Study of Additive-Epoxy Interaction of Thermally Reworkable Underfills

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ABSTRACT: Underfill is the material used in a flip-chip device to dramatically enhance its reliability as compared to a nonunderfilled device. Current underfills are mainly epoxy-based materials that are not reworkable after curing, which is an obstacle in flip-chip technology developments, where unknown bad die is a concern. Reworkable underfill is the key to address the nonreworkability of the flip-chip devices. The ultimate goal of this study is to develop epoxy-based thermally reworkable underfills. Our previous work showed that when incorporated into epoxy matrix, special additives could provide the epoxy formulation with die-removal capability around solder reflow temperature. The additive-epoxy interactions were studied and the results show that the additives do not adversely affect the epoxy properties. Moreover, when the additive decomposition temperature is reached, the decomposition of the additive causes a microexplosion within the epoxy matrix. Subsequently, the adhesion of the epoxy matrix is greatly reduced. Among the four additives studied, Additive1 and Additive2 may be used in reworkable underfills that can be reworked around solder reflow temperature, Additive3 cannot be used in underfill because it greatly reduces the shelf life of the underfill, and Additive4 may be used to develop reworkable underfill that withstands multiple reflows. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1868–1880, 2001

Key words: additive; epoxy; reworkable underfill; underfill; underfill encapsulant

INTRODUCTION

Flip-chip interconnection technique has been gaining acceptance in electronic packaging due to its good features of high I/O capability and short interconnects.[1] As the flip-chip technique becomes increasingly popular, the problem with coefficient of thermal expansion (CTE) mismatch between the IC chip and the organic substrate becomes critical. Due to the CTE mismatch between silicon IC chips (2.5 ppm/°C) and organic substrate, i.e., FR-4 printed wiring board (18–24 ppm/°C), temperature cycle excursions experienced by the device generate tremendous thermomechanical stress at the solder joints and can subsequently result in performance degradation of the packaged system. Underfill is an adhesive that serves to reinforce the physical and mechanical properties of the solder joints between the chip and the substrate. It provides not only drastic fatigue life enhancement, but also corrosion protection to the IC, resulting in a 10- to 100-fold improvement in fatigue life as compared to an unencapsulated package.[2,3] Due to these attractive traits, this new technique of underfill encap-

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sulation has been gaining acceptance in the chip-to-organic substrate attachment process.

Cycloaliphatic epoxies, combined with organic acid anhydrides as the hardener, have been widely used in flip-chip assemblies as the underfills. This is largely due to their low viscosity prior to curing combined with good adhesion properties after curing. Silica has been widely used as the filler in the underfill formulations to reduce the CTE of the epoxy resin. Up to 70% (by weight) of filler loading has been used in commercial products.

However, due to their intractability after curing, it is extremely difficult to replace a faulty chip with a new one in an epoxy underfilled device. This is a severe limitation to flip-chip technology development, where unknown bad die is still a concern, and often times defective devices have to be reworked to reduce costs. An effective way to address this problem is to make underfills reworkable, i.e., to make the underfill removable under certain conditions. Presently, reworkable underfills that are undergoing development can be classified into two categories: chemically reworkable underfills and thermally reworkable underfills.

Buchwalter et al. developed epoxy compositions that are soluble in organic acid after curing, which fits into the chemically reworkable category.[4–6] However, the use of chemicals makes localized repair difficult. Furthermore, it is time consuming for the chemicals to penetrate into the underfilled flip-chip package and dissolve the underfills between the chip and the substrate.[7] On the other hand, thermally reworkable materials offer the possibility of a fast, clean, and localized rework process. A few papers have been published in this area.[8–10]

Our goal is to develop thermally reworkable underfills that can provide good reliability to the flip-chip package while allowing the chip to be easily removed at elevated temperatures. One possible approach is to incorporate some special additives into epoxy matrix to convert the epoxies from nonreworkable to reworkable materials. Our previous work showed that when incorporated into epoxy matrix, special additives could provide the epoxy formulation with die-removal capability around solder reflow temperature.[11,12] This work is intended to thoroughly study the additive-epoxy interactions before, during, and after epoxy curing. The incorporation of these additives will greatly facilitate the development of reworkable underfills.

EXPERIMENTAL

Chemicals

The commercial epoxy resin, 3,4-epoxy cyclohexyl methyl-3,4-epoxy cyclohexyl carboxylate, was provided by Union Carbide under the trade name ERL4221, and was used as received. The hardener, hexahydro-4-methylphthalic anhydride (HMPA), was purchased from Aldrich Chemical Company, Inc., and was used as received. A catalyst, 1-cyanoethyl-2-ethyl-4-methylimidazole (EMZCN), was provided by Shikoku Company and was used as received. Other catalysts, including imidazole, 2-ethyl-4-methylimidazole (EMI), and triphenylphosphine (TPP) were purchased from Aldrich Chemical Company, Inc., and were used as received.

Four fine powder additives were obtained from a commercial source. The additives were dried at 100°C under vacuum before use.

Sample Preparation

ERL4221 was mixed with HMPA (mole ratio 1:0.8), and 4% of EMZCN by weight was used as the catalyst. The epoxy formulation obtained was called Epoxy0. Epoxy0 was mixed with four additives with 5% in weight as the additive level.

Characterization

Differential scanning calorimetry (DSC) study was performed on a modulated DSC (by TA Instruments, Model 2920). Approximately 10 mg of sample was used each time. Five °C/min ramping rate was used for all of the samples.

A thermo-gravimetric analyzer (TGA; by TA Instruments, Model 2940) was used to study the thermal decomposition of the epoxy formulations. Approximately 20 mg of material was used for each sample. The heating was from room temperature to 400°C at a ramping rate of 20°C/min. The purge gas was air.

A thermo-mechanical analyzer (TMA; by TA Instruments, Model 2940) was used to measure the CTEs of the epoxy formulations. The specimen preparation was the same as for DMA testing, except that the samples were cut into $5 \times 5 \times 3$ mm pieces. After the samples were mounted in the TMA, they were heated from room temperature to 250°C at a rate of 5°C/min.

Viscosities of the underfill formulations were measured using a rheometer (by TA Instruments, Model AR1000N). The measurement was done at

25°C using parallel plate geometry. The shear rate was controlled between 0.1 and 20 1/s while stepping in set increments. This means when a shear rate was applied, the same shear rate was held constant until five viscosity readings were taken within 5% tolerance from each other. This was done to ensure time dependent behavior of the viscosity was taken into consideration.

A fourier transform infrared spectrometer (FTIR; by Nicolet, Model Magna 560) was used to obtain IR absorbance spectrum of liquid and solid samples. Liquid and paste samples were measured in between a pair of NaCl plates, while solid samples were measured in pallet form diluted with KBr power. A high temperature demountable cell coupled with programmable temperature controller (by Spectra-Tech, Model 0019-019) was used to hold the sample at desired high temperatures during IR measurement.

The adhesion strengths of the underfill formulations to alumina substrate and silicon die were measured in shear mode using a bond tester (by Royce Instruments, model 550-100K). The die was 2 × 2 mm passivated with silicon oxide. Both the die and the alumina substrate were cleaned prior to testing. The cleaning procedure and adhesion test procedure followed those found in literature.[13] The test speed was 0.1 mm/s, with 0.05 mm tool lift.

RESULTS AND DISCUSSION

One approach to develop reworkable underfills is to incorporate some specific additives into nonreworkable epoxies. A group of chemicals has been identified that has the potential to be used as the additive to the epoxy formulation to provide thermal reworkability. The feature of these chemicals is that each of them decomposes at a specified temperature region. Once decomposed, each of them emits a large volume of gas. The reason that these chemicals provide reworkability to the epoxy matrix is directly due to this gas-emitting feature. After being embedded into the epoxy matrix and when the temperature reaches the decomposition temperature of the additive, the additive starts to decompose and emits gases, which causes a microexplosion within the epoxy matrix. This explosion causes delamination at underfill-chip and underfill-substrate interfaces. Moreover, the gas-emitting feature caused by the additive decomposition generates a lot of voids inside the epoxy matrix, which makes the residual epoxy left on the substrate after removal of the chip easy to clean.

Table I Thermal Decomposition Temperature Range of the Four Additives

Sample	Thermal Decomposition Temperature Range (°C)
Additive1	195–216
Additive2	228–235
Additive3	250–300
Additive4	271–300

However, the following criteria must be met before an additive can be incorporated into the epoxy resin to provide reworkability:

1. The additives should be inert to the curing reaction of the epoxy network and stable during thermal cycling of the flip-chip package.
2. The additives should not adversely affect the overall properties of the epoxy network.
3. The additive should readily cause dramatic change to the properties of the epoxy network under specific temperature, so that the network can be easily reworked.

The additive-epoxy interactions were thoroughly studied and the results are presented in this article. The interactions between the epoxy compositions and several additives before, during, and after epoxy curing were studied.

Additives

Because underfill typically cures around 150°C, the suitable additives must decompose at a higher temperature. Four additives that meet this requirement were selected. Table I lists their decomposition temperature ranges.

Our previous work showed that incorporation of 5% of Additive1 or Additive2 into epoxy formulation provided the epoxy chip-removal capability around solder reflow temperature.[11,12] In this study, the additive level was set to 5%.

Before Curing

Four additives were mixed with Epoxy0 and the mixtures were studied. Additive1 and Additive2 remained dispersed in Epoxy0, while Additive3 and Additive4 slowly dissolved in Epoxy0. The

Table II Viscosity Data of Epoxy 0 Incorporated with the Additives

Sample	Viscosity (Pa.S)	
	After Sample Preparation	After Sample Stored at −40°C for 1 Month
Epoxy0 w/Additive1	0.43	0.44
Epoxy0 w/Additive2	0.43	0.44
Epoxy0 w/Additive3	0.42	1.94
Epoxy0 w/Additive4	0.33	0.33

effects of the additives on the viscosity of Epoxy0 were studied by measuring the viscosities of the mixtures right after the mixtures were prepared, and after the mixtures were stored in a −40°C freezer for 1 month. The viscosity data is shown in Table II. It can be seen that the incorporation of Additive3 into Epoxy0 made its viscosity increase over time, even when Epoxy0 was stored at −40°C. The other three additives did not increase the viscosity of the epoxy stored at −40°C. Because Additive3 greatly reduced the shelf life of the epoxy, it is not good for underfill application.

During Curing

The behavior of the additives during epoxy curing is very important. An ideal additive should not interfere with the epoxy curing. The additive-epoxy mixtures were studied by oven curing test and DSC.

The oven curing test was done at 165°C for 30 min. The curing results showed that Additive1 and Additive2 did not seem to react with the epoxy composition, because they remained dispersed in the epoxy matrix after curing. The results also showed that both additives generated gas bubbles within the epoxy matrix under this curing condition. After being cured at 165°C for 30 min, both Additive3 and Additive4 formed homogenous single-phase mixtures with the epoxy matrix, which indicates both Additive3 and Additive4 did not interfere with epoxy curing.

The potential reaction between the additives and the main compositions of Epoxy0, ERL4221, and HMPA was studied by using DSC dynamic scan on the mixtures of ERL4221, HMPA, and 5% of the additives. Among the four additives, Additive3 acted as a catalyst in the epoxy-anhydride system, while Additive4 was totally inert. This explains why Additive3 increased epoxy viscosity during the epoxy storage. As shown in Figure 1, there seemed to be some interactions between Additive1, Additive2, and the epoxy-anhydride system when the temperature was above 170°C.

In order to investigate the possible interactions between the additives and the epoxy system, FTIR was used to study possible chemical interactions between Additive1, Additive2, and typical

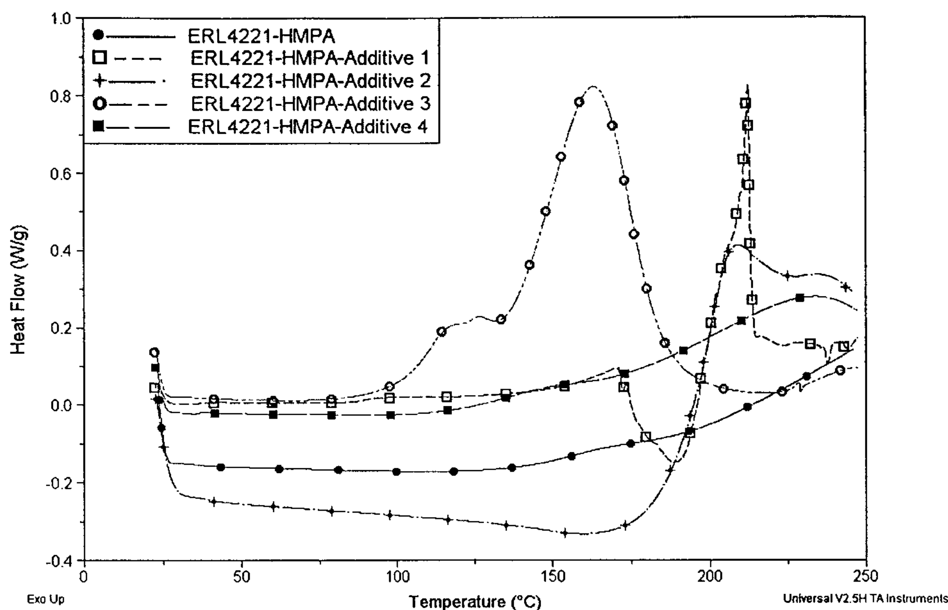

Figure 1 DSC curves of ERL4221-HMPA and ERL4221-HMPA with four additives.

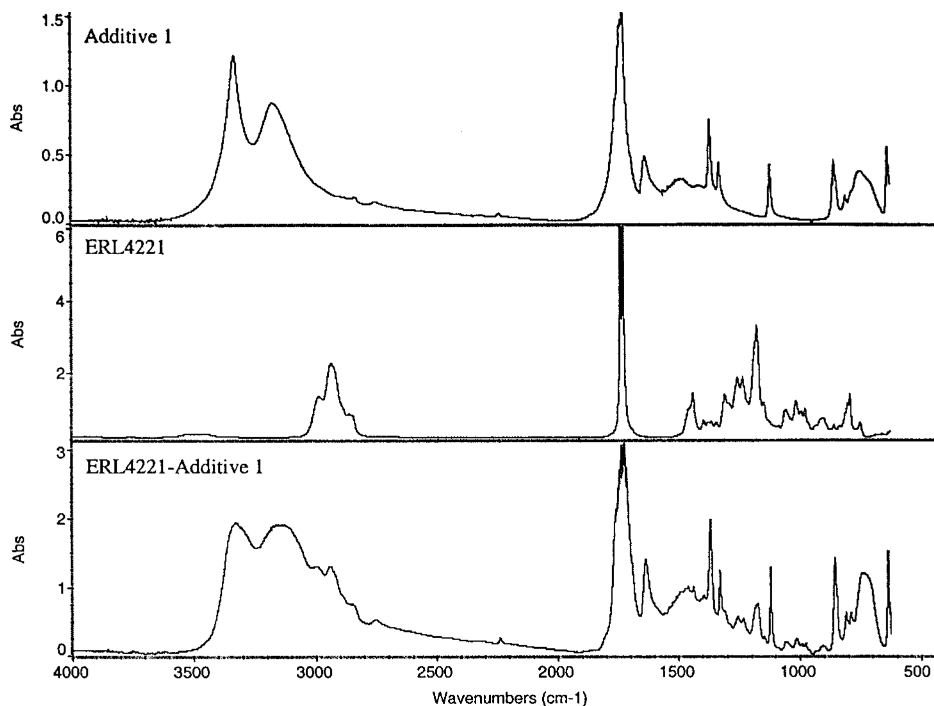

Figure 2 IR spectra of Additive1, ERL4221, and ERL 4221-Additive1 mixture.

epoxy compositions. All mixtures were prepared in 1:1 ratio in weight.

Figure 2 shows the IR spectra of Additive1, ERL4221, and their mixture at room temperature. Comparing the spectrum of the mixture to those of Additive1 and ERL4221, it is clear that all the peaks for the mixture are either from Additive1 or ERL4221, and there is no disappearance of existing peaks. It was also found that if the spectrum of Additive1 was subtracted from that of the mixture, the obtained spectrum was almost identical to the spectrum of ERL4221. All of these facts indicate that there is no chemical reaction between these two materials at room temperature.

Figure 3 shows the IR spectra of the Additive1-ERL4221 mixture measured at different temperatures. It shows that the spectrum did not change greatly at high temperatures. Actually, the only noticeable change is the decrease of ERL4221 peaks at high temperature, which is caused by its evaporation from the mixture. This figure shows that there is no chemical reaction between Additive1 and ERL4221 even at 250°C.

Figures 4 and 5 show the IR spectra of Additive1-HMPA mixture and Additive1-EMZCN mixture at room temperature. Like ERL4221, both HMPA and EMZCN do not react with Additive1 at room temperature. These two mixtures were also investigated by FTIR up to 250°C, with no sign of reaction. Other catalysts, including imidazole, EMI, and TPP were also mixed with Additive1 and were studied by FTIR, and the results all show that these do not react with Additive1 at room temperature or high temperature.

Based on these IR results, it is concluded that there is no chemical reaction between Additive1 and typical underfill composition, including ERL4221, HMPA, and catalysts.

Figures 6 through 9 show various IR spectra of the mixtures with Additive2. Like Additive1, Additive2 does not react with typical underfill composition, including ERL4221, HMPA, and catalysts at room or high temperature.

In order to investigate further the cause of the voiding problem during the curing, the interaction between Additive1, Additive2, and typical underfill compositions, including ERL4221, HMPA, and several catalysts, was studied. The catalysts studied included EMZCN, imidazole, EMI, and TPP. Each additive was mixed with ERL4221 and HMPA, and these catalysts individually in a 1:1 ratio in weight, and the mixtures were studied using DSC. Figure 10 shows the DSC curves of the mixtures with Additive1. The DSC curve of Additive1 was included in the figure for comparison. Figure 10 shows that ERL4221, HMPA, and all the catalysts tended to reduce the decomposition temperature of Additive1,

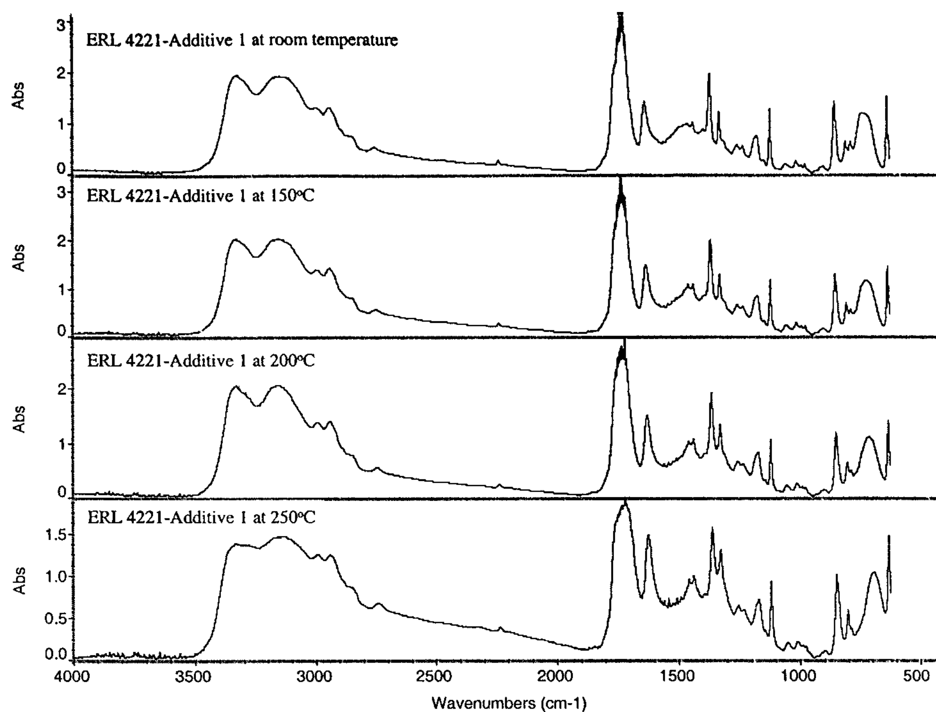

Figure 3 IR spectra of ERL4221-Additive1 mixture at different temperatures.

so they acted as activators to Additive1. This figure also shows that three imidazole-type catalysts reduced the decomposition temperature of Additive1 more than TPP, a nonimidazole-based catalyst. This indicates that imidazole-type catalysts are strong activators to Additive1. Figure 11 shows the

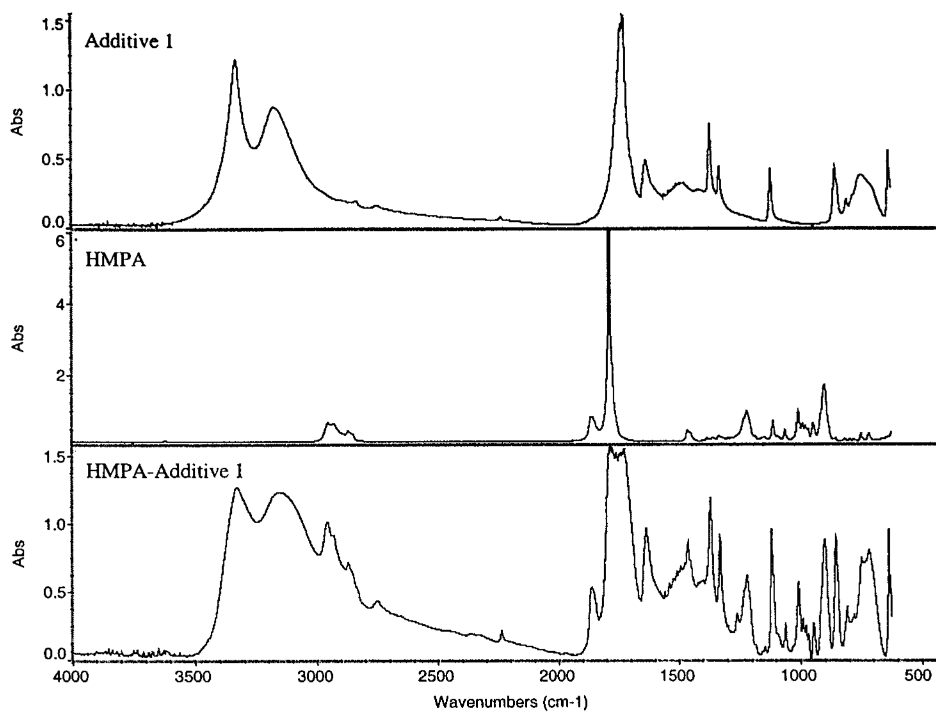

Figure 4 IR spectra of Additive1, HMPA, and HMPA-Additive1 mixture.

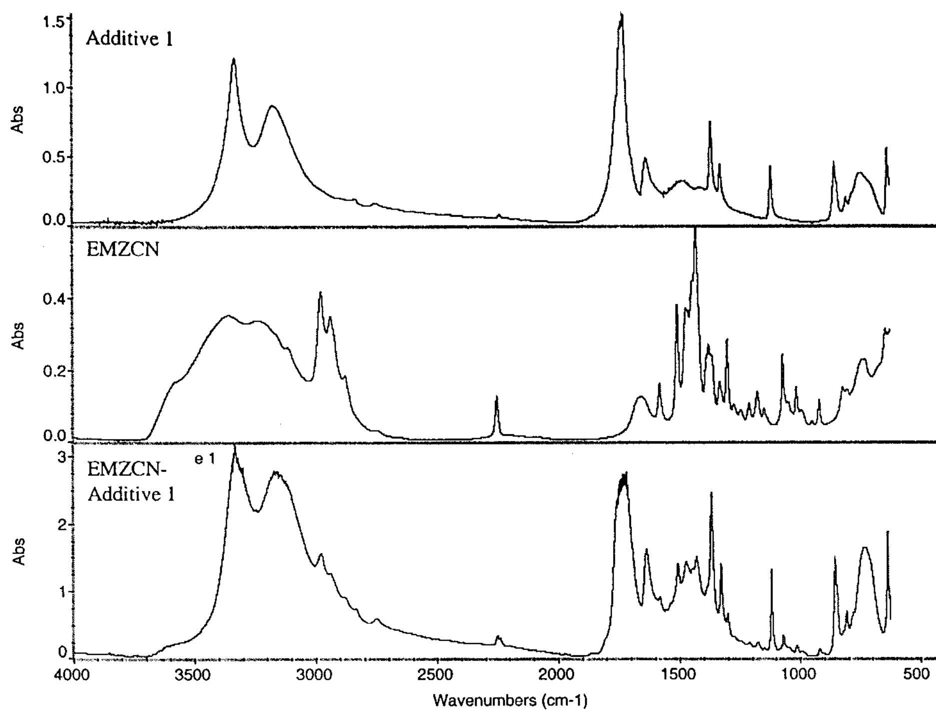

Figure 5 IR spectra of Additive1, EMZCN, and EMZCN-Additive1 mixture.

DSC curves of the mixtures with Additive2. It can be seen that Additive2 is quite similar to Additive1 in terms of its interaction with epoxy compositions.

A combination of IR and DSC results indicates that the voiding of the epoxy-anhydride system containing Additive1 and Additive2 during curing

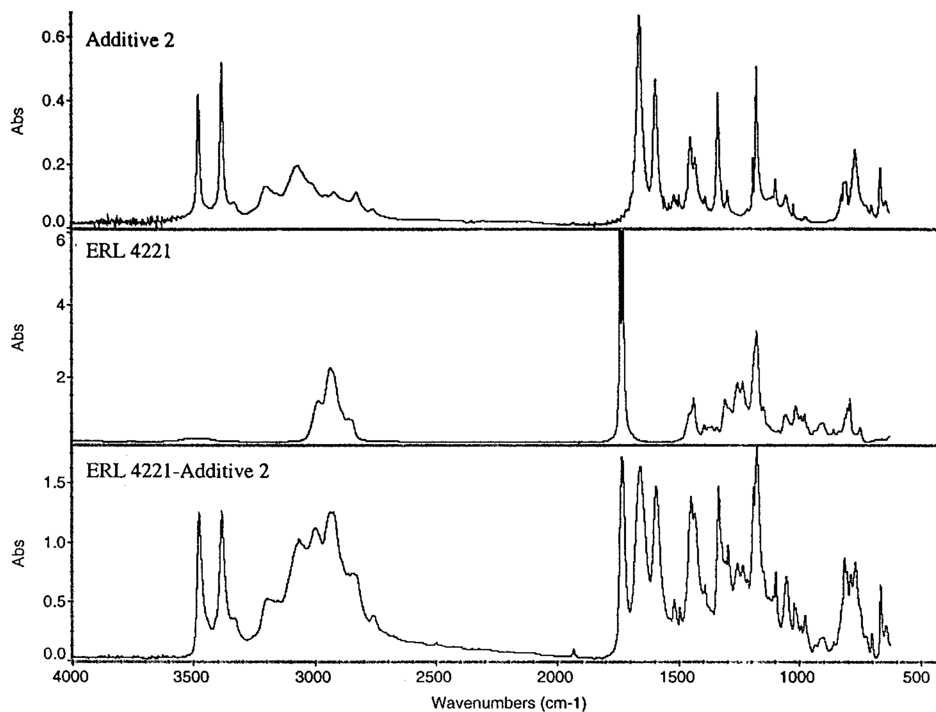

Figure 6 IR spectra of Additive2, ERL4221, and ERL4221-Additive2 mixture.

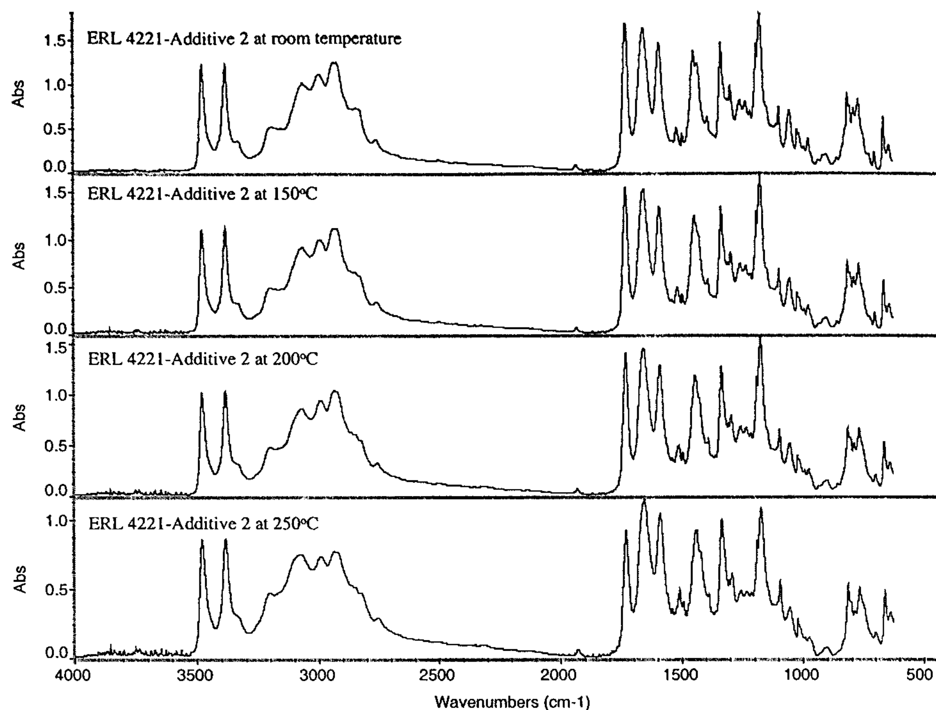

Figure 7 IR spectra of ERL4221-Additive2 at different temperatures.

is caused by the predecomposition of the additives activated by the underfill composition. Because epoxy curing is exothermic, when the curing temperature is 165°C, the temperature inside the epoxy during curing may be much higher than 165°C, which reaches the decomposition temper-

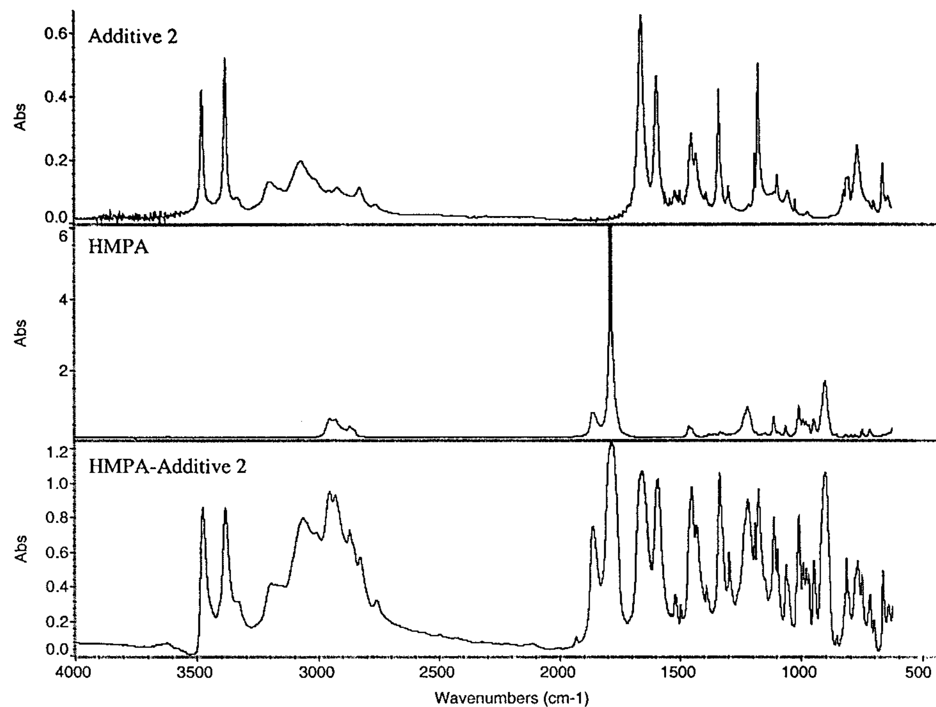

Figure 8 IR spectra of Additive2, HMPA, and HMPA-Additive2 mixture.

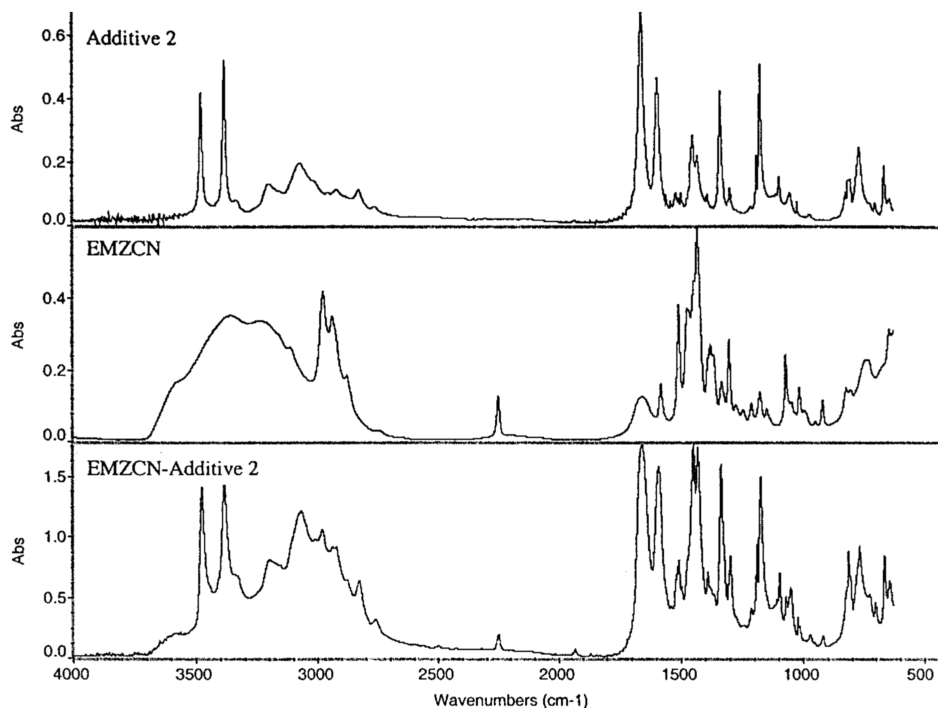

Figure 9 IR spectra of Additive2, EMZCN, and EMZCN-Additive2 mixture.

ature of the additive, which has been activated by the epoxy compositions. This overheating of the epoxy, combined with the activation of the additives by the epoxy composition, is believed to cause the voids of the epoxy containing Additive1 or Additive2.

To minimize this overheating effect, another curing scheme (slow cure) was then applied to these samples: from 80 to 140°C, the temperature was increased 10°C every 10 min; then the samples were heated up to 150°C and held for 20 min. This curing scheme was found to cure Epoxy0-

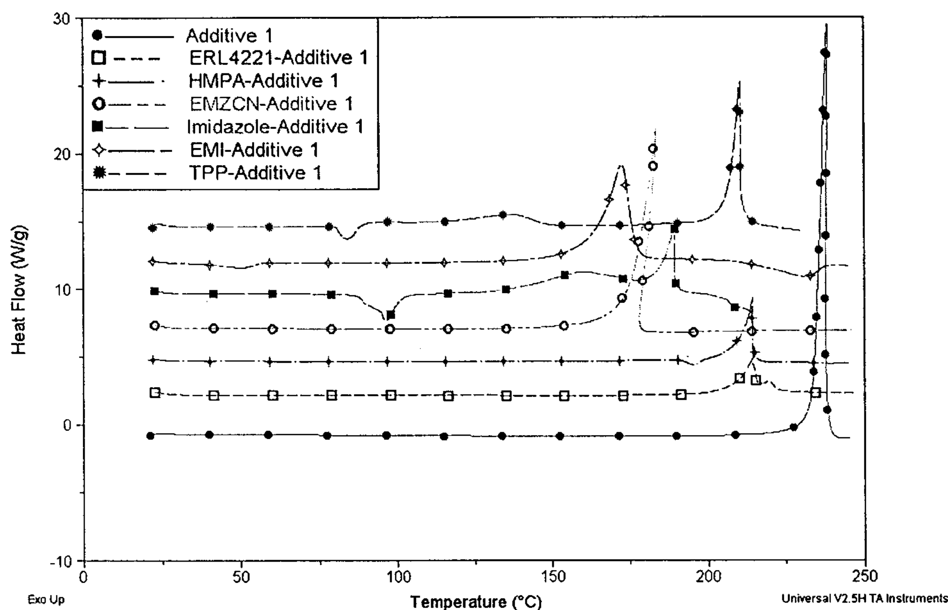

Figure 10 DSC curves of Additive1 and its mixtures with ERL4221, HMPA, and four catalysts.

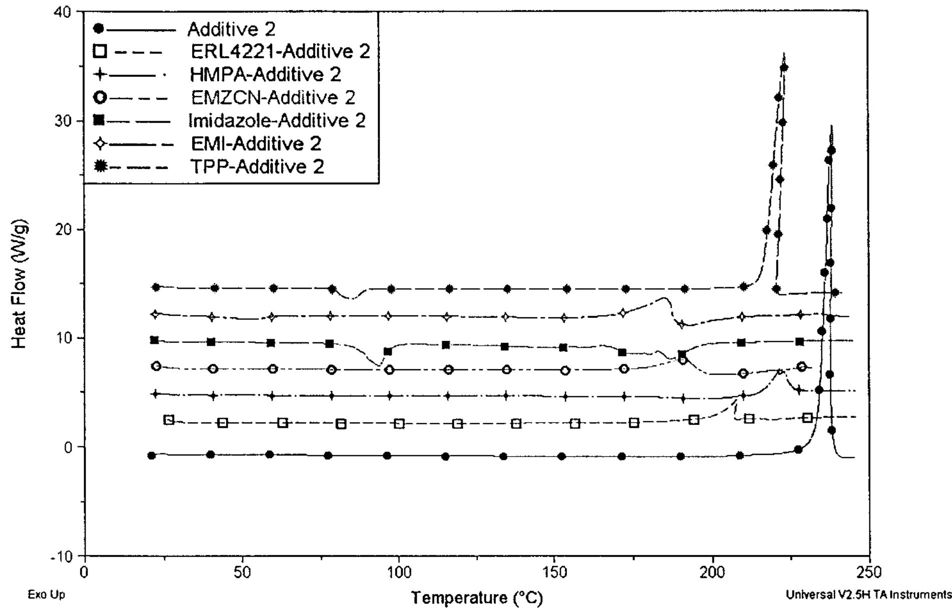

Figure 11 DSC curves of Additive2 and its mixtures with ERL4221, HMPA, and four catalysts.

Additive1 and Epoxy0-Additive2 without causing any voids within the cured epoxy sample.

After Curing

After the epoxy samples were cured according to the prescribed schedules (detailed in the section on curing), these samples were tested using TGA, TMA, and bond tester.

Figure 12 shows the TGA curves of Epoxy0 with four additives. Epoxy0 starts to lose weight around 350°C, while all four samples containing each of the four additives start to lose weight around additive decomposition temperature. This

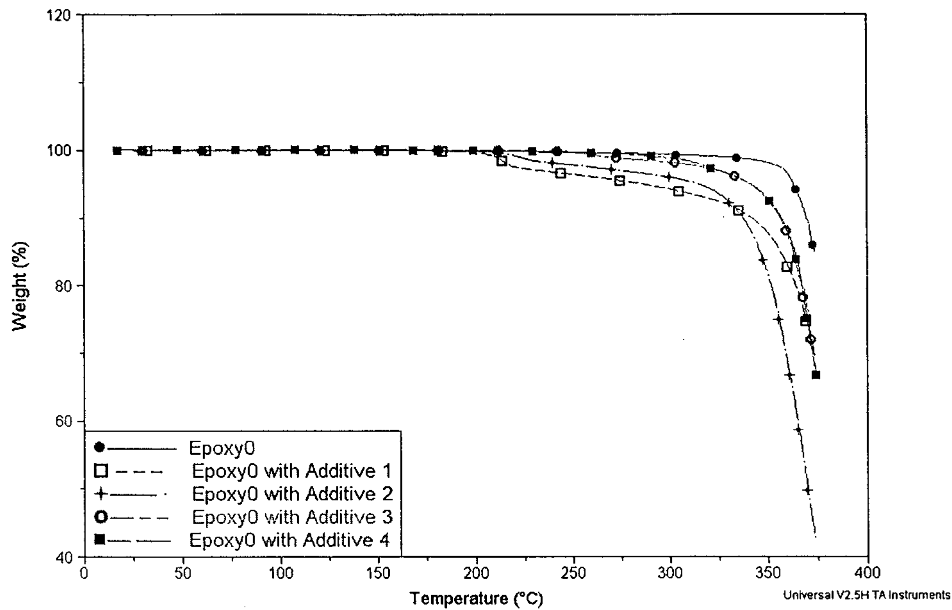

Figure 12 TGA curves of Epoxy0 and Epoxy0 with four additives.

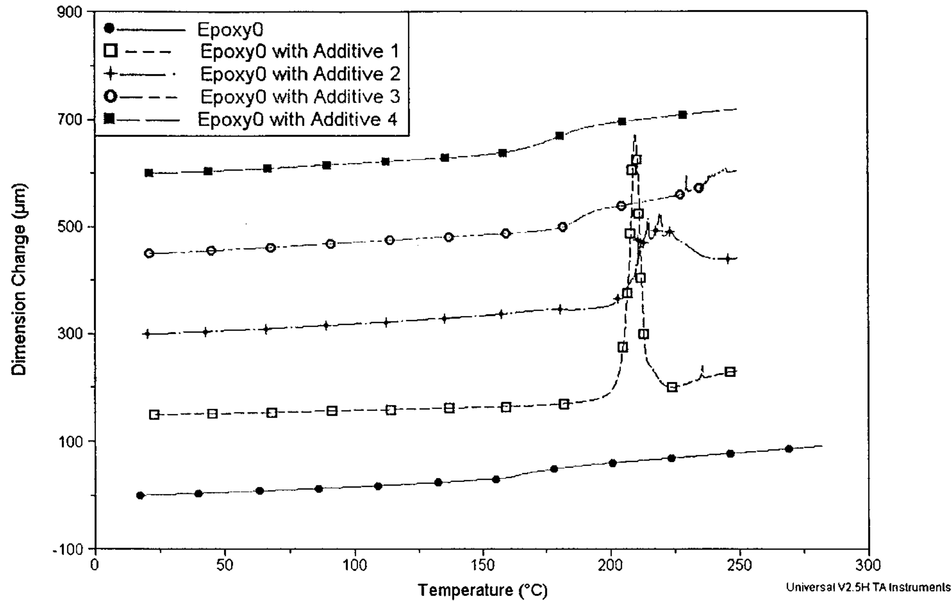

Figure 13 TMA curves of Epoxy0 and Epoxy0 with four additives.

indicates that these additives all maintained their decomposition and gas-emitting features within the epoxy matrix throughout the epoxy curing.

Figure 13 shows the TMA curves of Epoxy0 with four additives. It shows that the additives did not greatly affect α_1 (CTE before T_g) of Epoxy0. Moreover, when the temperature reached decomposition temperature of the additives, a microexplosion showed up on the TMA curve (represented as the TMA curve jump), which was caused by the gas-emitting of the additive. This explosion is most obvious for Epoxy0 with Additive1. For Epoxy0 with Additive3, there is only small curve jump around 250°C. No curve jump is observed for Epoxy0 with Additive4 up to 250°C, because the decomposition temperature of Additive4 is higher than that.

An ideal additive should not affect an epoxy's adhesion after curing, but it should greatly decrease the adhesion when the desired rework temperature is reached, to help the rework process. The adhesion of the epoxy formulations incorporated with the four additives was measured using a bond tester.

Figure 14 shows the adhesion data of Epoxy0 and its mixtures with Additive1 and Additive2. The slow cure scheme was used to prepare these samples for the adhesion test. Three thermal treatments were used in the test: curing, curing at 200°C for 5 min, and curing at 250°C for 5 min. In the figure, ASA stands for apparent strength of adhesion. This figure shows that incorporating Additive1 and Additive2 into the epoxy formulations did not affect their adhesion after curing. For Epoxy0 the thermal treatment at 200 and 250°C did not reduce its adhesion. Epoxy formulations incorporated with the additives showed little or no decrease of adhesion after 200°C for 5 min, but there was a large decrease after 250°C for 5 min. This indicates the additive decomposition greatly reduces the adhesion of the epoxy.

Figure 15 shows the adhesion data of Epoxy0 and Epoxy0 with Additive3 and Additive4. The curing scheme here was at 165°C for 30 min. Only 250°C was used as the thermal treatment after

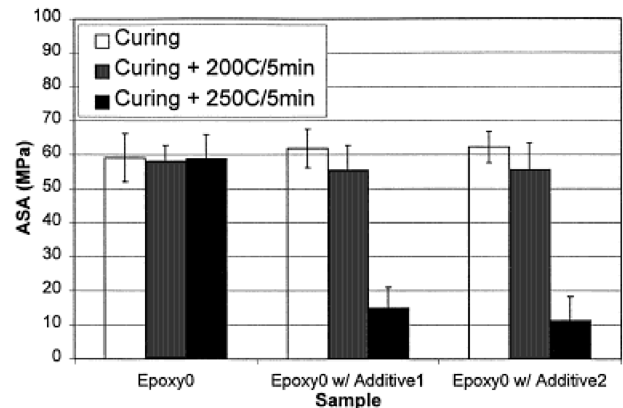

Figure 14 Adhesion data of Epoxy0 and its mixture with Additive1 or Additive2 after different thermal treatments.

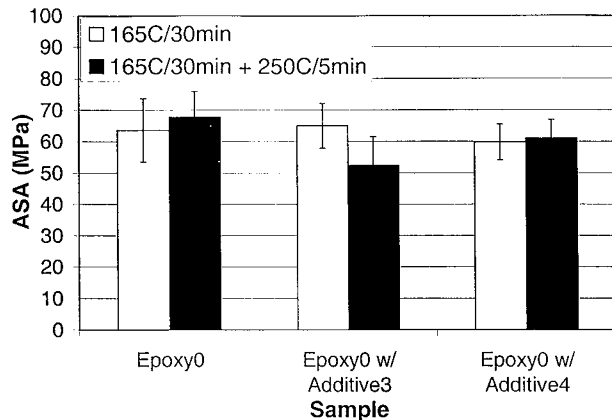

Figure 15 Adhesion data of Epoxy0 and its mixture with Additive3 or Additive4 after different thermal treatments.

curing because Additive3 and Additive4 decompose at that temperature. The figure shows the treatment at 250°C did not decrease the adhesion of Epoxy0 and Epoxy0 with Additive4, but it slightly decreased that of Epoxy0 with Additive3. This slight decrease might be caused by the decomposition of Additive3 at 250°C. Comparing Figure 15 with 14, one can see that two curing schema, 165°C/30 min and slow cure, did not affect the adhesion of Epoxy0.

Because the decomposition temperature of Additive1 and Additive2 is around the typical peak reflow temperature of eutectic solder (≈230°C), they can be used in reworkable underfills that are reworkable around solder reflow temperature. Additive3 cannot be used in underfill because it greatly reduces its shelf life. Due to its high decomposition temperature, Additive4 may be used to develop reworkable underfill that can withstand multiple reflows, for example, no-flow reworkable underfill.

CONCLUSIONS

Before Curing

Additive3 increases the viscosity of Additive3-Epoxy0 mixture during −40°C storage, so Additive3 is not a good additive to be used in underfill formulation because it greatly reduces the shelf life of the underfill. All of the other three additives do not increase the viscosity of the epoxy so they can be used in underfill application.

During Curing

Additive1 and Additive2 cause voiding in the sample during 165°C curing, while Additive3 is a catalyst to epoxy curing, and Additive4 is totally inert to epoxy curing. IR and DSC studies show that there is no chemical reaction between Additive1 and Additive2 and typical epoxy compositions, but these compositions tend to reduce the decomposition temperature of both additives. The voiding problem within the epoxy matrix can be eliminated by slow cure.

After Curing

When incorporated into the epoxy matrix, not all additives greatly affect the CTE before T_g and adhesion of the epoxy matrix, but they maintain their thermal decomposition feature within cured epoxy matrix. When the additive decomposition temperature is reached, the additive inside the epoxy matrix starts to decompose and it emits gasses to cause microexplosion within the epoxy matrix and adhesion reduction of the epoxy to the chip and the substrate.

In summary, our additive-epoxy interaction study indicates that Additive1 and Additive2 may be used in reworkable underfills that are reworkable around solder reflow temperature. Additive3 cannot be used in underfill because it greatly reduces its shelf life. Additive4 may be used to develop reworkable underfill that can withstand multiple reflows.

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