Preparation and Performance of High Refractive Index Silicone Resin-Type Materials for the Packaging of Light-Emitting Diodes

Xiongfa Yang,[1] Qian Shao,[1] Linlin Yang,[1] Xiaobiao Zhu,[2] Xilin Hua,[1] Qunliang Zheng,[2] Guangxin Song,[2] Guoqiao Lai[1]

[1]Key Laboratory of Organosilicon Chemistry and Material Technology of Education Ministry, Hangzhou Normal University, Hangzhou 310012, China

[2]Zhejiang Zhongzhou OPTO Co., Ltd., Hangzhou 311100, China

Correspondence to: X. Yang (E-mail: yangxiongfa@163.com) or
G. Lai (E-mail: hsdyjg@163.com)

ABSTRACT: A novel high refractive index and highly transparent silicone resin-type material for the packaging of high-power light-emitting diodes (LEDs) is introduced, which was synthesized by hydrosilylation of vinyl end-capped methylphenyl silicone resin and methylphenyl hydrosilicone oil catalyzed by Karstedt's catalyst. The vinyl end-capped methylphenyl silicone resins were prepared by hydrolysis−polycondensation method from methylphenyl diethoxysilane ($MePhSi(OEt)_2$), phenyl triethoxysilane ($PhSi(OEt)_3$), and vinyl dimethylethoxy silane ($Me_2ViSiOEt$) in toluene/water mixture catalyzed by cation-exchange resin. The vinyl end-capped methylphenyl silicone resins were characterized by ^{1}H-NMR and Fourier-transform infrared. The performances of the cured silicone resin-type materials for LED packaging have been examined in detail. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Compared with traditional filament-based lighting devices, light-emitting diodes (LEDs) exhibit various advantages, such as higher luminosity at low currents and voltages, longer service life, versatility in a variety of colors, and environmental friendliness, higher resistance to vibration, and higher tolerance to repeated power switching.[1–7] Because of these favorable characteristics, LEDs, especially high-power LEDs, are becoming more and more widespread and have replaced incandescent, fluorescent, and neon lamps.

Packaging technology is a key and necessary aspect for the practical application of LED lighting,[2] and the performance of the packaging material has a great impact on the brightness, exterior, and life of LEDs. Compared with the traditional packaging materials used for common LEDs, those for high-power LEDs have to endure a high intensity of UV light and a high working temperature, which will accelerate their aging. Therefore, packaging materials used for high-power LEDs should possess better integrated properties, especially UV resistance, thermal resistance, and transmittance.[2,6,8–10]

In the past two or three decades, most LEDs were packaged with epoxy resins. Normal epoxy resins, such as bisphenol A epoxy resins, undergo thermal and UV aging and display very pronounced yellowing or discoloration upon long-term exposure to light and heat, which will seriously decrease their luminous efficiency.[1,2,7,10–12] The improvement of the thermal- and light-aging resistances of LED encapsulation materials is a very important issue.

Silicone resins are emerging as ideal packaging materials for LEDs because of their outstanding performances, including stable thermo-optical properties, a wide range of service temperatures, good transparency, very low levels of ionic impurities, and minimal moisture absorption.[13–19] The cohydrolysis of alkoxy silanes with acids or bases can produce silicone resins.[16–19] However, the use of conventional acids or bases poses significant difficulties in handling and corrosive nature. Here, vinyl end-capped methylphenyl silicone resins have been prepared via a much easy handle method: cohydrolysis of alkoxy silane catalyzed by cation-exchange resin. Subsequently, a series of high refractive index silicone resin-type materials for the packaging of LEDs has been prepared from vinyl end-capped methylphenyl silicone resin and methylphenyl silicone oil by hydrosilylation

Additional Supporting Information may be found in the online version of this article.
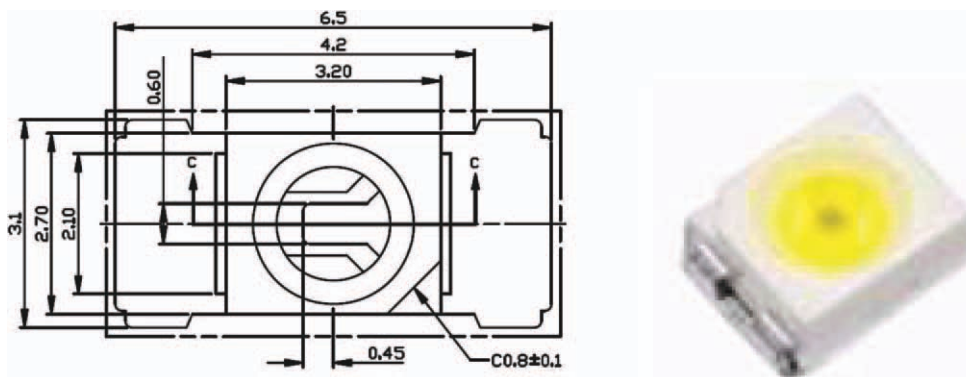
Figure 1. The structure graph of leadframe and packed LED. (a) The structure graph of leadframe and (b) the structure graph of packed LED. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

catalyzed by Karstedt's catalyst. The preparation and performances of these silicone materials have been investigated in detail.

EXPERIMENTAL

Raw Materials

$PhSi(OEt)_3$ and $Me_2ViSiOEt$ were obtained from Xinan Chemicals (Zhejiang Province, China). Octamethylcyclotetrasiloxane and tetramethylcyclotetrasiloxane were purchased from Dow Corning. $MePhSi(OEt)_2$ and methylphenyl cyclic oligomers, a mixture of cyclic trimer (trimethyltriphenylcyclotrisiloxane), tetramer (tetramethyltetraphenyl cyclotetrasiloxane), and pentamer (pentamethylpentaphenylcyclosiloxane), were prepared in our laboratory. Cation-exchange resin was purchased from Nantong Xingchen Synthetic Material (Jiangsu Province, China). 1,1,3,3-Tetramethyl-1,3-dihydrosiloxane was supplied by Zhejiang Sanmen Qianhong factory (Zhejiang Province, China). OE-6650 was from Down Corning (Dow Corning, Shanghai, China). $TiCl_4$ (A.R.), Ethanol (A.R.), and ammonium hydroxide (25%) were purchased from Alfa Aesar (Shanghai, China). Ln_2O_3 was obtained from Shanghai Yaolong factory (Shanghai, China). The rare earth solid super acid $SO_4{}^{2-}/TiO_2/Ln^{3+}$ was prepared according to Refs. [20–22]: $TiO_2 \cdot H_2O$ (10 g), the product of hydrolysis of $TiCl_4$ with dilute ammonia, was immersed in a sulfuric acid solution (25 mL) containing Ln_2O_3. The rare earth solid super acid was subsequently calcined at 550°C in a muffle furnace for 3 h. The structure graph of Leadframe [PPA, Figure 1(a)] and packed LED [Figure 1(b)] with chip(InGaN) for SMD package 5050 LED ($5.0 \times 5.0 \times 1.6$ mm^3) were supplied by Zhejiang Zhongzhou OPTO (Zhejiang Province, China). The packaged LED Red ink (Yingxiong Pai) was purchased from Shanghai fine stationary (Shanghai, China).

Preparation of Methylphenyl Hydrosilicone Oil

The liquid crosslinking agent for the packing of LED was synthesized by a new method, namely, ring-opening copolymerization of octamethylcyclotetrasiloxane (42.1 g), tetramethylcyclotetrasiloxane (3.307 g) with methylphenyl cyclic oligomers (81.1 g) at 80°C for 5 h. The reaction was catalyzed by a rare earth super acid (5 wt % of the total monomers), and the product was end capped with 1,1,3,3-tetramethyl-1,3-dihydrosiloxane (1.34 g) according to Ref. 22.

Preparation of the Vinyl End-Capped Methylphenyl Silicone Resins

The typical procedure for vinyl end-capped methylphenyl silicone resin was prepared by hydrolysis−polycondensation method from $MePhSi(OEt)_2$ (21.0 g, 0.10 mol), $PhSi(OEt)_3$ (53.2 g, 0.22 mol), and $Me_2ViSiOEt$ (7.3 g, 0.056 mol) in a toluene (81 g)/distilled water (20 g) mixture catalyzed by cation-exchange resin (5 wt % of the total silanes) at 78°C for 5 h. Then, the cation-exchange resin was removed by filtration. The solvent and water were then quickly removed on a rotary evaporator. The obtained products were colorless transparent viscous liquids. The synthetic scheme is shown in Figure 2.

Curing Procedures and Aging Tests

Methylphenyl hydrogen-containing silicone oil and the vinyl end-capped methylphenyl silicone resins were mixed according to the desired Si–H/Si–Vi ratio; the amount of Karstedt's catalyst was 8 ppm of the total mass of methylphenyl hydrogen-containing silicone oil and the vinyl end-capped methylphenyl silicone resin. The mixtures were degassed *in vacuo* and then poured into a cup-like LED bracket. The curing was conducted at 80°C for 0.5 h and then at 150°C for 2 h.
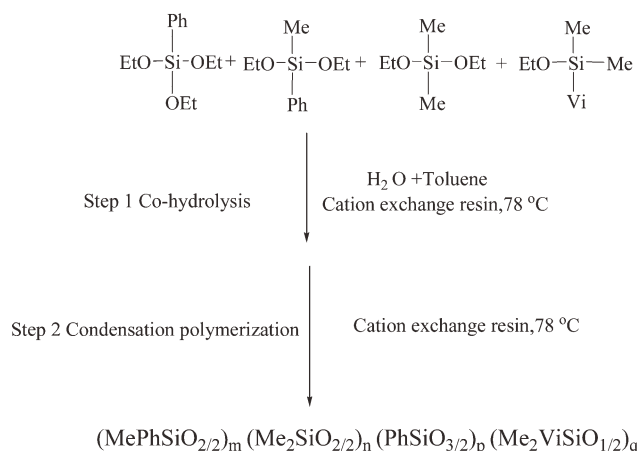
Figure 2. Synthetic scheme for the vinyl end-capped methylphenyl silicone resins.

Table I. The Vinyl End-Capped Methylphenyl Silicone Resins Prepared with Various Catalysts

Sample	Catalysts	Time (h)	Yield (%)	Appearance	Viscosity (cP)
Sample 1	5 wt % cation-exchange resin[a]	1	38.8	High transparent and flowable	2400
Sample 2		3	54.9		6950
Sample 3		5	78.5		8540
Sample 4		7	85.4	High transparent and sticky	11,800
Sample 5	100 ppm H_2SO_4[b]	3	72.6	Cream white and flowable	7580
Sample 6	100 ppm HCl[b]	3	67.1	Transparent and some of gel particles	6560
Sample 7	100 ppm KOH[b]	3	75.9	Transparent and some of gel particles	7450

Conditions: $m : n : p : q = 1.78 : 0 : 4.80 : 1$.
[a]Hydrolysis and polymerization at 78°C for a certain time, then distillation, taking off low-boiling residues under 150°C/0.096 MPa for 2 h, [b]Hydrolysis and polymerization at 78°C for a certain time, then washed with deionized water to pH as neutrality, taking off low-boiling residues under 150°C/0.096 MPa for 2 h.

Measurements

^{1}H-NMR spectra of the reaction products were recorded on a Bruker AVANCE AV400 (400 MHz) spectrometer in CDCl₃ at room temperature with tetramethylsilane as the internal reference. Fourier-transform infrared (FTIR) spectroscopic analysis of uncured silicone resin was carried out using a Perkin-Elmer FTIR 2000 spectrometer over the frequency range 4000–400 cm^{-1} using KBr pellets. Transmittance spectra of the cured samples (placed in a 10-mm-thick quartz absorption cell) were measured on a Unico UV-4802 UV/vis spectrophotometer (Unico Instrument, Shanghai) in the range 300–800 nm. The hardness of the cured samples was measured with an LX-D Shore D durometer (Haibao Instrument, China) according to ASTM D 2240. Refractive indices were measured with an Abbé refractometer at 25°C. Illuminance spectra were recorded on an LED300+ HAAS2000_V1_USB at 25°C. The dye test with red ink experiment was carried out in boiled red ink solvents of ethanol. The reflow soldering test was carried out three cycles (peak 260 ± 5°C). The variation performances of the packaging materials were measured by continuous room temperature light-up and high-current light-up aging for 1000 h.

RESULTS AND DISCUSSION

Synthesis of the Vinyl End-Capped Methylphenyl Silicone Resins

Vinyl end-capped methylphenyl silicone resin can be synthesized through cohydrolysis and cocondensation of chlorosilanes. Although this method poses significant risks in handling and disposal due to the corrosive nature of the materials, using an alkylalkoxy silane as the basic raw material, vinyl end-capped methylphenyl silicone resins can be prepared through a much more environmentally friendly process. However, the catalysts commonly used for hydrolysis, such as HCl and H_2SO_4, are very difficult to neutralize, and their residues have a significant impact on the viscosity and storage stability of the products. The effect of different catalysts on the vinyl end-capped methylphenyl silicone resins were investigated (listed in the Table I). The product catalyzed by H_2SO_4 was cream white and not suitable for LED packaging. There were some of gel particles in the products, when HCl or KOH was used as catalyst, and the gel particles should be filtered out. As can be seen from Table I, the yield and viscosity of the products increased with the prolongation of the reaction time when catalyzed by cation-exchange resin.

In this study, we chose cation-exchange resin as a catalyst to prepare vinyl end-capped methylphenyl silicone resins through the hydrolysis−polycondensation method from $MePhSi(OEt)_2$, $PhSi(OEt)_3$, and $Me_2ViSiOEt$ in a toluene/water mixture; thus, the cation-exchange resin was easily removed. Transparent vinyl end-capped methylphenyl silicone resins with different refractive indices and various R/Si ratios were prepared by changing the molar ratio of the starting materials. As can be seen from Table II and Figure 3, the refractive index of the products increased with increasing Ph content according to a linear relationship and attained a value as high as 1.5442. On the other hand, the lower the R/Si ratio, the higher the viscosity of the products obtained.

The ^{1}H-NMR spectrum of Sample 5 in Table II is shown in Figure 4. It is evident from this spectrum that the ethoxy groups
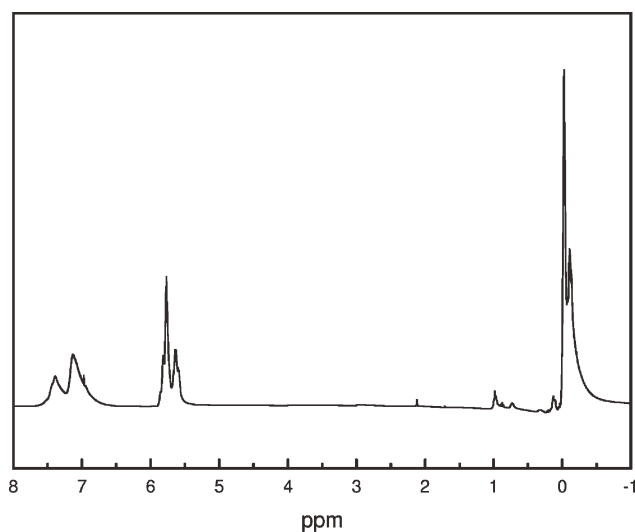
Table II. The Various Vinyl End-Capped Methylphenyl Silicone Resins Prepared

Sample	$m : n : p : q$	Ph/R (%)	R/Si Molar Ratio	Yield (%)	Vi (mol/g)	n_D^{25}	Viscosity (cP)
Sample 1	0.688 : 0.688 : 0.538 : 1	19.5	2.16	79.5	0.0033	1.4600	3200
Sample 2	3.33 : 0 : 1.67 : 1	44.1	1.89	81.8	0.0013	1.5135	4800
Sample 3	2.86 : 0 : 2.61 : 1	48.3	1.75	83.4	0.0012	1.5220	5350
Sample 4	2.45 : 0 : 3.40 : 1	51.8	1.65	76.3	0.0012	1.5308	6100
Sample 5	1.78 : 0 : 4.80 : 1	57.9	1.50	78.5	0.0012	1.5415	8540
Sample 6	0.81 : 0 : 5.07 : 1	61.0	1.41	81.2	0.0012	1.5442	10,500

Conditions: Hydrolysis and polymerization at 78°C for 5 h, then distillation, taking off low-boiling residues under 150°C/0.096 MPa for 2 h.
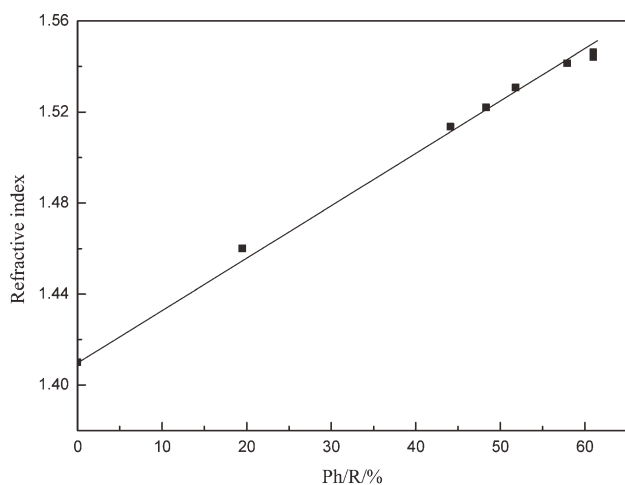
Figure 3. The relationship between refractive index and Ph/R ratio in the silicone resins prepared.
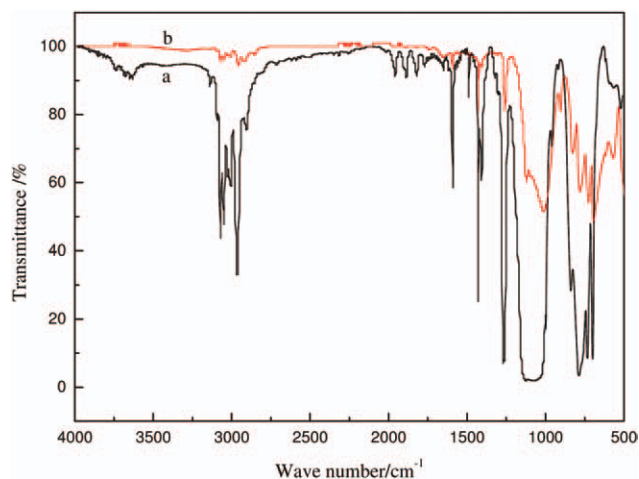

Figure 5. FTIR spectra of the silicone resin precured and postcured. (a) Silicone resin precured (Sample 5 in Table I) and (b) silicone resin postcured (Sample 4 in Table II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. 1H-NMR spectrum of Sample 5 in Table I.

had almost all been lost after the condensation. The signals of the phenyl group bonded to the silicon center can be clearly identified at 6.90–7.60 ppm. The signals at chemical shifts of

Table III. The Mechanical Properties of the Cured Silicone Resin-Type Packaging Materials with Various Si–H/Si–Vi Ratios

| Sample	Si-H/Si-Vi	Hardness/ Shore A	Tensile Strength (MPa)
Sample 1	0.9	63	2.2
Sample 2	1.0	72	2.5
Sample 3	1.2	80	3.2
Sample 4	1.5	92	3.8
Sample 5	1.8	72	3.5

Conditions: Silicone resin was Sample 5 in Table II. The amount of Karstedt's catalyst was 8 ppm. The silicone materials were cured at 80°C for 0.5 h then at 150°C for 2 h.

Figure 6. The appearance of Sample 4 in Table II. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
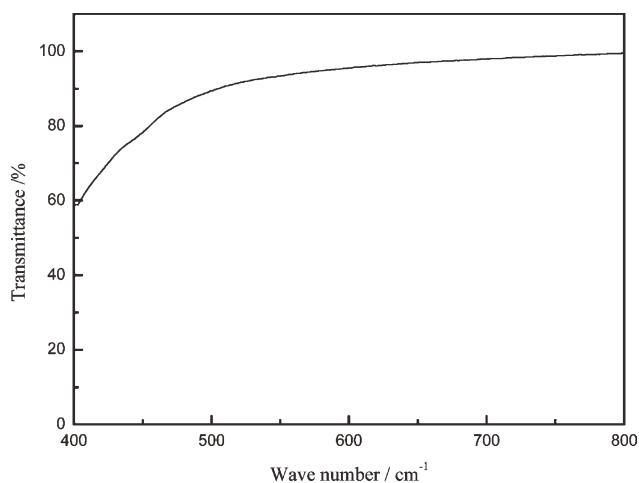
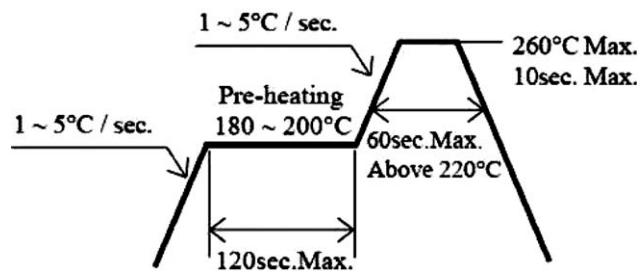**Figure 7.** The transmittance of Sample 4 in Table II.
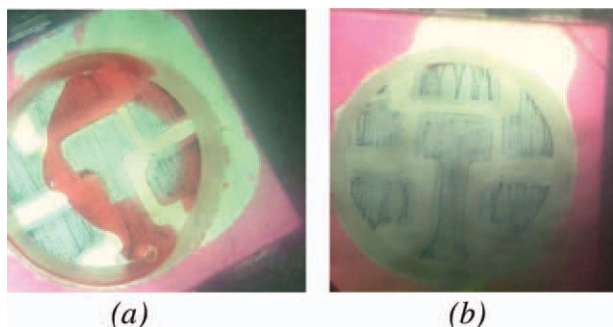
Figure 8. Photographs of an LED (packaged of Sample 4 in Table II) after the dye test examination. (a) The LED was dyed with penetrating red ink and (b) the LED packaged with the prepared silicone materials after a dye test with red ink. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. The thermal profile for the reflow soldering test.

0–0.65 ppm can be assigned to the ―CH$_3$ groups bonded to the silicon center. The characteristic signals located at 5.70–5.90 ppm in the ^{1}H-NMR spectrum can be attributed to the protons of the vinyl group, ―CH=CH_2, bonded to the silicon center.

Performance of the High Refractive Index Silicone Resin-Type Materials for the Packaging of High-Power LEDs

The Mechanical Properties of the Packaging Materials. The influence of the R/Si ratio on the packaging materials is well defined. With decreasing R/Si ratio, the viscosity of the vinyl end-capped methyphenyl silicone resin increased. When the

R/Si ratio reached 1.41, the viscosity was much too high for practical application; packaging materials with poor liquidity and not easy to handle. On the other hand, for cured packaging materials prepared with the vinyl end-capped methylphenyl silicone resins at higher R/Si ratio, the mechanical properties such as rigidity and tensile strength were unsatisfactory.

According to the desired Si–H/Si–Vi molar ratio, a mixture of the silicone resin (Sample 5, Table II), methylphenyl hydrosilicone fluid, and Karstedt's catalyst was stirred, debubbled through pressure reduction, and then cured, first at 80°C for 0.5 h and then at 150°C for 2 h. The mechanical properties of the cured silicone resin-type packaging materials at various Si–H/Si–Vi molar ratios were determined by tensile testing and hardness measurements. Their tensile strengths and hardnesses are shown in Table III. The mechanical properties are greatly affected by the cross-linking density, which is directly related to

Table IV. The Optoelectronic Properties of LEDs Packaged with Sample 4 in Table III

| Entry	I_f (mA)	V_f (V)	I_R (µA)	Φ (lm)	$Φ_e$ (mW)	Light Efficiency (lm/W)	I_p	x	y	T_c (K)	Ra
1	19.97	3.194	0	8.549	25.33	134.01	32687	0.3268	0.3546	5737	69.8
2	19.97	3.2	0	8.441	25.25	132.02	49967	0.324	0.3514	5859	71.3
3	19.97	3.193	0	8.403	25.87	131.75	52822	0.3156	0.3371	6300	72.4
4	19.97	3.192	0	8.561	25.21	134.25	54333	0.3289	0.3583	5646	69.7
5	19.97	3.19	0	8.545	25.22	134.13	54258	0.3284	0.3574	5666	69.7
6	19.97	3.19	0	8.531	25.1	133.86	54178	0.3293	0.359	5633	69.6
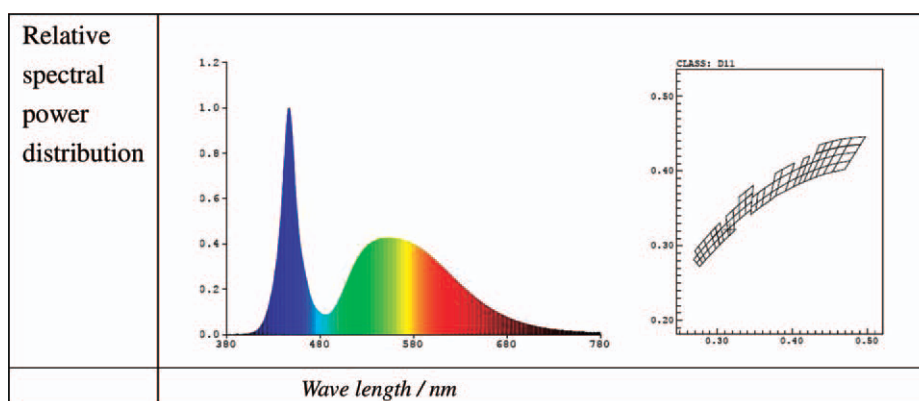
Figure 10. Illuminance spectrum for Entry 3 in Table III. $λ_d$ = 482.0 nm, R = 14.2%, G = 82.3%, B = 3.5%, Ra = 73.4. White light D11, integration time: 1091.00 ms, humidity: 40%, temperature: 118.6°C, aged by room temperature light-up and high-current light-up. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(a)

(b)

(c)
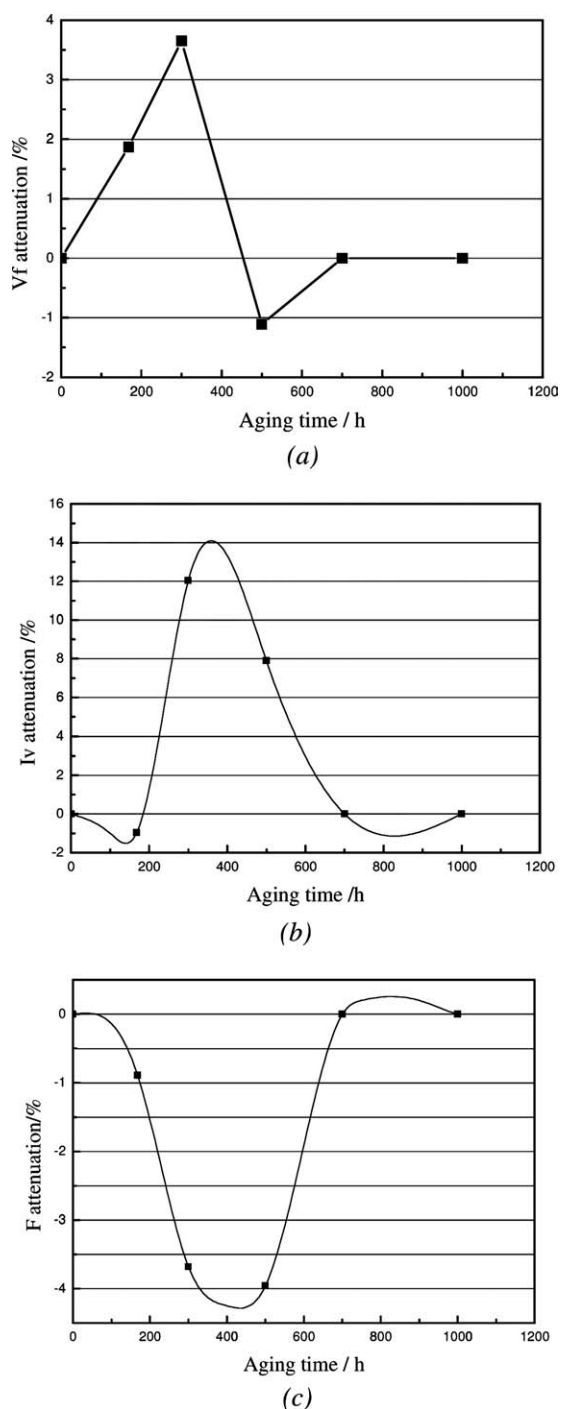
Figure 11. The packaged LEDs aged by room temperature light-up. (a) Direct voltage (V_f) variation diagram. (b) Forward current (I_f) variation diagram. (c) Luminous flux (Φ) variation diagram.

the Si–H/Si–Vi molar ratio. With increasing Si–H/Si–Vi ratio, the tensile strength and hardness of the packaging materials first increased and then decreased. At an Si–H/Si–Vi ratio of 1.5, both the tensile strength and the hardness were maximized. This indicated that the cured Sample 4 was very rigid because of a very high crosslinking density.
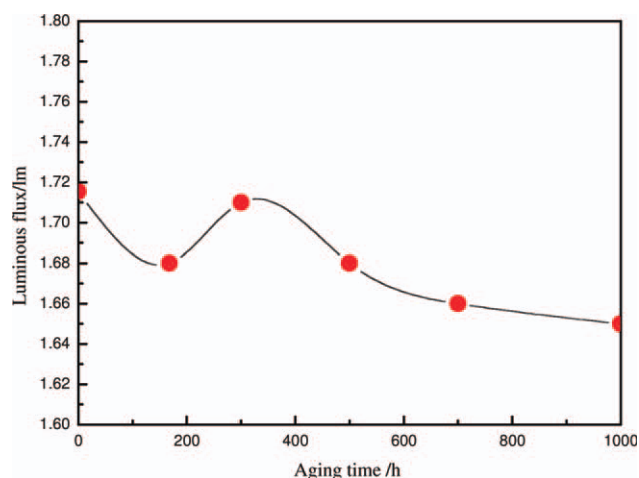
Figure 12. The packaged LEDs aged by high-current light-up. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The FTIR Spectra of the Silicone Resin Precured and Postcured. The FTIR spectra of the silicone resin precured and postcured (Sample 5 in Table II and Sample 4 in Table III, respectively) are shown in Figure 5. The relatively sharp single band at 1429 cm^{-1} can be assigned to the characteristic peak of the phenyl group in the MePhSiO unit, whereas the absorption peak at 1593 cm^{-1} can be attributed to the characteristic peak of the vinyl group bonded to the silicon center. The two absorptions at 1270 and 2965 cm^{-1} can be ascribed to the symmetric deformation vibration and stretching vibrations of the ─CH$_3$ groups bonded to silicon center, respectively. The results combined with the ^{1}H-NMR spectrum confirmed that the products obtained were vinyl end-capped methylphenyl silicone resins. It was also exhibited that the vinyl group bonded to the silicone center almost vanished after cured.
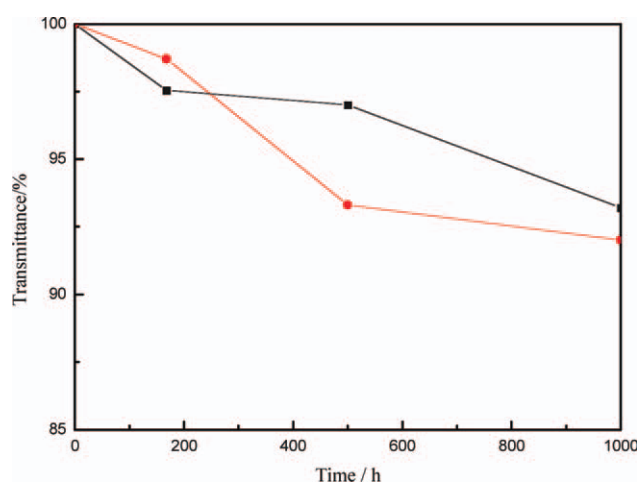
Figure 13. The packaged LEDs aged by blue light at room temperature. ■: The LED packaged with produced silicone materials. ●: The LED packaged with silicone materials from Dow Corning (OE-6650). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Transmittance of the Packaging Materials. A high optical transparency is an essential requirement for LED packaging materials. The silicone resins obtained were highly transparent, colorless liquids. Methylphenyl hydrosilicone oil with higher refractive index served as the cross-linking agent here. The cured silicone resin-type packaging materials were glassy with a high transparency and did not show any yellowing. Figure 6 shows the appearance, and Figure 7 shows the transmittance spectrum in the range 400−800 nm, respectively, for the cured silicone material denoted as Sample 4 in Table III.

Dye Test with Red Ink and Reflow Soldering Test on LEDs Packaged with the Prepared Materials. Good adhesive strength between the packaging materials and the LED leadframe (PPA) is an essential requirement, which is assessed by means of a dye test with red ink. The dye test with red ink experiment was carried out in boiled red ink for 3 h. As can be seen from Figure 8(b), there was no permeation during the course of the dye test with red ink.

The reflow soldering test was carried out according to Figure 9 for three cycles. Moisture sensitivity level is 2a and exposed to 30°C/60% Relative Humidity (RH) or less and floor life is 4 weeks. The prepared packaging materials did not break and remained adhered to the LED mount. Moreover, the examined LEDs all lit up, which means that the packaged LEDs withstood the reflow soldering test. The results of the dye test with red ink and reflow soldering test indicated that the prepared silicone resin-type packaging materials showed good adhesive properties to the LED leadframe and that the encapsulated LEDs produced showed little or no lamp failure.

The Optoelectronic Properties of the LEDs Packaged with the Prepared Materials. Table IV lists the optoelectronic properties on Sample 4 in Table III, and Figure 10 shows the illuminance spectrum for Entry 3 in Table IV. The results indicated that the LEDs packaged with the produced silicone resin-type materials exhibited low color temperature deviation and high light efficiency.

The Variation Performance of the Packaging Materials. The variation performance of the packaging materials has an important and direct effect on the luminous output degradation of LEDs. The LEDs packaged with the prepared silicone resin were aged by room temperature light-up (Figure 11) and high-current light-up (Figure 12) for 1000 h. The results indicated that the LEDs produced incurred low degrees of luminous output degradation of less than 5% over the 1000 h of test time. Furthermore, the silicone packaging materials did not turn yellow during the 1000 h of aging. Figure 11 shows up and down the V_f and photointensity in the middle of time point, which may be ascribed to the variation of the current density distribution and testing error.

The LEDs packaged with the prepared silicone resin and the OE-6650 from Down Corning were also aged by blue light at room temperature for 1000 h, respectively (Figure 13). The results exhibit that the transmittance of LEDs packaged with the produced silicone materials may be higher than that of LEDs packaged with OE-6650 after aged for 1000 h under certain condition.

CONCLUSIONS

A novel high refractive index and highly transparent silicone resin-type material for the packaging of LEDs has been synthesized by hydrosilylation of vinyl end-capped methylphenyl silicone resin and methylphenyl hydrosilicone oil catalyzed by Karstedt's catalyst. The vinyl end-capped methylphenyl silicone resins were prepared by hydrolysis−polycondensation of MePhSi(OEt)$_2$, PhSi(OEt)$_3$, and Me$_2$ViSiOEt in a toluene/water mixture catalyzed by cation-exchange resin. The refractive indices of the vinyl end-capped methylphenyl silicone resins were in the range 1.46−1.542. The structures of the vinyl end-capped methylphenyl silicone resins have been confirmed by ^{1}H-NMR and FTIR. The cured resins exhibited good mechanical properties and high optical clarity. LEDs packaged with the silicone materials showed low degrees of luminous output degradation of less than 5% over a test time of 1000 h. The silicone packaging material did not turn yellow during aging for 1000 h. A dye test with red ink and a reflow soldering test demonstrated that the prepared silicone resin-type packaging materials had good adhesive properties to the LED leadframe and that the LEDs produced showed little or no lamp failure. The silicone resin-type materials are thus quite suitable packaging materials for high-power LEDs.

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