Noncatalytic Curing of an Epoxy Siloxane Monomer with 1,2,4-Cyclohexanetricarboxylic Anhydride: Properties and Light-Emitting Diode Encapsulation

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ABSTRACT: The noncatalytic anhydride curing of an epoxy siloxane monomer, 1,3-bis[2-(3-{7-oxabicyclo[4.1.0]-heptyl})ethyl]tetramethyldisiloxane, with 1,2,4-cyclohexanetricarboxylic anhydride (H-TMAn) and methyl hexahydrophthalic anhydride (MeHHPA) was studied. Different H-TMAn concentrations, ranging from 13 to 58 mol %, were evaluated. The highest curing exotherm and highest glass-transition temperature were both found at 50 mol %. MeHHPA showed a sharp dependence of the thermal stability and thermal discoloration on the anhydride concentration. In contrast, the H-TMAn concentration did not much affect the thermal stability or thermal discoloration. H-TMAn could be diluted up to 3 times with MeHHPA to reduce the initial viscosity without a loss of noncatalytic reactivity. Unlike MeHHPA, H-TMAn experienced very little anhydride evaporation and weight reduction. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2301–2306, 2009

Key words: differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

INTRODUCTION

Epoxy resins are versatile thermosets used in a wide range of applications, including encapsulation, coating, adhesion, and composites. Light-emitting diode (LED) encapsulation is an important epoxy application that consists of methyl hexahydrophthalic anhydride (MeHHPA) along with various epoxy monomers.[1,2]

Ease of handling, a low viscosity, and a long storage life are the advantages of liquid-anhydride-cured epoxy systems. On the other hand, anhydride evaporation and catalyst residues are disadvantages. Anhydride evaporation causes volume shrinkage, and this generates internal stress within the package. An acceleration catalyst (a tertiary amine, imidazole, or phosphine) accelerates the photothermal discoloration and reduces the LED light output intensity as discolored epoxy absorb its own light emission.[3]

We have reported various improvements in epoxy-based LED encapsulation. Two epoxy monomers, both hydrogenated bisphenol A glycidyl ether[3,4] and epoxy siloxane monomer,[5–7] have been evaluated for minimum discoloration.

Hydrogenated trimellitic anhydride [1,2,4-cyclohexanetricarboxylic anhydride (H-TMAn)] was origi-nally developed as a precursor for various plasticizers.[8] Then, Mitsubishi Gas Chemical Co., Ltd. (Tokyo, Japan), invented liquid H-TMAn for noncatalytic anhydride curing.[9,10] H-TMAn can be reacted with epoxy groups without the addition of an acceleration catalyst.

Eliminating both photothermal discoloration and anhydride evaporation was our initial interest in H-TMAn. In surface-mounted LED devices that are very small and thin, anhydride evaporation causes significant internal stress and further reliability issues. In a previous article,[11] we evaluated the properties and cure shrinkage using hydrogenated bisphenol A glycidyl ether and H-TMAn. H-TMAn demonstrated a significant improvement in cure shrinkage. However, we could not confirm the discoloration behavior because of the thermal stability of the epoxy monomer itself.

In this article, we report the noncatalytic curing of an epoxy siloxane hybrid with H-TMAn. A detailed comparison of the curing behavior, cured epoxy properties, and thermal discoloration was made between H-TMAn and MeHHPA.

EXPERIMENTAL

Materials

An epoxy siloxane monomer of 1,3-bis[2-(3-{7-oxabicyclo[4.1.0]heptyl})ethyl]tetramethyldisiloxane (BEPDS) was prepared according to Crivello and Lee.[12]

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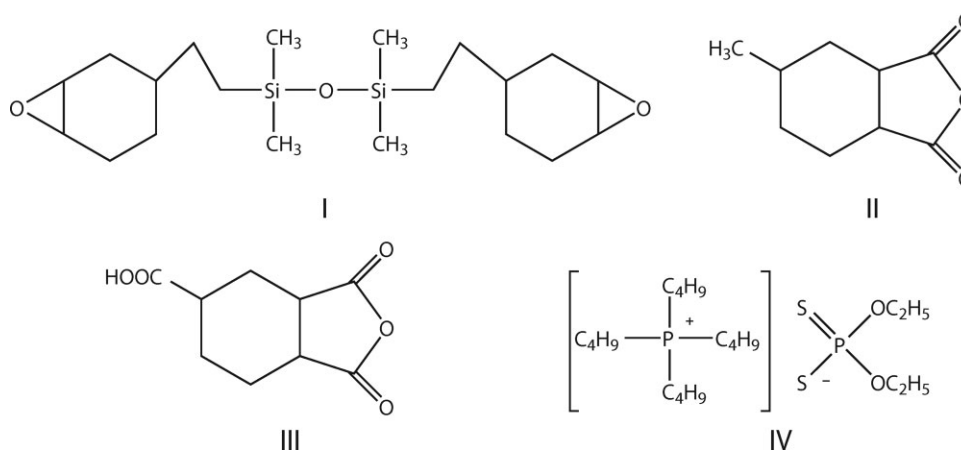
Scheme 1　Chemical structures of BEPDS (**I**), MeHHPA (**II**), H-TMAn (**III**), and PX-4ET (**IV**).

H-TMAn was a gift from Mitsubishi Gas Chemical. MeHHPA was obtained from New Japan Chemical Co., Ltd. (Kyoto, Japan). The acceleration catalyst tetra-*n*-butylphosphonium *o,o*-diethylphosphorodithioate (PX-4ET) was received from Nippon Chemical Industrial Co., Ltd. (Tokyo, Japan). All chemicals were used without further purifications. The chemical structures are illustrated in Scheme 1.

Curing of the epoxy siloxane

In a typical procedure, BEPDS and the anhydride were mixed in a flask and dried *in vacuo* to remove the oxygen. Then, the mixture was fed into a 2-mm-thick casting unit, as shown in Figure 1. This unit included a silicone tube and two glass plates attached to a silicone-coated polyester film. This was heated at 150°C for 3 h. After curing, a 2-mm-thick epoxy plate was removed from this unit. This bulk plate was cut into 2-cm square pieces for transpar-
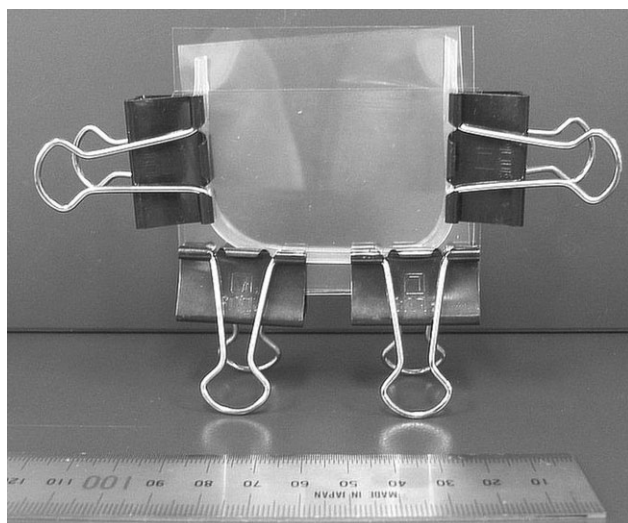
ency measurements and thermal discoloration testing.

Characterization

All thermal analysis was measured under the same conditions used in the previous report.[2–7] Differential scanning calorimetry (DSC) was performed with a Shimadzu (Kyoto, Japan) DSC60 at a heating rate of 5°C/min under a flow of nitrogen gas. Thermogravimetric analysis (TGA) was performed with a Shimadzu TG/DTA 60 at a heating rate of 10°C/min under a nitrogen atmosphere. Thermal mechanical analysis (TMA) was recorded on a Shimadzu TMA60 at a heating rate of 5°C/min under a flow of nitrogen gas. Dynamic mechanical analysis was performed with a Seiko Instruments (Chiba, Japan) DMS 6100 at a heating rate of 4°C/min with a fixed frequency of 10 Hz under a nitrogen atmosphere. The transmittance spectrum of the polymerized plaque was measured on a Shimadzu UV-3100 from 300 to 800 nm. The transmittance spectrum was first converted to color points (CIE X, Y, and Z), and then it was converted into the yellowness index

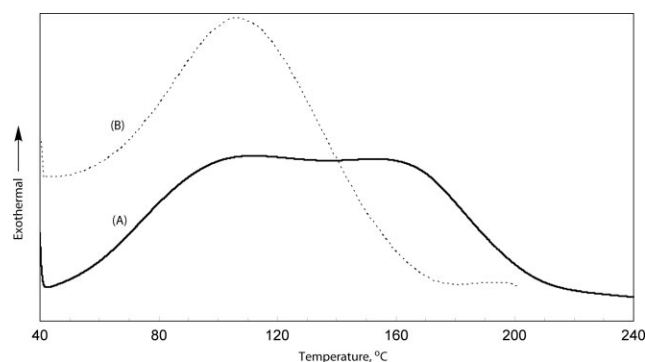**Figure 1**　Epoxy plate casting unit.

Figure 2　DSC thermograms of epoxy siloxane hybrid curing with (A) 50 mol % H-TMAn and (B) 49 mol % MeHHPA and 1 mol % PX-4ET (5°C/min ramp, 10 mg).

H-TMAn (mol %)[a]	Curing behavior by DSC[b]		T_g (°C)	Cured properties[c]		
	Curing reactivity (J/g)	Onset (°C)		CTE (ppm)		
				Below T_g	Above T_g	Difference
58	259.3	53	148.7	—	—	
55	283.5	57	177.3	95	121	26
50	398.9	53	199.4	—	—	
47	375.1	61	189.5	105	131	26
43	316.3	60	187.4	—	—	
38	256.8	64	145.8	124	161	37
31	211.7	70	131.8	131	182	51
23	81.8	96	81.7	136	230	94
13	60.3	95	—	—	—	

[a] No catalyst (BEPDS + H-TMAn = 100 mol %).
[b] Measured from 40 to 260°C with a 5°C/min ramp.
[c] Samples were cured at 120°C for 1 h and then at 150°C for 3 h.

according to ASTM Method E 313. These calculations were done by a computer program included with the Shimadzu UV-3100 spectrometer. The viscosity of the mixed epoxy siloxane monomer and anhydride before curing was measured with a Brookfield (Middleboro, MA) DV-II viscometer at 25°C at a speed of 20 rpm

RESULTS AND DISCUSSION

Effect of the H-TMAn concentration on the cured properties

The optimum cured properties [e.g., the highest crosslink density and the lowest coefficient of thermal expansion (CTE) both below and above the glass-transition temperature (T_g)] can be found in a stoichiometric mixture in many cases. A previous study of BEPDS with MeHHPA showed both the highest T_g value and the lowest CTE difference (from above T_g to below T_g) at a 1 : 1 ratio.[5] However, the optimal ratio of H-TMAn to the epoxy monomer could be different. The optimum ratio of hydrogenated bisphenol A glycidyl ether to H-TMAn was 1 : 0.75.[11]

In the first section, the effects of the H-TMAn concentration on the curing reactivity and properties were studied. Figure 2 shows a comparison of DSC thermograms for H-TMAn (noncatalytic) and MeHHPA (catalytic). Table I summarizes the curing behavior and cured properties.

According to the DSC thermograms, H-TMAn had a broader exothermal peak than MeHHPA. A similar result was observed with hydrogenated bisphenol A glycidyl ether. With the H-TMAn concentration increasing, the curing reactivity increased to the maximum at 50 mol % but decreased again at 58 mol %. At the same time, the highest T_g value of 199°C was observed. The highest possible H-TMAn concentration was 58 mol % because of the high viscosity and difficulty in the mixing process. The onset temperature decreased with the H-TMAn concentration increasing. For the lower side, 30 mol % was the lowest H-TMAn concentration that enabled both a 2-mm-thick plaque and a surface-mount-type LED (shown later in Fig. 8) to be cured. The thermal expansion of the cured hybrid, both below and above T_g, increased with the H-TMAn concentration decreasing. It is notable that the CTE difference (from above T_g to below T_g) was 26–50 ppm when the H-TMAn concentration was 30 mol % or higher.

With H-TMAn, the cured properties were much better than those obtained with MeHHPA. The highest T_g point with MeHHPA was 58°C lower (141°C), and the CTE difference was doubled (80–100 ppm).[5]
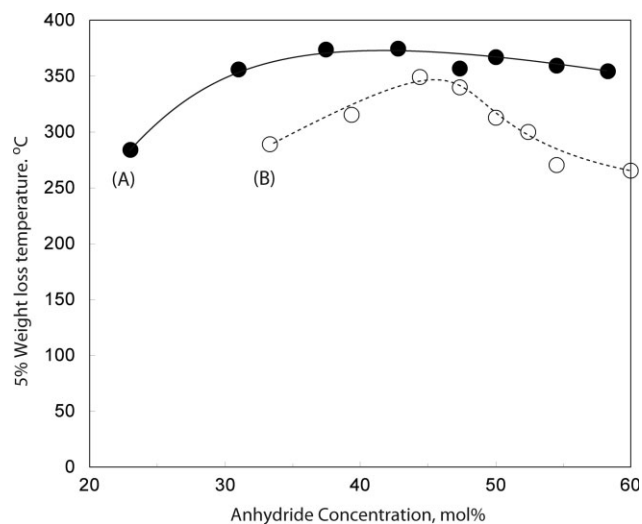

Figure 3 Thermal stability of the cured epoxy siloxane hybrid with different anhydride concentrations: (A) BEPDS–H-TMAn and (B) BEPDS–MeHHPA with 0.71 wt % PX-4ET as a catalyst.
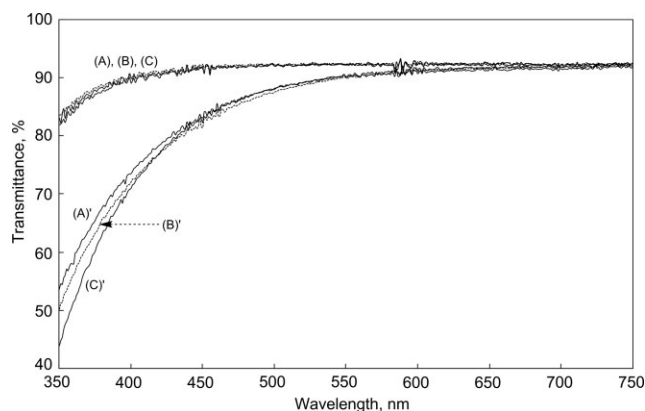
Figure 4 Transmittance spectra of the epoxy siloxane hybrid cured with different H-TMAn concentrations: (A,A′) 0.55, (B,B′) 0.47, and (C,C′) 0.31 mol % (thermal aging at 150°C for 72 h).

Thermal stability and discoloration

Figure 3 compares the thermal stability of the noncatalytic H-TMAn cure and the catalytic MeHHPA cure with different anhydride concentrations. The 5% weight loss temperature was used as an indicator of thermal stability. The epoxy siloxane cured with H-TMAn always showed higher thermal stability than that cured with MeHHPA. H-TMAn demonstrated constant thermal stability with a wider concentration range of 38–55 mol %. In contrast, the highest thermal stability was observed within a very narrow concentration range for MeHHPA.

On the basis of these results, the thermal stability of the cured epoxy was very sensitive to changes in the MeHHPA concentration but was very stable with changes in the H-TMAn concentration. For stabilization of the production quality, MeHHPA requires tight control of the mixing ratio.

Figure 4 shows the transmission spectrum of an epoxy siloxane hybrid with different H-TMAn concentrations before and after thermal discoloration. With increasing thermal discoloration, light absorption started from a shorter wavelength and then
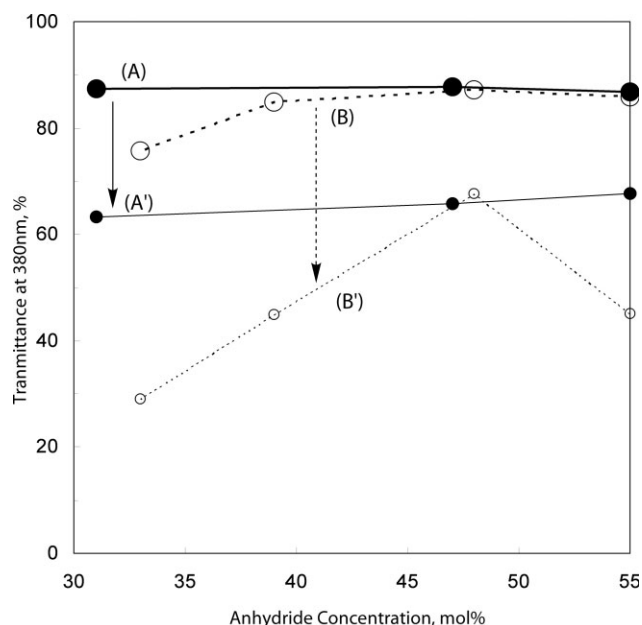

Figure 5 Transmission intensity change in the epoxy siloxane hybrid before and after thermal discoloration: (A,A′) BEPDS–H-TMAn and (B,B′) BEPDS–MeHHPA–PX-4ET (thermal aging at 150°C for 72 h).

shifted to a longer wavelength. To demonstrate white LED encapsulation, we evaluated the transmission change at 380 nm. Most commercial white LEDs consist of phosphors and LEDs with near-UV (peak wavelength = 380 nm) or blue (450–470 nm) emissions. Yttrium aluminum garnet is one of the most popular phosphors used for white LEDs; it converts blue light into yellow light. Figure 5 shows the transmission change before and after thermal discoloration (150°C 72 h) with different anhydride concentrations. When the anhydride concentration was about 50 mol %, thermal discoloration was at a similar level for both H-TMAn and MeHHPA. Significant thermal discoloration was observed with MeHHPA when its concentration was lower or higher than 50 mol %. H-TMAn showed constant thermal discoloration between 31 and 55 mol %.

TABLE II
Effect of the H-TMAn Concentration on the Curing Reactivity

Formulation (mol %)[a]				Curing behavior[c]		Cured properties[d]	
BEPDS	H-TMAn	MeHHPA	Viscosity (cP)	Curing reactivity (J/g)	Onset (°C)	5% weight loss (°C)	T_g (°C)
50	50	0	2798	398.9	52.8	367	199.4
50	37.5	12.5	1111	350.0	63.7	361	186.7
50	25	25	357	354.0	75.1	354	179.3
50	12.5	37.5	172	326.3	85.7	353	162.5
50	0	50	80	6.3	136.1	—	—
50	0	50[b]	92	175.8	121.5	355	145.0

[a] No catalyst.
[b] The sample contained 1.0 wt % PX-4ET as a catalyst.
[c] Measured by DSC from 40 to 260°C with a 5°C/min ramp.
[d] The samples were cured at 120°C for 1 h and then at 150°C for 3 h.

A new finding is that the H-TMAn concentration did not affect the thermal stability or thermal discoloration. The mixing ratio of the anhydride and epoxy monomer sometimes causes product quality variation. H-TMAn eliminates such variation without tight control of the mixing ratio.

Curing reactivity of BEPDS with MeHHPA-diluted H-TMAn

High viscosity is a major visible disadvantage of H-TMAn. Because H-TMAn can be dissolved in MeHHPA, the initial viscosity can be reduced by the replacement of H-TMAn with MeHHPA.[13] In Table II, we summarize the mixed viscosity, curing behavior, and cured properties.

The initial viscosity was dramatically reduced. For example, replacing half of H-TMAn with MeHHPA reduced the mixed viscosity by about an eighth. The reactivity and cured properties remained reasonable. With increasing MeHHPA concentration, the curing onset temperature was shifted higher, and the total exothermal energy decreased. When 75% of H-TMAn was replaced with MeHHPA, T_g decreased 37°C (from 199.4 to 162.5°C), but the thermal stability dropped only 14°C (from 367 to 353°C).

Replacing H-TMAn with MeHHPA may reduce its reactivity if no catalyst is added. Figure 6 shows DSC thermograms for different H-TMAn/MeHHPA ratios. With increasing MeHHPA concentration, both the onset and ending temperatures shifted higher.

Anhydride evaporation

Anhydride evaporation is one of the few disadvantages of MeHHPA. Evaporation happens during the cure reaction, and this causes volume shrinkage in the final cured epoxy. As we reported before, H-TMAn hardly evaporates during the epoxy cure.[11]
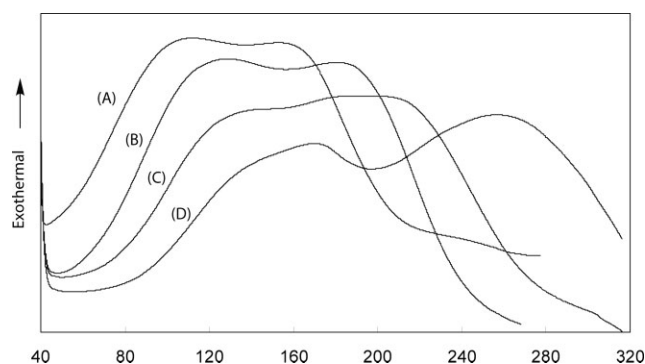

Figure 6 DSC thermogram of epoxy siloxane curing with an H-TMAn–MeHHPA mixture: (A) 100 mol % H-TMAn, (B) 75 mol % H-TMAn and 25 mol % MeHHPA, (C) 50 mol % H-TMAn and 50 mol % MeHHPA, and (D) 25 mol % H-TMAn and 75 mol % MeHHPA (5°C/min ramp, 10 mg).
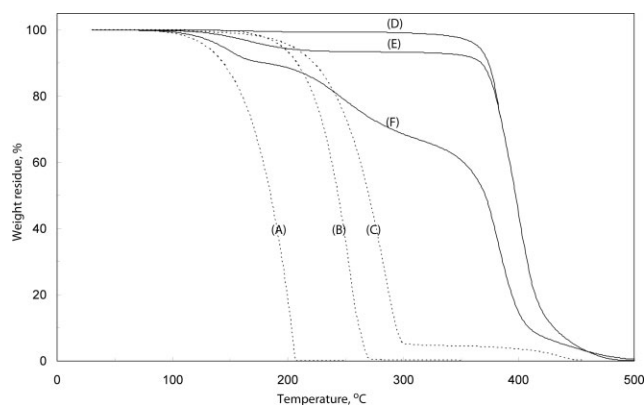

Figure 7 Thermal weight-loss behavior of the raw material and uncured epoxy mixture: (A) MeHHPA, (B) H-TMAn, (C) BEPDS monomer, (D) 100 : 100 : 0 BEPDS/H-TMAn/MeHHPA mixture, (E) 100 : 50 : 50 BEPDS/H-TMAn/MeHHPA mixture, and (F) BEPDS/MeHHPA/PX-4ET mixture.

Figure 7 illustrates TGA curves of the epoxy monomer, anhydrides, and mixed epoxy formulations. TGA of the uncured epoxy indicated weight loss during the cure.

MeHHPA lost its weight [Fig. 7(A)] much faster than H-TMAn [Fig. 7(B)] or BEPDS monomer [Fig. 7(C)]. The evaporation of MeHHPA started just above 100°C, and it completely evaporated by 210°C. The degradation of H-TMAn started at 150°C. This meant that no anhydride evaporation was expected when the curing temperature was below 150°C. In the mixed formulation with H-TMAn [Fig. 7(D)], weight loss started at 300°C. When half of H-TMAn was diluted with MeHHPA, a small weight loss was
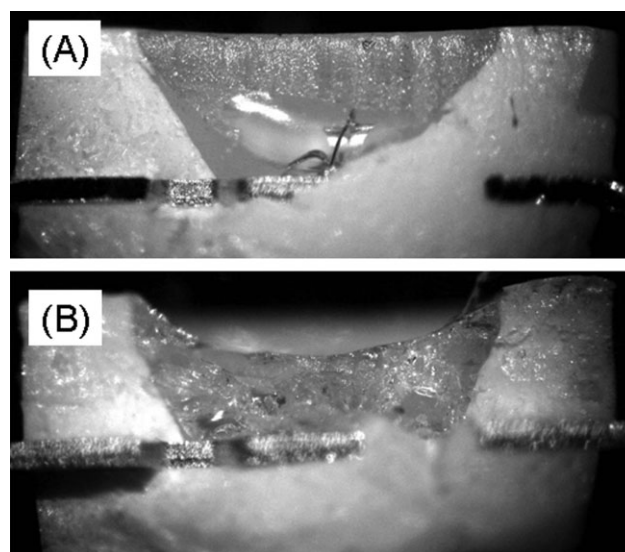

Figure 8 Cross-section pictures of surface-mount-type LED devices after encapsulation with (A) BEPDS–H-TMAn (100 : 100) and (B) BEPDS–MeHHPA–PX-4ET (100 : 99 : 1).

observed between 100 and 200°C [Fig. 7(E)]. The highest weight decrease was observed in a mixture of BEPDS, MeHHPA, and a catalyst [Fig. 7(F)]. On the basis of these results, noncatalytic H-TMAn experienced almost no anhydride evaporation during the cure process [Fig. 7(F)].

Figure 8 shows a cross-section picture of a surface-mount-type LED after curing. The surface of the encapsulant was flat with H-TMAn, but it was concave with MeHHPA. Anhydride evaporation caused this concavity. Besides this, there was no visual defect such as cracking or delamination in the two samples.

CONCLUSIONS

As a curing agent for the epoxy siloxane hybrid, H-TMAn was a better anhydride in terms of the cured properties and stability. A significant difference between H-TMAn and MeHHPA was seen in the thermal stability and thermal discoloration. These thermal properties highly depended on the MeHHPA concentration but not on the H-TMAn concentration. H-TMAn allowed a wider range of anhydride concentrations for the best cured properties. This is a quite desirable characteristic for production. The level of thermal discoloration for the H-TMAn-cured hybrid was similar to the best record for the MeHHPA-cured hybrid. The high viscosity of H-TMAn is a visible problem, but this can be improved by dilution with MeHHPA without the addition of an acceleration catalyst. In a more detailed investigation of this anhydride, we are evaluating LED encapsulation and its package reliability. Surface-mount-type device fabrication and the important moisture preconditioning reflow process will be reported soon.

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