

A Reworkable Epoxy Resin for Isotropically Conductive Adhesive

Haiying Li and C. P. Wong, *Fellow, IEEE*

Abstract—Electrically conductive adhesive (ECA) is a promising alternative to the toxic eutectic tin-lead solder as an interconnect material. Typical ECAs use epoxy resin as their matrix, which has superior properties over other polymers, such as high adhesion, and low dielectric constant. However, once cured, it is not reworkable. In this study, a liquid diepoxide was designed and synthesized, and used in isotropically conductive adhesive (ICA) formulations. This diepoxide has a molecular structure able to thermally decompose at mild temperature that allows selective individual removal of the bad component without damaging the board and its surroundings. The characterizations including proton and carbon 13 nuclear magnetic resonance, infrared spectroscopy indicated the success of the synthesis. A dual-epoxy system containing this secondary diepoxide and an equivalent bisphenol-A diepoxide were formulated and cured with an anhydride hardener and an imidazole catalyst. Thermal analyses, such as differential scanning calorimetry, thermo-gravimetry analysis (TGA), thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA) were employed for the curing kinetics, thermal degradation behavior, glass transition temperature, coefficient of thermal expansion (CTE), and mechanical modulus, respectively. The dual-epoxy system showed two exothermal curing peaks at 140 °C and 180 °C, respectively. The thermoset of this dual-epoxy system has a decomposition temperature around 234 °C, a glass transition temperature around 80 to 90 °C, and CTEs of 74 ppm/°C and 225 ppm/°C below and above its T_g, respectively. The rework test on a surface mount component bonded to copper surface showed this ECA can be easily and quickly removed from the copper surface. The bulk resistance and contact resistance of ICAs were measured before and during an accelerated aging process in a temperature/humidity chamber (85 °C/85% RH). The ECA showed good bulk resistivity and contact resistance comparable to its control and a commercial ECA on gold and copper surface finishes.

Index Terms—Coefficient of thermal expansion (CTE), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), electrically conductive adhesive (ECA), FT-IR, isotropically conductive adhesive (ICA), nuclear magnetic resonance (NMR), thermo-gravimetry analysis (TGA), glass transition temperature (T_g), thermo-mechanical analysis (TMA).

I. INTRODUCTION

CURRENTLY, lead-containing solders for soldering and interconnect in electronic products will soon be banned from electronics industry in developed countries. Electrically conductive adhesive (ECA) is one of the promising alternatives to

eutectic tin-lead solder as an interconnect material [1]–[3]. Typical ECAs use epoxy resin as their matrix, which has superior properties over other polymers, such as high adhesion, low dielectric constant [4]–[7]. However, once cured, it is infusible and insoluble [6], [7]. Therefore, after the removal of an ECA bonded component, the ECA residue left on the board is very difficult to clean without damaging the underlying substrate. As a result, the failure of a single component on a board usually leads to the disposal of the entire board. This is very critical as the integration density of both the component and the board increases, especially for the high density and more expensive board assemblies [8]. One promising approach to overcome this problem is to make the polymer matrix reworkable. A reworkable material is the one that can be degraded under certain circumstances, typically by heat and solvents. However, study of reworkable ECA is rarely reported in literature [9]. In contrary, reworkable underfill materials have been extensively studied since the 1990s, because similar problem was encountered in flip-chip and ball grid array technologies where epoxy resin is also employed as the major polymer matrix for the underfill materials. Four types of reworkable underfill materials have been proposed: thermoplastics; thermosets that are solvent dissolvable or cleavable; thermally cleavable; and additive-aided thermally reworkable [8], [10].

Among these approaches, thermally cleavable epoxy resins not only provide a rapid and localized chip/component removal at an optimal temperature range around 250 °C, but also keep their unique properties of high adhesion and low dielectric constant. Several studies in this area have been reported [10]–[15]. However, most of these resins exhibited their degradation either above 250 °C or below 200 °C as compared to 230–250 °C, the optimal temperatures for safe rework operations [10], [15]. Ober *et al.* has reported the syntheses and thermal properties of several six-membered-cycloaliphatic diepoxides containing secondary or tertiary ester linkages [10], [15]. They demonstrated that these diepoxides decomposed between 200–300 °C as compared with 350 °C or higher, the degradation temperature of a primary ester diepoxide of the same type. The advantages of this approach are the proper decomposition temperature range, which provides a localized component rework and the unique low viscosity at ambient temperature. Besides, the cured epoxy resins that resulted usually showed high adhesion and high glass transition temperature. We have reported the syntheses and characterizations of two series of thermally reworkable epoxides, with one containing carbamate group and the other incorporating carbonate moiety, all based on aliphatic six membered rings. All but one epoxide showed decomposition temperatures in the range of 200 °C–300 °C [11]–[14].

Manuscript received May 15, 2003; revised January 9, 2004. This work was supported by the National Science Foundation under Grant DMI-0217910, by the NSF-funded Packaging Research Center, by the Georgia Institute of Technology, by Lindau Chemicals, and by Ferro Corporation.

The authors are with the Packaging Research Center, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245 USA (e-mail: cp.wong@mse.gatech.edu).

Digital Object Identifier 10.1109/TADVP.2004.824939

However, aliphatic based epoxy materials essentially showed lower performance than the aromatic based counterparts. Aliphatic esters are usually vulnerable to hydrolysis especially when water is present. From the electronic packaging point of view, the resistance to hydrolysis is critical for encapsulant materials since these materials have to pass several important environmental/reliability tests, such as 85 °C/85% relative humidity (RH) and pressure cooking, in which test samples are exposed to high moisture or water at elevated temperatures. On the other hands, advantages of aromatic based epoxy materials, e.g., bisphenol-A and/or F type systems include better dielectric, mechanical and thermo-mechanical properties, interfacial adhesion, fatigue life, and reliability. Besides, the aromatic carbonate linkage provides outstanding impact resistance, which has been known since the 1960s.

In order to obtain diepoxides with both enhanced reliability and decomposition temperatures around 250 °C, our molecular design was to incorporate conjugated moieties combined with secondary or tertiary vinyl alcohols, since aryl, vinylic and acetylenic, substrates are not reactive toward nucleophilic substitutions.

In this study, a new diepoxide containing bisphenol-A moiety and two secondary carbonate linkages was synthesized, and used in isotropically conductive adhesive (ICA) formulations. With this molecular structure, this diepoxide may provide good mechanical properties, low moisture up-take, and proper decomposition temperature that allows individually removal of the bad component without damaging the board and its surroundings.

II. EXPERIMENTAL

A. Chemicals and Materials

Unless otherwise noted, all glassware was oven-dried and all plastic syringes were used as received. All reactions and subsequent manipulations involving moisture-sensitive reagents were conducted under an atmosphere of purified nitrogen with Schlenk or syringe techniques. Reagents and solvents were purchased from either Aldrich or Fisher and used as received. Poly (Bisphenol-A-co-epichlorohydrin, glycidyl end-capped) (Average molecular weight about 377) was obtained from Aldrich Chemical Company, Inc. and hexahydro-4-methylphthalic anhydride (HHMPA) was obtained from Lindau Chemicals. 1-Cyanoethyl-2-ethyl-4-methylimidazole (EMZCN) was from Shikoku Chemicals. Two types of silver flakes, SF-26LV and SF52, with particle size of 1.5–5 and 0.8–2.0 μm , respectively, were supplied by Ferro (formerly Degussa) Corporation. All compounds and materials were used as received without further treatment.

B. Synthesis of Bisphenol-A-Bis [2-(6-Methyl-5-en) Heptyl] Carbonate (1a)

A 250-mL three-neck round-bottomed flask equipped with a stirring bar, a reflux condenser, a dropping funnel, and a nitrogen bubbler was charged with 5.13 g (40 mmol) of 6-methyl-5-hepten-2-ol, 10-mL of anhydrous pyridine, and 50-mL methylene chloride. The mixture was stirred and cooled to -10°C with ice bath while 7.06 g (20 mmol) of bisphenol-A

bis (chloroformate) dissolved in 50-mL methylene chloride was added dropwise from the dropping funnel. After stirring for 3 h at 0 °C, a white precipitate was formed. The resulting solution was then heated with an oil bath and refluxed at 60 °C for 12 h. After the mixture was cooled to room temperature, the white precipitate was filtered and the solution was poured slowly into 500-mL of water and washed with dilute HCl solution. About 50-mL of methylene chloride was added and the organic phase was separated and treated with sodium bicarbonate aqueous solution and finally dried with MgSO_4 . The solvent was removed under vacuum and the resulting liquid product was purified with chromatography on a silica gel column (4 \times 60 cm) with hexane/ethyl acetate in a ratio of 5:1 to give 9.27 g, 86.3% yield of **1a**, as a colorless liquid. ^1H NMR (δ in CDCl_3): 7.23 (dd, 2H, aromatic), 7.20 (dd, 2H, aromatic), 7.08 (dd, 2H, aromatic), 7.05 (dd, 2H, aromatic), 5.10 (t, 1H, 2HC = C), 4.83 (oct, 1H, 2-C-O), 2.09 (dd, 2H, 2CH₂ C =), 1.84–1.66 (m, 2H, CH₂), 1.69 (s, 6H, 2CH₃ C =), 1.66 (s, 6H, 2CH₃ C-phenyl), 1.61 (s, 6H, 2CH₃ C =), 1.36 (s, 3H, 2CH₃ -C-O, isomer 1), 1.34 (s, 3H, 2CH₃-C-O, isomer 2) ppm; ^{13}C NMR (δ , in CDCl_3): 153.43, 149.07, 147.90, 132.51, 127.82, 123.04, 122.98, 120.49, 76.03, 75.98, 42.45, 35.76, 30.89, 2725.68, 23.86, 19.81, 17.63 ppm; FT-IR (film): 3070, 3023, 2979, 2921, 2839, 1716, 1608, 1453, 1378, 1326, 1301, 1236, 1134, 1073, 941, 856, 728, 706, 655 cm^{-1} .

C. Synthesis of Bisphenol-A-Bis [2-(6-Methyl-5, 6-Epoxy) Heptyl] Carbonate (1b)

In a 1000-mL four-neck round bottomed flask equipped with a mechanical stirrer and two dropping funnels, 5.38 g (1 mmol) of **1a**, 50-mL of methylene chloride, 50-mL of acetone, 85-mL of phosphate buffer solution (pH 8.0) and 0.5 g (1.7 mmol) of 18-crown-6 ether were placed. The resulting mixture was vigorously stirred and the temperature was lowered to 0 °C. In one of the dropping funnels, 30.0 g (44 mmol) of OXONE[®] (monopersulfate compound, 2KHSO₅ KHSO₄ K₂ SO₄) and 0.06 g of EDTA dissolved in 120-mL DI water was charged and added dropwise to the stirred mixture. The pH of the mixture was kept at 7–8 by slowly dropping 0.5 M aqueous KOH solution from the other dropping funnel. The resulting mixture was stirred at 0 °C for 5 h or until its pH was stable around 7.0. The organic phase was then collected and the aqueous phase was extracted with methylene chloride. The organic portions were combined and washed with water and dried over anhydrous MgSO_4 . The solvent was then removed under vacuum to give 4.96 g, 92.2% yield of **1b**, as a viscous colorless liquid. ^1H NMR (δ in CDCl_3): 7.23 (dd, 1H, aromatic), 7.20 (dd, 2H, aromatic), 7.08 (dd, 1H, aromatic), 7.05 (dd, 2H, CCH₃), 4.88 (m, 2H, CHO), 2.74 (m, 2H, CHO), 1.98–1.60 (m, 12H, CH₂), 1.66 (s, 3H, 2CH₃, CH₃ C-phenyl), 1.39 (s, 3H, 1 CH₃), 1.37 (s, 3H, CH₃), 1.31 (s, 3H, CH₃), 1.28 (s, 3H, CH₃) ppm; ^{13}C NMR (δ , in CDCl_3): 153.37, 148.98, 147.95, 127.82, 120.44, 76.09, 75.57, 63.70, 64.00, 58.41, 42.45, 32.75, 32.45, 30.90, 25.09, 24.80, 24.50, 19.91, 19.73, 18.68 ppm; FT-IR (film): 2982, 2937, 1716, 1608, 1435, 1379, 1351, 1302, 1241, 1140, 1063, 931, 861, 794 731, 652 cm^{-1} . The epoxide equivalent weight (EEW) value of **1b** was determined to be 386 (theoretical 284; 73.5%).

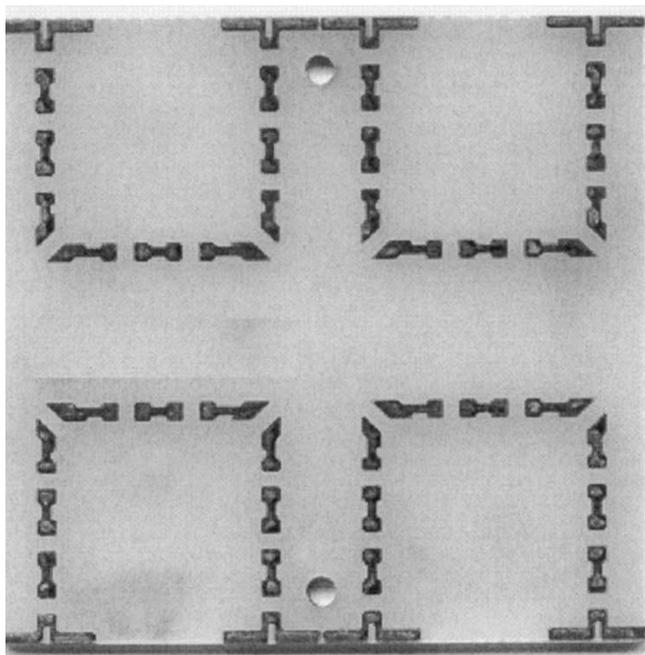


Fig. 1. Contact resistance test coupon.

D. Epoxide Equivalent Weight (EEW) Measurement

The EEW values of all epoxides were determined using the ASTM titration procedure D1652-90.

E. Formulations of Electrically Conductive Adhesives

The polymer matrix is based on an epoxy-anhydride (hardener)-organic base (catalyst) system. The epoxy used was either the synthesized diepoxide, **1b**, or a bisphenol-A epoxy resin (Aldrich Chemicals). An anhydride, hexahydro-4-methylphthalic anhydride (HHMPA, Lindau Chemicals) was used as the hardener, and 1-cyanoethyl-2-ethyl-4-methylimidazole (EMZCN, Shikoku Chemicals) was used as the catalyst. The conductive media employed was silver flake. Two types of silver flakes, SF-26LV and SF52 (Ferro, formerly Degussa Corporation) with particle size of 1.5–5 and 0.8–2.0 μm , respectively, were used.

F. Curing of Epoxides

The bulk matrix samples were cured at 120 °C for 30 min., at 150 °C for 60 min., and at 175 °C for another 30 min. ECA specimen and samples applied on test coupons were cured by ramping the temperature from room temperature to 175 °C in about 30 min. and staying at 175 °C for 60 min.

G. Test Coupons

The contact resistance test coupons were manufactured by Standley Circuits. The coupons all are 1.57 mm (0.062 in) thick FR4 boards with four loops etched on Cu clad. A schematic of the contact resistance test coupons is shown in Fig. 1. The coupons were plated or coated with one of three surface finishes: electroless Ni/immersion Au, Cu/organic solder preservative (OSP), and Tin. All coupons were cleaned with isopropanol and then ethanol, and dried under vacuum after plating or prior to use.

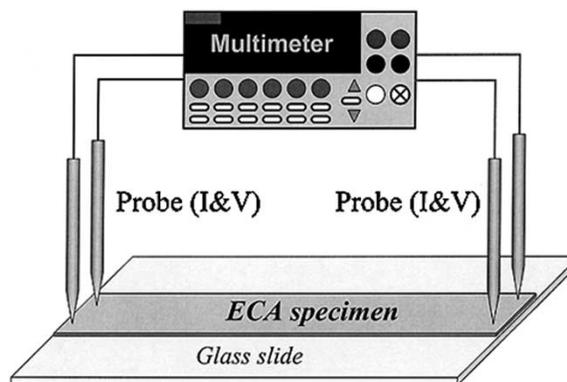


Fig. 2. Schematic of a bulk resistivity test coupon.

H. Equipment

To measure the bulk and contact resistance, a multimeter (Keithley 2000) was employed with four-point probe configuration for high accuracy. A profilometer (Sloan Dektak 3030) was used to measure the thickness of the rectangular film sample. A digital electrometer (Keithley 616) was used in the electrical potential measurement. The reliability test was conducted in an accelerated aging environment of 85 °C and 85% RH with a Lunaire environmental chamber (Model CEO932W-4).

I. Bulk Resistivity

The bulk resistivity was obtained on a rectangular film sample with a size about 78 mm (L) \times 6 mm (W) \times 0.5 mm (T). This sample was prepared by spreading uncured ECA on a glass slide and between two strips of Kapton tape or polyester tape applied on the glass slide using a blade. The sample was cured at 150 °C for 1 h in a convection oven and the tapes were peeled away afterward. A schematic of the bulk resistivity coupons is shown in Fig. 2.

J. Contact Resistance

The specimen for contact resistance test was prepared by stencil printing the uncured ECA paste on the test coupon to fill the gap between the neighboring copper traces and cover the trace ends. The stencil tool was custom made at Mini Micro Stencil, Inc. At least one coupon of each finish was used for each ECA formulation. After printing, the coupons were cured at 150 °C for 1 h in a convection oven. At room temperature, the total contact resistance of each loop was measured before and during aging periodically.

K. Spectroscopic Analyses

Infrared spectra were obtained as a thin film layer on a KBr pellet using a Nicolet Model 205 spectrometer. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Gemini Model 300 spectrometer.

L. Thermal Analyses

Modulated DSC was performed under nitrogen on a TA Instruments DSC (Model 2920) with a heating rate of 5 °C/min. Decomposition temperatures of the thermosets in nitrogen were determined using a TGA by TA Instruments (Model 2940) with

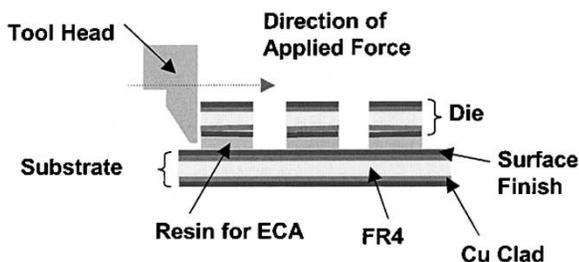


Fig. 3. Substrate shear test coupon configuration.

a heating rate of 10 °C/min. TMA was conducted on a TMA instrument by TA Instruments (Model 2940) and the sample was heated from 25 °C to 250 °C at a rate of 3 °C/min.

M. Substrate Shear Test and Sample Preparation

The modified substrate shear test coupons use 0.785 mm (0.031 in) thick FR4 boards with Cu clad laminated on both surfaces, which have been plated or coated with one of the surface finishes. Substrates of sizes 4 mm × 4 mm were used and the surfaces were cleaned prior to use according to the same procedure for test coupons for contact resistance. Nine smaller substrates were glued to a larger substrate with the formulated epoxides, and glass beads of 75 μm in diameter in the amount of 0.5 weight% were added to the formula to control the bond layer thickness. The amount of bonding layer applied under a small substrate was carefully controlled to avoid the formation of fillets. A schematic of the substrate shear coupon and test configuration are shown in Fig. 3. The bonding materials were then cured as described previously. The substrate shear test was performed using a die bond tester from Royce Instruments (Model 550-100 K) and the shear force observed was converted into shear strength by divided it over area of the corresponding small substrate. The area of each small substrate was measured with callipers.

N. Rework Test

A test vehicle was made of a plastic leaded chip carriers (PLCC 44) mounted on a piece of Cu clad laminated FR4 board with ECA to be tested. Rework test was conducted on a rework station by Summit (Model 1100HR).

III. RESULTS AND DISCUSSION

A. Synthesis

The synthesis of this new diepoxide using a modified method was achieved in two steps [14]. It started with commercially available 6-methyl-5-hepten-2-ol, and bisphenol-A bis (chloroformate), as illustrated in Fig. 4. The condensation of the secondary alcohol with the chloroformate in the presence of base gave a colorless liquid product, bisphenol-A-bis [2-(6-methyl-5-en) heptyl] carbonate (**1a**), in a high yield. The epoxidation of **1a** with OXONE®, a mixture of a monoperoxysulfate compound: 2KHSO₅·KHSO₄·K₂SO₄, in aqueous solution led to the formation of the corresponding diepoxide, Bisphenol-A-bis [2-(6-methyl-5, 6-epoxy) heptyl] carbonate (**1b**), a colorless liquid in a yield of 73.5% based on EEW

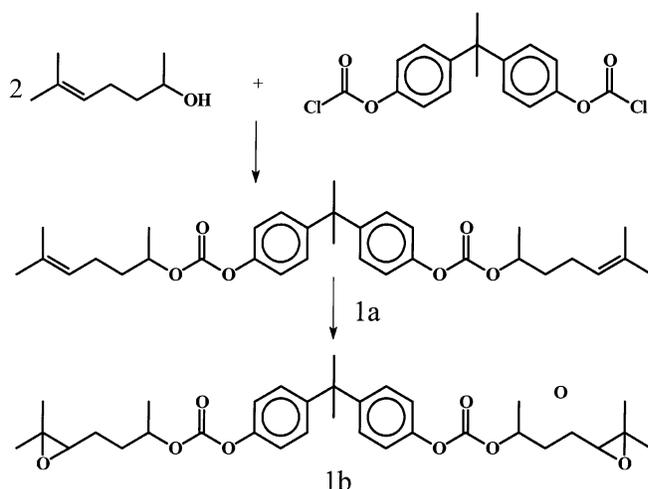


Fig. 4. Scheme of the synthesis of the diepoxide, **1b**.

value. The structures of both compounds were confirmed with ¹H and ¹³C NMR and FT-IR spectroscopies.

B. Formulation and Curing Reaction

Epoxy resins can be cured with amines, acids or anhydrides. In order to have a higher temperature curing system and avoid decomposition during curing, hexahydro-4-methyl-phthalic anhydride (HHMPA) and imidazole were selected as the hardener and the catalyst, respectively. Because **1b** has two weak carbonate linkages which may be hydrolyzed in the presence of acids or aminolysized by amines and lead to low crosslink density, **1b** mixed with HHMPA in a stoichiometric ratio based on the EEW value of the epoxides. However, the peak curing temperature of **1b** was found to be above 200 °C and at such high temperature the anhydride quickly evaporates before being incorporated into the polymer network. This is probably due to the steric hindrance of the two neighboring methyl groups of the epoxy carbons. One solution to this problem was to convert the anhydride into oligomer below its boiling point with a more active diepoxide. For this reason, a dual-epoxy system was prepared, in which a commercial bisphenol-A diepoxide was used together with **1b** and HHMPA in a molar ratio of 1:1:4, and imidazole was added as the catalyst. All were based on the EEW value of diepoxide (Table I).

The curing profile of this dual-epoxy system was determined with DSC as shown in Fig. 5. The two exothermic peaks centered at 147 °C, and 190 °C represent the exothermic curing reactions of bisphenol-A and **1b**, respectively.

C. Thermal Properties

Thermal stability of the cured dual-epoxy system was studied with TGA in a heating rate of 10 °C/min. (Fig. 6). From the TGA diagram it can be seen that this system started a fast weight loss at 234 °C. After about 50% of its weight was lost the weight loss slowed down until 380 °C, at which the weight drop accelerated again and all the remaining weight was lost around 400 °C.

The decomposition at lower temperature was probably caused by the thermal cleavage of the secondary carbonate linkage of **1b**, and the one at 380 °C may be due to the degradation of ester linkage formed between bisphenol-A and HHMPA which

TABLE I
ECA FORMULATIONS

| Compound | FW | Reworkable (mol.) | Control (mol.) |
|-------------------------|-------|-------------------|----------------|
| Diepoxide 1b | 568 | 0.5 | |
| Bisphenol-A epoxy resin | 377 | 0.5 | 1 |
| HHMPA | 168 | 2 | 2 |
| 2E4MZCN | 163.2 | 0.004 | 0.004 |
| Ag 52V | 107.9 | 40(wt%) | 40(wt%) |
| Ag26LV | 107.9 | 40(wt%) | 40(wt%) |

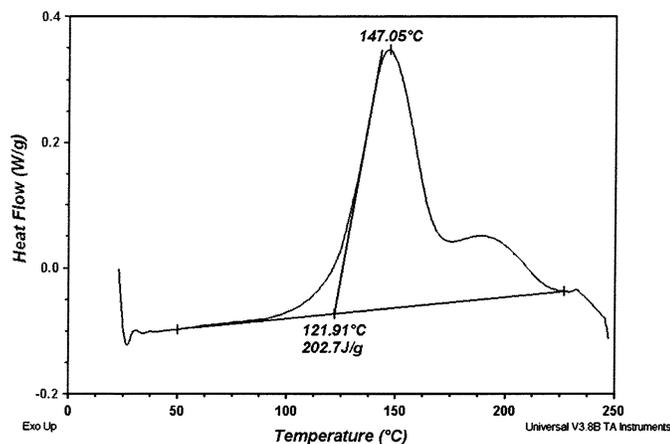


Fig. 5. DSC curing diagram of the dual-epoxy system.

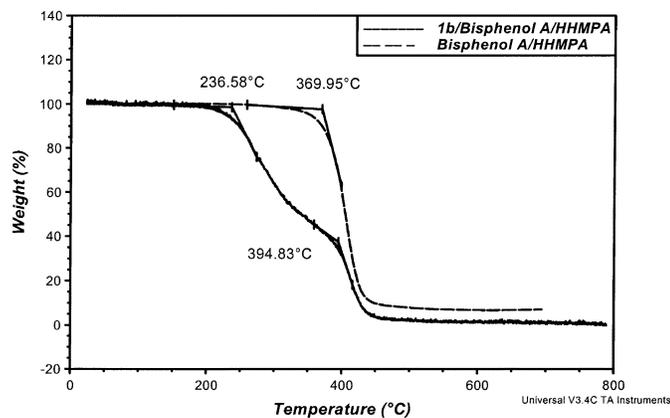


Fig. 6. TGA diagram of the dual-epoxy system and its control.

is believed to be the weakest bond after the breakdown of the secondary carbonate link. The comparison of TGA diagram of this system and the bisphenol-A-based control sample also indicates this is a reasonable assumption.

To study the degradation time at different temperatures, isothermal TGA was conducted at 200 °C, 225 °C, 250 °C, and 275 °C and the results are showed in Fig. 7.

Thermoset from control sample was stable at 250 °C, while at this temperature the cured dual-epoxy system lost 10 wt% in 6 min. At these test temperatures listed above, the time for the **1b** system to loss 10% of weight was 90, 24, 6, and 4 min, respectively. The suitable rework temperature and time that are safe to the board and surrounding components is believed around 250 °C for 5 min [12]. Therefore the thermal degradation property of this dual-epoxy system meets this requirement.

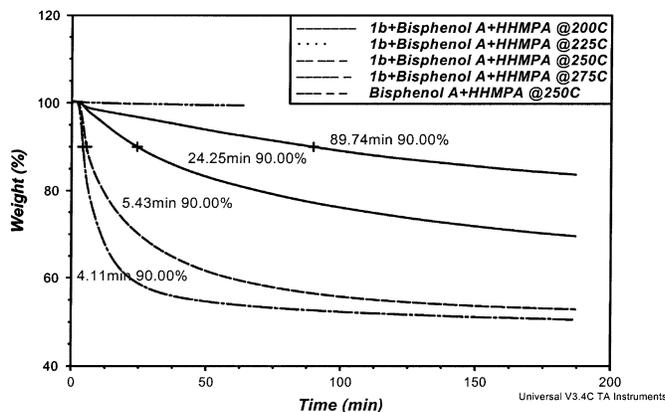


Fig. 7. Isothermal TGA diagrams of the dual-epoxy system at four different temperatures.

TABLE II
ACTIVATION ENERGY OF THERMAL DECOMPOSITION
CALCULATED FROM TGA KINETICS

| Sample | Activation Energy, E _a (kJ/mol) |
|------------------------------------|--|
| Bisphenol-A epoxy/HHMPA | 163.3 |
| 1b /Bisphenol-A epoxy/HHMPA | 72.0 |

Degradation kinetics of a polymer can be described as the relation between the conversion rate and the activation energy [10]

$$\ln R = \ln(d\alpha/dt) = F + \ln A - E/RT$$

where R is reaction rate, α is conversion, t is time, F is a constant, A is the pre-exponential factor, and E is activation energy. The activation energy of the thermal decomposition was derived from the TGA data using the equation above and listed in Table II. This average activation energy was obtained at low conversion, $\alpha = 0.01 - 0.10$, which is due to the initial decomposition of the weak linkages. The activation energy of **1b** system (secondary carbonate linkage) is lower than that of Bisphenol-A/HHMPA (primary ester linkage on HHMPA). These results are in good agreement with the onset decomposition temperatures.

The glass transition temperatures (T_g) of the cured resin from this dual-epoxy system were determined using TMA and DMA (Figs. 8 and 9). The T_g of this system was found to be 90 °C on the TMA diagram and 80 °C from the DMA diagram, while the corresponding data for the control were 137 °C and 149 °C, respectively. The coefficient of thermal expansion (CTE) data of the cured dual-epoxy system were also determined with TMA. The CTE were 74 ppm/°C below.

T_g and 225 ppm/°C above T_g, and those for the control were 69 ppm/°C and 194 ppm/°C, respectively. DMA diagram shown in Fig. 8 indicates that the dual-epoxy system has a comparable storage modulus as the control sample below its T_g.

D. Shear Strength From Substrate Shear Test

To measure the adhesion, small dies made from FR4 board were glued to a large FR4 substrate with this material, and

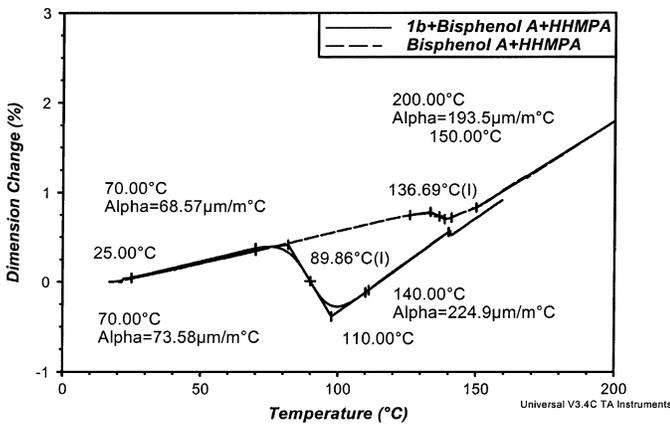


Fig. 8. TMA diagrams of the dual-epoxy system and its control.

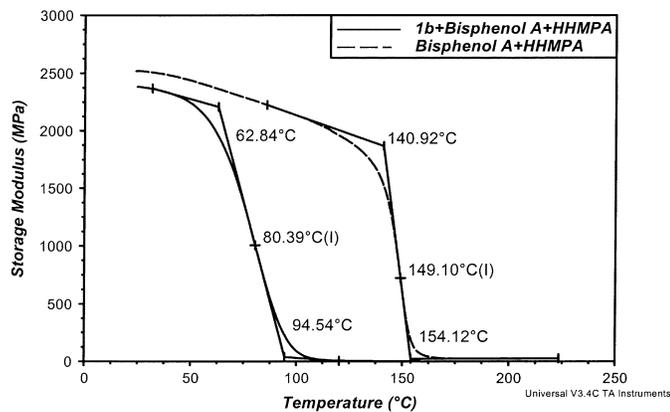


Fig. 9. DMA diagrams of the dual-epoxy system and its control.

after curing the shear strength of the material was measured. As shown in Fig. 10, the shear strength of this material was fair on gold surface finish but low in copper/OSP and tin surface finishes, as compared to the epoxy matrix reported in literature.

E. Component Rework Test

The reworkability of the dual-epoxy system was also characterized as an ECA for surface mount on board and went through a rework process on an industrial rework station. The process included chip removal and site cleaning. The test showed that after exposure to 250 °C (the temperature on the rework site) for 5 min., a component bonded with the dual-epoxy material containing 80 wt.% of silver flakes was easily removed, when a light twist force was applied. The site was quite easy to clean when the temperature was still high by scratching with a wooden applicator as shown in Fig. 11(b). The decomposed residue on the board was easily cleaned manually with a horse-hair-brush on an electrically driven tool. In Fig. 11(a) shows the a component mounted on a Cu laminated FR4 board, and Fig. 11(b) shows the site on the board after the component removal and the immediate site cleaning, and Fig. 11(c) shows the same site after final cleaning. It can be seen clearly in Fig. 11(c) that after cleaning the surface was essentially clean and without any damage, although slight silver color can still be seen on the site, which came from the very fine silver powder remaining on the site.

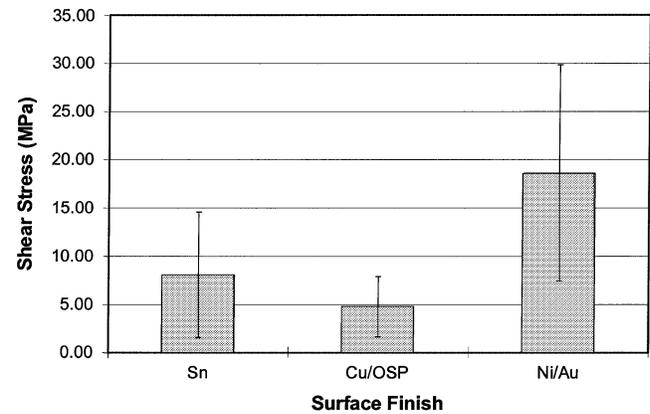


Fig. 10. Adhesion strength of the dual-epoxy system on three surface finishes.

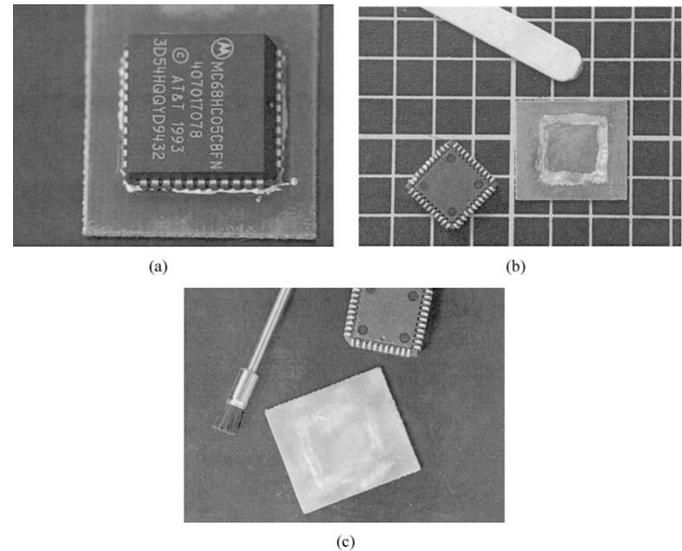


Fig. 11. Rework of surface-mounted component. (a) A component mounted on a Cu laminated FR4 board. (b) Site on board after component removal and immediate site cleaning. (c) Cleaned site.

F. Bulk Electrical Resistance

The bulk resistivity data of the ECA based on the dual-epoxy system, the control, and a commercial ECA are shown in Fig. 12. The addition of **1b** did not impair the electrical conductivity of the ECA as compared to the control sample. Fig. 12 also indicated that this ECA formulation is better than the commercial ECA in terms of its bulk electrical conductivity.

G. Contact Resistance

The tested contact resistance on this coupon is basically attributed to three parts: two bulk resistances in the ECA; and in the metal pads; and one contact resistance in the interface of metal pad. The resistance in the metal pads is negligible since the resistance of metal is comparably low.

Figs. 13–15 show the contact resistance change of the ECA on three different metal surfaces in the 85 °C/85% RH environment. On both gold and copper/OSP surfaces, the **1b** based ECA showed slightly better stability of contact resistance than the control, but a little bit lower than the commercial ECA. On the tin surface, all the three ECAs exhibited unstable resistance. This instability is common on nonnoble metal/alloy

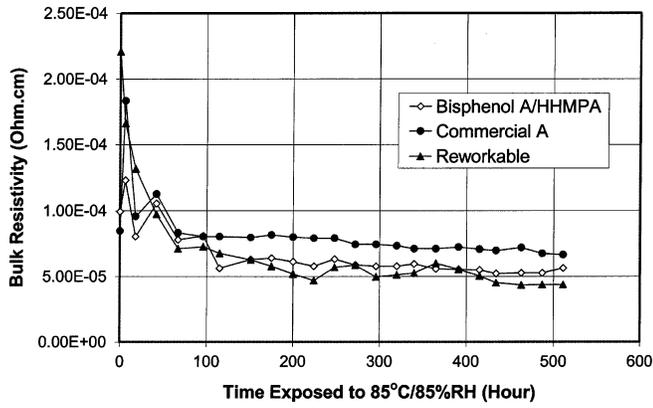


Fig. 12. Bulk resistivity of an ECA based on the dual-epoxy system, the control, and a commercial ECA.

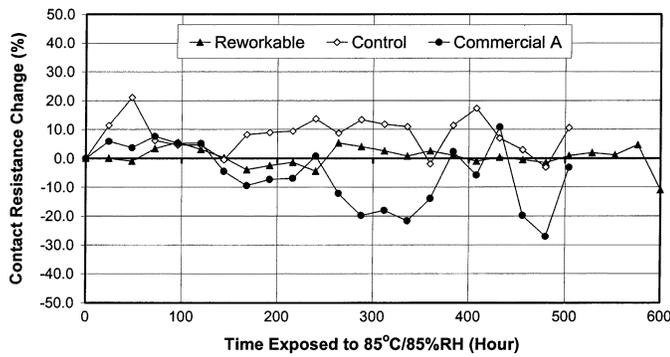


Fig. 13. Contact resistance change on Ni/Au surface.

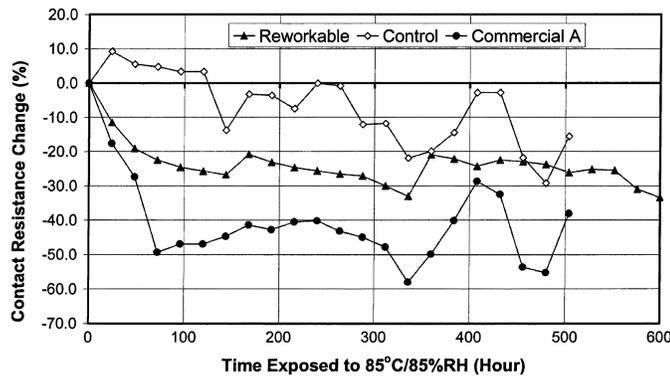


Fig. 14. Contact resistance change on Cu/OSP surface.

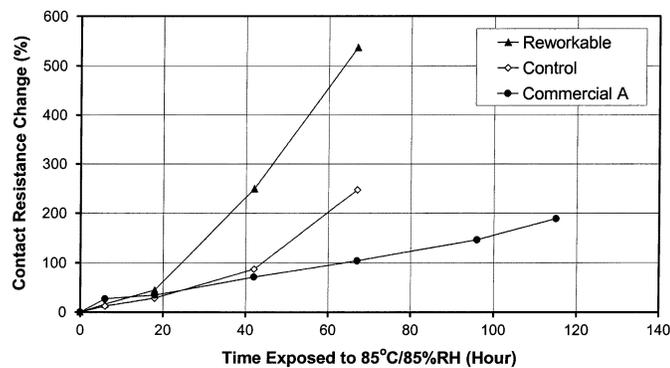


Fig. 15. Contact resistance change on tin surface.

surfaces and has been identified to be caused by Galvanic corrosion [16]–[18]. The stability of **1b** based ECA was comparable to its control and the commercial ECA in the first day of the test, however, as the time proceeded, the resistance increased faster than both the control and the commercial ECA. This early failure of contact resistance probably due to the high mobile ion content of the synthesized diepoxide, such as chloride and sulfate from the condensation and product treatment. It has been demonstrated that the contact resistance of ECAs on nonnoble surfaces can be effectively stabilized using oxygen scavenger or anode protection with sacrificial metal/alloys [17]–[21].

The decrease in both the bulk resistivity and the contact resistance during the 85 °C/85% RH environment test was due to the continued curing of the epoxy resins under the act of heat and moisture, which has been studied and reported in the literature [16], [17].

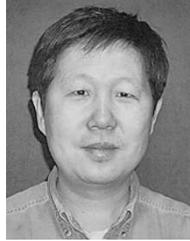
IV. CONCLUSION

A new diepoxide containing a bisphenol-A moiety and two secondary carbonate linkages was designed, synthesized and characterized with NMR and FT-IR spectroscopies. This diepoxide is a liquid at ambient temperature. A dual-epoxy system containing this secondary diepoxide and an equivalent bisphenol-A diepoxide were formulated and cured with an anhydride hardener and an imidazole catalyst. The curing properties of this diepoxide system was studied using DSC. Thermal properties of the cured resins of this diepoxide system were characterized with TGA, TMA, and DMA. The thermoset of this secondary diepoxide based dual-epoxy system showed a decomposition temperature around 240 °C, a glass transition temperature around 80 °C–90 °C, and a CTE of 74 ppm/°C below its T_g. The rework test on a surface mount component bonded to a copper surface showed this ECA can be easily and fast removed from copper surface. The reliabilities of bulk resistivity and contact resistance of the ECA on nickel/gold, copper/OSP, and tin surfaces with respect to 85 °C/85% RH aging were studied. The ECA showed good bulk resistivity and contact resistance that comparable to its control and a commercial ECA on gold and copper finishes, but poor on tin surface. In summary, the properties of the dual-epoxy system make it a promising reworkable ECA. The possible applications of this ECA could be rigid and flexible boards with Cu/OSP or Ni/Au surface finishes in a working temperature below 150 °C.

REFERENCES

- [1] K. Gilleo, "Introduction to conductive adhesive joining technology," in *Conductive Adhesives for Electronics Packaging*, J. Liu, Ed. London, U.K.: Electrochemical Publications, 1999.
- [2] J. E. Morris, "Conduction mechanisms and micro-structure development in isotropic electrically conductive adhesives," in *Conductive Adhesives for Electronics Packaging*, J. Liu, Ed. London, U.K.: Electrochemical Publications, 1999.
- [3] M. Zwolinski, J. Hickman, H. Rubon, and Y. Zaks, "Electrically conductive adhesives for surface mount solder replacement," in *Proc. 2nd Int. Conf. Adhesive Joining and Coating Technology and Electronics Manufacturing*, Stockholm, Sweden, June 3–5, 1996, pp. 333–340.
- [4] *Microelectronic Packaging Handbook*, pt. Part III, R. R. Tummala, E. J. Rymaszewski, and A. Klopfenstein, Eds., Chapman & Hall, New York, 1997.
- [5] J. H. Lau, *Chip on Board*. New York: Van Nostrand Reinhold, 1994, p. 504.

- [6] C. P. Wong, *Polymers for Electronic and Photonic Applications*, C. P. Wong, Ed. San Diego, CA: Academic, 1993, p. 195.
- [7] R. S. Bauer, *Polymers for Electronic and Photonic Applications*, C. P. Wong, Ed. San Diego, CA: Academic, 1993, p. 297.
- [8] Y. Tsukada, Y. Mashimoto, and N. Watanuki, "A novel chip replacement method for encapsulated flip-chip bonding," in *Proc. 43rd Electronic Components and Technology Conference*, 1999, p. 199.
- [9] S. Liang and C. P. Wong, "Development of thermoplastic isotropically conductive adhesive," in *Proc. 51st Electronic Components and Technology Conference*, Orlando, FL, May 2001, pp. 586–592.
- [10] S. Yang, J. Chen, H. Korner, T. Breiner, C. K. Ober, and M. D. Poliks, "Reworkable epoxies: Thermosets with thermally cleavable groups for controlled network breakdown," *Chem. Mater.*, vol. 10, pp. 1475–1482, 1998.
- [11] C. P. Wong and L. Wang, "Reworkable epoxy underfill encapsulants," U.S. Patent 617 214 1, Jan. 2001.
- [12] L. Wang and C. P. Wong, "Syntheses and characterizations of thermally degradable epoxy resins, I," *J. Polym. Sci., Part A: Polym. Chem.*, vol. 37, pp. 2991–3001, 1999.
- [13] L. Wang, H. Li, and C. P. Wong, "Syntheses and characterizations of thermally degradable epoxy resins, II," *J. Polym. Sci., Part A: Polym. Chem.*, vol. 38, pp. 3771–3782, 2000.
- [14] H. Li, L. Wang, K. Jacob, and C. P. Wong, "Syntheses and characterizations of thermally degradable epoxy resins, III," *J. Polym. Sci., Part A: Polym. Chem.*, vol. 40, pp. 1796–1807, 2002.
- [15] S. Yang, J. Chen, H. Korner, T. Breiner, C. K. Ober, and M. D. Poliks, "Design and characterization of a new reworkable epoxy using solvent free, thermally induced network breakdown," *Amer. Chem. Soc., Polymer Preprints, Div. Polymer Chem.*, vol. 38, no. 2, pp. 440–441, 1997.
- [16] D. Lu, C. P. Wong, and Q. K. Tong, "Mechanisms underlying the unstable contact resistance of conductive adhesives," *IEEE Trans. Comp., Packag., Manufact. Technol. C*, vol. 22, pp. 228–232, July 1999.
- [17] D. Lu, C. P. Wong, and Q. K. Tong, "Conductivity mechanisms of isotropic conductive adhesives," *IEEE Trans. Comp., Packag., Manufact. Technol. C*, vol. 22, pp. 223–227, July 1999.
- [18] D. A. Jones, *Principles and Prevention of Corrosion*, 2nd ed. Englewood Cliffs, NJ: Prentice-Hall, 1996.
- [19] H. Takezawa, T. Mitani, T. Kitae, H. Sogo, S. Kobayashi, and Y. Bessho, "Effects of zinc on the reliability of conductive adhesives," in *Proc. 8th Int. Advanced Packaging and Materials Symposium*, Stone Mountain, GA, Mar. 3–6, 2002, pp. 139–143.
- [20] C. P. Wong, H. Li, and K. Moon, "Electrical conductive adhesives for lead-free surface replacement with sacrificial anti-corrosion additives," U.S. patent pending, 2004.
- [21] H. Li, K. Moon, and C. P. Wong, "A novel approach to stabilize contact resistance of electrically conductive adhesives on lead-free alloy surfaces," *J. Electron. Mater.*, vol. 33, pp. 106–113, Feb. 2004.



Haiying Li received the B.S. degree in polymer science and engineering from the Beijing Institute of Chemical Technology, Beijing, China, in 1983, the M.S. degree in chemistry from Clark College, Atlanta, GA, in 1996, and the Ph.D. degree in polymer engineering from the Georgia Institute of Technology (Georgia Tech), Atlanta, in 2003.

After receiving the B.S. degree, he served as a Polymer Engineer in industry for ten years. He has authored or coauthored ten journal papers and over 30 proceedings articles. He is currently with the

Packaging Research Center, Georgia Tech.

Dr. Li received the Third Award of the Light Industry Ministry of China for Progress in Science and Technology in 1989 and 1991. He is a member of the American Chemical Society.



C. P. Wong (SM'87–F'92) received the B.S. degree in chemistry from Purdue University, West Lafayette, IN, and the Ph.D. degree in organic/inorganic chemistry from The Pennsylvania State University, University Park.

After his doctoral study, he was awarded two years as a Postdoctoral Scholar at Stanford University, Stanford, CA. He spent 19 years at AT&T Bell Laboratories. He is a Regents Professor with the School of Materials Science and Engineering and a Research Director at the NSF-funded Packaging Research Center, Georgia Institute of Technology (Georgia Tech), Atlanta. He holds over 40 U.S. patents, numerous international patents, has published over 400 technical papers and 300 key-notes and presentations in the related area. His research interests lie in the fields of polymeric materials, high T_c ceramics, materials reaction mechanism, IC encapsulation, in particular, hermetic equivalent plastic packaging, electronic manufacturing packaging processes, interfacial adhesions, PWB, SMT assembly, and components reliability.

Dr. Wong received the AT&T Bell Laboratories Distinguished Technical Staff Award in 1987, the AT&T Bell Labs Fellow Award in 1992, the IEEE Components, Packaging and Manufacturing Technology (CPMT) Society Outstanding and Best Paper Awards in 1990, 1991, 1994, 1996, and 1998, the IEEE Technical Activities Board Distinguished Award in 1994, the 1995 IEEE CPMT Society's Outstanding Sustained Technical Contribution Award, the 1999 Georgia Tech's Outstanding Faculty Research Program Development Award, the 1999 NSF-Packaging Research Center Faculty of the Year Award, the Georgia Tech Sigma Xi Faculty Best Research Paper Award, the University Press (London, UK) Award of Excellence, the IEEE Third Millennium Medal in 2000, the IEEE EAB Education Award in 2001 and was elected a member of the National Academy of Engineering in 2000. He is a Fellow of AIC and AT&T Bell Labs. He served as the Technical Vice President (1990 and 1991), the President (1992 and 1993) of the IEEE-CPMT Society, the IEEE TAB Management Committee (1993–1994), the Chair of the IEEE TAB Design and Manufacturing Committee (1994–1996), the IEEE Nomination and Appointment Committee (1998–1999), and the IEEE Fellows Committee (2001 to the present).