

Non-Catalytic Anhydride Curing of Hydrogenated Bisphenol-A Glycidyl Ether with 1,2,4-Cyclohexanetricarboxylic Anhydride and Light Emitting Diode Encapsulation

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ABSTRACT: Nuncatalytic anhydride curing of hydrogenated bisphenol-A glycidyl ether (YX8000) using hydrogenated trimellitic anhydride (1,2,4-cyclohexanetricarboxylic anhydride, H-TMA_n) and methylhexahydrophthalic anhydride (MeHHPA) were studied. Differential scanning calorimetry data shows no exothermal under 190°C using MeHHPA without catalyst because of the low reactivity. On the other hand, H-TMA_n had higher reactivity and it can be cured without catalyst. The effect of anhydride concentration both on curing and on properties was studied in detail. For example, the highest T_g was found when YX8000 : H-TMA_n = 100 : 75 or YX8000 : MeHHPA = 100 : 100. The highest curing exothermal was found at similar

ratio. Following, the encapsulation of light emitting diode (LED) was prepared with two anhydrides. Surface volume decrease was observed with MeHHPA by its evaporation, but H-TMA_n gave flat surface. After thermal cycle test of these LED, H-TMA_n was found to have better crack resistance than MeHHPA. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 962–966, 2006

Key words: epoxy resin; 1,2,4-cyclohexanetricarboxylic anhydride; methylhexahydrophthalic anhydride; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA); light-emitting diodes (LED)

INTRODUCTION

Epoxy resin has been used in a wide range of application such as coating, adhesive, and composite. Light emitting diode (LED) encapsulation is an important application for transparent epoxy resin. In this transparent epoxy resin, methylhexahydrophthalic anhydride (MeHHPA) and hexahydrophthalic anhydride (HHPA) are used as a curing agents.¹

Although the reactivity of these anhydride are low, they require acceleration catalyst such as tertiary amine, imidazole, or phosphine. The curing temperature also needs over 100°C for few hours to complete its curing.

Because of the recent development of LED, the emission spectrum wavelength are becoming shorter and light output intensity are rapidly growing.² At the same time, discoloration of epoxy encapsulant and decreased light output maintenance has become major issues.^{3,4}

To prevent the discoloration of epoxy resin, the author has reported the discoloration behavior of hydrogenated bisphenol-A glycidyl ether both with anhydride curing⁵ and with cationic polymerization⁶ In addition to this epoxy, we are interested in the epoxy-siloxane hybrid to improve discoloration. We have already reported the properties of the hybrid materials, both with anhydride curing⁷ and with cationic polymerization.⁸

From our series of studies, it is found that UV discoloration was greatly accelerated by unsaturated bond concentration in the catalyst, in most cases by catalyst concentration. Thermal discoloration has also been much correlated with catalyst concentration. Smallest catalysts concentration may minimize the discoloration, but the optimization of material properties becomes quite difficult. Until now, there were no other anhydrides that satisfy the optical transparency.

It is well know that carboxyl acids such as dimer fatty acid, nonanedioic acid, and trimellitic anhydride were good curing agent of epoxy resin, which are widely used in painting application. The reactivity of these acids is very fast and no catalyst is required because free carboxyl group accelerate the polymerization. In recent years, hydrogenated trimellitic anhydride is commercially available.^{9,10}

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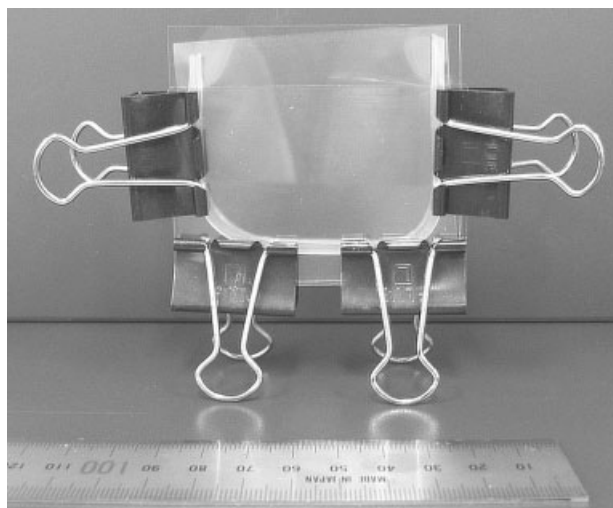


Figure 1 Plaque equipment.

In this study, noncatalytic anhydride curing of hydrogenated bisphenol-A glycidyl ether using hydrogenated trimellitic anhydride (1,2,4-cyclohexanetricarboxylic anhydride)¹¹ was performed. The reactivity, mechanical properties, and LED encapsulation were studied in detail.

EXPERIMENTAL

Materials

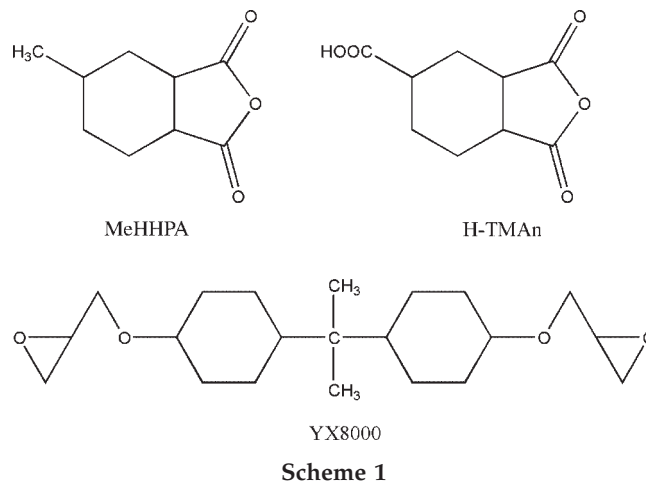
Hydrogenated bisphenol-A glycidyl ether (YX8000) was generously donated by Japan Epoxy Resin Co. Ltd. 1,2,4-cyclohexanetricarboxylic anhydride (H-TMA_n, Scheme 1) was gift from Mitsubishi Gas Chemical Co. Ltd. (Tokyo, Japan). Methyhexahydrophthalic anhydride (MeHHPA) was from New Japan Chemical Co. Ltd. (Kyoto, Japan). Tetra-*n*-butylphosphonium *o,o*-diethylphosphorodithioate (PX-4ET) was received from Nippon Chemical Industrial Co., Ltd. (Tokyo, Japan).

Curing of hydrogenated bisphenol-a glycidyl ether

Typical procedure: YX8000, Anhydride, and sometimes PX-4ET were mixed in flask and dried *in vacuo* to remove oxygen. H-TMA_n was heated to 60°C in advance to reduce the viscosity. Then, the mixture was fed into a 2-mm thick casting as shown in Figure 1. This unit included two glass plate attached with silicone coated polyester film and silicone tube. This was heated at 120°C for 2 h followed by 150°C for 2 h. After curing, the epoxy plaque was removed from this unit.

Measurement

Differential scanning calorimetry (DSC) was measured with Shimadzu DSC60 at heating rate of 5°C/



min under a flow of N₂ gas. Thermal gravimetric analysis (TGA) was done with Shimadzu TG/DTA 60 at a heating rate of 10°C/min under nitrogen atmosphere. Thermal mechanical analysis (TMA) was recorded on Shimadzu TMA60 at heating rate of 5°C/min under a flow of N₂ gas. Transmittance spectrum of polymerized plaque was measured on Shimadzu UV-3100 from 300 to 800 nm and yellowness index were calculated from these spectrum intensity. Shore D hardness was measured by Durometer.

Light emitting diode encapsulation

Light emitting diode encapsulation was evaluated with surface mounted devices that consist of silver plated copper lead frame and white plastic reflector. AMODEL A-4122NL polyphthalamide is used as the reflector materials, which come from Solvay Ad-

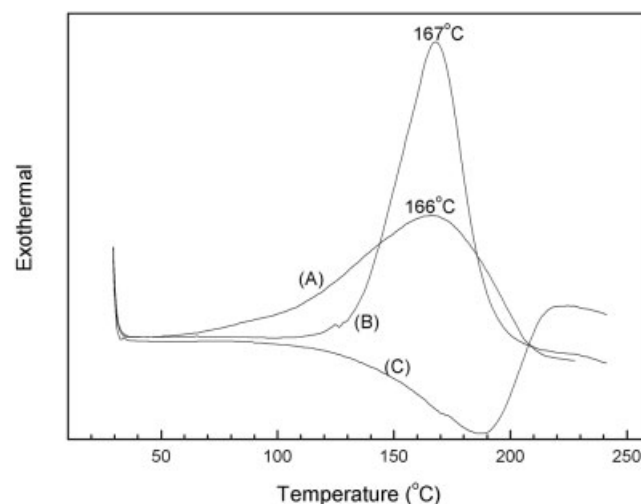


Figure 2 DSC thermograms of (A) YX8000 + H-TMA_n (100 : 100), (B) YX8000 + MeHHPA + PX-4ET (100 : 99 : 1) and (C) YX8000 + MeHHPA (100 : 100) without catalyst.

TABLE I
Polymerization of YX8000 with H-TMAN and MeHHPA

Formulation (mol ratio)		DSC			ΔH (J/g)	Peak (°C)
YX8000	H-TMAN	MeHHPA	PX-4ET			
100	100	0	0	286	166.5	
100	75	25	0	273	175.4	
100	50	50	0	205	193.5	
100	25	75	0	147	202.5	
100	0	100	0	75	228.7	
100	0	99	1	215	167.8	

Curing condition: 120 °C, 12 h.

vanced Polymers (Georgia, USA). This amide contains glass fiber and TiO₂. Mixed epoxy resin (3.1 μ L) was dispensed into concave of LED package and cured 120°C for 12 h. Thermal cycle test of LED devices was performed in thermal shock chamber. The lowest and highest exposure temperature is -40°C and 120°C, respectively, one cycle is 30 min with each 15 min.

RESULTS AND DISCUSSION

Curing reactivity of epoxy resin with 1,2,4-cyclohexanetricarboxylic anhydride

Using 1,2,4-cyclohexanetricarboxylic anhydride (H-TMAN), curing reaction of hydrogenated bisphenol-A glycidyl ether (YX8000) was proceeded without catalyst but completed within few hours. First, curing behavior of YX8000 with two anhydrides was compared by differential scanning calorimetry (DSC).

As shown in Figure 2, exothermal started from 50°C with H-TMAN and reached to maximum at 166°C. The total exothermal (ΔH) was 286 J/g. But curing with MeHHPA without catalyst, exothermal was not observed until 185°C and then reached to peak at 228°C. In this case, base line reduction was observed due to the anhydride evaporation. After DSC measurement, the polymer volume was apparently decreased. Then the acceleration catalysts of Tetra-*n*-butylphospho-

nium *o,o*-diethylphosphorodithioate (PX-4ET) was added (1 mol %) to MeHHPA. This catalyst has smaller discoloration as compared with other catalyst as reported in our previous paper.^{5,7} Exothermal was observed from 105°C, ΔH and peak temperature was 215 J/g and 167°C, respectively.

To compare the reactivity of anhydrides, curing reaction of H-TMAN and MeHHPA mixture under epoxy equivalent was monitored by DSC. As shown in Table I, ΔH was decreased with increasing MeHHPA concentration and peak exothermal temperature was increased. From these results, H-TMAN has higher reactivity than MeHHPA has.

Effect of anhydride concentration

Next, the effect of anhydride concentration both on reactivity and on polymer properties was studied. In the Bisphenol-A glycidyl ether, the effect of MeHHPA concentration on properties are well studied, and most optimal characteristics were appeared at equivalent concentration.¹²

Table II summarized the properties and H-TMAN concentration. Maximum ΔH was observed when the molar ratio between epoxy and H-TMAN was missing from 100 : 100 to 100 : 75. With decreasing H-TMAN concentration, ΔH was decreased, and exothermic peak temperature was increased.

TABLE II
Effect of H-TMAN Concentration on Polymerization and Properties

Formulation (mol ratio)		DSC		Polymer properties		
YX8000	H-TMAN	ΔH (J/g)	Peak (°C)	Hardness Shore D	5% weight loss (°C)	T_g , DSC (°C)
100	125	193	165	88	252	97
100	110	221	165	89	254	111
100	100	286	166	88	273	110
100	90	283	163	88	284	120
100	75	287	161	88	320	138
100	60	220	167	88	336	135
100	45	193	177	88	346	119
100	30	79	180	86	356	75
100	20	75	187	83	323	65
100	10	62	194	20	261	43

Curing condition: 120°C 2 h and then 150°C 3 h.

TABLE III
Effect of MeHHPA Concentration on Polymerization and Properties

Formulation (mol ratio)		DSC		Polymer properties		
YX8000	MeHHPA ^a	ΔH (J/g)	Peak (°C)	Hardness Shore D	5% weight loss (°C)	T_g , DSC (°C)
100	125	150	161	87	232	96
100	110	162	162	86	292	110
100	100	215	167	83	305	117
100	90	198	164	85	311	114
100	75	190	166	85	355	105
100	60	185	166	82	355	85
100	45	162	173	78	317	48
100	30	106	173	33	265	N/A

Curing condition: 120°C 2 h and then 150°C 3 h.

^a Contain 1.0 wt % PX-4ET in MeHHPA.

Table III shows the same experiment but with MeHHPA and 1.0 mol % of PX-4ET. Highest ΔH was observed only epoxy equivalent concentration and then ΔH was decreased with decreasing MeHHPA concentration. The maximum hardness was about 90 with both anhydrides. Higher hardness over 80 was maintained until 20 parts of H-TMAN, but fell quickly at 45 parts or less of MeHHPA.

The largest glass transition temperature (T_g) was 138°C when 75 part of H-TMAN was used, although 117°C was the largest with 100 part of MeHHPA. Thermal stability of polymer was evaluated by thermo gravimetric analysis (TGA) and 5% weight loss temperature was used as an index. The highest 5% weight loss temperature was almost same but this archived with 30 part of H-TMAN or 75–60 part of MeHHPA. Coefficient of thermal expansion (CTE) was measured by thermo mechanical analysis (TMA) and these results were shown in Table IV. T_g value seems to be similar with DSC measurement. CTE both α_1 and α_2 was decreasing with anhydride concentration and smallest CTE appeared at YX8000 : H-TMAN = 100 : 75 or YX8000 : MeHHPA = 100 : 100. H-TMAN gave smaller CTE both α_1 and α_2 as compared with MeH-

HPA. These lower CTE and higher T_g indicated that H-TMAN gave higher crosslinking density than MeHHPA did. Curing mechanism of epoxy resin with H-TMAN or with trimellitic anhydride was not reported before, but earlier mentioned results suggested that carboxyl group apparently contributed crosslinking.

Anhydride evaporation and LED encapsulation

Anhydride evaporation is a major issue, both for manufacturing and for product reliability. The amount of evaporation has related with reactivity. If the curing was completed faster using high reactive catalyst, total evaporation was smaller. Although such high reactive catalyst usually contains phenyl group and causes more discoloration under UV irradiation.⁵ The curing reactivity of YX8000 is smaller than other epoxy like glycidyl ether of bisphenol-A and cycloaliphatic epoxy resin.

We compared this new anhydride with MeHHPA, for surface mounted LED encapsulation.^{13,14} Considering the specific gravity, the cubic volume of those two should be the same.

Figure 3 shows the cross section picture of LED just after it was cured. The surface of encapsulant was flat with H-TMAN, whereas surface concave with MeHHPA. This concave surface will be the results after

TABLE IV
Effect of Anhydride Concentration on Mechanical Properties

Epoxy : Anhydride (mol ratio)		CTE (ppm)		T_g (°C)	
		α_1	α_2	TMA	DSC
100 : 125	H-TMAN	85	183	97	97
100 : 100		79	186	110	117
100 : 75		64	185	131	138
100 : 45		77	197	122	119
100 : 20		131	251	63	65
100 : 125		MeHHPA	98	202	97
100 : 100	77		207	108	117
100 : 75	92		222	103	105
100 : 45	134		261	51	48

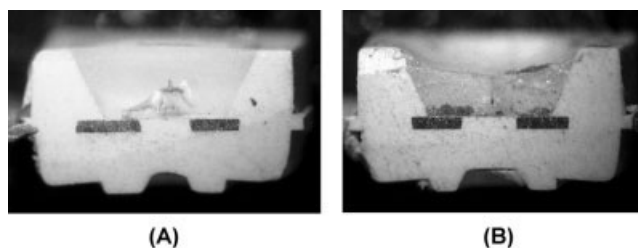


Figure 3 Cross section picture of LED devices after encapsulation with (A) YX8000 + H-TMAN (100 : 100), (B) YX8000 + MH-700 + PX-4ET (100 : 99 : 1). The cracks seen inside were caused when cross sectioning.

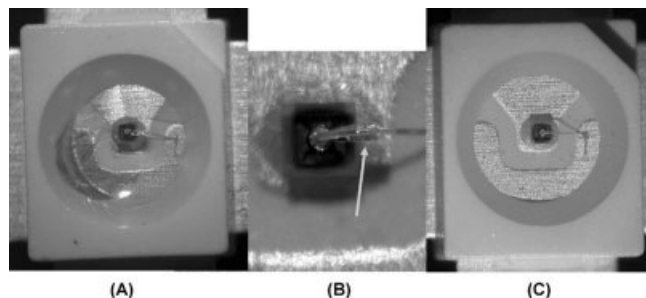


Figure 4 Picture of LED after thermal cycle test. (A) Encapsulated with YX8000 + MeHHPA + PX-4ET (100 : 99 : 1), (B) Details of (A) near Au wire bonding and (C) Encapsulated with YX8000 + H-TMAN (100 : 100). Thermal cycle condition: -40°C (15 min) to 120°C (15 min) 100 cycles.

anhydride evaporation. Beside this, there was no visual defect such as crack and delamination in any samples.

Next, thermal shock of these LED has been tested. As shown in Figure 4, crack was generated in the interface between top of lead flame and epoxy resin with MeHHPA before 50 cycles. Other minute cracks were also generated surrounding the gold wire, which connect a die and an electrode. On the other hand, we cannot find any errors in H-TMAN until 500 cycles.

The interfacial cracks between lead flame and epoxy resin may cause light reflection change. The reason why lead flame not only carry electron but reflect light output from LED die. The light output from LED die is going through transparent epoxy resin and reflect on Lead flame. When there was crack in this interface, some of light from epoxy resin could not reflect because of air is low reflective index. In addition, these cracks are growing cycle by cycle or LED operation.

This LED package evaluation may demonstrate the relative difference of properties, but it is very difficult to evaluate with properties quantitatively. Using MeHHPA, epoxy-anhydride ratio will be varied from surface to bottom by its evaporation, and crosslink density on surface should be lower than bottom, whereas, H-TMAN gave more homogeneous crosslink density. The cracks will be generated as a result of decreasing the crosslinking density. As mentioned

earlier, CTE increase and T_g decrease will also help the crack generation.

CONCLUSIONS

We found two advantages using H-TMAN for curing hydrogenated bisphenol-A glycidyl ether, as compared with conventional MeHHPA. One is high reactivity, which does not need a catalyst. Since a catalyst causes discoloration, noncatalytic curing expected to reduce its discoloration. The other advantage is smaller anhydride evaporation during curing as compared with MeHHPA. LED devices with H-TMAN encapsulation showed good thermal cycle resistance. H-TMAN should promise to be the efficient anhydride for thinner encapsulation. Further evaluation of this anhydride including curing with epoxy siloxane hybrid is now under investigation and these results will be reported soon.

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