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Chapter 8

Degradation and Failures of Polymers Used in Light-Emitting Diodes



M. Yazdan Mehr, W. D. van Driel, and G. Q. Zhang

1 Introduction

Solid-state lighting (SSL) technology is one of the novel technological accomplishments in the last decades. Light-emitting diode (LED), based on SSL technology, is rapidly increasing its share in the general lighting market [1]. LEDs are used widely in indoor lighting and also are more widely used in outdoor and industrial applications [1, 2]. Higher light output, smaller size, longer lifetime, eco-friendly, and more color controllability are the LED advantages compared to more traditional light sources (fluorescent lamps and tubes). In addition, LEDs have the lowest energy consumption per lumen produced among all available lighting sources [3, 4].

An LED lighting system is a complex system that consists of optical, electrical, or thermal functionality components at different levels. These components have dependence on the roles they have in the system. Around 30 failure modes have been reported in SSL devices, and these failures can occur at any system level [5]. These failure modes are unique to LED-based lighting products and are not comparable with the failure modes of other lighting devices.

Most commonly failures and most dramatic ones are limited to the LED chip, the LED package, and its solder interconnects [6, 7]. It is required for microelectronic

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components to protect against the aggressive system and environmental stresses. Protection is usually done by covering chips and other microelectronic components with a package that usually includes polymeric encapsulants to prevent the LED chip from being in direct contact with said environmental stresses. So, it is not unexpected that many of LED failures are related to the package and encapsulation. With that said, the best selection for packaging material is of crucial importance. The organic material used in LED applications should be stable enough to resist the heat and high photon fluxes that occur in LEDs.

The main purpose of this chapter is studying the degradation and aging mechanisms of different optical materials in solid-state lighting systems. In this chapter, first currently used optical polymers [8–15] are introduced. Then common optical degradation mechanisms that happened in the LED polymer lens and encapsulants are explained.

2 Optical Materials Used in LED-Based Systems

Basic knowledge of the structure of optical materials used in LED packages and lighting device is necessary to exploring different failure mechanisms in LEDs. Combination of thermal, optical, electrical, and mechanical properties are expected for organic materials used in LED devices. In order to have a reliable light source, lots of complexities and the technical challenge should be solved, and to solve material-related challenges optimization of materials are required. Silicone, epoxy, Bisphenol A-Poly carbonate (BPA-PC), and Poly Methyl Methacrylate (PMMA) are more common optical materials which are used widely in LEDs and LED-based products which will be briefly introduced. In next section (Sect. 3) the main failure mechanism of each organic materials will be explained thoroughly. Phosphor as a non-organic material has an essential role in the LED and LED-Based product to produce white light, and it also degrade during service life, but in this chapter, we do not explain the degradation of the phosphor.

2.1 Epoxy

Widely used polymer in electronic is epoxy, different factors make epoxy resins unique between all the thermoset resins [16–18], These factors can be listed as, Low fabrication pressure, low cure shrinkage and hence low residual stress in the cured product, use of a wide range of temperatures which leads to good control over the degree of crosslinking, low price, mechanical stabilities, and moisture resistance [19–22]. Because of these unique characteristics and useful properties of the network polymers, epoxy resins are widely used [23, 24] in different applications such as structural adhesives, surface coatings, engineering composites, and electrical laminates. Epoxy materials have the most significant share in the LED packaging

market [24]. Epoxies are commonly used as die-attach and underfill adhesives and are used in many printed circuit boards (PCBs).

Epoxy resins are known to have two significant weaknesses as LED encapsulants. These issues are brittleness of this resin and photo-degradation of epoxy under radiation at high temperatures. Huge chain scission takes place at said condition, causing in a discoloration. The main consequence of discoloration is reduction of transparency and a light output degradation.

2.2 Polycarbonate (BPA-PC)

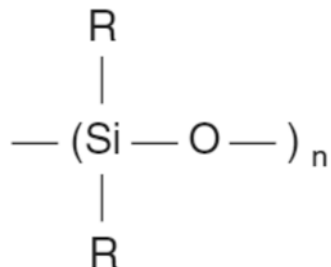
Another important class of polymers which are extensively used in microelectronic is polycarbonates. The first polycarbonate, a cross-linked material, was discovered in 1898, but the first linear thermoplastic polycarbonate was not made until 1953 and brought into commercial production in 1960 [25]. The polycarbonates are sturdy, engineering materials that will withstand a wide range of temperatures.

Bisphenol-A polycarbonate (BPA-PC) is one of the most common polymers which is used in LED and LED-based products as a secondary optics, due to its high elastic modulus, high fracture resistance, and excellent thermal stability. Much information about the structure, properties, and thermal/optical degradation mechanisms of polycarbonates is reported [26–36]. The main disadvantages of polycarbonate are yellowing and discoloration under exposure to radiation at high temperatures. Discoloration leads to decreasing light output. Polycarbonate degrades by an oxidation process that is strongly dependent depends on the composition of the polycarbonates.

2.3 Silicone

Silicone is a unique type of polymer, because of a combination of organic groups (methyl, vinyl, ...) with an inorganic backbone (Si—O) which leads to the semi-organic structure. Fig. 8.1 illustrates the schematic of silicone, where R can be methyl (CH₃), phenyl (C₆H₅), vinyl (CH=CH₂), or trifluoropropyl (C₃H₄F₃).

Fig. 8.1 Chemical structure of a general silicone



Silicone has unique properties such as higher purity, stronger stress absorbing, and more biocompatibility than other polymers. Also, silicone maintains its excellent electrical properties at high temperatures and under humid environments [37].

On the other hand, lower glass-transition temperature (T_g), a larger coefficient of thermal expansion (CTE), and poor adhesion to the housing listed as disadvantages of silicone. Siloxane-modified LED transparent encapsulant is usually used in order to improve the thermal and mechanical properties of silicone

2.4 Poly Methyl Methacrylate (PMMA)

Another commonly used thermoplastic polymer in LED lens, which is the cheapest options in the market and packaging is polymethylmethacrylate (PMMA) [38–40]. Processing and manufacturing of PMMA are straightforward than other polymers because of the glass transition temperature of PMMA, T_g -between 105 to 110 °C, which leads to the extensive use of PMMA.

Main advantage of PMMA is an excellent light/UV transmittance [41–45]. On the other hand, PMMA discolor under high water absorption, low heat resistance, and low abrasion resistance which is the disadvantage for PMMA [40–45].

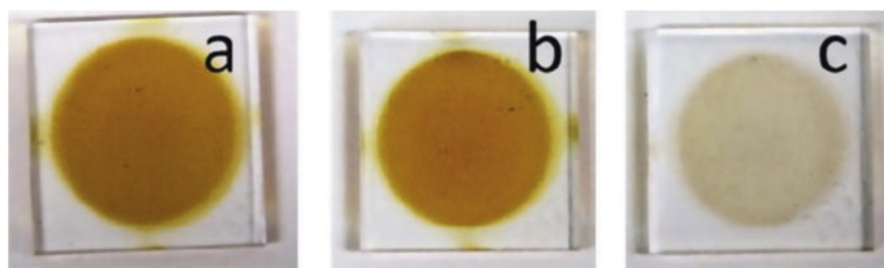
3 Degradation of Optical Materials

Among different failures in LED system, package-related failure mechanisms result in an optical degradation, color change, and severe discoloration of the encapsulant/lens Materials.

Chromaticity shift in the output light is one of the most common failures in LEDs [12–15]. It is considered as one of the most critical measures of quality and is often studied and reported [13–15]. LEDs have to work in different conditions such as high temperatures and humidity environments, moisture, ionic contaminants, heat, radiation, and mechanical stresses. Working in such harsh conditions can be highly detrimental to LEDs and LED-based products and may lead to device failures. Optical/package materials are expected to have some characteristics to withstand these harsh environments, to increase the light extraction efficiency, minimize the heat generated, conduct more heat out of the package, and resist heat and UV light. In this chapter, attention will be paid to essential failure mechanisms, with all having significant influences on the packaging failures. The focus will be on yellowing, lens cracking, delamination, and carbonization of polymeric materials used as encapsulants in LED packaging. Most observed and reported chromaticity shifts are due to either of these mechanisms or a combination of them, Table 8.1 summarizes mentioned failure mechanisms. Each mechanism will be explained in detail for some of the packaging materials in the next section.

Table 8.1 Summary of main failure mechanisms, which will have contribution to the color shift [12]

Failure mechanisms	Description
Discoloration	Oxidative degradation of the encapsulant/lens materials (BPA-PC, PMMA, silicone, and epoxy), resulting in yellowing <ul style="list-style-type: none"> • Oxidation degradation of reflective surfaces within the LED device
Cracking	Mechanical defects in the LED which change the average photon path through the phosphor
Delamination	Separation between different material interfaces, such as between the LED substrate and optical path materials
Carbonization	Over-absorption of blue light by the phosphor <ul style="list-style-type: none"> • Joule heating • Self-heating of phosphors • Radiation of lights with shorter wavelength

**Fig. 8.2** Picture of the sandwiched samples of the silicone glues after UV-exposure under vacuum using the ESTEC SUV facility [40, Reproduced with permission from authors]

3.1 Yellowing of Encapsulant/Lens

Chemical reactions of the polymeric materials under continued exposure to wavelength emission (blue/UV radiation), and working at high-temperature environment leads to discoloration and yellowing of optoelectronic materials. Enhanced molecular mobility, using additives such as flame retardant, scattering agent, and stabilizers are the main chemical reasons for discolorations in the opto-electronic materials [46]. In this section, different illustrations of the discoloration of different optoelectronic materials used in LED and LED-based products will be studied.

Photo degradation is influenced by the exposure time and the intensity of radiation. Besides, thermal effects, related to the junction temperature of the LED chip self-heating of the package [12], also play a significant role in polymer discoloration in LED-based products [12].

One of the examples of silicone yellowing is shown in Fig. 8.2, it is evident that the discoloration upon UV irradiation seems to be independent from the molecular structure of the silicones.

Another reason of discoloration is a failure because of the chemicals and contaminations which leads to the browning of polymeric materials. Figure 8.3 shows the degradation effect from a volatile organic compound (VOC) that permeated the silicone encapsulant and covered the LED chip [41].

Another reason for discoloration of the optoelectronics materials is humidity. Moisture and humidity have an accelerating effect on the rate of yellowing in epoxy molding compound (EMC) used in some LED packages [12]. An example of the effect of the humidity on the yellowing of EMC is shown in Fig. 8.4. The sample in the wet high temperature (95°C) operation lifetime (WHTOL 95°C/95%RH) showed slightly more yellowing the one which is only thermally aged at 105°C (HTOL 105 °C).

Hydrothermal degradation of silicone is together with the absorption of water, leads to the increasing the weight of the EMC epoxies.

Diffusion of the water in opto-electronics materials follows a Fickian law and the degradation reaction is controlled by hydrolysis, a model with a perfect agreement with experimental observations was proposed [48].

BPA-PC and PMMA are typically used as a secondary lens in LED packages, due to their comparatively lower costs. Yazdan Mehr et al. have extensively worked on the aging of the BPA-PC [46–48]. Thermal aging at low-temperature regime is associated with oxidation and rearrangement reactions, both having implications for discoloration of LEDs. A significant consequence of yellowing is a decrease in the transmissivity in LED lenses [50–55]. Whether the rearrangement or oxidation reactions control the discoloration depends on the temperature and oxygen contents.

Lu et al. [51, 52] examined the influence of temperature- and blue light radiation-induced degradation of BPA-PC and PMMA on their chromaticity shifts of LED devices. Figure 8.5 illustrates the differences between the yellowing of PC and PMMA samples [52].



Fig. 8.3 Influence of thermal aging on the discoloration of LED optical package [47, Reproduced with permission from authors]

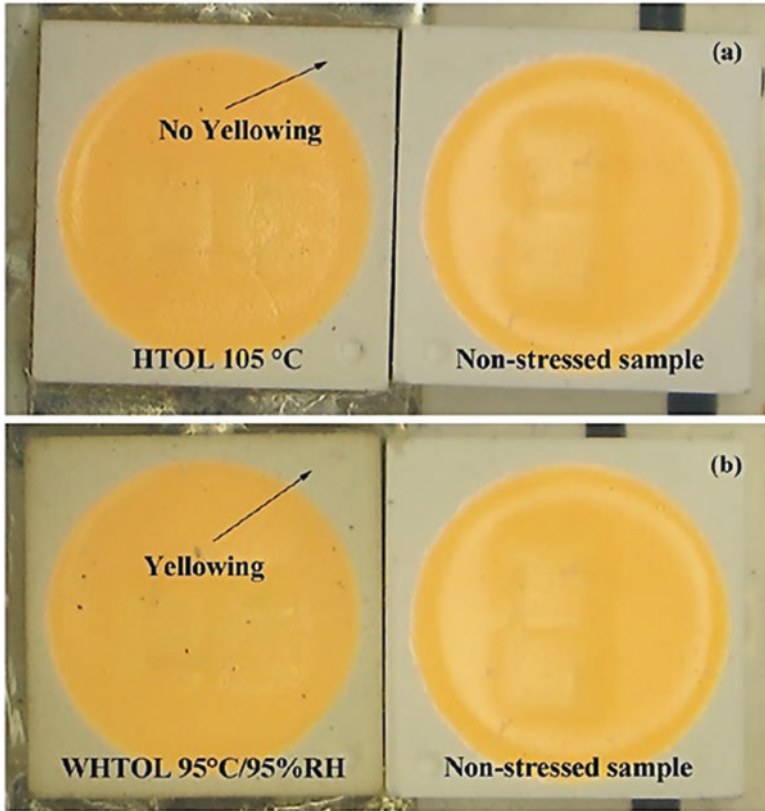


Fig. 8.4 Influence of humidity of the yellowing of EMC [10, reproduced with permission from authors]

3.2 Crack and Delamination

Delamination at the chip/phosphor interface is another crucial failure mechanism in high-powered LEDs, which leads to discoloration and chromaticity shifts in the yellow direction. Likewise, differences between the coefficients of thermal expansion (CTE) as well as temperature cycles during production and service are another commonly observed failure modes in LEDs debonding at the soldered areas. Figure 8.6 reported the severe delamination at the interface of lead frames, and epoxy molding compound (EMC) used to encapsulate the lead frame [23].

Delamination at the polymer/lead frame interface is shown in Fig. 8.7. Absorbed moisture accelerated the influence of oxygen and hydrogen ions [12].

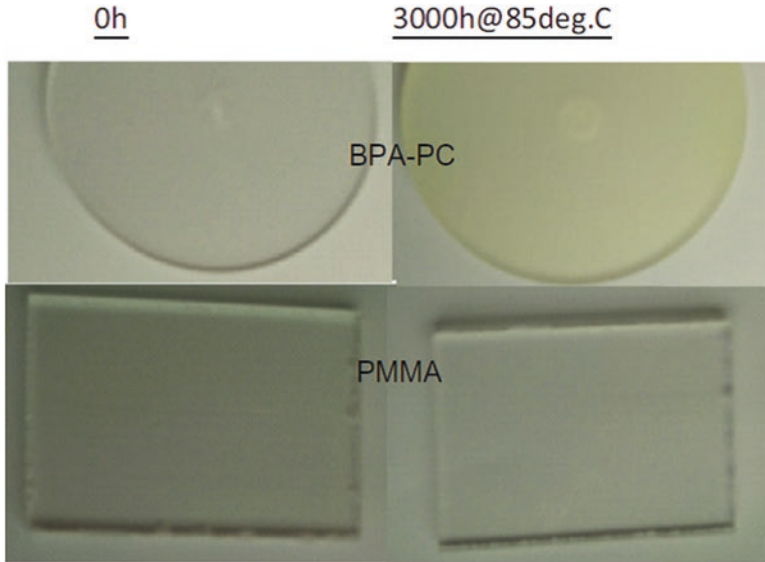


Fig. 8.5 Yellowing of PC versus PMMA [52, Reproduced with permission from authors]

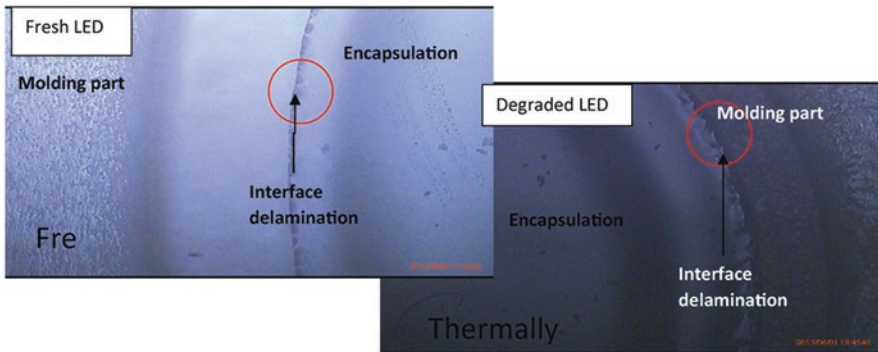


Fig. 8.6 Optical microscope images of interface delamination in white high-power LEDs [23, Reproduced with permission from Elsevier]

3.3 Carbonization

Another important reason for the discoloration and failure of the optical materials in LED and Led-based products is carbonization [12]. Silicone can undergo severe carbonization by applying adequate electrical current to the LED package [12].

Electrical overstress which leads to the formation of a conductive path across the LED is because of carbonization of the polymer material on the chip surface. Reduction of the insulation resistivity is also due to the carbonization of the polymeric materials used as encapsulants in LED-based products [12]. The

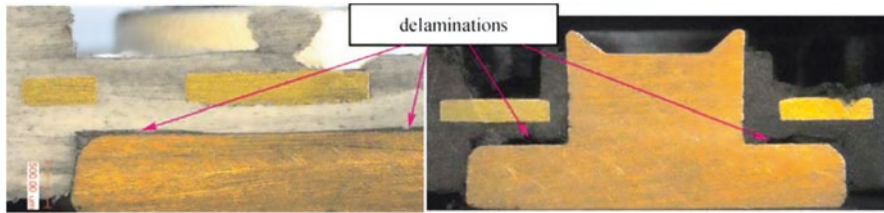


Fig. 8.7 Delaminations at the polymer packages of Luxeon [12, Reproduced with permission from authors]

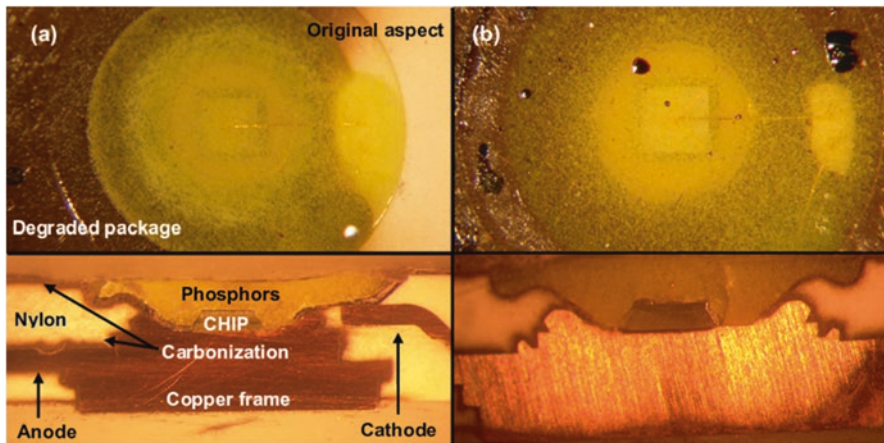


Fig. 8.8 Carbonization in LED package, (a) aged at 400mA and (b) aged at 220°C [55, Reproduced with permission from authors]

carbonization of the encapsulant leads to light output degradation and color shifting. Figure 8.8 shows the carbonization of the silicone materials in the LED package. Silicone encapsulant in the device is aged under temperature and current.

4 Color Shifting

The main result of above-explained failure mechanisms is the reduction of light output and color shifting of the light.

One of the most critical measures of quality of light is chromaticity shift [56–58]. Chromaticity shift is explained as the variation of chromaticity coordinate from its original values.

Color shift is defined as the change in the chromaticity coordinates from its original values. It is named chromaticity shift, in case CIE1976 (u',v') chromaticity diagram is used. The (u',v') coordinates are related to the CIE 1931 (x, y)

coordinates. The chromaticity coordinates of a source provide a numerical representation of the color of the light.

One of the examples of color shifting is shown for the Philips Lumileds Luxeon Rebel LED package in Fig. 8.9 [58]. Color shifting in these products happens in 3 stages which is due to the elevated temperature. It is illustrated that there is initially a fast shift in the chromaticity at all temperatures, followed by a plateau in which the shift is almost negligible. The third stage is accompanied by the decrease in $\Delta u'v'$. It is shown that by increasing the temperature plateau stage is shorter.

Degradation of optical components in LED packages is one of the most significant reasons for the chromaticity shift of LED devices, which means that optical components in LED packages and LED-based products have an essential role in the optical performance of LED devices by controlling the emission of light from the device.

The chromaticity shift can be determined by dominant degradation mechanisms occurring in the package, which depends on the package materials and methods of construction. Directions of chromaticity shift can be different from case to case, as shown in Fig. 8.10, and can be toward the yellow, blue, green, or red colors. Different package systems have shown distinct differences in the chromaticity shift signatures. Table 8.2 illustrates different commonly seen chromaticity shift mechanisms that can happen in LED lighting systems which are related to both organic materials (polymers) and inorganic materials (phosphors) which are widely used in LED and LED-based products.

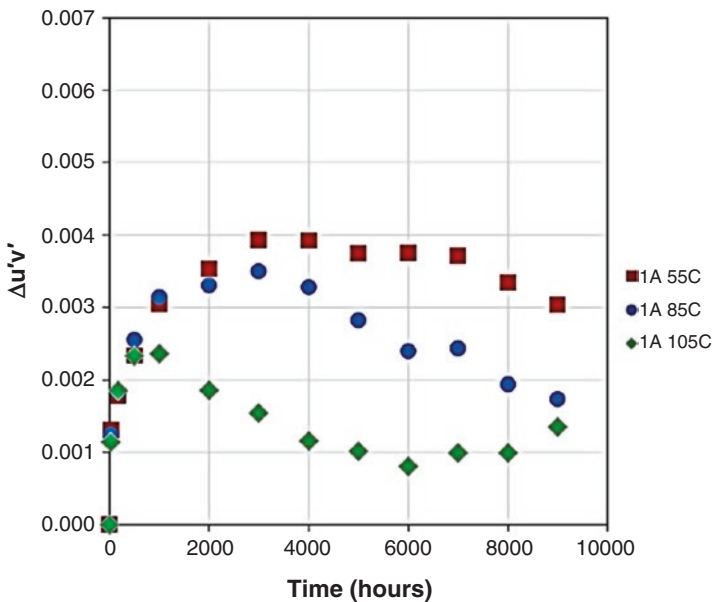


Fig. 8.9 Effects of temperature on the chromaticity shift ($\Delta u'v'$) of Luxeon LEDs operated at 1 amp [59, Reproduced with permission]

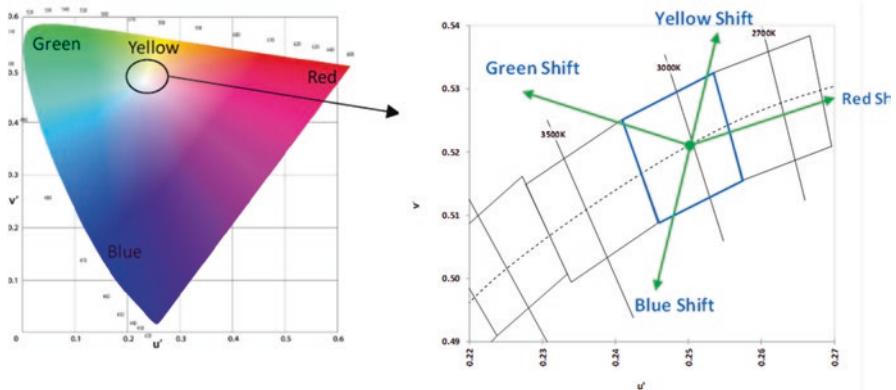


Fig. 8.10 Illustration of color shifts in the CIE 1976 color space. Any change in the spectral proportion of any colors results in a chromaticity shift [14, Reproduced with permission]

Table 8.2 Summary of main chromaticity shift mechanisms that can occur in LED lamps and luminaires [3]

Shift direction	Reason
Blue shift	<ul style="list-style-type: none"> – Oxidation of the molding compound in PLCC (plastic leaded chip carrier) or tarnishing of exposed metal surfaces such as lead frames and reflectors – Top-to-bottom fractures of the binder in the phosphor-binder layer, resulting in blue photons bypassing the phosphor layer
Yellow shift	<ul style="list-style-type: none"> – Increase in phosphor quantum efficiency due to chemical changes or temperature decreases – Cracking or delamination of phosphor-binder layer, which can lengthen the path of blue photons through the phosphor – Discoloration/oxidation of the lenses – Discoloration of the reflector
Green shift	<ul style="list-style-type: none"> – Chemical changes in the phosphor such as oxidation that shift emission intensity to lower wavelengths – Reduction in red emissions such as those from a red LED
Red shift	<ul style="list-style-type: none"> – Shift in emission properties of direct red emitter

5 Harsh Environments

Recently, Yazdan Mehr et al. studied the degradation of silicone used in secondary optical designs combined with an LED package under harsh environment conditions [58]. The effects of UV 360 nm exposure or blue 450 nm light exposure, combined with high temperature (100 °C), water environment (35 and 100 °C), and saline 100 °C water environment on the color, and radiant power intensities of silicone samples were studied. They have shown that silicone samples have a great degree of stability against light exposures (both UV and blue light). It is shown that 3500 h of radiation at 100 °C did not result in any aging in the optical properties of

silicone samples. Major adverse effects of harsh environment on silicone lens were exposure to saline and high-temperature environmental conditions.

Significant reduction in the transmission of samples in the visible light range, reduction in the maximum radiant power at 450 nm, and a change in the color chromaticity values are the main degradation of silicone samples under saline water exposure at 100 °C. Saline water exposure at 100 °C changed the also mechanical properties of silicone plates by making them more brittle.

Figure 8.12 shows the effects of exposure to a saline water on the FTIR spectra of silicone samples. Decrease in the transmission of degraded samples with exposure time in this case is quite significant.

This specifies that among various potential degrading factors in a harsh environment condition, Cl ions dissolved in water which shows the most negative contribution to the structural stability of silicone. Cl ions significantly accelerated the kinetics of degradation in silicone samples. Observing at the FTIR spectra, it can be concluded that chemical degradation was associated with breaking Si–O–Si bonds and decomposition of methyl groups attached to silicone atoms. Several papers also reported parallel results concerning hydrothermal stability of cross-linked silicone rubber [28–31] (Fig. 8.11).

A shear punch test was also conducted on as received and aged specimens with 3500 h of exposure to saline environment to study changes in the mechanical properties of the degraded specimens in a saline environment. Figure 8.13 compares force–displacement curves of these two samples, illustrating that exposure to a saline water environment was accompanied with embrittlement and a decrease in the ductility of specimens.

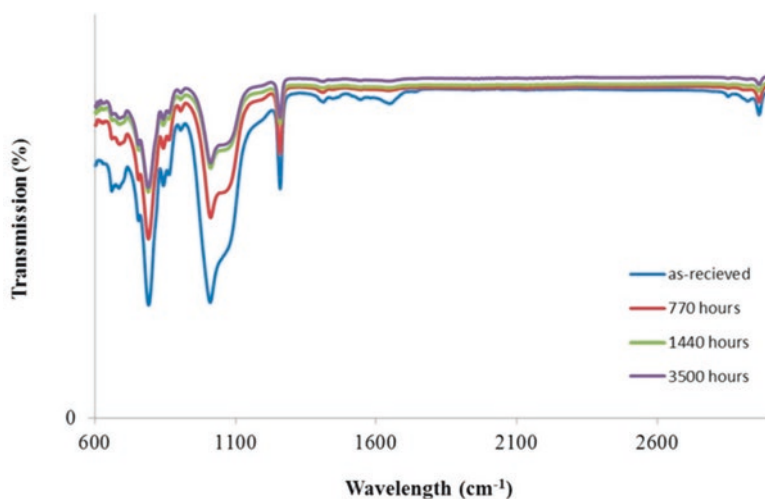


Fig. 8.11 FTIR-ATR spectra of aged Si in a salt batch at 100 °C

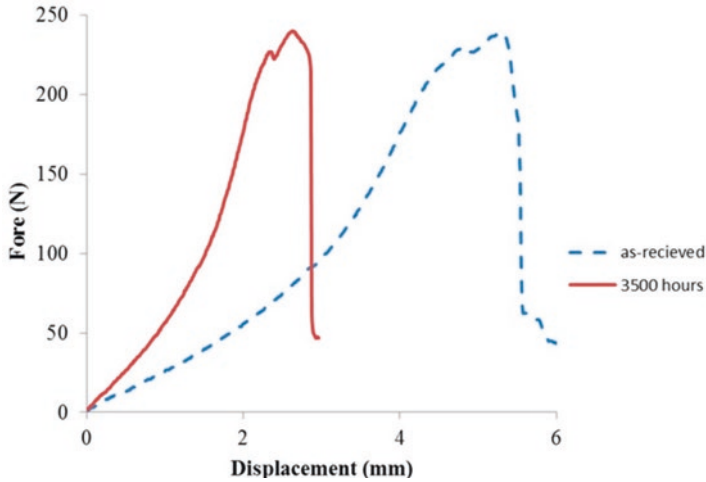


Fig. 8.12 Force displacement curve for aged silicone in a salt bath at 100 °C

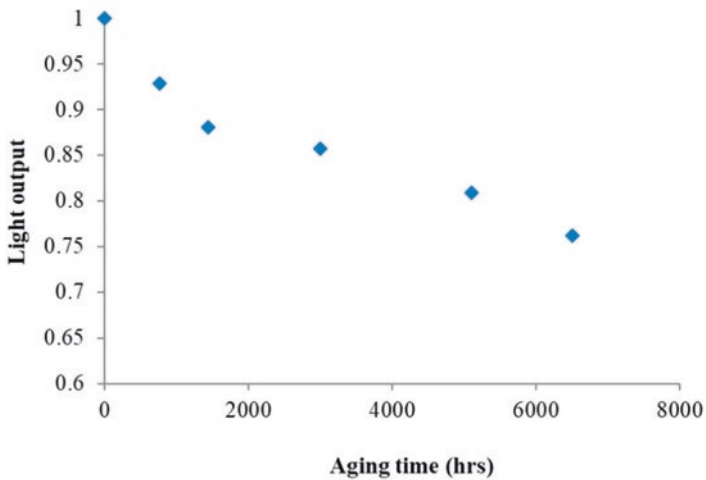


Fig. 8.13 Variation of maximum power intensity at 450 nm with exposure time under a saline water environment condition at 100 °C

Figure 8.13 illustrates the effects of aging time on the normalized maximum light output at 450 nm. Interestingly, there was a linear reduction of maximum light output with exposure time.

6 Reliability and High Accelerated Testing (HAST)

Degradation and failure of optical materials in LEDs are due to the operating under diverse stresses, including temperature, UV/Visible light, ionic contaminations, and humidity. Reliability of the LED-based products under different conditions in LED-based products are explained thoroughly in the literature [12, 35, 57]. In the high accelerated set up (HAST) [12, 35] the effects of both blue light intensity and the thermal stress on the lifetime and the kinetics of aging of phosphor plates used in LED-based products are well studied. Applying both thermal stress and light intensity in HAST set-up increases the rate of degradation. Three temperatures of 80, 100, and 120 °C were used, blue light is radiated on the sample with different light intensities of 825, 3300, and 13200 W/m² and samples are aged up to 3000 h.

LED lifetime is measured by lumen maintenance, which is how the intensity of emitted light tends to weaken over time. Reliability models predict the lifetime of the LED under different stress.

In the HAST experiments, where the light intensity is also used as an extra acceleration factor, the Eyring relationship is an appropriate reliability model, as below [49]:

$$R = \gamma_0 (I)^n \exp\left(\frac{-E_a}{KT}\right) \quad (8.1)$$

where R is the reaction rate, γ_0 is the pre-exponential factor, I is the intensity of blue light, n is the constant factor, E_a is the activation energy (eV) of the degradation reaction, K is the Boltzmann gas constant (eV/K), and T is the absolute temperature (K) [57]. The radiation of light obviously accelerates the aging of remote phosphor by a factor 1.01, 1.2, and 1.9 for blue light radiations of 825, 3300, and 13200 W/m², respectively [57]. The increase in acceleration factor by radiation of light indicates the effect of light intensity. It is also shown that the lifetime, defined as 30% lumen depreciation at 40 °C, is around 35 khrs, for the lowest energy power, which has almost the same lifetime as thermally aged phosphor. The lifetime of the phosphors with higher power energy is 25 khrs.

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