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ORIGINAL PAPER

Synthesis and characterization of a high refractive diglycidyl ether of thiodibenzenethiol epoxy resin

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Abstract High refractive index of epoxy resins used as encapsulant in light-emitting diode (LED) is essential in improving the light extraction efficiency, reducing heat and prolonging the service life of LED packages. In this study, diglycidyl ether of thiodibenzenethiol (DGETDBT), an epoxy resin with high refractive index, was synthesized via a novel method and its chemical structure was characterized with Fourier-transform infrared (FTIR) spectrometer and ^{1}H NMR spectrometer. Using *m*-xylylenediamine (MXDA) as curing agent, the curing behavior of DGETDBT was studied by differential scanning calorimetry (DSC) and was compared with that of diglycidyl ether of bisphenol A (DGEBA), a generally used encapsulant in LED. The thermal behavior and optical performance of these two resins were investigated with thermogravimetric analyses, UV–Vis scanning spectrophotometer, and Abbe refractometer, respectively. The results showed that DGETDBT/MXDA resin demonstrated similar curing and thermal behavior to DGEBA/MXDA resin. But its refractive index reaches 1.698, which is significantly

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higher than that of DGEBA/MXDA resin (1.604). Comparatively, DGETDBT resin can be expected to be a more effective encapsulant of LED.

Keywords Thermosetting resins · Optical material · Refractive index · Diglycidyl ether of thiodibenzenethiol (DGETDBT)

Introduction

Light-emitting diode (LED) is a new generation of solid-state light source with high efficiency, energy conservation, stability, durability, and compactness, and is expected to substitute incandescent lamp and fluorescent lamp [1]. To avoid stress shock and humidity corrosion, LED devices are mostly designed to be encapsulated. Transparent epoxy resins are generally used as encapsulant of LED due to their high transmittance, strong intensity, superior electric properties, anticorrosion, and low cost [2, 3]. However, the refractive index of the general diglycidyl ether of bisphenol A (DGEBA)/anhydride system is 1.53–1.54 (n_D^{25}, the same below), much lower than those of the LED dies [4]. The refractive index difference of these two mediums can cause total internal reflection when light travels from the die into the encapsulant at certain incident angles, and results in low light output [3]. Moreover, the trapped light is converted into heat and brings about many problems in LED packages. And these problems have became even worse nowadays as high-power LED is getting more and more popular and being considered as future light source [4–7].

As an average property of an integral material, the refractive index is mainly influenced by its molecular weight, density and the inherent molar refractivity of its molecular structure according to the Lorentz–Lorenz equation [8]. At present, introducing sulfur element into polymer is regarded as one of the best methods to realize high refractive index, and thioalcohol and thioether are usually used to prepare epoxy resin with high refractive index [9, 10]. Li et al. [11] co-cured the conventional DGEBA epoxy resin with bi-[2,2′-bis(mercaptomethyl)-1,1-biphenyl methylene] sulfide and aliphatic tetra-thiol (pentaerythritol tetrakis (3-mercaptopropionate)), and got a colorless encapsulant with the refractive index being 1.64. Katsumasa et al. [12] publicized a diglycidyl ether of thiodibenzenethiol (DGETDBT) epoxy resin with the refractive index of 1.669 in their patent, which is the ever-reported highest refractive index of extant epoxy resins. But there were no detailed data on the structure characteristics and performance of this resin. In addition, a large quantity of toxic solvents such as toluene and dioxane were involved in its preparation process.

In this study, a high refractive DGETDBT epoxy resin was synthesized via a novel method in which only a small amount of methyl isobutyl ketone was used. The chemical structure of DGETDBT was characterized by Fourier-transform infrared (FTIR) spectrometer and ^{1}H NMR spectrometer, and the performance of its uncured and cured resins was studied by differential scanning calorimetry (DSC), thermogravimetric analyses (TGA), UV–Vis scanning spectrophotometer, and Abbe refractometer.

Experimental section

Materials

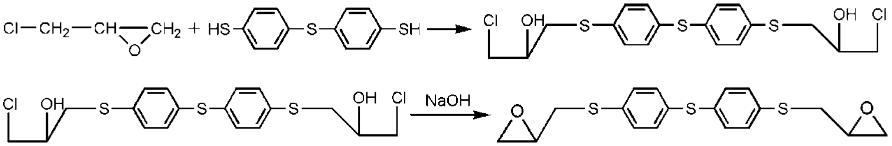
4,4′-Thiodibenzenethiol (TDBT) was provided by Zhejiang Shouerfu Chemical Co., China. Epichlorohydrin, methyl isobutyl ketone, and sodium hydroxide (NaOH) were supplied by Tianjing Guangfu Fine Chemical Research Institute, China. Curing agent *m*-xylylenediamine (MXDA) was obtained from Shanghai Chemical Co., China. Diglycidyl ether of bisphenol A (DGEBA, NPEL-128E) was obtained from Shenzhen Jiadida Chemical Co., China. All chemicals were used without further purification.

Synthesis of DGETDBT epoxy resin

The reaction process is divided into two steps as shown in Scheme 1. Briefly to say, TDBT (25 g) and epichlorohydrin (60 ml) were added into a four-neck round-bottom flask, which was equipped with thermometer, stirrer, reflux condenser and nitrogen inlet and was settled in a thermostatic water bath. Distilled water (0.5 ml) and NaOH (0.5 g) were added till TDBT was completely dissolved in epichlorohydrin, and the mixture was heated to 60 °C and refluxed for 3 h. The remaining epichlorohydrin was retrieved under vacuum at 80 °C for 1 h. Then methyl isobutyl ketone (25 ml) was added, and NaOH (8 g) were added at an interval of 0.5 h for four times at 60 °C. The mixture was further stirred and reacted for 1–2 h. After being filtered, the crude product was washed with deionized water to chlorine-free in a separatory funnel. Finally, the solvent was evaporated under vacuum and 32.6 g viscous yellow DGETDBT epoxy resin was obtained with the yield of 90.5 %.

Curing of epoxy resin

The stoichiometric mixture of DGETDBT and MXDA was prepared by uniformly mixing by a mixer. After being degassed, the resin was poured into a closed silicone rubber mold and cured sequentially at 50 °C for 3 h and 120 °C for 1 h. The DGETDBT/MXDA specimens with two kinds of thickness of 0.5 and 3 mm were prepared for transmission and refractive index measurement, respectively. The DGEBA/MXDA resin and its specimens were also prepared with the same method for comparison study.



Scheme 1 The reaction steps of DGETDBT's preparation

Characterization

The average molecular weight and molecular weight distribution of epoxy resins were determined via a Waters 515 gel permeation chromatography (GPC) system relative to polystyrene standards with THF as a solvent, and the results for DGETDBT are $M_n = 684$ and $M_w/M_n = 1.16$. The epoxide equivalent weight was tested with acetone–hydrochloride method and the viscosity of epoxy resin was measured on a NDJ-79 rotating viscometer, which results are calculated as 188.7 g mol^{-1} and about 1.0 Pa s at 25 °C for DGETDBT, respectively.

FTIR spectra were obtained by Nicolet 6700 FTIR spectrometer to identify the chemical structure of the specimens, which were prepared by attaching the samples to a potassium bromide (KBr) disc. ^{1}H NMR spectra were performed on a Varian INOVA NMR spectrometer at 400 MHz using $CDCl_3$ as solvent. Non-isothermal curing kinetics was studied by DSC with a TA DSC Q100 calorimeter under the protection of nitrogen flow. The heating rate was 10 °C min^{-1} from −40 to 200 °C. Calibration of the calorimeter with regard to temperature and energy was achieved by measurement of the temperature and enthalpy of melting of indium as standard material. TGA were carried out using TA Q50 TGA analyzer. The samples were heated from 25 to 550 °C at a rate of 20 °C min^{-1} under the protection of nitrogen flow. Transmittance spectra were recorded with UV1801 UV–Vis scanning spectrophotometer. Refractive indices were determined using WYA Abbe refractometer.

Results and discussion

Structure analysis of DGETDBT epoxy resin

FTIR spectra of DGETDBT epoxy resin and its monomer TDBT were given in Fig. 1. There was an absorption peak at 2,600 cm^{-1} in the spectrum line of TDBT for its S–H functional group, whereas the same peak was not found in that of DGETDBT, which suggested that TDBT was converted completely. The characteristic peaks of the three-member ring ether group at 927 and 854 cm^{-1} and the peak representing the stretching vibration of C–O–C at 1,267 cm^{-1} of DGETDBT were both seeking out in its FTIR spectrum. Furthermore, characteristic absorption peaks of phenyl at 3055, 1634, 1574, 1474, 1391, and 813 cm^{-1}, and the C–S–C stretching vibration at 1,095 and 1,010 cm^{-1} were also observed in Fig. 1 [13, 14]. The appearance of a broad absorption peak at 3,474 cm^{-1} and the characteristic peak of water at 1,631 cm^{-1} indicated that a small amount of water was absorbed by DGETDBT, as reported by Antoon et al. [15].

^{1}H NMR spectrum of DGETDBT epoxy resin was shown in Fig. 2, which further confirmed the chemical structure of this synthesized resin. In the spectrum, peaks at 2.56 and 2.78 ppm were assigned to protons of methylene in the oxirane ring, peak at 2.97 ppm were for protons of methine in the oxirane ring, peak at 3.15 ppm were attributed to the protons of methylene connected the thioether group and the oxirane ring of DGETDBT, and peaks at 7.24 and 7.32 ppm were specified to the protons of benzene rings group, respectively, according to some previous study [16].

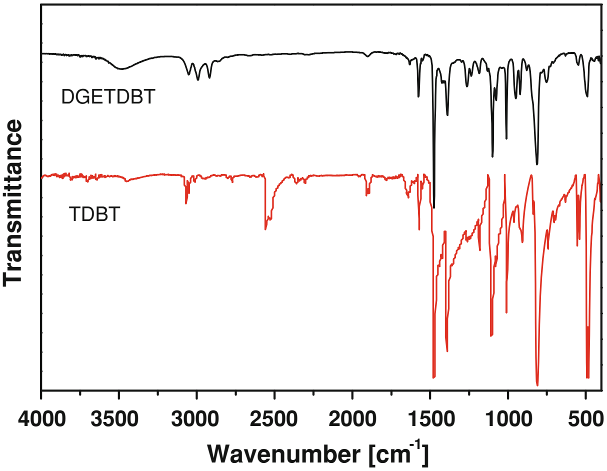


Fig. 1 The FTIR spectra of DGETDBT and TDBT

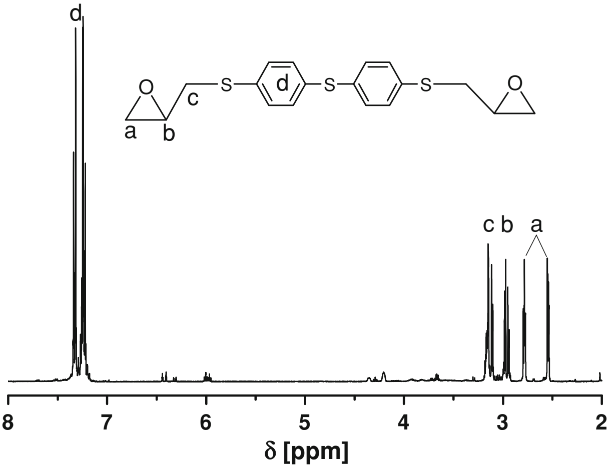


Fig. 2 The ^{1}H NMR spectra of DGETDBT

Thermal properties of DGETDBT and DGEBA epoxy resin

In present study, DSC was used to monitor the curing behavior and measure the glass transition temperatures (T_g) of DGETDBT/MXDA and DGEBA/MXDA resins. Thermograms of the two resins were obtained with twice DSC scans at a heat rate of 10 °C/min and were presented in Fig. 3. The first scan was designed to monitor the curing behavior of the uncured resins, and the second scan was aimed to measure T_g of the cured epoxy [17]. The detailed results were summarized in Table 1. Comparatively, even though the two resins showed similar exothermic behavior, DGETDBT/MXDA resin had broader exotherm range, lower onset

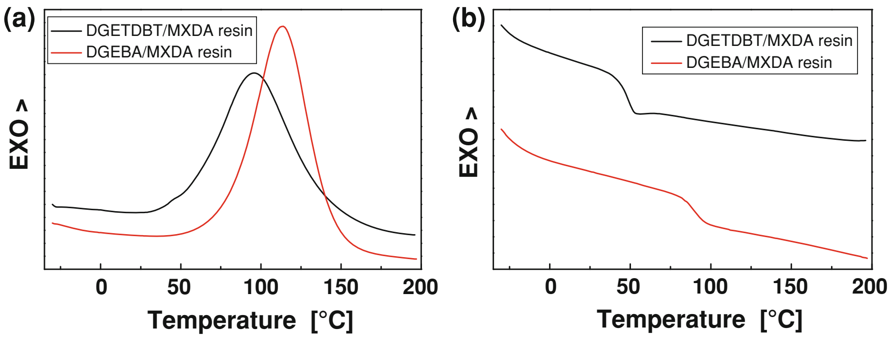


Fig. 3 The DSC thermograms of DGETDBT/MXDA and DGEBA/MXDA resins. **a** The first scan, **b** the second scan

Table 1 DSC heating scans of DGETDBT/MXDA and DGEBA/MXDA resins

Resins	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	T_g (°C)
DGETDBT/MXDA	29	96	194	389.0	49.2
DGEBA/MXDA	42	115	186	433.2	90.5

T_i onset temperature of the exothermic peak, T_p peak exothermic temperature, T_f ending temperature of the exothermic peak, ΔH heat of reaction

temperature of the exothermic peak (T_i), peak exothermic temperature (T_p), heat of reaction (ΔH), and T_g than DGEBA/MXDA resin, which indicated that the former was prone to be cured.

Figure 4 showed the TGA and its differential curves (DTG) of the two cured resins under nitrogen, which provided information regarding their thermal stability and thermal degradation behavior. Temperatures for 5 % weight loss and peak in DTG curves were 295.2 and 343.5 °C for the cured DGETDBT/MXDA resin, and 340.5 and 372.5 °C for the cured DGEBA/MXDA resin, respectively. Obviously, the cured DGETDBT/MXDA resin exhibited lower thermal stability than the cured DGEBA/MXDA resin because of the higher instability of thioether structure (C–S–C) in the former than ether structure (C–O–C) in the latter. But the cured DGETDBT/MXDA resin also meets the usage demand of LED.

Optical performance of DGETDBT and DGEBA epoxy resin

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 [18, 19]. In this study, optical transparency of the two cured epoxy was characterized with UV–Vis spectrometer at a wavelength range of 200–900 nm, and the thickness of the specimens was controlled to about 0.5 mm. Figure 5 showed the optical transmittance spectra of the cured DGETDBT/MXDA and DGEBA/MXDA resins. Obviously, the visible light transmittances of the two cured resins both

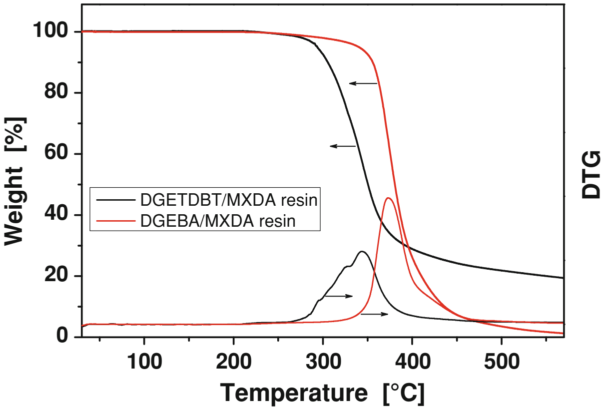


Fig. 4 The thermogravimetric differential curves of cured DGETDBT/MXDA and DGEBA/MXDA resins

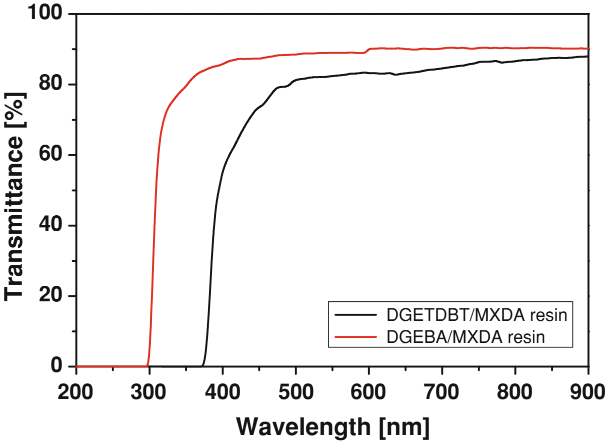


Fig. 5 The transmittance spectra of cured DGETDBT/MXDA and DGEBA/MXDA resins at the wavelength of 200–900 nm

reached to about 85 %, which indicates their excellent optical transparency in this region, and their transmittances were both nearly to zero at the wavelength of <300 nm. As far as the wavelength of 300–370 nm in UV region was concerned, the cured DGEBA/MXDA resin still showed very high transmittance, while that of the cured DGETDBT/MXDA resin was zero. This property would be very useful in protecting human eye from ultraviolet rays if the DGETDBT/MXDA resin was used as packaging materials in LED devices.

In this study, 3 mm thickness specimens of the cured resins were prepared for refractive index measurement. Liquid prepolymer and uncured resin specimens were normally measured directly. The results for DGETDBT and DGEBA in different states were shown in Table 2. The refractive indices of DGETDBT prepolymer, uncured, and cured DGETDBT/MXDA resins were 1.665, 1.656, and

Table 2 Refractive indices of prepolymer, uncured and cured resins of DGETDBT and DGEBA

Specimens	Prepolymers	Uncured resins	Cured resins
DGETDBT	1.665	–	–
DGEBA	1.570	–	–
DGETDBT/MXDA	–	1.656	1.698
DGEBA/MXDA	–	1.575	1.604

1.698, respectively, which were all significantly higher than the corresponding values of DGEBA prepolymer and DGEBA/MXDA resins. Sulfur atoms in DGETDBT have contributed to an obvious increase in its refractive index according to some recent literatures [9, 10].

Conclusions

Overall, a high refractive epoxy resin, DGETDBT, was synthesized via an environment-friendly method, and its structure was characterized with FTIR and ^{1}H NMR spectra. All curing behavior and thermal properties of the cured DGETDBT/MXDA resin meet the requirements of LED devices, similar to those of DGEBA, the generally used LED encapsultant. The most important is the sulfide groups in DGETDBT significantly improved its refractive index, which meets the development trend of LED encapsultant. Moreover, light transmittance of the cured DGETDBT/MXDA resin at the wavelength of <370 nm was zero, usage of which might shield people from UV radiation. Therefore, we have reasons to expect DGETDBT resin as one potential high-performance encapsulant of LED in practical application.

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References

1. Gunshor RL, Nurmikkob AV (1996) Wide bandgap semiconductors and their application to light emitting devices. Curr Opin Solid State Mater Sci 1:4–5. doi:10.1016/S1359-0286(96)80002-7
2. Rector L, Starkey D (2004) Performance of epoxy encapsulants for optoelectronie packaging. In: The 4th IEEE international conference on polymers and adhesives in microelectronics and photonics, Portland, USA, pp 211–215. doi:10.1109/POLYTR.2004.1402763
3. Huang JC, Chu YP, Wei M (2004) Comparison of epoxy resins for applications in light-emitting diodes. Adv Polym Technol 23:298–306. doi:10.1002/adv.20018
4. Edwards M, Zhou Y (2001) Comparative properties of optically clear epoxy encapsulate. Proc SPIE 4436:190–197. doi:10.1117/12.451299
5. Schubert E (2003) Light-emitting diodes. Cambridge University Press, Cambridge
6. Lin Y, Tran N, Zhou Y, He Y, Shi F (2006) Materials challenges and solutions for the packaging of high power LEDs. In: 2006 international microsystems, package, and assembly conference Taiwan, pp 177–180. doi:10.1109/IMPACT.2006.312173

7. Zhou Y, Tran N, Lin YC, He YZ, Shi F (2008) One-component, low-temperature, and fast cure epoxy encapsulant with high refractive index for LED applications. IEEE Trans Adv Packaging 31:484–489. doi:10.1109/TADVP.2008.924233
8. Brandrup J, Immergut EH (1980) Polymer handbook. Wiley, New York
9. Harumichi A, Yoshinobu K (1998) Sulfur-containing epoxy compound and sulfur-containing epoxy resin. JP10130250, Japan
10. Teruyuki N, Koju O, Tohru M (1990) Lens comprising a resin having a large refractive index and process for preparing the lens. EP0351073A2, Japan
11. Li HT, Hsu CW, Chen KC (2008) A novel high refractive transparent material in LED package applications. In: 10th international conference on electronics materials and packaging, pp 309–312. doi:10.1109/EMAP.2008.4784290
12. Katsumasa Y, Michio S, Koji S, Katsuya I (1997) Adhesive. JP9316421A, Japan
13. Martinez PA, Cadiz V, Ana M, Serra A (l985) Synthesis, characterization, and thermal behavior of new epoxy polyesterimide. Angew Makromol Chem 133:97–109. doi:10.1002/apmc.1985.051330108
14. Lee LH (1961) Mechanism of thermal degradation of phenolic condensation polymers. I. Studies on the thermal stability of polycarbonate. J Polym Sci Polym Chem 2:2859–2873. doi:10.1002/pol.1964.100020635
15. Antoon MK, Koening JI, Serafini T (1981) Fourier-transform infrared study of the reversible interaction of water and a crosslinked epoxy matrix. J Polym Sci Polym Phys 19:1567–1575. doi:10.1002/pol.1981.180191007
16. Pan GY, Du ZJ, Zhang C, Li CJ, Yang XP, Li HQ (2007) Synthesis, characterization, and properties of novel novolac epoxy resin containing naphthalene moiety. Polymer 48:3686–3693. doi:10.1016/j.polymer.2007.04.032
17. Agag T, Takeichi T (1999) Synthesis and characterization of epoxy film cured with reactive polyimide. Polymer 40:6557–6563. doi:10.1016/S0032-3861(99)00026-9
18. Gu Q, Zhou Q (1998) Preparation of high strength and optical transparent silicone rubber. Eur Polym J 34:1727–1733. doi:10.1016/S0014-3057(97)00098-0
19. Lin YH, You JP, Lin YC, Tran NT, Shi FG (2010) Development of high-performance optical silicone for the packaging of high-power LEDs. IEEE Trans Compon Packag Technol 33:761–766. doi:10.1109/TCAPT.2010.2046488