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Heat Resistant Underfill for Flip-chip Packaging

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DBMI-added underfill can show excellent thermal reliability, due to the superior properties of CTE, the elastic modulus, and water resistance. When the properties of a DBMI (2wt%)-added underfill were compared with those of a typical underfill (epoxy/anhydride system), the value of CTE was reduced to less than one-half at the solder reflow temperature (about 200 ^{o}C), the elastic modulus was reduced to less than one-half in the temperature region below Tg, and water resistance improved by 2 times.

Keywords: Underfill; Flip-chip packaging; Thermal reliability; DBMI

INTRODUCTION

The key to the success of flip-chip technology depend on the availability of successful underfill materials. However, the reliability of flip-chip technology using current underfill materials is generally found to be lower than that of conventional wire-bond connection packaging materials such as EMC. The main reasons are the high values of CTE (coefficient of thermal expansion) and the high values of moisture absorption ratio of cured underfill materials. Because the underfill materials contain a smaller amount of silica filler than EMC for good flowability during the underfilling process [1]. In this study, desbimide(DBMI), which has a low melting point (about 80 ^{o}C), was added in the underfill materials as a co-hardener. Properties such as the

CTE, modulus, and the glass transition temperature of underfill materials were evaluated according to the contents of the thermoset imide in the epoxy/anhydride system.

EXPERIMENTAL

Materials. The epoxy resin was 3, 4- epoxy cyclohexyl-3, 4-epoxy cyclohexyl carboxylate, and the hardener were hexahydro-4-methylphthalic anhydride (HMPA), which were purchased from Aldrich Chemical Company, Inc. and used as received. Co(II) acetylacetonate was used as the curing catalyst for this study. Also, the DBMI (synthesized in the lab.) was used as a co-hardener. The equivalent weight of epoxy resin was 120g, HMPA was 168.2g, and DBMI was 180g. The detail recipes of the underfill materials are summarized in Table I [2].

Synthesis of desbimide. Methylenedianiline (MDA) (Aldrich), maleic anhydride (MA) (Katayama Chemical), acetic anhydride (Ac_2O) (TEDIA), 1,4-diazobicyclo [2, 2, 2] octane (DBACO) (Janssen), and acetone (Janssen) were used without purification as raw materials of desbimide. A solution of 50g (0.5 mol) MA in 140 mL of acetone was added dropwise to a stirred solution of 50g (0.25mol) MDA in 350 mL of acetone. A yellow precipitate appeared immediately. Stirring was continued for 30 min at reflux temperature, after which 0.32g (2.9mmol) of DBACO and 71g (0.7mol) of Ac_2O were added. When the reaction mixture turned into a clear brown solution, the volatile components were removed by distillation using a rotavapor. The DBMI was obtained after washing with a sodium bicarbonate solution to remove

TABLE I The recipes for the underfill.

Materials	DBMI 0 (R=1.0)	DBMI 2 (R=1.0)	DBMI 4 (R=1.0)	DBMI 6 (R=1.0)	DBMI 8 (R=1.0)
Epoxy	7.29	7.29	7.29	7.29	7.29
DBMI	0	0.34	0.68	1.03	1.37
Anhydride	9.89	9.55	9.21	8.86	8.52
Catalyst	0.17	0.17	0.17	0.17	0.17
Epoxy silane	0.25	0.25	0.25	0.25	0.25
Filler	32.69	32.69	32.69	32.69	32.69
Sum	50.29	50.29	50.29	50.29	50.29

acetic acid in the product (MP, 60-80 °C). The DBMI is composed of 4, 4'-bismaleimidodiphenylmethane (BMI, about 25%), 4-maleimido-4' acetaimidodiphenylmethane (about 25%), 4-maleimido-4'-isomaleimidodiphenylmethane (about 10%), and etc [3].

Sample preparation. The specified quantities of hardeners such as HMPA and DBMI, were added into the epoxy resin, and the mixture was stirred for 1 hour at 60 °C. Thereafter, a specified quantity of the catalyst was added into the mixture, then the mixture was stirred for an additional 1 hour at 60 °C until the catalyst was homogeneously dissolved. The formulations were then stored in a refrigerator.

TMA measurement. The CTE of the composite was measured by using a bar-shaped specimen in a thermal mechanical analyzer (Perkin-Elmer, TMA 7e) with a static force (50mN) and a heating rate of 5℃ /min from 40 °C up to 250 °C. Also, the glass transition temperature (Tg_{TMA}) was determinated at the inflection point of the expansion ratio. The below equation was used to calculate the CTE:

$$\alpha = \frac{\Delta L}{L_0 \Delta T} \qquad (1)$$

where, α is the CTE, $\Delta L/L_0$ is the thermal expansion ratio of the sample, and ΔT is the difference of temperature.

DMA measurement. A dynamic mechanical analyzer (Perkin-Elmer Co., DMA 7e) was used to study the storage modulus of cured underfill materials from 100 °C to 250 °C at a heating rate of 5 °C/min under He purging (20ml/min) conditions. The sample was measured by the parallel plate method (diameter, 3mm), with a static force of 110mN, dynamic force of 100mN, and frequency of 1Hz. Also, the glass transition temperature (Tg_{DMA}) was determined at the peak point of tan δ.

Water resistance. A rectangular specimen (20×10×4mm) was polished with sandpaper before being immersed in water at 85 ℃. To measure the amount of water absorption, the surface of the immersed sample was fully dried by wiping off all moisture with dried cloth, then the sample's change in weight was measured every day.

RESULTS AND DISSCUSSION

The R value(R=Equiv. Wt of epoxy/(Equiv. Wt of HMPA+DBMI)) of the DBMI-added underfill was fixed as 1. The thermal reliability of the DBMI-added underfill as a function of the DBMI content were

evaluated. The CTE, the modulus, and water resistance were found to be important factors in the thermal reliability of the underfill.

CTE

CTE of the underfill was directly proportional to the Tg of the underfill. The consequent TMA- measured values of the Tg_{TMA} and the DMA-measured values of the Tg_{DMA} of the underfill as a function of DBMI content are shown in Fig. 1. The values of Tg_{TMA} and Tg_{DMA} of the DBMI-added underfill were higher than those of a typical underfill. In particular, when 2 wt% of DBMI was added to the underfill, Tg rapidly increased. In general, Tg of the underfill was increased by increasing the thermoset imide content because the thermal resistance group is contained in thermoset imide [4].

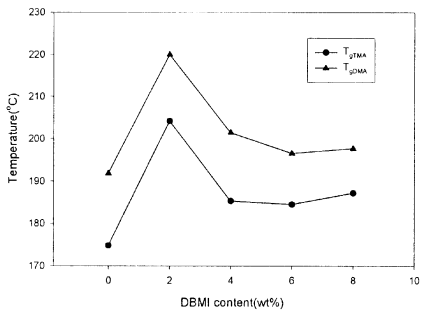

FIGURE 1. Glass transition temperature of the underfill as a function of DBMI content.

However, in the case of DBMI, when more than 4 wt% of the DBMI was added to the underfill, Tg of the underfill was decreased. This because the cure reaction of the epoxy/anhydride was interfered by reduced mobility of molecular and faster reaction of the underfill compared to the 2 wt% DBMI-added underfill. The CTE of cured underfill as a function of DBMI content are shown Table II. Table II shows that α_{200} (near the solder reflow temperature) of the 2 wt% DBMI-added underfill sharply decreased because of the high Tg of the underfill, though α_{150} in the region of below the Tg of the underfill was decreased by increasing the DBMI content. As results, when 2 wt% of DBMI was added to the underfill, Tg and CTE of the underfill improved markedly, compared to that of a typical underfill.

TABLE II. The CTE of the underfill as a function of DBMI content.

	α_1	α_2	α_{150}	α_{200}	α_{230}
DBMI 0wt%	91.20	473.60	84.27	139.89	154.50
DBMI 2wt%	97.90	696.20	75.07	86.25	136.10
DBMI 4wt%	83.25	557.00	74.32	124.77	141.50
DBMI 6wt%	85.88	666.84	71.83	132.86	147.20
DBMI 8wt%	80.70	825.50	71.64	131.54	143.40

*α_1 : CTE of below Tg, α_2 : CTE of upper Tg, α_{150}, α_{200}, α_{230} : CTE in the temperature range from 40°C to 150, 200, 230 °C

The modulus

In general, the crack resistance of materials against thermal stresses in IC operation is decreased by increasing the elastic modulus of materials. The elastic modulus of the material is directly proportional to Tg and the cross-linking density of materials. However, the elastic modulus of complex polymers is often decreased because one part of the complex polymers acts as a toughener regardless of Tg or the cross-linking density of materials. The DMA-measured elastic modulus of the cured underfill as a function of DBMI content is shown in Fig. 2. The elastic modulus of a small amount of DBMI (2~4wt%)-added underfill sharply decreased in the region below Tg. This is because DBMI, which has a longer chain than HMPA, act as a toughener in the epoxy/HMPA system.

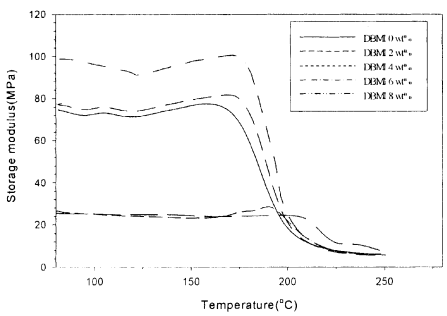

FIGURE 2. The storage modulus of the underfill as a function of temperature with the parameter of DBMI contents.

However, when more than 6 wt% of DBMI was added to the underfill, the elastic modulus was increased because of the self-additional reaction of DBMI.

Water resistance

The water resistance of the underfill as a function of DBMI content is shown in Fig. 3. A cured sample was prepared and an immersion test was carried out at 85 °C for 5 days in distilled water. The water absorption ratios of the underfill according to the DBMI content showed a minimum value at 2 wt% of DBMI. This is because the water absorption ratios of materials were inversely proportional to the cross-linking density, which can be evaluated by measuring Tg.

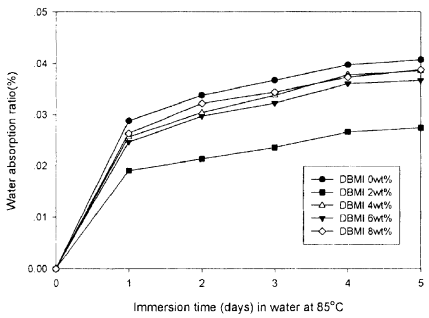

FIGURE 3. Water resistance of the underfill as a function of time with the parameter of DBMI contents.

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