

# Mechanical, Surface, and Thermal Properties of Polyamideimide–Polydimethylsiloxane Nanocomposites Fabricated by Sol–Gel Process

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**ABSTRACT:** Polyamideimide (PAI)–epoxysilane (coupling agent) composites were reacted with oligomeric polydimethylsiloxane (PDMS), a condensation product of difunctional silane, by using the sol–gel process, and were then dried into films. After this procedure, the surface, mechanical, and thermal properties were measured. The study showed that PDMS existed in the PAI matrix by the use of FTIR. With respect to mechanical properties, the maximum elongation and toughness were increased in the PAI with silane groups, although the maximum tensile strength was slightly decreased. In this experiment, PAI–30 wt % epoxysilane composite had the best mechanical properties. The intensive dispersion of the silane groups on the surface of PAI

was confirmed through XPS measurement. As a function of the siloxane contents, the TGA curve shows less thermal stability in terms of their initial weight loss. However, in an oxygen atmosphere at about 700°C, the series of PAI–siloxane composites indicated a significant increase in char concentration. In the end, PAI with a relevant amount of silane groups was improved in both toughness and surface properties. This experiment showed that PDMS added to PAI had better properties than those of classical materials. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1774–1783, 2004

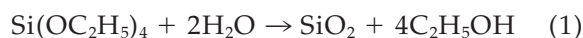
**Key words:** nanocomposites; polyamideimides; silicones; mechanical properties; ESCA/XPS

## INTRODUCTION

In the case of organic–inorganic compounds, adding an inorganic filler to the organic polymer material to enhance the mechanical properties or thermal stability was the widely used method in the past. If these materials are called first-generation composite materials, then the composition of organic–inorganic materials in the molecular level can be referred to as second-generation composite materials.<sup>1</sup> The sol–gel process belongs in the second category. In fact, the process does not simply put coupling agents on the reinforcing agent as in first-generation composite materials, but puts them on the polymer matrix. This is because the reinforcing agent is later formed by the sol–gel method.

The sol–gel process<sup>2–18</sup> is able to make and mass-produce ceramic-like substances by hydrolyzing organic metal compounds in the liquid state. In most cases the particles produce a dispersed sol and later become a cohered gel in the middle stage, leading to

the formation of ceramic in the final stage. This process has the merit of being able to mix substances in the liquid state by a molecular-level mixture at a lower temperature compared to the powder–mixture fusion, the method most widely used in the ceramic area, and also compose pure silica. This is also applied to various ceramic fillers, fibers, and ceramic coatings compared to other methods because of its superior chemical uniformity, mobility, gel-forming capability, and also the strong reaction of this gel.<sup>19,20</sup> Besides the advantage of the sol–gel process being performed at a low temperature, the ceramic formed in the polymeric phase is of nanomolecular size, or at the molecular level that increases the adhesion of the interface leading to nanoscale morphology. A material that is transparent with various properties is made from this process. An example of this would be the complex material of polyimide–silica. In this case, polyimide (which is the matrix) prevents the silica from forming a lump and keeps it at nanoscale.<sup>21–24</sup> These complex materials are called nanocomposites. The most important reaction on the sol–gel process is the hydrolysis formula, which is caused by the acid or base catalyst of tetraethyl orthosilicate (TEOS).<sup>4,5,25,26</sup>



TEOS is the most popularly used ceramic-producing material because it can easily increase the degree

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of purity by distillation, thus making it possible to obtain pure ceramic. This process occurs inside the organic material to produce an organic-inorganic mixed composite material. The organic materials used in this experiment should mostly be polymers and have the kind of functional group that will enhance the bonding between the newly made ceramic. The uniformity and cohesiveness between the organic (polymer) and inorganic (ceramic) can be improved by the use of a bonding agent.<sup>7,8,27-30</sup> Therefore using a bonding agent greatly affects the mechanical properties and the improvement in transparency. In the case of high-temperature polymers that do not have an abundance of functional groups, supplementation with a functional group or the addition of a bonding agent is used to enhance the coupling between the polymer and ceramic. However, the bonding agent is not necessarily needed in cases that involve special interactions such as hydrogen bonding. In the sol-gel process an acid or base catalyst is used to promote hydrolysis. Base catalysts such as ammonia and diethylamine are widely used because base catalysts volatilize easily, which makes it simple to eliminate them. When the hydrolysis of organic silicate-polymer is accomplished with plentiful amounts of silane, silica is produced in a continuous phase. The dispersed polymers exist in the continuous phase. Polymer (organic) and the transformed ceramic (inorganic) are called Ormocer<sup>31</sup> and Ceramer.<sup>32</sup>

Polyimide is produced from the precursor, polyamic acid, because it is insoluble and infusible. Despite the high thermal stability and mechanical strength, the fact that it has high brittleness and an insoluble characteristic continues to cause many problems in manufacturing. To solve this problem, the derivation of a proper monomer system and/or the induction of a new molecular structure that minimizes the decline in heat resistance and mechanical strength while increasing the chain's flexibility have been conducted.<sup>33</sup> Pratts, Johnstons, and other researchers have compounded silicon with polyimide to give better processibility. Also Yang composed *N,N'*-(pyromellitoyl)-diglycine with methyl groups to give processibility to polyimide. He reported the thermal properties after he polymerized various diamines with the substance described above.<sup>34</sup>

Polyimide has been widely applied in the field of microelectronics in which mechanical properties, thermal stability, adhesive properties, water resistance, and the dielectric constant are valuable in the production of circuit-printing films and semiconductor coating materials. PAI with improved toughness, by using low-temperature vulcanization that adapted the existing sol-gel process, was produced in this project. In the existing research, TEOS, a tetrafunctional silane group, was used to produce silica in the polymer matrix, and this increased the mechanical properties

such as tensile strength. However, dimethyldiethoxysilane (DEDMS), a difunctional silane group, was used to disperse the rubbery phase in the polymer (PAI) matrix, polydimethylsiloxane (PDMS), into nanoparticles. Increasing the toughness of PAI by this process would be the main objective of this project. This means the extension of the sol-gel process from the area of ceramics to the field of rubber and also a new toughening method for polymers. It shows a similar physical property to the existing segmented polyimide-PDMS block copolymer<sup>35,36</sup> because of similar structures. However, the composite material that was made by the sol-gel process does not need to synthesize PDMS with expensive functional groups and is easier to produce. Because of these advantages, this method is thought to be more useful. The polyamideimide-PDMS nanocomposites can be used as an insulator for semiconductors and be further used in the aerospace industry.

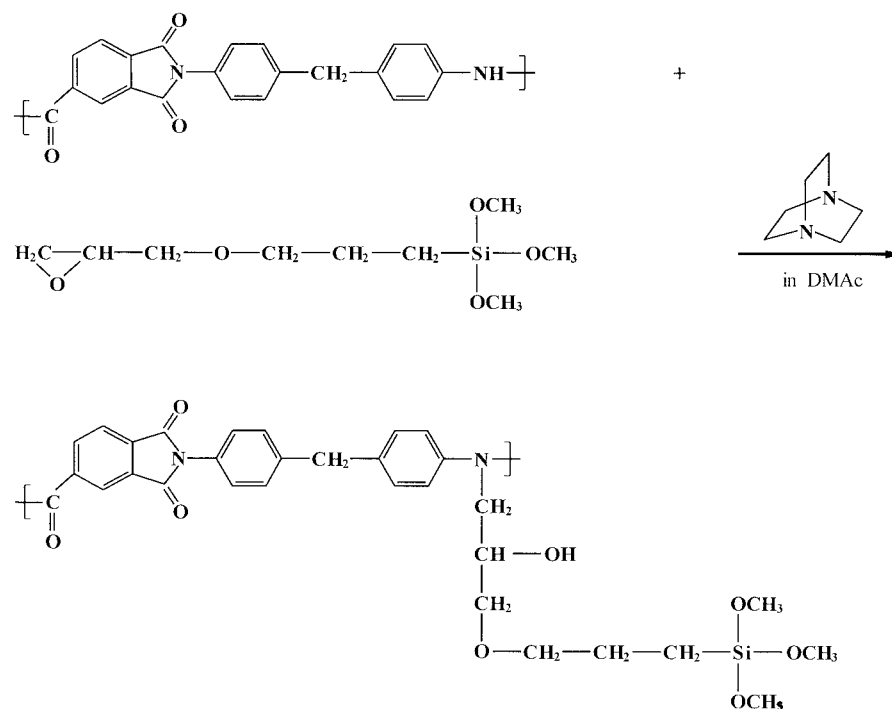
## EXPERIMENTAL

### Materials

Poly(trimellitic anhydride chloride-co-4,4'-methylenedianiline) was used to produce PAI. It was dried in a vacuum at the temperature of 60°C for 24 h before use. *N,N*-Dimethylacetamide (99.8%, anhydrous, DMAc) was used for the solvent and 3-glycidoxypropyltrimethoxysilane (98%) for epoxysilane, 1,4-Diazabicyclo[2.2.2]octane (triethylene diamine, 98%) and tin (II) 2-ethylhexanoate [2-ethylhexanoic acid, tin (II) salt] were used as catalysts. Diethylamine (99.5+%) and diethoxydimethylsilane (97%, DEDMS), which is a difunctional silane, were also used. All the materials used in this experiment were purchased from the Aldrich Chemical Co. (Milwaukee, WI).

### Synthesis of PAI with coupling agent

Some 20 g of PAI was charged to a 500-mL flask that contained a magnetic bar and 0.2 g of 1,4-diazabicyclo[2.2.2]octane was added to it. Then this mixture was dried in a 60°C vacuum drying oven for 24 h. After being dried, the flask was sealed by a rubber septum and a rubber balloon filled with N<sub>2</sub> gas was attached to it. The solvent (anhydrous DMAc; 200 mL) was charged to the flask containing PAI by the use of a syringe. This was put on a heating stirrer at a fixed temperature of 50°C for 4 h and the PAI completely dissolved. After this flask was cooled to room temperature, 3-glycidoxypropyltrimethoxysilane was added. The flask containing PAI-epoxysilane was put on a 60°C heating stirrer and the materials were reacted under constant stirring for 3 days.



**Scheme 1** Synthesis of PAI with epoxysilane coupling agent.

### Preparation of PAI-PDMS composition films

The product of the PAI-epoxysilane reaction was poured into a bottle. The chosen amount of diethoxydimethylsilane, diethylamine dissolved in DMAc, and water were added to create a hydrolysis and condensation reaction. Additionally, 5–6 drops of tin (II) 2-ethylhexanoate were added to accelerate the reaction. Then the bottle was kept in a shaking water bath at the temperature of 60°C for 12 h. This was cooled for a suitable time then poured into a Teflon mold. After this, PAI-PDMS composition films were manufactured by putting this 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

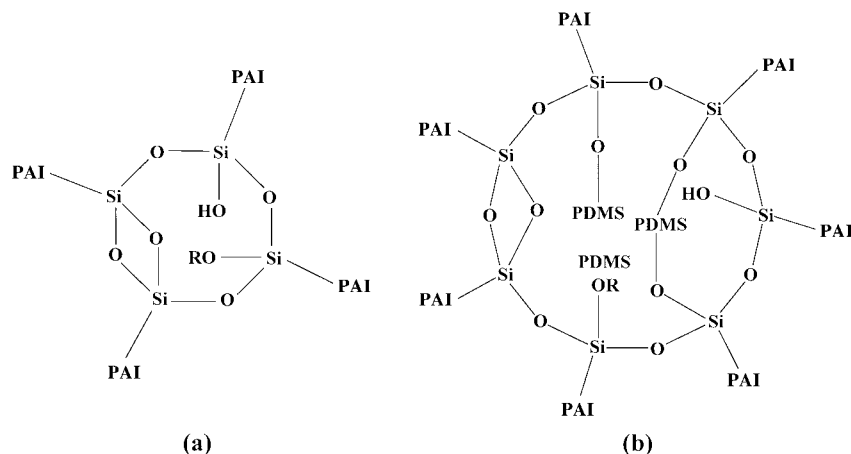
A Bruker IFS-66 FTIR apparatus (Bruker Instruments, Billerica, MA) was used for chemical analysis. The sample was fabricated as a thin film for the measurements. The mechanical properties were measured by a Lloyd's universal testing machine (Lloyd Instruments, Hampshire, UK). The extension rate was 5 mm/min, gauge length 25 mm, and sample dimensions were approximately 40 × 5 × 0.2 mm. For the surface analysis, a VG Microscop ESCA-2000 (Thermo VG Scientific, West Sussex, UK) was used to do wide scanning and depth profiling. Depth profiling collided the positive ion ( $\text{Ar}^+$ ) that was developed from the inert gas with high energy from the surface of the polymer

solid sample. By doing this, the surface was peeled by several angstroms/min. This process is used to analyze the change in formation and chemical condition of the depth that reaches to several thousand angstroms. The qualitative analysis of an element by the use of wide scanning and the relative quantitative analysis of the change in element content affected by the ion-sputtering time were used in this experiment. A TGA 2050 (TA Instruments, New Castle, DE) was used. The range of the measured temperature was 30 to 800°C; the heating rate was 20°C/min; and  $\text{N}_2$  and  $\text{O}_2$  gases were set at 50 mL/min. A DSC 2010 (TA Instruments) was used. The range of the measured temperature was 30 to 250°C; the heating rate was 10°C/min; and  $\text{N}_2$  gas was set at 50 mL/min.

## RESULTS AND DISCUSSION

### FTIR results

**Scheme 1** shows the reaction between PAI and epoxysilane. The epoxy group can react with the alcohol, amine, acid, and amide in the PAI. In this situation tertiary amine was used as the catalyst. Triethylene diamine was used in this experiment and DMAc was used as the solvent. For a complete reaction this was heated at 60°C for 2–3 days. From this process PAI with a silane group was formed and this silane group acts as a bridging material or a coupling agent by itself or by a condensation reaction of  $\text{SiO}_2$  or PDMS, as seen in Figure 1. This condensation process pro-



**Figure 1** Condensed product of PAI-epoxysilane: (a) PAI-epoxysilane composite; (b) PAI-epoxysilane composite with PDMS.

gressed at a relatively low temperature ( $<60^{\circ}\text{C}$ ) and a vacuum was used to remove the condensation product. The importance of this experiment is shown in the following comparison. In the case of polyimide, vulcanization by imidation occurred at a high temperature ( $>200^{\circ}\text{C}$ ), whereas the vulcanization of this silane group occurred at a low temperature.

To solve the problem of polyimide—the residual stress in the membrane or the thermal decomposition of the other nearby device during high-temperature vulcanization—a study on low-temperature vulcanization solubility has been in progress. This research can potentially provide a solution to this problem.

Figure 1(a) indicates the structure of a PAI-epoxysilane composite condensation. In this figure, the silane group acts as a bridging material and PAI has a grafting structure. This also contains small amounts of unreactive alcohol or alkoxy group. Figure 1(b) indicates oligomeric PDMS, which is the condensation of DEDMS added to a PAI-epoxysilane composite. In Figure 1(b), three forms are shown together: PDMS attached to both ends of structure (a), PDMS attached to one end, and a form that shows no attachment. The phase separation of PDMS and polyamide occurs here and the size is supposed to be at nanoscale. More details were confirmed by transmission electron microscopy (TEM). Figure 2 shows the change in FTIR spectra caused by the change in content of oligomeric PDMS that was produced by the condensation of difunctional silane. The condensation of difunctional silane and the successful reaction between the epoxy group and polyamide were confirmed from each spectrum.

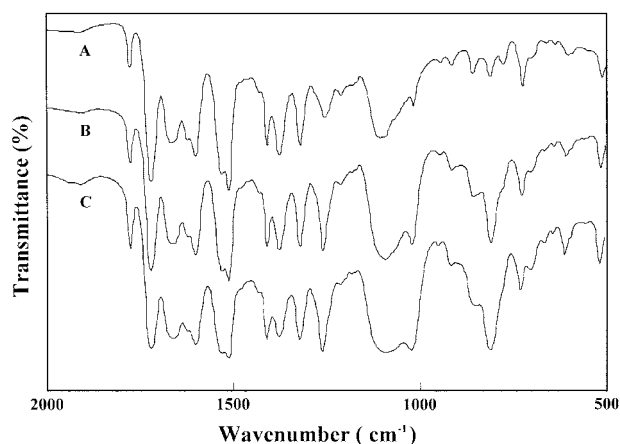
The Si—O—Si stretching vibration peak near  $1000\text{--}1100\text{ cm}^{-1}$  appeared with the C—O—C stretching vibration peak and as the content of PDMS increased the peaks became larger. This was caused by the increased content of PDMS that led to the increase in Si—O—Si.

Moreover, the peaks of  $\text{Si}(\text{CH}_3)_n$  ( $n = 1, 2, 3, 4$ ) near  $1250\text{--}1280\text{ cm}^{-1}$  and  $\text{Si}(\text{CH}_3)_2$  near  $800\text{--}850\text{ cm}^{-1}$  show that there was a noticeable difference caused by the difference in the content of difunctional silane. Because the Si—CH<sub>3</sub> group exists only in PDMS, the fact that the intensity of the peaks increased as the content of oligomeric PDMS increases was anticipated.

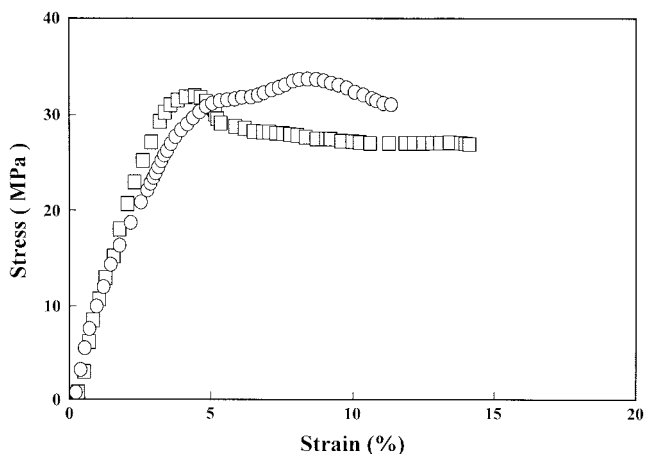
The Si—OH stretching vibration peak near  $950\text{ cm}^{-1}$  is very weak regardless of the PDMS contents, so the amount of remaining silanol group without condensation can be considered negligible.

### Measurement of mechanical properties

By using only PAI, film could not be made well and because of its tendency to break down easily it could not be used as a sample. High-temperature vulcaniza-



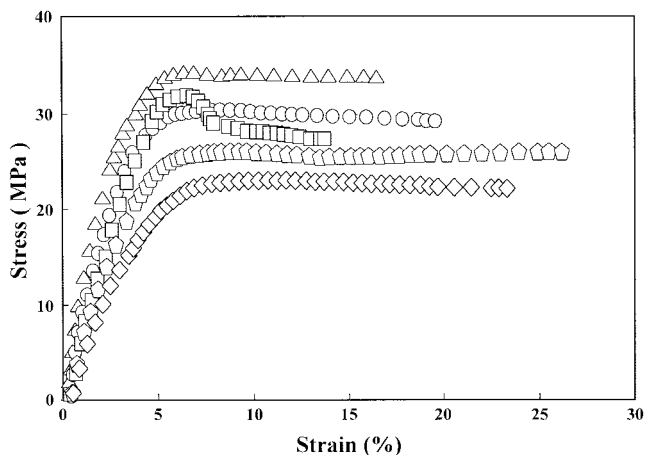
**Figure 2** FTIR spectra of PAI-epoxysilane (30 wt %) composite with various PDMS contents (in wt %): (A) 0; (B) 20; (C) 40.



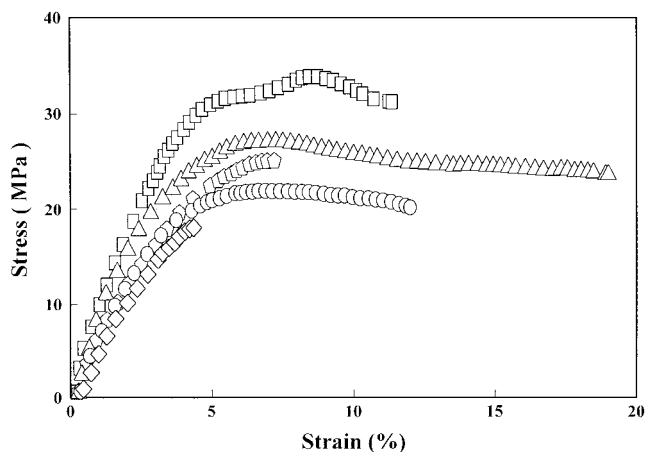
**Figure 3** Stress-strain curves for PAI with various epoxysilane contents (in wt %): (○) 15; (□) 30.

tion should be used to make a sample but this process was omitted in this experiment. On the other hand, high-quality film was produced from the condensation of epoxysilane in the PAI at a temperature that was under 70°C and measurement of mechanical properties was also possible. This proves that the bridge building of PAI was caused by the condensation reaction of the silane group and it also shows that low-temperature vulcanization is possible.

Figure 3 indicates the difference in mechanical properties attributed to the content of epoxysilane. In this figure, the tensile strength of PAI with 30 wt % epoxysilane had decreased compared to that of PAI with 15 wt % epoxysilane, although the maximum elongation and toughness of the former was substantially increased. This was seen as the composite improved in flexibility because of the flexible groups in epoxysilane. Figure 4 is a stress-strain curve that was



**Figure 4** Stress-strain curves for PAI-epoxysilane (30 wt %) composites with various PDMS contents (in wt %): (□) 0; (△) 10; (○) 20; (◇) 30; (◇) 40.



**Figure 5** Stress-strain curves for PAI-epoxysilane (15 wt %) composites with various PDMS contents (in wt %): (□) 0; (△) 10; (○) 20; (◇) 30; (◇) 40.

affected by various contents of oligomeric PDMS—the condensation product of diethoxydimethylsilane (difunctional silane)—added to PAI that was reacted with 30 wt % epoxysilane. When the amount of PDMS was increased, the maximum tensile strength increased at first but then gradually declined. Maximum elongation and toughness were increased proportionally as the PDMS content was increased, although a slight decrease was shown when 40 wt % was added. An excessive addition of PDMS compared to the coupling agent content is thought to be the reason PAI did not bond with it, causing a high degree of phase separation.

Figure 5 is the stress-strain curve that was given various changes in the PDMS content added to PAI that had already been reacted with 15 wt % epoxysilane. This shows that maximum tensile strength gradually declined as the PDMS content was increased. Maximum elongation and toughness increased to addition of 10 wt % PDMS but after this point, both properties decreased. Table I is a summary of Figures 2–4.

When the reactant of PAI-epoxysilane is compared to the changes caused by various contents of epoxysilane, the maximum tensile strength of high-content epoxysilane shows a slight decline, whereas maximum elongation and toughness increased. When PDMS was added to PAI with a fixed amount of epoxysilane, maximum tensile strength slightly decreased, whereas toughness and maximum elongation increased. This can be explained by the dispersion of PDMS particles of PAI with silane groups that led to the increase in toughness; however, physical properties declined when an excessive amount of PDMS was added. Because of excessive rubbery phase addition, this could not react with epoxysilane, the coupling agent, which led to macrophase separation. The weak-

**TABLE I**  
**Mechanical Properties of Polyamide-Epoxy silane Composites with Various PDMS Contents**

Epoxy silane contents (wt %)	Difunctional silane contents (wt %)	Maximum tensile strength (MPa)	Toughness (MPa)	Maximum elongation (%)
15	0	34.86	8.60	11.45
	10	27.04	19.40	19.09
	20	22.38	8.73	12.07
	30	25.63	4.05	7.60
	40	18.71	2.25	4.09
30	0	31.34	9.50	14.02
	10	34.36	15.18	16.83
	20	30.34	16.04	19.62
	30	26.48	21.15	26.35
	40	23.56	18.39	23.50

ening bonding between the phase-separated PAI and PDMS led to the decline of the physical properties of the PAI composite.

**Measurement of X-ray photoelectron spectroscopy (XPS)**

Some 20 years ago, XPS was a more commonly used method in the area of metal material science or physics than in chemistry. Within the past decade, XPS has become a new research area. Its increased use is attributed to the characteristic of XPS as an electron spectroscopy that shows the structure element of a surface of a solid and an interface or its chemical bonding condition. XPS is widely used in researches such as metal, catalyst, semiconductor device material, ceramic, thin film, and polymer film. This analytical method is designated electron spectroscopy for chemical analysis (ESCA). XPS uses X ray as the source of light and measures kinetic energy of the photoelectron by releasing photoelectrons from the inner electrons. The structure element of the surface and its chemical bonding condition can be determined from the minute difference in bonding energy obtained from the measurements.<sup>37</sup> XPS is the most commonly used method among other surface-analyzing devices (SEM, TEM, contact angle, etc.) because by using XPS quantitative analysis is possible and easily done. It also provides much more chemical information.

Table II indicates the bonding of the electron in each

orbit of an element and the relative intensity of the signals. The bonding of an electron is determined by subtracting the energy of the released photoelectron from the energy of the incident ray. In the case of XPS, quantitative analysis is possible, although the accuracy declines because of the following three reasons. First of all, the relative size of the photoelectron’s peak of each element is different. Another reason is the difference in the amount of released photoelectron according to the form of the sample even when the surface concentration of the element is the same. The last reason is the difference caused by the condition of the devices. The Scofield section shown here indicates the relative intensity of the signals when the same concentration element exists and this was referred to the work of R. N. King.<sup>38</sup> To obtain more accurate measurements, the highest intensity peak was used.

Polyimide is used as an adhesive or coating material in the electronic and aerospace industries and in these cases surface adhesive strength, water resistance, adhesion resistance, chemical resistance, and durability are considered to be very important characteristics. These surface characteristics are highly affected by the difference in the distribution of the surface and the inner part of the elements. XPS can uncover the difference in distribution of the surface and inner part by using a method that is nondestructive as well as destructive. An example of the nondestructive method is depth profiling. This is a method in which the possible infiltration depth of the X ray is indicated as  $d = 3\lambda \sin \theta$ . [ $\theta$  is the angle formed between the angle of the incidence ray and the sample. When this angle is changed, the possible infiltration depth ( $d$ ) will also change.] It also shows the concentration (which is calculated by the XPS signal) that is affected by the changes in  $d$ . An example of the destructive method is taking measurements after grinding the surface (chemically, physically, mechanically, and electronically). In this experiment, a positive ion ( $Ar^+$ ) was collided with the surface of the sample for 10 min to

**TABLE II**  
**Binding Energy of the Elements for Semiquantitative Elemental Analysis of XPS**

Element and line identification	Binding energy (eV)	Scofield section
C(1s)	285	1.00
O(1s)	531	2.93
Si(2s)	149	0.955

TABLE III  
Semiquantitative Elemental Analysis Through Ion Sputtering Time for Polyamide-Epoxy-silane (5 wt %) Composite with 10 wt % PDMS

Sputtering time (min)	Peak area			Normalized area				% Atomic		
	Si	C	O	Si	C	O	Total	Si	C	O
0	55	556	313	57.5	556	106.8	720.4	8.0	77.2	14.8
1	31	667	131	32.5	667	44.7	744.2	4.4	89.6	6.0
2	21	703	100	22.0	703	34.1	759.1	2.9	92.6	4.5
3	17	742	88	17.8	742	30.0	789.8	2.2	94.0	3.8
4	15	746	82	15.7	746	28.0	789.7	2.0	94.5	3.5
5	15	765	80	15.7	765	27.3	808.0	1.9	94.7	3.4
6	13	746	79	13.6	746	27.0	786.6	1.8	94.8	3.4
7	12	756	80	12.6	756	27.3	795.9	1.6	95.0	3.4
8	11	766	79	11.5	766	27.0	804.5	1.4	95.2	3.4
9	11	786	71	11.5	786	24.2	821.7	1.4	95.6	3.0
10	11	781	70	11.5	781	24.0	816.5	1.4	95.7	2.9

peel the surface using depth profiling. The change in relative content of the surface of the element resulting from the ion-sputtering time was analyzed and the results are shown in Table III. Figure 6, and Figure 7. The conversion of sputtering time to depth is possible but because this process is very complicated, the change in the element concentration (C, Si, O) caused by sputtering time was shown instead. XPS signals and the values given in Table II were used for calculation and the results are indicated in Table III.

Figure 6 shows the wide scanning of PAI with 5 wt % of epoxy-silane added to 10 wt % PDMS. (A) is the scanning result of the first condition and (B) is the scanning result shown after 10 min of ion sputtering. (A) showed that a large content of C, O, and Si also existed, although it was not a large amount. This result confirms the concentrated dispersion of siloxane on the surface of PAI. After 10 min of ion sputtering the results shown in (B) were as follows: C slightly increased, but O and Si decreased dramatically. In

conclusion, the Si—O group of siloxane dispersed on the surface gradually detached as the sputtering time increased.

Figure 7 indicates the atomic contents (%) of O and Si affected by the sputtering time. The two elements decreased as the time increased. Specific details can be recognized by comparing this to Figure 6. Polyimide that contains siloxane is known to have high water resistance, abrasion resistance, and good adhesion to metals. Organosilicate (ceramic) produced by the oxidation of siloxane when the surface is oxidized is also known to protect the inside, which is congruous with the results of this experiment. Moreover, it can be explained by the surface separation of siloxane with low surface tension that revealed all the good surface properties. Polyimide materials with improved physical properties are used as adhesives or coating materials in electric, electronic, and aerospace industries. Because this material has the necessary characteristics of an adhesive or coating material, it is expected to be widely applied in this area.

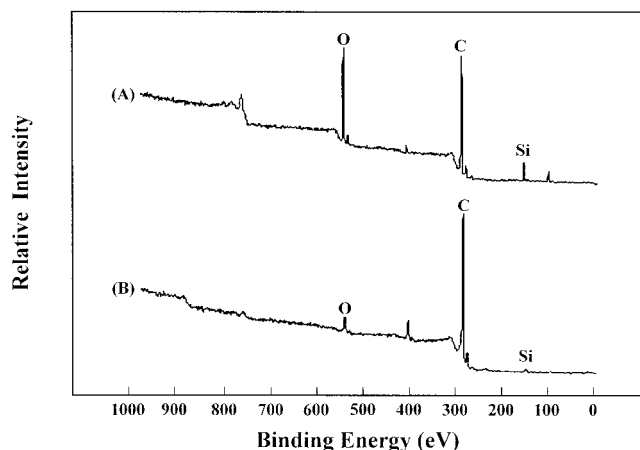


Figure 6 Wide scanning spectra of XPS for PAI-epoxy-silane (5 wt %) composite with 10 wt % PDMS: (A) the first scanning; (B) after sputtering time of 10 min.

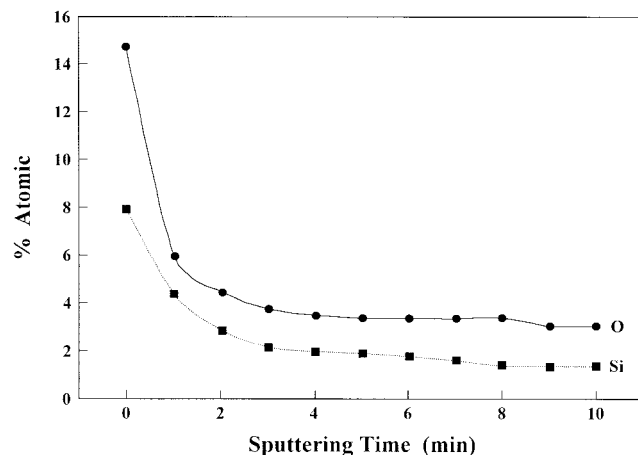


Figure 7 Atomic contents versus sputtering time for PAI-epoxy-silane (5 wt %) composites with 10 wt % PDMS content.

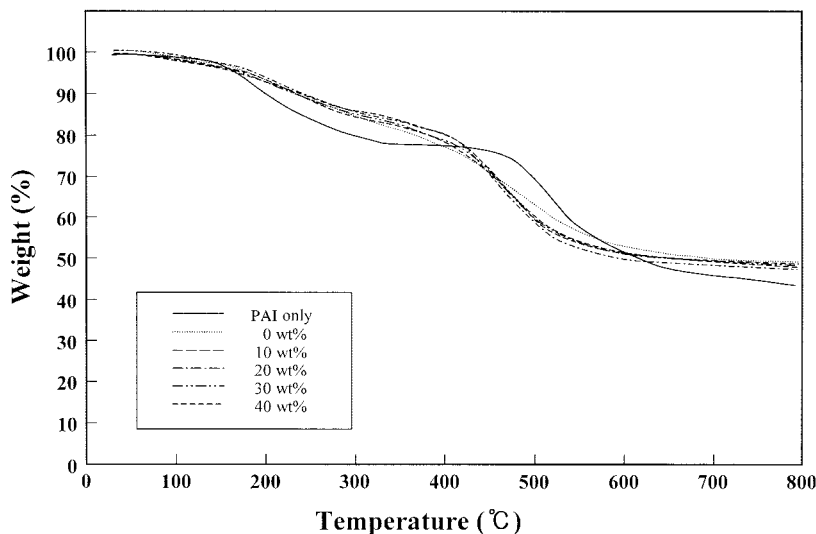


Figure 8 TGA curves in nitrogen atmosphere for PAI-epoxysilane (30 wt %) composite with various PDMS contents.

**Thermogravimetric analysis (TGA)**

Figure 8 presents the TGA curves of the thermal properties of PAI samples that contain various contents of PDMS in the presence of nitrogen current. In the case of pure PAI, a gradual weight loss was detected until the temperature reached 300°C, given that the substances containing fewer molecules leach out by the condensation reaction. Weight loss was found once again at temperatures over 450°C, which was caused by pyrolysis. The residue in an aromatic compound that does not decompose and exists before reaching 800°C, constituted a portion of about 40%. For the PDMS-containing PAI, the weight loss caused by the condensation reaction was smaller than that of pure PAI. The starting temperature of the pyrolysis for this

substance was 400°C, which is 50°C lower than that of pure PAI. This was attributed to the plentiful condensation reactions that had already taken place in the sol-gel process and the low thermal stability of the generated rubber phase. No further weight loss was found as the temperature reached >600°C. The reason for this is thought to be the stable silicate system ceramic that was formed after the pyrolysis. When the temperature reached near 800°C, the residue content of the PDMS-containing PAI was 45%, which was higher than that of pure PAI. In other words, when PDMS is added to PAI the pyrolysis temperature is lower in the presence of nitrogen current, although the amount of residue left in this experiment is greater.

Figure 9 illustrates the TGA curves that indicate the

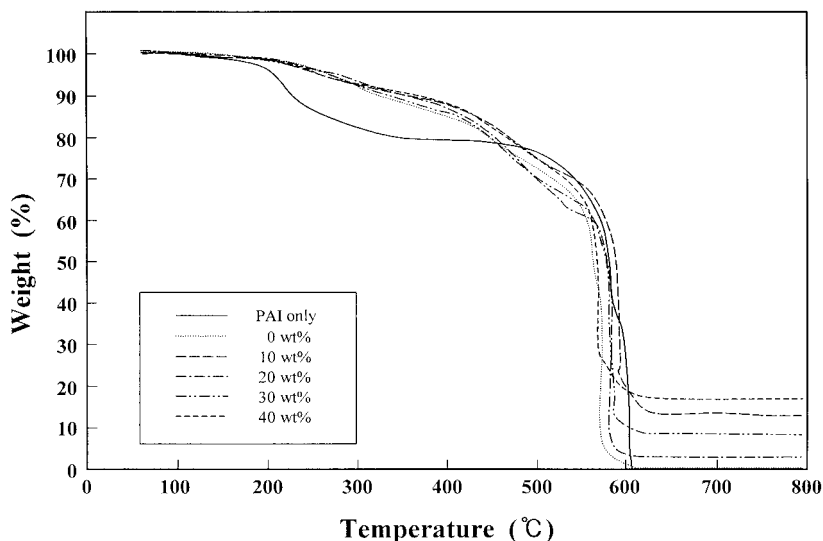


Figure 9 TGA curves in oxygen atmosphere for PAI-epoxysilane (30 wt %) composite with various PDMS contents.



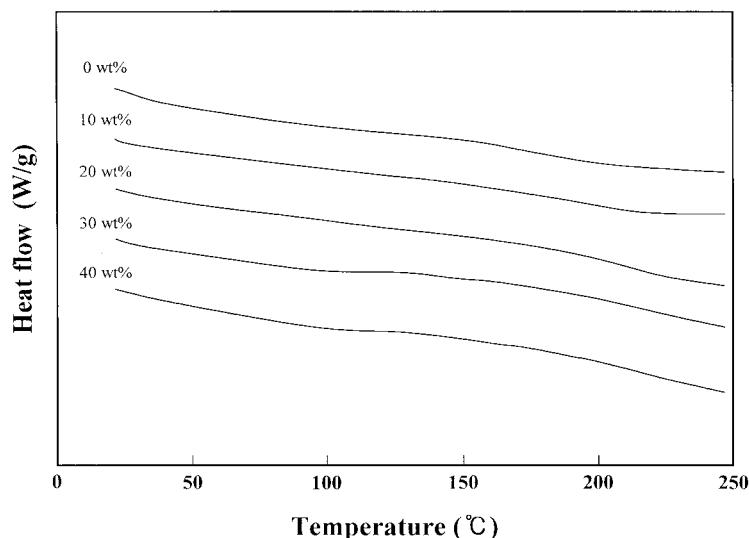


Figure 10 DSC curves for PAI-epoxysilane (30 wt %) composite with various PDMS contents.

thermal properties of the PAI-epoxysilane compounds with various amounts of added PDMS while they are conveyed through air. At temperatures under 558°C, the TGA curves were similar to those in the presence of nitrogen current and a dramatic weight loss attributed to oxidation was shown when the temperature approached 600°C. Whereas the residue for pure PAI was 0 because it was completely oxidized at 600°C, the residue of the PDMS-containing PAI was in proportion to the amount of PDMS added to the pure PAI. From other research, the residue from this experiment was confirmed to be silicate ceramic by using XPS analysis. This silicate char is known to interrupt combustion, which increases fire resistance and reduces the amount of smoke that erupts. The thin membrane of the ceramic formed by oxidation is thought to protect the inner material from severe environments.

#### Differential scanning calorimetry (DSC)

Because  $T_g$  was not shown clearly in the first measurement, a more specific graph was created from the measurements taken after quenching, although the exact  $T_g$  was still difficult to determine. It can be interpreted that the addition of PDMS did not affect the glass-transition temperature of PAI. For block copolymer that had only a slight phase separation, a similar phenomenon occurred (see Fig. 10). This means having two  $T_g$  values: the  $T_g$  of PAI and the  $T_g$  of PDMS. The  $T_g$  of PDMS is expected to appear near the temperature of  $-100^\circ\text{C}$  when low-temperature measurement using liquid nitrogen to lower the temperature to  $-180^\circ\text{C}$  is done.

#### CONCLUSIONS

PAI with silane group was produced by reacting PAI with epoxysilane (coupling agent) and a composite

material was made by oligomeric PDMS that was the condensation product of difunctional silane. The use of FTIR confirmed that the reaction progressed satisfactorily. Addition of epoxysilane increased the cohesiveness between PAI and oligomeric PDMS. When the content of oligomeric PDMS was increased in PAI with a fixed amount of epoxysilane, the maximum tensile strength decreased slightly, whereas maximum elongation and toughness increased substantially.

However, a decline in the physical properties was observed when too much PDMS was added; this phenomenon confirmed the importance of the content of the coupling agent. In this investigation, maximum toughness was obtained in the composite of 30 wt % oligomeric PDMS added to the product of 30 wt % epoxysilane and PAI. The concentrated distribution of Si—O group on the surface was validated from the results of XPS. This means that the addition of a small amount of silicone can dramatically change the surface characteristics. As a function of the siloxane contents, the TGA curve shows less thermal stability in terms of initial weight loss. However, in an oxygen atmosphere of about  $700^\circ\text{C}$ , these series of imide-siloxanes indicated a significant increase in the char concentration. Furthermore, a material can be produced with the various characteristics (water resistance, adhesive property, abrasion resistance, chemical resistance, etc.) needed for application in the fields of aerospace, electronic information, and communication.

The materials used in this experiment were toughened in low temperature by the condensation of silane. This method not only can solve the problems of the previously used method of high-temperature vulcanization by imidation but also can overcome the major defect of polyamideimide, which is low toughness.

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