

# Advanced Underfill for High Thermal Reliability

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**ABSTRACT:** The key to the success of flip-chip technology lies in 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 epoxy molding compound (EMC) because of the high coefficients of thermal expansion (CTE) and moisture absorption of cured underfill material. In this study desbimide (DBMI), which has a low melting point (about 80°C), was used in the underfill materials as a cohardener. As a result, DBMI-added underfill can show excellent thermal reliability, which is due to the superior properties of the CTE, the elastic modulus, and water resistance. When the properties of a 2 wt % DBMI-added underfill were compared with those of a typical underfill (epoxy/anhydride), the CTE value was reduced to less than one-half at the solder reflow temperature (about 200°C), the elastic modulus was reduced to less than one-half in the temperature region below the glass-transition temperature, and the water resistance was improved twofold. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2617–2624, 2002

**Key words:** underfill; flip-chip packaging; desbimide; thermal reliability; epoxy

## INTRODUCTION

Over the last few decades, the microelectronics industry in computer and communication devices for the fast treatment of huge amounts of data has grown rapidly in size. Thus, integrated circuits (ICs) with high performance are in demand. This demand has been increasing steeply.<sup>1–3</sup> According to this trend, typical plastic is being replaced by flip-chip technology. Flip-chip technology is very different from typical plastic packaging such as wire-bond connection packaging. In flip-chip technology, after soldering a chip directly onto the printed circuit board (PCB), underfill resin is then dispensed at 80°C. Capillary action is required to flow feed the dispensed un-

derfill resin under the die. Once the flow or underfilling is completed, the assembly is heated to an elevated temperature to cure the underfill resin (about 170°C).<sup>4</sup> The key to the success of flip-chip technology lies in 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 epoxy molding compound (EMC). The main reason is the high coefficient of thermal expansion (CTE) values and the moisture absorption ratio of the cured underfill material, because the underfill material contains a smaller amount of silica filler than EMC for good flowability during the underfilling process.<sup>5</sup> The thermal stress due to the difference of the CTE among the chips, the PCB, and the solder bump results in cracks in the solder bump, especially during the curing of the underfill. This problem may decrease the reliability of the IC operation.<sup>6</sup> To ob-

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**Table I** Raw Materials for Underfill

Chemical Names	Chemical Structures	Equiv. Weight
3,4-Epoxy cyclohexylmethyl-3,4-epoxy		236.5
Hexahydro-4-methylphthalic anhydride		168.2
Desbimide (BMI derived)		180.0
Cobalt(II) acetylacetonate		

tain a lower thermal expansion property of the EMC at high temperature, the epoxy resin was modified by a thermoset imide such as bismaleimide (BMI, melting point of 157°C), which is one of the high heat-resistant thermosetting materials. However, it is difficult to use for the underfilling process of underfill materials at low temperature (80°C) because most thermoset imides must be heated to at least 120°C to obtain the appropriate viscosity.<sup>7</sup> Also, it is expected that the desbimide (DBMI)-added underfill will provide good adhesion between the PCB and an underfill because the chemical structure of DBMI closely resembles that of the BMI triazine resin used for the PCB of the raw material.<sup>8</sup>

In this study DBMI, which has a low melting point (about 80°C), was used in the underfill materials as a hardener. Properties such as the viscosity at the flow temperature, CTE, modulus, and glass-transition temperature of the 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 was

hexahydro-4-methylphthalic anhydride (HMPA), which were purchased from Aldrich Chemical Company, Inc. and used as received. Cobalt(II) acetylacetonate was used as the curing catalyst for this study. The DBMI (lab synthesized) was used as a hardener. The equivalent weights of the epoxy resin, HMPA, and DBMI were 120, 168.2, and 180 g, respectively. Table I shows the chemical structures of the epoxy resin, the hardener, and the catalyst used in this study; the detailed recipes of the underfill materials are summarized in Table II.<sup>9</sup>

### Synthesis of DBMI

Methylenedianiline (MDA, Aldrich), maleic anhydride (MA, Katayama Chemical), acetic anhydride (Ac<sub>2</sub>O, TEDIA), 1,4-diazobicyclo[2,2,2]octane (DBACO, Janssen), and acetone (Janssen) were used without purification as raw materials of DBMI. A solution of 50 g (0.5 mol) of MA in 140 mL of acetone was added dropwise to a stirred solution of 50 g (0.25 mol) of MDA in 350 mL of acetone. A yellow precipitate appeared immediately. Stirring was continued for 30 min at reflux temperature, after which 0.32 g (2.9 mmol) of DBACO and 71 g (0.7 mol) of Ac<sub>2</sub>O 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 acetic

**Table II** Recipes for Underfill

Materials	DBMI 0 ( $R = 1.0$ )	DBMI 2 ( $R = 1.0$ )	DBMI 4 ( $R = 0.8$ )	DBMI 4 ( $R = 0.9$ )	DBMI 4 ( $R = 1.0$ )	DBMI 6 ( $R = 1.0$ )	DBMI 8 ( $R = 1.0$ )
Epoxy	7.29	7.29	6.5	6.9	7.29	7.29	7.29
DBMI	0	0.34	0.68	0.68	0.68	1.03	1.37
Anhydride	9.89	9.55	9.97	9.59	9.21	8.86	8.52
Catalyst	0.17	0.17	0.17	0.17	0.17	0.17	0.17
Epoxy silane	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Filler	32.69	32.69	32.69	32.69	32.69	32.69	32.69
Sum	50.29	50.29	50.26	50.28	50.29	50.29	50.29

acid in the product (mp 60–80°C). The DBMI is composed of 4,4'-bismaleimidodiphenylmethane (BMI, about 25%), 4-maleimido-4'-acetamidodiphenylmethane (about 25%), and 4-maleimido-4'-isomaleimidodiphenylmethane (about 10%).<sup>7</sup> The <sup>1</sup>H-NMR (300 MHz) spectra of DBMI in acetone-*d*<sub>6</sub> is shown in Figure 1.

### 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 h at 60°C. Thereafter, a specified quantity of the catalyst was added into the mixture, then the mixture was stirred for an additional 1 h at 60°C until the catalyst was homogeneously dissolved. The formulations were then stored in a refrigerator.

### Thermomechanical Analysis (TMA) Measurement

The CTE of the composite was measured by using a bar-shaped specimen in a thermal mechanical

analyzer (TMA 7e, Perkin–Elmer) with a static force of 50 mN and a heating rate of 5°C/min from 40 to 250°C. The glass-transition temperature ( $T_{gTMA}$ ) was determined at the inflection point of the expansion ratio. The equation below was used to calculate the CTE:

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

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

### Differential Scanning Calorimetry (DSC) Measurement

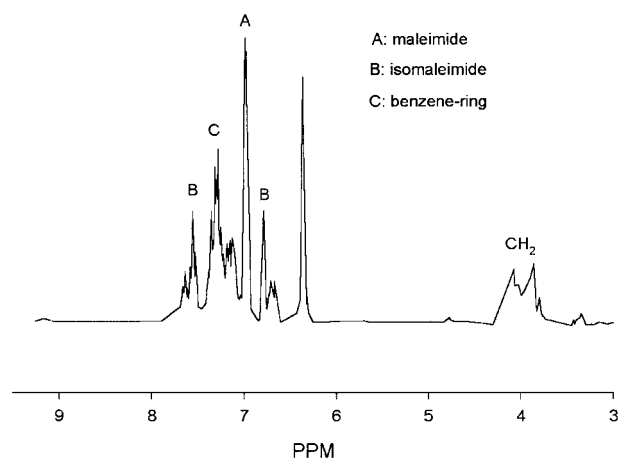
A Perkin–Elmer Pyris1 DSC was used to study the curing profile of the underfill material during curing at a heating rate of 10°C/min under N<sub>2</sub> purging (20 mL/min) conditions. The initiation temperature ( $T_i$ ) was the onset point of the curing area, the maximum temperature ( $T_{max}$ ) was the peak point of the curing area in the DSC thermogram, and the termination temperature ( $T_t$ ) was the end point of the curing area.

### Dynamic Mechanical Analysis (DMA) Measurement

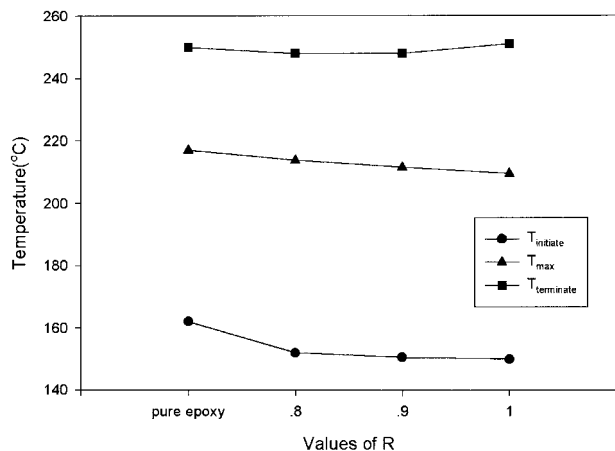
A Perkin–Elmer DMA 7e was used to study the storage modulus of the cured underfill materials from 100 to 250°C at a heating rate of 5°C/min under He purging (20 mL/min) conditions. The sample was measured by the parallel plate method (3-mm diameter) with a static force of 110 mN, a dynamic force of 100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

### Thermogravimetric Analysis (TGA) Measurement

A Perkin–Elmer TGA 7 was used to study the weight loss of the underfill material during cur-



**Figure 1** <sup>1</sup>H-NMR (300 MHz) spectra of DBMI in acetone-*d*<sub>6</sub>.



**Figure 2** The cure characteristics of the underfill as a function of  $R$ .

ing. The sample was heated in the TGA furnace at 20°C/min from room temperature to 270°C under  $N_2$  purging (20 mL/min). The percentage of the weight difference between 25 and 270°C was taken as the percentage of weight loss of the compound during the curing process.

#### Viscosity Measurement

A rheometer (RDAII, Rheometric Co.) was used to study the viscosity of the underfill. The sample was measured by the cone and plate method (25-mm diameter, 0.1 rad angle) with a frequency of 10 rad/s at 80°C.

#### Surface Tension Measurement

A tensometer (K101T, Krüss Co.) was used to study the surface tension of the underfill. The sample was measured by the plate method at 80°C.

#### Water Resistance

A rectangular specimen (20 × 10 × 4 mm) 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 a dried cloth, then the sample's change in weight was measured every day.

## RESULTS AND DISCUSSION

#### Properties with Value of $R$

To determinate the equilibrium weight ratio of DBMI as a cohardener of the epoxy/anhydride

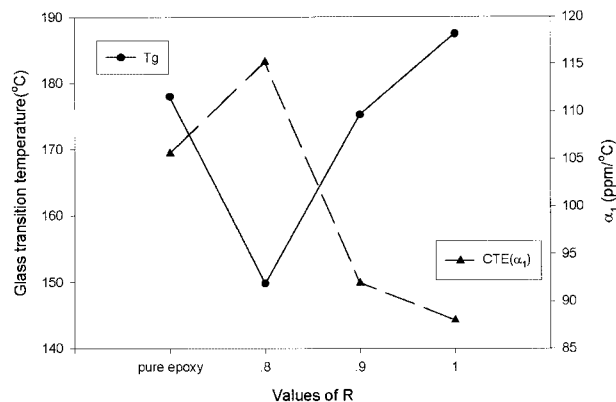
system, properties such as the curing characteristics,  $T_g$ , and the CTE of DBMI (4 wt % in epoxy/anhydride resin)-added underfill were evaluated according to the value of  $R$ , which is  $R = \text{epoxy equiv. wt.}/(\text{HMPA equiv. wt.} + \text{DBMI equiv. wt.})$ .

#### Curing Characteristics

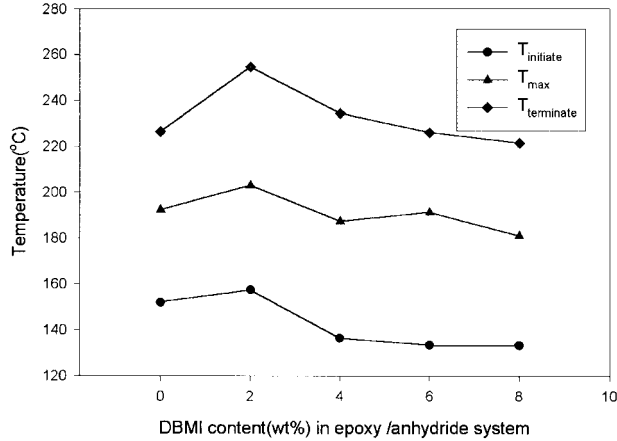
The  $T_i$ ,  $T_{\text{max}}$ , and  $T_t$  of DBMI (4 wt %)-added underfill as a function of the value of  $R$  are shown in Figure 2. Figure 2 shows that the  $T_i$  and  $T_{\text{max}}$  of the DBMI-added underfill were lower than that of a typical underfill (epoxy/HMPA system). Also, the  $T_i$  and  $T_{\text{max}}$  of the DBMI-added underfill were increased by decreasing the value of  $R$ , because a highly reactive group such as the urea group ( $-\text{CO}-\text{NH}-\text{CO}-$ ) in DBMI was reacted at a lower temperature than the reaction temperature of an epoxy/HMPA system.<sup>7</sup> However, the  $T_t$  of the DBMI-added underfill was increased by decreasing the value of  $R$ , which was due to the high temperature reactive group, such as BMI in DBMI, which is active at high temperature.

#### Physical Properties

The values of the  $T_{g\text{TMA}}$  and the CTE of the DBMI-added underfill as a function of the value of  $R$  are shown in Figure 3. The DBMI-added underfill was cured for 2 h at 170°C. Figure 3 shows that the  $T_g$  of the cured underfill was increased, but the CTE of the cured underfill was decreased by increasing the value of  $R$ , although the relative weight of the hardener was decreased. This indicates that DBMI reacted fully with the epoxy resin. As a result, when the  $R$  value of the DBMI-added underfill was 1, the cured underfill formed a full network structure with the epoxy/HMPA



**Figure 3** The glass-transition temperature and CTE of the underfill as a function of  $R$ .



**Figure 4** The curing characteristics of the underfill as a function of the DBMI content.

system. In addition, the DBMI-added underfill has a higher  $T_g$  and a lower CTE compared to a typical underfill.

**Properties of Underfill as Function of DBMI Content**

According to the above-mentioned results, the  $R$  value of the DBMI-added underfill was fixed as 1. The physical properties such as the cure characteristics, flowability, and thermal reliability of the DBMI-added underfill as a function of the DBMI content were evaluated.

**Curing Characteristics**

The  $T_i$ ,  $T_{max}$ , and  $T_t$  of the DBMI-added underfill as a function of the content of DBMI are shown in Figure 4.

The  $T_i$  of the DBMI-added underfill was rapidly decreased by increasing the DBMI content, because a highly reactive group such as the urea group ( $-\text{CO}-\text{NH}-\text{CO}-$ ) contained in DBMI reacted at a lower temperature than the reaction temperature of the epoxy/HMPA system. However, when less than 4 wt % of DBMI was added to the underfill, the  $T_i$  of the DBMI-added underfill was not decreased. The  $T_{max}$  of the DBMI-added underfill was not affected by the DBMI content. This means that the curing rate of the DBMI-added underfill was not affected by the DBMI content. As a result, when less than 4 wt % of DBMI was added to the underfill, the  $T_i$  and the rate of curing of the DBMI-added underfill closely resembled those of a typical underfill.

The outgasing weight is one of the important factors for the thermal reliability of underfill be-

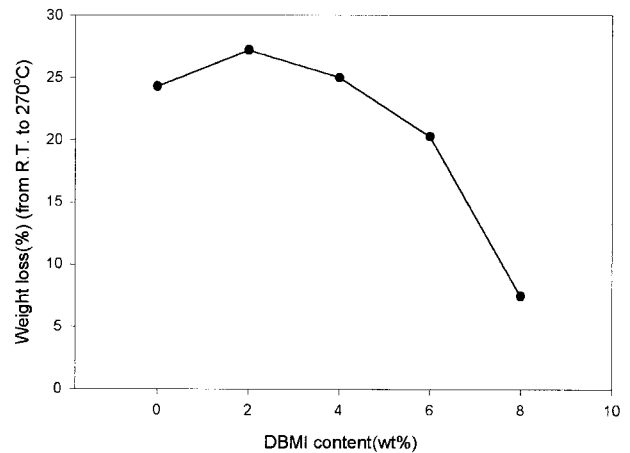
cause the voids of underfill are often formed by the outgasing weight of the underfill during the process of curing. The TGA-measured weight loss of the underfill as a function of the DBMI content during the curing reaction is shown in Figure 5. Generally, the weight loss of the underfill is related to the  $T_i$  and the curing rate of the underfill. Figure 5 shows that the weight loss of the underfill during the curing reaction was decreased by increasing the DBMI content because the  $T_i$  of the DBMI-added underfill was decreased by increasing the DBMI content. Also, the weight loss of the DBMI-added underfill in the range of 2–4 wt % was similar to that of a typical underfill because the  $T_i$  and the curing rate of the DBMI-added underfill were similar to those of a typical underfill.

**Capillary Action**

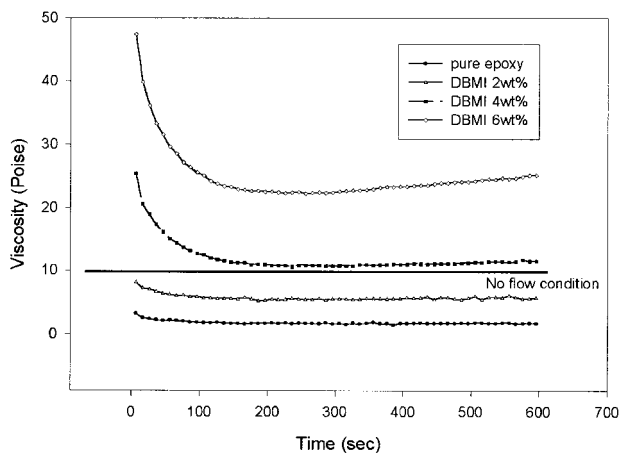
The viscosity and the surface tension of an underfill are very important factors in filling the gap between parallel plates by capillary action. To evaluate the flowability of underfill materials, the following equation suggested by Washburn<sup>10</sup> was used:

$$C_p = (\gamma \cos \theta) / 3\mu \tag{2}$$

where  $C_p$  is the coefficient of the planar penetrate,  $\gamma$  is the surface tension of the underfill,  $\theta$  is the wet angle, and  $\mu$  is the viscosity of the underfill. The coefficient of the planar penetrate signifies the penetrating power of a liquid into a gap between parallel plates, and it has units of velocity.

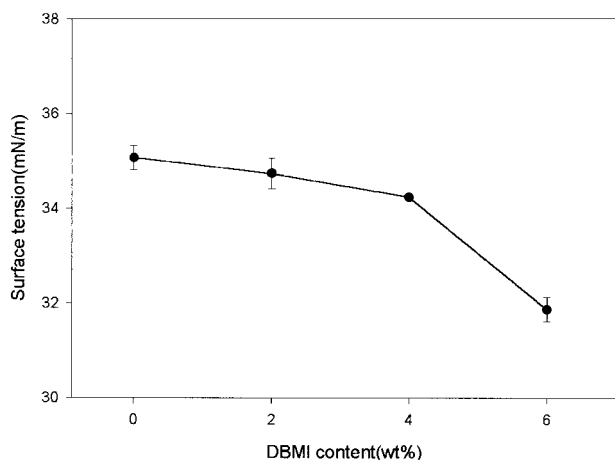


**Figure 5** The outgasing weight of the underfill during the curing reaction as a function of the DBMI content.

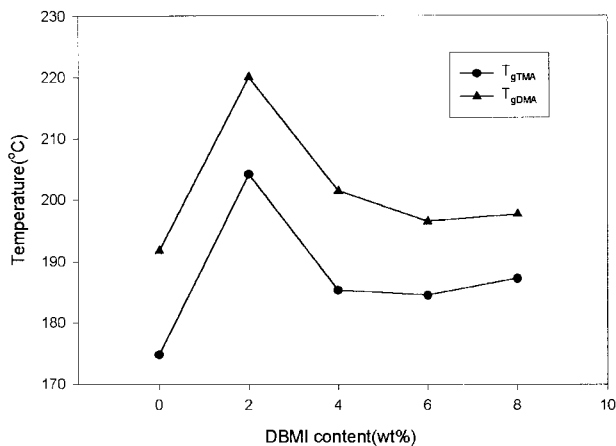


**Figure 6** The viscosity of the underfill at 80°C as a function of the DBMI content.

Typically, most underfill materials wet the parallel plates, resulting in a near-zero wet angle ( $\cos \theta \equiv 1$ ). Therefore, the flowability driven by capillary action between parallel plates is inversely proportional to the surface tension of the underfill and directly proportional to the viscosity of the underfill. In this study the viscosity was measured by an RDAII and the surface tension was measured by a tensometer. These properties of the underfill as a function of the DBMI content are shown in Figures 6 and 7, respectively. The sample for the viscosity measurement was prepared with fused silica (50 vol %), but the sample for the surface tension measurement was prepared without fillers to reduce the void effect of the underfill materials. Figure 6 shows that the viscosity of the underfill was rapidly increased by



**Figure 7** The surface tension of the underfill as a function of the DBMI content.



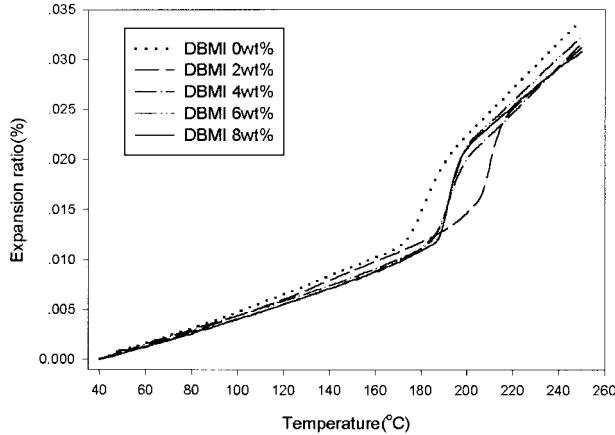
**Figure 8** The glass-transition temperature of the underfill as a function of the DBMI content.

increasing the DBMI content because the DBMI has a highly reactive group such as a urea group, it reacted with the epoxy/HMPA system at low temperature, and it has a higher molecular weight than HMPA. When more than 4 wt % of DBMI was added to the underfill, the viscosity of the underfill was higher than that of the no-flow condition as suggested by Pearson et al.<sup>4</sup> Therefore, fused-silica filled underfill (50 vol %) can achieve appropriate flowability when less than 4 wt % of DBMI is added to the underfill. However, a shear thinning effect of the underfill, which is prevented by segregation of the filler, was increased by increasing the DBMI content. When only 2 wt % of DBMI was added to the underfill, a segregation of the filler in the underfill was not observed during a 14-day period at  $-40^{\circ}\text{C}$ . Figure 7 shows that the surface tension of the underfill was decreased by increasing the DBMI content because of the inclusion in DBMI of low surface tension materials such as organic acids. As a result, the flowability by the capillary action of the underfill was very poor when more than 4 wt % of DBMI was added. However, when 2 wt % of DBMI was added to the underfill, the underfill had appropriate flowability and no segregation of the filler in the underfill was observed.

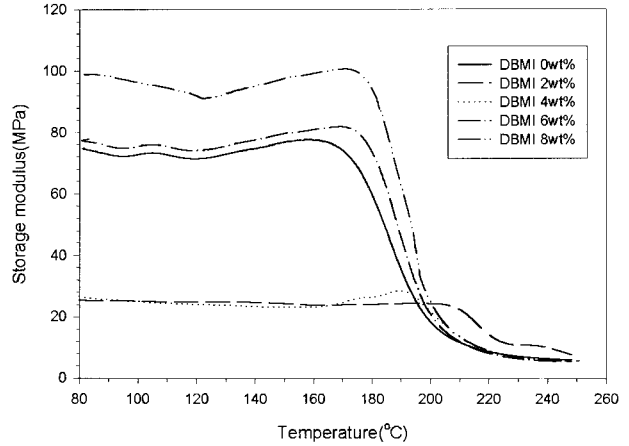
#### Thermal Reliability

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

**CTE.** The CTE of the underfill was inversely proportional to the  $T_g$  of the underfill. The conse-



**Figure 9** The thermal expansion ratios (%) of the underfill as a function of the temperature with the parameter of DBMI contents.



**Figure 10** The storage modulus of the underfill as a function of the temperature with the parameter of DBMI contents.

quent  $T_{gTMA}$  and  $T_{gDMA}$  values of the underfill as a function of the DBMI content are shown in Figure 8. The  $T_{gTMA}$  and  $T_{gDMA}$  values 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, the  $T_g$  rapidly increased. In general, the  $T_g$  of the underfill was increased by increasing the thermoset imide content because the thermal resistance group is contained in thermoset imide.<sup>11</sup>

However, in the case of DBMI, when more than 4 wt % of the DBMI was added to the underfill, the  $T_g$  of the underfill was decreased. This was because the cure reaction of the epoxy/anhydride was interfered with by the reduced mobility of the molecular and faster reaction of the underfill compared to the 2 wt % DBMI-added underfill. The thermal expansion ratio and a CTE of the cured underfill as a function of the DBMI content are shown in Figure 9 and Table III, respectively. Figure 9 shows that the thermal expansion ratio

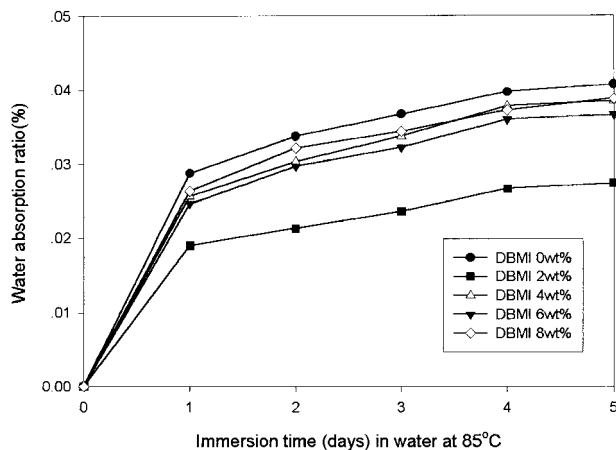
of the DBMI-added underfill decreased more than that of a typical underfill because the DBMI has a lower CTE than HMPA. Figure 9 and Table III show that the  $\alpha_{200}$  (near the solder reflow temperature) of the 2 wt % DBMI-added underfill was sharply decreased because of the high  $T_g$  of the underfill, although the  $\alpha_{150}$  in the region below the  $T_g$  of the underfill was decreased by increasing the DBMI content. As a result, when 2 wt % of DBMI was added to the underfill, the  $T_g$  and CTE of the underfill markedly improved compared to that of a typical underfill.

**Table III** CTE of Underfill as Function of DBMI Content

DBMI	$\alpha_1$	$\alpha_2$	$\alpha_{150}$	$\alpha_{200}$	$\alpha_{230}$
0 wt %	91.20	473.60	84.27	139.89	154.50
2 wt %	97.90	696.20	75.07	86.25	136.10
4 wt %	83.25	557.00	74.32	124.77	141.50
6 wt %	85.88	666.84	71.83	132.86	147.20
8 wt %	80.70	825.50	71.64	131.54	143.40

$\alpha_1$  CTE of below the  $T_g$ ;  $\alpha_2$ , CTE of upper  $T_g$ ;  $\alpha_{150}$ ,  $\alpha_{200}$ ,  $\alpha_{230}$ , CTE in the temperature range from 40 to 150, 200, and 230°C.

**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 the  $T_g$  and the crosslinking 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 the  $T_g$  or the crosslink density of the materials. The DMA-measured elastic modulus of the cured underfill as a function of the DBMI content is shown in Figure 10. The elastic modulus of a small amount of 2–4 wt % DBMI-added underfill sharply decreased in the region below the  $T_g$ . This is because DBMI, which has a longer chain than HMPA, acts as a toughener in the epoxy/HMPA system. However, when more than 6 wt % of DBMI was added to the underfill, because of the self-additional reaction of DBMI, the elastic modulus of the underfill was increased by increasing the DBMI content.



**Figure 11** The water resistance of the underfill as a function of the time with the parameter of DBMI contents.

**Water Resistance.** The water resistance of the underfill as a function of the DBMI content is shown in Figure 11. 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 the materials were inversely proportional to the crosslinking density, which can be evaluated by measuring the  $T_g$ .

## CONCLUSIONS

1. A DBMI was used as a cohardener in an epoxy/anhydride curing reaction.
2. When the  $R$  value of DBMI-added underfill was 1, a cured DBMI-added underfill formed a full network structure.
3. When a small amount of DBMI (2 wt %) was added to the underfill, the flowability of the underfill was appropriate and a seg-

regation of the filler in the underfill was not observed.

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

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