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THERMAL CHARACTERIZATION OF POLYMERIC MATERIALS USED IN SEMICONDUCTOR DIE BONDING*

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ABSTRACT

Several conductive and non-conductive epoxy systems recommended for use in microelectronic device bonding applications have been characterized by thermal analysis and spectrographic techniques. Data on such properties as degradation temperatures, weight changes as a function of temperature, coefficient of expansion, second-order transition temperature, shrinkage behavior, and peak exothermic reaction temperature of polymeric materials were determined to be important in order to optimize curing conditions for specific polymer applications. Thermal analysis has been successfully used in observing the shrinkage behavior of some conductive gold- and silver-filled epoxy resin systems and in understanding fluctuating contact resistance readings in ohmic die bonds using conductive epoxy systems.

INTRODUCTION

Several conductive and non-conductive filled epoxy systems were characterized for use in microelectronic die bonding. Our requirements included high thermal conductivity, low ionic content, low thermal coefficient of expansion, high degradation temperatures, and low shrinkage for conductive and non-conductive die bonding.

The use of thermal analysis techniques and emission spectroscopy to characterize polymeric materials offers a convenient means to the investigator in his selection and optimization for specific polymer applications, as it is sometimes necessary to use polymeric materials in construction of finished semiconductor electronic modules. Information concerning physical properties, chemical makeup, thermal characteristics, etc., is necessary to understand fully the material systems involved.

EXPERIMENTAL

All of the polymer specimens used for this investigation were formulated using commercially available materials. The samples consisted of filled non-conductive

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epoxy polymer systems and conductive epoxy systems filled with gold and silver. DTA, TMA, and TG analyses were the main thermal analysis methods used in this work.

Polymer specimens were cured at various temperatures as recommended by the commercial product data sheets. The samples were evaluated for coefficient of expansion before and after T_g. The T_g was recorded after the sample was cured and an effort made to increase the T_g to a higher temperature by post-curing.

The coefficient of expansion and second-order transition temperatures were measured simultaneously in the expansion mode. The temperature was programmed from 25 to 200°C at a heating rate of 5°C min^{-1}. Sample thickness varied depending on resin application.

RESULTS AND DISCUSSION

Epoxy A—filled non-conductive

The DTA thermogram of cured Epoxy A shows the degradation temperature to be just above 270°C. No degradation or rapid physical change was detected below this temperature. The sample was heated to approximately 350°C at 10°C min^{-1}. The decomposition temperatures shifted upward slightly after post cure.

The cured epoxy resin does change color over this temperature range. The resin

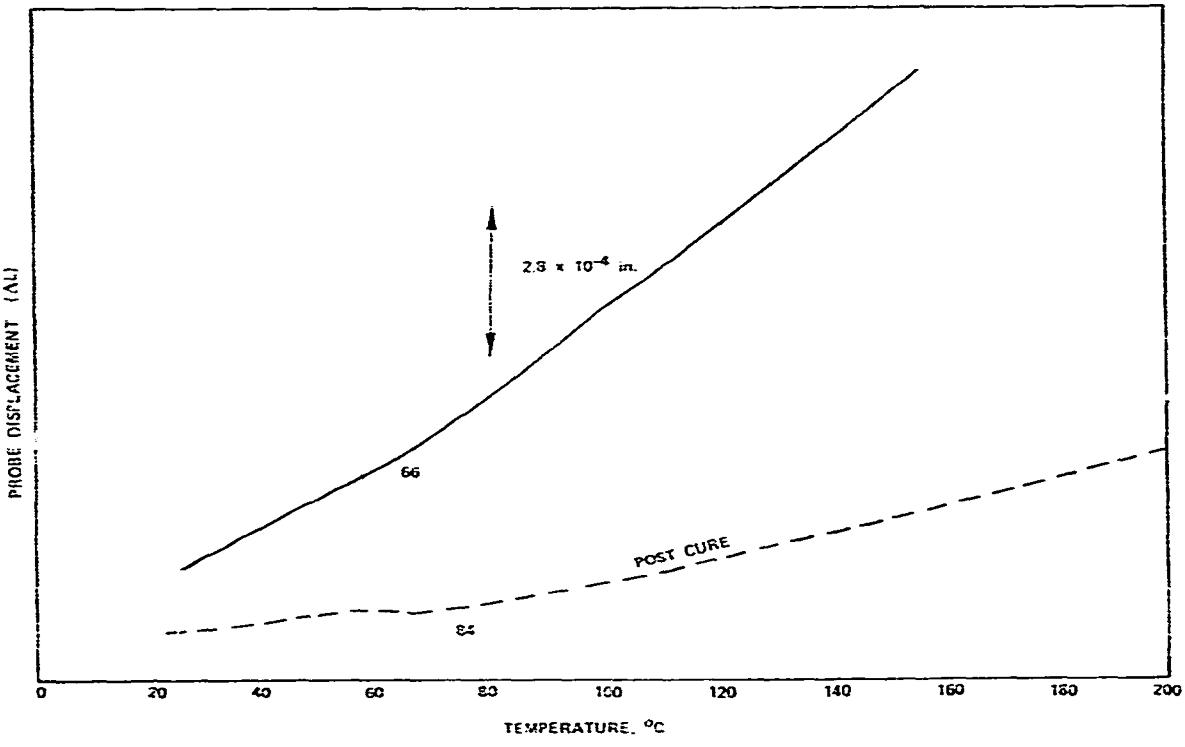

Fig. 1. Epoxy A TMA thermogram.

TABLE 1

THERMAL DATA

Materials A, B, C, D and F are non-conductive filled thermal epoxies; material E is a conductive filled epoxy preform. Materials C through E are one-mil glass cloth supported, tack-free, epoxy films.

Material name	*Cure cycle, °C*	*Coefficient of linear expansion (°C) 0–150°C*			*Decomposition temp. (°C)*		*% Filler*
		Before T_g	*After T_g*	*T_g (°C)*	*1°*	*2°*	
Epoxy A-Two Part	1 h, 120	1.6×10^{-4}	3.4×10^{-4}	66	270	385	74.4
	24 h post cure, 120	1.4×10^{-5}	10.4×10^{-5}	84	270	385	
Epoxy B-Two Part	1 h, 120	2.4×10^{-4}	7.4×10^{-4}	84	280	385	74.4
	24 h post cure, 120	1.0×10^{-4}	1.2×10^{-4}	86	310	385	
Resin							
Epoxy C-Preform	30 min, 150	11.6×10^{-4}	18.6×10^{-4}	108	385		38.6
	2 h, 150	9.7×10^{-4}	20.4×10^{-4}	109	385		
Epoxy D-Preform	30 min, 150	12.2×10^{-4}	20.5×10^{-4}	111	355		33.2
	2 h, 150	9.2×10^{-4}	20.5×10^{-4}	98	—		
Epoxy E-Preform	30 min, 150	13.5×10^{-4}	19.3×10^{-4}	116	380		73.0
	2 h, 150	11.0×10^{-4}	22.1×10^{-4}	109	—		

TABLE 2

EMISSION SPECTROGRAPHIC RESULTS

Materials A and B

50 ppm Ag, 500 ppm Cu, 10 ppm Ti, 50 ppm Sn,
10 ppm Al, 1000 ppm Ni, 10 000 ppm Mg, 100 ppm Ca,
10 000 ppm Si, 100 ppm Mn, 100 ppm B, no Na or K determined
Fillers suspected to be SiO_2, MgO, $CaCO_3$

Material C	*Material D*
Hi = Mg, Si, Al, Ca, Ti > 1%	Ca, Al, Si, Ti, Mg > 1%
0.05 = B, Cd	B, Pb
0.01 = Fe	Sn, Fe, Cu
0.001 = Pb, Cu	—
0.005 = Ag	Ag
0.0005 = Mn	Mn, Cr
0.025 = Na, K	0.05 = Na
	0.01 = K

Material E

Hi = Ag, Mg, Al, Si, Ca > 1%
0.05 = B
0.01 = Cu, Fe, Ti
0.001 = —
0.005 = —
0.0005 = Mn
0.08 = Na
0.01 = K
Note: Ag filled.

system is originally blue, and changes to green, and then to brown as the temperature increases. The color changes at the surface only. The core remains blue.

No gaseous products were detected to 150 °C, the approximate temperature at which the material turns brown. The gaseous decomposition products of a pyrolyzed sample were identified as CO, CO_2, H_2O, methane, and ethane.

From the thermal data on Table 1, the glass transition temperatures shifted upward approximately 20 °C and the coefficient of expansion was significantly lower before than after T_g on the post-cured resin, indicating a more completely cured resin. Optimized cure times are shown in Table 5.

Analysis of TG data, Table 1, showed that a rapid weight loss began at 270 °C, leveling off at 350 °C and starting again at 385 °C. This would indicate two decomposition reactions, occurring at 270 and 385 °C. This is most likely attributed to the modified epoxy, the additive decomposing at a different temperature than the epoxy. Emission spectroscopy data are shown in Table 2. From the cationic analysis, fillers are suspected to be silica and magnesium oxide.

Epoxy B—filled non-conductive

Epoxy B is very similar to Epoxy A with similar physical characteristics. The basic difference is in the use of a modified epoxy resin in Epoxy B, resulting in slightly better thermal properties.

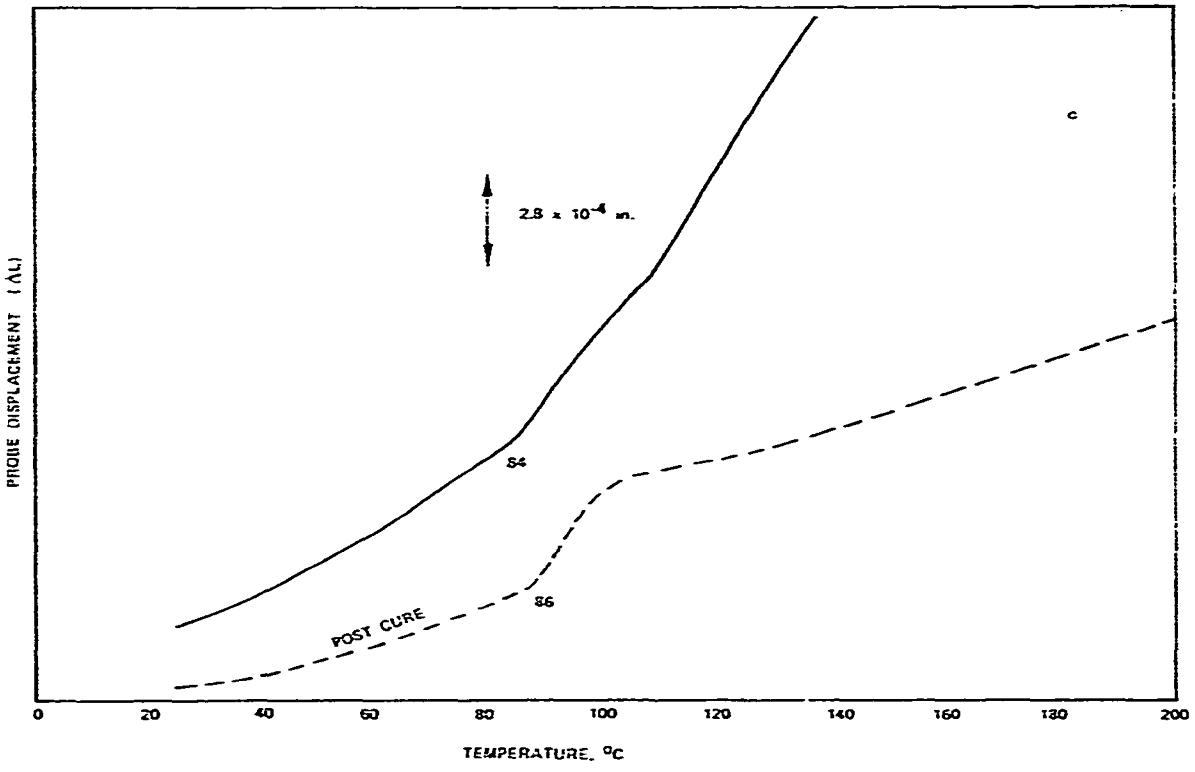

Fig. 2. Epoxy B TMA thermogram.

The TMA data in Table 1 show the glass transition temperatures shifted upward slightly, and the coefficient of expansion was significantly lower before and after T_g on the post-cured resin, indicating a more complete cure.

Analysis of TG (Table 2) data showed a rapid weight loss beginning at 280 °C, leveling off at 300 °C, and starting again at 385 °C. This indicates two decomposition reactions taking place in the same fashion as Epoxy A. DTA exothermic reaction temperatures correlate with TG data. Decomposition temperatures shifted higher on the post-cured sample, indicating a better cured resin for Epoxy B. Both resins A and B should be post-cured for optimum physical properties (Table 5) determined from thermal analysis.

Emission spectroscopy data are shown in Table 2. Note: 100 ppm of boron was found in Epoxies A and B, indicating that the resin systems may be BF_3 activated; which if present, could cause corrosion in some microelectronic systems, e.g., aluminum metallurgy.

Epoxies C, D, and E preforms

Conductive and non-conductive epoxy preform film adhesives potentially useful for semiconductor die bond operations were also evaluated. These adhesives are available commercially as prefrozen preforms, which contain a one mil glass cloth

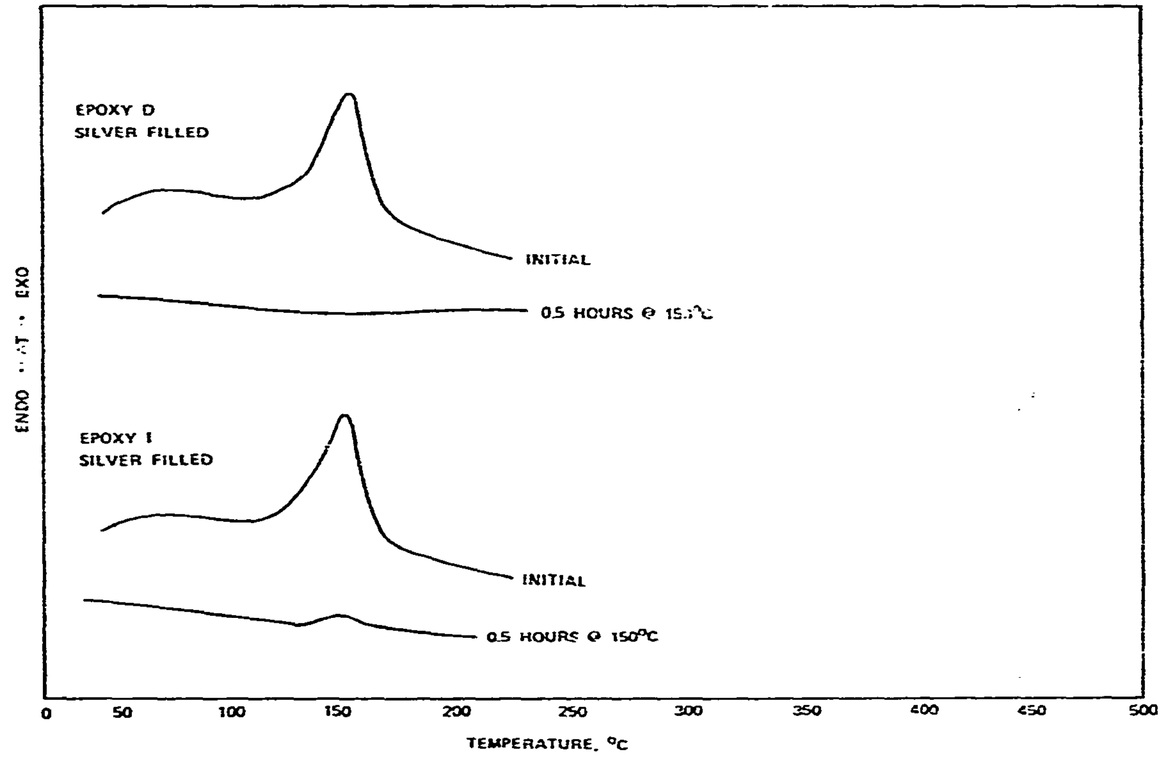

Fig. 3. DTA thermogram.

for support. After curing, the epoxy samples were characterized using DTA, TMA, TG and emission spectrographic techniques.

Epoxies C and D appeared completely cured after 30 min at 150 °C as indicated by the absence of any exothermic reaction from DTA (Fig. 3, Table 5).

Epoxy E, thermally conductive preform, showed a slight exothermic reaction after 30 min at 150°C, indicating a less complete cure. The sample appeared to be completely cured after 2 h at 105°C (Fig. 3, Table 5).

DTA, TG, and TMA data would suggest Epoxy C to be the most suitable candidate of the three resins. Thermal data can be found in Table 1.

Emission spectroscopy data for Epoxies C, D, and E are shown in Table 2. From this analysis, fillers for samples C and D appear to be a mixture of one or more of the following—alumina, calcium carbonate, magnesium oxide, silica, and titanium oxide. Epoxy E is a silver-filled film adhesive. (Note: 500 ppm of boron was found in Epoxies C, D, and E, indicating that the resin systems may be BF_3 activated; which, if present, could cause corrosion in some microelectronic systems, e.g., aluminum metallurgy.)

Epoxies F, G, H, and I—conductive paste epoxy adhesives

Electrically conductive Epoxies F, G, H, and I displayed an expansion-shrinkage phenomenon which made it difficult to measure the coefficient of expansion

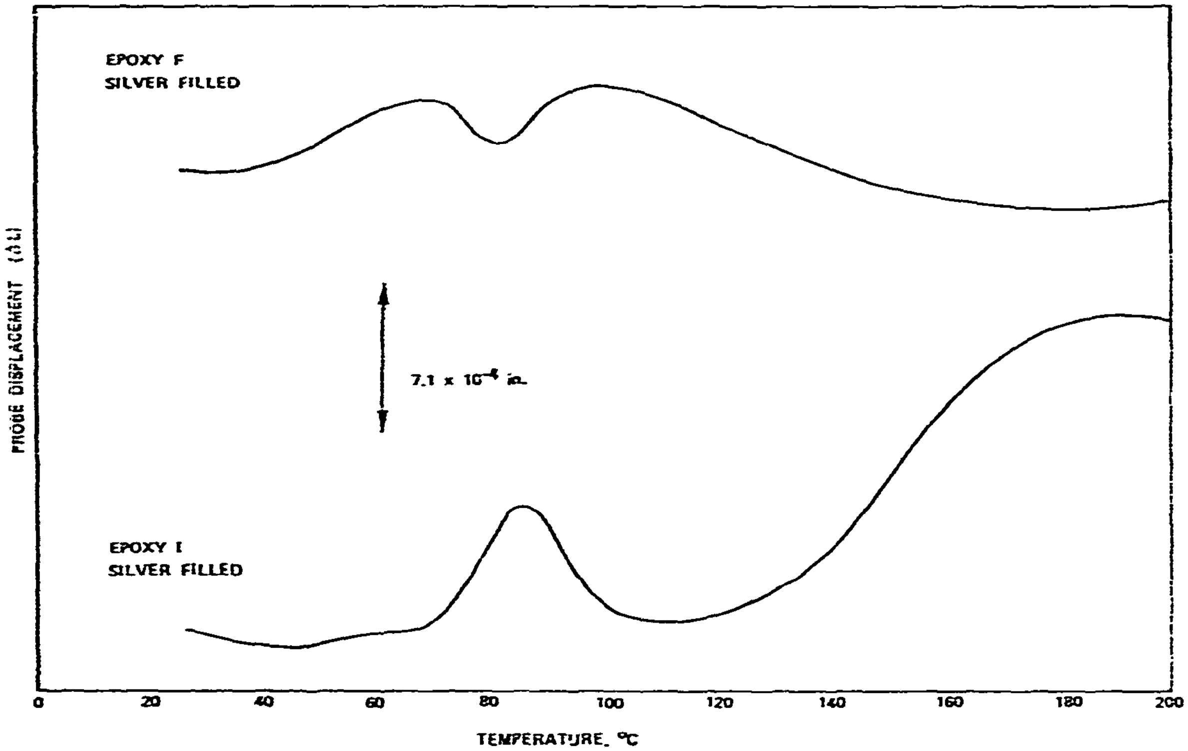

Fig. 4. TMA thermogram.

or determine a valid T_g. Coefficients of linear expansion were not measured on the conductive epoxies because of the alternating expansion–contraction phenomenon, displayed in Fig. 4, Table 2 and Table 4.

Expansion–contraction phenomenon is less evident in Epoxies G and H. Post-cure seemed to have very little effect on the expansion–contraction phenomenon of the conductive epoxies. Second-order transitions shifted positively as a direct function of time and temperature during the various cure cycles. Epoxy G had no significant exothermic reaction after 30 min at 100°C. This was compared with an uncured sample.

The degree of cure had no effect on degradation temperatures (Tables 3 and 4). No system had any appreciable weight loss prior to degradation temperature (Tables 3 and 4).

(Note: Cure data furnished in the literature do not always represent the polymer's true performance for a specific application. As a result of the thermal analysis; e.g., T_g and peak exotherm temperature, optimum cure times were developed

TABLE 3

THERMAL DATA

Material	*Cure cycle, °C*	*Second-order transition temp. T_g (°C)*	*Degradation temp. (°C)*	*Wt. loss prior to degradation temp. % Wt./Wt.*	*Wt. % Filler*
F	0.5 h, 150	39, 60, 70, 166	280	0.10	Not determined
	0.75 h, 150	45, 62, 79, 130	285	0.10	
	1.0 h, 150	66, 80, 95, 108	285	0.10	
	5.0 h, 150	65, 78, 105, 172	286	0.10	
	24.0 h, 150	70, 110, 139, 172	—	—	
	24.0 h, 100	54, 80, 113, 136	—	—	
G	0.5 h, 100	167, 180, 255	280	0.10	90.3
	1.0 h, 125	167, 180, 255	—	—	
	1.0 h, 150	253	—	—	
	5.0 h, 150	260	—	—	
H	0.25 h, 150	43, 56, 100	282	0.10	Not determined
	0.5 h, 150	53, 80, 106	—	—	
	0.75 h, 150	52, 106, 180	—	—	
	1.0 h, 150	50, 116, 170	—	—	
Note: Epoxies F, G and H are one-component filled conductive epoxy adhesives.					
I	0.5 h, 150	77, 187	280	0.10	66.5
Two	1.0 h, 150	58, 189	280	0.10	
Part	1.5 h, 150	94, 188	280	0.10	
Adhesive	2.0 h, 150	94, 181	280	0.10	
	3.0 h, 150	92, 184	280	0.10	
	5.0 h, 150	99, 180	280	0.10	
	24.0 h, 150	101, 181	280	—	
	2.0 h, 100	62, 147	—	—	
	24.0 h, 100	63, 146	—	—	

TABLE 4

EMISSION SPECTROGRAPHIC RESULTS—
PERCENT COMPOSITION ON CURED RESIN

Material	*10*	*1–10*	*0.01–0.1*	*0.01*
F	Ag		B, Si, Fe	Cu, Al, Pg, Mg, Au
G	Au		0.01 = Sn, Al, Mg Si, B; [0.05 = Ag]	0.005 = Pd 0.001 = Cu, Pb, Fe
H	Au		0.01 = Sn, Al, Mg Si, B; [0.05 = Ag]	0.005 = Pd, Pb, Cu, Fe
I	Ag		0.01 = Pb, Fe, Si; [0.05 = Au]	0.005 = Cu, Mg 0.001 = Pd, Al, Ca

TABLE 5

OPTIMIZED CURE TIMES

Material Part A & hardener	*Mix-ratio (A to hardener): parts by weight*	*Curing cycle (temp./time)*
A, B	10:1	(A) 250°F, 3/4 h
		(B) 200°F, 1.5 h
—		(C) 165°F, 4 h
		(D) 140°F, 24 h
C, D, E	Single Part	(A) 165°F, 3 h
		(B) 200°F, 2 h
		(C) 250°F, 1 h
		(D) 300°F, 0.5 h
F	Single Part A	(A) 120°C, 5 h
		(B) 150°C, 1 h
G	Single Part	(A) 150°C, 1 h
H	Single Part	(A) 150°C, 1 h
I	15:1	(A) 150°C, 1.5 h

and are shown in Table 5. Extension of time at the optimized temperatures should improve bonding properties.)

Emission spectroscopy data for Epoxies F, G, H, and I are shown in Table 4. Epoxies F and I are silver-filled, whereas Epoxies G and H are gold-filled. Note: substantial boron levels of up to 1,000 ppm maximum were found in the one-component conductive epoxies, Epoxies F, G, and H. The resins are suspected of using the following catalytic reaction for BF_3 activated epoxies:

a. $BF_3 + MEA$ (monoethylamine—or like amine) $\longrightarrow$ BF_3MEA salt[1]

Further reactions of BF_3MEA complex are[1]:

b. $BF_3MEA \xrightarrow[90\,°C]{}$ dissociation:

c. $BF_3MEA \xrightarrow[130\,°C]{} BF_3$ evaporated out of system:

Reactions of BF_3 (Lewis acid)[2]:

d. $4BF_3+6H_2O \longrightarrow 3H_3O^+ + 3BF_4^- + B(OH)_3$:

$BF_4^- + H_2O \longrightarrow [BF_3OH]^- + HF, k = 2.3 \times 10^{-3}$:

BF_4^-, fluoboric acid ion is very reactive.

Suspected reaction of BF_3MEA complex[3]:

e. $BF_3 + MEA \xrightarrow[180\,^\circ C]{} HF + BF_3$ gas:

Note: BF_3 gas is corrosive, as is BF_4^- ion, and HF will corrode aluminum conductors.

Current density

Conductive adhesives are usually filled with Ag or Au flake or powder and are commonly used for ohmic die bonds. Limited data presently exist regarding maximum current density levels for this type of device application. The most severe problem we experienced in the use of conductive epoxies for ohmic die bonds was fluctuating device contact resistance in microelectronic packages.

This has been thought to be due to the current-carrying capability of metal-filled thermosets[4].

Conduction through a metal-filled thermoset is based upon a complex series of parallel paths made up of many metal–metal construction sites. Any process that extends the polymer network and reduces the number of metal contacts will degrade the material conductivity. High current densities cause the polymer to thermally heat with a corresponding increase in material resistivity due to volume expansion and contact breaking followed by resistivity decreases above the polymer T_g. Current densities of 300 to 400 A in.$^{-2}$ will generally cause the problems described, whereas 100 A in.$^{-2}$ could cause intermittent problems. Non-uniform die bond areas will also cause high current densities. Non-uniform areas could be either device- or package-related[4].

Devices operating at 88 A in.$^{-2}$ using conductive epoxies for the ohmic die bond experienced only a few problems thought to relate to Item 1 above. However, in those cases of fluctuating contact resistances and intermittent device operation, failure analysis showed non-uniform backside device metallization. Therefore, it is believed that a large percentage of the current passed through the metallization "nodes", severely stressing the conductive epoxy die bond, causing it to experience current densities in excess of 175 A in.$^{-2}$. This results in thermal heating causing the expansion–contraction phenomenon described previously in Item 2.

CONCLUSIONS

Conductive and non-conductive epoxy systems recommended for die bonding of microelectronic devices were characterized by spectrographic analysis and analytical techniques. This investigation was useful in developing information to aid in the selection of materials for device-bonding applications.

Possible evidence of BF_3 activation was found in all epoxy systems investigated except Epoxy I. Boron levels of 100 to 1,000 ppm were determined by emission spectroscopy. BF_3, if indeed present, could cause corrosion in some microelectronic systems, especially in accelerated high-temperature, high-humidity environments. Certainly the use of one- or two-component epoxy systems, which do not contain fluoride, e.g., BF_3 activated, for microelectronic die bonding is warranted. (Much higher levels of boron would be present in the resin systems studied if boron, e.g., BN, was used as a filler material. SEM and OJ auger analysis for fluorine was not available at the time this work was under investigation.)

Fluctuating contact resistance in ohmic die bonds had been experienced in microelectronic packages and was felt to be primarily due to thermal heating of the polymer, with resultant expansion–contraction causing intermittent device operation.

Thermal analysis was used to provide data on such properties as degradation temperature, weight changes as a function of temperature, shrinkage behavior and peak exothermic reaction temperature of polymeric materials to optimize polymer cure conditions for specific polymer applications. Thermal analysis was also successfully used in observing the shrinkage behavior of some conductive gold- and silver-filled epoxy resin systems.

Thermal analysis techniques are being used for quality control purposes. Accurate determination of such properties as coefficient of expansion, glass transition temperature(s), decomposition temperatures, and percent filler are necessary to accurately control the quality and identity of incoming materials, e.g., polymers, filled polymer systems, metals, etc.

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GLOSSARY

α	TCE—Linear Thermal Coefficient of Expansion
DTA	Differential Thermal Analysis—the measurement of a temperature difference between a specimen and a thermally inert reference, continuously recorded as a function of furnace temperature. The process measures changes in heat content of the sample. Parameters that can be measured are fusion, crystallization, vaporization, condensation, decomposition, dehydration, T_g (ref. 5).
TMA	Thermal Mechanical Analysis—the measurement of the change of linear

	displacement divided by length vs. temperature = $\Delta L/L$ vs. T. A weighted probe is placed on a sample, the sample being heated at a programmed rate, with $\Delta L/L$ vs. temperature being recorded continuously. Thermal coefficient of expansion, α, and T_g can be determined[5].
TCE	Thermal Coefficient of Expansion
T_g	Glass Transition Temperature—the temperature at which a material changes from a crystalline state to a glassy (amphorous) state with a corresponding change in modulus, heat capacity, and TCE[5].
TG	Thermal Gravimetric Analysis—the measurement of a change in weight dependent on temperature and time as the sample undergoes various physical phase changes. The temperature is increased, or held isothermal, at a given programmed rate. Oxidation and decomposition temperatures can be determined[5].
DSC	Differential Scanning Calorimetry—gives DTA and TMA data.
PPM	Parts per million—used in emission spectroscopy, which is used to identify cationic contaminants and to identify fillers in filled polymer systems.

1.0% = 10,000 ppm
0.1% = 1,000 ppm
0.01% = 100 ppm
0.001% = 10 ppm
0.0001% = 1 ppm

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