

# Modification of Epoxy Resins with Polysiloxane TPU for Electronic Encapsulation. II

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## SYNOPSIS

Polyol or polysiloxane thermoplastic polyurethanes (TPU) were used to reduce microcracking in cresol-formaldehyde novolac epoxy resin cured with phenolic Novolac resin for electronic encapsulation application. A stable dispersion of TPU particles in an epoxy resin matrix was achieved via the epoxy ring opening with isocyanate groups of urethane prepolymer to form an oxazolidone. The effects of structure and molecular weight of TPU in reducing the stress of electronic encapsulant were investigated. The mechanical and dynamic viscoelastic properties and morphologies of TPU modified epoxy networks were also studied. A "sea-island" structure was observed via SEM. The dispersed polysiloxane TPU rubbers not only effectively reduce the stress of cured epoxy resins, by reducing flexural modulus and the coefficient of thermal expansion, but also increase the glass transition temperature because of the rigid oxazolidone structure formation. Electronic devices encapsulated with the polysiloxane TPU modified epoxy molding compounds exhibited excellent resistance to the thermal shock cycling test and resulted in extended device life.

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## INTRODUCTION

Epoxy molding compounds (EMCs) have been widely used as encapsulation materials for semiconductor devices to protect them from their surroundings and connect them to printed circuit boards.<sup>1</sup> Because of its excellent heat, moisture, solvent, and chemical resistance, superior electrical and mechanical properties, and good adhesion to many substrates, *o*-cresol-formaldehyde novolac epoxy (CNE) is the resin typically employed to encapsulate microelectronic devices. Upon cure, this multifunctional epoxy resin provides a densely crosslinked protective layer; however, it is relatively brittle.

The trend of electronics equipment is toward miniaturization and thinness. At the same time the scale of integration of large-scale integrated circuits (LSICs) is continuing upward, forcing the design toward larger chips, finer patterns, and higher pin

counts that are more susceptible to internal stress failure. The prevailing surface mount technology (SMT) also generates thermal stress to devices.<sup>2,3</sup> Internal stress may cause package cracking, passivation layer cracking, and aluminum pattern deformation, etc.<sup>4-6</sup> Therefore, the development of a higher ductility EMC is required for high-reliability semiconductor devices. The sources of internal stress resulting from the use of plastic encapsulants are considered to be shrinkage of the plastic upon curing and thermal mismatch between the resin and the device. In the case of EMC encapsulation, the first source, shrinkage, has been relatively minor; the second one, which is caused by the difference in thermal expansion coefficients between the resins and the silicon chip, is the dominant factor. The internal stress on IC devices caused by the difference between thermal expansion coefficients is expressed in the following equation<sup>7</sup>:

$$S = K \int (\alpha_r - \alpha_s) E_r dT$$

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where  $S$  is the internal stress in the encapsulant,  $K$  is a constant,  $\alpha_e$  is the thermal expansion coefficient of the encapsulant,  $\alpha_s$  is the thermal expansion coefficient of the silicon chip, and  $E_r$  is the flexural modulus of the encapsulant. Therefore, it is necessary to reduce the thermal expansion coefficient and the flexural modulus of EMCs to reduce internal stress or increase ultimate elongation.

Reductions of internal stress by lowering of either the thermal expansion coefficient or the flexural modulus of the encapsulant have been reported.<sup>8-17</sup> Increasing the amount of silica filler used in an encapsulant effectively lowers the thermal expansion coefficient.<sup>18</sup> However, silica may act as a stress concentrator, thus reducing EMC ductility and also increasing the elastic modulus and viscosity of the resin composition, resulting in poor moldability. Lowering the flexural modulus by modification with a rubber in a "sea-island" two-phase structure is considered to be more desirable than a one-phase structure in view of the thermal property needs.<sup>19</sup> Traditional modifiers, which can reduce the elastic modulus of the cured epoxy resins, include reactive liquid rubbers such as carboxy-terminated butadiene-acrylonitrile copolymer (CTBN).<sup>20,21</sup> When CTBN modifiers are incorporated into resin compositions, a two-phase morphology, consisting of relatively small rubber particles dispersed in a resin matrix, is generated that toughens the epoxy resins. However, phase separation depends upon the formulation, processing, and curing conditions. Inadequate phase separation can result in a significant lowering of the glass-transition temperature ( $T_g$ ).<sup>22</sup> Moreover, modifier presence in epoxy molding compounds raises the thermal expansion coefficient of the resultant EMC. The relatively high  $T_g$  of butadiene-acrylonitrile copolymer also limits their low-temperature applications. Polysiloxanes are known for their excellent thermal and thermooxidative stabilities, moisture resistance, good electric properties, low stress, and lower  $T_g$  ( $-123^\circ\text{C}$ ) values than conventional elastomers. Low-stress EMCs modified by vinyl or hydride terminated polydimethyl siloxanes<sup>23,24</sup> effectively reduced the stress of cured epoxy resins by reducing flexural modulus and the coefficient of thermal expansion. However, the  $T_g$ s were slightly sacrificed. Therefore, developing a material that not only reduces the stress of cured EMC but also increases  $T_g$  of the resultant EMC is a major task for the electronic packaging industry.

In this work, a stable dispersion of thermoplastic polyurethane (TPU) or polysiloxane TPU particles in an epoxy resin matrix was achieved via epoxy

ring opening with isocyanate groups of urethane prepolymer to form an oxazolidone. The effects of structure and molecular weight of TPU in reducing the stress of electronic encapsulant were investigated. The mechanical and dynamic viscoelastic properties and morphologies of TPU modified epoxy networks were also studied. The devices encapsulated by the TPU modified EMC were also evaluated by the thermal shock cycling test.

## EXPERIMENTAL

### Materials

The control epoxy resin was CNE (Quatrex3330, Dow Chemical Co., epoxy equivalent weight, EEW, 192]. A phenol-formaldehyde novolac resin was used as a curing agent with an average hydroxyl functionality of 6 and a hydroxyl equivalent weight of about 104 (Schenectady Chemical, HRJ-2210). Toluenediisocyanate (TDI), technical grade (80/20 mixture of 2,4 and 2,6 isomers) was purchased from Fluka AG. Polytetramethylene ether glycol (PTMG, Polymeg, Quaker Oats) was degassed under vacuum at  $65^\circ\text{C}$  and 2 mmHg for 3 h to remove any absorbed water, then stored over 4-Å molecular sieves. Polypropylene ether glycol (PPG) and polyethylene ether glycol (PEG, Naclai Tesque Inc., Kyoto, Japan) were degassed in the same manner as the PTMG. Polydimethylsiloxane- $\alpha,\omega$ -diol (PDMS-diol) with hydroxy numbers 62 (XF-6001) and 112 (X-22-160AS), giving a calculated molecular weight (MW) of 1810 and 1002, respectively, were purchased from Shin-Etsu Chemical Co., Ltd., Japan. The structure, MW, and designations of the polydiols used in the manufacture of the polyurethanes are listed in Table I. The structural formulas of CNE and methane diisocyanate (MDI) are also shown in the following. Stannous octoate was used as a catalyst in the syntheses of isocyanate terminated PDMS diols. 2-Phenylimidazole was used as a catalyst in the epoxide-isocyanate reaction to form oxazolidone.  $\text{Ph}_3\text{P}$  was the triphenylphosphine used as a curing accelerator.

### General Procedure for Urethane Prepolymer Synthesis

#### Urethane Prepolymer

To a flame-dried, 500-mL, four-necked, round-bottom flask, equipped with a water cooled condenser with a capped  $\text{CaCl}_2$  drying tube, a thermometer,  $\text{N}_2$

**Table I Polyols Used in Manufacture of Polyurethanes**

Common Name	Structure	Molecular Weight	Sample Designation
Polyethylene ether glycol, PEG	$\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$	2000	PEG
Polypropylene ether glycol, PPG	$\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$   $\text{CH}_3$	2000	PPG
Poly(tetramethylene ether) glycol, PTMG	$\text{HO}-(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$	2000	PTMG
Polydimethyl siloxane- $\alpha,\omega$ -diol, PDMS	$\text{HO}-\text{R}-\text{Si}(\text{CH}_3)_2-\text{O}-\left(\text{Si}(\text{CH}_3)_2-\text{O}\right)_n-\text{Si}(\text{CH}_3)_2-\text{R}-\text{OH}$ $\text{R} = (\text{CH}_2)_3$	1810 1002	S1810 S1002

inlet, a 150-mL addition funnel, and mechanical stirrer, was charged 1.0 mol of TDI that was heated to 80°C. To the TDI was added 0.5 mol of polyol (PEG, PPG, or PTMG) dropwise (i.e., NCO : OH = 2 : 1) under a nitrogen atmosphere. The mixture was stirred and maintained at 80°C until the absorption peak of the OH group (ca. 3500 cm<sup>-1</sup>) in the infrared (IR) spectra disappeared.

#### PDMS-Based Urethane Prepolymer

The reaction flask was equipped in the same manner as mentioned above. The PDMS-based urethane prepolymer was synthesized by adding dropwise 0.5 mol of PDMS (S1810 or S1002) with 0.15 wt % stannous octoate to 1.0 mol of TDI over a period of 1 h while maintaining the reaction at room temperature under a nitrogen atmosphere. Completion of the reaction was confirmed by IR for the disappearance of the absorption peak of the OH group.

#### General Procedure for TPU Modified CNE Preparation

To a 1-L, four-necked, round-bottomed flask, equipped with a CaCl<sub>2</sub> drying tube, heating mantle, N<sub>2</sub> inlet, stirrer, thermocouple, and temperature controller, was added 400 g of CNE. The epoxy resin was heated to 150°C and then vigorously stirred and dehydrated under vacuum (<10 mmHg) until the water content was less than 0.01% (measured by Karl Fischer). The reaction temperature was then

raised to 160°C and 350 ppm (based on CNE) of 2-phenylimidazole was added. To the stirring CNE was added 57.2 g of urethane or PDMS-based urethane prepolymer. The reaction temperature was held at 160°C for 2 h. Completion of the epoxide-isocyanate reaction was confirmed by IR spectroscopy for the disappearance of NCO group absorption. The resulted TPU or polysiloxane TPU modified epoxy resin contained ca. 12.5 wt % dispersed rubber and had an EEW of ca. 235.

#### Curing Procedure of Epoxy Resins

Various rubber modified epoxy resins were mixed with a stoichiometric amount of curing agent and Ph<sub>3</sub>P in a mill at moderate temperature to give a thermosettable epoxy resin powder. The resin powder was cured in a mold at a temperature of 150°C and 50 kg/cm<sup>2</sup> for a period of 1 h and then post-cured at 180°C for 2 h and 210°C for 3 h to obtain a cured specimen for dynamic viscoelastic analysis and SEM.

#### Encapsulation Formulation

A control resin and CNE modified with various TPU rubbers or silicone powder were formulated into seven electronic encapsulating formulations. The formulations were each cured at 175°C for 4 h. The detail of encapsulating formulations are given in a previous article.<sup>11</sup> The thermal mechanical proper-

ties of the cured encapsulating formulations were determined by the following tests.

### Measurement and Testing

#### EEW

EEWs of epoxy resins were determined by the  $\text{HClO}_4$ /potentiometric titration method.

#### IR Spectroscopy

IR spectra were recorded with a Perkin-Elmer 16PC FTIR spectrophotometer operated with a dry air purge. Signals of four scans at a resolution of  $4 \text{ cm}^{-1}$  were averaged before Fourier transformation.

#### Dynamic Viscoelastic Analysis

Dynamic viscoelastic analyses were performed on a Rheometrics RDA-II rheometer between  $-150$  and  $250^\circ\text{C}$ , with a heating rate of  $5$  or  $2^\circ\text{C}/\text{step}$  at a frequency of  $1 \text{ Hz}$ . The rectangular torsion mode was chosen and the dimensions of the specimen were  $51 \times 12.7 \times 0.76 \text{ mm}$ . The storage modulus  $G'$  and  $\tan \delta$  were determined. The peak of  $\tan \delta$  was identified as the glass transition temperature ( $T_g$ ) because a large decrease in  $G'$  occurred at this point.

#### Morphology

A JEOL JSM-6400 scanning electron microscope was employed to examine the morphology of cured rubber modified samples fractured cryogenically in liquid nitrogen. The fracture surfaces were vacuum coated with gold.

#### Flexural Properties

Flexural properties of cured resins were measured using a Shimadzu AGS-500 universal testing machine. Flexural strength and modulus were obtained at a crosshead speed of  $2 \text{ mm}/\text{min}$  according to ASTM D790-86. A 3-point loading system was chosen and rectangular bar specimens,  $80 \times 10 \times 4 \text{ mm}$ , were molded directly by a transfer molding process.

#### Thermal Mechanical Analysis

The coefficient of thermal expansion (CTE) was measured with a DuPont 943 thermal mechanical analyzer (TMA) in accordance with ASTM E831-86. A specimen  $4 \text{ mm}$  in length was used at a heating rate of  $5^\circ\text{C}/\text{min}$ . Normally, the thermal expansion increases with the increase in temperature and the CTEs were calculated from the slope. An abrupt

change in slope of the expansion curve indicates a transition of the material from one state to another.

#### Moisture Absorption

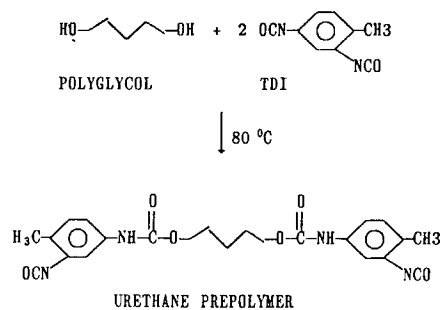
The moisture pick up was determined by placing preweighed  $3 \text{ mm}$  thick  $\times$   $50 \text{ mm}$  diameter cured disks in boiling water for  $100 \text{ h}$ . The disks were removed, cooled to ambient, wiped dry, and weighed to determine any weight gain.

#### Thermal Shock Cycling Test

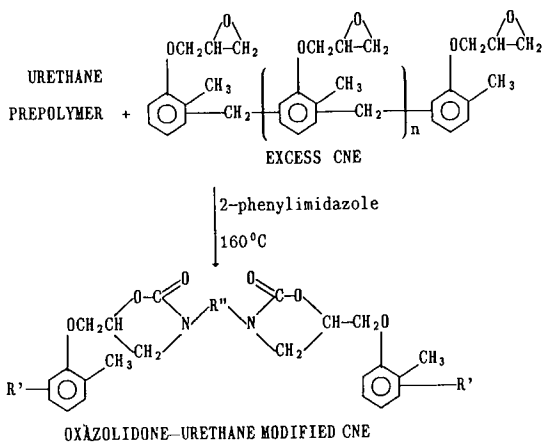
The thermal shock cycling test was carried out by the following procedure.<sup>25</sup> The device used was a 14-pin LM 324 quad operational amplifier with a single passivation layer. The device was encapsulated with an encapsulation formulation by a transfer molding process and subjected to a thermal cycling test. A cycle consisted of  $-65^\circ\text{C} \times 15 \text{ min}$  and  $150^\circ\text{C} \times 15 \text{ min}$ . The devices were inspected by an optical microscope for cracks after 250, 500, 750, 1000, 1500, 2000, 2500, 3000, 3500, 4000, and 4500 cycles. Any crack observed in the encapsulated device was counted as the failure of that device. The percentage of devices that failed (cracked), as a function of cycles, was plotted.

## RESULTS AND DISCUSSION

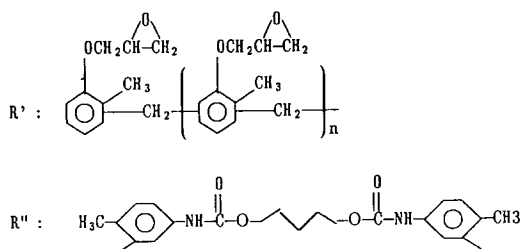
The incorporation of TPU or polysiloxane TPU as a soft segment into an epoxy resin matrix can be achieved in a two-step reaction. The first step involves the synthesis of urethane prepolymer or PDMS-based urethane prepolymer as shown in Schemes 1 and 2. The equation for the first step indicates the formation of an isocyanate terminated soft segment that is then grafted onto epoxy resin in the second step. This occurred via the epoxy ring opening in the presence of a catalyst (2-phenylim-



**Scheme 1.** The synthesis of urethane prepolymer.



Where

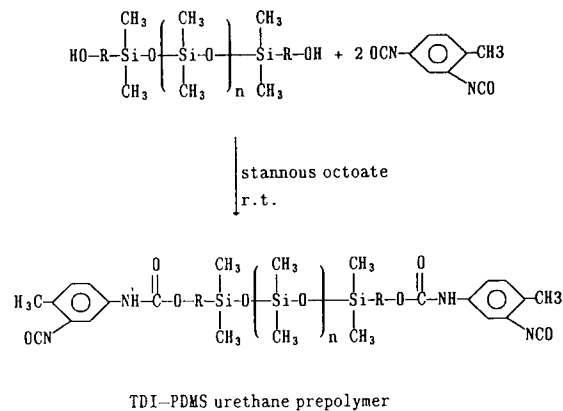


**Scheme 2.** The synthesis of PDMS-based urethane prepolymer.

imidazole) to form an oxazolidone yielding a stable dispersion of TPU particles in an epoxy resin matrix as shown in Schemes 3 and 4. These resulting TPU modified CNEs are multifunctional epoxy resins that show similar reactivity to other epoxy resins and can be cured with various curing agents.

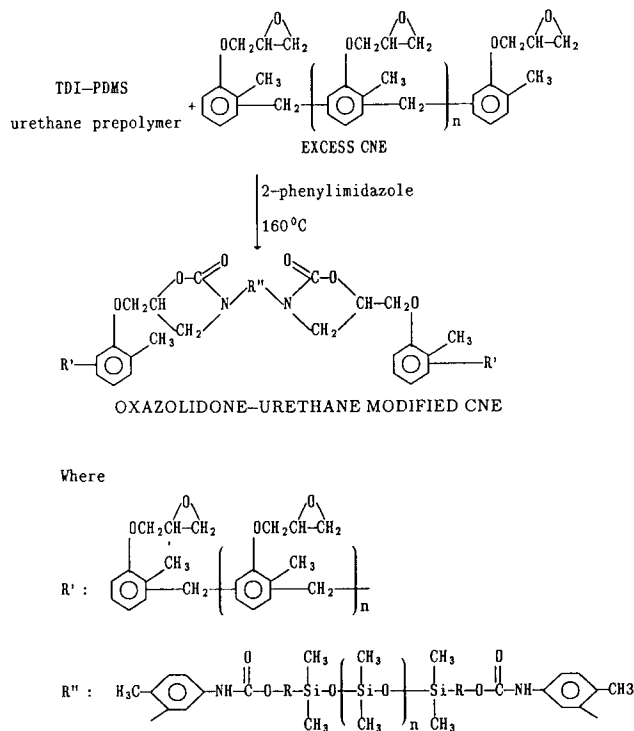
### Characteristic of TPU or Polysiloxane TPU Modified Epoxy Resins

Typical FTIR spectra of PDMS diol (X22-160AS), PDMS-based urethane prepolymer, and polysiloxane TPU modified CNE are shown in Figure 1. The completion of isocyanate terminated prepolymer formation was confirmed by the disappearance of the hydroxy group absorption peak at  $3444\text{ cm}^{-1}$  and the appearance of the absorption peak of urethane at  $3316\text{ (N-H)}$  and  $1736\text{ (C=O)}$ . The resulting isocyanate terminated urethane prepolymer was then grafted onto the epoxy resin via the epoxy ring opening in the presence of a catalyst (2-phenylimidazole) at  $160^\circ\text{C}$  to form an oxazolidone. The completion of this reaction was confirmed by the disappearance of the  $\text{—NCO}$  group absorption peak at  $2274\text{ cm}^{-1}$ . The trimerization of the NCO group to form an isocyanurate, a side reaction that can

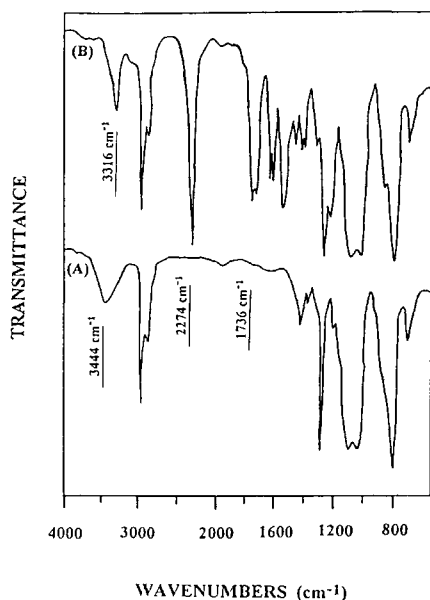


**Scheme 3.** The preparation of TPU modified CNE via epoxide-isocyanate reaction.

take place simultaneously with the oxazolidone formation, is known to be favored at a low reaction temperature. However, at a reaction temperature of  $160^\circ\text{C}$  and with 2-phenylimidazole catalyst, the oxazolidone formation is predominant. A typical IR spectrum of polysiloxane TPU modified CNE is given in Figure 2, which shows the IR characteristic absorption peak of oxazolidone at  $1758\text{ cm}^{-1}$  and without any absorption peak of isocyanurate at  $1700\text{--}1710\text{ cm}^{-1}$ .



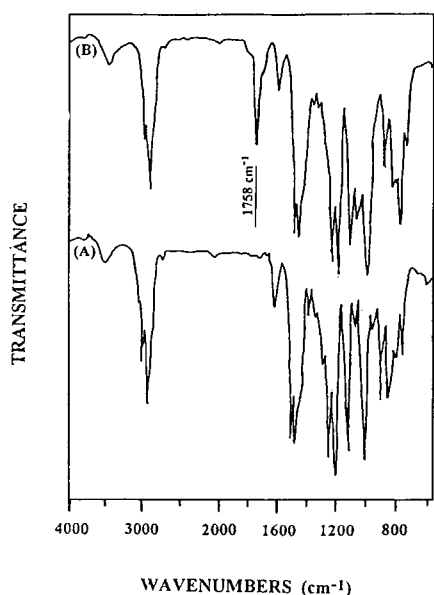
**Scheme 4.** The preparation of polysiloxane TPU modified CNE via epoxide-isocyanate reaction.



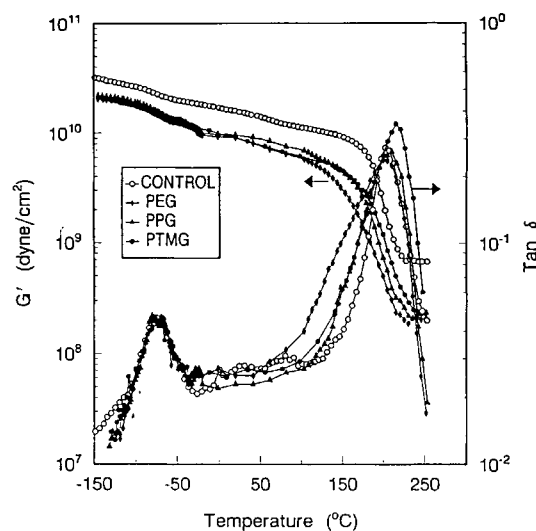
**Figure 1** FTIR spectra of (A) polydimethylsiloxane- $\alpha$ ,  $\omega$ -diol (X-22-160AS) and (B) PDMS-based urethane prepolymer. Note the disappearance of the OH group at  $3444\text{ cm}^{-1}$  and appearance of N—H and C=O bonds at  $3316$  and  $1736\text{ cm}^{-1}$ .

### Dynamic Viscoelastic Properties

The dynamic viscoelastic spectra are shown in Figures 3 and 4. The sample designations correspond

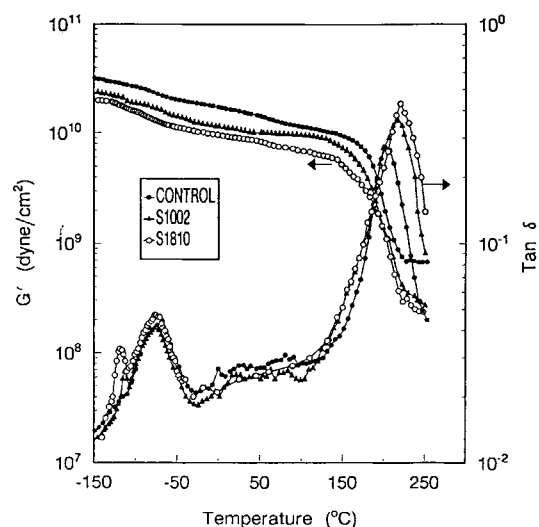


**Figure 2** FTIR spectra of (A) unmodified CNE and (B) polysiloxane TPU modified CNE (S1002). Note the disappearance of the NCO group at  $2274\text{ cm}^{-1}$  and the appearance of the oxazolidone structure at  $1758\text{ cm}^{-1}$ .



**Figure 3** Dynamic viscoelastic analysis for the control and various polyol TPU modified epoxy resins (no filler). The curing agent is phenol-formaldehyde novolac (HRJ-2210).

to those in Table I. Dynamic viscoelastic analysis can give information on the microstructure of cured rubber modified epoxy resins. Figure 3 shows the storage modulus  $G'$  and  $\tan \delta$  curves for the resins modified with various TPU particles and shows similar curves for cured polysiloxane TPU modified CNE. Storage moduli decreased with modification for all samples. The  $\tan \delta$  curves for the control



**Figure 4** Dynamic viscoelastic analysis for the control and various polysiloxane TPU modified epoxy resins (no filler). The curing agent is phenol-formaldehyde novolac (HRJ-2210).

**Table II Dynamic Viscoelastic Properties of Cured Neat Rubber Modified Epoxy Resin System**

Sample Designation	$T_g^a$ (°C) Matrix	Shear Modulus, 20°C, $\times 10^9$ dyn/cm <sup>2</sup>	$T_g^b$ (°C) Rubber
Control <sup>c</sup>	204	16.0	—
PEG	203	9.1	-68
PPG	207	9.4	-69
PTMG	213	9.0	-70
S1810	218	8.9	-117
S1002	215	10.8	-110

<sup>a</sup> Peak of  $\tan \delta$  at higher temperature.

<sup>b</sup> Peak of  $\tan \delta$  at lower temperature.

<sup>c</sup> Control, unmodified CNE.

epoxy network exhibit two major relaxations observed in most epoxy polymers<sup>26</sup>: a high-temperature or  $\alpha$  transition corresponds to the major  $T_g$  of the cured epoxy resins, above which significant chain motion takes place; the low temperature or  $\beta$  transition is attributed predominantly to the motion of the  $\text{CH}_2\text{—CH(OH)—CH}_2\text{—O}$  (hydroxyether) group of the epoxy. Figure 3 shows that the  $\alpha$ -relaxation peak in the  $\tan \delta$  curve became broader with PEG or PPG modification, but the peak position and the magnitude of the  $\alpha$ -relaxation peak hardly changed with respect to the control resin. However, the peak position of the  $\alpha$ -relaxation peak in the  $\tan \delta$  curve for the resin modified with PTMG shifted markedly toward higher temperature. This result can be attributed to the solubility between the epoxy resin and the TPU particles. The solubility of TPU particles in the epoxy resin decreases with increasing carbon number in the polyol and this lowering in solubility resulted in complete phase separation. The  $\beta$ -relaxation peak in the  $\tan \delta$  curves at ca.  $-100$  to  $-50^\circ\text{C}$  was observed without an additional peak for TPU. These results can be explained in that  $T_g$ s of the pure TPUs are around the  $\beta$ -relaxation peak of cured epoxy resin. Figure 4 shows that the peak position of the  $\alpha$ -relaxation peak in the  $\tan \delta$  curves for the resins modified with polysiloxane TPU shifted markedly toward higher temperature. This result can be attributed not only to a complete phase separation of polysiloxane TPU particles, but also to the formation of oxazolidone structure via the epoxy ring opening with isocyanate groups of the urethane. In addition to  $\alpha$  and  $\beta$  peaks, these curves all show an additional markedly small peak from  $-130$  to  $-100^\circ\text{C}$  with a center near  $-116^\circ\text{C}$  corresponding to the  $T_g$  of the polysiloxane

phase. This small peak further supports the multi-phase separation. The dynamic viscoelastic properties of the cured rubber modified epoxy resin systems including the major  $T_g$  and the rubber's  $T_g$  are shown in Table II.

### Morphology

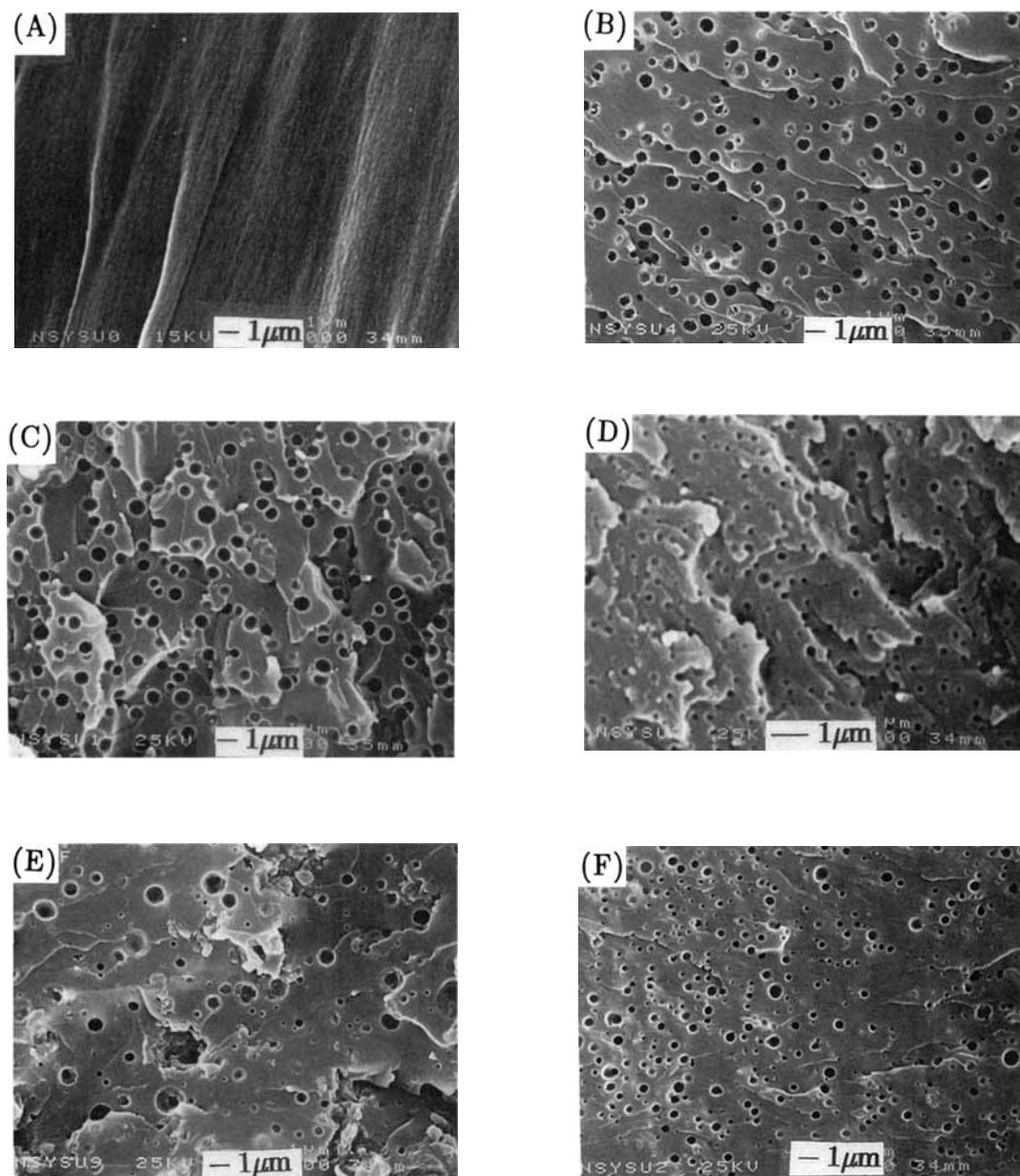
SEM photomicrographs of cold snap surfaces for the control and five TPU modified resins are given in Figure 5. A sea-island structure is observed in all rubber modified resins. Regardless of TPU or polysiloxane TPU modification, the spherical shape of rubber particles are quite the same. The sizes of the rubber particles are  $0.2\text{--}1\ \mu\text{m}$  and slightly proportional to the structure of the TPU modifiers. The polysiloxane TPU particles have slightly larger size than the polyol TPU particles. The cavity formation and deformation seem to be the toughening mechanism.

### CTE

Figure 6 shows the thermal mechanical properties. The CTE in the glassy state below the  $T_g$  was taken from  $60$  to  $100^\circ\text{C}$ , and the CTE above the  $T_g$  was taken from  $200$  to  $240^\circ\text{C}$ . For the CTE below  $T_g$ , all rubber modified encapsulants have approximately equal to or slightly lower CTE than the unmodified resin. This results in a small difference in CTEs between the encapsulant and the silicon chip.

### Glass-Transition Temperature

$T_g$ s were determined from tangents of the CTE as a function of temperature at  $100$  and  $200^\circ\text{C}$ . The



**Figure 5** Morphology of cold-snap fracture surfaces of cured epoxy resins modified with various TPU particles (12.5 wt %): (A) unmodified, (B) PEG, (C) PPG, (D) PTMG, (E) S1810, and (F) S1002.

results are shown in Figure 7. The  $T_g$ s are slightly lower for polyol TPU modification, while  $T_g$ s are slightly higher for polysiloxane TPU modification compared to the unmodified encapsulant. This observation is consistent with the viscoelastic investigation. The  $T_g$ s measured by the dynamic viscoelastic analyses (Figs. 3 and 4 where epoxy resins were cured without filler) correlate well with Figure

7 (with 70 wt % filler), although higher  $T_g$ s were shown without filler.

#### Flexural Test Properties

Figure 8 shows the result of the flexural test. The flexural moduli of the cured encapsulants were reduced markedly whether modified with polyol TPU



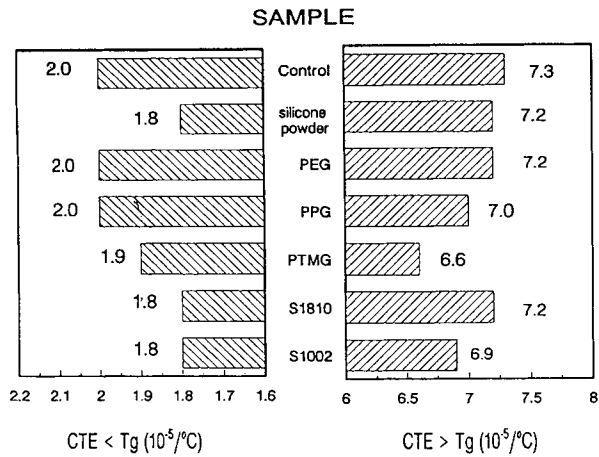


Figure 6 Coefficient of thermal expansion (CTE) for various TPU modified epoxy resin encapsulants.

or polysiloxane TPU. The flexural strengths of polysiloxane TPU modified CNE were approximately equal to or slightly larger than that of the control resin; however, the flexural strength was significantly reduced with the silicone powder modification (Fig. 8). This result indicates that physical blending, although improving the toughness of cured epoxy resin, lowers its strength.

Internal Stress

The internal stress of IC devices encapsulated by EMCs is closely related to the product of flexural modulus ( $E_{r1}$ ) and thermal expansion coefficient ( $\alpha_{r1}$ ) below the  $T_g$  of the cured EMCs.<sup>24</sup> Figure 9 shows the internal stress of the control and various rubber modified encapsulants. The polysiloxane TPU modified EMC (S1810) and TPU modified

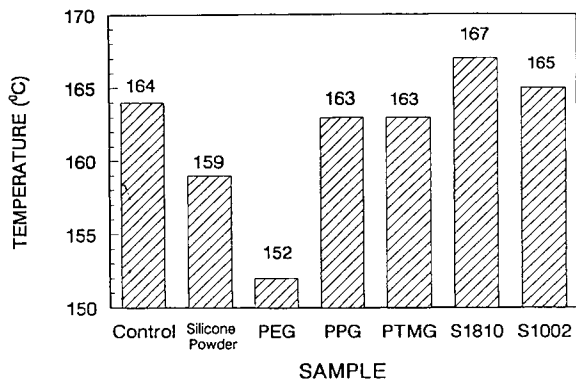


Figure 7 Glass-transition temperature for various TPU modified epoxy resin encapsulants.

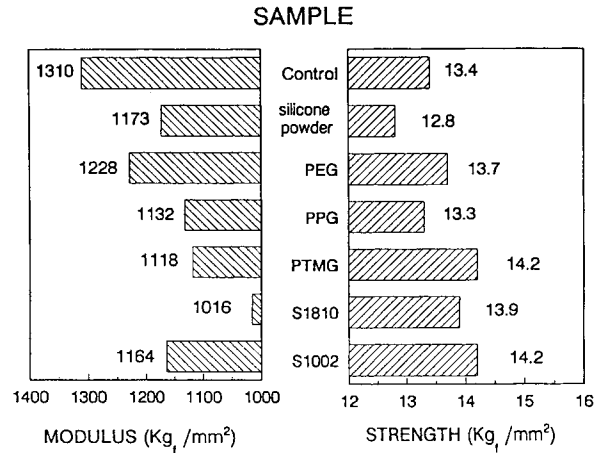


Figure 8 Flexural test properties for various TPU modified epoxy resin encapsulants.

EMC (PTMG) had a lower stress than that of the control.

Moisture Absorption

Absorbed moisture in the package was found to not only plasticize the epoxy resin, causing a lowering of the  $T_g$  and in turn affecting mechanical response, but also to cause package cracking.<sup>27</sup> This cracking (the so-called popcorn phenomenon) is caused by evaporation and expansion of absorbed moisture in the package at the temperature of reflow soldering (215–260°C) for mounting on printed circuits.<sup>28</sup> The moisture absorption results are given in Figure 10. S1810 encapsulant, consisting of polysiloxane moiety, absorbed the least moisture.

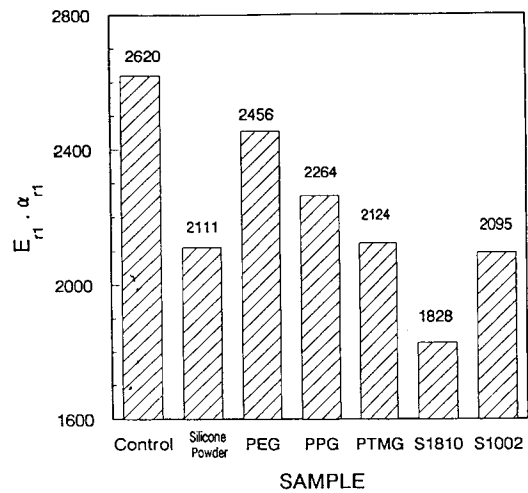


Figure 9 Comparison of stress for various TPU modified epoxy resin encapsulants.

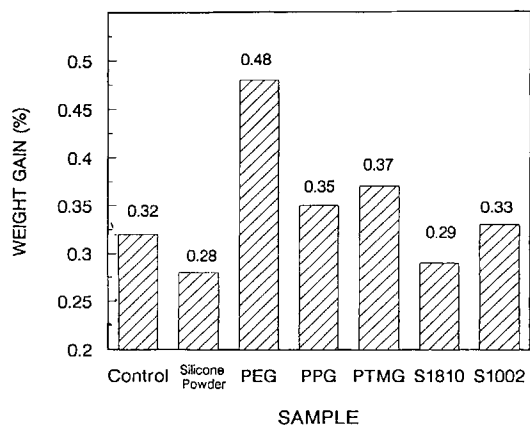
The polysiloxane TPU modified EMC (S1810) and TPU modified EMC (PTMG) had lower stress than that of the control; moreover, S1810 absorbs the least moisture and also has a higher  $T_g$  than the control. Both were chosen to encapsulate the semiconductor devices. The encapsulated devices were subjected to a thermal shock cycling test in comparison with the control resin.

### Thermal Shock Cycling Test

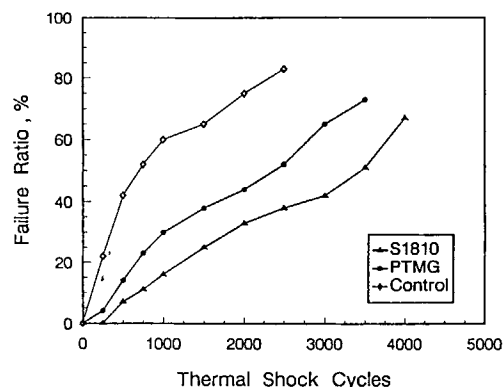
The thermal shock cycling test involves cycling the encapsulated devices at  $-65$  and  $150^\circ\text{C}$  and observing the crack (failure) of encapsulated devices at various intervals (after 250, 500, 750, 1000, 1500, 2000, 2500, 3000, 3500, 4000, and 4500 cycles). Any crack that occurred in a device is counted as failure for that device. The percentage of devices that failed vs. test cycles is given in Figure 11. The result indicates that for 50% of the devices, failure happened after 3600 cycles for the S1810 modified EMC and after 2400 cycles for the PTMG modified CNE compared to after 750 cycles for the control resin. (EMC specification is 1000 cycles, however it strives to be better than 2500 cycles.) S1810 modified EMC has much better thermal shock resistance, lower stress, higher  $T_g$ , and lower moisture absorption than the others.

### CONCLUSION

A process was developed to incorporate stable dispersed polyol TPU or polysiloxane TPU particles in an epoxy resin matrix that not only greatly re-



**Figure 10** Moisture absorption for various TPU modified epoxy resin encapsulants.



**Figure 11** Thermal shock cycling test results. Temperature cycle:  $-165^\circ\text{C} \times 15$  min and  $150^\circ\text{C} \times 15$  min.

duces the stress of cured EMCs but also increases  $T_g$  of the resultant EMC because of rigid oxazolidone structure formation. Reduction in internal stress of the encapsulant was greatly affected by the structure of the TPU. Electronic devices encapsulated with the polysiloxane TPU modified EMCs exhibited excellent resistance to the thermal shock cycling test and resulted in extended device life.

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