Synthesis and Modification of a Naphthalene-Containing Trifunctional Epoxy Resin for Electronic Applications

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ABSTRACT: A series of trifunctional epoxy resins were successfully synthesized by the condensation of 2,6-dimethylol-4-methylphenol with phenol , cresol, 2,6-dimethylphenol or 2-naphthol, respectively, followed by epoxidation with a halohydrin. The structures of the synthesized triphenols were characterized by elemental analysis (EA), mass spectrometry (MS), and nuclear magnetic resonance (NMR) spectrometry, including ¹H-NMR and ¹³C-NMR. The resulted epoxy resins were cured with 4-4'-diaminodiphenyl sulfone (DDS), and the cured products were investigated. The cured trifunctional 2,6-bis-(2-glycidyloxy-1-naphthyl-methyl)-4-methyl phenyl glycidyl ether had the highest glass transition temperature, highest thermal stability, the lowest coefficient of thermal expansion, and lowest moisture absorption of the epoxy resins studied. The internal stress of cured naphthalene-containing epoxy resin was reduced by modification with 12 wt % amino-terminated polydimethyl siloxane (ATPDMS), while the glass transition temperature was only slightly depressed. Phase separation of the silicone rubber-modified epoxy matrix was characterized by SEM. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1907–1921, 1998

Keywords: novolac; naphthalene; glass transition temperature; moisture absorption; thermal stability; morphology; internal stress

INTRODUCTION

Epoxy resins have been widely used for printed circuit board and semiconductor encapsulation applications, owing to their well-balanced properties including excellent heat, moisture, solvent, and chemical resistance, superior electrical and mechanical properties, and good adhesion to many substrates.¹ *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, the trend of IC packaging has shifted from conventional insertion mount devices, such as DIP (Dual Inline Package), to surface-mount devices, such as QFP (Quad Flat Package), SOP (Small Outline Package), and PLCC (Plastic Leaded Chip Carrier).² For mounting on a printed circuit board, both the semiconductor and circuit board have to be exposed to high temperatures of 215–260°C during reflow soldering. Many problems have been discovered 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 devices. Therefore, it was necessary to develop a high glass transition temperature (T_{σ}) , low moisture-absorbing, and low thermal-expansion resin system for high-reliability semiconductor devices.³ Many approaches have been reported to improve the heat resistance of epoxy resins, for example, increasing the crosslink

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density of cured epoxy resin, preparing a stiff main chain,⁴ or the introduction of a bulky structure such as biphenyl or naphthalene.⁵ A goal of the present study was the synthesis of a new, high-performance trifunctional epoxy resin containing a naphthalene structure that would provide both a high crosslink density and a bulky structure. To provide a clear reference point, other trifunctional phenol-type epoxy resins were also synthesized. The viscoelastic, thermal, and moisture absorption properties of the cured trifunctional epoxy resins were determined to provide a direct comparison.

The trend toward miniaturization and thinner electronic equipment and continuing increase in the scale of integrated circuits (IC) have forced the design of larger chips, finer patterns, and high pin counts that are more susceptible to thermal stress failure.^{6,7} Thermal stress causes package cracking, passivation layer cracking, aluminum pattern deformation, etc.⁸ Therefore, the development of a naphthalene-type epoxy resins modified with polydimethyl–siloxane to reduce internal stress while maintaining a high T_g was another purpose of this study.

EXPERIMENTAL

Materials

The paraformaldehyde was purchased from Hayashi Co. and used as received. p-Cresol and ocresol were purchased from Jansen, phenol from Feark, and 2,6-dimethylphenol from Acros. They were all vacuum distilled prior to use. 4-Toluenesulfonic acid 1-hydrate (PTSA) was purchased from Ferak and vacuum dried prior to use. 2-Naphthol purchased from Acros and epichlorhydrin (ECH) purchased from Janssn Co., were used without further purification. 4-4'-diaminodiphenylsulfone (DDS) obtained from Merck was used as a curing agent. All solvents were purified by standard methods before use. Amino-terminated polydimethyl siloxane (ATPDMS), with a number-average molecular weight of around 2300 $(\times 22-161c)$ was provided by Shin-Etsu Chemical Co., Japan. The A-1 catalyst was the (ethyl) triphenyl phosphonium acetate acetic acid complex that was used as an accelerator.

Preparation of 2,6-Dimethylol-4-methylphenol (DMMP)

Into a 500-mL four-heck round-bottom flask equipped with a heating mantle, mechanical stir-



Figure 1 Schematic diagram of the synthesis of 2,6dimethylol-4-methylphenol (DMMP).

rer, reflux condenser, was charged 40 mL of deionized water, which was heated to 50°C. While stirring, p-Cresol 54.6 g (0.5 mol) and paraformaldehyde 31.6 g (1 mol) were added. Aqueous sodium hydroxide (15 wt %,40 g) was added through a dropping funnel over a period of 20 min, which maintained the reaction temperature at 50°C. After the completion of sodium hydroxide addition, the reaction mixture was maintained at 50°C for an additional 8 h. The reaction mixture was then cooled to ambient temperature and poured into a beaker containing 600 mL of deionized water. This was then adjusted to pH = 3 with 10 wt % aqueous HCl, which resulted in precipitation of the product. The solid was collected by fltration and washed with deionized water until the pH value of the filtrate was neutral. A white powdery product (56.0 g, 65% yield) with a melting point of 124-125°C was obtained. The chemical structure of DMMP was confirmed by mass spectrometry, elemental analysis, and ¹H-NMR. The synthetic scheme is shown in Figure 1.

MS m/z 168 (65; M^+). Anal. Calcd. for C₉H₁₂O₃: C, 64.19; H, 7.14. Found: C, 64.27; H, 7.19. ¹H-NMR (Acetone, d₆): $\delta 2.19$ (s, 3H, CH₃), $\delta 4.48$ (t, 2H, methylene-OH), $\delta 4.71$ (d, 4H, CH₂), $\delta 6.91$ (s, 2H, aromatic), $\delta 8.33$ (s, 1H, OH).

General Procedure for the Preparation of Trifunctional Novolac Resins

Preparation of 2,6-Bis-(hydroxy-benzyl)-4-methylphenol (Ia)

To a 500-mL five-neck round-bottom flask equipped with a heating mantle, stirrer, thermometer, reflux condenser, and nitrogen inlet, was added a solution of *p*-toluenesulfonic acid (PTSA, 0.17 g) dissolved in 100 mL MIBK. After purging with nitrogen for 10 min, phenol (56.47 g, 0.6 mol) was added to the above solution at room temperature. 2,6-Dimethylol-4-methylphenol (16.82 g, 0.1mol) was added portionwise over a period of 40 min. After the completion of the addition, the reaction temperature



Figure 2 Schematic diagram of the synthesis of trifunctional novolacs, symbol [I], for all synthesized novolacs.

was allowed to increase to 50°C and was held at that temperature for 2 h. The solution was further heated to 65°C and maintained at that temperature for 5 h. The reaction product was washed with the deionized water until the wash solution was neutral. The organic phase was finally "rotovapped" at 195°C for 2 h to remove the excess phenol and solvent. A light amber-colored product (27.54 g, 86% yield) was obtained. Residual phenol content was less then 0.3% (as analyzed by L C) and the softening point 84°C with the number-average molecular weight $M_n = 322$ by GPC. The chemical structure of Ia was confirmed by elemental analysis (EA) and ¹³C-NMR spectroscopy. The synthetic scheme is shown in Figure 2.

ANAL. Calcd. for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.36; H, 6.53. The ¹³C-NMR spectrum is shown in Figure 3(a). As illustrated in Figure3(a), the characteristic carbons⁹ resonated at 36.03 ppm and 31.62–31.28 ppm for *para* and *ortho* positions of phenol, respectively. Judging from the integral spectral intensity, 74% was linked to *para* position and 26% to *ortho* position.

Preparation of 2,6-Bis-(hydroxy-2-methyl-benzyl)-4-methyl-phenol (Ib)

Ib was synthesized by a procedure analogous to the synthesis of a using *o*-cresol instead of phenol. A light amber-colored solid product in 76% yield was obtained. Residual cresol content was 0.27% (analyzed by liquid chromatography), and the softening point was around ambient temperature. The chemical structure of Ib was confirmed by mass spectrometry, elemental analysis, and ¹³C-NMR spectroscopy. The synthetic scheme is also shown in Figure 2.

MS m/z 348(52; M^+). Anal. Calcd. for C₂₃H₂₄O₃: C, 79.28; H, 6.944. Found: C, 78.50; H, 7.04. ¹³C-NMR is presented in Figure 3(b).

From its integral spectral intensity, the ratio of para to ortho is 80/20.

Preparation of 2,6-Bis-(4-hydroxy-3,5-dimethylbenzyl)-4-methyl-phenol (Ic)

To a 500-mL, five-neck round-bottom flask, equipped with a heating mantle, stirrer, ther-



Figure 3 Chemical shift and relative intensity of ¹³C-NMR for the methylene bridge in the *para* or *ortho* position: (a) DMMP with phenol, (b) DMMP with *o*-cresol.

mometer, and reflux condenser, nitrogen inlet, were charged 150 mL methanol, PTSA 0.34 g, and 2,6-dimethyl phenol 132.38 g (1.08 mol). The mixture was heated to 45°C under nitrogen atmosphere. 2,6-Dimethylol-4-methyl phenol 33.64 g (0.2 mol) was added portion wise by controlling the reaction temperature around 50°C. After the completion of addition, the mixture was heated to 70°C and maintained at that temperature for 38 h to complete the reaction. The reaction mixture was cooled to ambient temperature and then poured into ice water to precipitate product. The resulting solid was collected by filtration and thoroughly washed with methanol/water mixture. A white solid product of Ic (48.00 g, 64% yield) was obtained after vacuum drying , melting point 187–189°C. The chemical structure of Ic was confirmed by mass spectrometry, elemental analysis, and ¹H-NMR. The synthetic scheme is shown in Figure 2.

MS m/z 376 (66; M^+). Anal. Calcd. for $C_{25}H_{29}O_3$: C, 79.76; H, 7.50. Found: C, 79.49; H, 7.54. ¹H-NMR (CD₃OD): $\delta 2.129$ (s , 3H, CH₃), $\delta 2.163$ (s, 12H, CH₃), $\delta 3.778$ (s, 4H, CH₂) $\delta 6.639$ (s, 2H, aromatic), $\delta 6.744$ (s, 4H, aromatic).

Preparation of 2,6-Bis-(2-hydroxy-1-naphthylmethyl)-4-methyl phenol (Id)

Id was synthesized by a procedure analogous to the synthesis of Ia using 2-naphthol instead of phenol. The crude product was washed with methanol/water mixture thoroughly to remove residual 2-naphthol. A gray solid (52% yield), with a melting point of 223–225°C, was obtained. The chemical structure of Id was confirmed by mass spectrometry, elemental analysis, and ¹H-NMR. The synthetic scheme is also shown in Figure 2.

MS m/z 420 (56; M^+). Anal. Calcd. for C₂₉H₂₄O₃: C, 82.83; H, 5.75. Found: C, 82.86; H, 5.77.

¹H-NMR (acetone, d_6): δ 1.9142 (s, 3H, CH₃), δ 1.4163 (s, 4H, methylene), δ 7.2693 (d, 2H, C-3 of 2-naphthol), δ 9.0500 (broad, 2H, naphthol-OH).

General Procedure for the Preparation of Triglycidyl Ethers

Into a 500 mL four-neck round-bottom flask, equipped with a stirrer, heating mantle, thermocouple, temperature controller, condenser, nitrogen inlet, and addition funnel, were charged 0.05 mol of the trifunctional novolacs, 1.5 mol of epichlorohydrin (ECH), 27 g of isopropyl alcohol (IPA), and 4 mL water. The reaction mixture was heated to 65°C while stirring, and then 20 wt % aqueous NaOH 30 g (0.15 mol) was added dropwise over a period of 45 min. After the completion of aqueous sodium hydroxide addition, the reaction mixture was maintained at 65°C for an additional 15 min, and the bottom brine layer was removed by siphoning. The organic phase was further reacted with 20 wt % aqueous NaOH 15 g (0.075 mol) at 65°C for 30 min, and then the phases were separated. The organic phase was washed several times with deionized water to remove the residual sodium chloride. The organic phase after water washing was placed on a rotary evaporator under a full vacuum at 150°C to re-



IIa, R= 2,6-Bis- (glycidyloxy - benzyl) -4-methyl glycidyl phenyl ether

Figure 4 General scheme for the preparation of poly (glycidyl ether).

move excess ECH and solvent completely. The general schematic of the preparation of poly (glycidyl ether) is shown in Figure 4. The epoxy equivalent weight (EEW) and total chlorine content of each trifunctional epoxy resin were determined. Results are shown in Table I.

General Procedure for the Preparation of Silicone Rubber-Modified Trifunctional Naphthol-Type Epoxy Resins

Into a four-neck round-bottom flask, equipped with a heating mantle, stirrer, nitrogen inlet, condenser, thermocouple, and temperature controller, was added 20 g 2,6-bis-(2-glycidyloxy-1-naphthyl-methyl)-4-methyl phenyl glycidyl ether. The epoxy resin was heated to 160°C and dehydrated under a full vacuum over a period of 30 min. Under a nitrogen atmosphere, a mixture consisting of ATPDMS (2.86 g) and A-1 catalyst (0.05 g) was added dropwise over a 30-min period via a metering pump while maintaing the reaction temperature at 180°C. Upon completion of the ATPDMS addition, the reaction mixture was held at 180°C for an additional 2 h. The resulting epoxy resin contained ca. 12 wt % dispersed silicone rubber (EEW 334). Dispersed silicone rubber

Sample	IIa	IIb	IIc	IId
EEW Total Cl (ppm)	185	197	192	258
	782	635	416	120

Table IEEW and Total Chlorine Content ofTrifunctional Epoxy Resins

(20 wt %) (EEW 366)-modified epoxy resin was also prepared by the same procedure using 5.0 g ATPDMS and 0.09 g A-1 catalyst.

Curing Procedure for the Epoxy Resins

Unmodified and silicone rubber-modified trifunctional epoxy resins were heated under full vacuum to drive off any residual air bubbles and water in the epoxy resins.¹⁰ Each epoxy was then mixed well with a stoichiometric amount of curing agent at moderate temperatures to give a precured epoxy powder. The epoxy powder was poured into a aluminum tray ($20 \times 14 \times 5 \text{ mm}$) and cured in this mold under atmospheric pressure at 150°C for 1 h, 180°C for 2 h, and then postcured at higher temperature to obtain a specimen for SEM and dynamic viscoelastic analysis.

Measurement and Testing

The ¹H-NMR of DMMP was obtained on a Bruker Analytic WP-100, the spectra of other products were obtained on a Bruker AMX-400. ¹³C-NMR spectra was also obtained on the Bruker AMX-400. Samples were analyzed in deuterated acetone or deuterated methanol using tetramethylsilane (TMS) as an internal standard. Elemental analyses were obtained from a Heraeus CHN-Rapid Analyser, and mass spectrometric analyses were performed on a VG 70-250S GC/MS spectrometer. Infrared spectra were recorded with a Nicolet 520 FTIR spectrophotometer operated with a dry air purge. Thirty-two signal scans at a resolution of 4 cm⁻¹ were averaged before Fourier transformation. The EEWs of epoxy resins were determined by the HClO₄/potentiometric titration method. Dynamic viscoelastic properties were performed on a Perkin-Elmer 7 Series Thermal Analysis System, with DMA mode between -150and 300°C, with a heating rate of 10°C/min at a frequency of 1 Hz. The temp./time scan in a threepoint bending mode was chosen and the dimension of the specimen was 20 imes 12.7 imes 1 mm according to ASTM D790-95a; the distance of the

support span was 15 mm. The elastic modulus E'and tan δ were determined. The coefficient of thermal expansion (CTE) was measured with the TMA mode of the Perkin-Elmer 7 instrument. A specimen 1 mm in thickness was used at the same heating rate of 5°C/min. The CTEs were calculated from the slope below the glass transition (T_{g}) . A Hitachi S-4200 Field Emission Scanning Electron Microscope was employed to examine the morphology of cured rubber-modified samples after they were fractured cryogenically in liquid nitrogen. The fracture surfaces were vacuum coated with platinum. The thermal stability profiles were obtained using a Perkin-Elmer Thermogravimetric Analyzer (TGA) with a heating rate 10°C/min in nitrogen atmosphere. The moisture pickup was determined by placing preweighted $2.5 ext{ thick} imes 45 ext{ mm-diameter cured disks in water}$ at 23°C for 100 h. The disks were removed and wiped off with a dry cloth, and weighed to the nearest 0.001 g immediately. The density of the cured epoxy resin specimen was determined in a carbon tetrachloride-toluene density gradient column, the specific volume was taken as a reciprocal of density.

RESULTS AND DISCUSSION

Synthesis and Characterization

Trifunctional novolacs were produced by condensing DMMP with excess phenol or 2-naphthol (Fig. 2). With the large molar excess of phenol to DMMP combined with a slow addition of DMMP to phenol, the other polyfunctional novolacs were not detected by gel permeation chromatograph (GPC) and mass spectrometry. The preparation of triglycidyl ethers involved the reaction of novolacs with a halohydrin in the presence of an alkali metal hydroxide (Fig. 4).

The chemical structures of the synthesized trifunctional novolacs were confirmed by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies. From IR spectra of Ia and its triglycidyl ether (IIa), absorptions at $3400-3600 \text{ cm}^{-1}$ for the —OH functional group in the novolac, and at 910 cm⁻¹ for the oxirane in epoxy resin were observed. Judging from the intensities of methylene bridge in ¹³C-NMR, the ratios of *para/ortho* were found to be 76/26 for Ia and 80/20 for Ib. The mixed structures in Ia and Ib have made their softening points approach ambient temperature. For 2,6-dimethyl phenol, because only the *para* position was available to



STABLE DISPERSION IN EPOXY RESIN

Figure 5 Silicone rubber particle dispersed in epoxy resins via epoxy ring opening.

react with DMMP, a single structural product Ic (m.p. 187–189°C) was obtained, while for 2-naphthol, the methylene bridge was found at the most reactive C-1 position of naphthalene and a single structural product Id (m.p. 223–225°C) was obtained (as shown in Fig. 2).

The modification of the trifunctional naphthalene-containing epoxy resin IId was performed simply by the ring-opening of the oxirane ring in the epoxy resin with the amino-terminated polydimethylsiloxane (ATPDMS) in the presence of A-1 catalyst to form stable silicone rubber particles dispersed in the matrix resin in a "sea-island" structure ("islands" of silicone rubber dispersed in the "sea" of an epoxy resin, as shown in Fig. 5).

Dynamic Viscoelastic Analysis

The dyamic viscoelastic analysis can give us the information on the microstructure of cured epoxy resins. For cured phenol-type epoxy resins, from -150° C to the abrupt depression of viscoelastic curve (180°C, Fig. 6), the elastic modulus of IIc was higher than that of IIa and IIb epoxy resins, and this was attributed to the steric effect of two symmetric methyl substituents in IIc. At 180°C (below T_g), IIa, IIb, and IIc retained 82–89% of the orginal elastic moduli (25°C), while IId retained 65% (Table II). At 230°C (above T_g), the retentions was only 1% for IId, which was much



Figure 6 Dynamic viscoelastic analyses of cured IIa, IIb, and IId. The curing agent is 4-4'-diaminodiphenylsulfone (DDS); postcure temperature is 200°C.

Epoxies ^a	Elastic Modulus	*10	⁸ Pa	% Retention	
	25°C	180°C	230°C	180°C	230°C
IIa	11.58	10.30	2.28	89	20
IIb	10.22	8.35	1.32	82	13
IIc	13.95	12.43	2.02	89	14
IId	20.35	13.19	0.24	65	1

 $^{\rm a}$ Postcure condition: 200°C/4 h.

lower than 13–20% retention for IIa, IIb, and IIc. For IIa–c, the epoxy equivalent weights of these epoxy resins were almost the same, so the crosslink density of these network should be on the same level;¹¹ similar retentions of IIa–c were consistent with this conclusion. Lower retention represented lower crosslink density in naphthol than phenol systems. The lower mobility of naphthol-type than phenol-type epoxy resin had depressed its reactivity and residual uncured epoxy resin might act as a "plastizer" in the matrix. The rigid naphthol epoxy (IId) exhibited higher elastic modulus than that of IIa–c, as expected, and the stiffness can be modified by adding silicone rubber into the epoxy resins as shown in Figure 7.

The tan δ curves for the epoxy networks exhibited two major relaxations, as observed in most epoxy polymers:¹² a high temperature or α -transition corresponds to a major T_g of the cured epoxy resins, above which significant chain motion takes place; the low temperature or β -transition is attributed predominantly to the motion of the [CH₂-CH(OH)-CH₂-O] (hydroxy ether) group of the epoxy,¹³ which occurs at -100 to -30° C. The peak position of α -relaxation in the tan δ curves is related to the chemical structure. IId had a higher T_{σ} (220°C) than those of IIa–c under the same postcure temperature of 200°C (Table IV and Fig. 6). Several factors related to chemical structure were known to affect the glass transition temperature, and the most important factor was chain stiffness or flexibility of the polymer.¹⁴ Introduction of rigid naphthlene structure into the epoxy resin increased the difficulty of chain rotation, so the T_{σ} was higher. In Figure 7(b), the β -transition curve of the cured epoxy resin had shifted toward the lower the temperature region with the addition of ATPDMS.

Figure 7 shows the elastic modulus E' and tan δ curves for the naphthol-type (IId) epoxy resin

and its modification with 12 and 20 wt % ATP-DMS. The elastic moduli were decreased because of the polysiloxane modification. Besides the epoxy and peaks, the tan δ curves for the silicone rubber-modified products exhibited an additional small peak in the range of -150 to -120°C, with a center near -130°C, corresponding to the glass transition temperature of the silicone phase. This small peak further supported the multiphase separation. In addition, the α -relaxation peak and silicone rubber peak had all shifted slightly toward lower temperatures with the increasing ATPDMS content.

The heights of the α -transitions as shown in Figure 8, were dependent on crosslink density. When crosslink density was increased, the height of the α -transition was decreased.¹⁵ The tan δ curve was also shifted to a higher temperature when the postcure temperature was increased.

Network Structure for Cured Trifunctional Epoxy Resins

The model for network structures of the phenoltype and the naphthol-type epoxy resins cured with DDS near the crosslink point were proposed in Figure 9. Each amino group in DDS has two active hydrogens that could react with the oxirane group of epoxy resins. At stoichiometric ratio with sufficient energy, the amino group could react completely. For IIa-c, IIc had the highest modulus (Fig. 6) and the lowest coefficient of thermal expansion, α (Table IV), while IId, with two symmetric naphthalene groups in the backbone, had the lowest mobility and reactivity and, hence, required higher curing temperature than IIa-c for the amino group to react completely. The naphthalene structure being planar, it is natural to consider that the neighboring naphthalene groups should be oriented in a rectangular block



Figure 7 Dynamic viscoelastic analyses of cured unmodified modified naphthol-type epoxy resins (a) $-150-280^{\circ}$ C; (b) $-150-30^{\circ}$ C: (\bigcirc) unmodified; (\blacktriangle) 12 wt % silicone rubber; (\blacksquare) 20 wt % silicone rubber modification.



Figure 8 Dynamic viscoelastic analyses of cured naphthol-type epoxy resin (IId) at various postcure temperatures: (\bullet) 200°C; (\diamond) 230°C; (\Box) 260°C, 4 h.

network, as shown in Figure 9. The stacking of the network would result in the highest modulus (Fig. 6), highest glass transition temperature (Ta-



Figure 9 Network structure model near crosslink points in trifunctional epoxy II_{a-d} cured with DDS; rectangular block portion may be the stacked segment.

ble III),, and the lowest coefficient of thermal expansion (Table IV) for the naphthalene containing epoxy resin.

Specific Volume

The network structure model could also be used to explain the specific volume of the cured epoxy resin systems. For phenol-type epoxy resins IIa-c (200°C), IIc has more interfering methyl substituents and would require more space; therefore, the sequence of specific volumes was IIc > IIb > IIa(Table III). The naphthol-type epoxy resin IId (postcured at 200°C) had a larger specific volume than that of IIc (200°C), which might be due to an incomplete cure, while at higher postcure temperatures, a more dense specimen could be obtained and the sequence of specific volumes was IId $(200^{\circ}C) > IId (230^{\circ}C) > IId (260^{\circ}C). IId (260^{\circ}C)$ had the lowest value of 0.711 cc/g, while for phenol-type epoxy resin, for example, due to the nonplanar structure of IIb, the specific volume of IIb (260°C) was greater than that of IIb (200°C); sim-

Sample Designation ^a	EEW	Specific Volume (c.c/g)	$T_{g}^{\mathrm{b}},\mathrm{C}$ Rubber	$T_g^{ m c},~^{ m oC}$ Matrix
IIa (200°C)	185	0.784	_	210
IIb (200°C)	197	0.792	_	200
IIb (260°C)	197	0.796	_	211
IIc (200°C)	192	0.807	_	202
IId (200°C)	256	0.810	_	220
IId (230°C)	256	0.808	_	230
IId (260°C)	256	0.711	_	240
IId-12AS (200°C)	334	0.821	-130	218
IId-20AS (200°C)	366	0.819	-137	215

Table III Specific Volume and Dynamic Viscoelastic Properties of Cured Trifunctional Epoxy Resins

 $^{a}\left(\,\right)$ denotes the postcure temperature and all cured for 4 h.

 $^{\rm b}$ Peak of tan δ curve at lower temperature.

^c Peak of tan δ curve at higher temperature.

ilar phenomena were also reported in the diglycidyl ether of bisphenol A (DGEBA/DDS) system.¹⁶

Morphology

SEM photomicrographs of the cold snap surfaces for the cured naphthol-type epoxy resin and its rubber-modified epoxy networks were given in Figure 10. In Figure 10(a), bright streamer markings that emanate from the crack tip were the result of the tearing marks of ligaments as the crack began to advance. For the IId-12AS epoxy resin that contained 12 wt % liquid ATPDMS, the fracture surface shown in Figure 10(b) indicated extensive local yielding and shear. Large rubber particles were shown to be embeded in the epoxy matrix, and the presence of large holes suggested that those particle served as nucleation sites for local shear deformation, in many cases resulting from the particles being pulled out of the matrix. Electron micrographs revealed that rubber particles with a few micrometer or less in size had been dispersed in the matrix. The stress-whitening zone in the IId-20AS epoxy resin showed extensive overlapping regions of local shear deformation.

Coefficient of Thermal Expansion (CTE)

The thermal mechanical properties are shown in Table IV. The CTE in the glassy state below the T_g was taken from 50 to 180°C. The IId-12AS sample had the lowest CTE; in contrast, the IIa sample had the highest CTE. Under the same curing procedure and the postcure temperature (200°C), the sequence of CTE was IId < IIc < IIb

		E' (GPa)					
Epoxy ^a	T_g (°C)	<i>E</i> ′ _{20°C}	$E'_{\rm 180^{\circ}C}$	$E'_{ m ave}{}^{ m b}$	α (ppm/°C)	$E'_{\rm ave}*\alpha$ (KPa/°C)	Density (g/cc)
II _{a(200°C)}	210	1.16	1.03	1.10	63.94	70.33	1.2757
II _{b(200°C)}	200	1.02	0.83	0.93	56.80	52.82	1.2631
II _{b(260°C)}	211	2.91	1.51	2.21	49.20	108.73	1.2563
II _{c(200°C)}	202	1.40	1.24	1.32	54.71	72.22	1.2395
II _{d(200°C)}	220	2.05	1.32	1.69	47.03	79.48	1.2349
II _{d(230°C)}	230	2.39	1.54	1.97	45.26	89.16	1.2371
II _{d(260°C)}	240	3.09	2.30	2.70	39.85	107.60	1.4074
II _{d-12AS(200°C)}	218	1.68	0.58	1.13	10.96	12.38	1.2180
II _{d-20AS(200°C)}	215	1.36	0.38	0.87	18.62	16.20	1.2203

Table IV Viscoelastic Properties and Relative Internal Stress of Epoxy Resins Cured With DDS

 $^{a}\left(\,\right)$ denotes the postcure temperature and all cured for 4 h.

^b $E'_{\text{ave}} = (E'_{20^{\circ}\text{C}} + E'_{180^{\circ}\text{C}})/2.$



(b)



(c)



Figure 10 Morphology of the cold-snap fracture surfaces of cured naphthol-type epoxy resins modified with or without the silicone rubber: (a) IId (no silicone rubber); (b) IId-12AS (12 wt %); (c) IId-20AS (20 wt %).

< IIa, indicating that with the increasing steric hindrance the movements and rotations of the polymer chains were constrained. With the increase in curing extent (higher postcure temperature), the segments of the polymer chain would stack much more compactly, and the sequences of CTE for IIb and IId under various curing temperature were IIb (260°C) < IIb (200°C), IId (260°C) < IId (230°C) < IId (200°C). Also noteworthy, the IId-12AS had lower CTE than the unmodified IId, and the effect was similar to the results in our previous report.¹⁷ However, when the content of ATPDMS was increased to 20 wt %, the CTE of IId-20AS became higher than that of IId-12AS.

Glass Transition Temperature (T_g)

Glass transition temperatures (T_g) were determined from the peak of the tan δ curves, and the results were shown in Table III. At the 200°C postcure temperature, IId had a T_g of 220°C, and all the phenol-type epoxy resins provided T_g almost in the same level. The reasons for IId (200°C) having a T_g 20°C higher than the curing temperature might be due to the cure exotherm raising $T_{\rm CURE}$ above that of the oven temperature. For a more complete curing of IId, the curing temperature had to be raised to 260°Cto obtain a final, ultimate T_g (" T_g "). The highest T_g achieved for this system was about 240°C, while IIb (260°C) was 211°C. Silicone rubber-modified naphthalene-type epoxy resin IId-12AS and IId-20AS had slightly lower T_g than that of Iid itself.

Thermal Stability

The thermogravimetric analyses curves are shown in Figure 11, and the onset of the dynamic decomposition temperatures (T_d) were summarized in Table V. It was obvious that T_d was affected by the network structure, and they were all above 330°C. The epoxy resins containing a naphthalene structure exhibited better thermal stability than the epoxies containing phenyl structures. This difference may be attributed to the three resonance structures of naphthalene compared to two resonance structure for phenyl.¹⁸



Furthermore, T_d of the IId was increased with the silicone rubber modification, and this may be attributed to the thermal stability of the incorporated Si—O—Si structure.



Figure 11 Thermogravimetric analyses of various epoxy resins cured with 4-4'-diaminodiphenylsulfone (DDS).

Moisture Absorption

The absorbed moisture in the semiconductor package was found to plasticize the epoxy resin, causing a lowering of the T_g ,¹⁹ and also to cause the package to crack during the soldering process.²⁰ IIb and IIc have better hydrophobic properties than that of IIa, indicating that the incorporation of the hydrophobic methyl group had inhibited moisture absorption. The introduction of the naphthalene group into the backbone depressed the moisture absorption effectively, as shown in Table V. The addition of silicone rubber into IId had increased the specific volume (Table III) and reduced the crosslink density, so silicone modification of IId allowed more water diffusion into the structure.

Internal Stress

When the specimen was cooled from its curing temperature to room temperature, the internal stress would accumulate in the matrix. The internal stress of modified and unmodified epoxy resins can be approximated by the product of their elastic modulus and the CTE below T_g

 $(E'_{ave}*\alpha)$.^{21,22} Table IV Listed the elastic modulus E', CTE α , and $E'_{ave}*\alpha$ of the trifunctional epoxy resins investigated. The dispersed silicone rubber particles effectively reduce elastic modulus and the CTE of the naphthol-type epoxy resins. Therefore, the internal stress of IId can be reduced by modification with ATPDMS. This could be attributed to the complete separation of the rubber phase from epoxy matrix; this seperation acted as a stress reliever.

CONCLUSION

Trifunctional epoxy resins were synthesized by condensing 2,6-dimethylol-4-methylphenol with respective phenol, o-cresol, 2,6-dimethylphenol, and 2-naphthol followed by epoxidation with epichlorohydrin. A network structure of cured trifunctional epoxy resins was proposed to describe the curing behavior of the epoxy resins investigated. The naphthalene-containing epoxy resin IId has the highest elastic modulus, highest glass transition temperature (Ultimate T_g^u , 240°C), highest thermal stability, and the lowest CTE

$\operatorname{Epoxies}^{\operatorname{a}}$			Maintana	Der Derer
G=CH ₂ -CH-CH ₂	Resin (g/Eq)	$\begin{array}{c} Curing \ Agent \\ (g/Eq)^b \end{array}$	Absorption Gains (%)	Temp. (°C) T_d^{c}
$\begin{array}{c} OG \\ \downarrow \\ \downarrow \\ CH_2 \\ CH_3 \\ IIa \end{array} \begin{array}{c} OG \\ OG \\ CH_3 \\ IIa \end{array}$	3.744/0.020	1.256/0.020	0.97	330
$CH_{3} \xrightarrow{OG} CH_{2} \xrightarrow{OG} CH_{3} \xrightarrow{OG} CH_{3}$ $CH_{3} \xrightarrow{CH_{3}} CH_{3}$ IIb	3.793/0.019	1.207/0.019	0.70	346
$\begin{array}{c} CH_3 \\ OG \\ \hline \\ CH_3 \\ CH_3 \\ Hc \end{array} \begin{array}{c} OG \\ CH_2 \\ CH_3 \\ CH_3 \\ Hc \end{array} \begin{array}{c} CH_2 \\ CH_3 \\ CH_3 \\ CH_3 \end{array} \begin{array}{c} CH_2 \\ CH_3 $	3.778/0.020	1.222/0.020	0.74	346
$OG \longrightarrow OG \longrightarrow$	4.039/0.013	0.961/0.016	0.65	357
IId-12AS IId-20AS	4.216/0.013 4.275/0.012	0.784/0.013 0.725/0.012	$\begin{array}{c} 0.97\\ 0.82 \end{array}$	368 378

Table V Moisture Absorption and Thermal Stability

^a Curing condition: 150°C/1 h, 180°C/2 h, 200°C/4 h.

^b Curing agent: DDS.

° TGA test: heating rate of 10°C/min in the nitrogen atmosphere.

and moisture absorption properties; these characteristics will make IId an ideal candidate as a matrix resin for electronic applications. Modification of IId with amino-terminated silicone rubber, ATPDMS, has effectively reduced the elastic modulus and CTE of cured epoxy resin. The combination of lower elastic modulus and lower CTE will result in lower thermal stress, while the glass transition temperature is only slightly depressed.

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