

Cationic Copolymerization of Epoxy Siloxane Monomer with Liquid Poly-Butadiene and its Light Emitting Diode Encapsulation

Yasumasa Morita,^{1*} Seitarou Tajima,² Hiroshi Suzuki,² Hiroaki Sugino¹

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

²Toagosei Co. Ltd., 1-1 Funamicho Minato-ku Nagoya, 455-0027 Japan

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ABSTRACT: A novel epoxy siloxane hybrid was prepared using epoxy siloxane monomers of 1,3-bis[2-(3-{7-oxabicyclo[4.1.0]heptyl})ethyl]-tetramethyldisiloxane (BEPDS) with hydroxyl terminated hydrogenated polybutadiene (GI-1000), in different proportions. Apparent polymerization reactivity was decreased with increasing GI-1000 concentration but the normalized reactivity per epoxy group was slightly increased due to reaction between hydroxyl group and epoxy group. Increasing GI-1000 concentration showed significant flexibility improvement in epoxy siloxane hybrid. At 30 wt % of GI-1000 addition, glass transition temperature was decreased

from 116 to 21°C and shore D hardness was decreased from 75 to 46.5% weight loss temperature of these epoxy siloxane hybrid was decreased with increasing GI-1000 concentration, whereas thermal discoloration was increased. LED encapsulation with this epoxy siloxane demonstrated no crack when GI-1000 was 30 wt % or more. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1808–1813, 2008

Key words: epoxy siloxane; cationic polymerization; differential scanning calorimetry (DSC); dynamic mechanical analysis (DMA); light emitting diodes (LED)

INTRODUCTION

Transparent epoxy resins obtained by anhydride curing bisphenol-A glycidyl ether is commonly used in the light emitting diodes (LED) encapsulation.^{1,2} In recent years, significant improvements on light output efficiency have been reported in nitride-based blue LED. Most of white LED is fabricated from blue emitting LED chip with yellow phosphors. The light output intensity per LED device and the luminous efficiency are rapidly growing. The performance of white LED will be reached to that of fluorescent lamps within few years.^{3,4}

At the same time, the light output decrease due to epoxy discoloration becomes major issue for Blue LED or for White LED. To address these issues, we are investigating photo-thermally stable epoxy materials using hydrogenated bisphenol-A glycidyl ether^{5,6} or epoxy siloxane hybrid.^{7,8} Epoxy siloxane is expected for better photo-thermal stability but the hard and brittle nature is the biggest difficulties in the encapsulation. We evaluated epoxy siloxane monomer with longer siloxane segment length for more flexibility. These longer siloxane monomers

could improve both flexibility and photothermal discoloration.⁸

On the other hand, various stress modifiers can also control the crosslink density of epoxy thermosets. Hydroxyl terminated liquid rubber materials are well known stress modifier of epoxy resin.^{9,10} Considering blue light absorption in unsaturated bond, stress modifier should not contain unsaturated bond for LED application.

In this article, we report stress modification of epoxy siloxane using hydroxyl-terminated hydrogenated polybutadiene (GI-1000). The effect of GI-1000 concentration on polymerization reactivity and various cured polymer properties were studied in detail. In addition, we also demonstrated the LED encapsulation by this epoxy siloxane hybrid with different GI-1000 concentration.

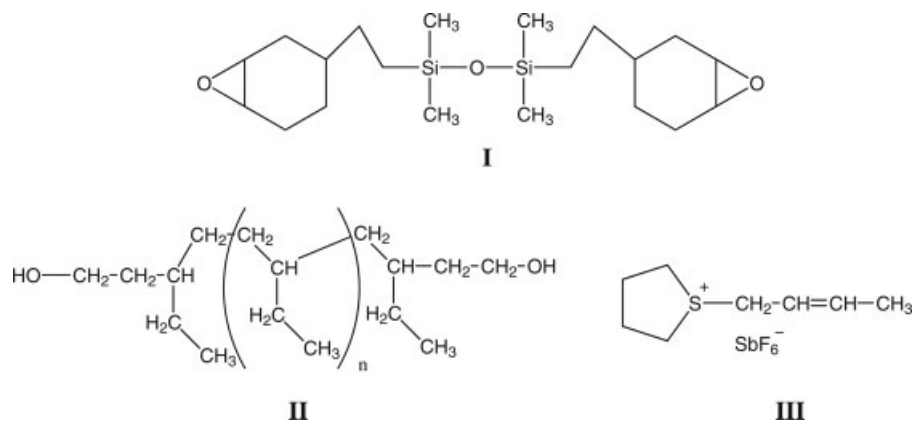
EXPERIMENTAL

Materials

Epoxy siloxane monomer of 1,3-bis[2-(3-{7-oxabicyclo[4.1.0]heptyl})ethyl]-tetramethyldisiloxane (**I**, BEPDS) was prepared according to Crivello et al.¹¹ Hydroxyl terminated hydrogenated 1,2-polybutadiene (**II**, GI-1000, M_n 1500) was received from Nippon-Soda (Tokyo, Japan). According to manufacturer's analysis, GI-1000 contained small amount of unsaturated group and its iodine value was less than

*Present address: Philips Lumileds Lighting Company, 370 West Trimble Road, San Jose, CA 95131.

Correspondence to: Y. Morita (yasumasa.morita@philips.com).



Scheme 1 Chemical structures of 1,3-bis[2-(3-[7-oxabicyclo[4.1.0]heptyl])ethyl]-tetramethyldisiloxane (I, BEPDS), Hydroxyl terminated hydrogenated 1,2-polybutadiene (II, GI-1000) and 3-methyl-2-butenyltetramethylenesulfonium hexafluoroantimonate (III, CP-77).

21 (mg/100 g). Propylene carbonate solution (66 wt %) of 3-methyl-2-butenyltetramethylenesulfonium hexafluoroantimonate (III, CP-77) was obtained from Asahi Denka (Tokyo, Japan). All chemicals were used without further purifications. These chemical structures are illustrated in Scheme 1.

Curing of epoxy siloxane

Typical procedure: BEPDS, GI-1000 and CP-77 were mixed in 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 silicone tube and two glass plates which attached with silicone-coated polyester film. This was heated at 120°C for 1 h followed by 150°C for 2 h. After curing, the epoxy plaque was removed from this unit.

Characterization

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

min under a flow of nitrogen 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 nitrogen gas. Dynamic mechanical analysis (DMA) was performed by Seiko Instruments DMS 6100 at a heating rate of 4°C/min with fixed frequency of 10 Hz under nitrogen atmosphere. Transmittance spectrum of polymerized plaque was measured on Shimadzu UV-3100 from 300 to 800 nm. Transmittance spectrum was once converted to color point (CIE X, Y, and Z) and then it converted into yellowness index, according to ASTM method E313. These calculations were done by computer program included in Shimadzu UV-3100 spectrometer. Shore D hardness of cured polymer was measured with Durometer. Scanning electron microscopy (SEM; Hitachi S-2460N) was used to analyze the fractured surface after coated with thin layer of gold prior to SEM observation.

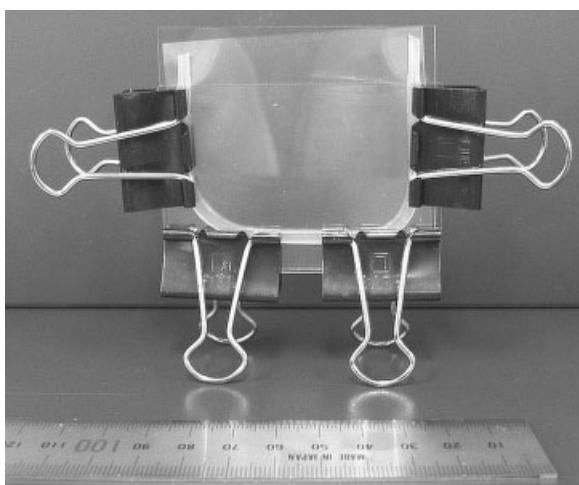


Figure 1 Epoxy plaque curing equipment.

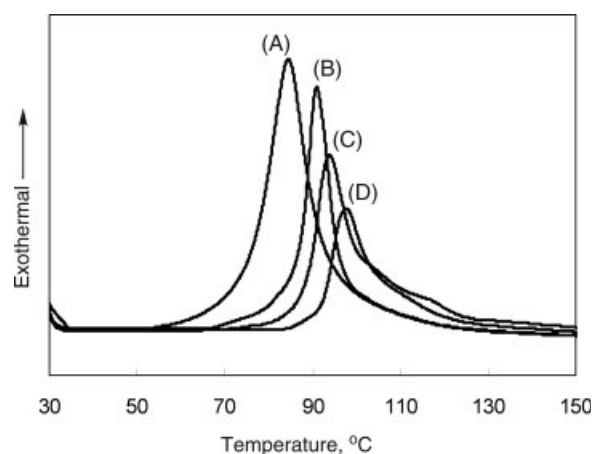


Figure 2 DSC thermograms of cationic copolymerization with different GI-1000 concentration but catalyst is fixed 0.2 wt %. (A) 0 wt %, (B) 10 wt %, (C) 30 wt % and (D) 50 wt %.

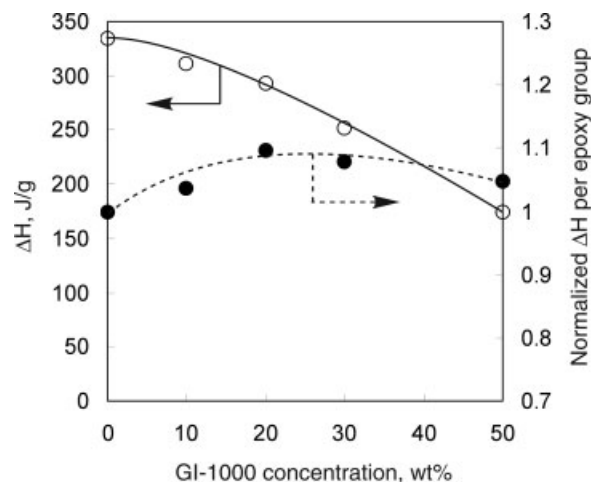


Figure 3 Effect of GI-1000 concentration on total exothermal (ΔH) and normalized ΔH per epoxy group.

Light emitting diode encapsulation

LED encapsulation was performed with surface mounted devices that consist of white plastic reflector and copper lead-flame with silver plated surface.¹² AMODEL A-4122NL polyphthalamide was used as the reflector materials, which come from Solvay Advanced Polymers (Georgia, USA). This amide contains glass fiber and Titanium dioxide. Blue LED chip, consisting from Indium Gallium Nitride (InGaN) was bonded on the center of the package using silver containing epoxy resin. Mixed epoxy siloxane (3.1 μL) was dispensed into concave of LED package and cured in the oven at 120°C for 1 h and then 150°C for 2 h. Encapsulation defect has been inspected just after the curing and then 12 h after left in the room temperature.

RESULTS AND DISCUSSIONS

Cationic polymerization

The cationic polymerization of epoxy siloxane monomer (BEPDS) with different GI-1000 concentration was monitored with DSC under the fixed (0.2 wt %)

catalyst concentration. Our previous study found that 0.2 wt % was minimum required catalyst concentration for a full cure.⁸ Before the curing, both GI-1000 and CP-77 were completely dissolved in BEPDS at room temperature.

Figure 2 describes DSC thermogram of curing epoxy siloxane hybrid with different GI-1000 concentration. With increasing GI-1000 concentration, total exothermal energy (ΔH) was decreased and the peak temperature was shifted to higher. Polymerization reactivity seems to be decreased with increasing GI-1000 concentration because epoxy is diluted with GI-1000. Figure 3 illustrates ΔH versus GI-1000 concentration normalized with epoxy group. From 0 to 20 wt %, ΔH was increased with increasing GI-1000 concentration. The increase in normalized ΔH is considered as ring-opening cationic copolymerization between epoxy group and hydroxyl group in addition to homo polymerization of epoxy. The presence of alcohol has considerable effect on the cationic ring opening polymerization of epoxides.^{13–15}

Properties of cured copolymers

Properties of cured epoxy siloxane hybrid with different GI-1000 concentration are tabulated in Table I. Thermal stability of copolymer was evaluated by thermo gravimetric analysis (TGA), and 5% weight loss temperature was used as indicator. With increasing GI-1000 concentration, thermal stability was decreased. Although decreasing its thermal stability by adding GI-1000, 30 wt % addition should be acceptable thermal stability for encapsulation. Lead-free soldering (Max 260°C within 1 min) should be the highest possible thermal stress against the encapsulation, and this process is widely used in the industry.¹⁶ Thermal weight losses at 260°C were less than 0.5 wt %, as shown in Table I.

Increased GI-1000 concentration led to a softer material because of the decrease in crosslink density resulting from the higher ratio of GI-1000 to epoxy siloxane.

More detail of thermal properties was observed from DMA. Since the mechanical property of the co-

TABLE I
Effect of GI-1000 Concentration on Hardness, CTE, and Thermal Stability

GI-1000 wt %	5% Weight loss temp, °C	Weight loss at 260 °C, %	CTE, ppm			$T_{g,r}$, °C ^a	Hardness shore D
			α_1	α_2	Average 25°C/150°C		
0	382	<0.5	162	207	174	116	75
10	372	<0.5	154	226	190	86	68
20	363	<0.5	–	242	242	50	54
30	359	<0.5	–	252	252	21	46
50	347	0.6	–	283	283	12	23

CP-77 0.2 wt %, 120°C 1 h + 150°C 2 h.

^a As determined by DMA.

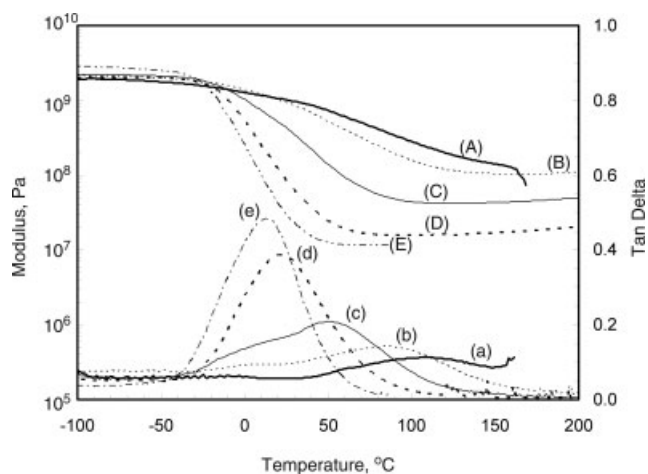


Figure 4 DMA curves of cured epoxy siloxane polymer with different GI-1000 concentration. (A) 0 wt %, (B) 10 wt %, (C) 20 wt %, (D) 30 wt % and (E) 50 wt %. Temperature scan rate = 4°C/min in nitrogen.

polymer is directly related to GI-1000 concentration, non GI-1000 addition is expected to give the stiffest and highest glass transition polymer.

DMA curves of cured epoxy siloxane hybrid are shown in Figure 4. The glass transition temperature (the peak temperature of loss tangent) was significantly decreased with increasing GI-1000 concentration.

The storage modulus at the lower temperature (< -20°C) was little difference between 0 and to 50 wt % of GI-1000 addition. However, 50 wt % of GI-1000 addition showed significant storage modulus increase in the lower temperature. The decline at 160°C with no GI-1000 addition was due to sample breaking by its own crack.

We also observed the fracture surface of cured epoxy siloxane hybrid with 50 wt % of GI-1000. Phase separation phenomenon can not be observed from the SEM micrograph up to 500 times of magnifications (Fig. 5). This observation suggested its homogeneity and compatibility after the cure in the micrometer range. However, there will be possible phase separation in nanometer range and this will be measured with TEM-EELS in the future.

Thermal discoloration

Thermal discoloration behavior of cured epoxy siloxane hybrid was evaluated. Figure 6 shows transmittance spectrum before and after thermal discoloration. Initial transmittance spectrum was almost same both 50 and 0 wt % of GI-1000 addition. The water transparent appearance became yellowish after 150°C for 100 h. More thermal discoloration was observed with GI-1000 50 wt % than non GI-1000 addition. Yellowish appearance means blue light absorption and this cannot be acceptable for LED encapsulation. Yellowness index change of different GI-1000 concentration provides detail information for thermal discoloration.

As shown in Figure 7, yellowness index was increased faster with increasing GI-1000 concentration. Yellowness index is not showing the exact amount of oxidation, although increasing yellowness index indicates more oxidation. Initially, yellowness index was increasing same speed, regardless the GI-1000 concentration. Yellowness index increased faster after induction period and higher GI-1000 concentration presented shorter induction period.

This thermal discoloration in the epoxy siloxane hybrid seems to be caused by multiple factors. Photo thermal oxidation of polyether is well known behavior.¹⁷ Residues both from catalyst and from unreacted epoxy group can accelerate thermal discoloration.⁵⁻⁸ In addition, lower thermal stability by increasing GI-1000 concentration may allow its thermal discoloration.

LED encapsulation

In the previous report, epoxy siloxane homopolymer showed good thermal stability and small discoloration both by UV and by high temperature. However, encapsulation in LED package was quite difficult because of cracks. Usually, there is no crack just after the curing when the LED is hot. Crack start appearing during the LED is cool down to the room temperature.

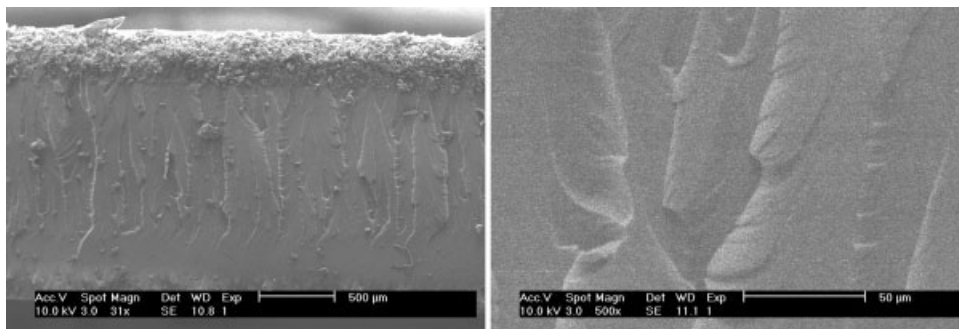


Figure 5 SEM micrograph of fracture surface of the cured epoxy siloxane hybrid with 50 wt % of GI-1000.

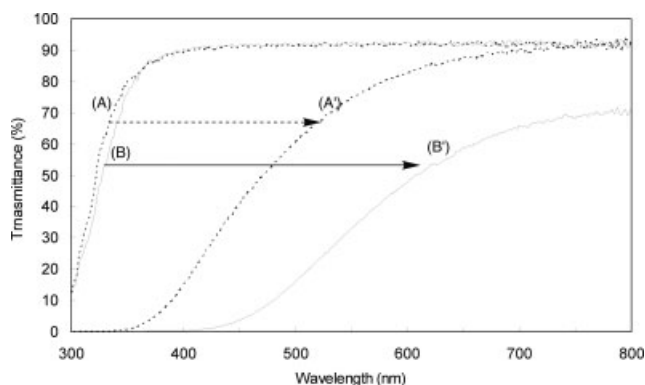


Figure 6 Transmittance spectra before and after thermal discoloration at 150°C 300 h. (A), (A'); Epoxy siloxane polymer no GI-1000 addition. (B), (B'); Epoxy siloxane with 50 wt % GI-1000.

To demonstrate the flexibility improvement by GI-1000, LED encapsulation was carried out with conventional surface mounting package. The curing condition of 120°C 1 h was determined from DSC and hardness change. Additional 150°C 2 h was added to increase the adhesive strength between reflector cup (polyphthalamide) and epoxy siloxane.¹²

Figure 8 shows the pictures of LED 12 h after the curing. No GI-1000 addition showed extensive cracks

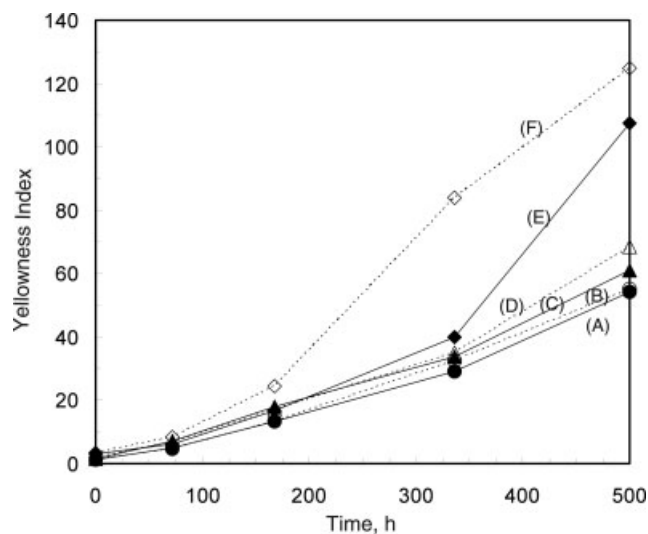


Figure 7 Effect of GI-1000 concentration on thermal discoloration. (A) 0 wt %, (B) 10 wt %, (C) 20 wt %, (D) 30 wt %, (E) 40 wt % and (F) 50 wt %.

across entire the encapsulation and delamination was also observed between reflector cup and epoxy siloxane encapsulant. With increasing GI-1000 concentration, the crack became smaller and then disap-

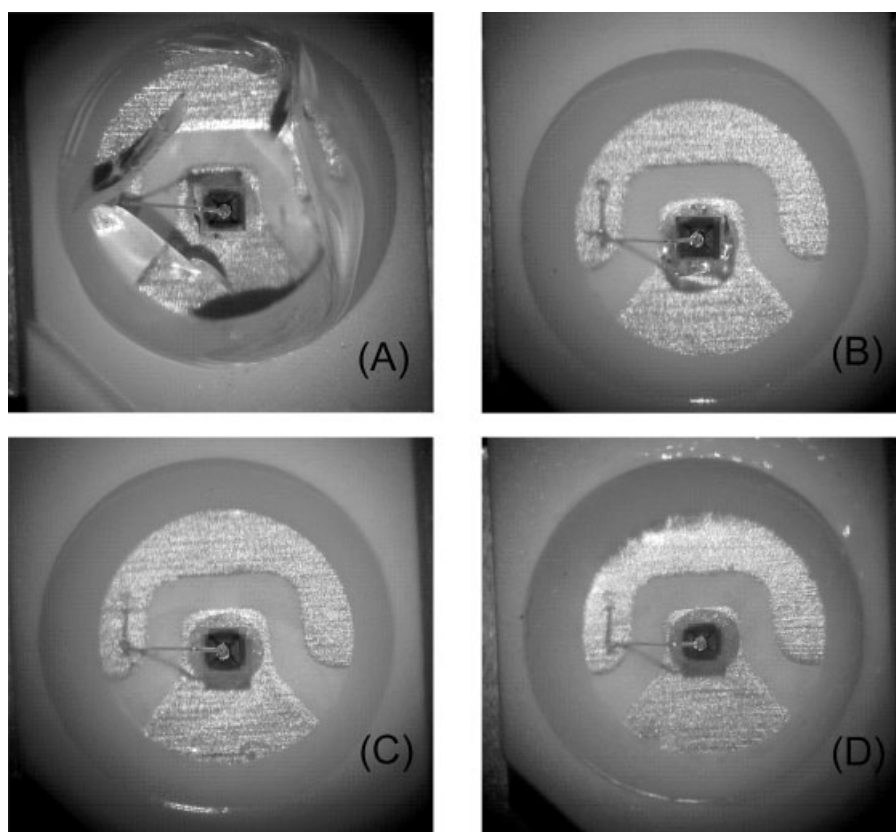


Figure 8 Pictures of LED encapsulation by epoxy siloxane with different GI-1000 concentration (A) 0 wt %, (B) 20 wt %, (C) 30 wt %, (D) 50 wt %.

peared, if GI-1000 concentration was 30 wt % or higher.

The significant stress modification enables crack free LED encapsulation. Compare 0 and 30 wt % of GI-1000 addition, average CTE increased 1.5 times between 25 and 150°C (Table I) but storage modulus decreased about 1/10 during that temperature.

CONCLUSIONS

A novel epoxy siloxane hybrid containing hydroxyl terminated hydrogenated 1,2-polybutadiene (GI-1000) was successfully improve its flexibility. GI-1000 was homogeneously mixed with epoxy siloxane before and after cure. Thermal stability of epoxy siloxane hybrid was decreased with increasing GI-1000 concentration, although this can be acceptable for encapsulation at least up to 30 wt % of GI-1000 addition. Thermal discoloration is still remaining as issue of this hybrid. Possible improvement will be using longer epoxy siloxane monomer and oxidation inhibitors. Those improvements and LED reliability will be reported soon.

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