

# Studies on UV-Stable Silicone–Epoxy Resins

Wei Huang, Ying Zhang, Yunzhao Yu, Youxue Yuan

*Institute of Chemistry, Chinese Academy of Science, Beijing 100080, People's Republic of China*

Received 24 October 2006; accepted 30 December 2006

DOI 10.1002/app.26188

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

**ABSTRACT:** Silicone–epoxy resins were synthesized through hydrosilylation of 1,2-epoxy-4-vinyl-cyclohexane with 1,3,5,7-tetramethylcyclotetrasiloxane. The silicone–epoxy resins showed high reactivity in the presence of aluminum complex/silanol compound catalysts. Curing of the resins was effected at extremely low concentrations of the aluminum acetylacetonate/ $\text{Ph}_2\text{Si}(\text{OH})_2$  catalyst to give hard materials with optical clarity. For the silicone–epoxy resins containing Si–H bonds,  $\text{Al}(\text{acac})_3$  alone is

effective for the curing. The cured silicone–epoxy resins showed excellent UV resistance. An improvement in the lifetime of UV-LEDs was achieved using the silicone–epoxy compositions as encapsulant. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3954–3959, 2007

**Key words:** silicone-epoxy resin; curing, UV stability; packaging material

## INTRODUCTION

Development of hightech appeals for high performance materials. Epoxy resins are versatile, they have been the standard choice in encapsulation of indicator LEDs.<sup>1</sup> However, they suffer from yellowing under the influence of heat and UV radiation.<sup>2</sup> Silicone resins are excellent in thermal stability and UV-resistance, but they are relatively weak in adhesion and mechanical strength.<sup>3–6</sup> Therefore, there is a need to combine the advantage of epoxy–resins, such as low cost, easy to process, excellent mechanical properties, and good adhesion, with the advantages of silicone. Modification of epoxy–resins with silicone has attracted much attention in recent years.<sup>7–11</sup>

Silicone–epoxy resins have been synthesized, and applied for encapsulating LED.<sup>12,13</sup> In these works curing of silicone-epoxies were effected using a curing agent such as acid anhydride. The use of anhydride reduced the proportion of silicone in the cured materials, and consequently their UV resistance and thermal stability were limited.

In this article, we synthesized a series of silicone–epoxy resins by the platinum-catalyzed hydrosilylation of 1,2-epoxy-4-vinylcyclohexane with 1,3,5,7-tetramethylcyclotetrasiloxane. These resins were very reactive in the presence of aluminum complex-silanol catalysts at very low concentrations. The cured silicone–epoxy resins show excellent optical clarity and UV resistance.

## EXPERIMENTAL

### Materials

1,3,5,7-Tetramethylcyclotetrasiloxane, 1,2-epoxy-4-vinyl-cyclohexane, aluminum acetylacetonate  $\text{Al}(\text{acac})_3$ , and 2-mercaptobenzothiazole were chemical reagents purchased from Adrich Chemical and used as received. Lamoreaux platinum catalyst and  $\text{Ph}_2\text{Si}(\text{OH})_2$  were obtained from Dow Corning Company. 3,4-Epoxy-cyclohexylmethyl-3,4-epoxycyclohexane carboxylate (ERL-4221), and diglycidyl ether of bisphenol A (DGEBA) were industrial products supplied by Dow and Shell Chemical, respectively. The acid anhydride curing agent, hexahydro-4-methylphthalic anhydride (MeHPPA), was a commercially available product of Lonza (Italy). Catalyst used to promote the epoxy-anhydride reactions was tetra-*n*-butylphosphonium *o,o'*-diethylphosphotodithioate purchased from Nippon Chemical (Japan).

### Synthesis of silicone–epoxy resins

To a 250-mL three-necked round bottom flask equipped with a reflux condenser and a nitrogen inlet, 24 g (0.1 mol) 1, 3, 5, 7-tetramethylcyclotetrasiloxane, 52.1 g (0.42 mol) 1, 2-epoxy-4-vinyl-cyclohexane, and 80-mL toluene was loaded. The reaction mixture was refluxed for 1 h. After cooling to room temperature, 1 drop of the platinum catalyst (0.75 wt % Pt) was added. Then the temperature of the reaction mixture was raised to 70°C and allowed to stand for 2 h. Completion of the reaction was indicated by disappearance of the IR band at  $2155\text{ cm}^{-1}$  for Si–H bonds and the  $^1\text{H-NMR}$  signal at 4.67 ppm. The reaction mixture was cooled to room temperature

Correspondence to: W. Huang (huangwei@iccas.ac.cn).

and 0.005 g 2-mercaptobenzothiazole was added to deactivate the catalyst. Toluene and the excess reactant were removed under 80°C/5 mmHg to give 67.95g of 1, 3, 5, 7-tetramethyl-1, 3, 5, 7-tetra [(3, 4-epoxycyclohexyl) ethyl]-cyclotetrasiloxane.

For the preparation of silicone-epoxies containing Si-H bonds, 0.2 mol or 0.3 mol, of 1,2-epoxy-4-vinyl-cyclohexane was used to react with 0.1 mol of 1,3,5,7-tetramethylcyclotetrasiloxane. The presence of Si-H bonds in the products was confirmed by IR and <sup>1</sup>H-NMR. After completion of the reaction, the remained vinyl group in the silicone-epoxy was below 0.3% based on <sup>1</sup>H-NMR spectrum. Viscosity of silicone-epoxies was determined using a rotation viscometer RHEOTEST 2 with a cone-and-plate measuring system. The data are given in Table I.

### Curing of silicone-epoxy resins

We dissolved 0.1 g Ph<sub>2</sub>Si(OH)<sub>2</sub> in 5 g DGEBA to give the catalyst component A, and 0.1 g Al(acac)<sub>3</sub> was dissolved in 5 g DGEBA to give the catalyst component B. We mixed 5 g silicone-epoxy with a given amount of the catalyst component A and the catalyst component B, the mixture was degassed under vacuum and then poured into a polycarbonate mold. The curing was carried out at 80°C for 30 min and then 120°C for 30 min. The gelation time of the silicone-epoxy composition was determined using an electrical hot plate. Anhydride-ERL-4221 and anhydride-DGEBA curing reactions were performed at 120°C for 1 h. The composition consisted of 100 parts by weight of ERL-4221 (or DGEBA), 60 parts (or 80 parts) by weight of MeHPPA, and 1.2 parts by weight of tetra-*n*-butylphosphonium *o,o'*-diethylphosphotodithioate.

### Tests for UV and thermal stability of the cured silicone-epoxy resins

Light transmission properties were determined on 10-mm thick specimens. The light transmittance over the range of 360 to 800 nm was measured by a UV-Vis spectrophotometer. Thermal aging studies were conducted in a circulating air oven at 150°C for 24 h. A mercury-vapor lamp with a wavelength band range 250–320 nm, and a power of 500 W was used for UV aging tests. The distance between the specimens and the UV lamp was 40 cm.

TABLE I  
Silicone-Epoxyes Synthesized

<i>m</i> Value of silicone-epoxy	Silicone content in silicone-epoxy (%)	Viscosity (Pa s)	Reaction yield (%)
2	49.2	0.6	95.8
3	39.2	0.5	94.5
4	32.6	0.3	92.3

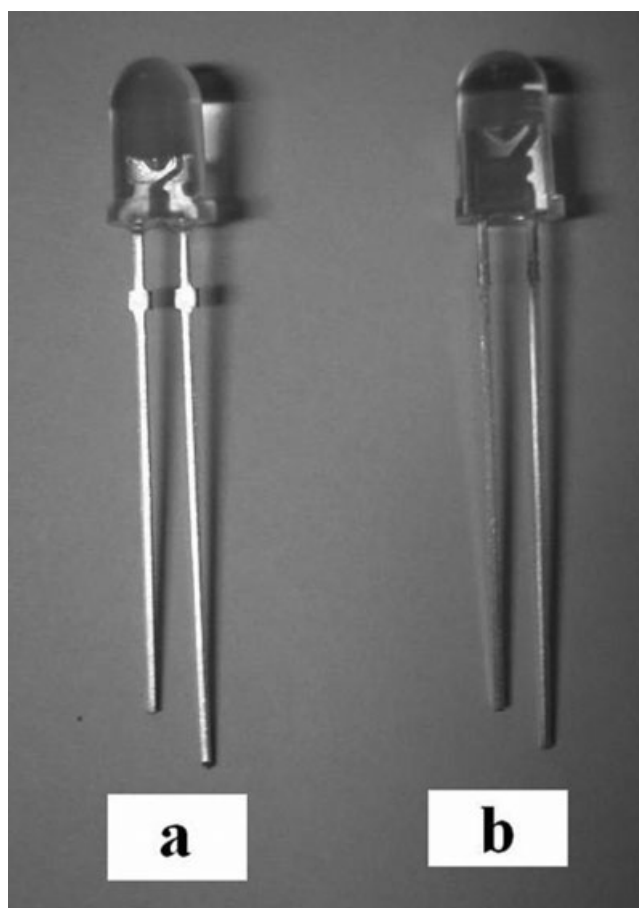


Figure 1 UV-LED encapsulated with silicone-epoxy (a) and the commercially available UV-LED SDL-5N3CUV (b).

### Packaging UV-LEDs with silicone-epoxies

The UV chips with a central wavelength at 393 nm and an electrical power of 10 mW were used to fabricate UV-LEDs. The chips were obtained from Gree (USA), which were based on silicon carbide (SiC) and gallium nitride (GaN) materials technology. Figure 1 shows the UV-LED encapsulated with silicone-epoxy (a) and the commercially available UV-LED SDL-5N3CUV (b). The chips of SDL-5N3CUV were also from Gree, and had the same properties as that of the chips we used. For the aging tests, UV LEDs were operated at a steady current of 20 mA. The light intensity was measured over time on a Photometric Colorimetric and Electric Test System for LED Lamps and Luminaires made by Everfine Photo-E-Info (People's Republic of China).

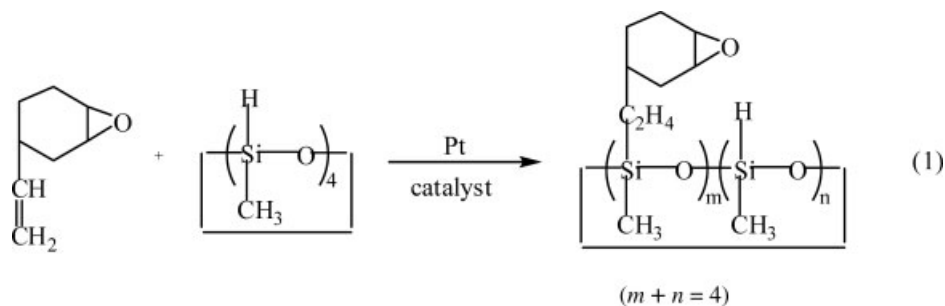
## RESULTS AND DISCUSSION

### Synthesis and curing of silicone-epoxy resins

The platinum-catalyzed hydrosilylation reaction is by far the most important method for the synthesis of silicone-containing compounds and polymers.

Many silicone-epoxies have been synthesized via hydrosilylation as described by Crivello and Lee.<sup>14</sup> The reaction used for the preparation of the silicone-

epoxy resin is shown in eq. (1). Typically, the reactions were carried out at between 60 and 90°C using toluene as solvent.



The average number of  $m$  and  $n$  was regulated by the ratio of the reactants. In eq. (1),  $n = 0$  means the Si-H bonds are completely converted, and the siloxane part makes 32.6 wt % of the product 1,3,5,7-tetramethyl-1,3,5,7-tetra[(3, 4-epoxycyclohexyl) ethyl]cyclotetrasiloxane. To ensure complete conversion of Si-H, an excess of 1,2-epoxy-4-vinyl-cyclohexane was used in the synthesis.

In the cases  $n = 1$  and  $n = 2$ , the fraction of the siloxane are higher, but a part of Si-H bonds is retained in the silicone-epoxy resin. When anhydride or amine is used as curing agent for the silicone-epoxy resin, Si-H bonds will take part in reactions, which result in hydrogen gas releasing.

To make silicone-epoxy resins with Si-H bonds viable encapsulants, a curing method is needed, in which Si-H bonds can survive the curing and transparent cured product can be obtained. We found that using the aluminum-complex/silanol as catalyst, silicone-epoxies can be cured without severing Si-H bonds. This was confirmed by retention of the IR band at 2155  $\text{cm}^{-1}$ .

Aluminum-complex/silanol catalyst was firstly used for curing of cycloaliphatic epoxy resins, through a cationic polymerization mechanism.<sup>15-17</sup> However, the catalyst system was sensitive to moisture in the atmosphere, and therefore the cured epoxy-resin usually showed a seriously wrinkled surface.

We found that the aluminum complex/silanol catalyst was very effective for the curing of silicone-epoxy resins, even at a concentration below 0.1 wt %, to give optically clear products.<sup>18,19</sup> The reaction was not significantly affected by moisture in the atmosphere, and the cured resins with a smooth surface were obtained.

Therefore, Si-H can be retained in the silicone-epoxy resin and the cured resins with different polysiloxane proportions were synthesized. Silicone-epoxies with different  $m$  values are listed in Table I. The silicone-epoxies were colorless liquids of low

viscosity. The yield was usually very high, especially for the silicone-epoxies containing Si-H bonds.

Side reactions involving platinum-catalyzed ring-opening polymerization of the epoxy groups are possible.<sup>20</sup> This is indicated by the viscosity enhance of the products. Since platinum complexes together with Si-H compounds are effective initiators for the ring-opening polymerization of epoxide,<sup>21</sup> the risk of gelation existed, because the silicone-epoxies are di-, tri-, or tetra-functional. To avoid gelation in the course of synthesis, the reaction temperature must be well controlled and 2-mercaptobenzothiazole must be added to deactivate the platinum catalyst before the step of solvent removing.

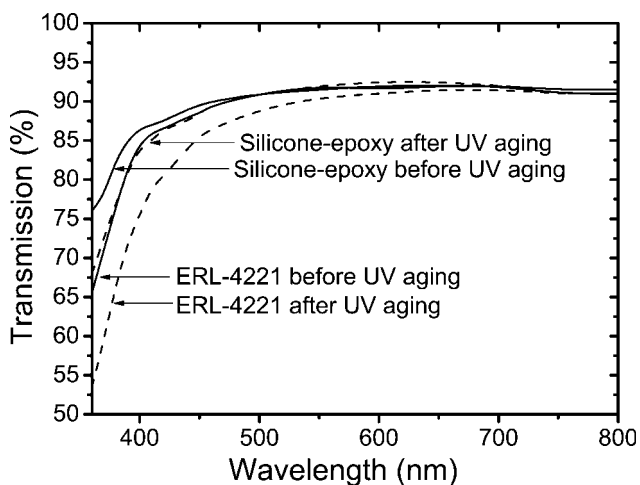
The neat silicone-epoxies were stable upon storage; no gelation was observed on heating at 100°C for 10 h. To cure the silicone-epoxies,  $\text{Al}(\text{acac})_3$  and  $\text{Ph}_2\text{Si}(\text{OH})_2$  were employed in this study. Other aluminum complexes and silanol compounds as reported in the literature<sup>15</sup> were turned out also effective.

Reactivity, in terms of gelation time, of silicone-epoxies with  $\text{Al}(\text{acac})_3/\text{Ph}_2\text{Si}(\text{OH})_2$  catalyst at a concentration of 0.02 wt %/0.02 wt % is shown in Table II. The resin without Si-H bond ( $m = 4$ ) had

**TABLE II**  
Reactivity of the Silicone-Epoxy Compositions

$m$ Value of silicone epoxy	$\text{Al}(\text{acac})_3$ content (wt %)	$\text{Ph}_2\text{Si}(\text{OH})_2$ content (wt %)	Temperature (°C)	Gelation time (min)
2	0	0	100	- <sup>a</sup>
2	0.02	0.02	80	4-5
2	0.02	0	80	4-5
3	0	0	100	- <sup>a</sup>
3	0.02	0.02	80	6-7
3	0.02	0	80	6-7
4	0	0	100	- <sup>a</sup>
4	0.02	0.02	80	9-10
4	0.02	0	100	- <sup>a</sup>

<sup>a</sup> No gelation after 10 h.



**Figure 2** Optical transmittance versus wavelength for the silicone-epoxy resin and the anhydride-cured ERL-4221.

a gelation time of 9–10 min at 80°C. The gelation time decreased to 6–7 min for the silicone-epoxy resin of  $m = 3$ , and 4–5 min for the silicone-epoxy resin of  $m = 2$ . It is suggested that the reactivity of the silicone-epoxies increases with the number of the Si–H bond in the molecule. Furthermore, the silicone-epoxies containing Si–H bonds could be cured using  $\text{Al}(\text{acac})_3$  alone as catalyst, while the concentration of  $\text{Ph}_2\text{Si}(\text{OH})_2$  showed little influence on the gelation time. On the contrary,  $\text{Ph}_2\text{Si}(\text{OH})_2$  was the indispensable component for curing of the silicone-epoxy resin without Si–H bonds ( $m = 4$ ): when  $\text{Ph}_2\text{Si}(\text{OH})_2$  was absent, gelation did not take place in 10 h at 100°C.

Using a schedule of heating at 80°C for 30 min and then 120°C for 30 min, the silicone-epoxies were cured to transparent materials of pencil hardness in the range of 2H–4H, which varied with the average number of  $m$ . The cured materials became softer as the polysiloxane fraction increased.

The mechanism of the polymerization of silicone-epoxies was believed to be cationic. Kinetic studies to illustrate the role of Si–H bonds in the curing reactions will be continued. It is likely that the Si–H bonds played the same role as they did in the ring-open polymerization of epoxides catalyzed by rhodium complexes together with Si–H containing compounds.<sup>22</sup>

#### UV and thermal stability of cured silicone-epoxy resins

The silicone-epoxies cured by  $\text{Al}(\text{acac})_3/\text{Ph}_2\text{Si}(\text{OH})_2$  have excellent UV stabilities.<sup>17,18</sup> Change of optical transmittance at different wavelength after UV-aging is shown in Figure 2 for the silicone-epoxy resin ( $m = 3$ ). The UV aging property of anhydride-cured cycloaliphatic epoxy resin ERL-4221 is also shown

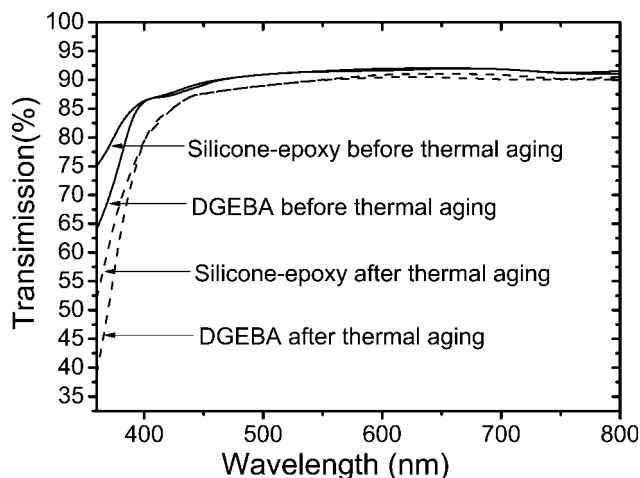
for comparison. The cycloaliphatic epoxy resin was considered to have excellent UV-resistance,<sup>1</sup> and the catalyst used in this study to promote the epoxy-anhydride reactions was a choice for the UV-stability of epoxy compositions.<sup>23</sup>

It is seen that the cured silicone-epoxy resin was more transparent in the range 360–500 nm compared with the anhydride-cured ERL-4221 resin. After UV-aging, the difference is even greater. For the anhydride-cured ERL-4221 resin, yellowing was easily noticed by the naked eyes. The silicone-epoxy resin was evidently superior to the anhydride-cured ERL-4221 resin in UV-resistance.

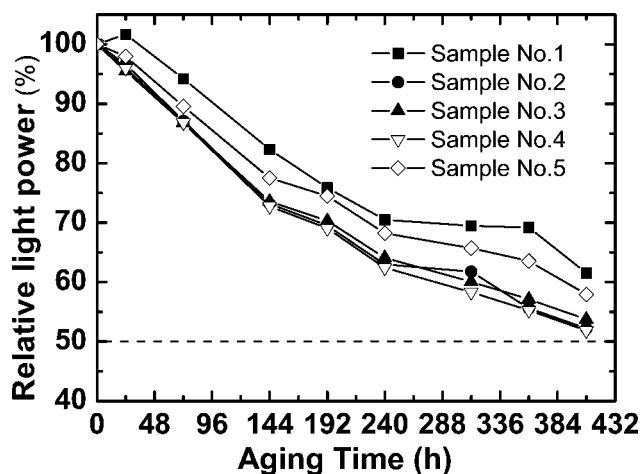
In Figure 3, a comparison between the silicone-epoxy resin and the anhydride-cured DGEBA epoxy resin in thermal aging properties is given. It is seen that the silicone-epoxy resin showed only a marginal improvement in thermal resistance compared with the conventional epoxy resin.

#### Lifetime of UV-LEDs packaged with silicone-epoxy resin

Since silicone-epoxy resins were excellent in UV-resistance, they were used for packaging of UV-LEDs. For comparison, UV-chips of the same batch were packaged using the silicone-epoxy resin  $m = 3$  and the anhydride-cured ERL-4221 resin respectively. LEDs were operated at a steady current 20 mA in the aging tests, and the light output was measured over time. The time when the light intensity attenuation reached 50% was taken as the lifetime of the LED. In Figures 4 and 5, the change of the relative intensity is shown. It is seen that the lifetimes of the LEDs packaged by silicone-epoxy exceeded 400 h, compared with 120 h for LEDs packaged by ERL-4221.



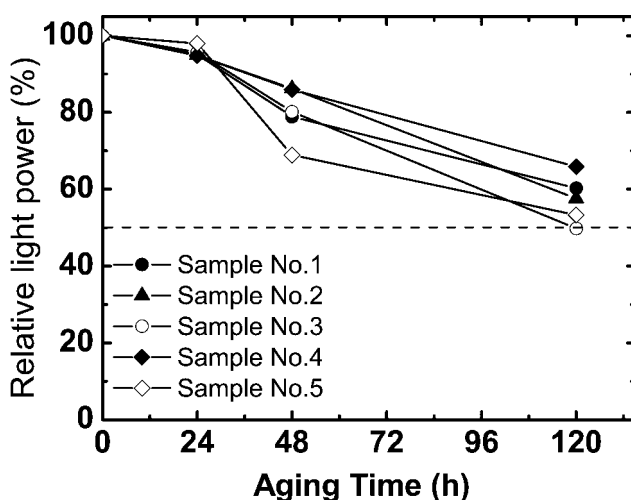
**Figure 3** Optical transmittance versus wavelength for the silicone-epoxy resin and the anhydride-cured DGEBA resin.



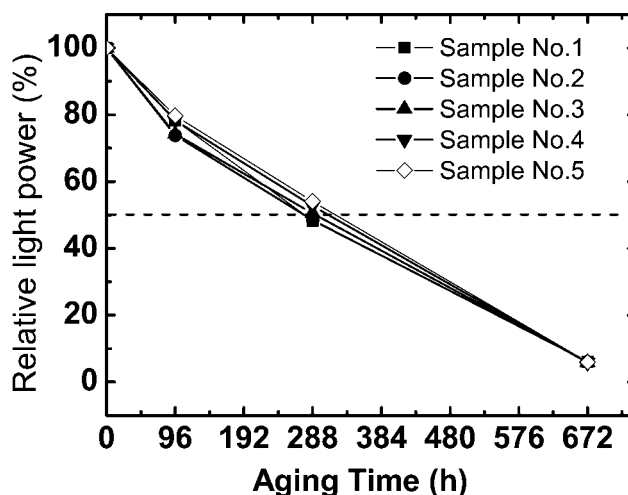
**Figure 4** Change of output light intensity over time for the UV-LEDs packaged by the silicone-epoxy resin operated at 20 mA.

Similar aging tests were conducted for the commercially available UV-LED SDL-5N3CUV, where UV-chips were of the same type as that used in our packaging tests described earlier. The results are shown in Figure 6. The lifetime of this commercial available LED was about 280 h. It should be pointed out that this is the longest lifetime among the similar UV LEDs available in the market at this time although we can buy easily white LEDs having at least 1000 h of lifetime in the store. We think this is mainly because the reduction in light transmittance of packaging material induced by UV irradiation is much more serious for UV LEDs compared with white LEDs that were made from blue chips.

Obviously, the long lifetime of the UV-LED packaged by silicone-epoxy resin can be attributed to the excellent UV-resistance of the packaging material. The silicone-epoxy resins have combined the advan-



**Figure 5** Change of output light intensity over time for the UV-LEDs packaged by the anhydride-cured ERL4221 resin operated at 20 mA.



**Figure 6** Change of output light intensity over time for the commercially available UV-LED SDL-5N3CUV operated at 20 mA.

tages of polysiloxane and epoxy resin; they might find applications in hightech areas.

## CONCLUSIONS

Silicone-epoxy resins with different silicone contents have been synthesized through hydrosilylation of 3,4-epoxy-1-vinylcyclohexane. They can be cured to optically clear materials using the  $\text{Al}(\text{acac})_3/\text{Ph}_2\text{Si}(\text{OH})_2$  catalysis at very low concentrations. For the silicone-epoxy resins containing Si-H bonds,  $\text{Al}(\text{acac})_3$  alone is effective for the curing. The cured silicone-epoxy resins are superior in UV-resistance compared with the anhydride-cured ERL-4221 resin. UV-LEDs packaged by silicone-epoxies have a lifetime significantly longer than that of LEDs packaged by the anhydride-cured ERL-4221 resin. Therefore, they are promising encapsulation materials for short-wavelength LEDs and other electronic devices.

## References

- Huang, J. C.; Chu, Y. P.; Wei, M.; Deanin, R. D. *Adv Polym Technol* 2004, 23, 298.
- Narendran, N.; Gu, Y.; Freyssonier, J. P.; Yu, H.; Deng, L. *J Cryst Growth* 2004, 268, 449.
- Carey, J. A.; Collins, D. W., III; Posselt, J. L. U.S. Pat. 6,204,523 (2001).
- Carey, J. A.; Collins, D. W., II; Posselt, J. L. U.S. Pat. 6,590,235 (2003).
- Miyoshi, K. U.S. Pat Application 20,040,116,640 (2004).
- Shimomura, K. U.S. Pat. 6,710,377 (2004).
- Ho, T. H.; Wang, C. S. *Eur Poly J* 2001, 37, 267.
- Gorczyca, T. B. U.S. Pat. 6,800,373 (2004).
- Kaji, S.; Usui, T. U.S. Pat. Application 20,050,272,896 (2005).
- Kashiwagi, T.; Shiobara, T. U.S. Pat Application 20,050,244,649 (2005).
- Morita, Y.; Ueki, H.; Nakanishi, K.; Furukawa, H. U.S. Pat. 7,105,614 (2006).

12. Rubinsztajn, M. I.; Rubinsztajn, S. U.S. Pat. 6,916,889 (2005).
13. Rubinsztajn, M. I.; Rubinsztajn, S. U.S. Pat. 7,144,763 (2006).
14. Crivello, J. V.; Lee, J. L. *J Polym Sci Part A: Polym Chem* 1990, 28, 479.
15. Hayase, S.; Ito, T.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1981, 19, 2185.
16. Hayase, S.; Ito, T.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1981, 19, 2997.
17. Hayase, S.; Onishi, Y.; Yoshikiyo, K.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1982, 20, 3155.
18. Huang, W.; Yu, Y. Z.; Yuan, Y. X. *Chin Pat. Application* 200510130312.5( 2005).
19. Huang, W.; Yu, Y. Z.; Yuan, Y. X. *Chin Pat. Application* 200610083846.1( 2006).
20. Crivello, J. V.; Bi, D. S. *J Polym Sci Part A: Polym Chem* 1993, 31, 2563.
21. Crivello, J. V.; Fan, M. X. *Makromol Chem Macromol Symp* 1992, 54, 179.
22. Crivello, J. V.; Fan, M. X. *J Polym Sci Part A: Polym Chem* 1992, 30, 1.
23. Morita, Y. *Jpn. Pat.* 2,003,012,896 (2003).