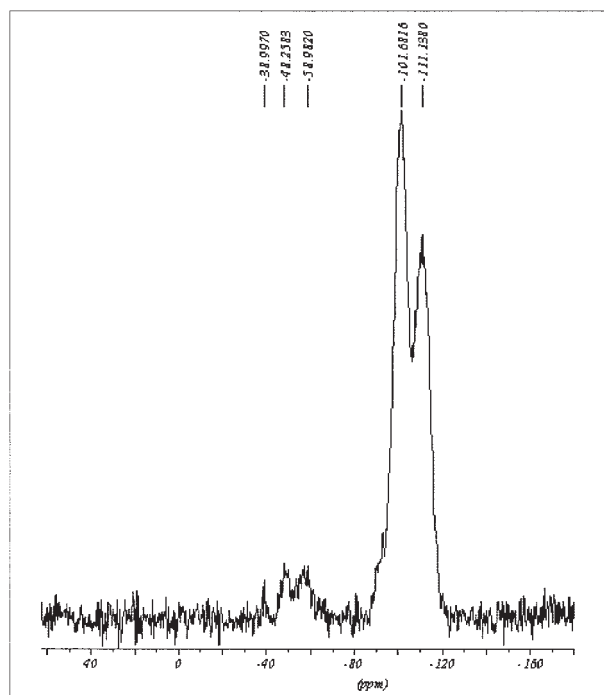


Figure 3 ^{29}Si CP/MAS NMR spectrum of polymer-modified silica, PMMA/SiO₂.

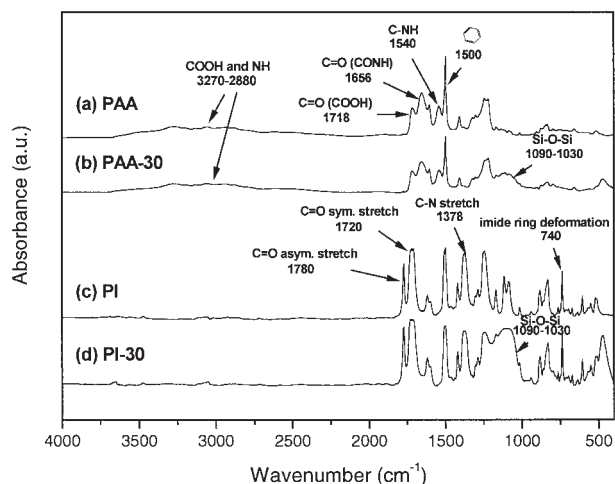


Figure 4 FTIR spectra of (a) PAA, (b) PAA-30, (c) PI, and (d) PI-30.

polymer-modified silica, PMMA/SiO₂. The ²⁹Si CP/MAS NMR spectrum of PMMA/SiO₂ also shows three peaks at about -92, -101, and -111 ppm corresponding to Q², Q³, and Q⁴, respectively.

Structural characterization of PAA, PI, and PI/SiO₂ hybrid films was carried out using the FTIR analysis. Figure 4 shows the FTIR spectra of pure PAA, pure PI, PAA-30, and PI-30 films, where 30 means the wt % of PMMA/SiO₂ in composites. The absorption bands at 1540, 1656, and 1718 cm⁻¹ in PAA film are attributed to the C—NH, C=O (CONH), and C=O (COOH) characteristic band, respectively, [Figs. 4(a) and 4(b)]. Another broad absorption band at 2880–3270 cm⁻¹ indicates the presence of the OH (COOH) and NH groups in PAA. After the thermal imidization of PAA, the C—NH stretching band, COOH and NH bands in PAA were not observed in the spectra [Figs. 4(c) and 4(d)]. Instead, new bands corresponding to PI were observed at 1780 cm⁻¹ (C=O, asymmetric stretching), 1720 cm⁻¹ (C=O, symmetric stretching), 1376 cm⁻¹ (C—N stretching), and 740 cm⁻¹ (imide ring deformation) in imide groups for all samples, which indicates the successful chemical imidization of PI. Also, the characteristic absorption bands representing Si—O—Si asymmetric stretching are observed at 1030–1090 cm⁻¹ in the spectra of hybrid films.

Figure 5 shows the FTIR spectra of pure PI and PI/SiO₂ hybrid films containing various contents of polymer-modified silica. A broad Si—O—Si band is observed around 1030–1090 cm⁻¹ in spectra, but the differences between PI-2.5 and PI-7.5 could not be clearly observed because of the low silica contents in the prepared hybrid materials. However, this absorption band over 7.5 wt % of polymer-modified silica is broader and the intensity of absorption band also increases with increasing polymer-modified silica content.

Microstructure analysis

The SEM results can give important information on the morphology of hybrid materials. The surfaces of pure PI and PI/SiO₂ hybrid films containing various amounts of polymer-modified silica observed by SEM are shown in Figure 6, where the bar of each picture represents 300 nm. It can be observed from Figure 6 that the fairly spherical silica particles were embedded into the PI matrix and the average diameter of the silica domains is estimated to be about 80 nm, indicating the formation of a nanocomposite. The polymer modification of silica surface seems to generate the interphase region between the outer surfaces of two silica particles due to the attached polymer chains and thus has a tendency to prevent the aggregation of the silica particles. In this regard, this modification may increase the phase compatibility between organic and inorganic phases, giving a fine dispersion of silica particles in the PI matrix. However, as the silica content increases, the aggregation tendency caused by the increase in particle number appears to increase, which brings about the macrophase separation [Figs. 6(f) and 6(g)]. Particle agglomeration and poor phase compatibility may act as a weak point in the hybrid materials when an external stress is applied to them, thereby resulting in the deterioration of properties involved. On the other hand, as shown in Figure 6(h), for the PI-U-5 film containing 5 wt % unmodified silica, particles are agglomerated because of a poor interfacial adhesion between organic and inorganic phases, and hence, a significant coarsening during phase separation is observed as compared to the PI/SiO₂ hybrid films based on polymer-modified silica.

Thermomechanical properties

The thermal properties of the hybrid films can also be effectively improved by the introduction of the poly-

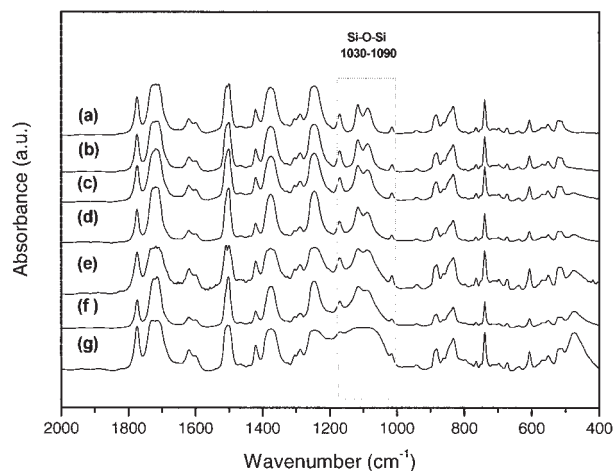


Figure 5 FTIR spectra of pure PI and PI/SiO₂ hybrid films: (a) PI; (b) PI-2.5; (c) PI-5.0; (d) PI-7.5; (e) PI-10; (f) PI-20; and (g) PI-30.

mer-modified silica in nanosize, on the basis of the fact that these materials have inherently good thermal stability. Figure 7 shows the TGA curves of pure PI and PI/SiO₂ hybrid films with various silica contents. The thermal decomposition temperatures (T_d 's) of prepared films are listed in Table II together with the data on T_g 's (see later). Continuous weight losses are observed below 200°C corresponding to the release of water and solvent during heating (Fig. 7). The decomposition temperature at 5% weight loss (T_{d5}) of hybrid films increases with the increase in silica content up to a silica content of 10 wt %. The final residue at 900°C is regarded as the real silica and is proportional to the silica content, suggesting the successful incorporation of silica in the PI/SiO₂ hybrid materials.

For pure PI and PI/SiO₂ hybrid films, thermal degradation occurred in two stages, as observed in the differential thermogravimetric curve (DTG curve, Fig. 8). The first stage appeared during 25–200°C with 2% weight loss, as a result of the release of water and

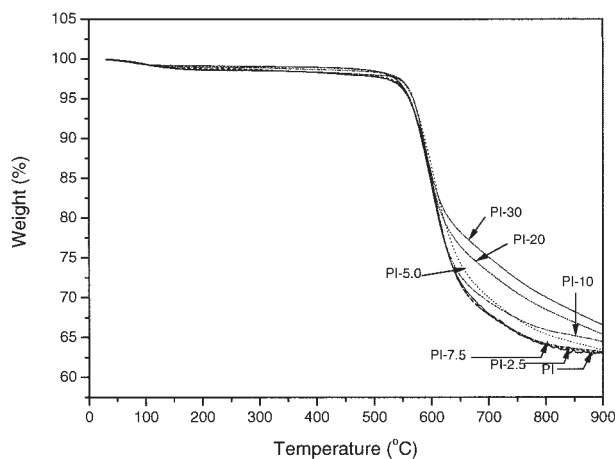


Figure 7 TGA curves of pure PI and PI/SiO₂ hybrid films with different polymer-modified silica contents.

solvent, and the second stage appeared between 550 and 570°C because of the degradation of imide segment. Notably, the maximum temperature at the second stage increased with the silica content when the modified silica was incorporated below 10 wt %, because of the favorable reinforcing effect of polymer-modified silica. In other words, 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 PI matrix and the silica particles. When the silica content exceeded 10 wt %, the T_d and the degradation rate of hybrid films were slightly reduced, but were still higher than that of pure PI. Thus, the introduction of polymer-modified silica into the PI matrix certainly improved the thermal stability of the resulting hybrid composites.

The silica content and dispersion state of silica particles within PI matrix can also affect the cooperative motions of the polymer chains at T_g . The thermal T_g and dynamic T_g of PI and PI/SiO₂ hybrids obtained from DSC (Fig. 9) and RDA (Fig. 10), respectively, are summarized in Table II. It is observed that both types of T_g 's increase with increasing silica content until 7.5 wt %, though with some definite differences in magnitude mainly because of the difference in operational principles,²⁴ in agreement with the general expectations. This increase in T_g may result from the strong interaction between silica particles and PI matrix, thereby limiting the movement of PI molecules (i.e., the segmental mobility), due to the combined effect of the use of nano-sized silica particles and the polymer modification of silica surface.²⁵

On the other hand, the dynamic T_g by RDA is a prominent relaxation associated with the dynamic mechanical transition between chain segments in the amorphous region. So, it can also give information on dynamic thermal property of polymer chains via the glass transition besides the T_g value. Typically, the

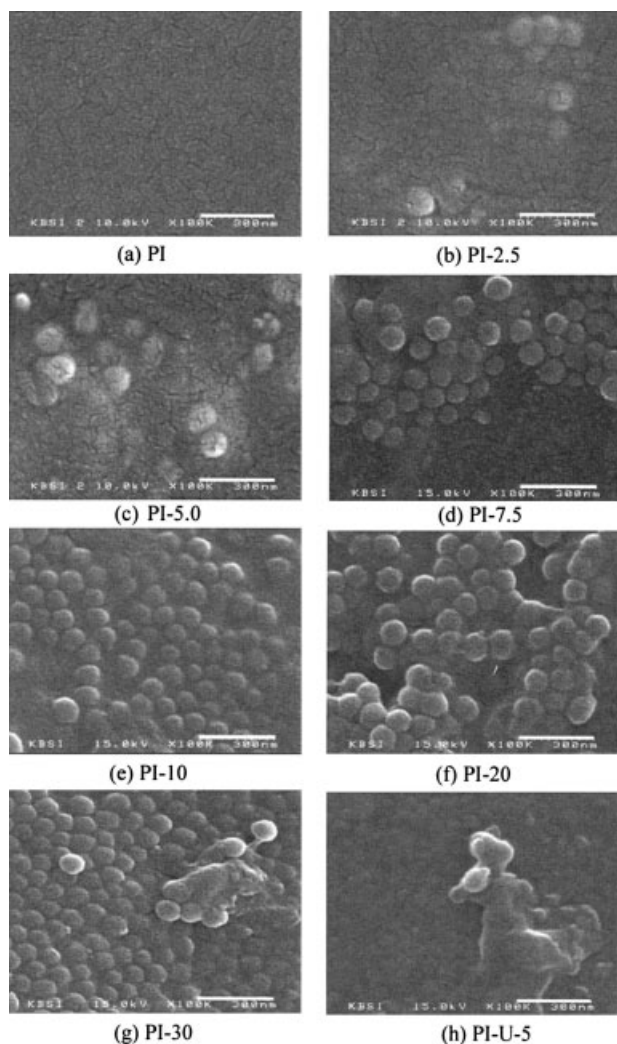


Figure 6 SEM micrographs of pure PI and PI/SiO₂ hybrid films.

TABLE II
Thermal Properties of Pure PI and PI/SiO₂ Hybrid Composites

| Sample | Thermal decomposition | | | | T_g (°C) | |
|--------|-----------------------|------------------|------------------|--------------------------|------------------|------------------|
| | T_{d5}^a (°C) | T_{d10}^b (°C) | T_{max}^c (°C) | Residue ^d (%) | DSC ^e | RDA ^f |
| PI | 558.87 | 580.89 | 598.57 | 62.86 | 265.6 | 285.5 |
| PE-2.5 | 562.75 | 583.60 | 602.79 | 63.06 | 267.9 | 289.7 |
| PI-5.0 | 567.10 | 588.79 | 609.25 | 63.43 | 269.8 | 292.1 |
| PI-7.5 | 568.26 | 586.44 | 601.77 | 63.21 | 273.0 | 294.2 |
| PI-10 | 568.68 | 586.03 | 599.05 | 64.49 | 269.8 | 303.0 |
| PI-20 | 562.13 | 583.52 | 595.37 | 65.38 | 268.2 | — |
| PI-30 | 561.77 | 582.64 | 589.99 | 66.56 | 266.8 | — |

^a Thermal decomposition temperature corresponding to 5% weight loss.

^b Thermal decomposition temperature corresponding to 10% weight loss.

^c Maximum rate temperature of weight loss corresponding to the decomposition of PI.

^d Residual ash at 900°C from TGA results.

^e T_g from the second heating traces of DSC measurements conducted with a heating rate of 10°C/min in nitrogen.

^f T_g determined by RDA measurements conducted with a heating rate of 5°C/min at 1 Hz.

magnitude of $\tan \delta$ at T_g , being a measure of the energy-damping, decreases with increasing silica content in PI/SiO₂ composites.^{11,26} However, such a trend is not clearly observed in our system (see Fig. 10). By contrast, the breadth of $\tan \delta$ relaxation reflecting the cooperative nature of polymer chains in motion at T_g is generally broadened for a simple particle-filled system.^{26,27} In our system, too, the broadening of $\tan \delta$ via the T_g can be observed at moderate silica contents. This may suggest that the cooperativity of polymer chains moving in concert via the transition decreased by the addition of silica particles in PI matrix due to the result of the restricted movement of PI chains caused by silica particles acting as transient crosslink points in the well-dispersed composite system.

Mechanical properties

The achievement of reinforcement by the incorporation of silica in PI matrix can be well reflected in

mechanical properties of hybrid composites. Usually, the properties of hybrid materials are determined by the nature of the interface between the constituting phases. Thus, a great variety of properties can be obtained with hybrid materials just by alteration of the morphological or interface properties. As stated before, the present PI/SiO₂ hybrid composites exhibited a good interfacial adhesion due to the polymer modification of nano-sized silica particles, thus the external stress can be distributed and transferred efficiently from the matrix to the particle.

Typical stress-strain curves of the pure PI and PI/SiO₂ hybrid films with various polymer-modified silica content are presented in Figure 11 and the results are summarized in Table III. In addition, ultimate properties (tensile strength and elongation at break) and initial tensile modulus of the pure PI and PI/SiO₂ hybrid films are given in Figure 12 as a function of the polymer-modified silica content. Interestingly, when 5 wt % silica was introduced, the tensile strength of

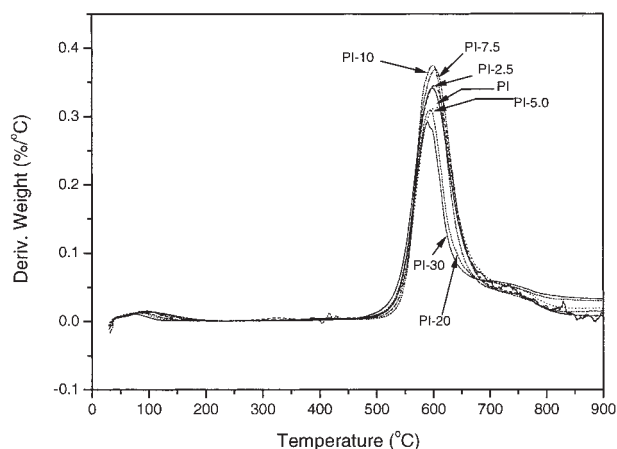


Figure 8 DTG curves of pure PI and PI/SiO₂ hybrid films with different polymer-modified silica contents.

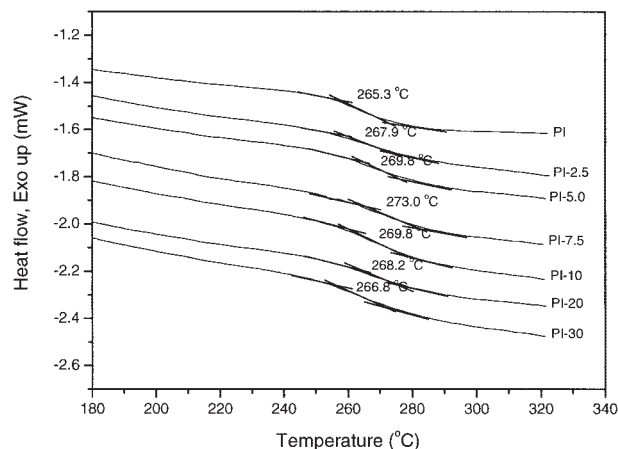


Figure 9 DSC thermograms of pure PI and PI/SiO₂ hybrid films with different polymer-modified silica contents.

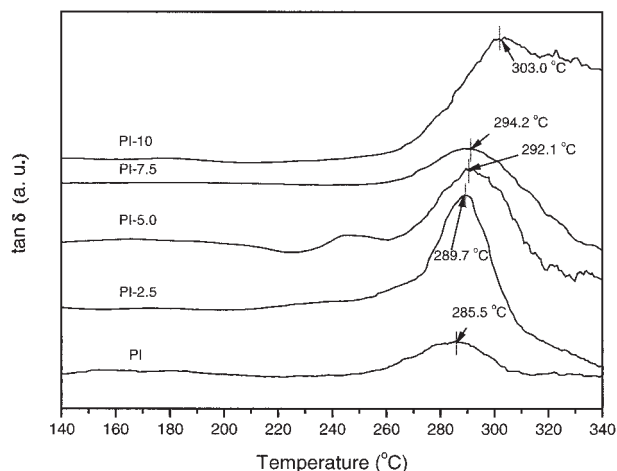


Figure 10 Tan δ versus temperature curves of pure PI and PI/SiO₂ hybrid films with various polymer-modified silica contents.

hybrid films increased by 83% (from 105.51 MPa for PI to 193.67 MPa for PI-5), and furthermore, the elongation at break increased by 39% (from 10.90% for PI to 15.19% for PI-5).

As shown in Table III, the initial tensile modulus of hybrid films also obviously increased by 23% (from 1.69 GPa for PI to 2.08 GPa for PI-5), indicating the increase of rigidity of hybrid materials probably due to the enhanced interfacial adhesion between PI and silica in the present sample. However, when the polymer-modified silica content was further increased to 5.0 wt %, the mechanical properties were decreased. This may be due to the macrophase separation caused by the aggregation effect of silica particles occurring at higher silica contents, as confirmed by the SEM observation (Fig. 6).

Before closing, significant improvements in thermal and mechanical properties for the current PI/SiO₂

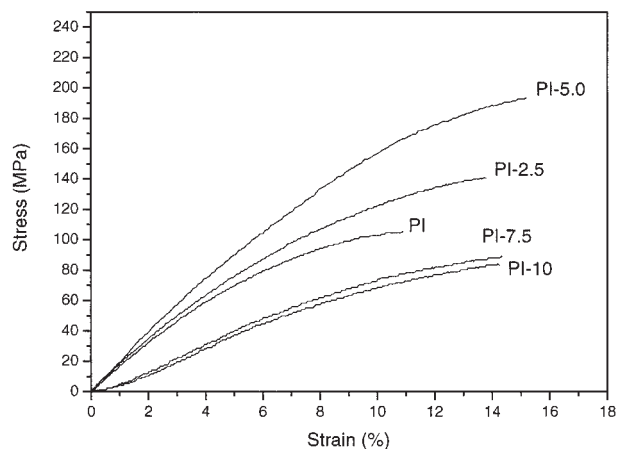


Figure 11 Stress-strain curves of pure PI and PI/SiO₂ hybrid films with various polymer-modified silica contents.

TABLE III
Mechanical Properties of Pure PI and PI/SiO₂ Hybrid Composites

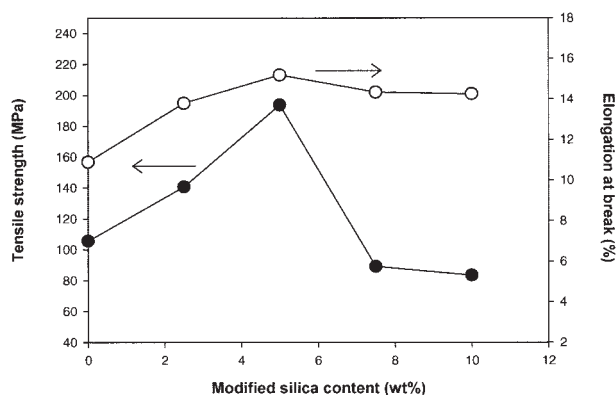
| Sample | Silica content ^a (wt %) | Tensile modulus ^b (GPa) | Tensile strength ^c (MPa) | Elongation at break (%) |
|--------|------------------------------------|------------------------------------|-------------------------------------|-------------------------|
| PI | 0 | 1.69 | 105.51 | 10.90 |
| PI-2.5 | 2.5 | 1.79 | 140.63 | 13.80 |
| PI-5.0 | 5.0 | 2.08 | 193.67 | 15.19 |
| PI-7.5 | 7.5 | 0.87 | 89.18 | 14.34 |
| PI-10 | 10 | 0.71 | 83.42 | 14.26 |

^a It refers to the content of polymer-modified silica, PMMA/SiO₂.

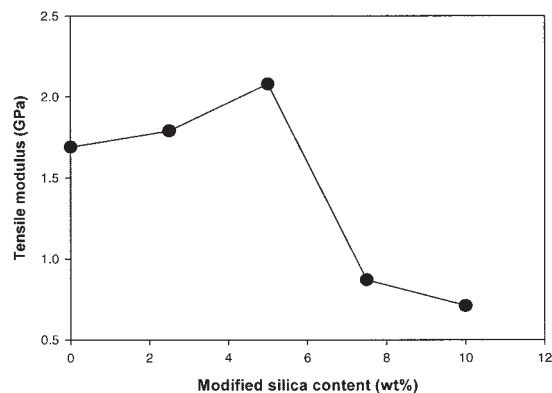
^b Initial slope of the stress-strain curve.

^c Stress at break.

hybrids compared with pure PI and PI/unmodified silica should be attributed to the enhanced interfacial adhesion (or compatibility) based on polymer-modification of nano-sized silica particles. Therefore, we believe that the present study can give a novel route to the preparation of polyimide/silica hybrid composites of high performance.



(a)



(b)

Figure 12 Effect of polymer-modified silica content on tensile strength, elongation at break (a) and tensile modulus (b) of the PI/SiO₂ hybrid films.

CONCLUSIONS

To improve the affinity of silica particles for the polyimide (PI) matrix, new PI/SiO₂ hybrid composites were successfully prepared using polymer-modified silica based on nano-sized colloidal silica in this work. The formation of polymer-modified silica, PMMA/SiO₂, and the conversion of PAA into PI and hybrid composites were confirmed by the ²⁹Si CP/MAS NMR and FTIR spectra, respectively. The SEM observation on hybrid films pointed to the existence of miscible inorganic-organic phase, which resulted in significant improvement in mechanical properties due to the fine dispersed morphology. Thermomechanical studies by TGA, DSC, and RDA also exhibited the higher thermal stability and the higher *T_g* than pure PI and PI/unmodified silica hybrid films because of the enhanced interfacial adhesion between polymer-modified silica and PI.

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