

Synthesis of Tetrafunctional Epoxy Resins and Their Modification with Polydimethylsiloxane for Electronic Application

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SYNOPSIS

High-performance tetrafunctional epoxy resins were synthesized by reacting a suitable tetraphenols which were obtained by the condensation of appropriate dialdehyde with phenol followed by epoxidation with a halohydrin. The structure of the synthesized tetraphenols was confirmed by infrared (IR), mass spectra (MS), and nuclear magnetic resonance (NMR) spectroscopy. Dispersed silicone rubbers were used to reduce the stress of the synthesized tetrafunctional epoxy resin cured with phenolic novolac resin for electronic encapsulation application. The dynamic viscoelastic properties and morphologies of neat rubber-modified epoxy networks were investigated. The thermal mechanical properties and moisture absorption of encapsulants formulated from the synthesized tetrafunctional epoxy resins were also studied. The results indicate that a low-stress, high glass transition temperature (T_g), and low-moisture-absorbing epoxy resin system was obtained for semiconductor encapsulation application. © 1996 John Wiley & Sons, Inc.

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 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.^{2,3} Thermal stress causes package cracking, passivation layer cracking, aluminum pat-

tern deformation, etc.^{4,5} Moreover, 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).⁶ 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 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 devices. Therefore, it is necessary to develop a low-stress, high glass transition temperature (T_g), and low-moisture-absorbing resin system for high-reliability semiconductor devices.

Many approaches have been reported to improve the heat resistance of epoxy resins, e.g., increasing the crosslink density of cured epoxy resin,⁷ preparation of stiff main chain,⁸ or introduction of a bulky

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structure such as biphenyl or naphthalene.⁹ A goal of the present study was the syntheses of new, high-performance tetrafunctional epoxy resins for printed circuit board and semiconductor encapsulation application. These novel materials may fulfill the deficiencies in the current materials.

Many studies have been reported on the enhancement of mechanical properties, especially the toughness of cured epoxy resin, by the incorporation of low levels of a reactive liquid rubber such as a carboxy-terminated butadiene-acrylonitrile copolymer (CTBN)¹⁰⁻¹³ or acrylate rubber¹⁴ or modification with a ductile engineering thermoplastic polymer such as bisphenol-A-based polycarbonate (PC)¹⁵ or polyetherimide.¹⁶ In our previous articles,¹⁷⁻¹⁹ a series of organosiloxane polymers with various functional groups were used to reduce the stress of cured epoxy resins. Therefore, the development of high T_g resins modified with polydimethyl-siloxane to withstand stress while maintaining high T_g was another purpose of this study.

EXPERIMENTAL

Materials

The dialdehydes were purchased from Merck Co. and consisted of 40 wt % aqueous glyoxal, terephthalaldehyde, and 25 wt % aqueous glutaraldehyde. 2,6-Dimethylphenol was purchased from Ferak and vacuum-dried prior to use. Epichlorohydrine (ECH) was purchased from Janssen Co. 4-4'-diaminodiphenyl sulfone (DDS) obtained from Merck was used as a curing agent. All solvents were purified by a standard method before use. Amine-terminated polydimethylsiloxane (ATPDMS) with a number-average molecular weight of around 1500 (X22-161B) was provided by Shin-Etsu Chemical Co., Japan. The structural formula of ATPDMS is shown in the following. The A-1 catalyst was the (ethyl) triphenylphosphonium acetate acetic acid complex, and Ph_3P was the triphenylphosphine that was used as a curing accelerator.

General Procedure for the Preparation of Tetraphenols

The Preparation of 1,1,2,2-Tetrakis(4-hydroxy-3,5-dimethylphenyl)ethane (THDMPE)

Into a 5 L four-neck round-bottom flask, equipped with a heating mantle, mechanical stirrer, reflux condenser, thermocouple, and temperature controller, were added 2000 g of 2,6-dimethylphenol, 40 mL

hydrochloric acid, and 750 mL methanol, being heated to 70°C while stirring. Aqueous glyoxal (40 wt %, 160.5 g) was added dropwise via a metering pump to the reaction mixture over a 2 h period. The reaction mixture was refluxed for approximately 36 h. The reaction mixture was cooled to 25°C with an ice bath and a solid product precipitated from the reaction mixture. The solid was collected by filtration and washed with methanol until the filtrate was clear and the product appeared white. A rotovap was then used to remove the remaining methanol and unreacted 2,6-dimethylphenol. The resulting white solid product was 380.5 g of the tetraphenol ethane (THDMPE). The chemical structure of tetraphenols was confirmed by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The synthesis scheme is shown in Figure 1.

¹H-NMR(DMSO): δ 2.07 (s, 24H, CH_3), δ 2.92 (s, 2H, CH), δ 4.63 (s, 4H, OH), δ 6.86 (s, 8H, aromatic). MS m/z 510 (25; M^+).

The Preparation of 1,1,4,4-Tetrakis(4-hydroxy-3,5-dimethylphenyl)p-xylene (THDMPPX)

THDMPPX was synthesized by a procedure analogous to the synthesis of THDMPE with the exception of dialdehyde being terephthalaldehyde. An orange-colored tetraphenol (THDMPPX) was obtained.

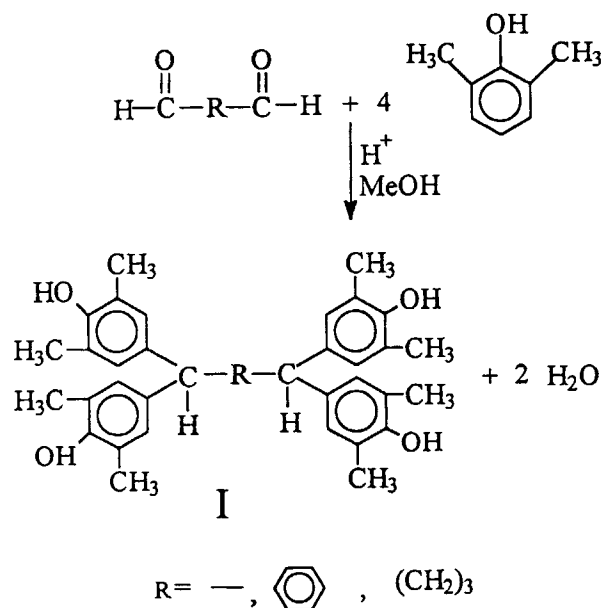


Figure 1 Schematic diagram of the synthesis of tetraphenol.

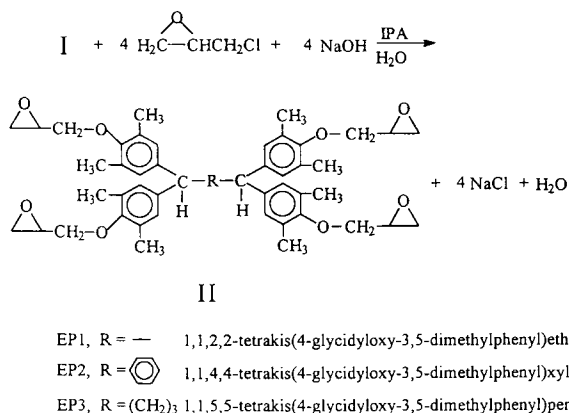


Figure 2 General schematic of the preparation of poly(glycidyl ether).

¹H-NMR(DMSO): δ 2.07 (s, 24H, CH₃), δ 2.91 (s, 2H, CH), δ 5.24 (s, 4H, OH), δ 6.71 (s, 8H, aromatic), δ 7.05 (s, 4H, aromatic). MS m/z 586 (40; M⁺).

The Preparation of 1,1,5,5-Tetrakis(4-hydroxy-3,5-dimethylphenyl)pentane (THDMPP)

THDMPP was synthesized by a procedure analogous to the synthesis of THDMPE with the exception of dialdehyde being 25 wt % aqueous glutaraldehyde. A yellowish brown tetraphenol (THDMPP) was obtained.

¹H-NMR(CDCl₃): δ 1.98 (p, 2H, CH₂), δ 2.22 (s, 24H, CH₃), δ 3.64 (t, 2H, CH), δ 4.65 (s, 4H, OH), δ 6.82 (s, 8H, aromatic). MS m/z 552 (22; M⁺).

General Procedure for the Preparation of Polyglycidyl Ether of the Tetraphenols

Into a 3 L four-neck round-bottom flask, equipped with a stirrer, heating mantle, thermocouple, temperature controller, condenser, nitrogen inlet, and addition funnel, were charged 0.5 mol of tetraphenol, 10 mol of epichlorohydrin (ECH), 540 g of isopropyl alcohol (IPA), and 230 mL water. The reaction mixture was heated to 65°C while stirring, and 20% aqueous NaOH was added dropwise in three separate increments of 200, 180, and 100 g, each increment being added over a period of 30 min. After completion of each addition, the reaction mixture was reacted for another 30 min and then the bottom brine layer was removed by siphoning. The organic phase was finally rotovapped at 150°C to remove excess ECH and solvent. The general schematic of the preparation of poly(glycidyl ether) is shown in Figure 2.

Dehydrohalogenation²⁰

The crude poly(glycidyl ether) of the tetraphenol (200 g) was dehydrohalogenated by dissolving in 300 mL of methyl isobutyl ketone and stirred with 1300 mL of 5% aqueous NaOH in a 5 L four-neck round-bottom flask equipped with a heating mantle, thermocouple, stirrer, reflux condenser, and nitrogen inlet. The reaction mixture was heated to reflux temperature (about 88°C) 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 each time. The organic layer, after washing, was allowed to cool to room temperature and stood overnight to crystallize the product. The product was filtered, washed with hexane, and dried overnight in a vacuum oven at 50°C. The epoxy equivalent weight (EEW) and total chlorine content of each tetrafunctional epoxy resin were determined. Results are shown in Table I.

General Procedure for the Preparation of Silicone Rubber-Modified Tetrafunctional Epoxy Resin

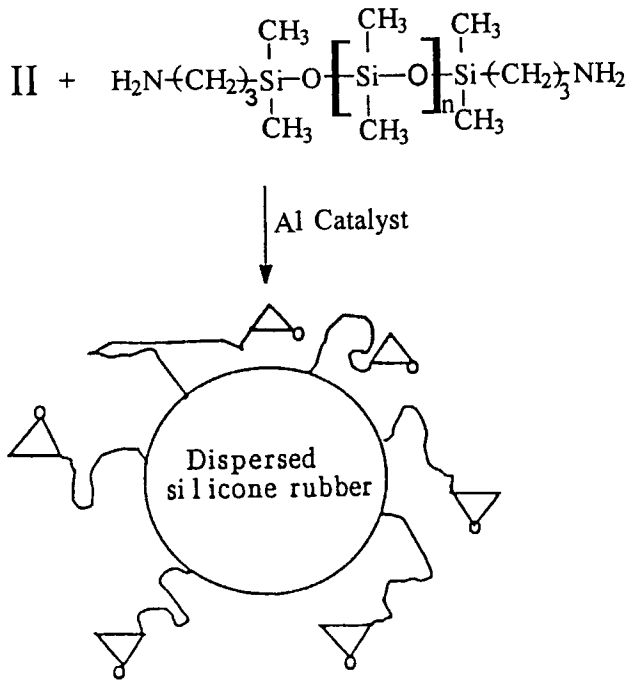
Into a four-neck round-bottom flask, equipped with a heating mantle, stirrer, nitrogen inlet, condenser, thermocouple, and temperature controller, were added 384 g of tetrafunctional epoxy resin. The epoxy resin was heated to 150°C and dehydrated under vacuum until the water content was less than 0.01 % (measured by a Karl Fischer). Under a nitrogen atmosphere, mixtures consisting of ATPDMS (43 g) and A-1 catalyst (0.8 g) was then added dropwise over a 1 h period via a metering pump while maintaining the reaction temperature at 150°C. Upon completion of the ATPDMS addition, the reaction mixture was held at 150°C for an additional 2 h. The resulting epoxy resin contained ca. 10 wt % dispersed silicone rubber.

Curing Procedure of Epoxy Resins

Unmodified and rubber-modified tetrafunctional epoxy resins were mixed with a stoichiometric amount of curing agent and Ph₃P in a mill at mod-

Table I The EEW and Total Chlorine Content of Epoxy Resins

Sample	EEW	Total Cl (ppm)
EP1	192	485
EP2	207	515
EP3	202	504



STABLE DISPERSION IN EPOXY RESIN

Figure 3 Silicone rubber particle dispersed in epoxy resins via the epoxy ring opening.

erate temperature to give a thermosettable epoxy resin powder. The resin powder was cured in a mold at temperature of 170°C and 50 kg/cm² for a period of 1 h and then postcured at 180°C for 2 h and 210°C

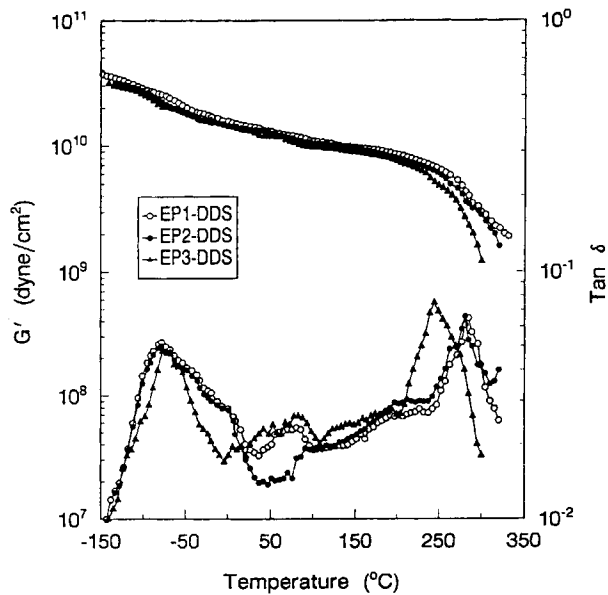


Figure 4 Dynamic viscoelastic analysis for the cured neat tetrafunctional epoxy resins (no filler). The curing agent is 4-4'-diaminodiphenyl sulfone (DDS).

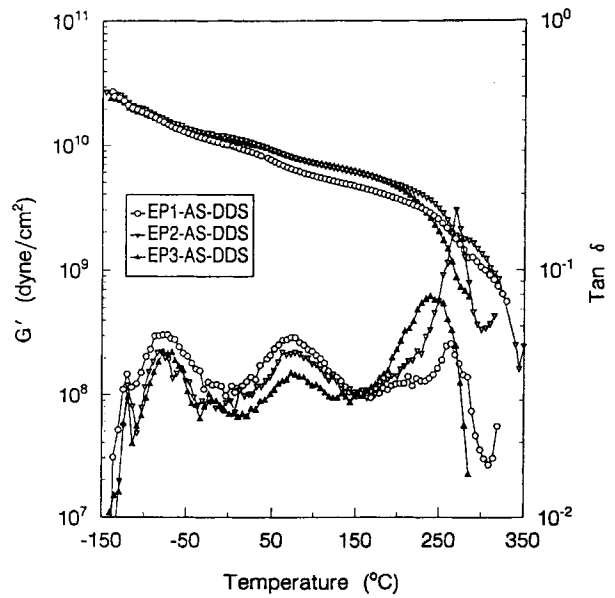


Figure 5 Dynamic viscoelastic analysis for the cured neat tetrafunctional epoxy resins with aminosiloxane modification (no filler).

for 4 h to obtain a cured specimen for SEM and dynamic viscoelastic analysis.

Measurement and Testing

¹H-NMR was obtained on a Burkert Analytic WP100 NMR. Samples were analyzed in deuterated di-

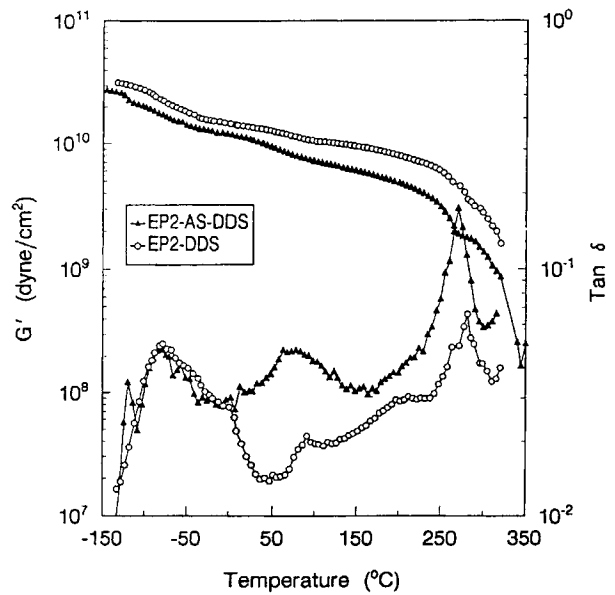


Figure 6 The comparison of storage modulus *G'* and tan δ curves between the cured neat epoxy resins with or without aminosiloxane modification.

Table II Dynamic Viscoelastic Properties of Cured Neat Tetrafunctional Epoxy Resin System

Sample Designation	T_g^a , °C Matrix	Shear	
		Modulus, 20°C, $\times 10^9$ dyne/cm ²	T_g^b , °C Rubber
EP1	282	14.4	—
EP2	279	13.7	—
EP3	243	13.2	—
EP1-AS	265	8.97	-120
EP2-AS	270	10.9	-120
EP3-AS	240	10.2	-119

^a Peak of $\tan \delta$ at higher temperature.

^b Peak of $\tan \delta$ at lower temperature.

methyl sulfoxide (DMSO) or deuterated chloroform (CDCl₃). Mass spectrometric analyses were performed on a VG 70-250 S GC/MS spectrometer with a solid inlet. Infrared spectra were recorded with a Perkin-Elmer 16PC FTIR spectrophotometer operated with a dry air purge. Signals for four scans at a resolution of 4 cm⁻¹ were averaged before Fourier transformation. The molecular weight of tetraphenols was obtained on a Shimadzu C-R4A gel permeation chromatograph (GPC) using a Shimadzu GPC-8025 column. Samples were analyzed by a Shimadzu RID-6A reflex indicator. The EEW of epoxy resins were determined by the HClO₄/potentiometric titration method. Dynamic viscoelastic properties were performed on a Rheometrics RDA-II rheometer between -150 and 350°C, with a heating rate of 5°C/step at a frequency of 1 Hz. The rectangular torsion mode was chosen and the dimensions of the specimen were 51 × 12.7 × 0.76 mm. The storage modulus G' and $\tan \delta$ were determined. 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 of cured resins were obtained using a Shimadzu AGS-500 universal testing machine. Flexural strength and modulus were obtained at a crosshead speed of 2 mm/min according to ASTM D790-86. A three-point loading system was chosen and rectangular bar specimens, 80 × 10 × 4 mm, were molded directly by a transfer-molding process.

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 mm in length was used at a heating rate of 5°C/min. Normally, the thermal expansion increase with 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. The moisture pickup was determined by placing preweighed 3 thick × 50 mm diameter cured disks in boiling water for 100 h. The disks were removed and cooled to ambient temperature and then wiped dry and weighed again.

RESULTS AND DISCUSSION

Synthesis and Characterization

Tetraphenols were produced by condensing the appropriate dialdehyde with the appropriate phenol.²¹ This condensation reaction is generally affected by reacting an excess amount of phenol with the dialdehyde (Fig. 1). The preparation of poly(glycidyl ethers) involve reacting the tetraphenol with a halohydrin in the presence of an alkali metal hydroxide (Fig. 2).

The structure of the synthesized tetraphenols was confirmed by infrared (IR), mass spectra (MS), and nuclear magnetic resonance (NMR) spectroscopy. From the IR spectra of THDMPE and its poly(glycidyl ether) (EP1), we can see a strong absorption peak at 3400–3600 cm⁻¹ representing the —OH functional groups of the synthesized tetraphenol, and a peak appeared at 910 cm⁻¹ representing the oxirane ring absorption of tetrafunctional epoxy resins.

Dispersed silicone rubbers in tetrafunctional epoxy resins can be prepared simply by the ring-opening of the oxirane ring in the epoxy resins with the amino group of ATPDMS in the presence of the 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. 3).

Dynamic Viscoelastic Analysis

The dynamic viscoelastic spectra are shown in Figures 4–6. Dynamic viscoelastic analysis can give information on the microstructure of cured rubber-modified epoxy resins. The $\tan \delta$ curves for the unmodified epoxy network exhibit two major relaxations observed in most epoxy polymers²²: 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 (hydroxyether) group of the epoxy.

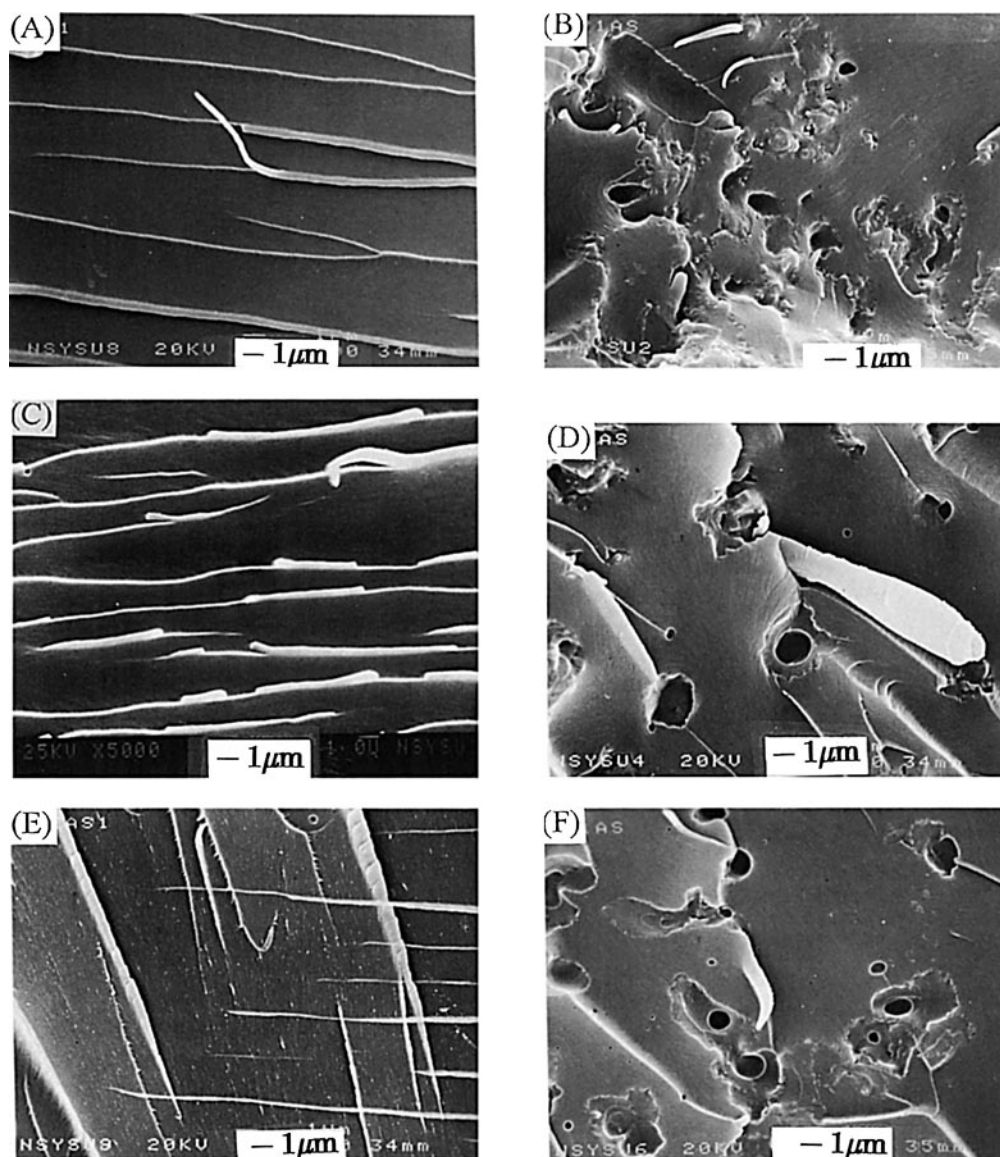


Figure 7 Morphology of cold-snap fracture surfaces of cured neat epoxy resins modified with or without silicone rubber particles (10 wt %): (A) EP1; (B) EP1-AS; (C) EP2; (D) EP2-AS; (E) EP3; (F) EP3-AS.

Figure 4 shows the storage modulus G' and $\tan \delta$ curves for the three cured tetrafunctional epoxy resins with different backbone structure. It can be seen from Figure 4 that the peak position of α -relaxation peak in the $\tan \delta$ curves is related to the chemical structure. The EP1 sample has the highest T_g ; in contrast, the EP3 sample has the lowest T_g . Several factors related to chemical structure are known to affect the glass transition temperature (T_g). The most important factor is chain stiffness or flexibility of the polymer.²³ The long-chain aliphatic group builds flexibility into a polymer (EP3) and lowers

the T_g ; the rigid group including the aromatic structure (EP2) raises the T_g .

Figure 5 shows the storage modulus G' and $\tan \delta$ curves for the resins modified with ATPDMS. A comparison of storage modulus G' and $\tan \delta$ curves between the cured unmodified and rubber-modified epoxy resins is shown in Figure 6. The storage modulus decreased with rubber modification. In addition to the epoxy α and β peaks, the $\tan \delta$ curve for the silicone rubber-modified product shows an additional markedly small peak from -130 to -105°C with a center near -120°C corresponding to the glass

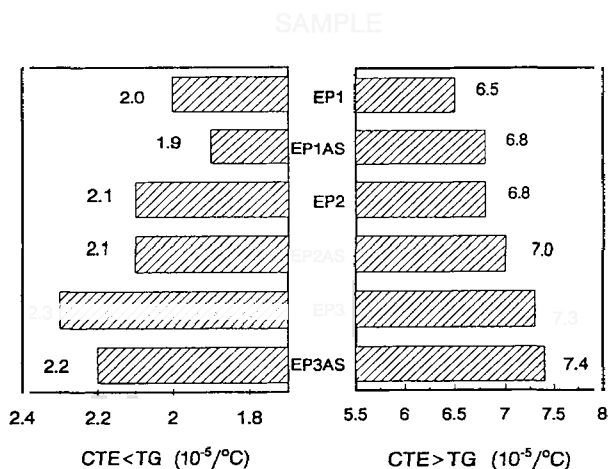


Figure 8 Coefficient of thermal expansion (CTE) for various tetrafunctional epoxy resin encapsulants with or without aminosiloxane modification.

transition temperature (T_g) of the siloxane phase. This small peak further supports the multiphase separation. In addition, the α -relaxation peak in the $\tan \delta$ curve for the resin modified with polysioxane became broader and the peak position slightly shifted toward lower temperature.

The dynamic viscoelastic properties of the cured tetrafunctional epoxy resin system including the major T_g and the rubber's T_g are shown in Table II. From Table II, a slight depression in the matrix T_g with rubber modification was observed. This result

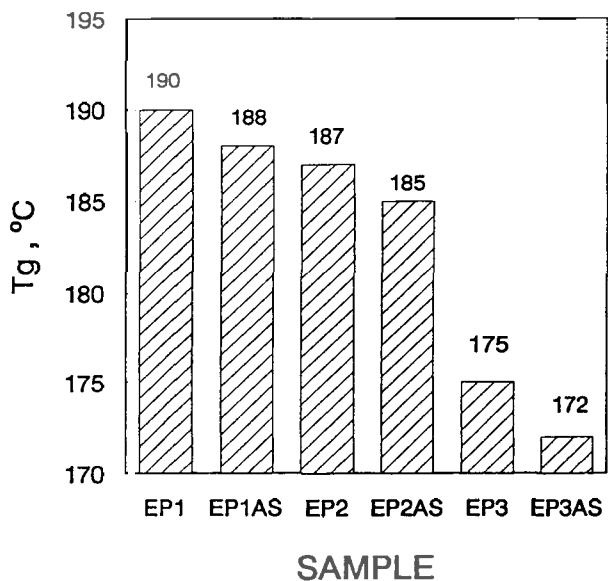


Figure 9 Glass transition temperature for various tetrafunctional epoxy resin encapsulants with or without aminosiloxane modification.

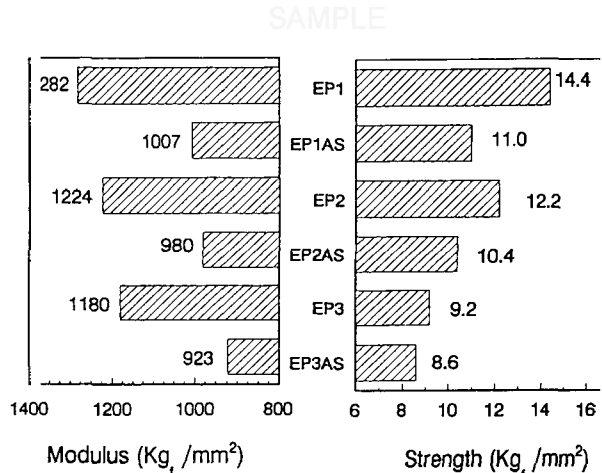


Figure 10 Flexural test properties for various tetrafunctional epoxy resin encapsulants with or without aminosiloxane modification.

can be attributed to an increase in the number-average molecular weight between crosslinks (M_c) of epoxy networks created by the incorporating of silicone rubber, even though the multiphase separation was observed.

Morphology

SEM photomicrographs of cold snap surfaces for the cured tetrafunctional epoxy resins and their rubber-modified epoxy networks are given in Figure 7. Electron micrographs reveal that rubber particles with a few micrometers or less in size have been dispersed in the matrix.

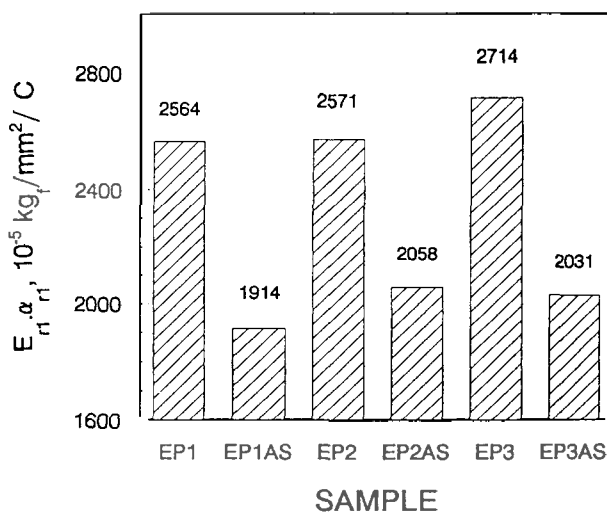


Figure 11 The comparison of the thermal stress pa-

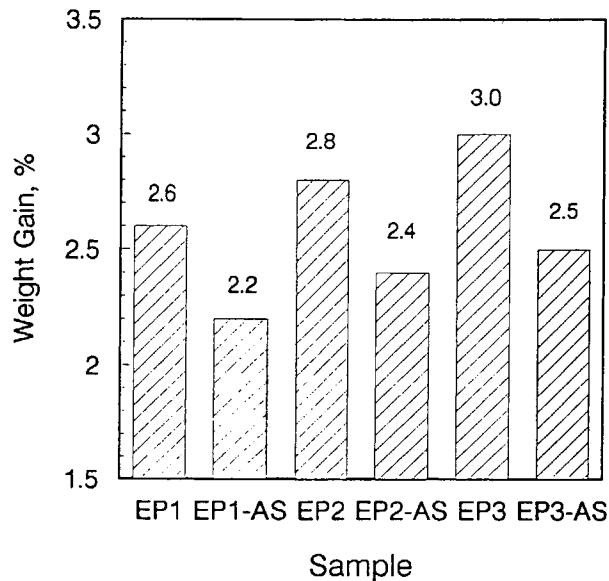


Figure 12 Moisture absorption of various tetrafunctional epoxy resin encapsulants with or without aminosiloxane modification.

Encapsulation Formulation

Three tetrafunctional epoxy resins and their rubber-modified resins were formulated into six electronic encapsulating formulations. An encapsulation formulation typically contains an epoxy resin, a curing agent, and a filler material such as silica.¹⁸ In the encapsulation process, the electronic part is cast with a molten encapsulation formulation which is then subjected to suitable conditions to cure the epoxy resins. The formulations were each postcured at 175°C for 4 h. The thermal mechanical properties of the cured encapsulating formulations were determined by the following tests.

Coefficient of Thermal Expansion (CTE)

The thermal mechanical properties are shown in Figure 8. The CTE in the glassy state below the T_g was taken from 80–140°C and the CTE above the T_g was taken from 230–300°C. Below the T_g , the rubber-modified encapsulants all have slightly lower CTEs than those of the unmodified resins and this will result in a small difference in CTEs between encapsulant and the silicon chip.

Glass Transition Temperature (T_g)

T_g 's were determined from the tangent of the CTE as a function of temperature at 140 and 230°C. The results are shown in Figure 9. Conventional epoxy

resins such as *o*-cresol-formaldehyde novolac epoxy which is predominately used in encapsulation compositions generally has a T_g of $\sim 160^\circ\text{C}$. The encapsulation compositions based on the synthesized tetrafunctional epoxy resins provide a T_g greater than 170°C while some greater than 185°C, no matter whether or not the resins are modified with silicone rubber. The T_g 's are slightly lower for silicone rubber modification compared to the unmodified encapsulant. This observation is consistent with the viscoelastic investigation.

Flexural Test Properties

Figure 10 shows the result of the flexural test. The magnitude of flexural moduli and flexural strength of the cured encapsulants (EP1 > EP2 > EP3) is related to the chemical structure of the tetrafunctional epoxy resins. This tendency corresponds to dynamic viscoelastic analysis of the tetrafunctional epoxy resins or the T_g 's measured via TMA of the cured encapsulants. The flexural moduli of all cured encapsulants with rubber modification were reduced markedly from the unmodified resins and this will result in a large decrease in thermal stress between encapsulant and silicon chip; however, the flexural strength of the cured encapsulants were also reduced. The amount of reduction in flexural strength by silicone rubber modification is dependent on the chemical structure of the tetrafunctional epoxy resins and is greatest for EP1.

Thermal Stress

The thermal stress of IC devices encapsulated by the encapsulation formulation is closely related to the product of the flexural modulus (E_{r1}) and thermal expansion coefficient (α_{r1}) below the T_g of the cured encapsulants.¹⁸ Figure 11 shows the thermal stress parameter ($E_{r1} \times \alpha_{r1}$) of the unmodified and their rubber-modified encapsulants. The result shows that the dispersed silicone rubbers effectively reduce the stress of all three cured epoxy resins by reducing the flexural modulus and CTE.

Moisture Absorption

The results of the moisture-absorption test are given in Figure 12. The absorbed moisture in the package was found not only to plasticize the epoxy resin causing a lowering of the T_g ,²⁴ but also to cause the package crack during the soldering process.⁶ All three rubber-modified encapsulants containing the

polysiloxane moiety absorbed less moisture than did the unmodified encapsulants.

CONCLUSION

High-performance tetrafunctional epoxy resins were synthesized by condensing a dialdehyde with phenol followed by the epoxidation of the resulting tetraphenol with epichlorohydrin. Dispersed silicone rubbers effectively reduce the stress of the synthesized tetrafunctional epoxy resins by reducing the flexural modulus and the coefficient of thermal expansion. The results indicate that a low-stress, high glass transition temperature (T_g), and low-moisture-absorbing epoxy resin system can be obtained for semiconductor encapsulation application.

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