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Synthesis and Modification of Trifunctional Epoxy Resin with Amine Terminated Polydimethyl Siloxanes for Semiconductor Encapsulation Application

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Abstract: Epoxy resins based on the triglycidyl ether of tris(hydroxyphenyl)methane (TETM) possess a very high heat distortion temperature and superior thermal oxidative stability over other types of epoxy resins. The high performance trifunctional epoxy resin (TETM) was synthesized by the condensation of a hydroxybenzaldehyde with phenol followed by epoxidation with a halohydrin. The structure of the synthesized TETM was confirmed by infrared (IR), mass spectra (MS), and nuclear magnetic resonance (NMR) spectroscopy. Amine terminated polydimethylsiloxanes (ATPDMS) were used to reduce the stress of trifunctional epoxy resin cured with phenolic novolac resin for electronic encapsulation applications. The dispersed silicone rubbers effectively reduce the stress of cured epoxy resins by reducing the coefficient of thermal expansion (CTE) and flexural modulus, while the glass transition temperature (T_g) is depressed by only a small amount.

Keywords: Triglycidyl ether of tri(hydroxyphenyl)methane (TETM), Amine terminated polydimethyl siloxane (ATPDMS), Stress, Flexural modulus.

Introduction

Owing to their excellent heat, moisture, solvent and chemical resistance, superior electrical and mechanical properties, and good adhesion to many substrates,epoxy resins have been widely used as an encapsulation material (called epoxy molding compound, EMC) for semiconductor devices. Epoxy novolac is the resin typically employed in the encapsulation of microelectronic devices. However, there is a considerable gap between epoxy novolac and polyimides in their thermal stability, and the latter also carry much higher price premiums and processing difficulty. Epoxy resins based on the triglycidyl ether of tris(hydroxylphenyl)methane isomers and higher oligomers are multifunctional resins which are known to posses improved thermal oxidative stability over other types of epoxy resins [1-4]. Upon cure, this multifunctional epoxy resin provides a densely crosslinked protective layer with a very high T_g; however, it is relatively brittle. The scale of integration of very large scale integrated circuits (VLIs) is continuing to increase, forcing the design of large chips and finer patterns which are more susceptible to internal stress failure. The prevailing surface mount technology also places heat stress on devices [5-6]. Internal stress causes package cracking, aluminum pattern deformation, passivation layer cracking etc. [7-8]. Therefore, the development of a low-stress EMC with high T_g is required for high-reliability semiconductor devices. Although a failure in toughening of a highly crosslinked epoxies (tri-and tetra-functional resins) has been reported [9], polydimethylsiloxanes were used in this study to achieve the reduction in internal stress of the cured trifunctional epoxy resins.

The thermal stress as produced by the differences of thermal expansion coefficients between a silicon chip and its encapsulant is expressed in the following equation [7, 10]:

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$$S = K\int_{T_1}^{T_2} Er(\alpha_r - \alpha_s)\,dT$$

Where S is the thermal stress; K, a constant; Er, the flexural modulus of the resin;
α_r, the thermal expansion coefficient of the resin; and α_s, the thermal expansion coefficient of the silicon chip. Therefore, the stress generated on the semicondutor can be approximated by the product of the elastic modulus of the resin and the difference in the thermal expansion coefficients between the resin and the chip.

Reductions in thermal stress by lowering either the thermal expansion coefficient or the flexural modulus of the encapsulant have been reported [11-17]. The lowering of the elastic modulus by modification with a rubber in a "sea-island" structure consisting of rubber particles and an epoxy matrix is considered to be more desirable than a one-phase structure in view of the thermal property needs. In this paper, the synthesis of a high T_g trifunctional epoxy resin and the preformation of a stable dispersion of rubbery particles in the uncured TETM epoxy resin via "ring-opening" using aminosiloxane were studied. The thermal mechanical properties and flexural test of EMC were also investigated.

Experimental

1. Materials

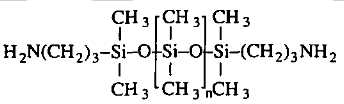
All reagents and solvents were reagent grade or were purified by standard methods before use. Reagent grade phenol, p-toluene sulfonic acid and 4-hydroxybenzaldehyde were the starting materials used in novolac synthesis. Epichlorohydrin and isopropyl alcohol were the reagents for the epoxidation reaction. Methyl ethyl ketone was used as a purification solvent.

A phenol-formaldehyde novolac resin was used as curing agent with an average hydroxyl functionality of 6 and a hydroxyl equivalent weight of about 104 (Schenectady Chemical, HRJ-2210). The A-1 catalyst was (ethyl)triphenylphosphonium acetate acetic acid complex, Ph_3P was triphenylphosphine that was used as curing accelerator. The aminosiloxanes were purchased from Shin-Etsu, their structure and molecular weight (M.W.) are shown in Table I.

2. Synthesis of trifunctional novolac resin (TM) [9]

To a 5 L reaction vessel equipped with a temperature controller, indicating means and a reflux condenser were added 2823.8 g phenol and 12.84 g p-toluene sulfonic acid (PTSA). At 70 °C, 305.5 g of 4-hydroxylbenzaldehyde was added dropwise over 40 min to the above stirred mixture. Upon completion of the addition, the reaction mixture was further stirred for one hour at 90 °C. The completion of the reaction was confirmed by the disappearance of 4-hydroxybenzaldehyde with LC. Aqueous NaOH 6.48 g was added to neutrallize the PTSA, and then the whole reaction mixture was placed on a rotary evaporater to remove excess phenol under reduced pressure and heat until 170 °C and 5 mmHg was reached. The molten trisphenol novolac was poured onto aluminum foil, and solid trisphenol novolac was obtained.

Table I. Aminosiloxanes for the modification of TETM.

Abbr	Structural formula	M.W.	Supplier
AS1	 $H_2N(CH_2)_3-\overset{CH_3}{\underset{CH_3}{Si}}-O\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_3NH_2$	900	Shin-Etsu
AS2		1680	Shin-Etsu
AS3		3000	Shin-Etsu
AS4		4600	Shine-Etsu

^1H NMR (DMSO-δ_6): δ 2.01 (s,1H, CH), δ 6.95 (s,12H, aromatic), δ 6.75 (s, 3H, OH). MS m/z: 292 (100; M^+).

3. Synthesis of trifunctional novolac epoxy resin (TETM) [9]

Trifunctional movolac (TM, 300 g), 493.3 g epichlorohydrin, 267.8 g isopropyl alcohol and 43.2 g deionized water were added to a 1 L flask for epoxidation. Upon stirring at 65 °C, 193.6 g of 20% NaOH was added within 45 min. Phases were separated, and the organic phase was further reacted with 86.4 g 20% NaOH and stirred for 30 min. The water-phase was separated and the organic phase was washed with deionized water for several times, and then dehydrated under vacuum at 150 °C to obtain the epoxy with an epoxy equivalent weight (EEW) of ca. 159.

4. General procedure for the preparation of silicone rubber modified epoxy resin [16]

To a four-neck round-bottom flask equipped with a heating mantle, stirrer , thermocouple and temperature controller was added 384 g of triglycidyl ether of tri-(hydroxylphenyl) methane (TETM). The epoxy resin was heated to 120 °C and then vigorously stirred and dehydrated under vacuum (<10 mmHg) until the water content was less then 0.01% (as measured by a Karl Fischer barometer). Under a nitrogen atmosphere, a mixture of aminosiloxane (42.7 g) and A-1 catalyst (0.8 g) was added dropwise *via* a metering pump over a period of 4 h while maintaining the reaction temperaure at 120 °C. Upon completion of the aminosiloxane addition, the reaction temperature was held at 120 °C for an additional 2 h. The resulting creamy silicone rubber-modified epoxy resin contained ca. 10 wt% of dispersed silicone rubber and had an EEW of ca. 177.

5. Curing procedure of epoxy resins

The various aminosiloxane-modified TETM epoxy resins were mixed with a stoichiometric amount of curing agent and 0.2 wt% Ph_3P in a mill at 25 °C to give a thermosettable epoxy resin powder. The resin powder was cured in a mold at 150 °C under a pressure of 50 kg/cm^2; 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.

6. Measurement and testing

Infrared spectra were recorded with a Perkin-Elmer 16 PC FTIR spectrophotometer operated with a dry air purge. Mass spectrometric analyses were performed on a VG70-250s GC/MS spectrometer with a solid inlet. ^{1}H NMR was obtained on a Burker Analytic WP100NMR and sample was analyzed in deuterated dimethylsulfoxide (DMSO). EEW of epoxy resin and rubber-modified epoxy resin were determined by the $HClO_4$/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 storage modulus G' and tan δ were determined. A JEOL JSM-6400 scanning electron microscope was employed to examine the morphology of the cured rubber-modified samples fractured cryogenically in liquid nitrogen. The fracture surface were vacuum coated with gold. Mechanical properties of cured resins were measured with a Shimadzu AGS-500 universal testing machine. Flexural strength and modulus were obtained at a crosshead speed of 2 mm/min according to ASTM E790-84a. The coefficient of thermal expansion (CTE) was measured with a DuPont 943 thermal mechanical analyzer in accordance with ASTM E831-86. The specimens were heated at a rate of 5 °C/min.

Results and Discussion

1. Synthesis and characterization

Tri-(hydroxyphenyl) methane (TM) was produced by condensing 4-hydroxybenzaldehyde with the appropriate phenol [18]. This condensation reaction is generally affected by reacting an excess amount of phenol with the 4-hydroxybenzaldehyde (Figure 1). The preparation of polyglycidyl ether involves reacting the TM with a halohydrin in the presence of an alkali metal hydroxide as shown in Figure 2.

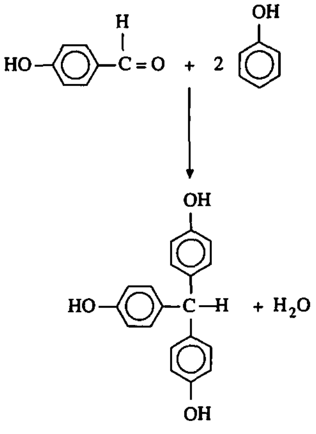

I

Figure 1. Schematic diagram of the synthesis of tris (hydroxyphenyl)methane.

The structure of the synthesized TM was confirmed by mass spectrum(MS), nuclear magnetic resonance (NMR), and infrared (IR) spectroscopy. From the IR spectra of TM and its polyglycidyl ether (TETM), a strong absorption peak at 3200 to 3400 cm^{-1}; representing the –OH functional group of the synthesized TM, and a peak at 910cm^{-1}; representing the oxirane ring absorption of trifunctional epoxy resins (TETM), were observed.

Dispersed aminosiloxane rubber in trifunctional epoxy resins was prepared by the ring-opening of oxirane ring in the epoxy resins with amino group of ATPDMS in the presence of A-1 catalyst to form stable silicone rubber particles dispersed in the ma-

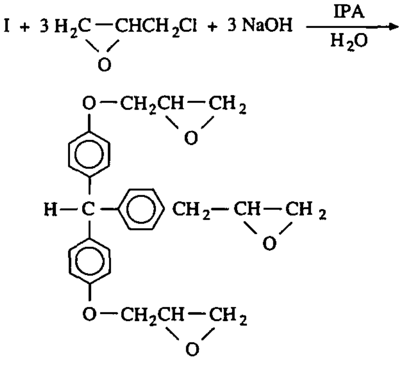

II

Figure 2. Schematic diagram of the preparation of triglycidyl ether.

trix resin in a "sea-island" sturcture ("islands" of silicone rubber dispersed in the "sea" of an epoxy resin as shown in Figure 3). Phenol-formaldehyde novolac cured TETMs exhibited T_g of around 260 °C (Table II) which is far superior to ordinary epoxy novalac (T_g around 180 °C).

2. Dynamic viscoelastic analysis

Dynamic viscoelastic analysis can give information about the structure of cured rubber-modified epoxy resin. The tan δ curves for the control epoxy network exhibit the two major relaxations observed in most epoxy polymers [19]. Figure 4 shows the storage modulus G' and tan δ curves of the cured unmodified and rubber-modified epoxy resins. The storage modulus decreased with modification. In addition to the epoxy α and β peaks, these curves show an additional markedly small peak from -130 to -110 °C with a center near -120 °C, corresponding to the glass transition temperature of the siloxane phase. This small peak further supports the multiphase separation. In addition, the α-relaxation peak in the tan δ curve for the resin modified with polysiloxane became broader and the peak position slightly shifted toward lower temperature. The dynamic viscoelastic properties of the cured trifunctional 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. It is interesting to note that the matrix T_g of the AS_4; aminosiloxane modification is higher than that of other aminosiloxane modifications. This result can be explained in terms of an incomplete phase separation that could result from the higher solubility of the lower M.W. siloxane rubber in the matrix resin, and this greater solubility has resulted in a depression of the glass transition temperature of the modified epoxy resin.

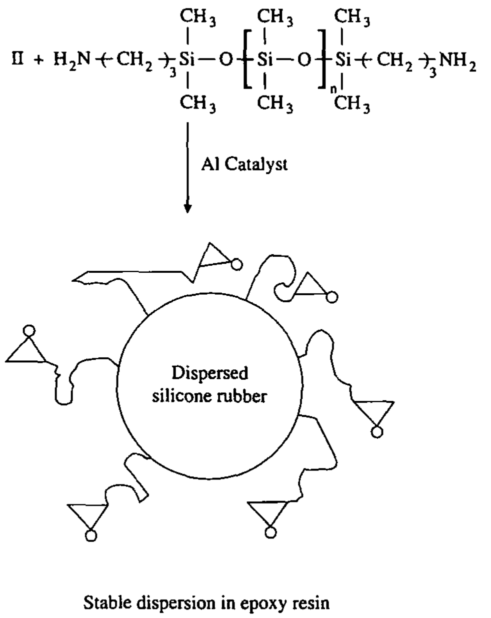


Figure 3. Silicone rubber particle dispersed in expoxy resins *via* the epoxy ring-opening.

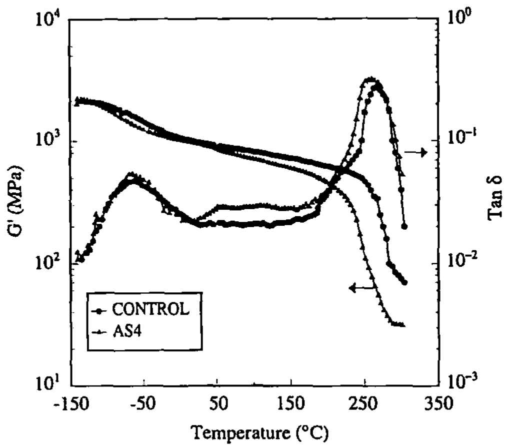


Figure 4. Dynamic viscoelastic analysis for the cured neat trifunctional epoxy resin with amino-siloxane modification.

Table II. Dynamic mechanical properties of cured neat rubber-modified trifunctional epoxy resin system

Sample Designation	$T_g^{(a)}$(°C) Matrix	$T_g^{(b)}$(°C) Rubber
control[c]	265	–
AS1	249	-104
AS2	253	-107
AS3	256	-109
AS4	260	-110

(a) Peak of tan δ at higher temperature.
(b) Peak of tan δ at lower temperature.
(c) Control: unmodified cured trifunctional epoxy resin.

3. Morphology

SEM photomicrographs of cold-snap surfaces for the aminosiloxane modified resins are shown in Figure 5. The two-phase structure is observed in all aminosiloxane-modified resins and the phase seperation is better for higher M.W. siloxane modifiers. The size of rubber particles is about 1 μm.

4. Encapsulation formulation

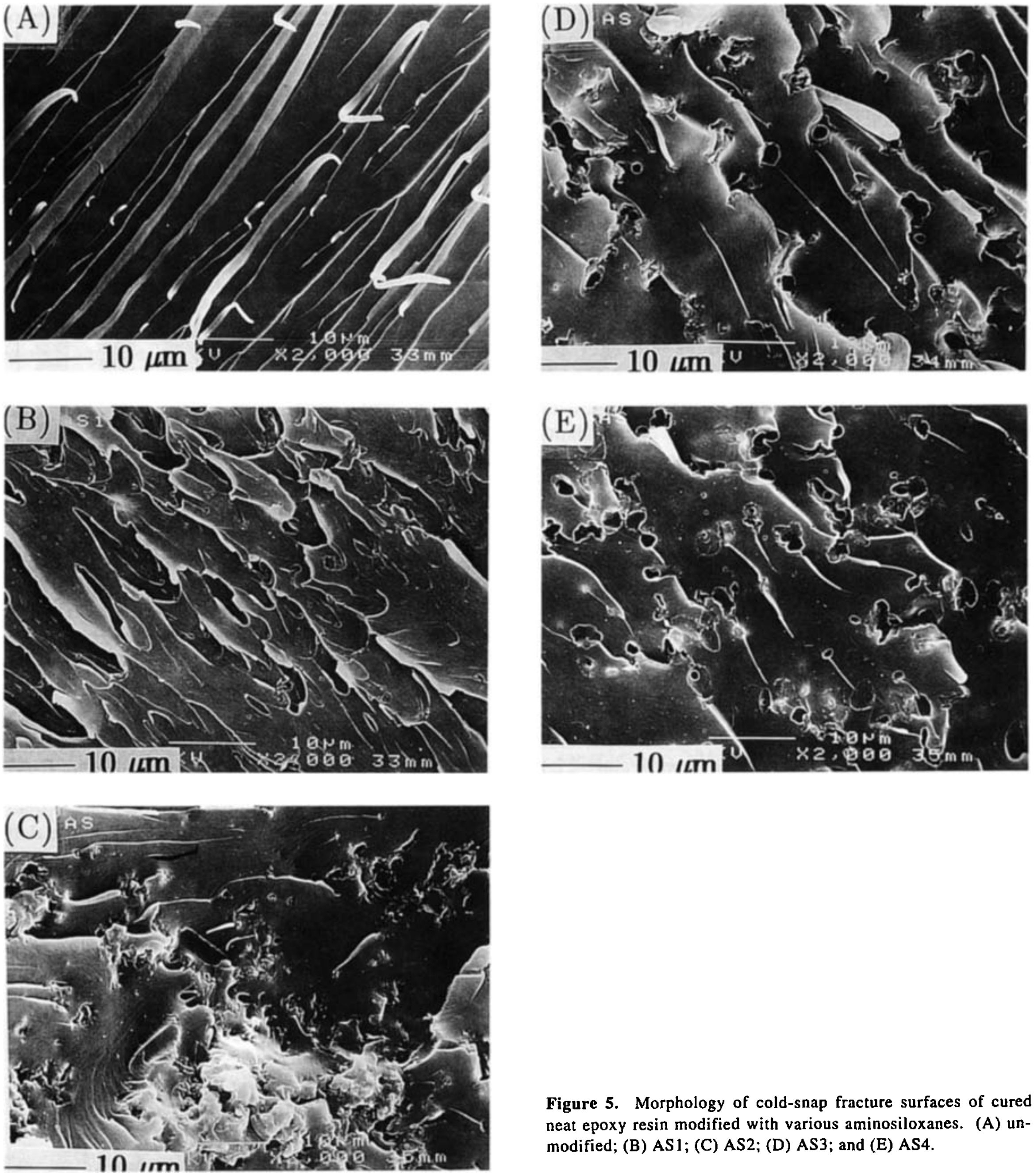


Figure 5. Morphology of cold-snap fracture surfaces of cured neat epoxy resin modified with various aminosiloxanes. (A) unmodified; (B) AS1; (C) AS2; (D) AS3; and (E) AS4.

The trifunctional epoxy resin and TETM modified with various silicone rubbers or silicone powder were formulated into six electronic encapsulating formulations. Encapsulation formulation typically contains an epoxy resin, a curing agent, and a filler material such as silca [20]. The formulations were cured at 175 °C for 4 h. The encapsulating formulations are given in Table III. The thermal mechanical properties of the cured encapsulating formulations were determined by the following tests:

5. Coefficient of thermal expansion (CTE)

The CTE in the glassy state below the glass

Table III. Typical encapsulating formulation.

Ingredient	Weight%
Fused silica (GP-71 HARBISON-WALKER)	68.5
Mold release (HOECHST WAX OP&E)	0.4
Carbon blake	0.4
Silane coupling agent (DC X-6040)	0.4
Antimony trioxide	1.0
Triphenyl phosphine accelerator	0.2
Phenolic hardner (HRJ-2210)	9.1
Cresol epoxy novolac	17.5
Brominated epoxy resin	2.5

transition temperature (T_g) was measured from 200 to 240 °C, and the results are shown in Figure 6. For CTE below T_g, all rubber-modified encapsulants have slightly lower CTE than the unmodified resin, and this will result in a small difference in CTEs between encapsulant and silicon chip. For the CTE below the T_g, the rubber-modified encapsulant of AS4 has a slightly lower CTE than the unmodified resin, and this results in a small difference in CTEs between encapsulant and the silicon chip.

6. Glass transition temperature (T_g)

Figure 7 shows the glass transition temperature of a control resin and various aminosiloxane modified TETM. Glass transition temperature (T_g) was determined from tangents of the CTE as a function of temperature at 100 and 200 °C. The T_g of cured TETM is relatively unaffected by the modification with AS4 aminosiloxane. However, the AS1-modified resin has a significantly lower T_g, and this may result from the smaller M.W. and greater solubility of AS1 modifier into the matrix resin than the others.

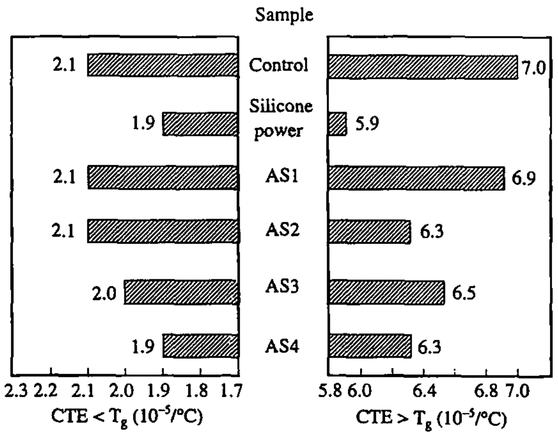


Figure 6. Coefficient of thermal expansion for TETM and various aminosiloxane modified encapsulants.

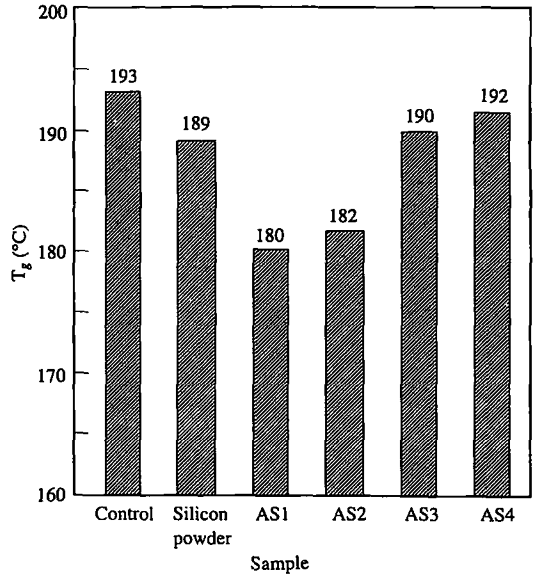


Figure 7. Glass transition temperature for TETM and various aminosiloxane modified encapsulants.

7. Flexural test properties

The flexural modulus values of the cured resin were reduced markedly with aminosiloxane modifications; the results are shown in Figure 8. The flexural strength of aminosiloxane-modified resin remained approximately equal to or slightly larger than that of the control resin. These results indicate that aminosiloxane-modification effectively improve the

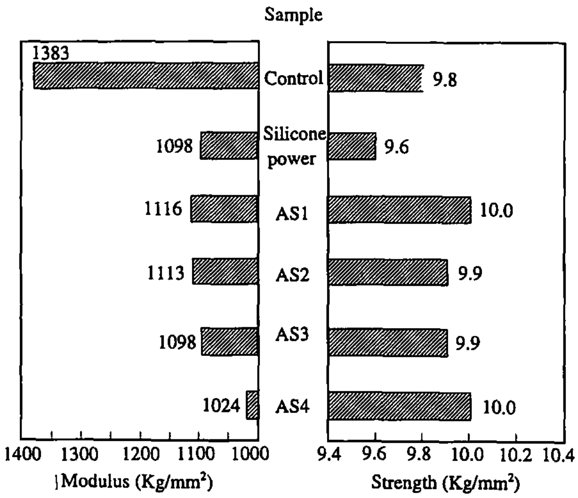


Figure 8. Flexural test properties for TETM and various aminosiloxane modified encapsulants.

toughness of cured epoxy resin without lowering its strength.

8. Internal stress

Internal stress of the cured encapsulant can be approximated by the product of the flexural modulus and the CTE below the T_g ($E \cdot \alpha_{r1}$). The stress of the control and various aminosiloxane-modified encapsulants are shown in Figure 9. The results indicate that AS4 aminosiloxane is a better modifier than other lower M.W. siloxanes in reducing stress. This can be attributed to the complete separation of the rubber phase from the epoxy matrix and the rubber phase acting as a stress reliever.

Conclusion

High performance trifunctional epoxy resin was synthesized by condensing a hydroxybenzaldehyde with phenol followed by the epoxidation of the resulted TM with epichlorohydrin. Epoxy resin based on the triglycidyl ether of tris(hydroxyphenyl) methane has high T_g and superior thermal properties over conventional resins. It is the best candidate resin for electronic encapsulation application to meet the challenges of surface mount technology.

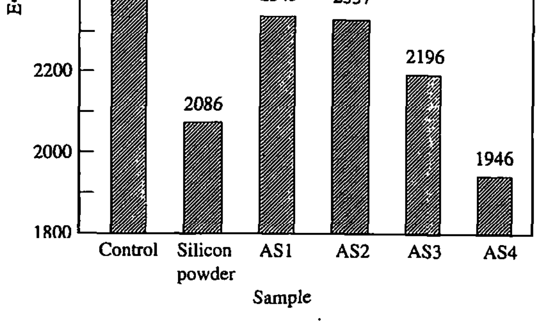


Figure 9. Comparsion of stress for TETM and various aminosiloxane modified encapsulants.

A process was developed to toughen multifunctional epoxy resin by incorporating stable dispersed aminosiloxane rubber particles in the resin matrix, which reduced the CTE and the modulus of cured TETM epoxy resin. AS4 is an excellent modifier for trifunctional epoxy resin, greatly reducing the internal stress without lowering the glass transition temperature of the cured trifunctional epoxy resin.

Acknowledgement

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