

# Surface and Electrical Characteristics of Poly(amide imide)–Poly(dimethylsiloxane) Nanocomposites

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**ABSTRACT:** A series of poly(amide imide)–poly(dimethylsiloxane) (PDMS) nanocomposites were fabricated through the reaction of poly(amide imide), epoxysilane (coupling agent), and diethoxydimethylsilane (DEDMS) via a sol–gel process. Nanocomposite films were obtained through the hydrolysis and condensation of DEDMS in poly(amide imide) solutions. The existence of the condensation product of DEDMS in the poly(amide imide) matrix was confirmed with Fourier transform infrared (FTIR). The concentration of PDMS on the surface of the poly(amide imide) matrix was observed through a comparison of FTIR and attenuated total reflection spectra. The contact angle of the poly(amide imide)–PDMS composites increased more than 40° with respect to that of pure poly(amide imide). The

alternating-current (ac) breakdown strength was obtained through the measurement of the ac breakdown voltage at the temperature of liquid nitrogen. As the PDMS concentration in poly(amide imide) increased, the characteristics of the insulation breakdown improved greatly. The best ac breakdown strength was observed in a poly(amide imide)–epoxysilane (30 wt %) nanocomposite with 30 wt % PDMS. The samples at the temperature of liquid nitrogen were brittle, as in a glassy state. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 342–347, 2004

**Key words:** polyimides; nanocomposites; mechanical properties; polysiloxanes

## INTRODUCTION

The sol–gel process has been in the spotlight of the ceramic industry because it has made it possible to obtain ultrapure ceramics at low temperatures through the hydrolysis and condensation of organometallic compounds.<sup>1–4</sup> With this process, a new type of hybrid composite, an organic–inorganic hybrid composite, has been produced.<sup>5–17</sup> An organic–inorganic hybrid composite includes an inorganic ceramic phase that is formed in the polymer phase by a sol–gel process. The continuous phase (the polymer) functions as the matrix, and the disperse phase (the ceramic) acts as a filler. Most polymers that have functional groups can be used as a matrix, and tetraethyl orthosilicate (TEOS) has been widely used as the formative substance of ceramic fillers. The most popularly used material in the electronics and aerospace industries is polyimide matrix because it is a high-performance polymer material with a low dielectric constant and good mechanical and thermal properties. Studies on hybrid composites produced through the

formation of silica in polyimide matrix have shown great progress. A polyimide–silica hybrid composite<sup>18–24</sup> that was produced at an early stage showed mechanical failure in areas such as the tensile strength and elongation at break because of weakening in the interfacial bonding strength between the polymer phase and ceramic phase.<sup>19</sup> These problems were solved by either the attachment of functional groups that reacted with silica on the main chain of polyimide or the use of coupling agents that enhanced the interfacial bonding strength between the two phases.<sup>20,25–29</sup> The greatest weakness of the polyimide–silica hybrid composite, which had superior mechanical strength and transparency, was its low impact strength. Efforts to enhance the toughness and elongation were made in some studies; they included the formation of a ceramic phase and a rubbery phase together in the polymer phase<sup>30,31</sup> and the production of a rubbery phase.<sup>28</sup> In this research, diethoxydimethylsilane (DEDMS) was added to a poly(amide imide) solution instead of TEOS, and with a sol–gel process, poly(dimethylsiloxane) (PDMS) was produced. The poly(amide imide)–PDMS hybrid composite that was produced showed improved toughness and elongation in comparison with the polyimide–silica hybrid composite. In previous studies, polyimides with enhanced characteristics in various areas, including surface properties, were produced with the block copolymer form of polyimide and polysiloxane.<sup>32–35</sup> The poly(amide imide)–PDMS hybrid composite produced

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during this research is expected to show surface properties and electronic characteristics similar to those of PDMS because of the PDMS dispersed on the surface of the poly(amide imide). Poly(amide imide)-PDMS hybrid composites that have excellent water resistance and electronic insulation can be used as flexible circuit boards or insulators between turns of superconducting transformers and can also be applied in the aerospace industry, this being the final objective.

## EXPERIMENTAL

### Materials

Poly(trimellitic anhydride chloride-co-4,4-methylenedianiline) was used as the poly(amide imide) and was dried in a vacuum-drying oven at 60°C for 24 h before use. *N,N*-Dimethylacetamide (DMAc; 99.8%, anhydrous) was used as the solvent, 3-glycidoxypropyltrimethoxysilane (98%, epoxysilane) was used as the coupling agent, and the difunctional silane DEDMS (97%) was used to produce PDMS for the rubber phase in the polymer phase. 1,4-Diazabicyclo[2.2.2]octane (triethylenediamine; 98%) was used to speed up the reaction between the poly(amide imide) matrix and coupling agent, and a small amount of tin(II) 2-ethylhexanoate (2-ethylhexanoic acid tin(II) salt) was also used. Calculated amounts of diethylamine (>99.5%) and H<sub>2</sub>O were added for the hydrolysis of DEDMS. All the materials used in this experiment were purchased from Aldrich.

### Synthesis of the poly(amide imide) coupling agent

A fixed amount of poly(amide imide) was poured into a 500-mL flask and was then dried in a vacuum-drying oven at 60°C for 24 h. After the addition of a small amount of 1,4-diazabicyclo[2.2.2]octane, the solvent (anhydrous DMAc) was poured into the flask. Then, the flask was put on a heated stirrer that was fixed at 50°C for 4 h to completely dissolve the poly(amide imide). The flask that contained the poly(amide imide) was cooled to room temperature, and afterward the coupling agent was added to it. The flask containing the poly(amide imide)-epoxysilane reactant was reacted with agitation for 3 days on a heated stirrer that was fixed at 60°C.

### Production of the poly(amide imide)-PDMS nanocomposites

A chosen amount of DEDMS was added to the poly(amide imide)-epoxysilane reactant, and calculated amounts of diethylamine and H<sub>2</sub>O, which were dissolved in DMAc, were added to generate the hydrolysis and condensation reaction. Five to six drops of tin(II) 2-ethylhexanoate were added to accelerate the reaction. The mixture that was produced from this procedure was

kept in a shaking water bath, which was fixed at 60°C for 12 h. After it was cooled down for a certain amount of time, the mixture was poured into a Teflon mold and kept in a vacuum-drying oven at 80°C for 24 h to produce a poly(amide imide)-PDMS nanocomposite film. The nanocomposite film was stored in the vacuum-drying oven until the property measurements.

### Instruments

A chemical analysis was performed with a Bruker IFS-66 Fourier transform infrared (FTIR) instrument. Samples were made into thin films for the measurement of the transmittance, and attenuated total reflection (ATR) was used to observe their surface compositions. For the observation of the surface properties, the static contact angle was measured. The static contact angle of each sample was measured as follows: the filmlike samples were fixed on a flat plate and then water was dropped at a regular speed. The alternating-current (ac) breakdown voltage was measured, and the ac breakdown strength was calculated to observe the electronic characteristics. Aluminum was placed by vacuum deposition on both sides of the samples to form an electrode and was placed on a specially made sample holder. The insulation breakdown characteristics were measured by its deposition in liquid nitrogen and the impression of the ac voltage. Figure 1 presents the apparatus for the ac breakdown voltage measurements. The mechanical properties were measured with a Llyod Co. universal testing machine. 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. The samples were cooled in a Styrofoam cup with liquid nitrogen. A hole was made in the bottom of the cup for the samples, and the leaks were sealed with silicone vacuum grease.

## RESULTS AND DISCUSSION

The epoxy group in epoxysilane can react with the alcohol, amine, acid, and amide that exist in polyimide, and a tertiary amine is usually used as the catalyst. In this research, triethylenediamine was used as the catalyst, and DMAc was used as the solvent. With FTIR, the existence of the Si—O—Si peak near 1100–1000 cm<sup>-1</sup>, which did not exist in the pure polyimide, and the Si—CH<sub>3</sub> peak near 815–800 cm<sup>-1</sup>, which was the characteristic peak of PDMS, was confirmed. Also, as the DEDMS content increased, the strength of the two peaks increased as well. These results showed that the polyimide and epoxy groups reacted and that the condensation product of DEDMS, PDMS, existed in the polyimide matrix.

Unlike ordinary infrared (IR) measurements, which obtain information through the IR absorption region when a ray of incident light transmits through a sam-

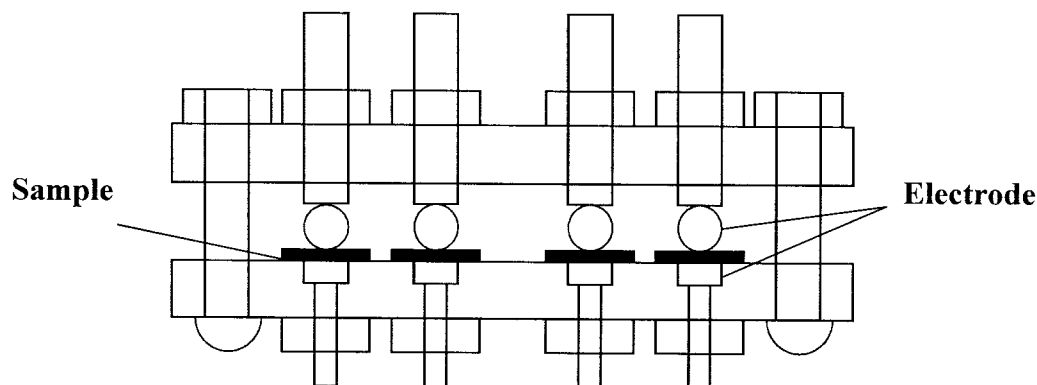


Figure 1 Apparatus for the measurement of the ac breakdown voltage.

ple, ATR is an analysis method based on internal reflection. In this research, ATR spectra were used to observe the surface compositions of the composite samples. Figure 2 presents a comparison of FTIR and ATR spectra of a sample formed by the addition of 30 wt % PDMS to a poly(amide imide)-epoxysilane (30 wt %) hybrid composite. The strength of the Si—O—Si peak of ATR was higher than that of FTIR near  $1000\text{--}1100\text{ cm}^{-1}$ , and the Si—CH<sub>3</sub> peak near  $815\text{--}800\text{ cm}^{-1}$  was stronger in the ATR spectrum. The results show that PDMS was dispersed on the surface of poly(amide imide) because of its low surface tension.

The most widely used method for measuring the contact angle is the Wilhelmy plate method. This method uses more than two liquids, the surface tensions of which are already known, to measure the

contact angle. This method provides various interface data as well. However, the complexity of the measurement process is the defect of this method. In this research, the contact angle was measured directly with water and a sample that was simple to measure and that gave an accurate measurement. Figure 3 presents the contact-angle measurements of pure poly(amide imide), a poly(amide imide)-epoxysilane compound, and a poly(amide imide)-epoxysilane compound with various PDMS concentrations. The contact angle of pure poly(amide imide) was  $71^\circ$ , and that of the poly(amide imide)-epoxysilane compound was  $113^\circ$ . For the samples with 10, 20, 30, and 40 wt % PDMS, the contact angles were 112, 111, 113, and  $113^\circ$ , respectively. The contact angles of epoxysilane and the PDMS samples were  $40^\circ$  higher on average than

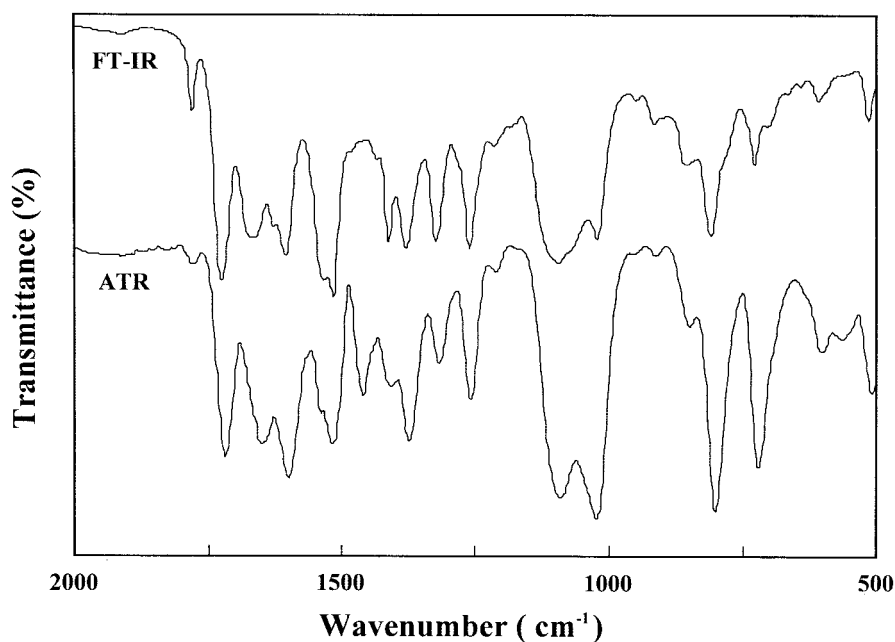
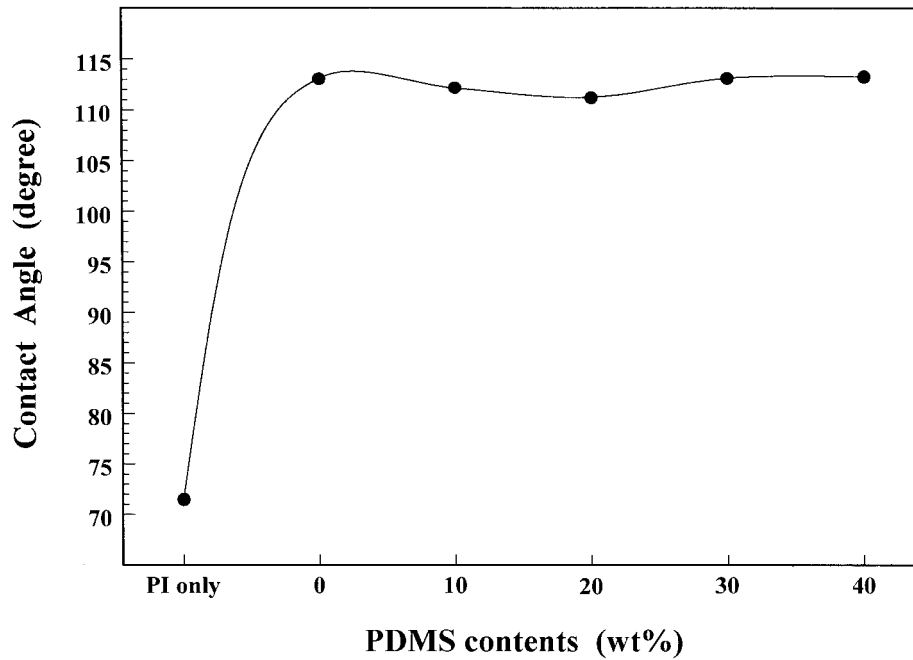


Figure 2 Comparison of the ATR and FTIR spectra of a poly(amide imide)-epoxysilane (30 wt %) composite with 40 wt % PDMS.

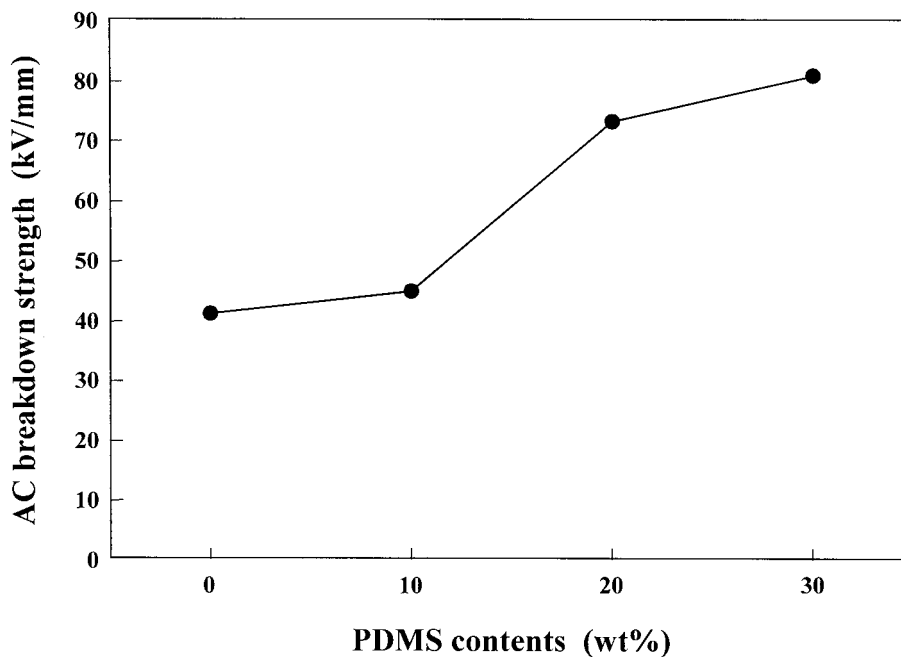


**Figure 3** Contact angles of poly(amide imide) and poly(amide imide)–epoxysilane (30 wt %) composites with various PDMS contents.

those of pure poly(amide imide). This was caused by siloxane, which had a hydrophobic characteristic. Even a small amount of siloxane could form a thin film on the surface of the poly(amide imide) and show water-resisting qualities. The concentrated distribution of siloxane groups on the surface was also proved

by X-ray photoelectron spectroscopy.<sup>36</sup> This surface characteristic is thought to be suitable for industries that are affected by moisture, such as the semiconductor and electronics industries.

Figure 4 shows the measurements of the ac breakdown strength of poly(amide imide)–epoxysilane (30



**Figure 4** Curve of the ac breakdown voltage for poly(amide imide) (30 wt %) composites with various PDMS contents at the temperature of liquid nitrogen.

**TABLE I**  
**Breakdown Voltage for Poly(amide imide)—Epoxy silane**  
**(30 wt %) Composites with Various PDMS Contents at**  
**the Temperature of Liquid N<sub>2</sub>**

PDMS (wt %)	AC breakdown voltage (kV)	Thickness (mm)	AC breakdown strength (kV/mm)
0	13.60	0.33	41.21
10	13.50	0.30	45.00
20	9.20	0.12	73.67
30	9.70	0.12	80.83

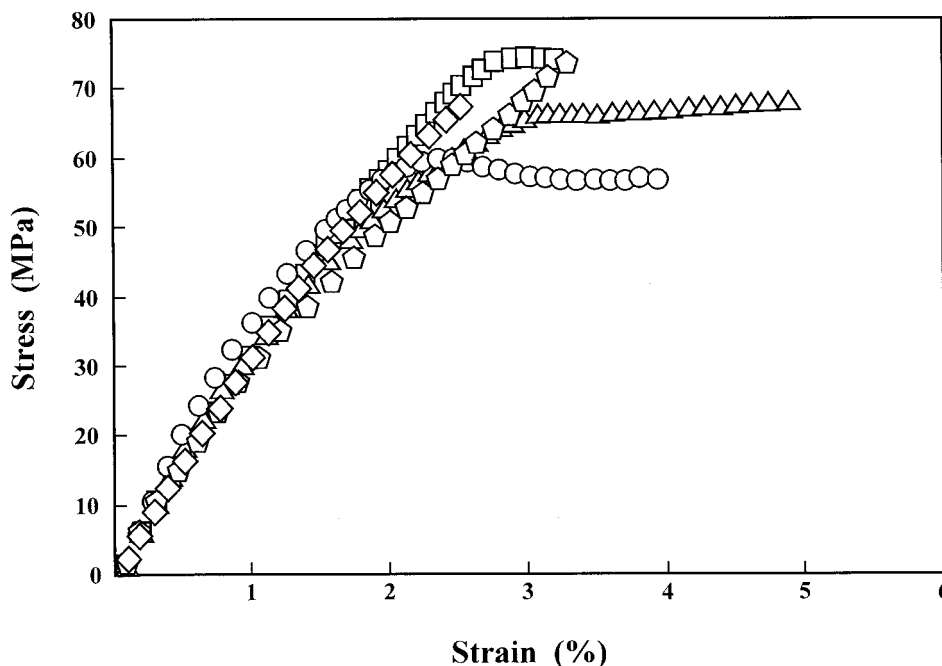
wt %) with various contents of oligomeric PDMS, a condensation product of DEDMS at the temperature of liquid nitrogen. The ac breakdown strength of the PDMS-added reagent was stronger than that of the poly(amide imide)—epoxy silane compound. The ac breakdown strength increased as the amount of PDMS increased. As shown in Table I, the ac strength of the poly(amide imide)—epoxy silane compound was 41.21 kV/mm, and those of the samples with 10, 20, and 30 wt % PDMS were 45.00, 73.67, and 80.83 kV/mm, respectively. The ac breakdown strength of the poly(amide imide)—epoxy silane compound with 30 wt % PDMS was 80.83 kV/mm, which was the highest measurement. This was due to the increase in the content of PDMS, which enhanced the electric insulation characteristic of the sample. The effect of the thickness on the ac breakdown strength was thought to be negligible. The poly(amide imide)—PDMS nanocomposite produced in this experiment is expected to be a sub-

stitute for Kapton, an insulating material used between turns of a superconductor, because of its excellent mechanical characteristics and electric insulation characteristics at low temperatures.

Figure 5 presents a stress–strain curve at the temperature of liquid nitrogen with various changes in the PDMS content added to poly(amide imide) that had already been reacted with 30 wt % epoxy silane. The tensile strength of the samples was more than twice that measured at room temperature<sup>36</sup> (Table II), and the toughness and elongation at break were greatly reduced. These results are characteristic of a glassy state. The toughness of the samples increased until 10 wt % of PDMS was added; after this point, there was a slight decrease in the toughness. The toughness of polyimide–epoxy silane with 30 wt % PDMS was similar to that of poly(amide imide)—epoxy silane without PDMS. The elongation at break of these samples was 3–5%, and that of polyimide coatings in electronic packages is approximately 1–3%.

## CONCLUSIONS

New nanocomposites with a PDMS rubber phase formed in the poly(amide imide) matrix were produced with a sol–gel process. The reaction between epoxy silane (coupling agent) and poly(amide imide) was confirmed with FTIR spectra. Also, the existence of PDMS, the condensation product of DEDMS, in the poly(amide imide) matrix was confirmed. The fact that the addition of PDMS greatly affected the surface



**Figure 5** Stress–strain curve for poly(amide imide)—epoxy silane (30 wt %) composites with various PDMS contents at the temperature of liquid nitrogen.

TABLE II  
Mechanical Properties of Poly(amide imide)-PDMS Composites with Various PDMS Contents at Room Temperature and at the Temperature of Liquid N<sub>2</sub>

Temperature Liquid N <sub>2</sub>	Difunctional silane content (wt %)	Maximum tensile strength (MPa)	Toughness (MPa)	Maximum elongation (%)
Temperature Liquid N <sub>2</sub>	0	74.68	5.64	3.24
	10	72.66	9.08	5.03
	20	59.70	6.75	4.07
	30	74.61	5.26	3.30
	40	68.01	3.81	2.77
Room Temperature <sup>36</sup>	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

composition of poly(amide imide) was shown in a comparison of ATR and FTIR spectra. This was due to the dispersion of siloxane on the surface of poly(amide imide). Also, the contact angle of the epoxysilane and PDMS-added sample increased more than 40° over that of pure poly(amide imide) because of siloxane. Even a small amount of siloxane, which is hydrophobic, can form a thin film on the surface of poly(amide imide) and lead to strong water-resisting surface properties. The ac breakdown voltage was measured at the temperature of liquid nitrogen to observe the electrical characteristics, and through this, the proportionality of the ac breakdown strength and the PDMS contents was confirmed. This was caused by PDMS, which has excellent electronic insulation properties, being in the poly(amide imide) matrix. The nanocomposites produced through a low-temperature hardening process (<60°C) by the condensation of silane, rather than a high-temperature hardening process (>200°C) by imidization, showed excellent electronic insulation, surface, and mechanical properties and adhesion with metals. Because of these properties, the nanocomposites are expected to be suitable as insulating materials between turns of superconducting transformers and as flexible circuit board materials in the electronics industry. The mechanical properties of the samples at the temperature of liquid nitrogen were brittle in comparison with those measured at room temperature. These results were characteristic of a glassy state. The toughness of poly(amide imide)-epoxysilane with 30 wt % PDMS was similar to that of poly(amide imide)-epoxysilane without PDMS. The elongation at break of these samples was 3–5%, which was better than that of polyimide coatings in electronic packages.

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