

High-performance optical silicone for high power LED packages

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Abstract

Silicone materials with a relatively high refractive index have been introduced for the encapsulation of high power LEDs and LEDs with relatively short wavelengths. However, most of those existing silicone encapsulants, they still suffer thermal and radiation induced degradations and thus cause reliability issues and shorten the lifetime. A new high performance silicone has been developed and its performance has been compared with other silicone products in the packaging of high power blue and white LEDs. The new materials has been found to suffer less loss in the optical output during the aging test, high temperature/high humidity test, as well as JEDEC reliability test. Thus, this material is excellent for the packaging of high power white LEDs and high power colored LEDs, because of its ability in maintaining high transparency and great radiation/thermal resistance.

Key words: high power LEDs, packaging, silicone, reliability, transmittance, refractive index

Introduction

The applications of light emitting diodes (LEDs) are continued to grow in recent years. The LEDs had been used in the general lighting as well as applications in automobiles, LCD laptop, mobile phones and television back-lighting systems. Presently, the research of white LEDs had been conducted by many manufactures and academics. One of the popular methods for making white LEDs is to use YAG:Ce phosphors with GaN LEDs to produce white light emitting diodes. The phosphor was embedded in an optical grade resin, such as epoxy or silicone, and excited by blue or UV-visible light generated from the GaN chip. High power LEDs can have high cost-effectiveness in large display, lighting, and automotive application. Surface mount device (SMD) LEDs were a mainstream for high power LED packaging due to thermal advantage, low-profile design, and reduced assembly costs [1]-[2].

The LED package includes LED chip mounted onto the lead frame, wire bonding for electrical connection, and protecting the LED device by encapsulant. There are several functions for LED encapsulant. First, it protects the device from dust and moisture. Second, it behaves as a lens focusing the light in the desired way. Third, it improves the light output of LED device by increasing light-extraction from LED chip to air. A major challenge for the LED encapsulant is to achieve high light-extraction efficiency, especially for high power LED in general illumination application. Due to the relatively low refractive index of the encapsulant, a relatively high critical angle loss of light emitting was

between the LED chip and the encapsulant. The critical angle θ_c can be calculated using the Shell's equation

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

Where n_1 is the refractive index of the LED chip and n_2 is the refractive index of the encapsulant.

The critical angle θ_c is decreased, when a LED chip is encapsulated in a low refractive index medium. Thus, low light-extraction efficiency is at the interface between the LED chip and the encapsulant. The refractive index of a LED chip is between 2.5 and 3.5. However, the refractive index of an encapsulant, such as the epoxy or silicone, is between 1.4 and 1.6. As the light passing through the boundary of a LED chip and an encapsulant, a part of the light is reflected back at the interface of the two media because of the difference of refractive index. In order to reduce the light reflected back and increase light-extraction efficiency, materials with high refractive index ($n > 1.5$) and TiO₂ nanoparticle loaded encapsulant are always used in LED packaging [3].

The optical grade epoxy has been used as the materials of LED encapsulant for many years due to its good light transmission, high refractive index, and high glass transition temperature (T_g). However, several problems had been found in high power LED package. The first problem is the yellowing issue of optical grade epoxy during the epoxy encapsulant exposed to blue or ultra-violet (UV) light. The yellowing of the epoxy is the result of a significant loss of light output over time. Another issue is the high power LEDs can generate too much heat at the chip surface, which

induce the yellowing of surrounding encapsulant. The optical grade silicone had been used in LED encapsulating materials for replacing epoxy due to several advantages of silicone, such as suitable refractive index 1.4 to 1.57, good UV and thermal resistance, low impurity levels, high optical clarity, and low modulus. The chemical structure of silicone consists of silicon (Si) and oxygen (O). The bonding of siloxanes (Si-O) is inorganic and has a higher bond energy of 444 kJ/mol than the carbon-oxygen (C-O) of 339 kJ/mol or the carbon-carbon (C-C) of 356 kJ/mol. Hence, for high power LED package, inorganic silicone encapsulants have better reliability than organic encapsulants, i.e. epoxy, polymethyl methacrylate (PMMA), or poly carbonate [4].

Experimental

A. Materials

An optical grade epoxy, the epoxy/anhydride system, was obtained from Henkel Corporation. The high refractive index (RI) silicone was also commercial available and gotten from Dow Corning Corporation. It is a two-parts encapsulating materials for high power LEDs. This product has refractive index 1.53 and high transparency. The high performance silicone consisting of a mixture of a vinyl terminated polydimethylsiloxane and a methylhydrosiloxane-dimethylsiloxane copolymer was bought from United Chemical Technologies and formulated by Shi's lab. The preferred catalyst for this hydrosilylation reaction was a platinum carbonyl cyclovinyldimethylsiloxane complex. All these three LED encapsulating materials were cast in 2 mm bars for transmittance and refractive index measurement. The cure schedules for epoxy and silicone were 120°C for 1.5 hours and 150°C for 2 hours, respectively.

B. Packaging

A surface mount device (SMD) LED package was used for making testing device in this experiment. The schematic diagram of high power SMD LEDs is shown in Fig. 1. A LED chip (SemiLED SL-V-B40AC) with a central wavelength of 455 nm was mounted on Cu substrate by die attach materials, and wire-bonded with gold wire to lead frame to make a circuit. And then it was bounded to a print circuit board (PCB) for the purpose of thermal dispersion. The SMD LEDs were encapsulated with optical grade epoxy, high RI silicone or high performance silicone, mixed with phosphor to produce white light. The light output of these packaged LEDs was measured by Labsphere SLMS LED spectral light measurement system.

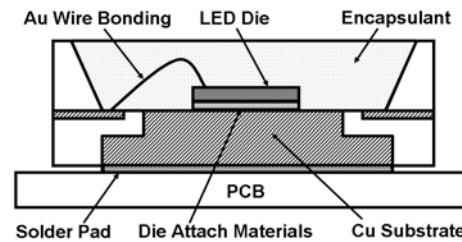


Fig. 1. A cross-sectional schematic structure of SMD LEDs

C. Aging and reliability test

The 2mm bars of optical grade epoxy, high RI silicone, and high performance silicone were made for materials aging test. In UV-radiation aging test, these specimens were exposed to 300–400 nm UV-irradiance at the power of 200 W/m² for different aging time. The UV-radiation aging machine was manufactured by Hitachi Chemical. For thermal aging test, all of the 2 mm bars were thermal-aged at 120°C in the constant temperature oven. Combining UV-radiation and 120°C thermal aging test was also carried out. The loss of transmittance for different aging conditions, the UV-radiation aging, thermal aging, and UV-radiation/thermal aging, was measured by Shimadzu UV2010PC, UV-VIS scanning spectrophotometer.

The in-device aging of 1 Watt LED device was tested in 350 mA constant current at room temperature. These high power LEDs were packaged with different encapsulants of optical grade epoxy, high RI silicone, and high performance silicone. The JESD22 Method A101-B reliability test of LEDs packaged with encapsulating materials of optical grade epoxy, high RI silicone, or high performance silicone was done under a wet and high temperature operating conditions, 85°C and 85% relative humidity. A temperature-humidity reliability testing chamber, model GLMP50, was made by Chemkorea Corporation.

Results and discussion

A. Properties of the cured silicone and epoxy

The platinum catalyzed hydrosilylation reaction is one of the most important methods for formulating silicone elastomers. The platinum cured silicone is an addition cured formula, and without byproducts. The hydrosilylation of vinyl functional siloxanes by hydride functional siloxanes is the basis of addition cure chemistry used in 2-part formulation of silicone. The vinyl groups react with the hydrides, in the presence of a platinum catalyst, to crosslink the polymers into the desired elastomers [5]–[6]. In theory, the reaction of hydride functional siloxanes with vinyl functional siloxanes takes place at 1:1 stoichiometry. In practice,

the ratio of hydride to vinyl is much higher from 1.5:1 to 5:1. The optimum cure ratio is usually determined by measuring the hardness of cured elastomers at different ratios. The optical grade epoxy resin compositions obtained by a bisphenol A type epoxy resin, or alicyclic epoxy resin and an acid anhydride curing agent are generally used. This epoxy resin for LED encapsulation was always thermal-cured and two-part liquid system. The two-part epoxy had to be precisely in stoichiometry.

Optical clarity, a factor to judge LED encapsulating materials, is expressed as the percentage of light transmission through a certain path length at the wavelength of interest [7]. For commercial white LED encapsulation made by phosphor and resin, the high transmittance at the wavelength of either near UV (380nm) or blue (450-470nm) is required. The transmittance of optical grade epoxy, high refractive-index silicone, and high performance silicone was compared in Fig. 2. The cured bulk materials of optical grade epoxy, high refractive-index silicone, and high performance silicone were in 2mm thickness and measured by UV2101PC, UV-VIS scanning spectrophotometer at the range of 300-800 nm for the transmittance. The optical grade epoxy resin was more transparent than high RI silicone and high performance silicone at the wavelength of 360-800 nm. Some additive in silicone for increasing adhesion may cause loss of transmittance, when high refractive-index silicone and high performance silicone were designed for LED encapsulation. Due to the aromatic functional group in bisphenol-A based epoxy resin, the transmittance was reduced a lot when the wavelength was less than 360 nm, as shown in black line of Fig. 2.

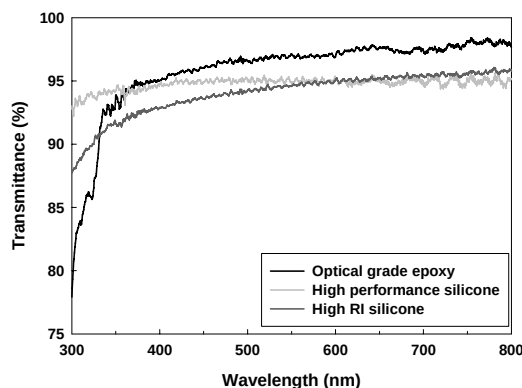


Fig. 2. The transmittance as a function of the incident wavelength between 300 and 800 nm for the cured optical grade epoxy, high refractive index silicone, and high performance silicone

The function of the phenyl groups in causing high refractive index was in the commercial high refractive-index silicone. This phenyl group can also cause the reduction of transmittance at 300-400nm of ultraviolet

wavelength. For the high performance silicone, there was no phenyl group in it. Therefore, the transmittance of this high performance silicone was high and in constant at a wide range of wavelength, 300nm-700nm.

The refractive index (n) is a major optical property for materials of LED encapsulant. The refractive index of LED chip, greater than 1.8, is higher than encapsulating materials, at range of 1.4 to 1.6. By Snell's law, decreasing the difference of refractive index between LED chip and encapsulating materials is a method to increase light extraction. Hence, the larger the refractive index of the encapsulating materials, the higher the light extraction of the LED device [8]. As shown in Fig. 3, the wavelength-dependent refractive indices of optical grade epoxy, high refractive index silicone, and high performance silicone were measured at the wavelength of 486-656 nm. Due to optical grade epoxy contains aromatic ring, the refractive index of optical grade epoxy was 1.5 at the wavelength of 486 nm. The refractive index of cross-linked silicone can be adjusted by varying the phenyl group content in the polymer. The correlation between the phenyl group and the refractive index is proportional. The more phenyl group in silicone can get the higher refractive index. Fig. 3 shows the refractive index of high RI silicone and high performance silicone are 1.55 and 1.41 at 486nm wavelength. For high refractive index silicone, it contains at least 30% of phenyl group. But, the high performance silicone is without any aromatic functional group and at low refractive index.

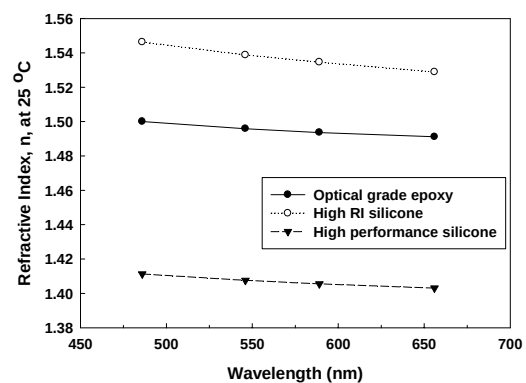


Fig. 3. The wavelength-dependent refractive index of optical grade epoxy, high refractive index silicone, and high performance silicone at the wavelength of 486-656 nm

B. UV and thermal stability of the cured silicone and epoxy

Most of optical polymer suffers the yellowing phenomena when it is under UV radiation or thermal aging. Typically, this phenomenon was due to the aromatic group or free radical in optical polymer. The degree of yellowing phenomena can be judged by the loss of transmittance. The main reason for the decreasing of light output in LED package is the

yellowing of encapsulating materials. Hence, measuring the loss of transmittance in an encapsulant of epoxy or silicone is a method to understand the LED reliability [9]. The epoxy and silicone were made in 2 mm bars and aged at different conditions, which are UV aging, 120°C thermal aging, and UV aging combined with 120 °C thermal aging. The loss of transmittance was measured by UV2101PC, UV-VIS scanning spectrophotometer and by comparing the initial transmittance to the transmittance at aging time. This measurement was based on the loss of transmittance at a wavelength of 460 nm.

Fig. 4 shows the loss of transmittance in optical grade epoxy, high RI silicone, and high performance silicone. Under the UV aging, the transmittance loss of optical grade epoxy was higher than high RI silicone and high performance silicone, as shown in Fig. 4(a). A lot of transmittance loss was also in high RI silicone, compared with high performance, almost zero loss of transmittance. The loss of transmittance under UV aging seems depending on the amount of aromatic functional group. Hence, the more amount of aromatic functional group, the higher loss of transmittance [10]-[11]. Fig. 4(b) shows the optical grade epoxy, high RI silicone, and high performance silicone under 120 °C thermal aging at different time. The optical grade epoxy still suffers serious transmittance loss. However, the high RI silicone just loses less than 5% of transmittance after 480 hours thermal aging. For high performance silicone, the loss of transmittance keeps low at less than 1%. As shown in Fig. 4(c), all these three samples were aged and measured under the condition of combining UV and thermal aging. At 480 hours aging time, the transmittance loss of optical grade epoxy was higher than 40%, and the high RI silicone also had 20% of transmittance loss. Therefore, combining the UV and thermal aging will reduce a lot of transmittance for optical grade epoxy and high RI silicone due to the aromatic functional group in them. No matter what kind of aging test was applied in high performance silicone, it was still in high transmittance.

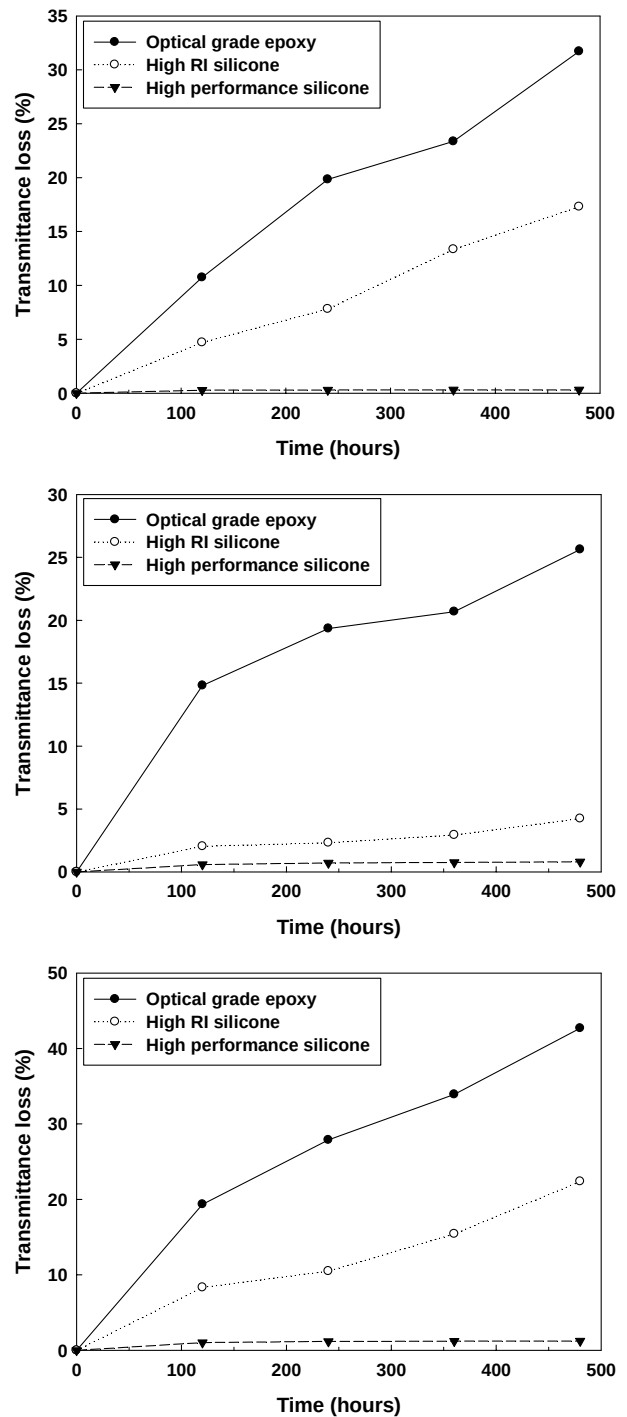


Fig. 4. The transmittance loss of optical grade epoxy, high RI silicone, and high performance silicone: (a) UV aging (b) 120°C thermal aging (c) UV and 120°C thermal aging

C. JEDEC reliability test of silicone and epoxy encapsulant

The JEDEC 22-A101-B test method is a steady-state temperature humidity bias life test for the purpose of evaluating the reliability of nonhermetic packaged solid-state device in humid environment. Fig. 5 shows the degradation of lumen for LEDs packaged with encapsulants of high RI silicone, high performance silicone, and optical grade epoxy at different aging time. The moisture resistance had been tested at high humidity (85% RH) and high temperature 85°C under the standard of JEDEC 22-A101-B. The penetration of moisture through the encapsulant materials or along the interface between encapsulants and lead frames was accelerated in the condition of temperature, humidity, and bias. The separation of adjacent, bonded material layers caused by the absorption of moisture is phenomena of delamination [12]-[13]. The delamination between encapsulants and polyphthalamide (PPA) lead frame is a reliability risk for LED package. More delamination can be observed in the boundary between high RI silicone and PPA lead frame due to more stress in high RI silicone, which is with higher hardness and the coefficient of thermal expansion (CTE) than high performance silicone[14]-[15]. In LEDs encapsulated with high RI silicone, moisture is easy to penetrate through the delamination and cause the degradation of lumen. The lumen drops 10% for high RI silicone and 5% for high performance silicone at the aging time of 500 hours. There is no delamination in optical grade epoxy, but the interface between chips and epoxy turns brown and loses transmittance. The lumen degradation of LEDs packaged with optical grade epoxy is more than 50% at aging time more than 300 hours. Therefore, different mechanisms induce the lumen degradation of LEDs in encapsulant materials of silicone and epoxy under JEDEC reliability test.

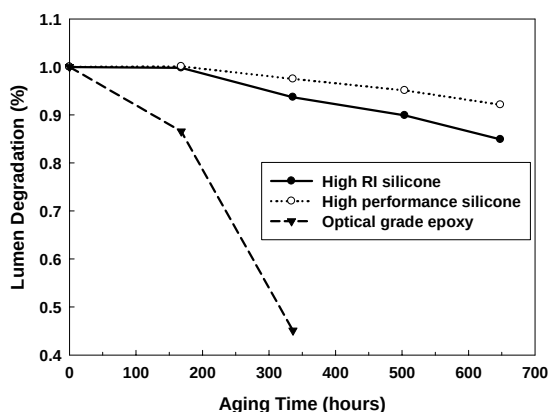


Fig. 5. The lumen degradation of LEDs in encapsulants of high RI silicone, high performance silicone, and optical grade epoxy at different aging time.

Conclusion

The encapsulant materials for light emitting diodes (LEDs) were made by organic polymers, such as epoxy or acrylic, because of their hardness, high refractive index, and low cost. Recently, silicone with high refractive index was also used in LED encapsulant materials. All of these encapsulant materials have reliability issue under high temperature and radiation power in high power LED. A new high performance optical silicone elastomer had been prepared, and compared with high refractive index silicone and optical grade epoxy in high power LED package. The high performance optical silicone had less light output loss than high refractive index silicone and optical grade epoxy under UV radiation test and thermal test. The high performance silicone, high refractive index silicone, and optical grade epoxy were also tested under JEDEC reliability standard for moisture sensitivity test. Therefore, maintaining high transparency and good heat resistance make high performance silicone suitable for high power LED encapsulant materials.

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