

# Encapsulants for light-emitting diodes from visible light-cured epoxy monomers

Walter F. Schroeder, Ignacio E. dell'Erba, Gustavo F. Arenas, Silvana V. Asmussen and Claudia I. Vallo\*



During the last decade, light-emitting diodes (LEDs) have replaced incandescent, fluorescent, and neon lamps due to their ability to produce high luminosity at low currents and voltages. LEDs are currently encapsulated by thermally curable epoxy resins. However, long periods of curing at high temperature result in high consumption of energy and require stringent process control to avoid failure of the devices. In addition, the thermal cure results in yellowing of the encapsulant, which decreases the efficiency of the LED. In recent years, photoinitiated polymerization has received much interest as it congregates a wide range of economic and ecological benefits. Cationic photoinitiators, such as diaryliodonium salts, generate Brønsted acid *in situ*, which initiates polymerization. The process can be triggered on demand by irradiating the mixture with light. Results from the present research reveal that cycloaliphatic epoxy monomers, photoactivated with an iodonium salt and Camphorquinone, polymerize readily under visible light irradiation (470 nm) in the absence of external heating. The partial replacement of cycloaliphatic epoxy with aromatic diglycidyl ether of bisphenol-A (DGEBA) is an effective means of improving the refractive index of the material and consequently the efficiency of the photoemission. Visible light polymerization of DGEBA pure proceeds at a slow rate; however, it is enhanced by the increase in temperature during the polymerization of the highly reactive cycloaliphatic monomer. From results obtained in the present research, it may be concluded that visible light polymerization of epoxy monomers is a promising route for the processing of LED encapsulants. Copyright © 2013 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this paper

**Keywords:** photopolymerization; visible light; light emitting diodes; epoxy; cationic polymerization

## INTRODUCTION

During the last decade, light-emitting diodes (LEDs) have replaced incandescent, fluorescent, and neon lamps due to their ability to produce high luminosity at low currents and voltages.<sup>[1]</sup> Besides, they have low-power consumption, comparatively longer service lives, and can be formed into different shapes. LEDs are used in a variety of lighting applications, including automotive lighting, indoor and outdoor lighting and backlighting for liquid-crystal display laptops, mobile phones, and televisions. The LED package includes a LED chip mounted on a lead frame, gold wires for electrical connection, and an encapsulant.<sup>[1,2]</sup> The encapsulant is an optical grade polymer that protects the device from dust and moisture. It behaves as a lens focusing the light in the desired way, and it improves the light output of LED device.

LEDs are currently encapsulated by thermally curable epoxy resins. These resins exhibit good thermal stability and mechanical properties and for that reason are widely used for electronic packaging application.<sup>[3,4]</sup> Epoxy monomers employed for LEDs encapsulation are either aromatic diglycidyl ether of bisphenol-A (DGEBA) or cycloaliphatic epoxides cationically cured using thermal cationic initiator or cured thermally by an anhydride.<sup>[1]</sup> However, there are several disadvantages associated with the thermal cure of epoxy formulations such as high cure temperature (>120 °C), long period of curing schedules requiring stringent process control to avoid failure of the devices, and high consumption of energy.<sup>[1,5–7]</sup> A typical curing schedule reported by Lee *et al.* for the cationic polymerization of DGEBA consisted of 70 °C for

30 min, then 140 °C for 2 h, and 1 h at 200 °C.<sup>[5]</sup> In another report, Morita carried out the cationic polymerization of aromatic and cycloaliphatic epoxy monomers at 120 °C for 12 h.<sup>[7]</sup> A drawback associated to the thermal cure (>120 °C) of the aromatic DGEBA is its increase of attenuation due to yellowing. The yellowing of the epoxy results in a significant loss of light output over time and decreases the efficiency of the photoemission.<sup>[7–10]</sup> Recent advances on the fabrication of high-power LEDs have been accompanied by increased interest in the development of novel materials for the LED encapsulant with improved properties.<sup>[11–13]</sup> In the present study, we report results on visible light photopolymerization of epoxy monomers, which exhibits interesting properties for the fabrication of LED encapsulant. We studied photopolymerizable epoxy resins formulations, which result in comparatively shorter cure times in the absence of external heating.

In recent years, photoinitiated polymerization has received much interest as it congregates a wide range of economic and ecological benefits.<sup>[14]</sup> Cationic photopolymerization has become an important method of crosslinking epoxy and vinyl

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ether monomers. The use of cationic photoinitiators, such as diaryliodonium and triarylsulfonium salts, provides a convenient method of generating powerful Brønsted acid *in situ*, which is the primary species that initiates polymerization, and obviates the difficulties of preparing and handling these materials.<sup>[15,16]</sup> The cationic photoinitiators can be dissolved into a multifunctional monomer, and then the polymerization can be triggered on demand by irradiating the mixture with light in the absence of external heating. Furthermore, this process has the added environmental benefits of totally eliminating the use of solvents as well as inherently low-energy-input requirements. The high rate of crosslinking achieved on irradiation is ideal for high-speed applications. Although the major absorption bands of cationic photoinitiators fall in the deep UV region, the spectral sensitivity of onium salts can be broadened to longer wavelengths by the use of photosensitizers.<sup>[16,17]</sup>

In this research, two cycloaliphatic epoxy monomers and blends of one cycloaliphatic epoxy with the aromatic DGEBA were examined. The resins were photoactivated with a diaryliodonium salt in combination with Camphorquinone and polymerized by irradiation with visible light (470 nm). The conversion of epoxy groups was measured by Fourier transform infrared (FTIR). The polymerized materials were characterized by means of optical transmittance measurements, dynamic mechanical analysis, and thermogravimetric tests.

Original results on visible-light photopolymerization of epoxy monomers presented in this research, which to our knowledge have not been previously reported, involve the measurement of conversion of epoxy monomers in thick specimens and studies of photobleaching of CQ in epoxy monomers during visible light irradiation.

## EXPERIMENTAL

### Materials and radiation source

The epoxy monomers used in this study were 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (UVR-6110 Dow Chem. Co.), 1,3-Bis (3,4-epoxycyclohexyl-2-ethyl),1,1,3,3-tetramethyldisiloxane (SIB 1092.0 Gelest Inc) and diglycidylether of bisphenol A (DGEBA DER 332 Dow Chem. Co.) The iodonium salt was p-(octyloxyphenyl) phenyliodonium hexafluoroantimonate ( $\text{Ph}_2\text{ISbF}_6$ , OMAN071 Gelest Inc.). Camphorquinone (CQ) and ethyl-4-dimethylaminobenzoate (EDMAB) were from Sigma Aldrich. (Structures of these chemicals shown in Fig. 1-Suppl Inform).

Blends of UVR and DGEBA at mass fraction DGEBA/UVR equal to 25/75, 50/50 and 75/25 were prepared. The resins were activated for visible light polymerization by the addition of 2 wt.%  $\text{Ph}_2\text{ISbF}_6$ , 1 wt.% CQ, and 1 wt.% EDMAB. The radiation source was a LED unit (VALO, Ultradent, USA) with a wavelength range 410–530 nm and irradiance equal to 600 mW/cm<sup>2</sup>.

### Measurement of conversion of epoxy groups

FTIR spectra were acquired with a Nicolet 6700 Thermo Scientific. Near-infrared spectroscopy (NIR) spectra were acquired over the range 4500–7000 cm<sup>-1</sup> from 32 co-added scans at 4 cm<sup>-1</sup> resolution. The background spectra were collected through an empty mold assembly fitted with only one glass slide to avoid internal reflectance patterns. The resins were sandwiched between two glass plates separated by a 2 mm rectangular rubber spacer containing a 10-mm circular hole. The glass plates

were previously treated with a releasing agent in order to avoid the adhesion between the epoxy and the glass after polymerization. The glass plates containing the resins were tightly attached to the sample holder using small clamps. With the assembly positioned vertically, the light source was placed in contact with the glass surface, and the specimens were irradiated at regular time intervals. Spectra were collected immediately after each exposure interval. The conversion of epoxy groups from the DGEBA was assessed from the decay of the absorption band at 4530 cm<sup>-1</sup> using the band at 4620 cm<sup>-1</sup> as reference. The epoxy groups from the UVR monomer were monitored by attenuated total reflectance (ATR) using a diamond crystal. The extent of reaction of the UVR monomer was assessed at the surface of specimens used in the NIR experiments (10 mm diameter and 2 mm thick). Mid-infrared (MIR) spectra were acquired over the range 400–4000 cm<sup>-1</sup> from 32 co-added scans at 4 cm<sup>-1</sup> resolution. The conversion of epoxy groups was calculated from the decay of the band at 788 cm<sup>-1</sup> using as internal reference the peak centered at 1508 cm<sup>-1</sup>.

The conversion of epoxy groups from the DGEBA was assessed at different temperatures by MIR spectroscopy. A drop of the monomer containing the photoinitiator system was sandwiched between two KBr crystal discs separated by a 50  $\mu\text{m}$  aluminium spacer ring used to regulate the sample thickness. The assembly was placed in a sample oven HT-32 (Spectra-Tech Inc., Shelton, CT) with programmable temperature control, which was then mounted into the spectrometer. A thermocouple (K-type) was directly plunged into the reactive mixture to record the real temperature of the system during reaction. The temperature was kept within 57–98 °C ( $\pm 0.5$  °C). The specimens were irradiated at regular time intervals, and spectra were collected immediately after each exposure interval. The conversion of epoxy groups was calculated from the decay of the absorption band located at 915 cm<sup>-1</sup> using the band at 1508 cm<sup>-1</sup> as internal reference.

### Temperature evolution during photopolymerization

The temperature during polymerization was monitored with fine K-type thermocouples (Omega Engineering, Inc., USA) embedded in the monomer specimens in the upper half of the sample where the temperature is more uniform.<sup>[18]</sup> This was verified after the experiment by visual examination of the sample with a magnifying lens. The thermocouples were connected to a data acquisition system that registered temperature every 2 s. Three replicates were conducted for each experiment. The studies were carried out in 2-mm thick and 10-mm diameter samples identical to those used in measurements of conversion.

### Refractive index

The refractive index of liquid samples was measured on an Abbe refractometer (ATAGO Co. Ltd., NAR-2T, Japan). First, the refractive index of degassed water was measured at  $290.3 \pm 0.1$  K and was in good agreement with the literature<sup>[19]</sup> within an experimental error  $\pm 0.001$ . Then, the refractive index of a series of samples was measured at the temperature  $T = 290.3 \pm 0.1$  K.

### Measurements of transmittance

The absorption spectra in resins containing of CQ were measured with an UV-visible spectrophotometer (1601 PC, Shimadzu) at room temperature (ca 20 °C) at the wavelength range of 300–800 nm. The photobleaching of the CQ photoinitiator was

studied in  $3.0 \pm 0.2$  mm thick samples sandwiched between 1-mm thick glass microscope slides separated by a rubber gasket. The geometry of the sample specimens was identical to that used in measurements of conversion. An identical cell containing the corresponding epoxy monomer was used as the reference.

### Dynamic mechanical analysis

The dynamic mechanical properties (DMA) of DGEBA/UVR blends were studied in the three-point bending mode on prismatic samples of dimensions 20 mm  $\times$  5 mm  $\times$  2 mm using a Perkin-Elmer DMA 7-e. Each sample was scanned from 20 to 300 °C at a heating rate of 10 °C per min under nitrogen atmosphere. During heating, the samples were subjected to strain at a frequency of 1 Hz, while the storage modulus ( $E'$ ) and the damping factor ( $\tan \delta$ ) were recorded.

### Thermogravimetric analysis

Thermogravimetric tests were performed using a SHIMADZU TGA-50 Thermogravimetric Analyzer. Sample masses of about 5 mg were placed into alumina pans. Runs were performed from 20 °C to 950 °C at a heating rate of 10 °C/min under air flow (20 ml/min).

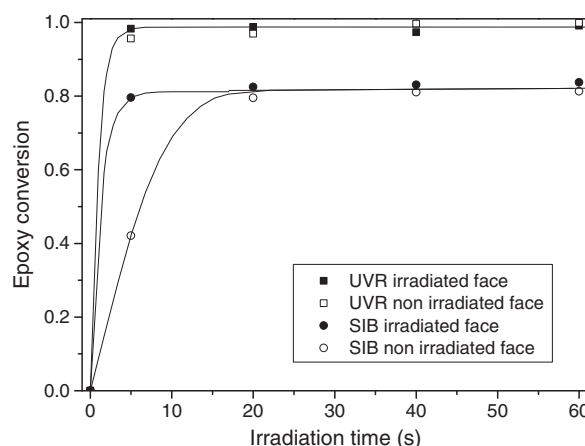
### Compressive strength

Compressive tests were carried out in an Instron testing machine (Model 4467) at a cross-head displacement rate of 2 mm/min. Samples for compression testing were made by injecting the monomers into glass cylindrical disposable molds of 6 mm internal diameter. The molds were previously treated with a releasing agent in order to avoid the adhesion between the epoxy and the glass after polymerization. Compressive specimens were irradiated for 20 s on each side, respectively. All test specimens were photopolymerized in ambient atmosphere at room temperature ( $20 \pm 2$  °C). Prior to mechanical testing, the specimens were stored at ( $20 \pm 2$  °C) for about 24 h. Cylindrical specimens having a length/diameter ratio of 1.5 were deformed between metallic plates lubricated with molybdenum disulfide. The deformation was calculated directly from the cross-head speed. True stress–deformation curves were obtained by dividing the load by the cross-sectional area. The compressive yield strength,  $\sigma_y$ , was determined at the maximum load. The results are the average of four measurements

## RESULTS AND DISCUSSION

### Visible light photopolymerization of cycloaliphatic epoxy resins

The conversion of epoxy groups versus irradiation time of UVR and SIB in 2-mm thick specimens is presented in Fig. 1. After 5 s irradiation, the conversion of UVR, containing 2 wt%  $\text{Ph}_2\text{ISbF}_6$  in combination with 1 wt% CQ and 1 wt% EDMAB was 98% at both irradiated and non irradiated face. Similarly, the conversion after 10 s irradiation of SIB containing 2 wt%  $\text{Ph}_2\text{ISbF}_6$  with 1 wt% CQ in the absence of EDMAB was approximately 80%. UVR polymerized readily and to high conversion in the presence of the CQ/EDMAB pair. However, no polymerization was detected after 60 s of irradiation in the absence of EDMAB. Results presented in Fig. 1 reveal that very high conversion of UVR and SIB occurs in the absence of external heating.



**Figure 1.** Monomer conversion versus irradiation time in 2-mm thick specimen of UVR containing 2 wt%  $\text{Ph}_2\text{ISbF}_6$  with 1 wt.% CQ/EDMAB and SIB containing 2 wt%  $\text{Ph}_2\text{ISbF}_6$  and 1 wt.% CQ.

The possible initiating mechanism in systems containing a diaryliodonium salt in combination with CQ has been proposed by previous researchers.<sup>[20–22]</sup> Irradiation of the CQ with visible light results in the formation of its singlet state, which is rapidly converted to its triplet state by intersystem crossing.<sup>[23]</sup> The excited CQ molecule is initially reduced by a hydrogen donor (monomer or amine) to the ketyl radical which in turn is oxidized back to CQ by the iodonium salt.<sup>[20–22]</sup> The resulting strong Brønsted acid derived from this process initiate the cationic ring-opening polymerization. In the case of the CQ/EDMAB pair, it is assumed that the mechanism involves the generation of  $\alpha$ -amino radicals by the abstraction of a hydrogen atom from the amine by the photoexcited CQ.<sup>[21]</sup> The diaryliodonium salt oxidizes the  $\alpha$ -amino radicals to the respective cations, which initiate the polymerization.<sup>[21]</sup> The function of the aromatic amine in the cationic polymerization is dictated by its basicity and nucleophilicity toward the propagating cationic center. If the amine has low basicity and the carbocation is less electrophilic, then the amine mainly functions as coinitiator. Otherwise, it will function as a terminator. The efficient polymerization of SIB in the absence of EDMAB is attributed to the fact that this silicone epoxy resin can act both as monomer and hydrogen donor molecule. This advantage of SIB over UVR will be discussed in more detail later.

The reactivity of a wide variety of epoxy monomers has been studied by Crivello *et al.*<sup>[24,25]</sup> Based on the results of those studies, the author concluded that epoxide ring strain is one of the most important factors in determining their reactivity. On the other hand, epoxide monomers containing ester carbonyl groups undergo polymerization at substantially slower rates than those monomers that do not contain those groups.<sup>[24]</sup> This effect is due to both the higher nucleophilic and basic character of the ester carbonyl, which leads to a different mechanism of propagation in these compounds. The ester carbonyl group can either directly interact with the protonated epoxide group in an inter- or intramolecular fashion to produce a comparatively low reactivity dialkoxycarbenium ion. Alternatively, the carbonyl group may reduce the activity of epoxide monomers through hydrogen bonding with the protonated epoxide group produced during the initiation process. Conversely, silicone-epoxide monomers that incorporate both epoxycyclohexane groups and siloxane linkages such as SIB are among the most reactive

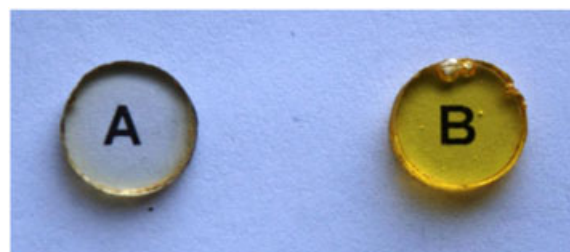
epoxide monomers.<sup>[25]</sup> Crivello *et al.* proposed that the outstanding reactivity of this monomer can be attributed to two major factors.<sup>[25]</sup> First, the ring strain inherent in the epoxycyclohexane ring system is probably the largest contributing factor. Second, there are no basic groups in the structure of SIB that can compete with the epoxide oxygen for either the initiating photogenerated acid or the positively charged growing chain ends. In addition, siloxane (Si-O-Si) bonds are not ether-like and are not readily protonated.

### Temperature evolution during photopolymerization

The reactivity of the two epoxy monomers can be assessed by the evolution of the temperature during polymerization. When 1 wt% CQ was added to the UVR monomer containing 2 wt%  $\text{Ph}_2\text{ISbF}_6$  and irradiated with visible light no appreciable polymerization took place. In contrast, Fig. 2 shows that when 1 wt% EDMAB was added the temperature of UVR raised to 213 °C. The temperature reached during irradiation of SIB containing  $\text{Ph}_2\text{ISbF}_6$ /CQ in absence of EDMAB amine (Fig. 2) was 115 °C. Results presented in Fig. 2 show a very effective photopolymerization of UVR and SIB monomers under 10 s continuous irradiation with visible light.

### Transmittance spectra

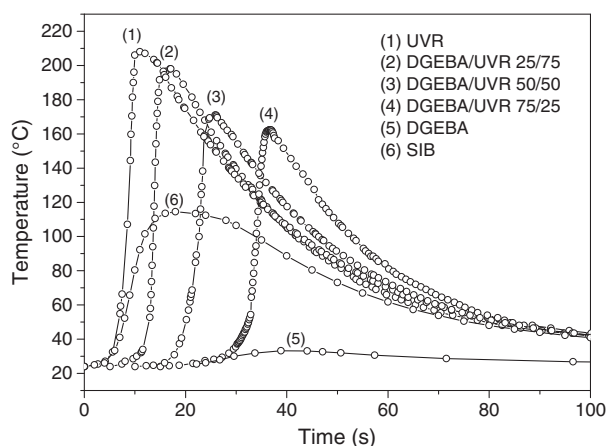
The photolysis of CQ dissolved in UVR and SIB monomers during visible light photopolymerization was examined. During irradiation, CQ absorbs visible light due to the  $n, \pi^*$  transition of the  $\alpha$ -dicarbonyl chromophore to produce an excited singlet state which passes into an excited triple state and interacts with oxidizable species, thus decomposing into colorless products.<sup>[26,27]</sup> Spectral changes measured by UV-vis experiments during irradiation of UVR and SIB monomers containing the photoinitiator system with visible light are presented in Figures 2 Suppl. Inf. Figure 3 shows the clean photobleaching of CQ in SIB monomer after 40 s irradiation. On the other hand, the photodecomposition of CQ in UVR in the presence of EDMAB is accompanied by the appearance of light absorbing by-products (Fig 2-B Suppl. Inf). The presence of light absorbing photoproducts in the



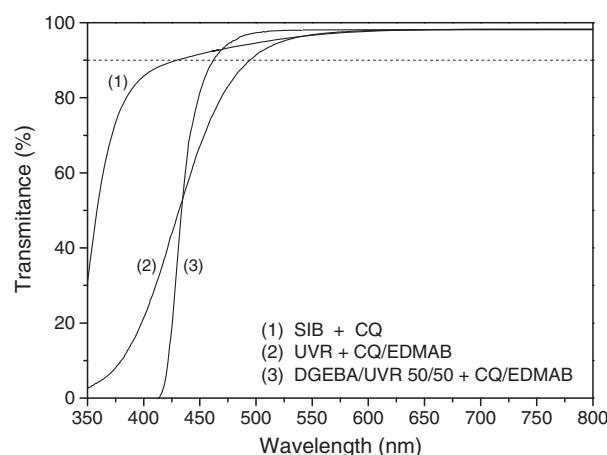
**Figure 3.** Photobleaching of CQ during polymerization of SIB photoactivated by 2 wt%  $\text{Ph}_2\text{ISbF}_6$  and 1 wt.% CQ (A) after 40 s irradiation (B) after 5 s irradiation.

polymerized resin has a direct effect on the optical properties of the encapsulant.

Optical transparency is an important property of materials used for LED and other optical encapsulants.<sup>[2,8–10]</sup> The optical transparency measures the percentage of light transmission through a certain path length of a material at the wavelength of interest. The increase in the transparency of an encapsulant results in higher light extraction out of the LED package. In the ideal case, an encapsulant material should be 100% transparent to visible light. The transmittance of 1-mm thick specimens of UVR and SIB monomers photopolymerized with visible light is compared in Fig. 4. The polymers derived from UVR and SIB monomers were highly transparent in the range of visible wavelengths, namely 470–700 nm. The SIB monomer exhibited a high transmittance at a wide range of wavelength (370–800 nm). The percentage of transmittance was 80% at 375 nm and increased to 90% at 400 nm. This is attributed to the clean photobleaching of the CQ during irradiation (Fig. 3) and to the absence of aromatic functional group which are known to reduce transmittance. The comparatively lower transmittance of UVR photoactivated with CQ/EDMAB at wavelengths lower than 450 nm is attributed to the presence of light-absorbing photoproducts. Above 550 nm, the two systems reached comparable values of transmittance (97%). Figure 4 also shows that the transmittance of the DGEBA/UVR 50:50 blend was greater than 90% in the range 460–800 nm. It is seen a more rapid increase of transmittance with wavelength in the range 400–460 nm compared with



**Figure 2.** Temperature evolution during photopolymerization of SIB and DGEBA/UVR blends. The SIB monomer was photoactivated with 2 wt%  $\text{Ph}_2\text{ISbF}_6$  and 1 wt.% CQ. The DGEBA/UVR blends were photoactivated by 2 wt%  $\text{Ph}_2\text{ISbF}_6$  with 1 wt.% CQ and 1 wt.% EDMAB. The curves were shifted along the time axis in order to make the plot clearer.



**Figure 4.** Transmittance of 1-mm thick samples of (1) SIB photoactivated with 2 wt%  $\text{Ph}_2\text{ISbF}_6$  and 1 wt.% CQ, (2) UVR photoactivated by 2 wt%  $\text{Ph}_2\text{ISbF}_6$  with 1 wt.% CQ and 1 wt.% EDMAB, and (3) DGEBA/UVR 50:50 photoactivated by 2 wt%  $\text{Ph}_2\text{ISbF}_6$  with 1 wt.% CQ and 1 wt.% EDMAB. The resins were irradiated 40 s.



that observed in the UVR monomer. This different trend resulting from addition of DGEBA to the UVR monomer is attributed to the presence of different absorbing by-products resulting from irradiation of the CQ/EDMAB pair in different epoxy monomers.<sup>[28]</sup> From results presented in Fig. 4, it emerges that one advantage of SIB is that it can be polymerized with CQ in the absence of amine (Fig. 3). This results in encapsulants with excellent optical transparency over a wide range of wavelength (> 90% at 400–800 nm).

It is worth mentioning that the presence of light absorbing photoinitiators in a photocuring resin inevitably results in attenuation of the light intensity along the radiation path and often limits the cure depth in a sample to be polymerized.<sup>[18,26,27]</sup> This effect occurs when the light fails to reach the deeper layers of a sample because the absorbing species near the irradiated surface absorb most of it. As a result of light attenuation in 2-mm thick specimens of methacrylate monomer photoactivated with 1 wt % CQ/EDMAB, the values of conversion at the irradiated surface was about 18% higher than that at the non irradiated surfaces.<sup>[18]</sup> On the other hand, the values of conversion of UVR and SIB at the irradiated and non-irradiated surfaces in 2-mm thick specimens were similar (Fig. 1). This is attributed to the well-known “dark cure” or “postpolymerization” effect typical of cationic process.<sup>[29,30]</sup>

### Compressive strength

Crosslinked epoxy resins are brittle in nature. Like other brittle materials, they are weak in tension but quite strong in compression and capable of yielding under uniaxial compression. Therefore, the yield strength was determined in compression. Typical registers of compression tests of SIB and UVR monomers are shown in Fig. 3 Suppl Inf. Results presented in Table 1 show that the polymer resulting from irradiation of UVR monomer displays a much higher compressive strength compared with that of the polymer derived from SIB. This is one advantage of the UVR monomer for situations that require high mechanical strength.

### Refractive index

There are three loss mechanisms that decrease photoemission of LEDs: absorption of the photons within the LED material itself, critical angle loss, and Fresnel loss.<sup>[2,12,13]</sup> These mechanisms and the role of the encapsulant material on the efficiency of photoemission can be described as follows. When a light beam crosses a boundary between media of different refractive indices, the light beam will be partially refracted at the boundary surface and partially reflected. However, if the angle of incidence is greater than a certain value known as critical angle, then the light beam will be totally reflected back internally or trapped

inside the die causing low light output (Fig. 4 Suppl Inf). This can only occur when light travels from a medium with a higher to one with a lower refractive index. The value of the critical angle,  $\theta_c$  is given by the Snell's law:

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

where  $n_1$  and  $n_2$  are the refractive index of each medium and  $n_1 > n_2$ . According to the Snell's law, the larger the refractive index of the encapsulant, the higher the light extraction from the LED device. In addition to critical angle loss, a portion of the light emitted from the LED chip is reflected back at discontinuities of refractive index. Light that is reflected back into the LED chip is lost, and, therefore, the efficiency of light extraction is reduced. The light reflection is caused by a change in the refractive index that occurs at the interface between the LED chip and the encapsulant material. This reflection loss is referred to as the Fresnel reflection loss. The portion of incident light (light of normal incidence) that is reflected back into the source can be approximated from the following relationship.

$$R = \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2 \quad (2)$$

$R$  is the fraction of the incident light reflected,  $n_1$  is the refractive index of the LED chip, and  $n_2$  is the refractive index of the encapsulant material. It is clear from eqns (1)–(2) that the higher the refractive index of the encapsulant, the more efficient light extraction from the LED. The values of refractive index of the cycloaliphatic epoxy monomers are shown in Table 1. A drawback of the SIB monomer is its relatively low refractive index ( $n = 1.48$ ) compared to UVR monomer ( $n = 1.50$ ).

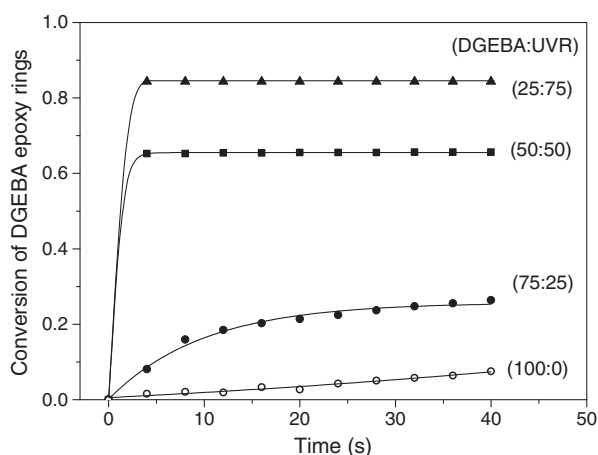
From results presented, it emerges that the excellent optical transparency exhibited by SIB photopolymerized with  $\text{Ph}_2\text{ISbF}_6/\text{CQ}$  is accompanied with lower refractive index and compressive strength compared with UVR photopolymerized with  $\text{Ph}_2\text{ISbF}_6/\text{CQ}/\text{EDMAB}$ . In addition, UVR reached complete conversion after 10 s irradiation in the absence of external heating while the extent of reaction of SIB under similar conditions was 80% (Fig. 1). The refractive index of the aromatic epoxy DGEBA is 1.573; therefore, UVR was blended with DGEBA to raise the refractive index of the resin and thus increase the photoemission efficiency. The characterization of the blends is described in the following points.

### Visible light photopolymerization of DGEBA/UVR blends

The efficiency of the polymerization of DGEBA/UVR blends was assessed by monitoring the conversion of epoxy groups versus time in resins photoactivated with 2 wt%  $\text{Ph}_2\text{ISbF}_6$  with 1 wt% CQ and 1 wt% EDMAB. Figure 5 shows a marked effect of the

**Table 1.** Compressive strength ( $\sigma_y$ ), refractive index ( $n_D$ ), glass transition temperature ( $T_g$ ) and conversion of UVR at non-irradiated and irradiated face measured by ATR. The refractive index of DGEBA is 1.573

Resin	$\sigma_y$ (MPa)	$n_D$	$T_g$ (°C)	UVR conversion
SIB	36.4 ± 0.6	1.481	187	-
UVR/DGEBA (100/0)	145.7 ± 3.2	1.502	185	0.982 / 0.996
UVR/DGEBA (75/25)	147.9 ± 0.5	1.525	183	0.997 / 1
UVR/DGEBA (50/50)	146.6 ± 0.6	1.541	172	0.996 / 1
UVR/DGEBA (25/75)	144.7 ± 2.3	1.558	171	0.615 / 0.682

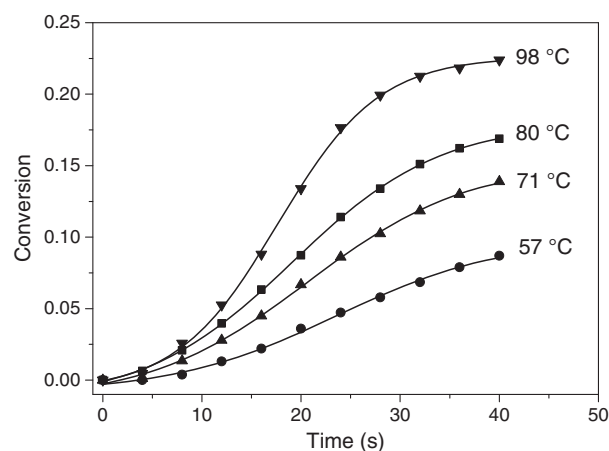


**Figure 5.** Conversion of epoxy groups from DGEBA in DGEBA/UVR blends versus irradiation time measured by NIR in 2-mm thick specimen. The blends were photoactivated with 2 wt%  $\text{Ph}_2\text{ISbF}_6$  with 1 wt.% CQ and 1 wt.% EDMAB. The conversion of epoxy groups from UVR are shown in Table 1.

composition of DGEBA/UVR blends on the extent reaction of epoxy groups from DGEBA. No significant polymerization of pure DGEBA was detected after 40 s of irradiation. However, this monomer polymerized readily and to relatively high conversion when UVR monomer was present. The conversion of DGEBA in the 25:75 and 50:50 DGEBA/UVR blends after 5 s irradiation was 82% and 62%, respectively, while in the 75:25 blend, the conversion was only 23 % after 40 s irradiation. The conversion of epoxy groups from the UVR monomer in DGEBA/UVR blends measured by ATR is shown in Table 1. It is seen that the UVR monomer reached complete conversion after 20 s irradiation in the absence of external heating. The temperature evolution during irradiation of DGEBA/UVR blends is shown in Fig. 2. No significant change in temperature was recorded during irradiation of pure DGEBA monomer. Conversely, a sharp temperature rise in DGEBA/UVR blends is seen in Fig. 2. The polymerization reaction of the UVR monomer is highly exothermic, which results in an increase in the sample temperature during the process, and this effect becomes more important as the proportion of UVR in the DGEBA/UVR blends increases. A higher sample temperature induces an increase of the mobility of the reaction environment (i.e. monomer, propagating species, and polymer) and consequently increases the reaction rate parameters. This assumption will be examined later by measuring the conversion of DGEBA at different temperatures.

### Conversion of DGEBA versus temperature

Figure 6 shows that the conversion of epoxy groups in DGEBA pure under irradiation with visible light increases markedly with cure temperature. No change in temperature was recorded during irradiation of thin films, which ensures that the polymerization was carried out under isothermal conditions. Results presented in Fig. 6 highlight the effect of the temperature on the cationic polymerization of the DGEBA photoinitiated with visible light. It is worth mentioning that conversion versus time plots in Fig. 6 were not carried out in real time and the resins polymerized in the dark during the process of data acquisition of the FTIR equipment. This made impossible the calculus of



**Figure 6.** Conversion of epoxy groups from DGEBA versus irradiation time measured by MIR in thin films at different temperatures. The DGEBA was photoactivated with 2 wt%  $\text{Ph}_2\text{ISbF}_6$  with 1 wt.% CQ and 1 wt.% EDMAB.

the activation energy of the cationic polymerization of DGEBA photoinitiated by CQ/EDMAB. From results presented, it may be concluded that the greater conversion of epoxy groups from the DGEBA with increasing proportions of UVR in DGEBA/UVR blends is attributed to thermal effects.

Original results on visible-light photopolymerization of epoxy monomers presented in this study, which to our knowledge have not been previously reported, may be summarized as follows. (i) The conversion of epoxy monomers was assessed during polymerization in thick specimens. The analysis of studies reported in the literature show that the degree of conversion of cycloaliphatic epoxy monomers has been measured by either dynamic scanning calorimetry or by MIR spectroscopy. Both techniques use thin films (thickness  $\sim 50 \mu\text{m}$ ). Conversely, in this research, the conversion of cycloaliphatic epoxy groups at the surface of 2 mm thick samples was evaluated by ATR technique whereas the conversion of aromatic epoxy groups in 2 mm thick specimens was assessed by near-IR. The measurement of conversion in thick specimens is relevant to applications that require thick layers such as encapsulants for LEDs instead of applications that require thin films such as coatings. (ii) The photobleaching of CQ was examined in order to assess the presence of colored photoproducts which might affect the optical properties of the cured material. Since the decomposition of CQ is assisted by association with tertiary amines and involves some ionic intermediates, the rate of reaction is expected to be affected by the polarity of the solvent. Thus, the photodecomposition of CQ was studied under visible light irradiation of epoxy monomers. The assessment of the photodecomposition of CQ is relevant to applications that require cured materials with high light transmission.

### Dynamic mechanical properties

DMA was used to measure the dynamic mechanical properties of epoxy blends prepared with different mass fractions DGEBA/UVR. A sharp drop in modulus and a peak in  $\tan \delta$  during DMA runs indicates the glass-to-rubber transition. Typical registers of the storage modulus (in MPa) and the  $\tan \delta$  as a function of temperature are shown in Figure 5 Suppl Inf. The glass transition temperature,  $T_g$ , was assessed from the maximum in  $\tan \delta$  versus temperature. The  $T_g$  values of resins prepared with different proportion of

UVR/DGEBA are summarized in Table 1. As seen in Table 1 the T<sub>g</sub> of blends UVR/DGEBA was not appreciably affected by the composition of the resins. The differences in T<sub>g</sub> are not large but are statistically significant.

### Compressive strength

Table 1 shows results from the compression tests performed on blends DGEBA/UVR. Similar to DMA analysis, it is seen that the compressive strength of blends DGEBA/UVR was not appreciably affected by the composition of the resins.

### Thermogravimetric analysis

The results of studies of thermal stability of the polymers derived from the photopolymerization of DGEBA/UVR blends by TGA are shown in Fig. 6 Suppl. Inf. Despite the very different structure of these two monomers, the thermal stabilities of the blends are similar. The crosslinked polymers display quite good stability out to approximately 300 °C. All three blends show a characteristic weight loss at temperatures above 300 °C that occurs in two major steps.

## CONCLUSION

Cycloaliphatic monomers photoactivated with an iodonium salt and CQ or CQ/EDMAB polymerize readily under visible light irradiation in the absence of external heating. This eliminates the problems associated with thermal cure at high temperature during long times, such as stringent process control to avoid failure of the devices and high consumption of energy.

The SIB monomer containing a siloxane group polymerized with CQ in the absence of amine giving as a result a clean photo-bleaching of the CQ and an excellent optical transparency. However, this advantage was accompanied with lower refractive index and compressive strength compared with the UVR monomer.

The partial replacement of cycloaliphatic UVR epoxy with DGEBA is an effective means of improving the refractive index of the material, and consequently the efficiency of the photo-emission. In spite of the fact that visible light polymerization of DGEBA proceeds at a slow rate, it is enhanced by the high temperature reached during the highly exothermic polymerization of UVR.

From results obtained in the present research, it may be concluded that visible light polymerization of epoxy monomers is a promising route for the processing of LED encapsulants.

Further experiments are required to assess the effect of different encapsulants on the efficiency of the photoemission of LEDs devices assembled from LEDs chip mounted on lead frames, gold wires, and encapsulants.

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## REFERENCES

- [1] Y. C. Lin, Y. Zhou, N. T. Tran, F. G. Shi, LED and Optical Device Packaging and Materials. In: *Materials for Advanced Packaging*, (Eds: D. Lu, C. P. Wong), Springer, Berlin, **2009**, 629–680.
- [2] Y. H. Lin, J. P. You, Y. C. Lin, N. T. Tran, F. G. Shi, *IEEE Trans. Compon. Packag. Manuf. Technol.* **2010**, *33*, 761–766.
- [3] P. L. Teh, M. Jaafar, H. M. Akil, K. N. Seetharamu, A. N. R. Wagiman, K. S. Beh, *Polym. Adv. Technol.* **2008**, *19*, 308–315.
- [4] R. Voo, M. Mariatti, L. C. Sim, *Polym. Adv. Technol.* **2012**. DOI: 10.1002/pat.3039
- [5] G. H. Kwak, S. J. Park, J. R. Lee, *J. Appl. Polym. Sci.* **2000**, *78*, 290–297.
- [6] R. N. Kumar, L. Y. Keem, N. C. Mang, A. Abubakar, *J. Appl. Polym. Sci.* **2006**, *100*, 1048.
- [7] Y. Morita, *J. Appl. Polym. Sci.* **2005**, *97*, 1395–1400.
- [8] S. C. Yang, J. S. Kim, J. H. Jin, S. Y. Kwak, B. S. Bae, *J. Appl. Polym. Sci.* **2010**, *117*, 2140–2145.
- [9] C. W. Hsu, C. C. Ma, C. S. Tan, H. T. Li, S. C. Huang, T. M. Lee, H. Tai, *Mater. Chem. Phys.* **2012**, *134*, 789–796.
- [10] J. S. Kim, S. C. Yang, S. Y. Kwak, Y. Choi, K. W. Paik, B. S. Bae, *J. Mater. Chem.* **2012**, *22*, 7954.
- [11] W. Liu, Z. Wang, Z. Chen, L. Li, J. Zhao, *Polym. Adv. Technol.* **2012**, *23*, 367–374.
- [12] Y. Zhou, N. Tran, Y. C. Lin, Y. He, F. G. Shi, *IEEE Trans. Compon. Packag. Manuf. Technol.* **2008**, *31*, 484–489.
- [13] F. W. Mont, J. K. Kim, M. F. Schubert, E. F. Schubert, R. W. Siegel, *J. Appl. Phys.* **2008**, *103*, 083120.
- [14] Y. Yagci, S. Jockusch, N. J. Turro, *Macromolecules* **2010**, *43*, 6245–6260.
- [15] J. Crivello, J. Jiang, H. Hua, J. Ahn, R. A. Ortiz, *Macromol. Symp.* **2004**, *215*, 165.
- [16] B. Aydogan, B. Gacal, A. Yildirim, N. Yonet, Y. Yuksel, Y. Yagci, *Photochemistry and UV Curing: New Trends*, Chapter 17 (Ed.: J. P. Fouassier), Kerala, India, **2006**.
- [17] J. Crivello, *J. Polym. Sci. Polym. Chem.* **2001**, *39*, 343.
- [18] V. Mucci, W. D. Cook, C. I. Vallo, *Polym. Eng. Sci.* **2009**, *49*, 2225–2233.
- [19] D. R. Lide, *Handbook of Chemistry and Physics* (82nd ed.) CRC Press, Boca Raton, FL, **2001**.
- [20] J. Crivello, *J. Polym. Sci. Polym. Chem.* **2009**, *47*, 866.
- [21] J. D. Oxman, D. W. Jacobs, M. C. Trom, V. Sipani, B. Fiek, A. B. Scranton, *J. Polym. Sci. Polym. Chem.* **2005**, *43*, 1747.
- [22] C. S. Pinzino, C. C. Chappelow, A. J. Holder, J. A. Morrill, C. D. Harris, M. D. Power, J. D. Eick, *J. Appl. Polym. Sci.* **2002**, *85*, 159–168.
- [23] J. Jakubiak, X. Allonas, J. P. Fouassier, A. Sionkowska, E. Andrzejewska, L. A. Linden, J. F. Rabek, *Polymer* **2003**, *44*, 5219–5226.
- [24] J. Crivello, U. Varlemann, *J. Polym. Sci. Polym. Chem.* **1995**, *33*, 2473–2486.
- [25] M. Jang, J. Crivello, *J. Polym. Sci. Polym. Chem.* **2003**, *41*, 3056.
- [26] S. Asmussen, G. Arenas, W. D. Cook, C. I. Vallo, *Dent. Mater.* **2009**, *25*, 1603.
- [27] S. Asmussen, G. Arenas, W. Cook, C. I. Vallo, *Eur. Polym. J.* **2009**, *45*, 515–522.
- [28] S. Asmussen, C. I. Vallo, *J. Photochem. Photobiol. A* **2009**, *202*, 228–234.
- [29] B. A. Ficek, A. M. Thiesen, A. B. Scranton, *Eur. Polym. J.* **2008**, *44*, 98–105.
- [30] V. Sipani, A. B. Scranton, *J. Photochem. Photobiol. A* **2003**, *159*, 189.