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# Synthesis of novel trifunctional epoxy resins and their modification with polydimethylsiloxane for electronic application

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The modification of novel trifunctional epoxy resins with silicon rubber to reduce stress while maintaining a high glass transition temperature is described. Trifunctional epoxy resins were synthesized from the condensation of 4-hydroxybenzaldehyde, chloroacetaldehyde or crotonaldehyde with phenol, followed by epoxidation with a halohydrin. The structure of the synthesized triphenols was characterized by infra-red, mass, and nuclear magnetic resonance spectrometry. Toughening of trifunctional epoxy resins was achieved by hydrosilation with side chain methyl hydrogen siloxanes. The dynamic viscoelastic properties and morphologies of neat silicon rubber-modified epoxy networks were investigated. The mechanical properties of encapsulants formulated from the synthesized silicone rubber-modified epoxy resins were also studied. The dispersed silicon rubbers effectively reduced the internal stress of cured epoxy resins by reducing Young's modulus and the coefficient of thermal expansion, while the glass transition temperature was slightly depressed. © 1997 Elsevier Science Ltd. All rights reserved.

**(Keywords: trifunctional epoxy resins; methyl hydrogen siloxane; low stress encapsulant)**

## INTRODUCTION

Since epoxy resins have excellent heat, moisture, and chemical resistance, superior electrical and mechanical properties, and good adhesion to many substrates, they are widely used in the field of coatings, adhesives, casting, potting, composites, laminates, and encapsulation of semiconductor devices. Recently, in integrated circuits (ICs) and large scale integrated circuit (LSI) sealed with epoxy moulding compounds (EMCs), the chip size has been increasing while the dimension of package has become smaller and thinner, which is more susceptible to the thermal stress failure. The stress causes package cracking, passivation layer cracking, aluminium pattern deformation and delamination[1–3]. The thermal stress as produced by the differences in thermal expansion coefficient between the silicon chip and the encapsulant is expressed in the following equation[1]:

$$S = K\int_{T_1}^{T_2} (\alpha_{r1} - \alpha_s)E_{r1}dT \quad (1)$$

where $S$ is thermal stress, $K$ is a constant, $\alpha_{r1}$ is the thermal expansion coefficient of the resin, $\alpha_s$ is the thermal expansion coefficient of the silicon chip, and $E_{r1}$ is the Young's modulus of the resin. Since $\alpha_{r1} \gg \alpha_s$, equation (1) may be simplified as:

$$S = K\int_{T_1}^{T_2} \alpha_{r1}E_{r1}dT \quad (2)$$

Therefore, the stress generated on the semiconductor can be approximated from the product of the Young's modulus of the resin and the thermal expansion coefficient of the resin. Moreover, the trend of IC packaging has shifted from conventional insertion mount devices, such as Dual Inline Package (DIP) to surface mount devices, such as Quad Flat Package (QFP), Small Outline Package (SOP), and Plastic Leaded Chip Carrier (PLCC)[4]. The prevailing surface mount technology, exposing devices to a soldering temperature of 250°C also generates heat stress to devices. Therefore, a low-stress and high glass transition temperature ($T_g$) EMC is strongly required.

Many studies have been reported to enhance the heat resistance of epoxy resins, for example increasing the crosslink density of cured epoxy resin[5], preparation of

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a stiff main chain[6], or introduction of a bulky structure such as biphenyl or naphthalene[7]. There are several ways to improve the toughness of the cured epoxy resins. Much attention has been paid to the addition of a carboxy terminated butadiene acrylonitrile elastomer (CTBN) to the epoxy resin[8–10]. However, the superior toughness of the rubber-modified epoxy resin was obtained only with a considerable sacrifice in $T_g$. Other studies have utilized high performance thermoplastic[11,12], liquid crystalline polymer[13], and acrylic rubber[14].

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[1,15]. In a previous investigation[15], side chain methyl hydrogen siloxanes (MHSs) have been reported as effective modifiers for the *o*-cresol formaldehyde novolac epoxy (CNE). In this paper, the synthesis of high $T_g$ trifunctional epoxy resins and the preformation of a stable dispersion of rubbery particles in the uncured trifunctional epoxy resins via hydrosilation using side chain MHSs were studied. The thermal mechanical properties and flexural behaviour of EMC were also investigated.

## EXPERIMENTAL

### *Materials*

4-Hydroxybenzaldehyde and *p*-toluene sulfonic acid (PTSA) were purchased from Ferak Co. Chloroacetaldehyde was purchased from Tokyo Chemical Industry Co. Crotonaldehyde was purchased from Merck Co. Epichlorohydrin (ECH) was purchased from Janssen Co. All solvents were reagent grade or were purified by standard methods before use. 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 side chain MHS, with a number-average molecular weight of around 6000, was purchased from Shin-Etsu Co. The A-1 catalyst was (ethyl)triphenyl phosphonium acetate acetic acid complex. $Ph_3P$ was triphenylphosphine, that was used as curing accelerator. $H_2PtCl_6$ (5 wt% in isopropanol) was used as a catalyst in hydrosilation.

### *General procedure for the preparation of triphenols*

*The preparation of tri(hydroxyphenyl) methane (THM).* To a 5-l four-neck round-bottom flask equipped with a heating mantle, mechanical stirrer, reflux condenser, thermocouple and temperature controller was added 2820 g (30 mol) of phenol. After reaction temperature was raised to 70°C, added 12.84 g (0.0675 mol) of PTSA. At 70°C, 305 g (2.5 mol) of 4-hydroxy-benzaldehyde was added dropwise to the reaction mixture over a period of approximately 40 min. Upon the completion of 4-hydroxybenzaldehyde addition, the reaction temperature was raised to 90°C and the mixture was stirred for an additional hour. Completion of the reaction was confirmed by liquid chromatography (LC), and the reaction mixture was charged with 6.48 g (0.081 mol) of sodium hydroxide to neutralize the PTSA. A rotovap was then used to remove the unreacted phenol. The chemical structure of the THM was confirmed by mass (m.s.), infra-red (i.r.) and nuclear magnetic resonance (n.m.r.) spectroscopy. The synthesis scheme is shown in *Figure 1*.

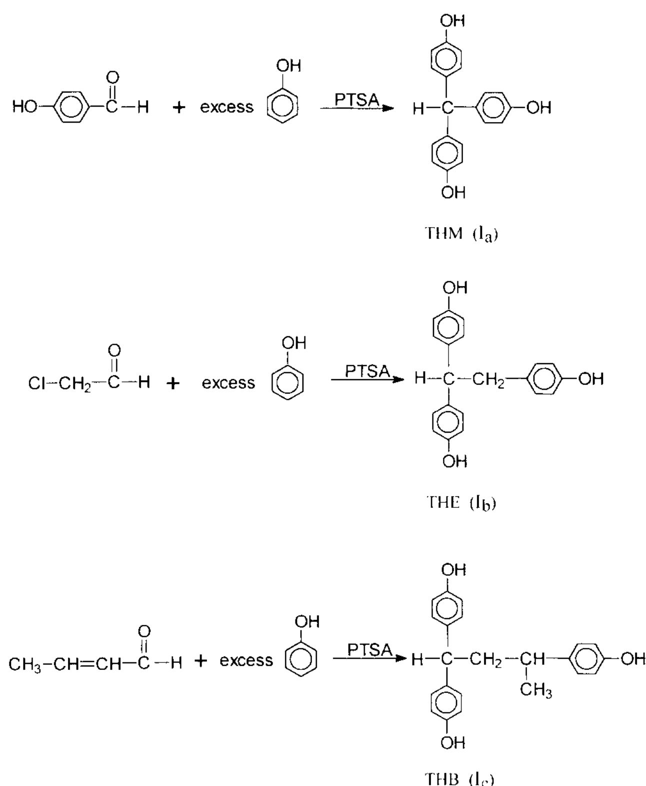


**Figure 1** Schematic diagram of the synthesis of triphenol

$^1$H n.m.r. (DMSO-$d_6$): $\delta$ 2.01 (*s*, 1H, CH), $\delta$ 6.95 (*s*, 12H, aromatic), $\delta$ 6.75 (*s*, 3H, OH). Ms $m/z$ 292 (100; $M^+$).

*The preparation of tri(hydroxyphenyl) ethane (THE).* THE was synthesized by the procedure analogous to the synthesis of THM, with the exception of aldehyde being replaced with chloroacetaldehyde.

$^1$H n.m.r. (DMSO-$d_6$): $\delta$ 2.11 (*t*, 1H, CH), $\delta$ 2.35 (*d*, 2H, $CH_2$), $\delta$ 6.9–7.2 (*m*, 12H, aromatic), $\delta$ 6.56 (*s*, 1H, OH), $\delta$ 6.76 (*s*, 2H, OH). M.s. $m/z$ 320 (100; $M^+$).

*The preparation of tri(hydroxyphenyl) butane (THB).* THB was synthesized by the procedure analogous to the synthesis of THM, with the exception of aldehyde being replaced with crotonaldehyde.

$^1$H n.m.r. (DMSO-$d_6$): $\delta$ 1.25 (*d*, 3H, $CH_3$), $\delta$ 2.19 (*t*, 1H, CH), $\delta$ 2.45 (*m*, 2H, $CH_2$), $\delta$ 2.91 (*m*, 1H, $\underline{CH}$-$CH_3$), $\delta$ 6.92–7.3 (m, 12H, aromatic), $\delta$ 6.02 (*s*, 1H, OH), $\delta$ 6.68 (*s*, 2H, OH). M.s. $m/z$ 334 (100; $M^+$).

### *General procedure for the preparation of polyglycidyl ether of the triphenols*

To a 2-l four-neck round-bottom flask equipped with a stirrer, heating mantle, thermocouple, temperature controller, condenser, nitrogen inlet, and additional funnel, were charged 0.5 mol triphenol, 6 mol epichlorohydrin (ECH), 270 g of isopropyl alcohol, and 50 ml water. The reaction mixture was heated to 65°C while stirring, and 20 wt% aq. NaOH (0.9 mol) was added dropwise over a period of 45 min. After completion of the additions, the reaction mixture was further reacted for another 20 min, and then the bottom brine layer was removed by

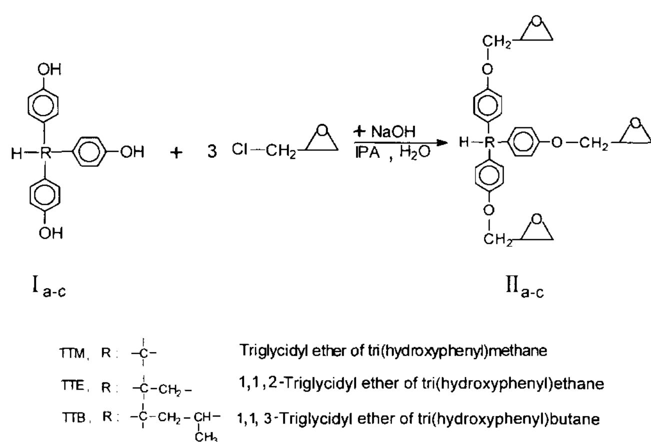


**Figure 2** General schematic of the preparation of polyglycidyl ether

siphoning. The organic phase was further reacted with 20 wt% aq. NaOH (0.4 mol) at 65°C for 30 min, and then the phases were separated. The organic layer was washed several times with deionized water and then rotovapped at 150°C to remove excess ECH and solvent. The general schematic of the preparation of polyglycidyl ether is shown in *Figure 2*.

*General procedure for the preparation of silicon rubber-modified trifunctional epoxy resin*

To a 500-ml four-neck round-bottom flask equipped with a heating mantle, stirrer, reflux condenser, thermocouple and temperature controller, was added 210 g of trifunctional epoxy resin. The epoxy resin was heated to 120°C, and then vigorously stirred and dehydrated under vacuum (< 10 mm Hg) until the water content was less than 0.01% (measured by Karl Fischer's method). The mixture of 2-allylphenol (2-AP, 6.3 g) and A-1 catalyst (0.5 g) was added dropwise via a metering pump over a period of 30 min, while maintaining the reaction temperature at 120°C. After the completion of 2-AP addition, the reaction temperature was maintained at 120°C for an additional 1.5 h. Completion of the reaction was confirmed by gas chromatography (g.c.) for the disappearance of the reactant (2-AP) in the reaction mixture. The resultant epoxy resin thus had a double bond in the molecule. To a 1-l flask equipped with a heating mantle, thermocouple and temperature controller, stirrer and a Dean–Stark trap with a reflux condenser were added the above resultant epoxy resins, 200 ml of toluene and 24 g MHS. The contents were mixed thoroughly and the temperature was raised to remove water by azeotrope with toluene for 1 h. $H_2PtCl_6$ solution (5 wt%, 0.2 g) was added and the mixture was allowed to reflux until the completion of the hydrosilation reaction. After the completion of hydrosilation, the reaction mixture was then heated to 150°C under a full vacuum for 2 h to remove the solvents. Upon cooling to room temperature, a creamy MHS-modified epoxy resin was obtained. The resulting epoxy resin contains *ca* 10 wt% dispersed silicon rubber.

*Curing procedure of epoxy resins*

Unmodified and silicon rubber-modified trifunctional epoxy resins were mixed with a stoichiometric amount of curing agent and $Ph_3P$ in a mill at moderate temperature to give a thermosettable epoxy resin powder. The resin powder was cured in a mould at temperature 170°C and $50\,kg\,cm^{-2}$ for a period of 1 h, and then postcured at 180°C for 2 h and 210°C for 4 h to obtain a cured specimen for scanning electron microscopic (SEM) and dynamic viscoelastic analysis.

*Measurement and testing*

Epoxy equivalent weight (EEW) of MHS-modified epoxy resin was determined by the $HClO_4$/potentiometric titration method. The i.r. spectra were carried out with a Perkin Elmer PC-16 Fourier transform (*FT*) i.r. Dynamic viscoelastic properties were performed on a Rheometrics RDA-II rheometer between −150 and 350°C, with a heating rate of 5°C per step at a frequency of 1 Hz. The rectangular torsion mode was chosen and the dimensions of the specimen were 51 mm × 12.7 mm × 0.76 mm. The storage modulus $G'$ and $\tan\delta$ were determined. The JEOL JSM-6400 SEM was employed to examine the morphology of cured rubber-modified samples fractured cryogenically in liquid nitrogen. The fracture surfaces 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 $2\,mm\,min^{-1}$ according to ASTM E790-86. A three-point loading system was chosen and rectangular bar specimens, 80 mm × 10 mm × 4 mm, were moulded directly by a transfer moulding process. The coefficient of thermal expansion (CTE) was measured with a DuPont 943 thermal mechanical analyser (TMA) in accordance with ASTM E831-86. A specimen 4 mm in length was used at a heating rate of $5°C\,min^{-1}$. Normally, the thermal expansion increase with the increase in temperature and the CTEs were calculated from the slope. An abrupt change in slope of the expansion curve indicates a transition of the material from one state to another.

## RESULTS AND DISCUSSION

*Synthesis and characterization*

Triphenols were produced by condensing the appropriate aldehyde with the appropriate phenol. This condensation reaction is generally effected by reacting an excess amount of phenol with the aldehyde (*Figure 1*). The preparation of polyglycidyl ethers involves reacting the triphenol with a halohydrin in the presence of an alkali metal hydroxide (*Figure 2*).

The structure of the synthesized triphenols was confirmed by i.r., m.s., and nuclear magnetic resonance (n.m.r.) spectroscopy. From the i.r. spectra of THM and its polyglycidyl ether (TTM), we can see a strong absorption peak at 3400 to $3600\,cm^{-1}$ representing the –OH functional groups of the synthesized triphenol, and a peak appears at $908\,cm^{-1}$ representing the oxirane ring absorption of trifunctional epoxy resins.

Dispersed silicon rubbers in epoxy resins can be prepared in two steps: The first step involves the vinylization of part of the epoxy groups in the TTM (or TTE, TTB) with 2-allylphenol to form a reactive macromonomer as shown in *Figure 3*. The second step is the hydrosilation of the resultant macromonomer with MHS in the presence of a catalyst (5 wt% $H_2PtCl_6$ in isopropanol) to form a stable silicon rubber particle dispersed in the matrix resin in a 'sea-island' structure ('island' of silicon rubber dispersed in the 'sea' of an

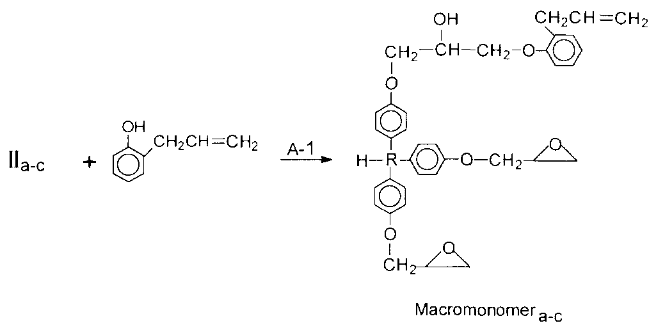


**Figure 3** Vinylization of an epoxy resin to form a macromonomer

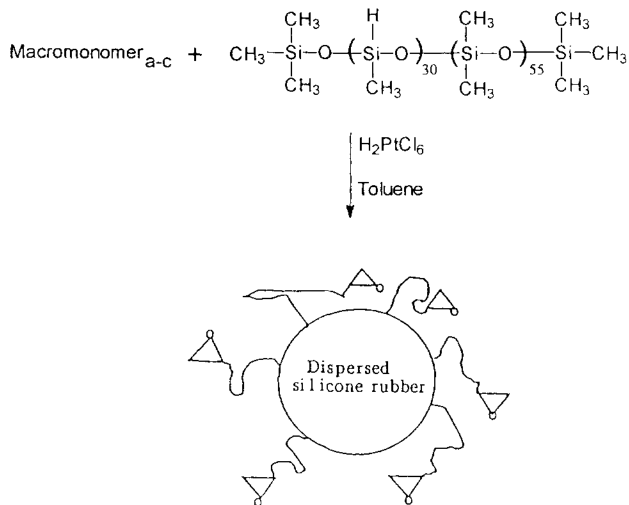


**Figure 4** Macromonomer and methyl hydrogen siloxane via 'hydrosilation' to form a dispersion

**Table 1** Epoxy equivalent weight (EEW) of unmodified and MHS-modified trifunctional epoxy resins

| Sample designation | EEW |
|---|---|
| TTM (triglycidyl ether of tri(hydroxyphenyl)methane) | 160 |
| TTE (1,1,2-triglycidyl ether of tri(hydroxyphenyl)ethane) | 180 |
| TTB (1,1,3-triglycidyl ether of tri(hydroxyphenyl)butane) | 196 |
| TTMS (methyl hydrogen siloxane-modified TTM) | 195 |
| TTES (methyl hydrogen siloxane-modified TTE) | 237 |
| TTBS (methyl hydrogen siloxane-modified TTB) | 239 |

epoxy resin as shown in *Figure 4*). In the vinylization step, some epoxy rings in epoxy resins were reacted, therefore, the epoxy equivalent weights of MHS-modified epoxy resins were increased. The results are listed in *Table 2*. The hydrosilation of MHS-modified epoxy resin was confirmed by i.r. spectroscopy. I.r. spectra of MHS, TTM and MHS-modified TTM are shown in *Figure 5*. The characteristic band of Si–O at 1118 $cm^{-1}$ is apparent from the spectrum of the MHS-modified TTM. The MHS-modified TTM also shows an absorption at 2162 $cm^{-1}$, which is attributable to residual Si–H in MHS.

*Dynamic viscoelastic analysis*

Dynamic viscoelastic analysis can give information on the microstructure of cured rubber-modified epoxy

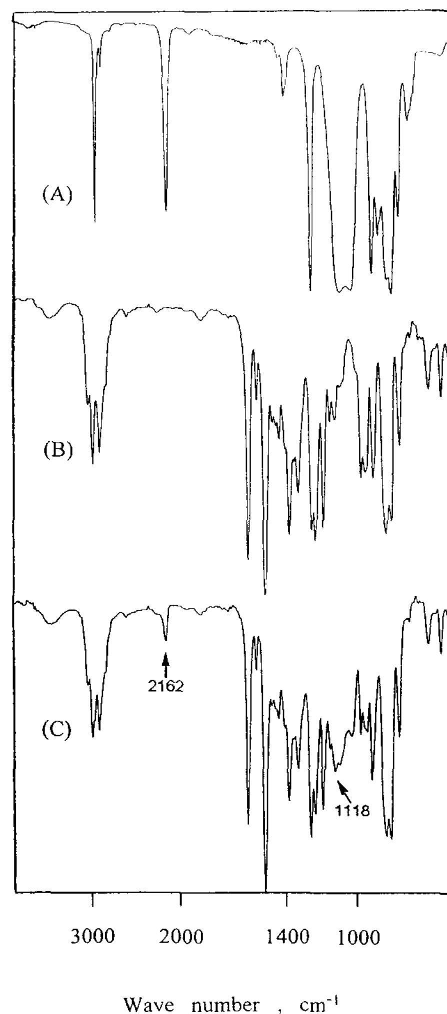


**Figure 5** I.r. spectra: (A) MHS; (B) TTM; (C) MHS-modified TTM

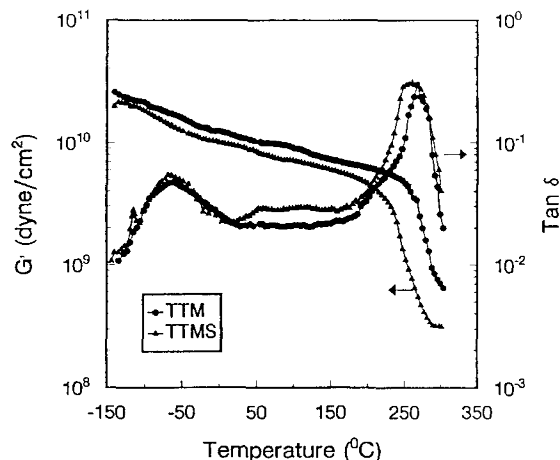


**Figure 6** The comparison of storage modulus $G'$ and $\tan\delta$ curves between the cured neat epoxy resins with or without MHS modification

resins. The $\tan\delta$ curves for the unmodified epoxy network exhibit two major relaxations observed in most epoxy polymers[16]: a major high-temperature or $\alpha$ transition corresponds 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 $CH_2$–CH(OH)–$CH_2$–O (hydroxyether) group of the epoxy. A comparison of storage modulus $G'$ and $\tan\delta$ curves between the cured

**Table 2** Dynamic viscoelastic properties of the cured neat trifunctional epoxy resin system

| Sample designation | $T_g{}^a$, matrix (°C) | Shear modulus 20°C ($\times 10^9$ dyne $cm^{-2}$) | $T_g{}^b$, rubber (°C) |
|---|---|---|---|
| TTM | 268 | 11.3 | – |
| TTE | 257 | 10.8 | – |
| TTB | 243 | 9.89 | – |
| TTMS | 260 | 9.45 | −115 |
| TTES | 251 | 9.41 | −113 |
| TTBS | 238 | 9.36 | −114 |

[a] Peak of tan $\delta$ at higher temperature
[b] Peak of tan $\delta$ at lower temperature

unmodified and rubber-modified epoxy resin is shown in *Figure 6*. The storage modulus decreased with rubber modification. In addition to the epoxy $\alpha$ and $\beta$ peaks, the tan $\delta$ curve for the silicon rubber-modified product shows a markedly small peak from −125 to −105°C with a centre near −115°C corresponding to the $T_g$ of the siloxane phase. This small peak further supports the multiphase separation. In addition, the $\alpha$-relaxation peak in the tan $\delta$ 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 system including the major $T_g$ and the rubber's $T_g$ are tabulated in *Table 2*.

*Morphology*

SEM photomicrographs of cold-fracture surfaces for the cured trifunctional epoxy resins and their rubber-modified epoxy networks are shown in *Figure 7*. Electron micrographs reveal that rubber particles a few micrometres or less in size have been dispersed in the matrix.

*Encapsulating formulation*

Three trifunctional epoxy resins and their MHS-modified

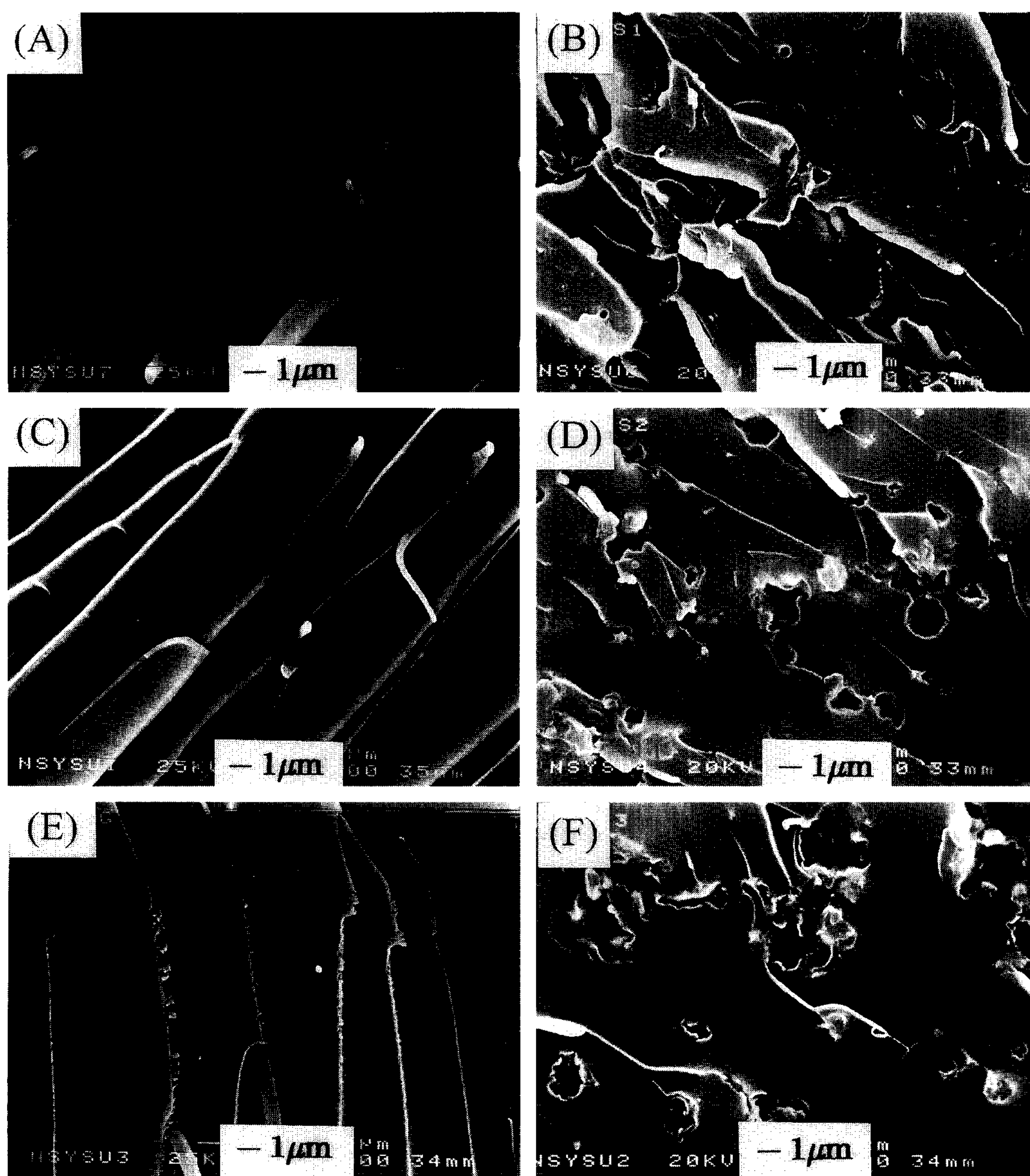


**Figure 7** Morphology of cold-fracture surfaces of cured neat epoxy resins modified with or without silicon rubber particles (10 wt%). (A) TTM; (B) TTMS; (C) TTE; (D) TTES; (E) TTB; (F) TTBS

resins were formulated into six electronic encapsulating formulations. Encapsulation formulations typically contain an epoxy resin, a curing agent, and a filler material such as silica[12]. The formulations were each cured 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*

*Figure 8* shows the thermal mechanical properties. The CTE in the glassy state below the $T_g$ was taken from 60 to 100°C and the CTE above the $T_g$ was taken from 200 to 240°C. For CTE below $T_g$, all of the MHS-modified encapsulants have either no change or a slightly lower CTE than the unmodified resin and this lowering of CTE will result in a smaller difference in CTEs between encapsulant and silicon chip.

*Glass transition temperature*

$T_g$s were determined from tangents of the CTE as a function of temperature at 100 and 200°C. The results are shown in *Figure 9*. MHS-modified resins have a slightly lower $T_g$ than the original resin, however the effect is very minimal indicating a good phase separation in all modified resins. This observation is consistent with the viscoelastic investigation.

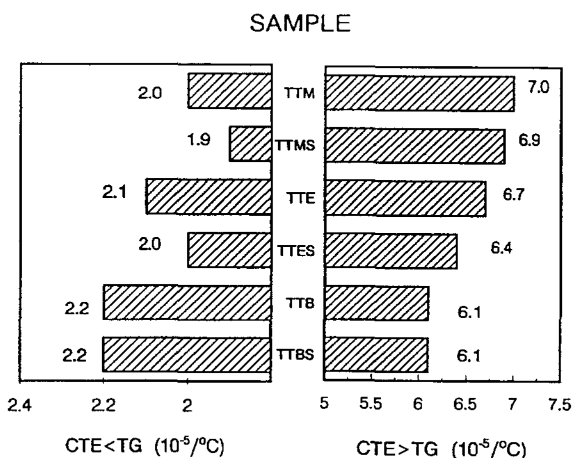


**Figure 8** CTE for various unmodified and MHS-modified trifunctional epoxy resin encapsulants

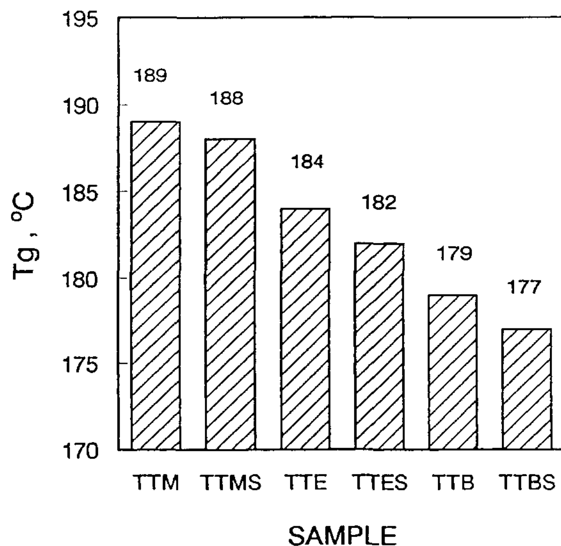


**Figure 9** $T_g$ for various unmodified and MHS-modified trifunctional epoxy resin encapsulants

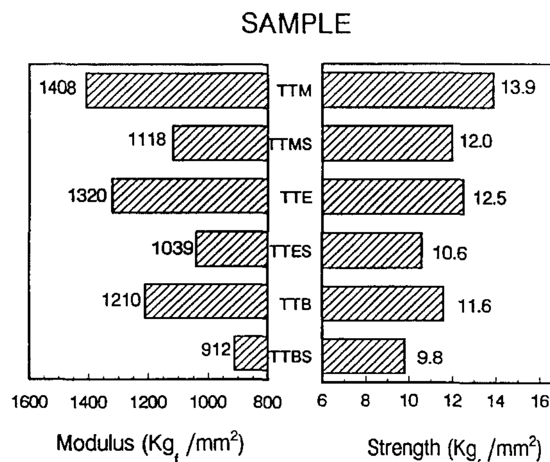


**Figure 10** Flexural test properties for various unmodified and MHS-modified trifunctional epoxy resin encapsulants

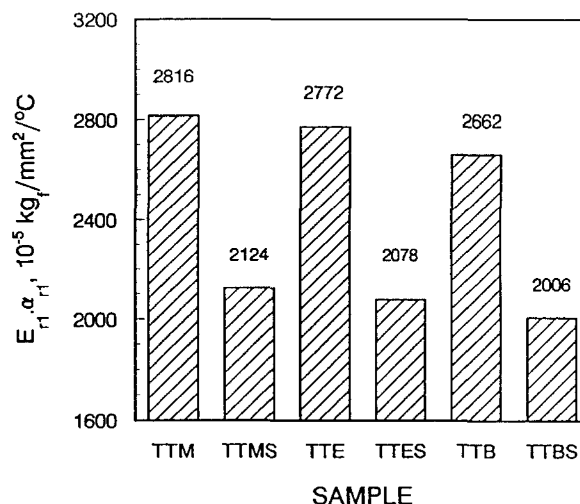


**Figure 11** Comparison of stress for various unmodified and MHS-modified trifunctional epoxy resin encapsulants

*Flexural test properties*

*Figure 10* shows the result of the flexural test. The flexural moduli of the three types of MHS-modified epoxy were reduced markedly. The flexural strengths of the three types of MHS-modified epoxy remained approximately equal to the unmodified epoxy resin. These results can be explained by MHS effectively improving the toughness of cured epoxy resin without lowering the strength.

*Internal stress*

Internal stress of the cured encapsulants can be approximated from the product of Young's modulus ($E_{rl}$) and thermal expansion coefficient ($\alpha_{rl}$) below the $T_g$ of the cured encapsulants. *Figure 11* shows the stress of unmodified epoxy resins and various MHS-modified encapsulants. The dispersed silicon rubber particles effectively reduce the internal stress. This can be attributed to the complete separation of rubber phase from epoxy matrix and acts as a stress relieving agent.

## CONCLUSIONS

High performance trifunctional epoxy resins were synthesized by the condensation of appropriate aldehyde with phenol followed by epoxidation with a halohydrin. A process was developed to incorporate stable dispersed silicon rubber particles in a trifunctional epoxy resin matrix, which greatly reduces the modulus of cured trifunctional epoxy resins. The results indicate that MHS is an excellent modifier for trifunctional epoxy resins, which greatly reduces the stress and only slightly decreases the $T_g$ of the cured trifunctional epoxy resins.

## ACKNOWLEDGEMENT

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## REFERENCES

1 Kuwata, K., Iko, K. and Tabata, H. *IEEE Trans. Comp. Hybrids Manuf. Technol.* 1985, **8**, 486
2 Steiner, T. O. and Suhl, D. *IEEE Trans. Comp. Hybrids Manuf. Technol.* 1987, **10**, 209
3 Suhl, D. *IEEE Trans. Comp. Hybrids Manuf. Technol.* 1990, **13**, 940
4 Kimura, H., Ohizumi, S., Nishioka, T., Nakao, M. and Haraa, M. *IEEE* 1992, **15**, 1035
5 Ogata, M., Kawata, T. and Kinjo, N. *Kobunshi Ronbunshu* 1987, **44**, 193
6 Matsumoto, A., Hasegata, K. and Fukuda, A. *Polym. Int.* 1993, **31**, 275
7 Ohta, K., Kosaka, W. and Yanagisawa, K. Eur. Patent 0,428,871 A2, 1991
8 Verchere, D., Sautereau, H., Pascault, J. P., Moschiar, S. M., Riccardi, C. C. and Williams, R. J. J., *J. Appl. Polym. Sci.* 1990, **41**, 467
9 Manzione, L. T., Gillham, J. K. and Mcpherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 889
10 Chen, T. K. and Jan, Y. H. *Polym. Eng. Sci.* 1991, **31**, 557
11 Bucknall, C. B. and Gilbert, A. H. *Polymer* 1989, **30**, 213
12 Iijima, T., Tomoi, M., Tochimoto, T. and Kakiuchi, H. *J. Appl. Polym. Sci.* 1991, **43**, 463
13 Carfagna, C., Nicolais, L., Amendola, E., Jr, C. C. and Filippov, A. G. *J. Appl. Polym. Sci.* 1992, **44**, 1465
14 Nakamura, Y., Tabata, H., Suzuki, H., Iko, K., Okubo, M. and Matsumoto, T. *J. Appl. Polym. Sci.* 1986, **32**, 4865
15 Ho, T. H. and Wang, C. S. *J. Appl. Polym. Sci.* 1994, **54**, 13
16 Yorkgitis, E. M., Eiss, Jr. N. S., Tran, C., Wilkes, G. L. and McGrath, J. E. in 'Advances in Polymer Science' (Ed. K. Dušek, Vol. 72, Springer-Verlag, New York, 1985, p. 79