Mechanical and Thermal Properties of Ceramic-Modified Poly(amide imide)

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ABSTRACT: Poly(amide imide)–epoxysilane (coupling agent) composites were reacted with silica, a condensation product of tetraethylorthosilicate (TEOS), by a sol–gel process and were then cast into films. After this procedure, the chemical characteristics and mechanical and thermal properties were measured. Fourier transform infrared showed that silica existed in the poly(amide imide) matrix. When a proper amount of silica was added to the poly(amide imide) matrix, the tensile strength, elongation, and toughness increased greatly. A poly(amide imide)/30 wt % epoxysilane composite with 20 wt % TEOS had the best mechanical properties. Thermogravimetric analysis under nitrogen and oxygen atmospheres indicated that the char contents increased with the amount of silica. The glass-transition temperatures of the poly-(amide imide)–silica nanocomposites were observed around 170–180°C with differential scanning calorimetry. This approach may be a new method for the low-temperature thermal curing of poly(amide imide). © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1780–1788, 2004

Key words: nanocomposites; silicas; toughness

INTRODUCTION

In the sol–gel process, a liquid-phase organometallic compound is hydrolyzed and condensed to form a ceramic substance. First, a sol in which particles are dispersed is produced, and these particles form a coagulated gel, eventually forming a ceramic.[1,2] This method has an advantage, in that high-purity ceramics can be fabricated at lower temperatures than those used in the regular ceramic process. This has led to various studies for the past 20 years. The most representative reaction in the sol–gel process is the hydrolysis of tetraethylorthosilicate (TEOS) by an acidic or basic catalyst:[3–6]

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \quad (1)$$
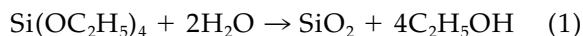
TEOS has been used most frequently because it can be purified easily by distillation, and high-purity ceramics can be obtained via eq. (1). Starting in the field of ceramics, the sol–gel process has been extended to the field of polymers and thus has become the basis for research into organic–inorganic hybrid composites.[7–19] Organic–inorganic hybrid composites are new hybrid composites in which ceramic particles are dispersed in polymer solutions by the sol–gel process. They are also called *ceramers* and *ormocers*.[20,21] Various types of polymers (rubbers, glass-phase polymers, and semicrystalline polymers) can be applied as the organic phases of these new hybrid composites. Extensive research has been conducted on heat-resistant materials, such as polyamide[22–25] and polyimide.[26–32] In particular, polyimide has been investigated intensively because of its wide applications for printed circuit films and semiconductor coating materials in the microelectronics industry, which are due to the high tensile strength, high modulus, low heat-of-thermal-expansion coefficient, low dielectric constant, chemical resistance, and thermal stability of polyimide. However, highly heat-resistant polymers such as polyimide have low reactivity. This causes phase separation, which results from the weak interfacial bond strength between the organic polymer and inorganic ceramic and ultimately degrades entire properties. These problems can be resolved by the direct attachment of reacting groups to the polyimide chain or by the addition of a coupling agent.[25,27] The use of coupling agents improves the bond strength of the two phases, and this enhances the transparency of the hybrid composites; therefore, the produced ceramic particles become smaller.[7,16,18,22–24,26,29,33] When inorganic ceramic particles in organic–inorganic hybrid composites become nanosize, they are called *nanocomposites*. In this research, we fabricated poly(amide imide) (PAI)–silica hybrid nanocomposites that showed increased toughness because of low-temperature ther-

mal curing. New PAI–silica hybrid nanocomposites may have wide applications in areas ranging from semiconductor coating materials to the aerospace industry. In particular, we expect them to be applicable to new insulating materials between turns of superconducting coils.

EXPERIMENTAL

Materials

Poly(trimellitic anhydride chloride-*co*-4,4-methylenedianiline), used as PAI, was dried in a vacuum drying oven at 60°C for 24 h before being used. *N,N*-Dimethylacetamide (DMAc; 99.8%, anhydrous) was used as a solvent. 3-Glycidoxypropyltrrimethoxysilane (98%, epoxysilane) and 1,4-diazabicyclo [2.2.2]octane (98%, triethylenediamine) were used as the coupling agent and catalyst, respectively. TEOS (98%) was used to form the ceramic particles. Calculated amounts of water and diethylamine (>99.5%) dissolved in DMAc were used to catalyze hydrolysis. Every reagent was purchased from Aldrich Chemical Co.(Milwaukee, WI).

Synthesis of the PAI coupling agent

PAI (20 g) was placed in a 500-mL flask that contained a magnetic bar, and 0.2 g of 1,4-diazabicyclo[2.2.2]-octane was added. Then, the mixture was dried in a 60°C vacuum drying oven for 24 h. After the mixture was dried, the flask was sealed with a rubber septum, and a rubber balloon filled with N_2 gas was attached to it. The solvent (anhydrous DMAc; 200 mL) was placed in the flask containing PAI with a syringe. This was placed on a heating stirrer that was fixed at 50°C for 4 h, and PAI completely dissolved. After this, the flask was cooled at room temperature, and 3-glycidoxypropyltrimethoxysilane was added. The flask containing PAI and epoxysilane was placed on a 60°C heating stirrer, and the materials were reacted during 3 days of stirring.

Preparation of the PAI–Silica composition films

The product of the PAI–epoxysilane reaction was placed in a bottle. TEOS, diethylamine dissolved in DMAc, and water were added to produce hydrolysis and condensation. Then, the bottle was kept in a shaking water bath at 60°C for 12 h. This mixture was cooled for a suitable time and then poured into a Teflon mold. After this, PAI–Silica composition films were manufactured by the placement of the mixture into a vacuum drying oven that was set at 80°C for 24 h. The composition films were kept in the vacuum oven until the physical properties were measured.

### Characteristics of the compounds and equipment

An IFS-66 Fourier transform infrared (FTIR) instrument (Bruker Instruments, Billerica, MA) was used for chemical analysis. Each sample was fabricated as a thin film for the measurements. Attenuated total reflection (ATR) was used for surface analysis. The mechanical properties were measured with a universal testing machine (Lloyd Instruments, Hampshire, United Kingdom). The extension rate was 5 mm/min, the gauge length was 25 mm, and the sample dimensions were approximately 40 mm × 5 mm × 0.2 mm. A TGA 2050 (TA Instruments, New Castle, DE) was used. The range of measured temperatures was 30–800°C. The heating rate was 20°C/min, and the rate of N_2 and O_2 gas was set at 50 mL/min. A DSC 2010 (TA Instruments) was used. The range of the measured temperatures was 30–250°C. The heating rate was 10°C/min, and the rate of N_2 gas was set at 50 mL/min.

RESULTS AND DISCUSSION

Chemical characteristics

Scheme 1 indicates the reaction of PAI and epoxysilane. Epoxy groups were reacted with alcohol, amine, acid, and amide groups in PAI, and a tertiary amine was used as the catalyst. Triethylenediamine and DMAc were used as the catalyst and solvent, respectively. For the completion of the reaction, the mixture was reacted for 2–3 days via heating at 60°C. The product was PAI with a silane group, and this silane group could act as a coupling agent and crosslinking agent by self-condensation or condensation with SiO_2. The strong interaction between the silica and polymer (polyamide) by the epoxysilane coupling agent has already been proven with scanning electron microscopy photographs.[22] This condensation reaction was performed at a relatively low temperature (<60°C), and the low-molecular-weight condensation products were eliminated *in vacuo*. The base (diethylamine) catalyst was chosen for its volatility, which made its removal easy. The hydrolysis and condensation rates of TEOS were relatively slow and easily controllable. The films of hybrid materials containing up to 40% silica were transparent. In comparison with polyimide, which is cured via imidification at a high temperature (>200°C), this silane group can be cured at a relatively low temperature. This is the significance of the reaction. When polyimide is used as an insulating material for electronic appliances, it can damage the circuit or shear stress can remain because of its high curing temperature. For these reasons, polyimide may affect the stability of products adversely. However, this new method is thought to resolve these issues.

Figure 1(a) shows the structure of a self-condensation product of a PAI–epoxysilane composite. In this
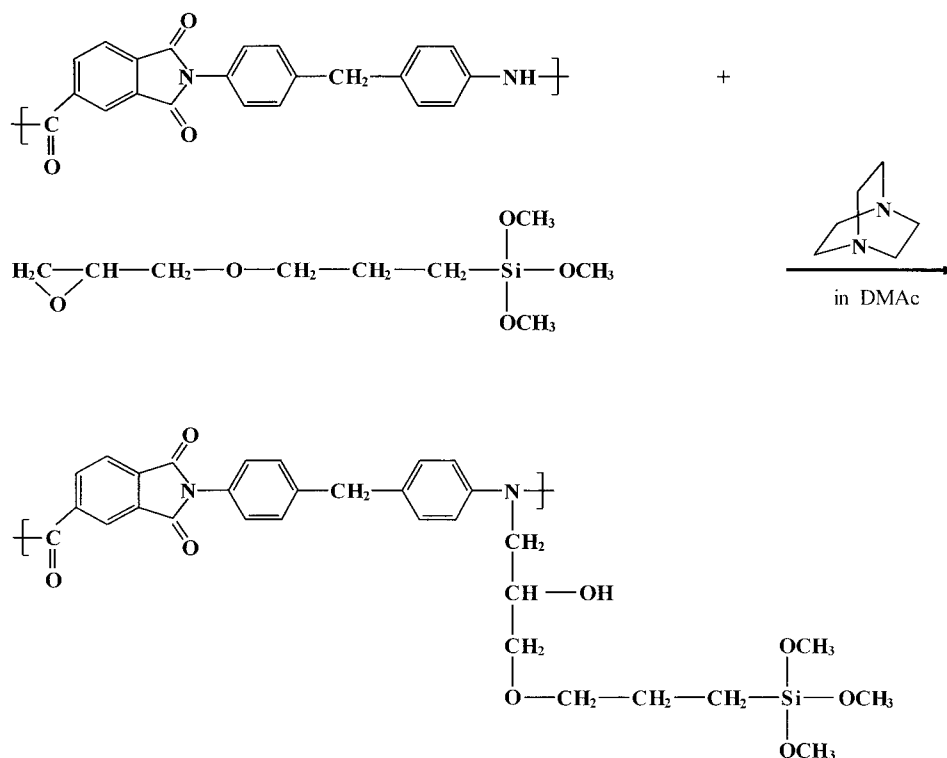
Scheme 1 Synthesis of PAI with the epoxysilane coupling agent.

structure, silane acts as a crosslinking agent, PAI has a grafted structure, and a small portion of unreacted alcohol or alkoxy groups exist. Figure 1(b) shows the case in which silica, the condensation product of TEOS, is added to a PAI–epoxysilane composite. Through the crosslinking of silane groups, a Si—O network structure is formed, and much PAI can be grafted. The structure is thought to enhance the efficiency of the curing reaction and increase the crosslinking density. Depending on the reaction conditions, the silica–polymer composites can have a variety of morphologies, which range from particulate
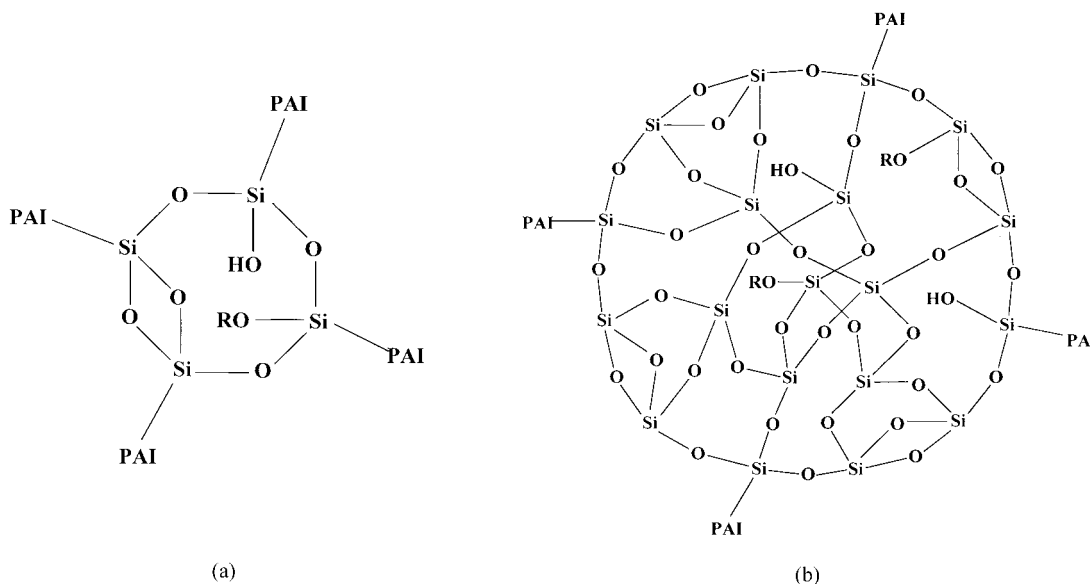

Figure 1 Condensed products of PAI and epoxysilane: (a) PAI–epoxysilane composite and (b) PAI–epoxysilane composite with silica.
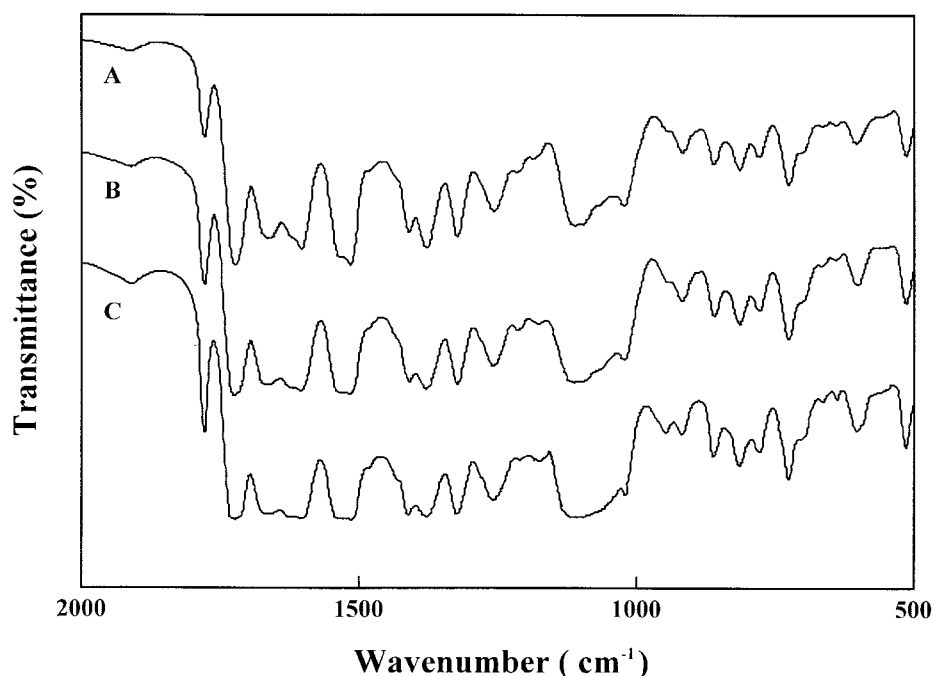
Figure 2 FTIR spectra of PAI–epoxysilane (30 wt %) composites with various silica contents: (A) 0, (B) 10, and (C) 30 wt %.

ceramic particles within the organic matrix to interpenetrating network phases and polymeric domains within the ceramic matrix. The morphologies of the chemically bonded organic–inorganic hybrids, which are to be silica particles, are connected by polymer chains, as shown in Figure 1.

Figure 2 illustrates the changes in the FTIR spectra for composites with various TEOS contents. Near 1100–1000 cm^{-1}, a Si—O—Si stretching vibration peak and a C—O—C stretching vibration peak overlap, and as the TEOS concentration increases, these absorption peaks increase. This results from the increase in Si—O—Si with the increase in the TEOS concentration. These results confirmed that the epoxy group and PAI reacted well and that silica, the condensation product of TEOS, existed. Figure 3 compares the FTIR and ATR spectra for PAI–epoxysilane composites (30 wt %) with 20 wt % TEOS. The intensity of the Si—O—Si peak near 1100–1000 cm^{-1} became stronger with the ATR method than with the transmittance method. This implies that abundant silica existed on the surface, and this was expected to improve the water resistance and abrasion resistance.

Mechanical properties

Fabricating a film out of polyimide is not simple, and it is almost impossible to make samples because it breaks easily. However, PAI–epoxysilane composites can be produced in the form of fine-quality films under 70°C so that the mechanical properties may be monitored. This shows that the condensation of silane

groups leads to the crosslinking of PAI and that low-temperature thermal curing is possible, as mentioned previously. The mechanical properties of composites with various silica contents are shown in Figure 4. The tensile strength was slightly lower for PAI with 30 wt % silane than for the composite with 10 wt % silane, whereas the elongation and toughness were greater. This shows that the crosslinking reactions via the self-condensation of silane groups increased the molecular weight, and this enhanced the impact strength.

Figure 5 presents stress–strain curves for PAI with 30 wt % silane and various TEOS concentrations. The elongation and toughness had a tendency to decrease, whereas the tensile strength increased as the TEOS concentration increased. This could be explained by the molecular weight and the extent of the curing reaction. When PAI is high-molecular-weight, a coupling agent increases the crosslinking density and makes PAI brittle. However, when PAI is low-molecular-weight, a coupling agent increases the molecular weight and acts as a crosslinking agent simultaneously. It is already known that all mechanical properties are enhanced with an increase in the molecular weight. We produced various other reagents to demonstrate this. Also, like polyimide, a high temperature is required for the silane group to react to form a network structure. However, the curing was performed at a low temperature in this research, so the condensation reaction was estimated to occur incompletely, and this may have contributed to the improvement in the softness. Thus, it is thought that a brittle material will be obtained if it is cured at a high tem-
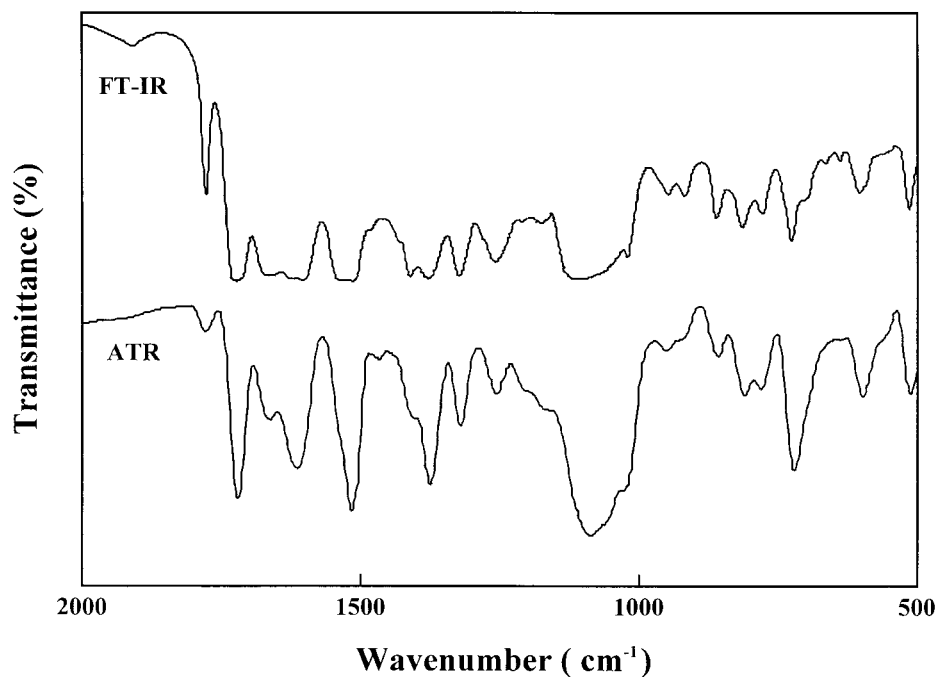
Figure 3 Comparison of ATR and FTIR spectra for PAI–epoxysilane (30 wt %) composites with 30 wt % silica.

perature (~300°C). However, after TEOS contents exceeded 30 wt %, the tensile strength, elongation, and toughness started to decrease. These results shows that silica is not able to bond with PAI because of its excessive concentration in comparison with the coupling agent substance, and so extra phase separation could happen. Figure 6 presents stress–strain curves for PAI–epoxysilane (10 wt %) composites with various silica contents. The tensile strength gradually increased with an increase in the TEOS concentration.
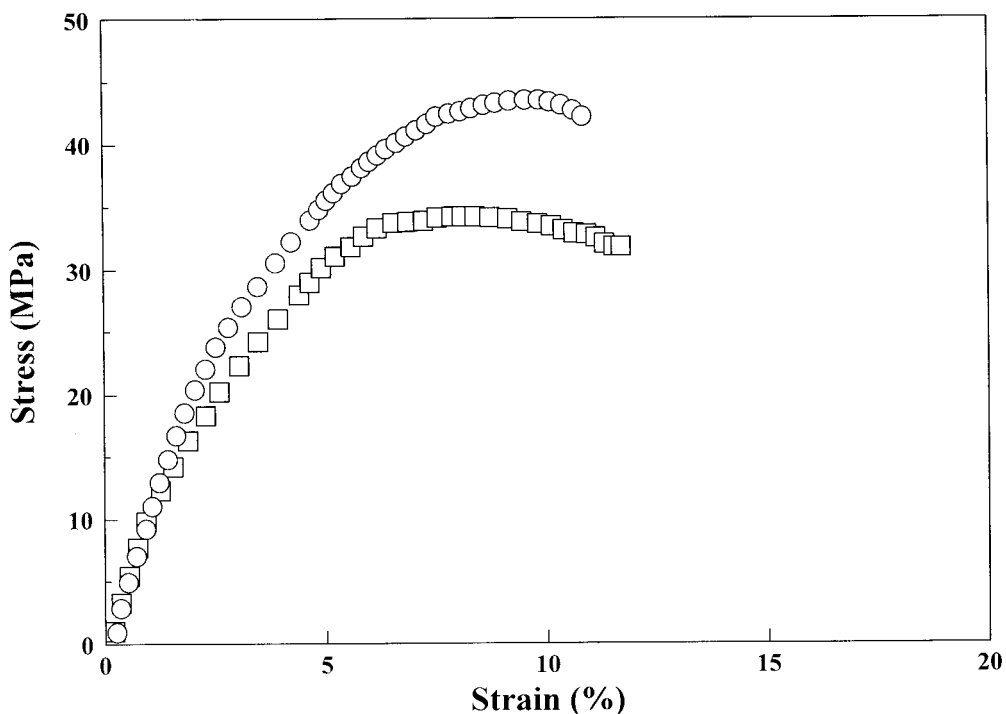

Figure 4 Stress–strain curves for PAI with various epoxysilane contents : (◯) 10 and (□) 30 wt %.
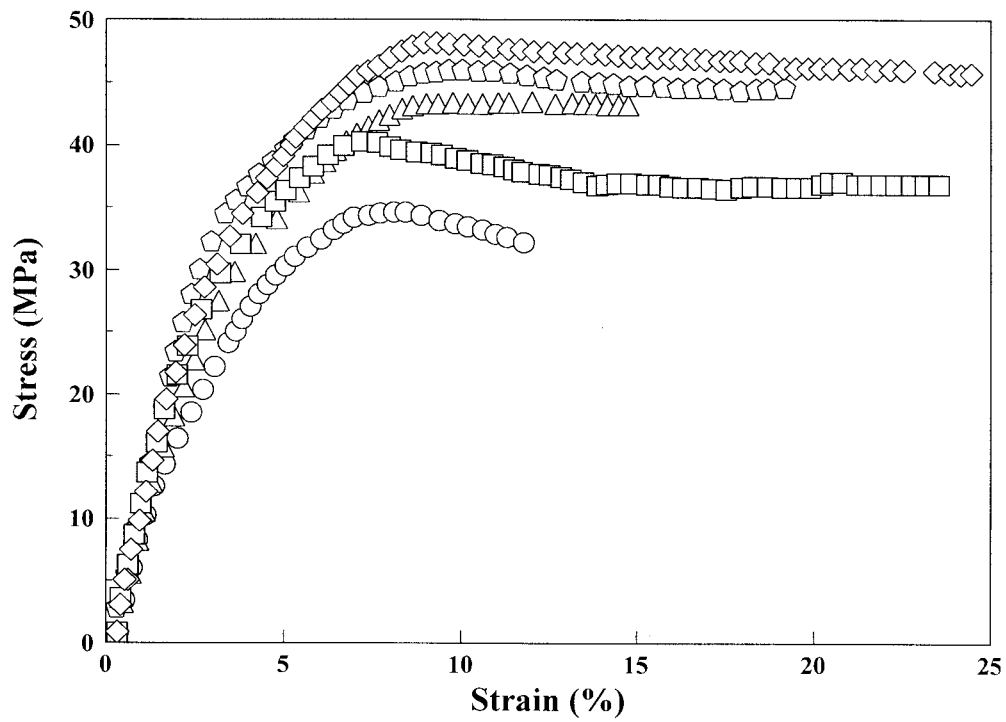
Figure 5 Stress–strain curves for PAI–epoxysilane (30 wt %) composites with various silica contents : (○) 0, (□) 10, (◇) 20, (⬠) 30, and (△) 40 wt %.
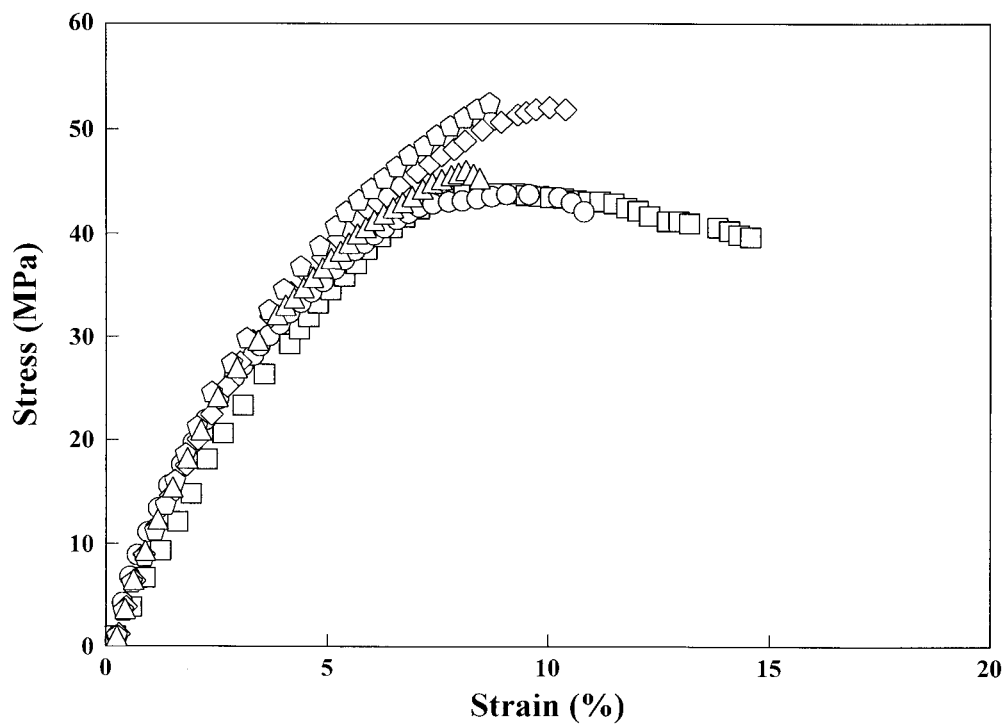

Figure 6 Stress–strain curves for PAI–epoxysilane (10 wt %) composites with various silica contents : (○) 0, (□) 10, (◇) 20, (⬠) 30, and (△) 40 wt %.

TABLE I
Mechanical Properties of PAI–Epoxysilane Composites with Various Silica Contents

Epoxysilane (wt %)	TEOS (wt %)	Maximum tensile strength (MPa)	Maximum elongation (%)
10	0	43.28	11.04
	10	43.72	14.83
	20	51.13	10.62
	30	50.70	8.75
	40	44.66	8.72
30	0	34.14	11.81
	10	38.26	23.64
	20	47.62	24.88
	30	46.47	19.20
	40	44.38	14.76

The elongation and toughness increased until 10 wt % TEOS was used, whereas they decreased when more than 10 wt % TEOS was added. Table I arranges Figures 4–6. Comparing the PAI–epoxysilane composites with changes in the epoxysilane contents, we found that the tensile strength somewhat decreased in the samples with higher epoxysilane contents, whereas the elongation and toughness increased. When TEOS was added to PAI and a standard amount of epoxysilane was added as well, the tensile strength, elongation, and toughness tended to increase until the ratio of epoxysilane to TEOS was 1:1. However, property deterioration was observed when excessive TEOS was added. This could be explained by the fact that the silica particles could not react with epoxysilane, and so extra phase separation might have happened.

Thermal properties

Thermogravimetric analysis (TGA)

Figure 7 shows TGA curves under a nitrogen atmosphere for PAI–epoxysilane (30 wt %) composites with various TEOS contents. The weight decreased gradually until 300°C for pure PAI because the low-molecular-weight substance was eliminated by condensation. A weight decrease by pyrolysis occurred again near 450°C. The final char (i.e., stable aromatic compounds) was not pyrolyzed until it reached 800°C, and 40% existed. A weight decrease by condensation for PAI with TEOS was smaller than that for pure PAI because condensation had already occurred during the sol–gel process. The pyrolysis starting temperature was 450°C for every sample. A weight decrease did not happen over 600°C. This indicated that a stable ceramic was produced after pyrolysis. The char contents near 800°C were greater in the composites with TEOS than in pure PAI, and they increased in proportion to the increase in the TEOS concentration.

Figure 8 presents TGA curves of PAI–epoxysilane composites with various TEOS contents; the curves represent the thermal properties of the samples.
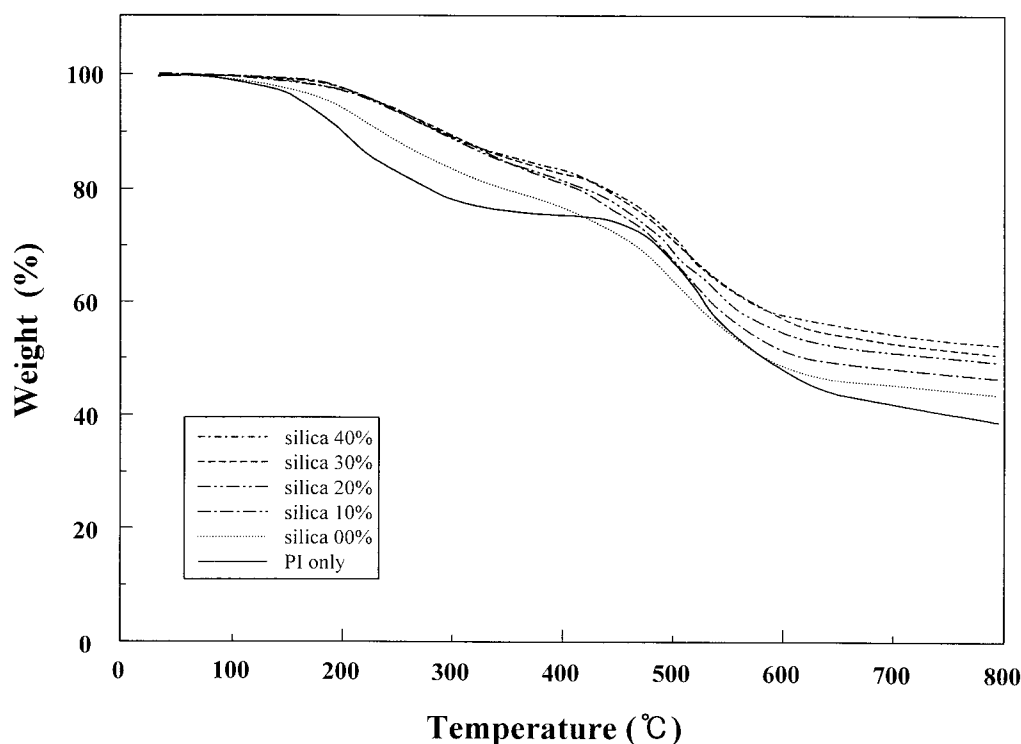

Figure 7 TGA curves under a nitrogen atmosphere for PAI–epoxysilane (30 wt %) composites with various silica contents.
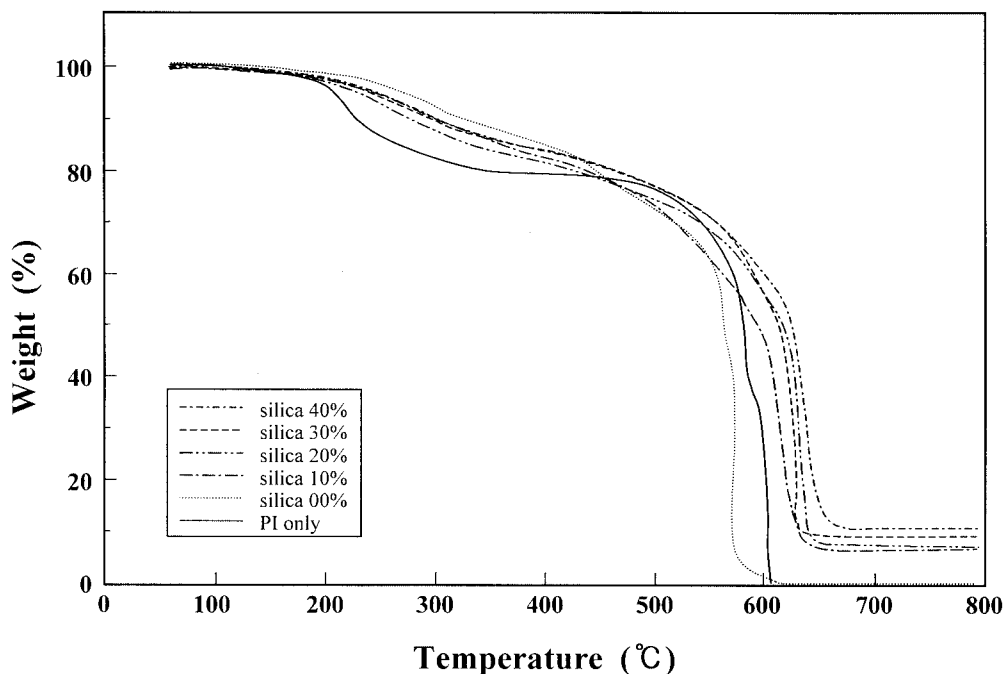
Figure 8 TGA curves under a oxygen atmosphere for PAI–epoxysilane (30 wt %) composites with various silica contents.

Under a temperature of 550°C, the curve was similar to that of a sample under a nitrogen atmosphere, and around 600°C, a drastic weight decrease was observed. The char contents of the samples with TEOS increased in proportion to the TEOS concentration, whereas pure PAI was fully oxidized and had no char.

Differential scanning calorimetry (DSC; Fig. 9)

Because the glass-transition temperature (T_g) did not appear clearly at first, it was measured again after quenching (Fig. 9). A thermal transition estimated to be T_g near 170–180°C was observed for most samples. This implied that T_g changes
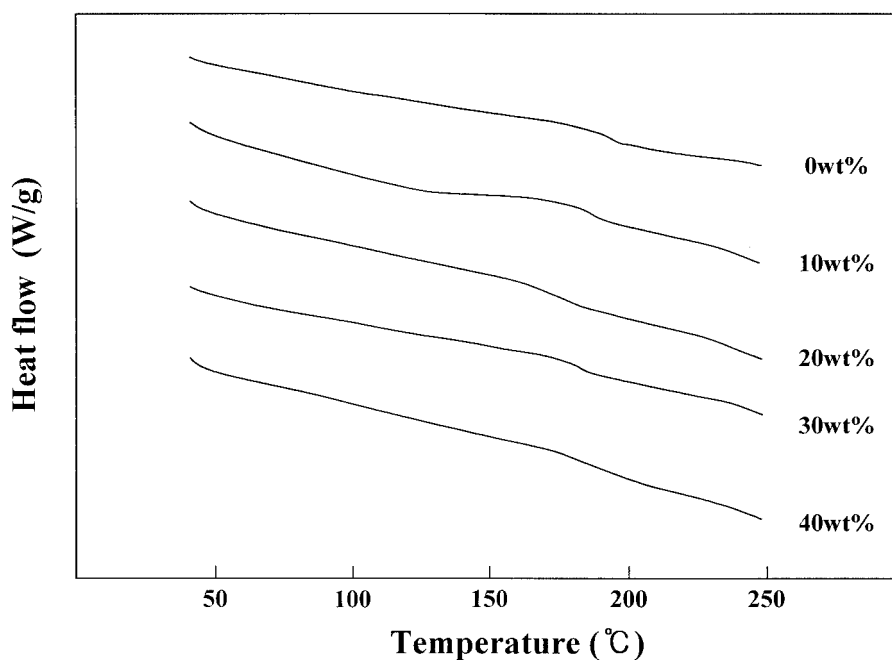

Figure 9 DSC curves for PAI–epoxysilane (30 wt %) composites with various silica contents.

with respect to the TEOS concentration did not occur.

DISCUSSION

PAI–epoxysilane (coupling agent) composites were reacted with silica, the condensation product of TEOS. FTIR spectroscopy verified that the reaction had proceeded. With the addition of epoxysilane, the bond strength between PAI and silica condensed with TEOS was enhanced. PAI–epoxysilane (1:1) composites with TEOS increased in tensile strength, elongation, and toughness. Excess TEOS, however, degraded the properties, and the content of the coupling agent also had a critical effect. The experiment showed that a PAI–epoxysilane (30 wt %) composite with 20 wt % TEOS had the best mechanical properties. The TGA curves under nitrogen and oxygen atmospheres confirmed that the char contents increased with respect to the TEOS concentration. A thermal transition estimated to be T_g near 170–180°C was observed, and T_g changes with respect to the TEOS concentration were not observed. The materials used in these experiments were processed by low-temperature (60°C) thermal curing through the condensation of silane. This is an epoch-making method that can solve the problems that occur in the high-temperature thermal curing of PAI and also enhance the toughness of PAI.

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