Low Temperature Curable Epoxy Siloxane Hybrid Materials for LED Encapsulant

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ABSTRACT: A thermally cured epoxy-siloxane hybrid material that is curable at low temperature (L-expoxy hybrimer) was investigated for use as an LED encapsulant. This new hybrimer was fabricated using thermally initiated, cationic polymerization of cycloaliphatic epoxy oligosiloxane (CAEO) resin, derived from non-hydrolytic sol–gel, mixed with oxetane hardener in the presence of a hexafluoroantimonate-type thermo-cationic initiator. The L-epoxy hybrimer was cured at a lower temperature (below 120°C) than previously reported for an epoxy hybrimer with anhydride hardener (above 180°C). The L-epoxy hybrimer showed high thermal resistance to yellowing under long-term high temperature condition, and maintained good optical transmittance. Also, it had a high refractive index (up to 1.57), as well as the hardness (Shore D 80), and low water-vapor permeability, when the new hybrimer was used to encapsulate an LED, it showed good adhesion without cracks or delamination and maintained their initial performance after the long-term aging tests (120 and 85°C at 85% humidity). © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39968.

INTRODUCTION

Light-emitting diodes (LEDs) have received much attention in the fields of lighting and display due to their high luminescent efficiency and ability to be driven at low voltage condition.[1] Due to these properties, LEDs have been tried for a number of applications including display backlighting, bright illumination, and as parts of energy storage systems.[1–5] As part of the LED packaging, an LED chip is encapsulated within a transparent material to protect the LED chip from a number of harmful aspects of the external environment (e.g., dust, humidity, and shock). Also, this encapsulant acts as a medium (light converter) due to the presence in it of dispersed phosphor particles. It can also reduce light loss by minimizing the difference between the refractive indices of the light emitter and the surrounding air.[4–11] Therefore, a good LED encapsulant is essential for the long-term reliability and high performance of an LED.

Conventionally, epoxy resins have been studied and used as LED encapsulants due to their good optical (for light transmission) and mechanical properties such as high glass transition temperature (T_g).[4,5,11,12] However, conventional epoxy resins are susceptible to yellowing from long-term exposure to UV light, and from exposure to the high temperatures generated by the LED.[11] For this reason, silicone materials have also received a lot of attention as encapsulants because they show good resist-

ance to yellowing from thermal exposure.[4,5,13,14] The thermal resistance of silicone materials originates from their strong siloxane bonds. The siloxane bond is relatively stable under long-term exposure to UV light and to high temperature. Also, properties such as hardness and refractive index can be controlled by replacing the organic substituents on the silicone atoms of the silicone material.[15] For example, the refractive index and hardness of silicone materials can be increased by replacing methyl organic substituents with phenyl groups.[14–17] The presence of phenyl groups, in particular, can increase thermal resistance due to the unique properties derived from their aromatic molecular orbitals.[17] However, silicone materials also suffer from problems such as poor moisture resistance, poor physical properties, and the need for an outer layer of protection.[4,11] Given this background, a polymer-siloxane hybrid material (hybrimer), derived from oligosiloxane resin synthesized from sol–gels, seemed a good candidate LED encapsulant that might take advantage of the benefits of both silicone and epoxy materials.[11] The polymer-siloxane hybrid materials have benefits from being a combination of organic and inorganic materials (e.g., effective barrier, optical transparency, refractive index, and thermal resistance). In particular, the epoxy-siloxane hybrimers have recently been introduced for applications related to OLED barrier coating, passivation layers, and LED encapsulant.[16,18,19] One example of interest was a thermally curable
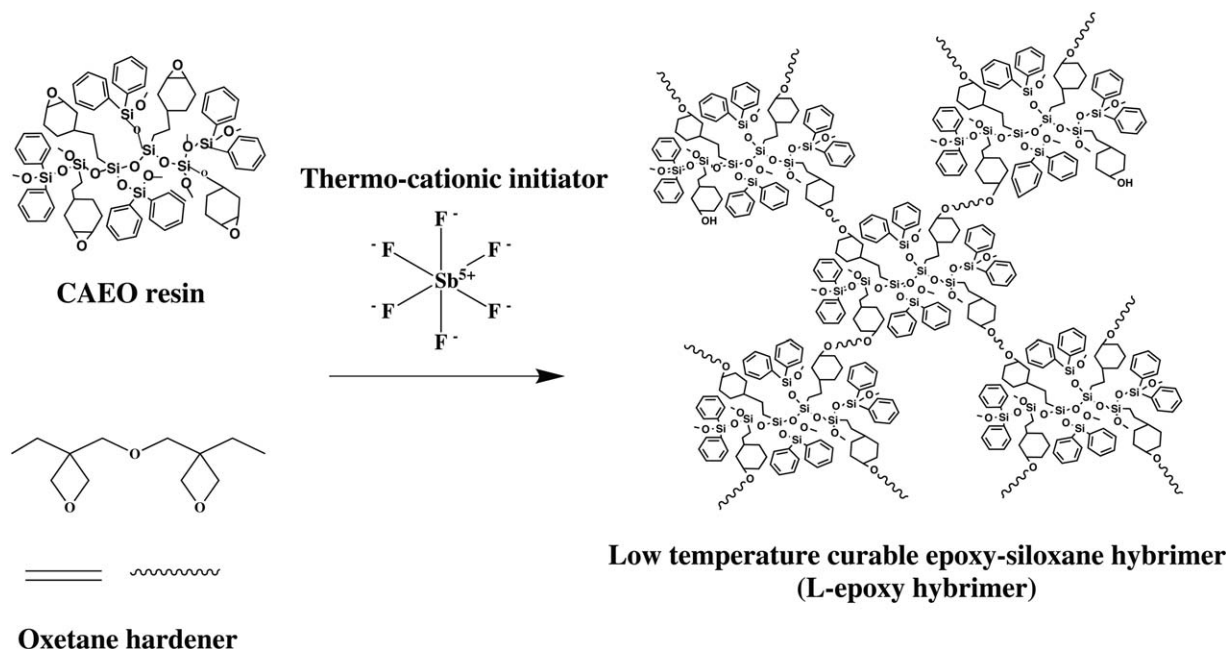
Scheme 1. Fabrication of the low temperature curable epoxy-siloxane hybrimer (L-epoxy hybrimer) using mixed resin of CAEO resin and oxetane hardener in the presence of thermo-cationic initiator.

epoxy-siloxane hybrid material hardened using anhydride (A-epoxy hybrimer).[15] The A-epoxy hybrimer showed a high refractive index (1.55) and showed little yellowing under long-term thermal aging at 120°C. However, the A-epoxy hybrimer requires a long time to cure and a very high curing temperature (above 180°C). This combination can distort its shape by thermal shrinkage, and decrease the performance of the LED due to the limited thermal resistance of the reflector cup.[3–5,18] For these reasons, a new ultraviolet (UV)-curable epoxy-siloxane hybrimer using an oxetane hardener (UV-epoxy hybrimer) was fabricated to overcome these problems.[1] The oxetane hardener provided low viscosity, and high cross-linking density, which promoted rapid curing.[20,21] The UV-epoxy hybrimer was used to an LED encapsulant without changing its flat shape. However, the UV-epoxy hybrimer had low thermal resistance due to the presence of onium salt, and thus required the large amount of anti-oxidants.[22] Therefore, the fast thermally curable epoxy-siloxane hybrimer at low temperature can be a new candidate for LED encapsulants having high thermal resistance to yellowing.

Recently, Liu et al.[23] reported on polymerization of a cycloaliphatic epoxy resin in the presence of a thermo-cationic initiator. Thermally initiated, cationic polymerization has some advantages including lower curing temperature, fewer environmental by-products and less toxicity.[24] Also, the blended resin is chemically stable under ambient conditions, and cures rapidly at a relatively low temperature compared to the conventional curing system using anhydride hardener.[24–26]

In this study, we report a low temperature curable epoxy-siloxane hybrid material (L-epoxy hybrimer) that is resistant to yellowing due to thermal exposure, as a candidate for LED encapsulant. We fabricated the new hybrimer by thermal curing

of cycloaliphatic epoxy oligosiloxane (CAEO) resin and oxetane hardener as represented in Scheme 1. A hexafluoroantimonate type of thermo-cationic initiator was used for the polymerization. The CAEO resin was synthesized using the sol–gel condensation reaction of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and diphenylsilanediol as reported previously.[16] Curing behaviors of the mixed resin, and resistance to yellowing due to thermal exposure of the L-epoxy hybrimer, were also investigated. Finally, the major physical properties relevant to the use of this new material as an LED encapsulant were characterized.

EXPERIMENTAL

Fabrication of L-Epoxy Hybrimer

Cycloaliphatic epoxy oligosiloxane (CAEO) resin was synthesized by a sol–gel condensation reaction between 1.0 mol of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTS, Gelest) and 1.5 mol of diphenylsilanediol (DPSD, Gelest, USA) with barium hydroxide monohydrate (Aldrich) as a basic catalyst.[16] The CAEO resin was mixed with 3-ethyl-3[[(3-ethyloxetane-3-yl)methoxy]methyl]oxetane (DOX, Toagosei, Japan) with a weight ratio of 1.0 : 0.2 for the CAEO resin. The hexafluoroantimonate-type initiator (ICAM-8409, Shenzhen Initial Create Applied Material, China) was mixed as a thermo-cationic initiator of polymerization between the epoxide and oxetane rings. For minimum yellowing, and maximum thermal stability and resistance of the L-epoxy hybrimer, the minimized initiator content (0.1 wt % for CAEO resin) was mixed with the CAEO/oxetane resin. The L-epoxy hybrimer (thicknesses of 2 and 5 mm) was cured at 120°C for 60 min in air, to analyze resistance to yellowing due to thermal exposure and thermal stability, as well as its optical and physical properties. As represented in Table 1, to be able to compare the characteristics of L-epoxy hybrimer,
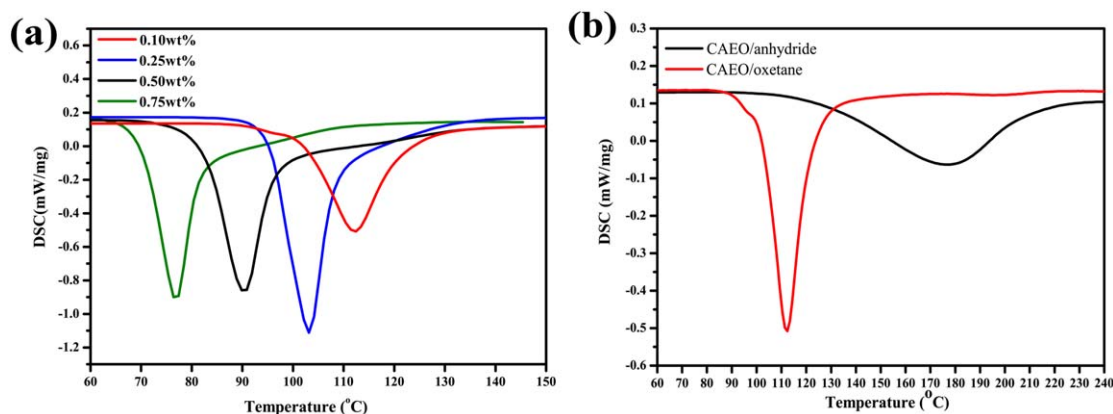
Figure 1. DSC curves of the (a) CAEO/oxetane resins with various thermo-cationic initiator contents and (b) the optimized CAEO/oxetane resin compared to the CAEO/anhydride resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

batches of thermally curable CAEO/anhydride hybrimer (A-epoxy hybrimer) was cured at 180°C for 180 min[15] and UV-curable CAEO/oxetane hybrimer (UV-epoxy hybrimer) was cured in the presence of a photo-cationic initiator using an Hg lamp for 2 min (80 mW/cm^2, 365 nm, Oriel 97453) under air.[1]

Characterization of L-Epoxy Hybrimer

To analyze the thermal curing behavior of the A-epoxy thermally curable CAEO/anhydride hardener resin and the L-epoxy low temperature curable CAEO/oxetane hardener resin in the presence of thermo-cationic initiator, the differential scanning calorimetry (DSC, Netzsch, Germany) was performed. The same amount (1.5 mg) of each sample was loaded on an Al pan and heated 5°C/min under air. The thermal stability (or heat decomposition behavior) of the epoxy hybrimers was analyzed using a thermogravimetric analyzer (TGA Q50, TA Instruments) under nitrogen and at a heating rate of 5°C/min. The optical transmittance of the epoxy hybrimers (L-epoxy hybrimer, A-epoxy hybrimer, UV-epoxy hybrimer, thickness 2 mm) was analyzed using an ultraviolet, visible, near-infrared (UV/VIS/NIR) spectrophotometer (UV3101PC, Shimadzu, Japan) at a normal wavelength range of 380–780 nm. YI was calculated using a color analysis program (ASTM, D1925) in the normal wavelength range of the UV/VIS/NIR spectrophotometer. The refractive index of the L-epoxy hybrimer (thickness 2 mm) was measured at room temperature by a prism coupler (2010 Prism Coupler, Metricon) at a wavelength 632.8 nm. The shore D hardness of the L-epoxy hybrimer (thickness 5 mm) was measured by a shore durometer (HPSD, Schmidt, Germany) at room temperature. The water-vapor permeability of the L-epoxy hybrimer (thickness 2 mm) was assessed by permeability analysis (AQUATRAN Model 1, MOCON). The photoluminescence (PL) intensity of an LED encapsulated by the L-epoxy hybrimer was measured by a photospectrometer (DARSA PRO 5100, PSI Trading, Korea) at room temperature using a xenon lamp (500 W) as an excitation source.

RESULTS AND DISCUSSION

Low Temperature Curing of Epoxy Oligosiloxane Resin with Oxetane

The degree of condensation of the siloxane bond in the cycloaliphatic epoxy oligosiloxane (CAEO) resin synthesized by the sol–gel reaction of ECTS and DPSD, was confirmed by ^{29}Si-NMR.[16] There was a high degree (over 90%) of siloxane bonding networks.[16] Therefore, in this study, we used the CAEO resin to fabricate the L-epoxy hybrimer as shown in Scheme 1. The thermo-cationic initiator can lower the curing temperature and strengthen the anti-yellowing property in an epoxy hybrimer. In a previous study, methylhexahydrophthalic anhydride was used for thermal curing of the CAEO resin to improve thermal resistance of an epoxy hybrimer.[18] However, it needed an additional anhydride-hardener, ring-opening catalyst (tetrabutylphosphonium methanesulfonate) which resulted in a need for curing at high temperature and for a long time.[18] Therefore, due to both the high curing temperature, and the intrinsic characteristics of the anhydride hardener, epoxy hybrimers are discolored from clear to a light yellow.

As the initiator content increases, the onset curing temperature decreases. However, excess amounts of catalyst can produce large numbers of free radicals that cause yellowing in the epoxy hybrimer during long-term thermal aging.[28] For this reason, we minimized the initiator content down to 0.1 wt % of CAEO resin. Figure 1(b) presents the DSC curves indicating the curing behavior of the optimized thermo-cationic initiator CAEO/oxetane resin compared to that of the CAEO/anhydride resin. The exothermic peak of the CAEO/anhydride resin was observed between 124.0 and 211.4°C with the maximum peak at 176.9°C. However, the exothermic peak of the CAEO/oxetane with optimized thermo-cationic initiator resin was observed at a range of significantly decreased temperature (between 101.1 and 122.4°C), with the maximum peak at 112.2°C. In contrast, the exothermic energy change (ΔH) was almost the same for the two: −115.8 J/g and −120.3 J/g, respectively. Based on the sharp gradient and narrow range of the DSC curves, we can conclude that the CAEO/oxetane resin has a faster curing rate, and cures at lower temperature, than the CAEO/anhydride resin. These results are caused by the presence of the oxetane hardener and thermo-cationic initiator. The oxetane hardener, which has high ring strain, encourages a fast curing rate, and the thermo-cationic initiator enables low temperature curing.[20,21] Therefore, the thermo-cationic initiator and oxetane hardener are suitable for polymerization of the CAEO resin.
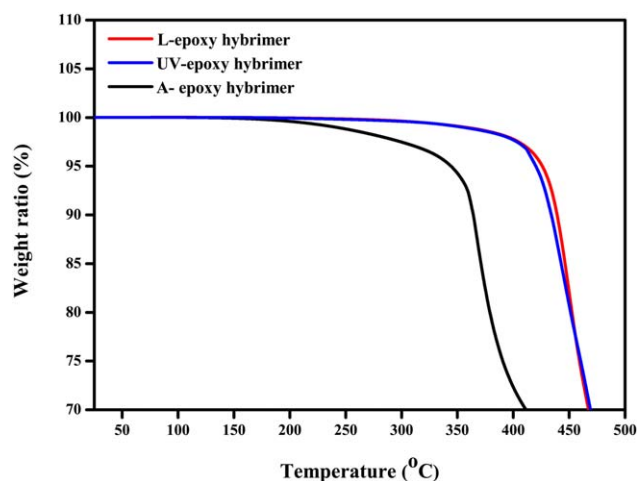
Figure 2. TGA curves of the epoxy hybrimers, representing 5% weight loss temperatures of L-epoxy hybrimer (425.9°C), UV-epoxy hybrimer (420.1°C), and A-epoxy hybrimer (344.2°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

### Thermal Stability of L-Epoxy Hybrimer

Prolonged exposure of LED encapsulants to high junction temperatures (about 120°C) can cause an adverse effect on their light-emission performance.[29,30] For long-term reliability of the LED encapsulant, it should have high thermal stability to pre-

vent heat related decomposition (measured by TGA), as well as resistance to yellowing caused by heat exposure. Figure 2 presents the heat decomposition behaviors of the epoxy hybrimers. The temperature at which a 5% weight loss occurred for the L-epoxy hybrimer was 426°C, while that for the A-epoxy and UV-epoxy hybrimers were lower (344 and 420°C, respectively). These higher thermal stability results of the CAEO/oxetane (L-epoxy and UV-epoxy) hybrimers originated from high density cross-linking in the oxetane hardener, which has difunctional reactive sites and low molecular weight.[31] Similarly, epoxy rings in the CAEO resin have high density cross-linking because of the multifunctional structure and short siloxane bonds in the CAEO resin.[32] Therefore, the thermal stability of the L-epoxy hybrimer is much higher than those of other siloxane based LED encapsulants (around 350°C).[27]

The refractive index of the LED encapsulant is a significant characteristic for achieving high luminescence flux. The L-epoxy hybrimer has a high refractive index (up to 1.57) at a wavelength of 632.8 nm. A large number of polarized phenyl groups, results in a relatively high refractive index compared to conventional epoxy LED encapsulants (1.53).[33] They are also responsible for the degree of hardness and low water-vapor permeability required for the LED encapsulant to protect the LED from environmental factors such as shock and humidity. The L-epoxy hybrimer is harder (Shore D hardness: 80) than commercial
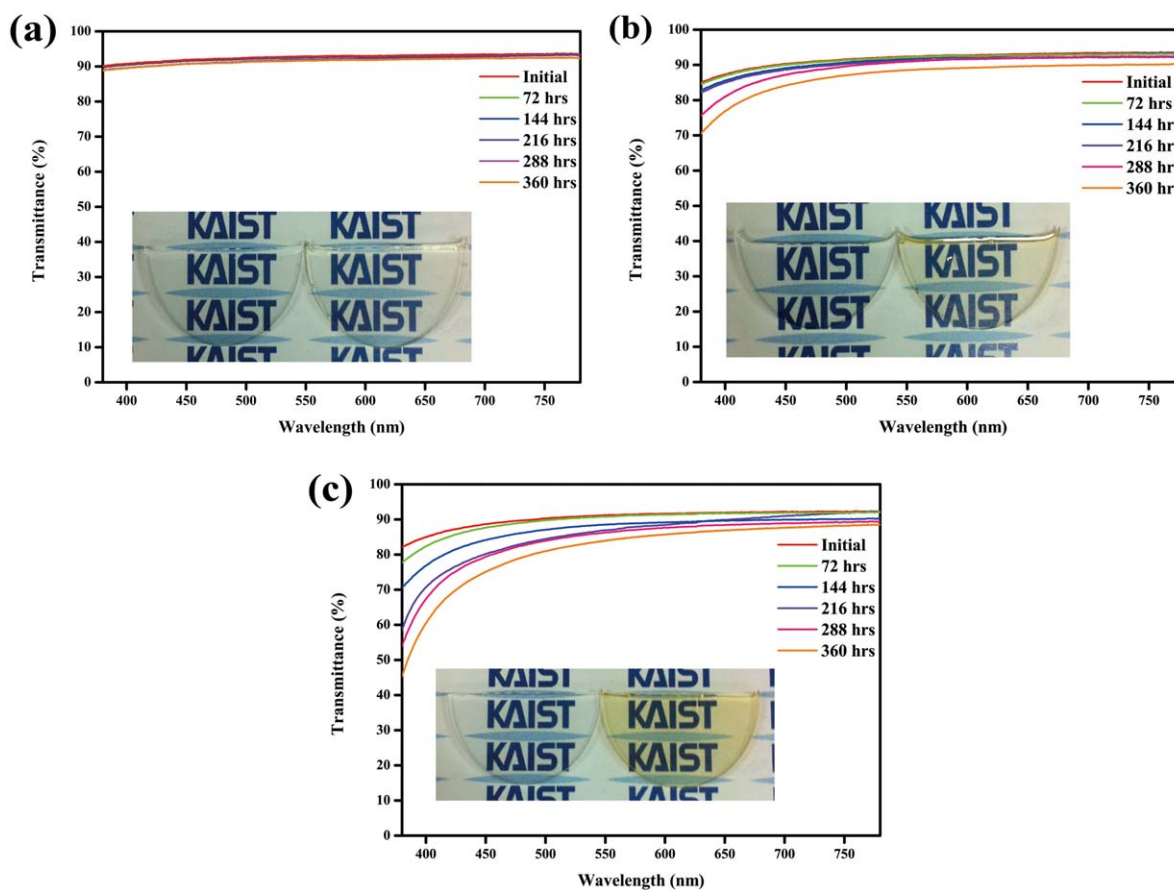
Figure 3. UV/VIS/NIR spectra of the epoxy hybrimers (2 mm) before and after thermal aging at 120°C for 360 h in air (a) L-epoxy, (b) A-epoxy, and (c) UV-epoxy hybrimer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
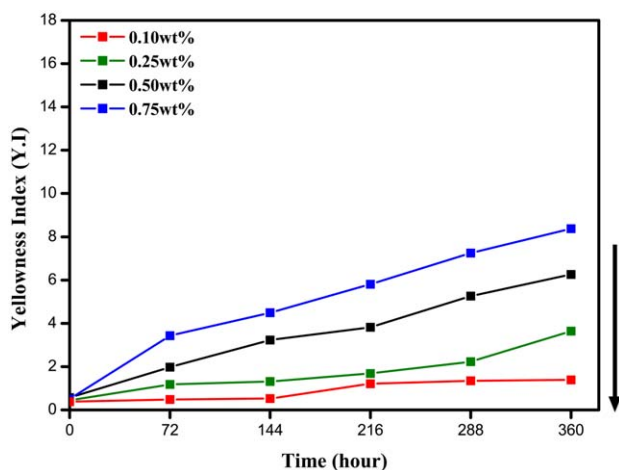
Figure 4. Changes in yellowness index of the L-epoxy hybrimer with various thermo-cationic initiator contents as a function of thermal aging time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

silicone LED encapsulants such as OE-6630 (Dow corning, Shore D hardness: about 40). The increase in hardness originates from the rigid structure characteristic of phenyl groups and the high density cross-linking of the CAEO/oxetane resin.[17,31,32] Moreover, the L-epoxy hybrimer has lower water-vapor permeability (about 1.09 g m^{-2} day^{-1}) compared to OE-6630 (Dow corning, water vapor permeability: about 3.1 g m^{-2} day^{-1}). This is because the large amount of hydroxyl groups generated by the epoxy polymerization can effectively prevent the penetration of water-vapor by polar–polar interaction. Penetration of water-vapor is also inhibited by the high density epoxy cross-linking.[16] These characteristics of L-epoxy hybrimer are summarized in Table 2. Also, the viscoelastic behavior of cycloaliphatic epoxy oligosiloxane hybrimer is characterized by weak and broad glass-transition behaviors over wide temperature ranges unlike long chain polymer such as PET. This weak glass-transition behavior originates from the high crosslinking density as expected from the multi-functional structure of the CAEO coupled with their short cross-linkable cycloaliphatic epoxy groups.[36–38]

Thermal Resistance of L-Epoxy Hybrimer

The epoxy hybrimers were subjected to a thermal aging test at 120°C for 360 h in air to compare their resistance to thermal degradation. In Figure 3, the transmittance spectra of the epoxy hybrimers were analyzed before and after thermal aging at a normal wavelength range of 380–780 nm in every 72 h. All the epoxy hybrimers had high initial optical transmittance (up to 90%) before thermal aging. After long-term thermal aging, the optical transmittance of the A-epoxy hybrimer was reduced from 90% to 80%, and that of the UV- epoxy hybrimer from 90% to 70%, at a wavelength of 450 nm. In contrast, the L-epoxy hybrimer maintained its initial transmittance (around 90%) even after thermal aging for 360 h. These transmittance results are well matched with the yellowing characteristics, as shown in the pictures of Figure 3.

A yellowness index (YI) was analyzed before and after the long-term thermal aging test using a color analysis program, based

on optical transmittance using an UV/VIS/NIR spectrophotometer. We measured the optical transmittance to compare the yellowness of the epoxy hybrimers before and after thermal aging at 120°C for 360 h in air. The yellowness index was calculated using the following equation.

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

where X_{CIE}, Y_{CIE}, and Z_{CIE} represent CIE tristimulus values for red, green, and blue. Figure 4 presents the change in YI of the L-epoxy hybrimer according to the thermo-cationic initiator content. The YI was reduced as the initiator content decreased. Experimentally, we observed the yellowing by eye when the YI value was above three. Thus, yellowing appeared in the L-epoxy hybrimer when the content of initiator was 0.25, 0.50, or 0.75 wt %, after long-term thermal aging. However, the L-epoxy hybrimer with 0.10 wt % initiator content did not show yellowing even after long-term thermal aging. The yellowing occurred due to oxidative degradation by large numbers of free radicals, easily provided by excessive initiator.[34] Therefore, the content of the initiator should be minimized.

Figure 5 represents changes in the YI of L-epoxy hybrimer, with 0.1 wt % of initiator content, compared to changes in the YIs of the A-epoxy and the UV-epoxy hybrimers. The YIs of the UV-epoxy and A-epoxy hybrimers rose to 8 and 16, respectively, after long-term thermal aging for 360 h, as shown in Figure 5. They changed from transparent to an opaque yellow, because they contained large amounts of the UV-cationic initiator and the anhydride hardener that are sources of free radicals under high temperature conditions.[34] On the other hand, the L-epoxy hybrimer did not show yellowing, and its YI value was less than two, after the long-term thermal aging test. The high thermal resistance of the L-epoxy hybrimer indicates that it provides almost no free radicals from sources such as non-polymerized organic reactive sites, or thermo-cationic initiators, during aging condition.[28,34] The lack of yellowing was also because the L-epoxy hybrimer has high density cross-linking between the oxetane and epoxy rings, and contains very small amounts of
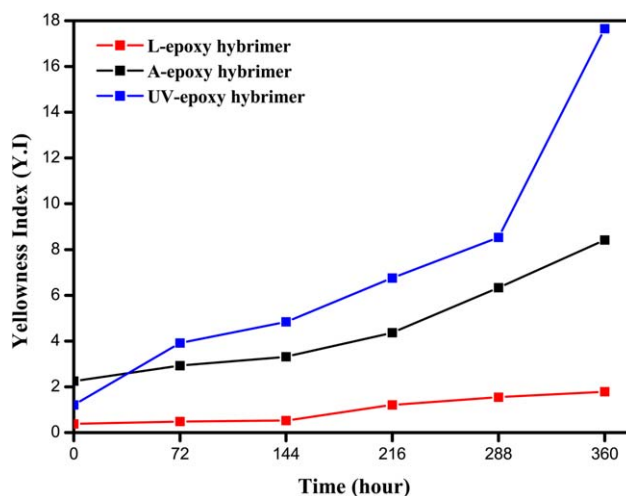
Figure 5. Changes in yellowness index of the epoxy hybrimers as a function of thermal aging time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
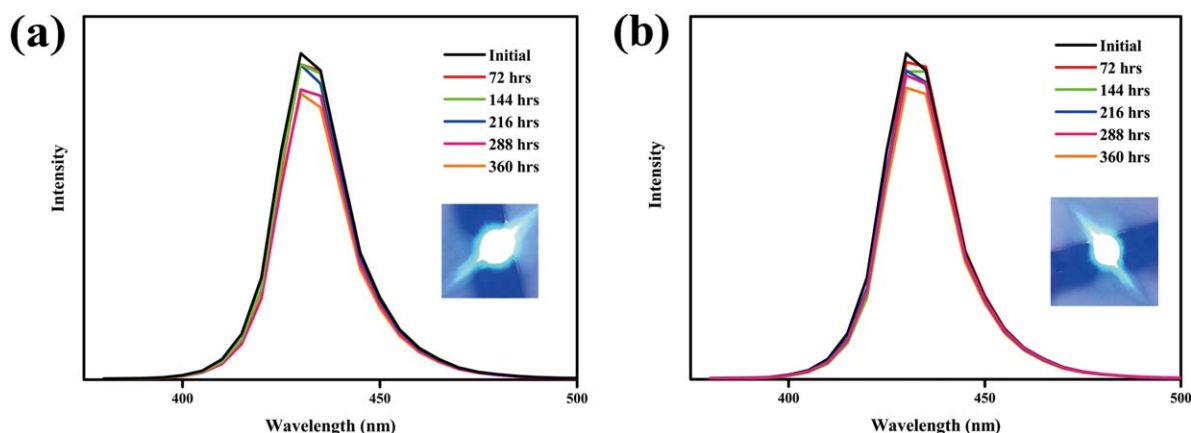
Figure 6. Change in PL intensity of blue LED encapsulated by the L-epoxy hybrimer under (a) 120°C thermal aging and (b) 85°C /85% humidity aging test for 360 h in air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Formulations and Notations of Cycloaliphatic Epoxy Hybrimers

Epoxy hybrimer	Resin	Oxetane (hardener)	MHHPA (hardener)	Cationic initiator
L-epoxy hybrimer	CAEO	20 wt %	None	0.1 wt %
A-epoxy hybrimer	CAEO	None	Equivalent ratio for epoxy groups	None
UV-epoxy hybrimer	CAEO	20 wt %	None	1.2 wt %

MHHPA, methylhexahydrophthalic anhydride (Aldrich, USA).

initiators.[31,32] In addition, the large number of phenyl groups and the high degree of condensation of the CAEO resins, encourage high thermal resistance in the L-epoxy hybrimer.[16–18]

That the yellowing tendencies of the epoxy hybrimers are well matched with optical transmittance results is clearly shown in Figure 4. The L-epoxy hybrimer with minimized initiator content had high thermal resistance under long-term thermal aging, showed no discoloration and maintained high optical transparency. According to the results of optical transmittance and the YI analysis, the L-epoxy hybrimer can promote long-term reliability of LEDs at high junction temperatures (about 120°C) in its role as an LED encapsulant.

LED Encapsulation of the L-Epoxy Hybrimer

The L-epoxy hybrimer is suitable as an LED encapsulant, because it satisfies the requirements for an effective LED encapsulant: high optical transparency, high refractive index, proper hardness, low water-vapor permeability, and in particular, high thermal resistance. In addition, L-epoxy hybrimer has good adhesion properties because it has many hydroxyl groups created when epoxide-ring-opening, thermo-cationic polymerization occurs.[1,35] Moreover, it showed no cracks or distortion when it was used to encapsulate an LED. Therefore, we encapsulated a blue LED with L-epoxy hybrimer to analyze the change of photoluminescence (PL) intensity before and after long-term thermal (120°C), and humidity (85°C at 85%) aging tests for 360 h in air. Figure 6 presents the change of PL intensity every 72 h from initial to final state of the two aging

conditions. According to the PL analysis, the L-epoxy hybrimer encapsulated blue LED had good resistance to both high temperature and humidity. Based on these analyses, the L-epoxy hybrimer can now be considered a practical LED encapsulant due to its excellent reliability under severe conditions.

CONCLUSION

In conclusion, we synthesized the cycloaliphatic epoxy oligosiloxane (CAEO) resin by a non-hydrolytic sol–gel reaction, and oxetane hardener was introduced to achieve rapid curing of the resin resulting in fully cured epoxy-siloxane hybrimer (L-epoxy hybrimer). A thermo-cationic polymerization initiator was used to enable curing at low temperature. The low temperature curing can reduce cracks in the encapsulants and preserve the LED's initial light-emitting performances which can be degraded in high temperature curing condition. Also, this low

Table II. Characteristics of the Low Temperature Curable Epoxy-Siloxane Hybrimer (L-Epoxy Hybrimer)

Property	Unit	Value
Transmittance	% (at 450 nm)	~90
Refractive index	n (at 632.8 nm)	1.568
5 wt % loss temperature	°C (5°C/min, N_2)	452.9
Hardness	Shore D	80
Water vapor permeability	g m^{-2} day^{-1}	1.09

temperature curing coupled with a short curing time is beneficial for the implementation in actual production process. The L-epoxy hybrimer showed excellent thermal resistance against yellowing under the LED's high junction temperature condition, which ensured preservation of the high optical transmittance. The L-epoxy hybrimer was successfully encapsulated on the blue LED without any cracks and distortion. Most noticeably, the encapsulated LED showed good light-emitting performance even after 360 h of thermal aging at 120°C and humidity aging (85°C at 85%) tests. Based on these excellent non-yellowing property as well as other good characteristics, the L-epoxy hybrimer may be considered a potential candidate for high-performance LED encapsulant.

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