

Thermal Resistance of Cycloaliphatic Epoxy Hybrimer Based on Sol-Gel Derived Oligosiloxane for LED Encapsulation

SeungCheol Yang, Joon-Soo Kim, JungHo Jin, Seung-Yeon Kwak, Byeong-Soo Bae

Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

Received 18 August 2009; accepted 31 October 2009

DOI 10.1002/app.31702

Published online 7 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cycloaliphatic epoxy hybrimer bulk was successfully fabricated by thermal curing of cycloaliphatic epoxy oligosiloxane resin synthesized by a sol-gel condensation reaction with methylhexahydrophthalic anhydride (MHHPA) and tetrabutylphosphonium methanesulfonate (TBPM). The composition of MHHPA and TBPM in the resin was optimized to minimize yellowness of the cycloaliphatic epoxy hybrimer bulk. The sample with the optimized composition showed little discoloration upon thermal aging at 120°C for

360 h under an air atmosphere. On the basis of its high thermal stability with appropriate hardness and a high refractive index of 1.55, cycloaliphatic epoxy hybrimer bulk can be used as a LED encapsulant for white LEDs. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2140–2145, 2010

Key words: oligomers; transparency; light-emitting diodes (LED); UV-vis spectroscopy; differential scanning calorimetry (DSC)

INTRODUCTION

White light-emitting diodes (white LEDs) have received considerable attention for lighting and displays as they have properties of extended lifespan, driving at low voltage, and high luminescence efficiency, and they are also heavy metal-free. Blue LED chips are generally used as light sources to make the white LEDs incorporating yellow phosphor. Blue light emitted by the blue LED chip is converted into white light when it passes through phosphors dispersed in the LED encapsulant. Among these components of white LEDs, the LED encapsulant plays an important role for obtaining high luminescence efficiency. The luminescence efficiency of white LEDs can be further increased by increment of the encapsulant's refractive index and their structural design for inhibiting total reflection and refraction of light. In addition to a high refractive index, for application as a LED encapsulant candidate materials must meet several requirements: transmittance

over 90%, thermal and UV resistance to yellowness, and hardness to protect the LED chip.

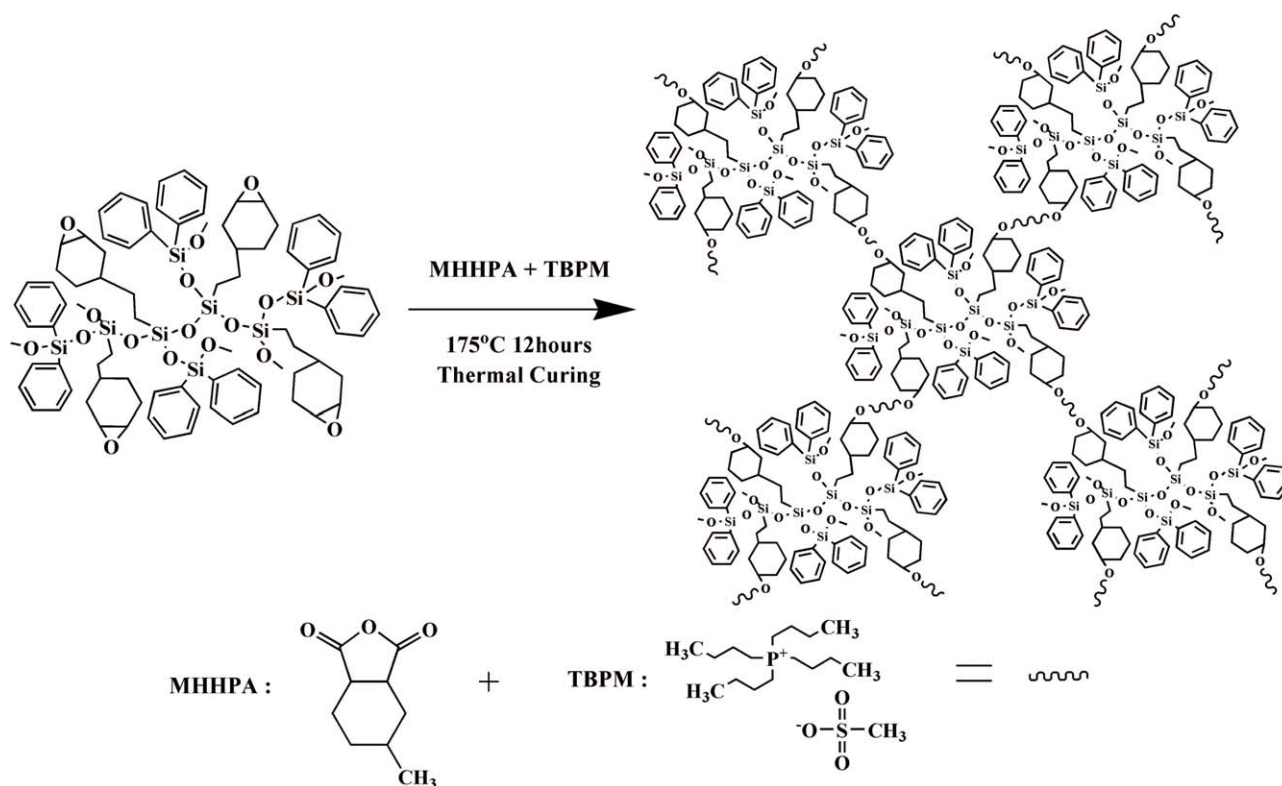
Aromatic epoxy resins such as bisphenol A epoxy resin have typically been used as material for LED encapsulation.¹ However, aromatic epoxy resins are susceptible to yellowing upon UV exposure or thermal degradation. Siloxane-based resins with excellent transmittance as well as light resistance have also been proposed as a resin suitable for white LED encapsulation.^{2–4}

Inorganic-organic nanohybrid materials (hybrimers) based on sol-gel derived oligosiloxane are candidate materials for the encapsulation of white LEDs due to their excellent transparency.^{5–7} Hybrimers are also optimal materials in terms of providing a high refractive index for high luminescence efficiency, because their refractive index is controllable according to their composition.⁸

In this study, we synthesized cycloaliphatic epoxy oligosiloxane resin by a sol-gel condensation reaction between 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTS) and diphenylsilanediol (DPSD). Hybrimer bulk with 2 mm thickness was fabricated with the oligosiloxane resin mixed with a hardener and a catalyst and its thermal resistance was investigated. The thermal resistance of the fabricated hybrimer was maximized by optimizing the hardener and catalyst composition in the resin. Also, the refractive index and the hardness of the hybrimer were examined to confirm its feasibility for use as an encapsulant for white LEDs.

Correspondence to: B.-S. Bae (bsbae@kaist.ac.kr).

Contract grant sponsor: National Research Foundation of Korea (NRF), Korea Government (MEST); contract grant numbers: R11-2007-045-03002-0, R01-2007-000-20815-0.



Scheme 1 Fabrication of cycloaliphatic epoxy hybrimer bulk using cycloaliphatic epoxy oligosiloxanes.

EXPERIMENTAL

Synthesis of cycloaliphatic epoxy oligosiloxane resin and fabrication of hybrimer bulk

We synthesized cycloaliphatic epoxy oligosiloxane resin (ED50) using a method described in a previous article.⁹ ED50 was synthesized by a simple sol-gel condensation reaction between 0.05 mol of ECTS (Gelest, Morrisville, PA) and 0.05 mol of DPSD (Gelest) at 80°C for 4 h under N₂ purging. Barium hydroxide monohydrate (Ba(OH)₂·H₂O, 98%, Aldrich, St. Louis, MO) was added as a catalyst to promote the reaction.

Methylhexahydrophthalic anhydride (MHPA, 97%, Aldrich) and tetrabutylphosphonium methanesulfonate (TBPM, Fluka, St. Louis, MO) were added as a hardener and a catalyst, respectively. ED50, MHPA, and TBPM were mixed in various compositions to minimize the yellowing upon thermal aging. Mixed resins were fed into a 2-mm thick mold made with hexamethyldisilazane (Aldrich) treated glass. The mold was kept in vacuum condition to remove oxygen from the mixed resin and then thermally cured at 140°C for 2 h followed by 175°C for 12 h under a vacuum condition. (Scheme 1) Fabricated cycloaliphatic epoxy hybrimer bulks with various compositions were heated at 150°C for 72 h under air to test for yellowing. The thermal resistance of cycloaliphatic epoxy hybrimer bulks with an optimized composition was estimated at 120/150/180°C

for 72 h and at 120°C for 360 h under an air atmosphere.

Characterization of cycloaliphatic epoxy hybrimer bulk

Differential scanning calorimetry (DSC, Netzsch, Germany) were performed under a nitrogen atmosphere with a heating rate of 5°C/min to confirm thermal curing behavior of the cycloaliphatic epoxy group in ED50 and the reactivity of TBPM as a catalyst. Transmittance measurements of cycloaliphatic epoxy hybrimer bulks before and after thermal aging were performed with an ultraviolet-visible-near infrared (UV/VIS/NIR) spectrophotometer (UV3101PC, Shimadzu, Kyoto, Japan) in a wavelength range of 300–800 nm. The yellowness index from the transmittance was calculated with the color analysis program of a UV/VIS/NIR spectrophotometer (ASTM, D1925). The refractive index of the cycloaliphatic epoxy hybrimer was obtained using a prism coupler (2010, Metricon, Pennington, NJ) at a wavelength of 632.8 nm. Shore D hardness of cycloaliphatic epoxy hybrimer bulks was measured with a shore D Durometer (HPSD, Schmidt, Waldkraiburg, German). Thermal stability of the cycloaliphatic epoxy hybrimer bulks was assessed with a thermogravimetric analyzer (TGA Q50, TA Instruments, New Castle, DE) under a N₂ condition with a heating rate of 5°C/min.

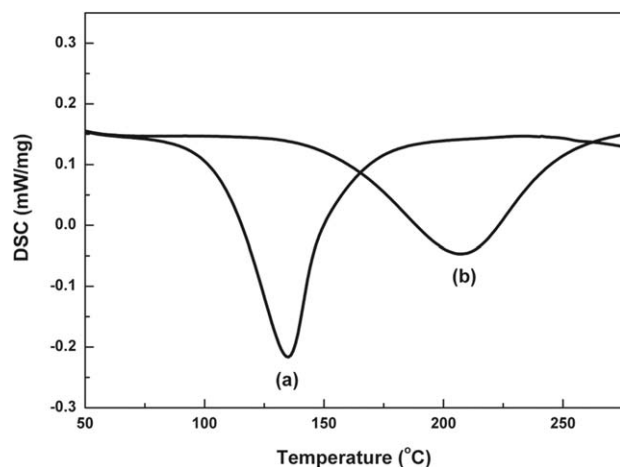


Figure 1 DSC curve of cycloaliphatic epoxy oligosiloxane resin (a) 9 mol % catalyst content and (b) 0.01 mol % catalyst content.

RESULTS AND DISCUSSION

Curing behaviors of cycloaliphatic epoxy oligosiloxane resin

Tertiary amines such as benzyl dimethyl amine (BDMA) are generally used as catalysts for the formation of polyester between epoxy groups and anhydrides by thermal curing.¹⁰ However, amine groups induce yellowness of the constitutive materials by thermal oxidation.¹¹ Thus, we used a quaternary phosphonium salt such as TBPM in our experiment to minimize the yellowing by catalysts such as tertiary amines. Quaternary phosphonium salts generally have rapid curing rates at moderately elevated temperature and do not degrade the electrical and mechanical properties of the cured resin.¹⁰

The thermal curing behavior of the cycloaliphatic epoxy groups was measured by DSC to confirm the ability of TBPM as the catalyst. The equivalent molar ratio between the cycloaliphatic epoxy groups in the resin and MHHPA was fixed at 1 : 1. Figure 1 shows the DSC curve according to catalyst content of 0.01 mol % and 9 mol % in the anhydride. The exothermic peak for 0.01 mol % catalyst content in the anhydride is observed between 155.7°C and 248.0°C with the maximum peak at 207.6°C. The exothermic peak for 9 mol % catalyst content is observed at lower temperature between 108.4°C and 151.6°C, with the maximum peak at 134.8°C in strong contrast with that for 0.01 mol % catalyst content. However, the exothermic energy (−163.2 J/g) for 0.01 mol % catalyst content is similar to that (−152.0 J/g) for 9 mol % catalyst content.

We also plotted the maximum peak temperature and exothermic energy, as a function of catalyst content depending on the measured DSC curve. (Fig. 2)

The maximum peak temperature decreases with increment of the catalyst content and the exothermic energy dose not show any relationship with the various catalyst contents, as shown in Figure 2. This indicates that full curing of cycloaliphatic epoxy groups in the resin is possible with a small amount of catalyst content and proper curing temperature. Depending on these DSC results, we found that TBPM is a suitable catalyst for the thermal curing of cycloaliphatic epoxy groups

Effect of anhydride and catalyst contents on thermal yellowness

Yellowness index was calculated using a color analysis program with the transmittance of a UV/VIS/NIR spectrophotometer (ASTM, D1925). The yellowness index is represented as the following equation.

$$YI = [100(1.28X_{CIE} - 1.06Z_{CIE})]/Y_{CIE}$$

X_{CIE} , Y_{CIE} , and Z_{CIE} are the CIE tristimulus values for red, green, and blue, respectively.

We optimized the anhydride content in the cycloaliphatic epoxy hybrimer bulk with this yellowness index. Catalyst content was fixed at 1 mol % in the anhydride. After thermal aging at 150°C for 72 h under air, degree of yellowness was represented according to the change in the yellowness index via the following equation (ASTM, D1925).

$$\Delta YI = YI_{final} - YI_{initial}$$

ΔYI is the change in yellowness index, $YI_{initial}$ is the yellowness index before thermal aging, and YI_{final} is the yellowness index after thermal aging. Figure 3 shows ΔYI as a function of anhydride content after thermal aging at 150°C for 72 h under air.

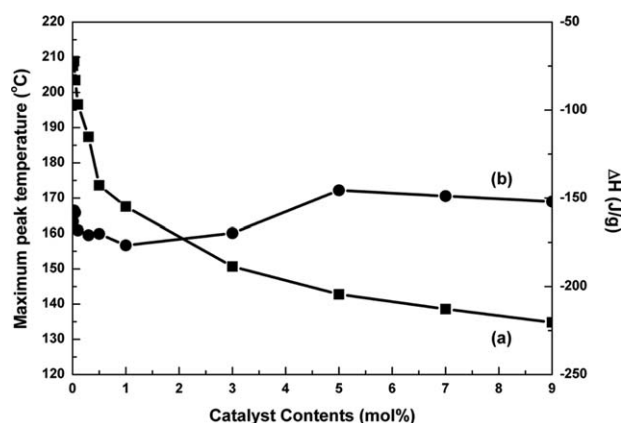


Figure 2 (a) Maximum peak temperature and (b) exothermic energy of cycloaliphatic epoxy oligosiloxane resin depending on the catalyst contents.

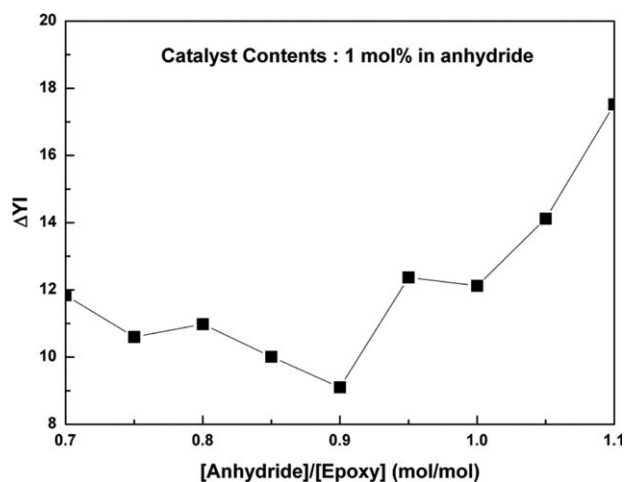


Figure 3 Effect of anhydride content on thermal yellowness of cycloaliphatic epoxy hybrimer bulk.

In Figure 3, the yellowness of the cycloaliphatic epoxy hybrimer bulk is minimized when the equivalent molar ratio between anhydride and cycloaliphatic epoxy group is 0.9. As insufficient crosslinking caused by excess anhydride and unreacted cycloaliphatic epoxy group acts as a source of thermal oxidation, which appears as yellowness, minimum yellowness occurs at roughly an equivalent concentration between anhydride and cycloaliphatic epoxy groups.^{2,11}

We plotted the calculated ΔYI as a function of catalyst content to verify the effect of the latter on yellowness of cycloaliphatic epoxy hybrimer bulk after thermal aging at 150°C for 72 h under air.

Figure 4 indicates that yellowness of cycloaliphatic epoxy hybrimer bulk is minimized when the catalyst content ranges between 0.3 and 0.5 mol % in anhydride. Even though we used quaternary phosphonium salts to minimize yellowness by the catalysts, excess catalyst content causes yellowness of the cycloaliphatic epoxy hybrimer bulk due to thermal oxidation of the catalyst. An insufficient amount of catalyst also causes yellowness of the cycloaliphatic epoxy hybrimer bulk, as it may lead to insufficient crosslinking under fixed thermal curing conditions.^{2,11}

Transmittance of cycloaliphatic epoxy hybrimer bulk

We applied thermal aging at 120/150/180°C for 72 h to three samples to verify the thermal resistance of the cycloaliphatic epoxy hybrimer bulk with the optimized compositions. Before and after thermal aging, the transmittance spectra of each sample were measured at a range of 300–800 nm (Fig. 5), and then we checked the transmittance of each sample at the wavelength of 450 nm.

The transmittance at 450 nm before thermal aging is 90%. After thermal aging at 120/150/180°C for 72 h, the transmittance at 450 nm is 90/82/38%, respectively. The cycloaliphatic epoxy hybrimer bulk does not show any change in transmittance upon thermal aging at 120°C for 72 h. We also measured the transmittance of cycloaliphatic epoxy hybrimer bulk after thermal aging at 120°C for 360 h to verify its capacity to withstand sustained thermal aging. (Fig. 6)

After thermal aging at 120°C, the transmittance at 450 nm remained above 87% even after 360 h. Through observation of the transmittance spectra, we confirmed that the transmittance of the cycloaliphatic epoxy hybrimer bulk shows almost no degradation upon thermal aging at 120°C for a long period of time. From Figures 5 and 6, we found that the cycloaliphatic epoxy hybrimer bulk can withstand thermal aging at 120°C under air.

Thermal stability of cycloaliphatic epoxy hybrimer bulk

Because heat generated by a LED chip can degrade the performance of individual components in the LED, the thermal stability of LED encapsulants is important. The thermal stability of cycloaliphatic epoxy hybrimer bulk with optimized compositions was characterized by TGA. Figure 7 shows a TGA curve of the cycloaliphatic epoxy hybrimer bulk.

In Figure 7, the 5% weight loss temperature of cycloaliphatic epoxy hybrimer bulk is $\sim 350^\circ\text{C}$. The high thermal stability of the cycloaliphatic epoxy hybrimer bulk is similar to that of other siloxane based LED encapsulants and is appropriate for the demands required by application as an LED encapsulant.²

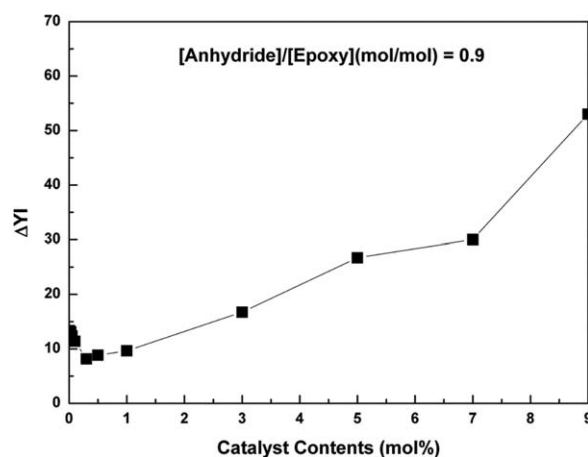


Figure 4 Effect of catalyst content on thermal yellowness of cycloaliphatic epoxy hybrimer bulk.

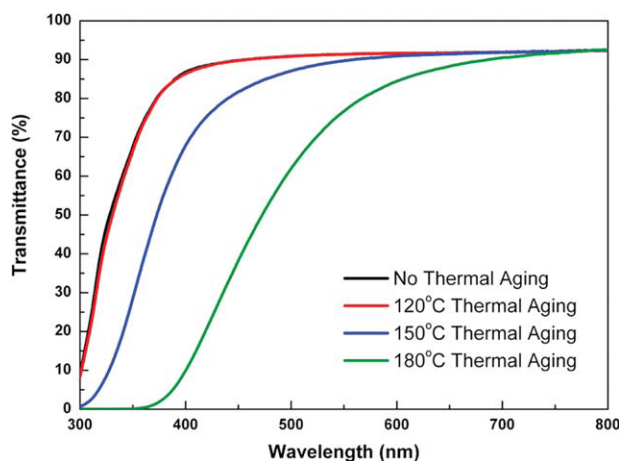


Figure 5 Transmittance spectra of cycloaliphatic epoxy hybrimer bulk before/after thermal aging at 120/150/180°C for 72 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Physical characteristics of cycloaliphatic epoxy hybrimer bulk for LED encapsulation

The refractive index of a LED encapsulant is the main factor to develop high luminescence efficiency in a white LED through enhancement of the light extraction efficiency. As conventional epoxy resin has a refractive index under 1.53, it is not suitable as LED encapsulants in terms of obtaining a white LED with high luminescence efficiency. Cycloaliphatic epoxy hybrimer bulk fabricated by sol-gel condensation and thermal curing, meanwhile, has a higher refractive index of 1.55 at a wavelength of 632.8 nm compared to that of a conventional epoxy encapsulant.^{12,13} The high refractive index of cycloaliphatic epoxy hybrimer bulk originates from high polariz-

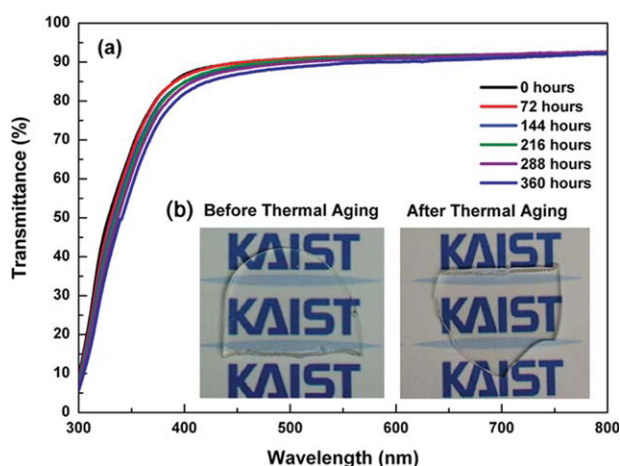


Figure 6 (a) Transmittance spectra of cycloaliphatic epoxy hybrimer bulk before/after thermal aging at 120°C for 72/144/216/288/360 h. (b) Photographs of cycloaliphatic epoxy hybrimer bulk before/after thermal aging at 120°C for 360 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

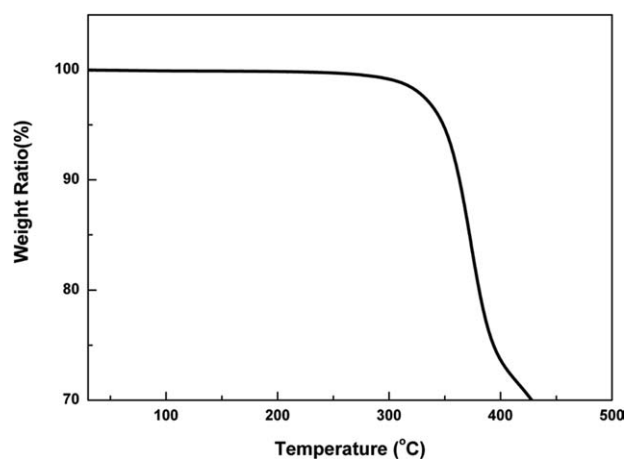


Figure 7 TGA curve of cycloaliphatic epoxy hybrimer bulk.

ability of phenyl groups in the cycloaliphatic epoxy hybrimer bulk.⁸ Therefore, cycloaliphatic epoxy hybrimer bulk is a suitable material for application as an LED encapsulant to produce a white LED with high luminescence efficiency.

Another requirement for LED encapsulants is material hardness, so as to protect the LED chip after encapsulation of the LED. The hardness of materials used as a LED encapsulant is generally estimated on the basis of the shore D hardness. Cycloaliphatic epoxy hybrimer bulk has a shore D hardness of 87, which is higher relative to other siloxane based encapsulants. The high shore D hardness of the fabricated cycloaliphatic epoxy hybrimer bulk is attributed to the rigid property of the constitutive phenyl groups.¹⁴

CONCLUSIONS

Cycloaliphatic epoxy oligosiloxane resin was synthesized by a sol-gel condensation reaction. MHHPA and TBPM were used for thermal curing of cycloaliphatic epoxy groups in this resin. Yellowness of the cycloaliphatic epoxy hybrimer bulk was minimized by control of the anhydride and catalyst content in the resin. The bulk with optimized compositions showed almost no yellowness upon thermal aging at 120°C for 360 h under air. The cycloaliphatic epoxy hybrimer bulk had high thermal stability exceeding 300°C, and its refractive index was higher compared to that of conventional epoxy encapsulants. The cycloaliphatic epoxy hybrimer bulk had high shore D hardness. Given these properties, cycloaliphatic epoxy hybrimer bulk is a candidate for use as a LED encapsulant.

References

1. Bogner, G.; Debray, A.; Hoehn, K. *Proc SPIE* 2000, 3938, 249.
2. Morita, Y. *J Appl Polym Sci* 2005, 97, 946.
3. Norris, A. W.; Bahadur, M.; Yoshitake, M. *Proc SPIE* 2005, 5941, 594115.

4. Huang, W.; Zhang, Y.; Yu, Y.; Yuan, Y. *J Appl Polym Sci* 2007, 104, 3954.
5. Yang, S. C.; Kim, J. H.; Jin, J. H.; Bae, B. S. *J Polym Sci Part B: Polym Phys* 2009, 47, 756.
6. Lee, T. H.; Kim, J. H.; Bae, B. S. *J Mater Chem* 2006, 16, 1657.
7. Yang, S. C.; Kwak, S. Y.; Jin, J. H.; Bae, B. S. *ACS Appl Mater Interfaces* 2009, 1, 1585.
8. Vorotilov, K. A.; Petrovsky, V. I.; Vasiljev, V. A.; Sobolevsky, M. V. *J Sol-Gel Sci Technol* 1997, 8, 581.
9. Jung, K. H.; Bae, B. S. *J Appl Polym Sci* 2008, 108, 3169.
10. Ellis, B. *Chemistry and Technology of Epoxy Resins*; Blackie Academic: London, 1993.
11. Nagajima, M.; Kania, C. M.; Mcquown, S. G.; Rechenberg, K. S.; Campbell, S. A.; Humbert, K. A.; Barkac, K. A. U.S. Pat. 6,863,982 (2004).
12. Zhou, Y.; Tran, N.; Lin, Y. C.; He, Y.; Shi, F. G. *IEEE Trans Adv Packaging* 2008, 31, 484.
13. Edwards, M.; Zhou, Y. *Proc SPIE* 2001, 4436, 190.
14. Morita, Y.; Tajima, S.; Suzuki, H.; Sugino, H. *J Appl Polym Sci* 2006, 100, 2010.