

# Synthesis of Aralkyl Novolac Epoxy Resins and Their Modification with Polysiloxane Thermoplastic Polyurethane for Semiconductor Encapsulation

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**ABSTRACT:** A series of phenol-based and naphthol-based aralkyl epoxy resins were synthesized by the condensation of *p*-xylylene glycol with phenol, *o*-cresol, *p*-cresol, or 2-naphthol, respectively, followed by the epoxidation of the resulting aralkyl novolacs with epichlorohydrin. The incorporation of stable dispersed polysiloxane thermoplastic polyurethane particles in the synthesized epoxy resin's matrix was achieved via epoxy ring-opening with the isocyanate groups of urethane prepolymer to form an oxazolidone. The mechanical and dynamic viscoelastic properties of cured aralkyl novolac epoxy resins were investigated. A sea-island structure was observed in all cured rubber-modified epoxy networks via SEM. The results indicate that a naphthalene containing aralkyl epoxy resin has a low coefficient of thermal expansion, heat resistance, and low moisture absorption, whereas phenol aralkyl type epoxy resins are capable of imparting low elastic modulus result in a low stress matrix for encapsulation applications. Modification of the synthesized aralkyl epoxy resins with polysiloxane thermoplastic polyurethane have effectively reduced the stress of cured epoxy resins, whereas the glass transition temperature was increased because of the formation of the rigid oxazolidone structure. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1905–1916, 1999

**Key words:** aralkyl novolac epoxy resin; naphthalene; polysiloxane TPU

## INTRODUCTION

The mainstream of the modern semiconductor industry involves resin-encapsulated diodes, transistors, ICs, LSIs, and super LSIs. Among various resin compounds for encapsulating semiconductor devices, epoxy molding compounds (EMCs) are the most popular in use, owing to their well-balanced properties including excellent heat, sol-

vent, moisture, and chemical resistance, superior mechanical and electrical properties, and good adherence to many substrates.<sup>1</sup> *o*-Cresol-formaldehyde novolac epoxy is the resin typically used to encapsulate microelectronics devices. Upon cure, this multifunctional epoxy resin provides a densely crosslinked protective layer; however, it is relatively brittle.

The trend of semiconductor devices is toward an increasingly higher degree of integration, forcing the design toward larger chip, finer patterns, and higher pin counts<sup>2,3</sup> that are more susceptible to internal stress failure.<sup>4,5</sup> Packages, on the other hand, are designed to be smaller and thinner in outer dimensions to meet the demands of

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compactness and light weight for electronic equipment. Furthermore, as to the attachment of semiconductor parts on circuit boards, surface mounting of semiconductor parts is now often used for the reasons of increased part density on boards and reduced board thickness.<sup>6</sup> The prevailing surface mount technology also causes thermal stress to devices. For mounting of semiconductor parts on a printed circuit board, the technique is to dip entire semiconductor devices in a solder bath or to pass them through a hot zone of molten solder. Both the semiconductor and printed circuit board have to be exposed to a high temperature of 215–260°C during reflow soldering process. Many problems have been realized after the soldering process, such as package cracking (popcorn phenomenon), delamination, and poor performance in humidity testing. These problems are caused mainly by the explosive vaporization and expansion of the absorbed moisture in the semiconductor device encapsulating resin layers.<sup>7</sup> Therefore, it is necessary to develop a higher ductility, high glass transition temperature ( $T_g$ ), and low-moisture-absorbing resin system for high-reliability semiconductor devices.

Reductions of internal stress by lowering either the coefficient of thermal expansion (CTE) or the flexural modulus of the encapsulant have been reported.<sup>8–14</sup> Increasing the filler loading in an encapsulant effectively lowers the CTE.<sup>15</sup> However, high silica loading not only increases the elastic modulus, but also decreases the molding properties because of high viscosity at melting condition and increases the possibility of wire deformation. There are two principal methods of lowering the flexural modulus of an epoxy compound: one is to change the overall composition of the formulation and the other is to start with materials which by themselves have a low flexural modulus.<sup>16</sup> One of the purposes of the present study was the synthesis of phenol-based aralkyl novolac epoxy resins that have a low internal stress by lowering the flexural modulus for semiconductor encapsulation application.<sup>17</sup>

Many approaches have been reported to improve the heat resistance of epoxy resins; for example, increasing the crosslink density of cured epoxy resin,<sup>18</sup> preparation of a stiff main chain,<sup>19</sup> or introduction of a bulky structure such as biphenyl or naphthalene.<sup>20</sup> Another goal of the present study was the synthesis of naphthol-based aralkyl epoxy resins, which have a planar structure and, being dense in molecular packing, can allow the resulting resin composition to have a low CTE, excellent thermal impact resistance,

soldering heat resistance and moisture resistance after soldering.

Many studies have been reported on the enhancement of mechanical properties, especially the toughness of cured epoxy resin, by changing the molecular structure such as incorporating long chains,<sup>21</sup> including sea-island structures,<sup>22</sup> by blending silicones synthetic rubber,<sup>23,24</sup> or polyester elastomers; however, these may be accompanied by lowering the  $T_g$ .<sup>25</sup> In our previous articles,<sup>26–28</sup> a process was developed to incorporate stable dispersed polysiloxane thermoplastic polyurethane (TPU) particles in an epoxy resin's matrix that not only greatly reduces the stress of cured EMCs but also increases the  $T_g$  of the resultant EMC. Therefore, the development of phenol-based or naphthol-based aralkyl epoxy resins modified with polysiloxane TPU to withstand stress while maintaining high  $T_g$  was the purpose of this study.

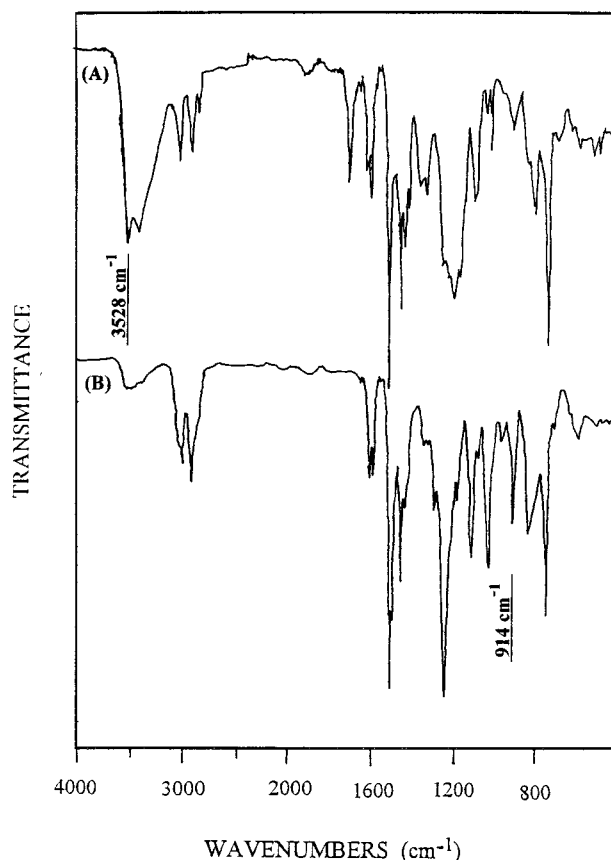
## EXPERIMENTAL

### Materials

Phenol, *o*-cresol, and *p*-cresol were purchased from Aldrich. They were all vacuum-distilled before use. *p*-Toluene sulfonic acid 1-hydrate (PTSA) was purchased from Ferak and vacuum-dried before use. 2-Naphthol was obtained from Aldrich, *p*-xylylene glycol was purchased from TCI, and epichlorohydrin (ECH) was purchased from Ferak; all were used without further purification. All solvents were purified by standard methods before use. Methylene bis(4-phenyl isocyanate) (MDI) (Multrathane, Mobay Chemical) was distilled under reduced pressure (170°C at 0.05 mmHg). Polydimethylsiloxane- $\alpha$ ,  $\omega$ -diol (PDMS-diol) with hydroxyl numbers 62 (XF-6001), giving a calculated MW of 1810, was purchased from Shin-Etsu Chemical Co., Ltd. (Japan). Stannous octoate was used as a catalyst in the synthesis of isocyanate-terminated PDMS-diol. 2-Phenylimidazole was used as a catalyst in the epoxide-isocyanate reaction to form oxazolidone. A phenol-formaldehyde novolac resin was used as a curing agent with an average hydroxyl functionality of 6 and a hydroxyl equivalent weight of approximately 104 (Schenectady Chemical, HRJ-2210). Triphenylphosphine ( $\text{Ph}_3\text{P}$ ) was used as a curing accelerator.

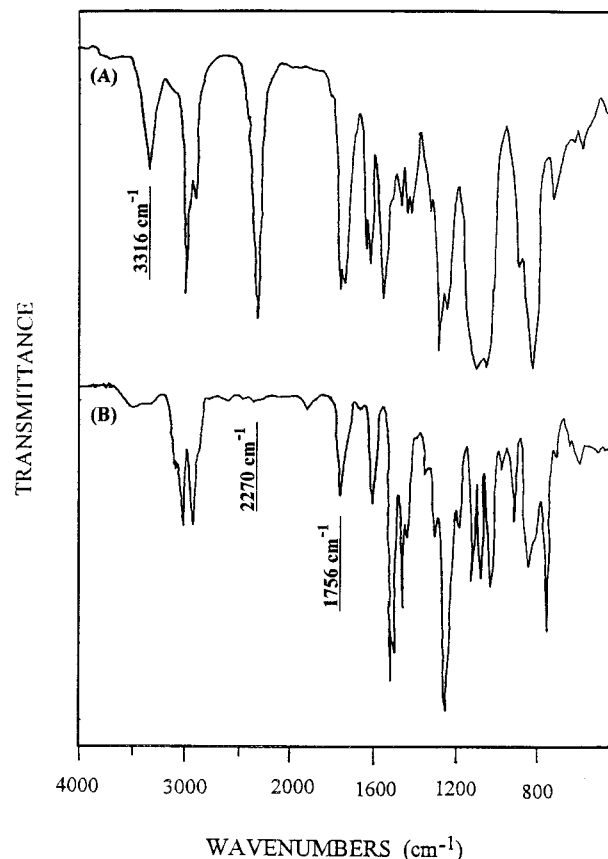
### General Procedure for the Preparation of Aralkyl Novolac Resins

Into a 1-L three-necked flat-bottomed flask, equipped with a heating mantle, thermocouple,



**Figure 1** Fourier Transform infrared (FTIR) spectra of (A) novolac resin, I<sub>a</sub>; (B) epoxy resin, II<sub>a</sub>.

and temperature controller, magnetic stirrer, and a Dean-stark trap with a reflux condenser, was added a solution of 69 g (0.5 mol) of *p*-xylylene glycol in 200 mL of 1-butanol and 1.5 mol of phenol (141 g), *o*-cresol (159 g), *p*-cresol (159 g), or 2-naphthol (216 g), respectively. After purging with nitrogen for 10 min, PTSA, (1.0 g) was added to the above solution at room temperature. The mixture was allowed to react with stirring at 115 to 120°C for 10 h under a reduced pressure (ca. 200 mmHg), in the meantime, removing water by azeotropeing with 1-butanol and returning the distilled 1-butanol to the system. The resulting mixture was neutralized with a dilute aqueous potassium hydroxide solution and washed with deionized water until the wash solution was neutral. The organic phase was finally "rotavapped" at 195°C under full vacuum for 3 h to remove the excess phenol to less than 0.3% (as analyzed by LC). Measurements by gel permeation chromatography (GPC) and infrared (IR) absorption spectroscopy were made on the resins and the results are shown in Figures 1 and 2 and Table I.



**Figure 2** FTIR spectra of (A) PDMS-based urethane prepolymer; (B) polysiloxane TPU-modified epoxy resin, II<sub>a</sub>-S.

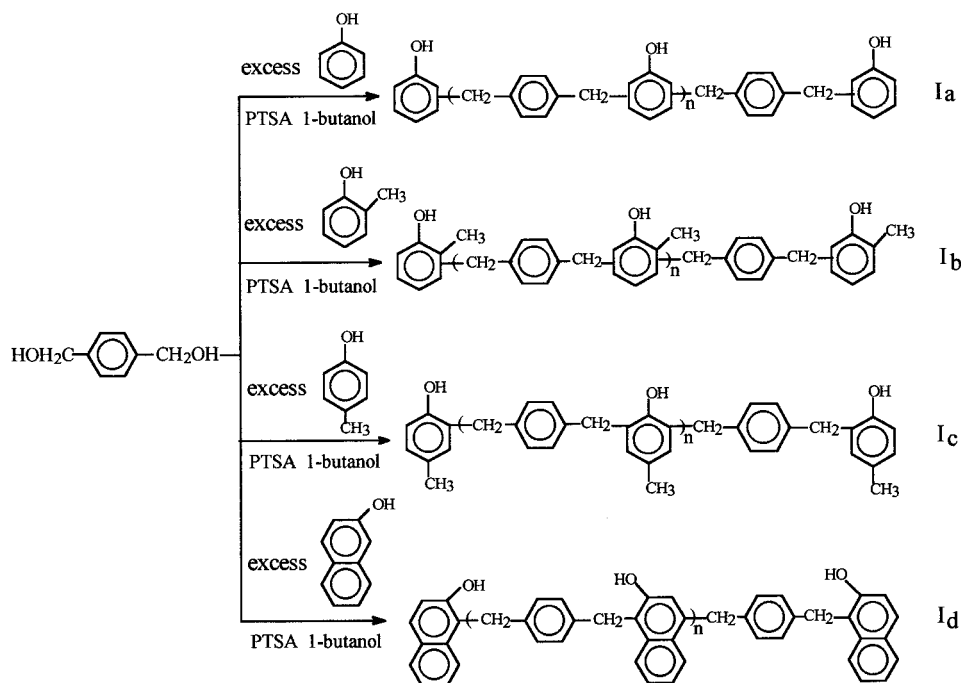
The synthetic scheme is shown in Scheme 1.

#### General Procedure for the Preparation of Polyglycidyl Ether of the Aralkyl Novolac Resins

To a 1-L four-neck round-bottomed flask, equipped with a stirrer, heating mantle, thermocouple, temperature controller, and a Dean-Stark trap with a reflux condenser, was added 0.5 equivalent of the above synthesized aralkyl novolac resin, 5 mol of ECH, and 80 g of the methyl ether of propylene glycol (1-methoxy-2-hydroxy propane) as a solvent.

**Table I** Average Molecular Weights of Novolac Resins Measured Via GPC

Novolac	$\overline{M}_n$	$\overline{M}_w$
I <sub>a</sub>	886	1099
I <sub>b</sub>	753	908
I <sub>c</sub>	719	1045
I <sub>d</sub>	791	959



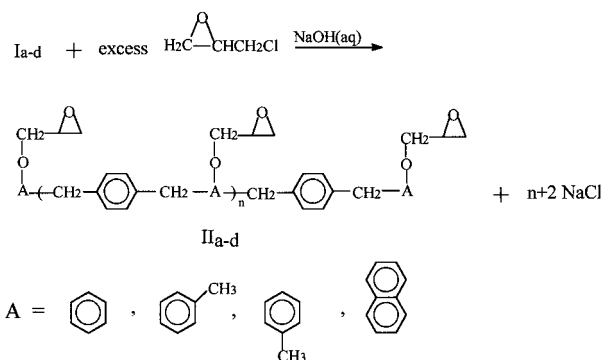
**Scheme 1** The syntheses of aralkyl novolac resins.

After stirring at room temperature and atmospheric pressure to thoroughly mix the contents, the temperature was raised to 65°C and the pressure was reduced to 160 mmHg absolute. To the resultant solution was continuously added 42 g, of a 48 wt % sodium hydroxide solution at a constant rate via a metering pump over a period of 3 h while maintaining the reaction temperature at 65°C under a reduced pressure. During the addition of the NaOH, the water was removed from the system by codistilling with ECH and solvent; in the meantime distilled ECH and solvent were returned to the system. Upon completion of the addition, the reaction mixture was maintained at 65°C for an additional 30 min. The resulting mixture was neutralized with a dilute aqueous potassium hydroxide solution and washed with deionized water. The organic phase was "rotavapped" at 190°C under full vacuum over 3 h to remove the excess ECH and solvent. The residue was extracted with methyl isobutyl ketone (MIBK), the extract was washed four times with deionized water, and the MIBK was distilled off at 190°C to recover 103 g of an epoxy resin. The general schematic for preparation of poly(glycidyl ether) is shown in Scheme 2.

### Dehydrohalogenation

The crude poly(glycidyl ether) of the aralkyl novolac resin (100 g) was further dehydrohaloge-

nated by dissolving in 150 mL of MIBK and stirred with 31.5 g of 5 wt % aqueous KOH in a 500-mL flask equipped with a hot plate, magnetic stirrer, and a reflux condenser. The reaction mixture was heated to reflux temperature and held for 2 h. The lower water layer was removed, and the organic layer was washed four times with warm (40°C) deionized water. The organic layer, after washing, was "rotavapped" at 190°C under full vacuum over 3 h to remove the solvent. The epoxy equivalent weight and total chlorine contents of each aralkyl epoxy resin were determined. Results are shown in Table II.



**Scheme 2** The preparation of poly(glycidyl ether) of aralkyl novolac resins.

**Table II The EEW and Total Chlorine Content of Aralkyl Epoxy Resins**

Epoxy Resin	EEW	Total Cl (ppm)
II <sub>a</sub>	215	485
II <sub>b</sub>	244	651
II <sub>c</sub>	298	530
II <sub>d</sub>	295	432

### General Procedure for the Synthesis of Urethane Prepolymer

To a flame-dried 500-mL four-necked round-bottomed flask, equipped with a water-cooled condenser with a capped CaCl<sub>2</sub> drying tube, a thermometer, N<sub>2</sub> inlet, a 150-mL addition funnel and mechanical stirrer, was charged 1.0 mol of MDI and heated to 85°C. To the MDI was added 0.5 mol of PDMS-diol with 0.15 wt % stannous octoate dropwise over a period of 1 h while maintaining the reaction temperature at 65°C 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 the Preparation of TPU-Modified Aralkyl Epoxy Resin

To a 500-mL 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 200 g of epoxy resin. The epoxy resin was heated to 150°C and then vigorously stirred and dehydrated under vacuum until the water content was less than 0.01% (measured by a Karl Fischer). The reaction temperature was then raised to 160°C, and 350 ppm (based on epoxy resin) of 2-phenylimidazole was added. To the stirring mixture was added 28.6 g of PDMS-based urethane prepolymer. The reaction temperature was held at 160°C for 2 h. Completion of epoxide-isocyanate reaction was confirmed by IR spectroscopy for the disappearance of the NCO group absorption. The resulting polysiloxane TPU-modified epoxy resin contained ca. 12.5 wt % dispersed rubber.

### Curing Procedure of Epoxy Resins

Each unmodified and polysiloxane TPU-modified epoxy resin was 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 kgcm<sup>-2</sup> for a period of 1 h and then postcured at 180°C for 2 h and 210°C for 3 h to obtain a cured specimen.

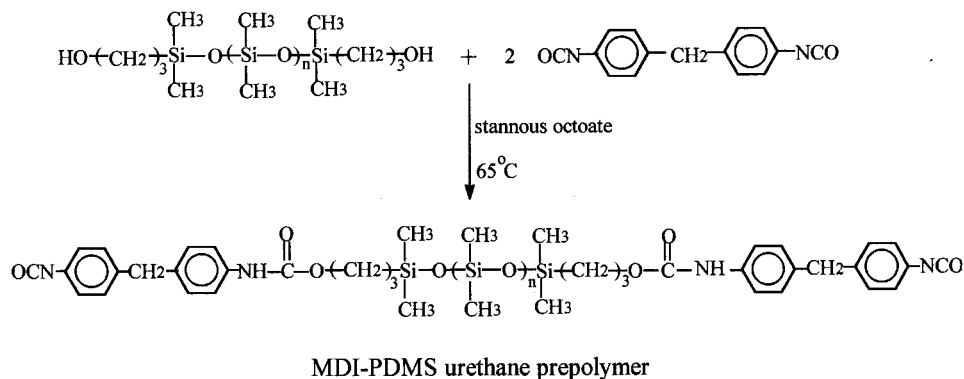
### Measurement and Testing

IR spectra were recorded with a Perkin-Elmer 16PC FTIR. Spectrophotometer operated with a dry air purge. Signals of 32 scans at a resolution of 4 cm<sup>-1</sup> were averaged before Fourier transformation. Mass spectrometric analyses were performed on a VG70-250S GC/mass spectra spectrometer. The molecular weight of aralkyl novolac resin was obtained on a Shimadzu C-R4A gel permeation chromatograph using a Shimadzu GPC-8025 column. Samples were analyzed by a Shimadzu RID-6A reflex indicator. The epoxy equivalent weight of epoxy resins was determined by the HClO<sub>4</sub>/potentiometric titration method. Dynamic viscoelastic properties were studied on a Perkin-Elmer 7 series thermal analysis with a DMA mode between -150 and 300°C with a heating rate of 5°C/min at a frequency of 1 Hz. The temp/time scan in a three-point bending mode was chosen and the dimensions of the specimen were 15 × 5.5 × 1.5 mm according to ASTM D790-95a; the distance of the support span was 10 mm. The elastic modulus E' and tan δ were determined. The CTE was measured with the TMA mode of the Perkin-Elmer 7 instrument in accordance with ASTM E831-86. A specimen 2 mm in thickness was used at a heating rate of 5°C/min. The CTE values were calculated from the slope. An AEOL JSM-6400 SEM was used to examine the morphology of cured rubber-modified samples fractured cryogenically in liquid nitrogen. The fracture surfaces were vacuum-coated with gold. The moisture pick-up was determined by placing preweighed 3-mm thick × 50-mm diameter cured disks in boiling water for 100 h. The discs were removed and were cooled to ambient and then wiped dry and weighed to determine any weight gain. The thermal stability profiles were obtained using a Perkin-Elmer thermogravimetric analyzer with a heating rate of 10°C/min in nitrogen atmosphere. The decomposition temperature (T<sub>d</sub>) was measured as the onset temperatures from thermogravimetric analyzer curves.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

Phenol-based or naphthol-based aralkyl novolacs were synthesized by condensing *p*-xylylene glycol



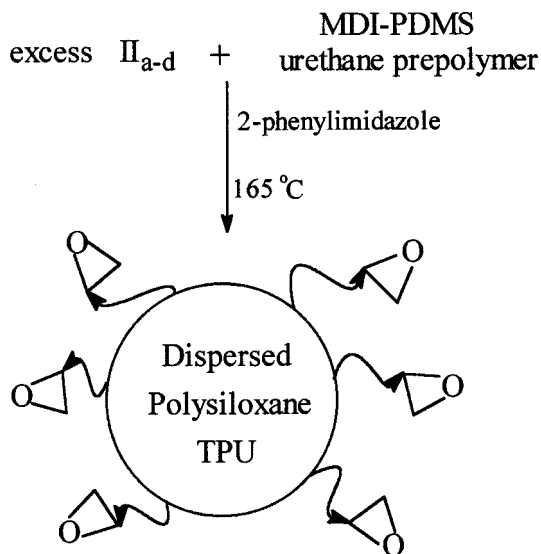
**Scheme 3** The synthesis of urethane prepolymer.

with excess phenol, *o*-cresol, *p*-cresol or 2-naphthol, respectively, using *p*-toluene sulfonic acid as a catalyst (Scheme 1). GPC measurement of the four novolacs were performed and the average molecular weights ( $\overline{M}_n$  and  $\overline{M}_w$ ) as shown in Table I were calculated by use of a GPC calibration curve. The preparation of aralkyl epoxy resin involves reacting the novolac with a halohydrin in the presence of an alkali metal hydroxide is shown in Scheme 2. The structure of the synthesized aralkyl novolacs was confirmed by IR and mass spectra. From the IR spectra (Fig. 1) of  $I_a$  and its poly(glycidyl ether) ( $II_a$ ), we can see a strong absorption peak at  $3400\text{--}3600\text{ cm}^{-1}$  representing the  $\text{—OH}$  functional groups of the synthesized aralkyl novolac, and a peak appeared at  $914\text{ cm}^{-1}$  representing the oxirane ring absorption of aralkyl epoxy resin. The incorporation of polysiloxane TPU as a soft segment into an epoxy resin's matrix can be achieved in a two-step reaction in accordance with the reported procedures of our previous studies.<sup>26</sup> The first step involving the synthesis of urethane prepolymer is shown in Scheme 3. The equation for the first step indicates the formation of an isocyanate-terminated soft segment, which is then grafted onto epoxy resin in the second step via epoxy ring opening in the presence of a catalyst (2-phenylimidazole) to form an oxazolidone to give a stable dispersion of polysiloxane TPU particles in an epoxy resin's matrix as shown in Scheme 4. The completion of this reaction was confirmed by the disappearance of the  $\text{—NCO}$  group absorption peak at  $2255\text{--}2270\text{ cm}^{-1}$ , whereas the IR characteristic absorption peak of oxazolidone appeared at  $1750\text{--}1760\text{ cm}^{-1}$ . The IR spectra are shown in Figure 2.

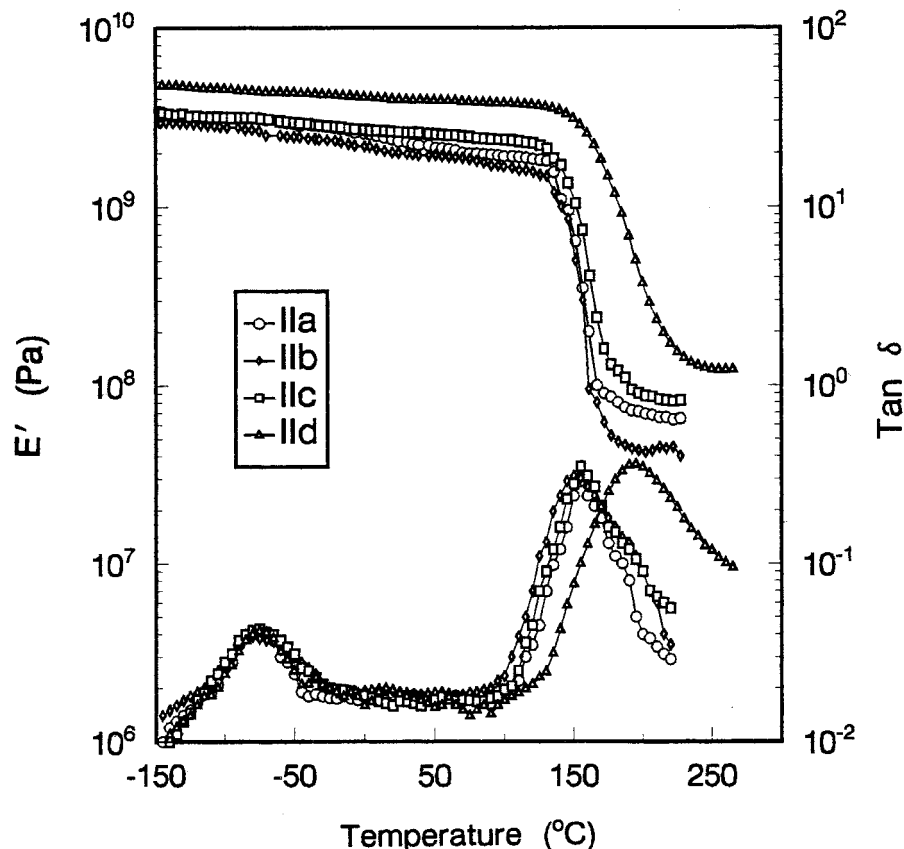
#### Dynamic Viscoelastic Analysis

The dynamic viscoelastic spectra are shown in Figures 3 and 4. Dynamic viscoelastic analysis

can give information on the microstructure of cured epoxy resins. The  $\tan \delta$  curves for the cured epoxy resins exhibit two major relaxations observed in most epoxy polymers<sup>29</sup>: a high-temperature  $\tan \delta$  peak corresponds approximately to the  $T_g$  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  $\text{CH}_2\text{—CH(OH)—CH}_2\text{—O}$  (hydroxy ether) group of the epoxy. Figure 3 shows the storage elastic modulus  $E'$  and  $\tan \delta$  curves for the four cured aralkyl epoxy resins with different structures. It can be seen from Figure 3 that the elastic modulus and the peak position of  $\alpha$ -relaxation peak in the  $\tan \delta$  curves are related to the chemical structure. The elastic moduli and the peak position of  $\alpha$ -relaxation peak in the  $\tan \delta$  curves of phenol-based epoxy resins ( $II_{a-c}$ ) are lower than that of naphthol-based ep-



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



**Figure 3** Dynamic viscoelastic analyses of cured phenol-based and naphthol-based aralkyl epoxy resins. The curing agent is phenol-formaldehyde novolac (HRJ-2210).

oxy resin (II<sub>d</sub>). This can be attributed to the rigid naphthalene structure. The rigid naphthol-based epoxy (II<sub>d</sub>) exhibited higher elastic modulus than that of phenol-based epoxy (II<sub>a-c</sub>) as expected. Several factors related to chemical structure are known to affect the  $T_g$ . The most important factor is chain stiffness or flexibility of the polymer.<sup>30</sup> Introduction of a rigid naphthalene structure into the epoxy resin increases the difficulty of chain rotation, and hence the  $T_g$  is higher. A comparison of elastic modulus  $E'$  and  $\tan \delta$  curves between the cured unmodified and rubber-modified epoxy resin is shown in Figure 4. The elastic modulus decreases with rubber modification. In addition to the epoxy  $\alpha$  and  $\beta$  peaks, the  $\tan \delta$  curve for the rubber-modified product shows an additional markedly small peak from  $-125$  to  $-105^\circ\text{C}$  with a center near  $-115^\circ\text{C}$  corresponding to the  $T_g$  of the polysiloxane phase. Figure 4 also shows that the peak position of the  $\alpha$ -relaxation peak in the  $\tan \delta$  curves for the resins modified with polysiloxane TPU shifts markedly toward higher temperature. This result can be attributed

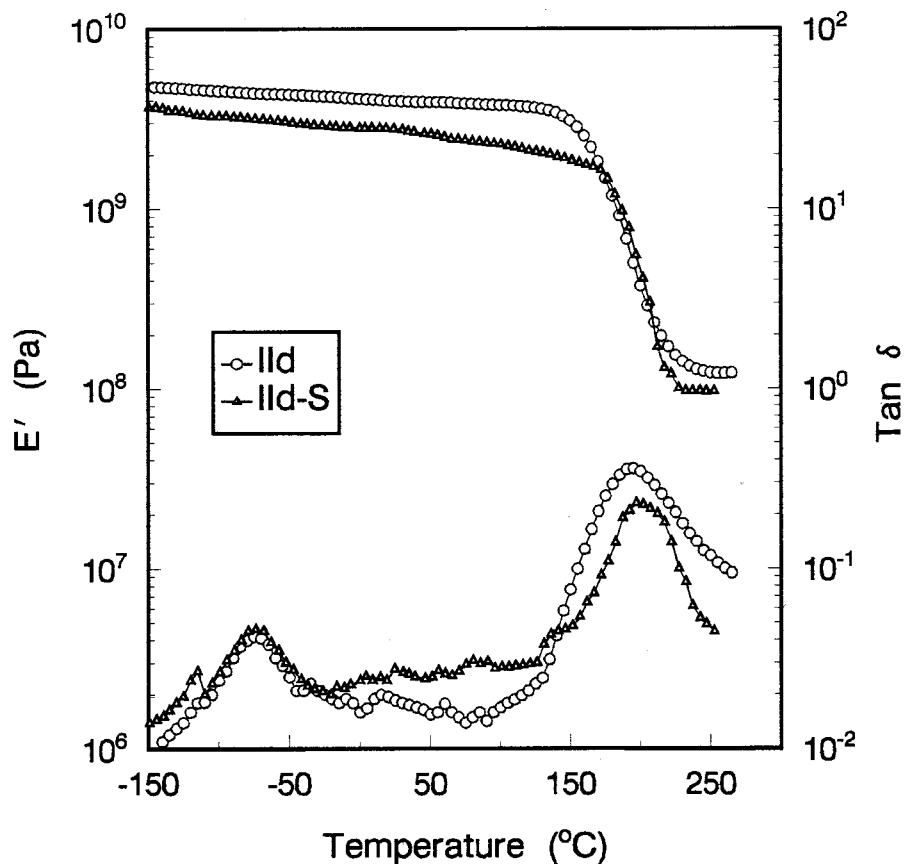
not only to the complete phase separation of polysiloxane TPU particles but also to the formation of oxazolidone structure via epoxy ring opening with the isocyanate groups of urethane. The dynamic viscoelastic properties of the cured aralkyl epoxy resin systems, including the major  $T_g$  and the rubber's  $T_g$ , are shown in Table III.

### Morphology

SEM photomicrographs of freeze-fractured surfaces for the cured aralkyl epoxy resins and their rubber-modified epoxy networks are given in Figure 5. Electron micrographs reveal that rubber particles  $1 \mu\text{m}$  or less in size are dispersed in rubber-modified resins in a "sea-island" structure ("island" of polysiloxane TPU dispersed in the "sea" of an epoxy resin).

### Thermal Mechanical Properties

Table IV shows the thermal mechanical properties. The CTE in the glassy state below the  $T_g$  was taken



**Figure 4** Comparison of dynamic viscoelastic properties of cured rubber-modified and unmodified aralkyl epoxy networks.

from 60 to 100°C and the CTE above the  $T_g$  was taken from 180 to 230°C. For the CTE, all cured naphthol-based epoxy resins ( $\text{II}_d$  and  $\text{II}_d\text{-S}$ ) are lower than those of phenol-based epoxy resins, no

matter whether the resins are modified with polysiloxane TPU or not. For the CTE below  $T_g$ , all rubber-modified resins have CTE approximately equal to or slightly lower than those of the unmodified

**Table III** Dynamic Viscoelastic Properties of Cured Rubber-Modified and Unmodified Aralkyl Epoxy Networks

Sample Designation	$E'$ (GPa)			$T_g^b$ (°C) Matrix	$T_g^c$ (°C) Rubber
	$E'_{20^\circ\text{C}}$	$E'_{100^\circ\text{C}}$	$E'_{\text{avg}}^a$		
$\text{II}_a$	2.38	1.91	2.15	150	—
$\text{II}_b$	2.01	1.67	1.84	147	—
$\text{II}_c$	2.64	2.36	2.50	152	—
$\text{II}_d$	3.98	3.78	3.88	197	—
$\text{II}_a\text{-S}^d$	1.92	1.61	1.77	154	116
$\text{II}_b\text{-S}$	1.73	1.39	1.56	152	113
$\text{II}_c\text{-S}$	2.08	1.71	1.90	158	118
$\text{II}_d\text{-S}$	2.81	2.29	2.55	200	117

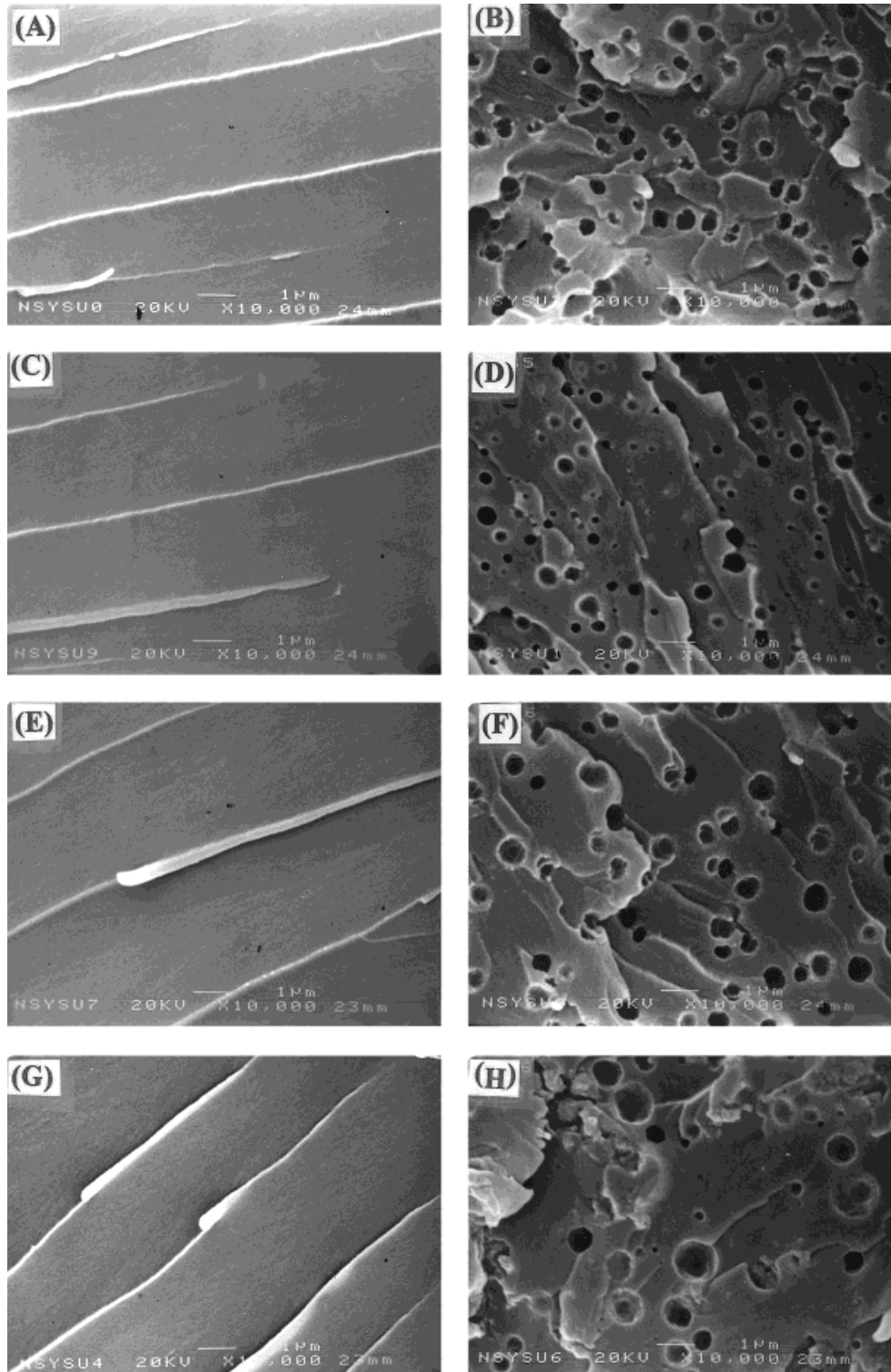
<sup>a</sup>  $E'_{\text{avg}} = (E'_{20^\circ\text{C}} + E'_{100^\circ\text{C}})/2$ .

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

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

<sup>d</sup> The character S represents the epoxy resin modified with polysiloxane TPU.





**Figure 5** Morphology of cold-snap fracture surfaces of cured epoxy resins modified with or without polysiloxane TPU rubber particles (12.5 wt %): (A) II<sub>a</sub>; (B) II<sub>a</sub>-S; (C) II<sub>b</sub>; (D) II<sub>b</sub>-S; (E) II<sub>c</sub>; (F) II<sub>c</sub>-S; (G) II<sub>d</sub>; (H) II<sub>d</sub>-S.

resins and this will result in a small difference in CTEs between encapsulant and silicon chip in semiconductor encapsulation application.

$T_g$  values were determined from the tangents of the CTE as a function of temperature at 100 and 180°C, and the results are shown in Table IV.

**Table IV Thermal Mechanical Properties of Epoxy Resins Cured with Phenol-Formaldehyde Novolac (HRJ-2210)**

Sample	$T_g$ (°C)	CTE ( $10^{-5}/\text{K}$ )	
		$<T_g$	$>T_g$
II <sub>a</sub>	134	8.86	23.6
II <sub>b</sub>	133	9.01	22.4
II <sub>c</sub>	139	8.12	20.3
II <sub>d</sub>	178	6.51	14.6
II <sub>a</sub> -S	139	8.52	21.6
II <sub>b</sub> -S	138	8.62	22.0
II <sub>c</sub> -S	145	7.91	17.9
II <sub>d</sub> -S	182	6.11	13.8

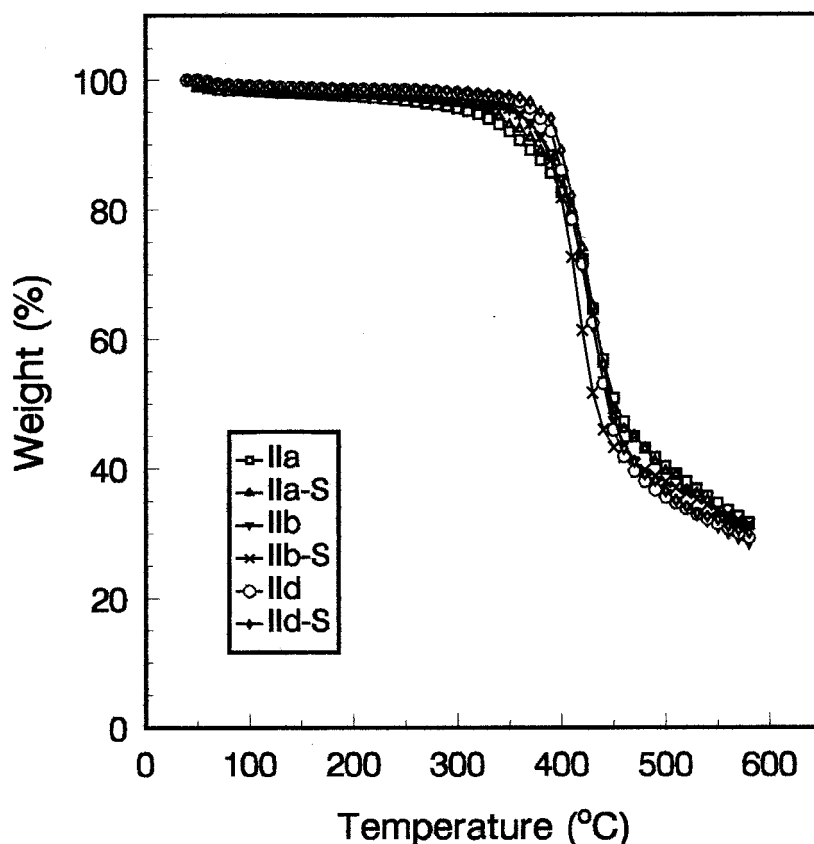
For the  $T_g$ , all cured naphthol-based epoxy resins are higher than those of phenol-based epoxy resins. This result can be attributed to the rigid naphthalene structure in the backbone of epoxy resins as observed in the viscoelastic investigation. Furthermore, in the phenol-based epoxy resin system,  $T_g$  became higher in the order, II<sub>a</sub>,

II<sub>b</sub>, < II<sub>c</sub>. This result is in agreement with that reported in earlier work.<sup>31</sup> Moreover, all rubber-modified resins have  $T_g$  values higher than those of the unmodified resins. This observation is also consistent with the viscoelastic investigation. It can be attributed to the formation of oxazolidone structure via epoxy ring opening with the isocyanate group of urethane.<sup>26</sup>

Because the naphthalene structure is planar and dense in molecular packing, it is natural to consider that the neighboring naphthalene groups should be oriented in a rectangular block network as shown in our previous article.<sup>32</sup> The stacking of the network would result in the highest modulus (Fig. 3), highest  $T_g$  (Tables III and IV), and the lowest CTE for the naphthalene containing epoxy resin.

### Thermal Stability

The thermogravimetric analyses traces are shown in Figure 6 and the  $T_d$  are summarized in Table V. The  $T_d$  value was determined by heating the sample at a rate of 10°C/min and observing the onset of degradation (a weight loss). It can be

**Figure 6** Thermogravimetric traces of cured epoxy resins.

**Table V** Moisture Absorption and Thermal Stabilities of Cured Epoxy Resins

Sample	Moisture Absorption Gains (wt %)	$T_d^a$ (°C)
II <sub>a</sub>	2.34	385.42
II <sub>b</sub>	2.08	379.77
II <sub>c</sub>	2.01	387.64
II <sub>d</sub>	1.48	391.38
II <sub>a</sub> -S	2.23	386.73
II <sub>b</sub> -S	1.98	380.15
II <sub>c</sub> -S	1.83	388.93
II <sub>d</sub> -S	1.41	393.35

<sup>a</sup> The onset temperature of TGA curve.

seen that the epoxy resins containing naphthalene structure exhibited better thermal stability than the epoxides containing phenyl structure. This can be attributed to the three resonance structures of naphthalene compared with the two resonance structures for phenyl as shown in our previous study.<sup>32</sup> Furthermore,  $T_d$ s are slightly higher for polysiloxane TPU-modified resins compared with the unmodified resins. This result may be attributed to the thermal stability of the incorporated Si—O—Si structure and the formation of rigid oxazolidone structure.

### Moisture Absorption

The results of the moisture absorption test are given in Table V. Absorbed moisture in the package was found not only to plasticize the epoxy resin, causing a lowering of the  $T_g$  and in turn affecting mechanical response, but also to cause the package to crack during the soldering process.<sup>33</sup> In the phenol-based aralkyl epoxy resin system, II<sub>b</sub> and II<sub>c</sub> have better hydrophobic properties than that of II<sub>a</sub>, indicating that the introduction of the hydrophobic methyl group to the benzene ring had inhibited moisture absorption. Furthermore, the incorporation of the naphthalene group into the backbone depressed the moisture absorption effectively as shown in Table V. All four rubber-modified epoxy resins containing the polysiloxane TPU moiety absorbed less moisture than did the unmodified epoxy resins.

### Internal Stress

The sources of internal stress are considered dominantly to be cooling of the cured epoxy resin specimen from its curing temperature to room temperature, meanwhile the internal stress

would accumulate in the resin matrix. The internal stress of cured specimens is closely related to the product of the elastic modulus ( $E'_{avg}$ ) and the CTE ( $\alpha_{r1}$ ) below the  $T_g$  of the cured epoxy resins.<sup>8</sup> Table VI lists the elastic modulus ( $E'_{avg}$ ), CTE ( $\alpha_{r1}$ ), and the internal stress parameter ( $E'_{avg} \times \alpha_{r1}$ ) of the unmodified and their rubber-modified epoxy resins investigated. The result shows that the internal stresses of all phenol-based epoxy resins are lower than those of naphthol-based epoxy resins, no matter whether the resins are modified with silicone rubber or not. Furthermore, the dispersed polysiloxane TPU particles effectively reduce the stress of all four cured epoxy resins by reducing the elastic modulus and CTE. This could be attributed to the complete separation of the rubber phase from epoxy matrix resulting in an island structure and the dispersed rubber particles acting as a stress-relieving agent.

### CONCLUSION

Phenol-based and naphthol-based aralkyl epoxy resins were synthesized by condensing *p*-xylylene glycol with phenol, *o*-cresol, *p*-cresol, and 2-naphthol, respectively, followed by the epoxidation of the resulting aralkyl novolacs with epichlorohydrin. The results indicate that epoxy resins based on phenol aralkyl resins are capable of imparting low elasticity, resulting in a low-stress encapsulant for semiconductor encapsulation, whereas a naphthalene ring-bearing aralkyl epoxy resin has a low coefficient of thermal expansion, heat resistance, and low-moisture absorption. These characteristics will make it an ideal candidate as a matrix resin for electronic applications. Modification of the synthesized aralkyl epoxy resins with

**Table VI** The Internal Stress Parameter of Cured Epoxy Resins

Sample	$E'_{avg}$ (GPa)	$\alpha_{r1}$ ( $10^{-5}/K$ )	Internal Stress $E'_{avg} \times \alpha_{r1}$ (kPa/K)
II <sub>a</sub>	2.15	8.86	190.49
II <sub>b</sub>	1.84	9.01	165.78
II <sub>c</sub>	2.50	8.12	203.00
II <sub>d</sub>	3.88	6.51	252.59
II <sub>a</sub> -S	1.77	8.52	150.80
II <sub>b</sub> -S	1.56	8.62	134.47
II <sub>c</sub> -S	1.90	7.91	150.29
II <sub>d</sub> -S	2.55	6.11	157.34

polysiloxane TPU effectively reduced the stress of cured epoxy resins, whereas the  $T_g$  is increased because of the formation of the rigid oxazolidone structure.

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