

Curing of Epoxy Siloxane Monomer with Anhydride

Yasumasa Morita*

Stanley Electric Co. Ltd., 2-14-1 Eda-nishi Aoba-ku Yokohama, 225-0014 Japan

Received 9 September 2004; accepted 13 January 2005

DOI 10.1002/app.21900

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Epoxy siloxane monomer, 1,3-Bis[2-(3-{7-oxabicyclo[4.1.0]heptyl})ethyl]-tetramethyldisiloxane, was cured with methylhexahydrophthalic anhydride, and the catalysts, *N,N*-dimethylbenzylamine (BDMA) and tetra-*n*-butylphosphonium *o,o*-diethylphosphorodithioate (PX-4ET), were compared. The curing reactivity of BDMA was higher than that of PX-4ET, but the thermal stability of the polymer was lower. PX-4ET caused less thermal discoloration, which increased in proportion to catalyst concentration. The optimum was 0.71–0.35 mol %. Maximum hard-

ness and glass transition temperature as well as minimum coefficient of thermal expansion and thermal discoloration was achieved with equivalent amounts of epoxy and anhydride. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 946–951, 2005

Key words: epoxy siloxane; anhydride; thermosets; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

INTRODUCTION

Silicone-containing epoxy derivatives are well known,¹ but they are not as widely used as epoxy resin. Currently, silane coupling and electron beam curing² are important applications of such derivatives. Epoxy siloxane can be synthesized from double-bond-containing epoxy and silane by hydrosilylation.³

Currently, encapsulation of light-emitting diode (LED) is accomplished with a transparent epoxy resin, diglycidyl ether of bisphenol A, and methylhexahydrophthalic anhydride. Recent improvements include using blue and near-ultraviolet light as well as increasing intensity.^{4,5} As a result, discoloration of the epoxy resin has become a major issue, because it decreases light output during LED operation. To improve this problem, I studied the discoloring effects of hydrogenated bisphenol A glycidyl ether during anhydride curing⁶ and cationic polymerization.⁷

Epoxy siloxane offers the benefits of both silicone resin and epoxy resin. The siloxane bond is stable in response to heat and ultraviolet light, and epoxy resin has high adhesive strength. Use of silicone resin alone would avoid discoloration but its poor adhesive strength may cause optical delamination between the semiconductor and its encapsulant.

Synthesis and cationic polymerization of epoxy siloxane were reported,^{8,9} but anhydride curing has not. Here we describe anhydride curing of epoxy siloxane with methylhexahydrophthalic anhydride and the effect of catalyst on polymerization and discoloration.

EXPERIMENTAL

Materials

Epoxy siloxane monomers of 1,3-Bis[2-(3-{7-oxabicyclo[4.1.0]heptyl})ethyl]-tetramethyldisiloxane (BEPDS) were prepared according to Crivello et al. by Toagosei Co. Ltd., Nagoya, Japan (Scheme I).³ Methylhexahydrophthalic anhydride (MeHHPA) was acquired from New Japan Chemical Co. Ltd. (Kyoto, Japan). Tetra-*n*-butylphosphonium *o,o*-diethylphosphorodithioate (PX-4ET) was acquired from Nippon Chemical Industrial Co., Ltd. (Tokyo, Japan). *N,N*-dimethyl benzylamine (BDMA) and 2,4-di-*tert*-butyl-hydroxytoluene (BHT) were purchased from Aldrich (St. Louis, MO). All chemicals were used without further purification.

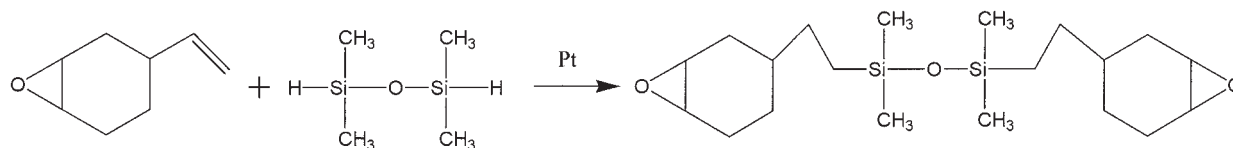
Curing of BEPDS

BEPDS, MeHHPA, and catalyst were mixed in flask and dried *in vacuo* to remove oxygen. Then, the mixture was fed into a 2-mm-thick casting (Fig. 1). This unit included two glass plates attached with silicone-coated polyester film and silicone tube. This was heated at 120°C for 1 h followed by 150°C for 1 h. After curing, the plaque was removed from this unit.

Thermal aging and UV irradiation

Thermal aging of epoxy plaques was done at 150°C for 72 h. UV irradiation was performed with a high-pres-

*Present address: Y. Morita, Lumileds Lighting, 370W Trimble Road, MS-91ML, San Jose, CA 95131; yasumasa.morita@lumileds.com.



Scheme 1.

sure mercury lamp equipped with a deep-cut filter to block wavelengths shorter than 350 nm. The light output distribution spectrum is shown in Figure 2. The radiation intensity of the resin surface was 5000 mW/cm² and the spot diameter was 5 mm.

Measurement

Differential scanning calorimetry (DSC) was measured with a Shimadzu DSC60 apparatus at a heating rate of 5°C/min under a flowing nitrogen gas. Thermogravimetric analysis (TGA) was done with a Shimadzu TG/DTA 60 at a heating rate of 10°C/min in a nitrogen atmosphere. Fourier transformation infrared (FTIR) spectra were recorded with a Shimadzu FTIR-8300. Transmittance spectrum of polymerized plaque was determined on a Shimadzu UV-3100 in the range of 300–800 nm, and yellowness indices were calculated from spectrum intensity.¹⁰ Shore D hardness of cured plaque was measured with a durometer.

RESULTS AND DISCUSSION

Curing of BEPDS

An acceleration catalyst is required for anhydride curing of epoxy resin, and many compounds such as amine, imidazole, and phosphine are used for this

purpose. Polymerization reactivity and properties of cured materials vary according to the catalyst employed. We have reported the effect of catalyst structure on UV discoloration by using hydrogenated bisphenol A glycidyl ether.⁶ UV discoloration varied directly with the unsaturated bond concentration in catalyst.

Initially, the effects of two catalysts, BDMA and PX-4ET, on curing were investigated. With these catalysts, transparent materials were produced when bisphenol A glycidyl ether and hydrogenated bisphenol A glycidyl ether were used as epoxy resin.⁶ Completion of polymerization was confirmed by FTIR spectra. By this time, the absorbance peak of epoxy groups of BEPDS at 890 cm⁻¹ completely disappeared, and the absorbance peak of carbonyl group in the anhydride appeared at 1750 cm⁻¹ (Fig. 3). A DSC thermograph monitored polymerization (Fig. 4). Catalyst concentration was fixed at 0.03 mol % in anhydride, and the ratio between epoxy groups in BEPDS and anhydride was 1 : 1. The onset temperatures of polymerization was 45°C with BDMA and 50°C with PX-4ET. Enthalpy (ΔH) was 155 mJ/mg with BDMA and 115 mJ/mg with PX-4ET. These results indicated that the reactivity of BDMA was higher than that of PX-4ET.

UV and thermal discoloration

During cationic polymerization with hydrogenated bisphenol A glycidyl ether, catalyst concentration

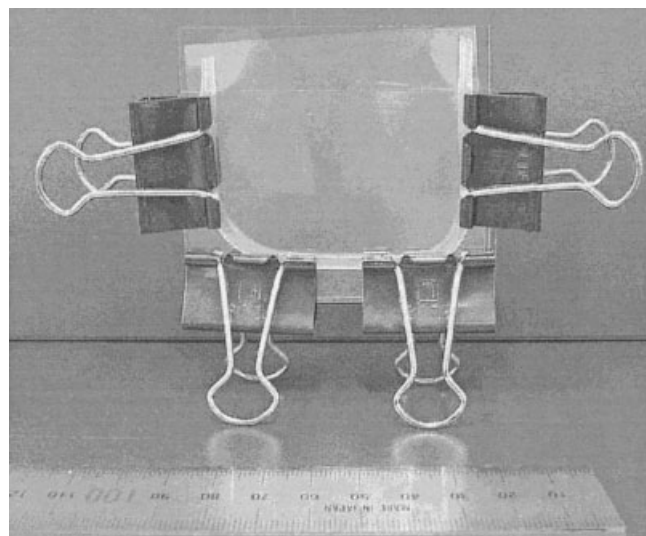


Figure 1 Plaque equipment.

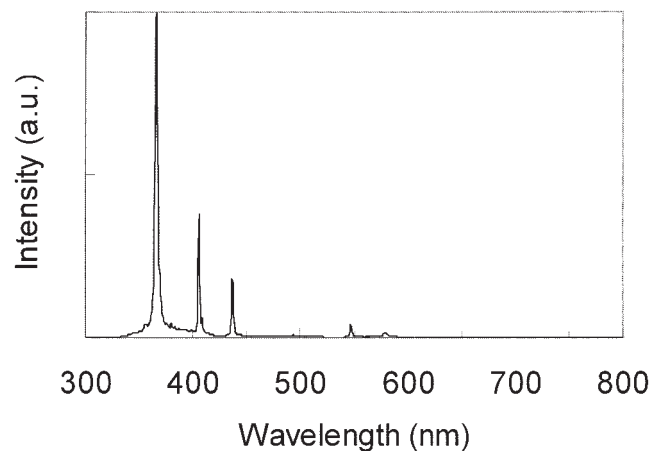


Figure 2 Light output distribution spectrum of UV light source.

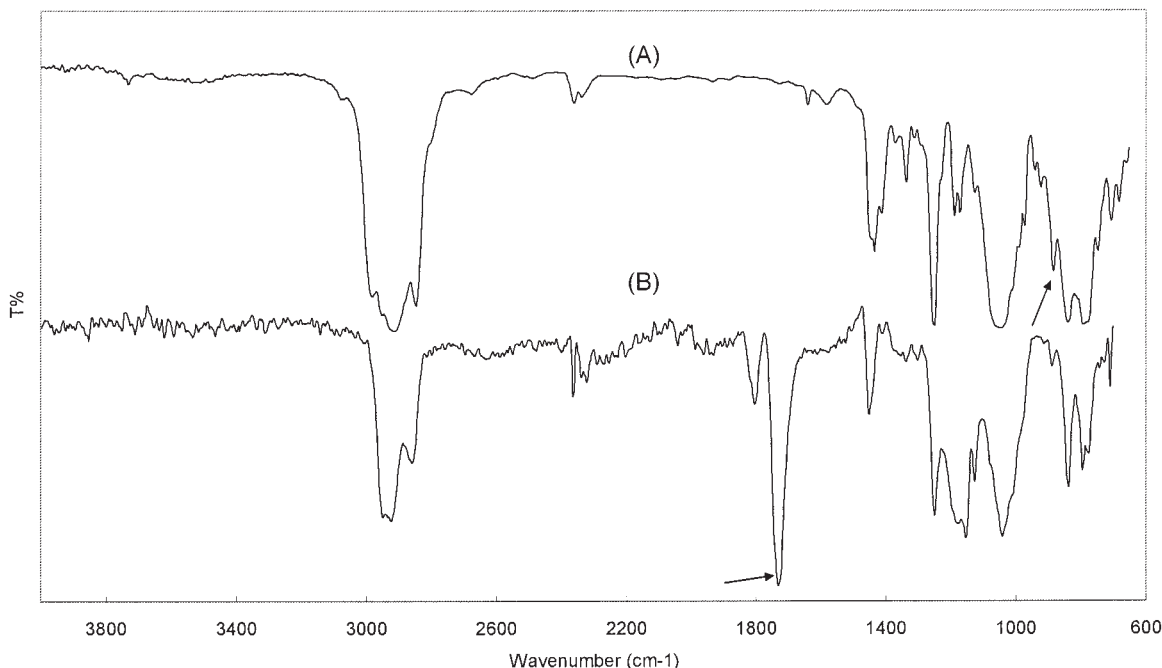


Figure 3 FTIR spectrum of epoxy siloxane: (A) monomer, (B) polymer cured with MeHHPA and PX-4ET.

affects thermal discoloration (Fig. 5). Before thermal aging, plaques were transparent, and the yellowness index was less than 1.5. After aging at 150°C for 72 h, discoloration decreased at first and then varied directly with increasing catalyst concentration. Discoloration was higher with BDMA than PX-4ET. Minimum discoloration occurred at 0.5 mol % with BDMA and 0.5–0.71 mol

% with PX-4ET. Thermal stability was confirmed by TGA analysis of the BEPDS monomer and cured material (Fig. 6). PX-4ET cured materials were more stable than those cured with BDMA. Maximum stability was obtained when the PX-4ET concentration was 0.71 or 1.50 mol %, and the 5% weight loss temperature was 310°C.

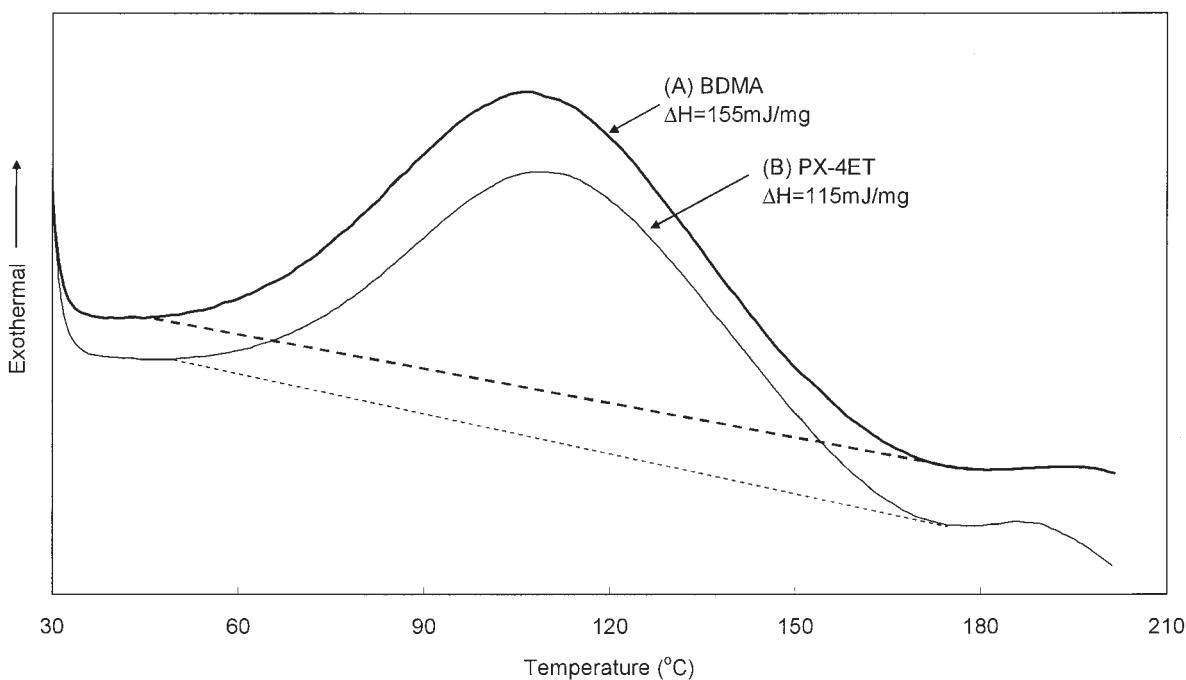


Figure 4 DSC thermograph of polymerization: (A) BDMA, (B) PX-4ET. BEPDS : MeHHPA : catalyst = 1 : 1 : 0.03 (mole ratio).

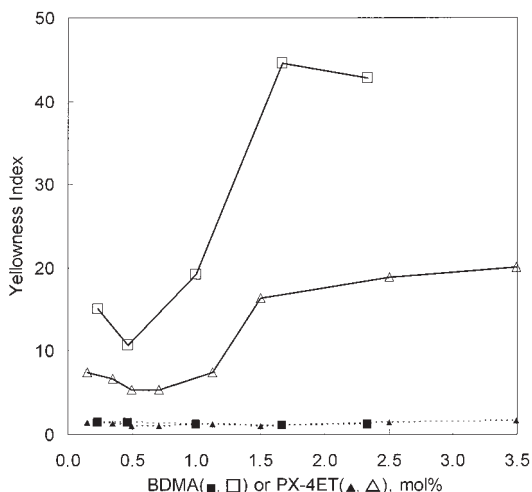


Figure 5 Effect of catalyst concentration on thermal discoloration. (■,□) BDMA; (▲,△) PX-4ET. Solid mark, initial; open mark, after 150°C 72 h. Curing condition; 120°C for 2 h and then 150°C for 2 h.

The effect of catalyst concentration on UV irradiation for further UV-LED encapsulation also was examined. To create conditions similar to a UV-LED light output spectrum, the UV irradiation source was equipped with a deep-cut filter that blocked wavelengths shorter than 350 nm. Light output intensity exceeded 10,000 mW/cm². As expected, UV discoloration first appeared at the surface before oxidation occurred at progressively deeper levels (Fig. 7). The effect of PX-4ET concentration

TABLE I
Effect of PX-4ET Catalyst Concentration on UV Irradiation

PX-4ET (mol %)	3.50	1.50	0.71	0.35	0.15
4 h	+/-	+	+	+	+
36 h	--	+/-	+	+	+
64 h		--	+	+	+/-
135 h			+	+	--
184 h			+/-	+/-	
207 h			+/-	+/-	
278 h			+/-	+/-	
350 h			-	--	

+, Water clear; +/-, slightly yellow; -, dark yellow; --, burned.

on UV irradiation is summarized in Table I. As catalyst concentration increased catalyst concentration, discoloration and oxidation occurred earlier. The optimum catalyst concentration for minimizing UV and thermal discoloration was 0.71 mol %. These results indicate that discoloration is caused both from catalyst and from low thermal stability.

Effect of anhydride concentration on discoloration and properties

The effect of anhydride concentration on properties was reported in detail by using bisphenol A glycidyl ether with MeHHPA.¹¹ Optimum anhydride concentration varied according to the specific applica-

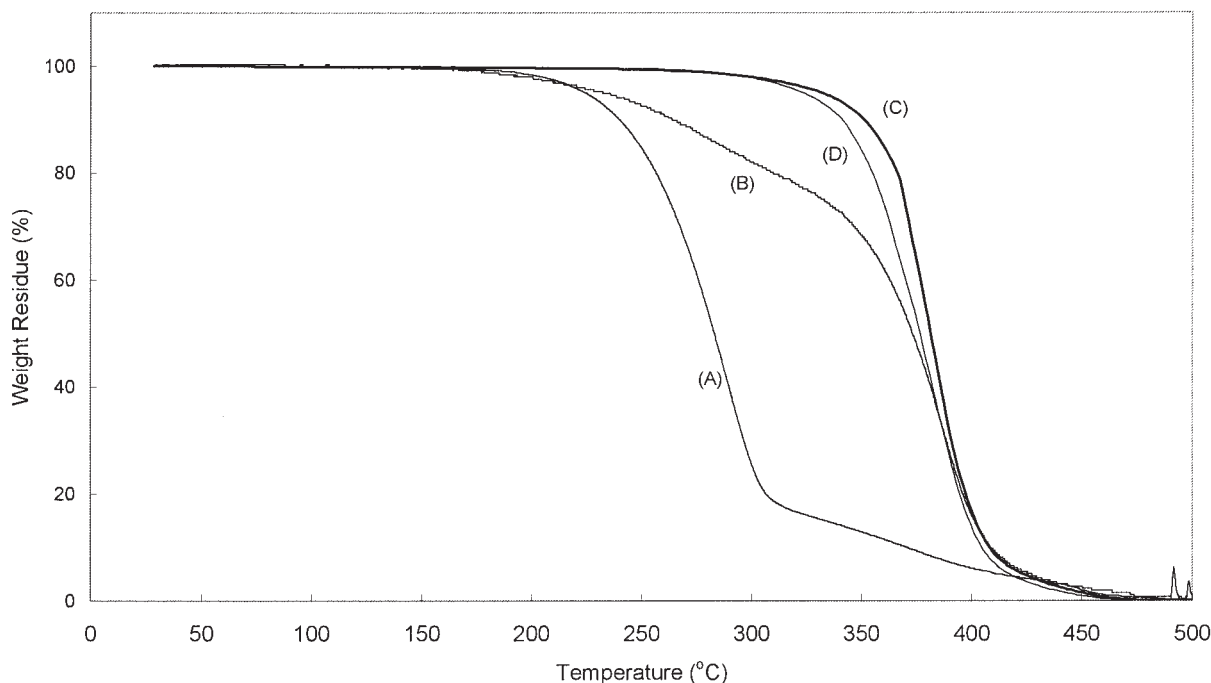


Figure 6 TGA curves of (A) BEPDS monomer and (B, C, D) MeHHPA-cured polymer. BEPDS : MeHHPA = 1 : 1 (mol ratio), (B) BDMA 0.23 wt %, (C) PX-4ET 1.5 mol %, (D) PX-4ET 3.50 mol %.

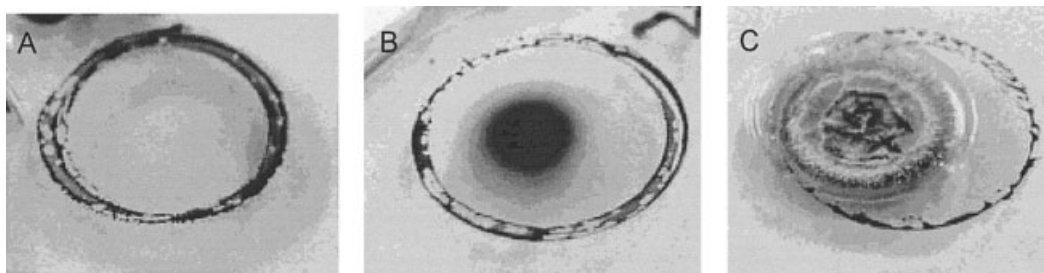


Figure 7 Discoloration behavior of cured plaque by UV irradiation; (A) before UV irradiation, (B, C) after UV irradiation.

tion, but in most cases acceptable properties appeared when the epoxy group and anhydride were equivalent. Here, the effect of anhydride concentration on thermal discoloration and material properties was studied. The relationship between thermal discoloration and anhydride concentration is shown in Figure 8. Minimum discoloration occurred at equivalent concentrations. Table II shows the 5% weight loss temperature, glass transition temperature (T_g), and coefficient of thermal expansion (CTE). Thermal stability varied inversely with anhydride concentration. The maximum 5% weight loss temperature was 349°C when the epoxy group and anhydride ratio was 100 : 80. T_g varied inversely with anhydride concentration and reached a maximum at 132°C when the ratio was 100 : 90. CTE above and below the T_g varied directly with anhy-

dride concentration, and both minimums appeared at equivalent concentrations.

From these results, it appears that the use of BEPDS increases thermal stability in the polymer network as a result of dimethylsiloxane bonding stability. This in turn increases T_g and decreases thermal discoloration. The rigid network structure of BEPDS reduces CTE. Insufficient crosslinking in an excess of anhydride or BEPDS leaves some groups unreacted, increasing CTE and thermal oxidation and reducing T_g .

CONCLUSION

During anhydride curing of epoxy siloxane monomer using a catalyst, BDMA has higher reactivity but caused more thermal discoloration than PX-4ET. Thermal and UV discoloration varied directly with catalyst

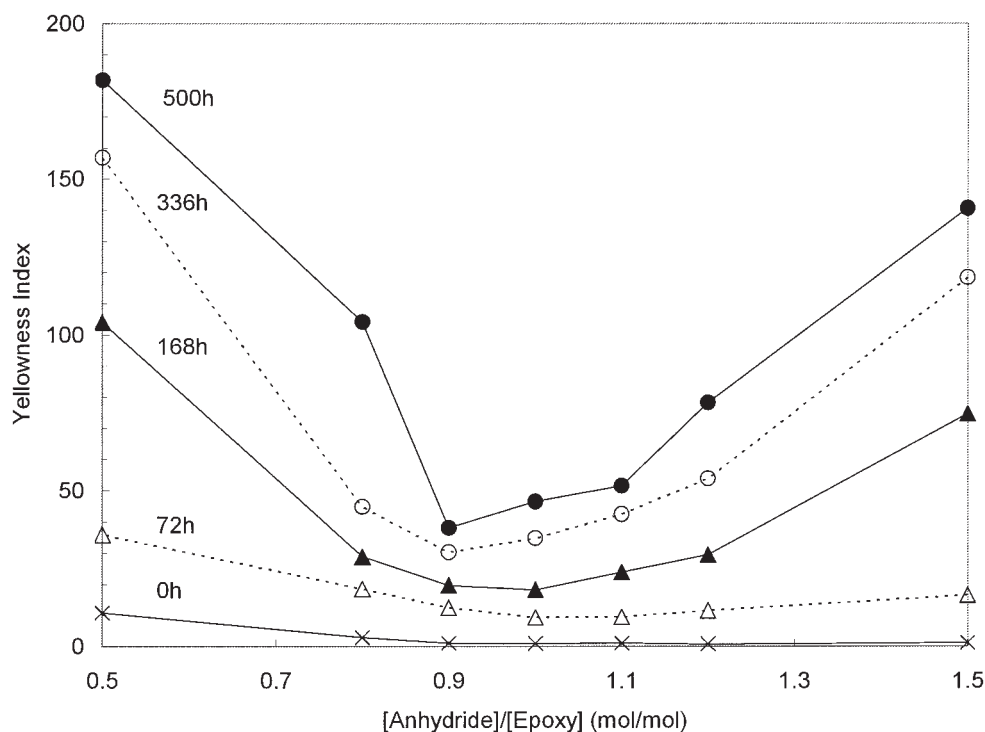


Figure 8 Effect of anhydride concentration on thermal discoloration. PX-4ET 0.71 mol %. Curing condition, 120°C for 2 h and then 150°C for 2 h.

TABLE II
Effect of Anhydride Concentration on Typical Properties

Formulation (mol ratio)		T_g , °C		CTE, ppm		5% Weight Loss. Temperature, °C
BEPDS	MeHHPA	DSC	TMA	Below T_g	Above T_g	
100	150	96	102	141	241	266
100	120	130	115	110	221	270
100	110	137	121	112	209	300
100	100	141	123	109	198	310
100	90	137	132	121	213	340
100	80	129	117	124	216	349
100	65	87	89	143	221	313
100	50	54	54	146	245	289

PX-4ET 0.71 mol %.

Curing condition, 120°C for 2 h and then 150°C for 2 h.

concentration, and minimum thermal discoloration is obtained with 0.71–0.35 mol % of PX-4ET. Anhydride concentration affects the physical properties of the materials. Maximum T_g as well as minimum CTE and thermal discoloration are achieved when epoxy and anhydride are present in equivalent amounts.

The author expresses gratitude to Toagosei for providing epoxy siloxane samples. The author also thanks Dr. Sugino of Stanley Electric and Mr. Tajima of Toagosei for helpful discussions.

References

- Kornilove, Y. I.; Bereesneva, N. K. *Rus. Pat.* 1967, 202524; *Chem. Abstr* 1968, 68, 87874.
- Crivello, J. V.; Lee, J. L. *J Polym Sci, Part A: Polym Chem Edn* 1990, 28, 479.
- Pleuddemann, E. P.; Fanger, G. J. *Am Chem Soc* 1959, 1, 2632.
- Craford, M. G.; Holonyak, N.; Kish, F. A. *Sci Am* Feb. 2001, 83–88.
- Nakamura, S. *Blue Laser Diodes*; Springer: Berlin, 2000, Chapter 1.
- Morita, Y. *Jpn J Adhesive Soc* 2003, 39, 410.
- Morita, Y. *J Appl Polym Sci* to appear.
- Crivello, J. V.; Song, K. Y.; Ghoshal, R. *Chem Mater* 2001, 13, 1932.
- Jang, M.; Crivello, J. V. *J Polym Sci, Part A: Polym Chem Edn* 2003, 41, 3056.
- Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates 2000; ASTM E313–00, 2000.
- New Japan Chemical Co. Ltd., Data sheet of MH-700 methyl-hexahydrophthalic anhydride, 1994.