Toughening of Epoxy Resins by Modification with Dispersed Acrylate Rubber for Electronic Packaging

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SYNOPSIS

Dispersed acrylate rubbers were used to improve the toughness of cresol–formaldehyde novolac epoxy resin cured with phenolic novolac resin for electronic encapsulation application. The effect of the alkyl group of the acrylate monomer on the phase separation of resultant elastomers from epoxy resin was investigated. The dispersed acrylate rubbers effectively improve the toughness of cured epoxy resins by reducing the coefficient of thermal expansion (CTE) and flexural modulus, while the glass transition temperature (T_g) was hardly depressed. Electronic devices encapsulated with the dispersed acrylate rubber-modified epoxy molding compounds have exhibited excellent resistance to the thermal shock cycling test and have resulted in an extended device use life. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Since epoxy resins have excellent heat, moisture, solvent, and chemical resistance, superior electrical and mechanical properties, and good adhesion to many substrates, they are widely used in the field of coatings, adhesives, castings, pottings, composites, laminates, and encapsulation of semiconductor devices. *o*-Cresol–formaldehyde novolac epoxy (CNE) is the resin typically employed to encapsulate microelectronic devices. Upon cure, this multifunctional epoxy resin provides a densely cross-linked protective layer but it is relatively brittle.

The scale of integration of LSIs is continuing upward, forcing the design of large chips and finer patterns that are more susceptible to internal stress failure. The prevailing surface mount technology also generates heat stress to devices.[1,2] Internal stress causes package cracking, passivation layer cracking, aluminum pattern deformation, etc.[3–5] The source of internal stress with plastic encapsulants are considered to be (1) shrinkage due to the curing process and (2) differential shrinkages between the device and the resin. In the case of epoxy resin encapsulation, the first source (shrinkage) is relatively minor, whereas the second one, which is the difference of thermal expansion coefficients, is the dominant effect. The thermal stress as produced by the differences of thermal expansion coefficient is expressed in the following equation:

$$S = K \int (\alpha_r - \alpha_s) E_r \, dT$$

where S is thermal stress; K, a constant; α_r, the thermal expansion coefficient of the resin; α_s, the thermal expansion coefficient of the silicon chip; and E_r, Young's modulus of the resin. Reductions of thermal stress by lowering of either the thermal expansion coefficient or the flexural modulus of the encapsulant have been reported.[6–16] Increasing the amount of silica filler used in an encapsulant effectively lowers the thermal expansion coefficient; however, this approach not only increases the elastic modulus, but also increases the viscosity of the resin composition, resulting in poor moldability. 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.[3,17] Traditional modifiers include functionalized rubber such as carboxyl terminated butadiene–acrylonitrile copoly-

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mers (CTBN). When CTBN modifiers are incorporated into resin compositions, a two-phase morphology consisting of relatively small ($\sim$ 0.1–5 μm) rubber particles dispersed in a resin matrix is generated that toughens epoxy resins.[18–21] However, phase separation depends upon the formulation, processing, and curing conditions.[22–26] Incomplete phase separation can result in a significant lowering of the glass transition temperature (T_g). Moreover, the rubber phase that separates during cure is difficult to control and may result in uneven particle size. The differences in the morphology and volume of the separated phase affect the mechanical performance of the product. To minimize these problems, the preformation of a stable dispersion of rubbery particles in the uncured epoxy resin via *in situ* polymerization of acrylate monomers in the epoxy resin was investigated.

EXPERIMENTAL

Materials

All reagents and solvents were reagent grade or were purified by standard methods before use. The control epoxy resin was *o*-cresol–formaldehyde novolac epoxy resin (CNE) (Quatrex 3330, Dow Chemical Co., epoxy equivalent weight [EEW] 192). 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 acrylate monomers were purchased from Aldrich Chemical Co. and consisted of methacrylic acid (MAA), ethyl acrylate (EA), *n*-butyl acrylate (*n*-BA), isoamyl acrylate (iso-AA), and 2-ethyl hexyl acrylate (2-EHA). Glycidyl methacrylate (GMA) was used as a compatibilizer and cross-linker for the elastomer. The CTBN rubber used was Hycar 1300 × 8 (Goodrich): It has an 18% acrylonitrile content with a number-average molecular weight around 3600. The A-1 catalyst was (ethyl)triphenylphosphonium acetate acetic acid complex, Ph_3P was triphenylphosphine that was used as curing accelerator, and *t*-butyl peroxy-2-ethyl hexanoate and 1,1-bis-(*t*-butyl peroxy)-3,3,5-trimethylcyclohexane were used as free radical initiators.

General Procedure for the Preparation of Acrylate Rubber-modified Epoxy Resin

To a four-neck round-bottom flask, equipped with a heating mantle, stirrer, reflux condenser, thermocouple, and temperature controller were added 384 g of *o*-cresol–formaldehyde novolac epoxy resin (CNE). The epoxy resin was heated to 120°C and dehydrated under vacuum (< 10 mmHg) until the water content was less than 0.01% (measured by Karl Fischer). The mixture of methacrylic acid (MAA, 2.4 g) and A-1 catalyst (0.4 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 MAA addition, the reaction temperature was maintained at 120°C for an additional 1.5 h. Completion of the reaction was confirmed by GC for the disappearance of the reactant, MAA, in the reaction mixture. The resultant epoxy resin thus had a radically polymerizable double bond in the molecule. Under a nitrogen atmosphere, a mixture consisting of alkyl acrylate monomers (40 g), GMA (2 g), and free-radical initiator (0.8 g) was then added dropwise over a 4 h period via a metering pump while maintaining the reaction temperature at 120°C. Upon completion of the alkyl acrylate monomer addition, the reaction temperature was held at 120°C for an additional 3 h. The reaction mixture was then heated at 150°C under a full vacuum for 30 min to remove unreacted monomers and decompose the radical initiator. The resulting epoxy novolac contained ca. 10 wt % dispersed acrylate rubber and had an EEW of ca. 225.

Curing Procedure of Epoxy Resins

Various acrylate rubber-modified 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 mold at temperature of 150°C and 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.

Measurement and Testing

Epoxy equivalent weight (EEW) of rubber-modified epoxy resin was determined by the $HClO_4$/potentiometric titration method. Dynamic viscoelastic properties were performed on a Rheometrics RDS-2 rheometer between −130 and 250°C, with a ramp rate of 5°C/step at a frequency of 1 Hz. The rectangular torsion mode was chosen and the dimensions of the specimens was 51(L) × 12.7(W) × 0.76(T) mm^3. The storage modulus G' and tan δ were determined. The peak of tan δ was identified as the glass transition temperature (T_g) because a large decrease in G' occurred at this point. Mechan-

ical 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. The thermal expansion was proportional to the temperature and the CTEs were calculated from the slope. The thermal shock cycling test was carried out by the following procedure[27,28]: The device used was a 14-pin LM 324 quad operational amplifier with a single passivation layer. The device was encapsulated with an encapsulation formulation by a transfer molding process and then subjected to a thermal cycling test. A cycle consisted of −65°C × 15 min and 150°C × 15 min. The devices were inspected by an optical microscope for cracks after 250, 500, 750, 1000, 1500, 2000, 2500, 3000, 3500, 4000, and 4500 cycles. Any crack observed in the encapsulated device is counted as the failure of that device. The percentage of devices that failed (cracked), as a function of cycles, is plotted.

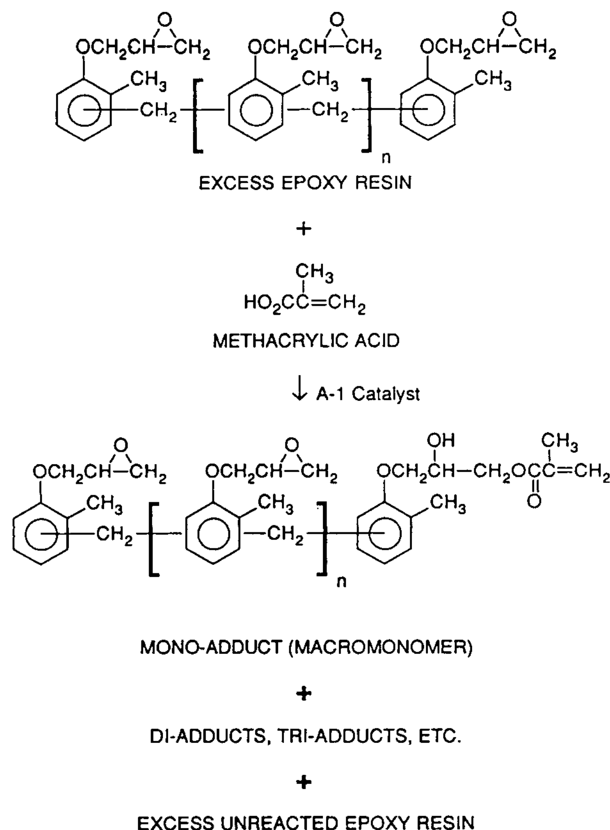

Figure 1 "Vinylization" of epoxy resin to form a macromonomer.

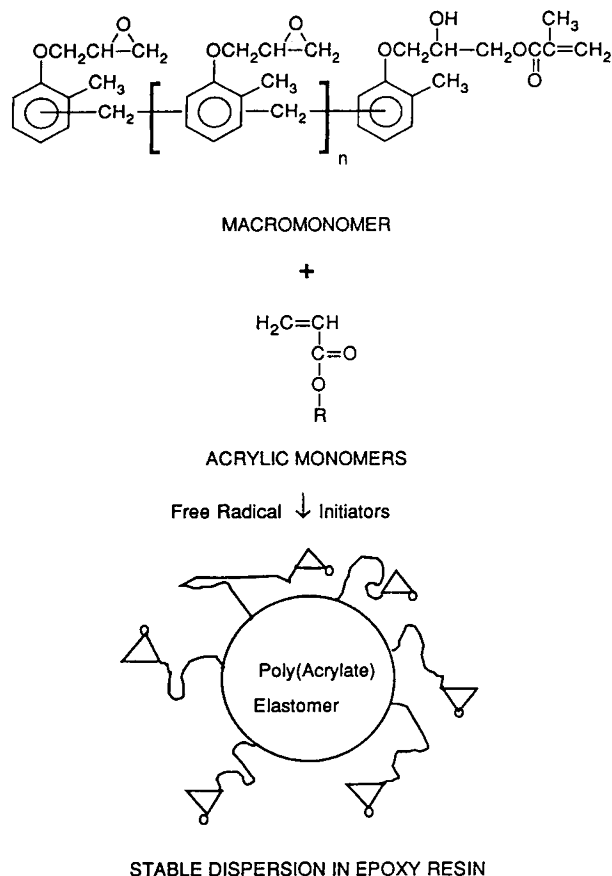

Figure 2 Vinyl *in situ* polymerization to form a dispersion.

RESULTS AND DISCUSSION

Dispersed acrylate rubbers in epoxy resins can be prepared in two steps: The first step involves the vinylization of part of the epoxy groups in the cresol–formaldehyde novolac epoxy resin (CNE) with methacrylic acid to form a reactive macromonomer as shown in Figure 1. The second step is the polymerization of the resultant macromonomer with various acrylate monomers in the presence of a radical polymerization initiator to form stable acrylate rubber particles dispersed in the matrix resin in a "sea-island" structure ("islands" of acrylate rubber dispersed in the "sea" of an epoxy resin as shown in Fig. 2).

Dynamic Viscoelastic Analysis of the Modified Resins

Dynamic viscoelastic analysis can give information on the microstructure of cured rubber-modified epoxy resins. The tan δ curves for the control epoxy

network exhibit the two major relaxations observed in most epoxy polymers[29]: A high-temperature or α transition corresponds to the major T_g of the cured epoxy resin above which significant chain motion takes place. The low temperature or β transition is attributed predominantly to the motion of the $CH_2-CH(OH)-CH_2-O$ (hydroxyether) group of the epoxy. Figure 3 shows the storage modulus G' and tan δ curves for the resins modified with various acrylate rubbers. The storage modulus decreased with modification. In addition, the α-relaxation peak in the tan δ curve shifted gradually toward lower temperature and became broader with a decreasing carbon number of the alkyl group of the acrylate monomer and several new relaxations appeared in the region ca. 0–100°C. However, the peak position and the magnitude of the α-relaxation peak in the tan δ curve for the resin modified with 2-EHA hardly changed with respect to the control resin. The broadness of the α-relaxation and the presence of new relaxations can be attributed to the formation of a matrix phase containing both the parent epoxy and the dissolved acrylate rubber in various amounts. The major T_g of the cured rubber-modified epoxy resins are shown in Table I and the 2-EHA-modified CNE has approximately the same T_g as that of the unmodified resin. It is concluded that the solubility between the epoxy resin and acrylate rubber depends greatly on the size of the alkyl group in the acrylate monomers. The solubility of acrylate rubbers in the epoxy resin increases when the alkyl ester group becomes smaller and this greater solubility has resulted in a depression of the glass transition temperature of the modified epoxy resin. The β-relaxation peak in the tan δ curves are about the same and no peak based on the added rubber was observed at ca. −65 to −40°C. These results can be explained in that the T_g's of the pure rubbers are around the β-relaxation peak of the epoxy resin. However, the β-relaxation peak for 2-EHA-modified CNE has broadened slightly, indicating a more complete phase separation of 2-EHA rubber particles from the matrix resin than in other acrylate rubber-modified systems.

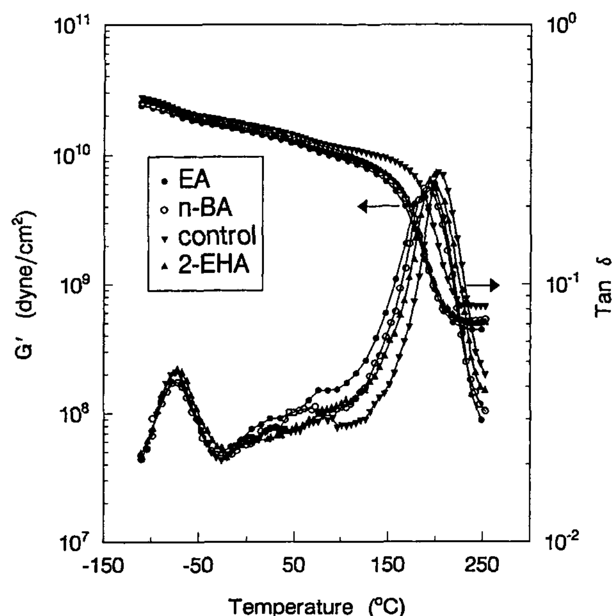

Figure 3 Dynamic viscoelastic analysis for various modified epoxy resins (no filler). The curing agent is phenol–formaldehyde novolac (HRJ-2210).

Table I T_g's of Various Cured Epoxy Resins

	Control[b]	EA	n-BA	2-EHA
T_g[a] (°C)	202	189	194	199

[a] Temperature at peak of tan δ.
[b] Control: unmodified CNE.

Encapsulation Formulation

A control resin and CNE modified with various acrylate rubbers or CTBN rubber were formulated into 6 electronic encapsulating formulations. The formulations were each cured at 175°C for 4 h. The encapsulating formulations are given in Table II.

Table II Typical Encapsulating Formulation

Ingredients	Weight (%)
Cresol epoxy novolac	17.5
Phenolic hardener (HRJ-2210)	9.1
Brominated epoxy resin	2.5
Fused silica (GP-71 Harbison-Walker)	68.5
Mold release (Hoechst Wax OP&E)	0.4
Carbon black	0.4
Silane coupling agent (DC Z-6040)	0.4
Antimony trioxide	1.0
Triphenylphosphine accelerator	0.2

Procedure
1. B-Stage melt mix at 95°C for approx. 7 min.
2. Cool and grind to a uniform powder.
3. Transfer molding of powder at 175°C for 90 s.
4. Postcure at 175°C for 4 h.

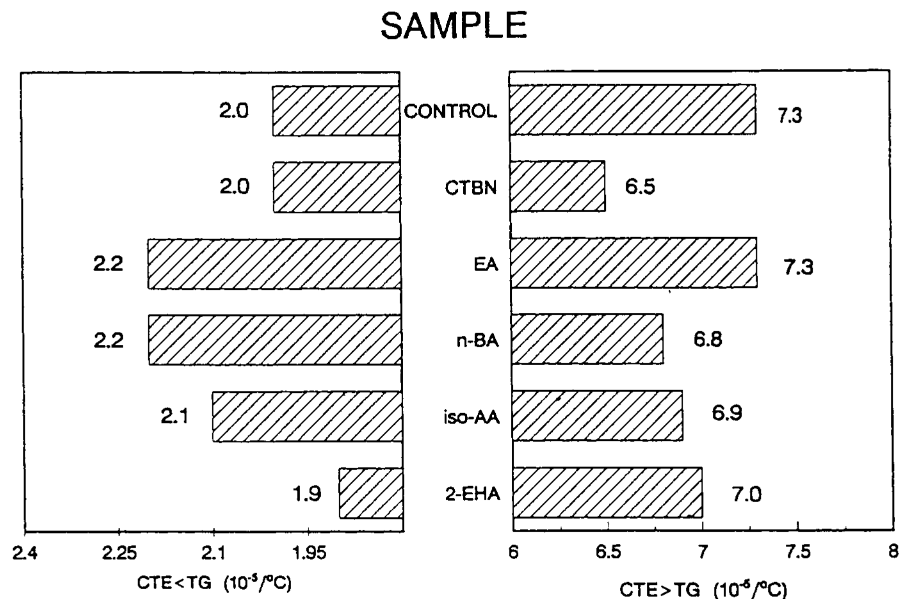

Figure 4 Coefficient of thermal expansion (CTE) for various rubber-modified epoxy resins.

The thermal mechanical properties of the cured encapsulating formulations were determined by the following tests:

Coefficient of Thermal Expansion (CTE)

Figure 4 shows the thermal mechanical properties. The CTE in the glassy state below the glass transition temperature (T_g) was taken from 60 to 100°C and the CTE above the T_g was taken from 200 to 240°C. For the CTE below the T_g, 2-EHA-modified CNE has a minimum value that will result in the least difference in CTEs between the encapsulant and silicon chip.

Glass Transition Temperature (T_g)

Glass transition temperatures (T_g) were determined from tangents of the CTE as a function of temperature at 100 and 200°C. The results are shown in Figure 5. The T_g of cured CNE is relatively unaffected by the modification with 2-EHA, but slightly depressed when modified with other acrylates with a small alkyl group. This result suggests that the 2-EHA rubber is not soluble in the epoxy matrix and remains phase-separated throughout the cure process. This observation is consistent with the viscoelastic investigation. This result is quite different from CTBN modification wherein an increase in toughness is accompanied by a decrease in the T_g, indicating an incomplete phase separation of CTBN rubber from matrix resin. This is in agreement with previous observations.[30,31]

Flexural Test Properties

Figure 6 shows the result of the flexural test. The flexural moduli of the cured resins were reduced markedly no matter whether modified with CTBN or various acrylate rubbers. However, the flexural strength remained equal to or larger than that of the control resin. The amount of reduction in the flexural modulus by the acrylate rubbers is dependent on the size of the alkyl group in the acrylate rubbers and is greatest with 2-EHA modification.

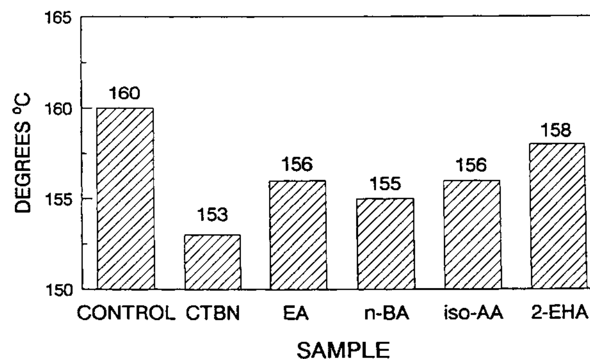

Figure 5 Glass transition temperature for various rubber-modified epoxy resins.

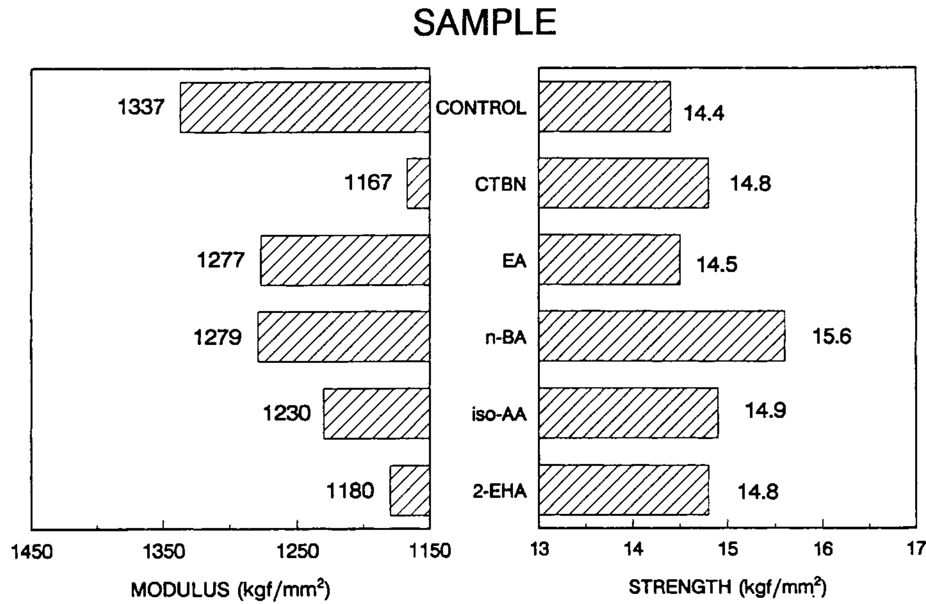

Figure 6 Flexural test properties for various rubber-modified epoxy resins.

From the test results of thermal mechanical properties, it is concluded that the solubility between the acrylate rubber and the matrix resin greatly affects the T_g, flexural modulus, and CTE of the cured resins. 2-EHA-modified CNE, which has a lower CTE and flexural modulus than those of CNE and has the same glass transition temperature as that of CNE, was chosen to encapsulate the semiconductor devices. The encapsulated devices were subjected to a thermal shock cycling test in comparison with the control resin.

Thermal Shock Cycling Test

The thermal shock cycling test involves cycling the encapsulated devices at −65 and 150°C and observing the crack (failure) of encapsulated devices at various intervals (after 250, 500, 750, 1000, 1500, 2000, 2500, 3000, 3500, 4000, and 4500 cycles). Any crack that occurred in a device is counted as failure for that device. The percentage of devices that failed vs. test cycles is given in Figure 7. The result indicates that for 50% of the devices failure happened after 3500 cycles for the 2-EHA-modified CNE compared to after 750 cycles for the control resin. 2-EHA-modified CNE has much better thermal shock resistance.

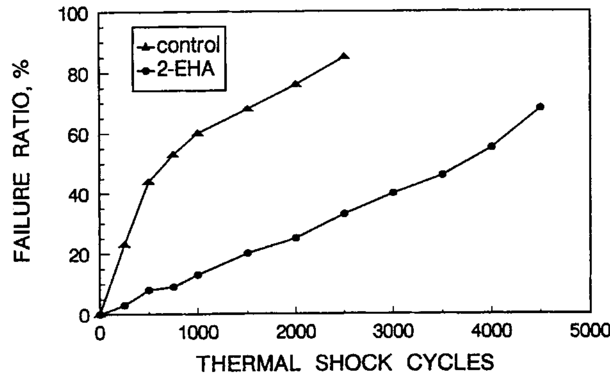

Figure 7 Thermal shock cycling test results. Temperature cycle: −65°C × 15 min and 150°C × 15 min.

CONCLUSION

A process was developed to incorporate stable dispersed acrylate rubber particles in an epoxy resin matrix that greatly improves the toughness of cured epoxy resins. Phase separation of the resultant acrylate elastomers from epoxy resin was greatly affected by the size of the alkyl groups on the acrylate monomer. 2-EHA is the best modifier for epoxy resins, which significantly reduces the flexural modulus and CTE while maintaining the T_g of cured epoxy resins. In electronic encapsulation applications, the encapsulant from 2-EHA-modified CNE has exhibited excellent thermal shock resistance and resulted in an extended device use life.

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