Synthesis and Thermal Stability of a Novel Cycloaliphatic Epoxy Resin System

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ABSTRACT: A novel cycloaliphatic epoxy resin was synthesized from dicyclopentadiene, ethylene glycol, and nadic anhydride. The chemical structures of the resultant epoxy resin and its precursor were characterized with Fourier transform infrared spectroscopy, ^{1}H-NMR, and mass spectrographic analyses. The thermal stability of the cured polymer was investigated with differential scanning calorimetry and thermogravimetric analysis. Compared with the thermal stability of the commercial cycloaliphatic epoxy resin 3,4-epoxy cyclohexyl methyl-3′,4′-epoxy cyclohexyl carboxylate, a higher thermal stability for the cured polymer of the novel epoxy resin was observed. The results imply that the novel cycloaliphatic epoxy resin has good potential applications in electronic encapsulation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 518–522, 2008

Key words: high performance polymers; resins; structure; synthesis; thermal properties

INTRODUCTION

An important trend in developing advanced integrated circuits is the development of high density and complex functionality for electronic products.[1–4] The last step of integrated circuit fabrication is encapsulation. The development of the electronic industry promotes encapsulation technology, and encapsulation materials must meet higher requirements.[5] That is, encapsulation materials must protect components from chemicals and mechanical stress, ensure good electrical insulation, and offer good thermal stability. Because of the lower cost and easier processing, over 90% of encapsulation materials are polymers.[6,7] Among these polymers, epoxy resins are the most widely used because of their outstanding properties, such as good heat resistance, high modulus, good heat resistance, and high electrical resistance.[8–10] At present, glycidyl ether of *o*-cresol novolac epoxy is most widely used as an encapsulation material. However, the high moisture absorption under a higher temperature and the melt viscosity of the resin have limited its usage in ultra-large-scale integrated circuits.[11] The development of novel epoxy resins to enhance the heat resistance and electric resistance of thermosetting polymers for use in electrical and microelectronic devices is attracting considerable attention.[12–14]

Cycloaliphatic epoxies, which are characterized by their saturated cycloaliphatic ring structure and lack of any aromatic groups, have been considered potential candidates for future printing circuit board (PCB) markets[15–20] because of their low viscosity before curing, outstanding heat and chemical resistance, and superior mechanical and electrical properties after curing.[21,22] The objective of this article is to describe the synthesis and structure of a novel cycloaliphatic epoxy resin derived from dicyclopentadiene (DCPD), ethylene glycol, and maleic anhydride. The thermal properties of the cured polymer were investigated with several methods and compared with those of the commercial cycloaliphatic epoxy resin 3,4-epoxy cyclohexyl methyl-3′,4′-epoxy cyclohexyl carboxylate (ERL-4221).

EXPERIMENTAL

Materials

Industrial product DCPD, reagent-grade ethylene glycol, *p*-hydroxylphenyl methyl ether, and maleic anhydride were commercially available and used as received; nadic anhydride (NA) was prepared from maleic anhydride and cyclopentadiene, which was freshly cracked from its dimer DCPD just before its use according to the literature.[23] *m*-Chloroperoxybenzoic acid (*m*-CPBA) was used as an epoxidizing

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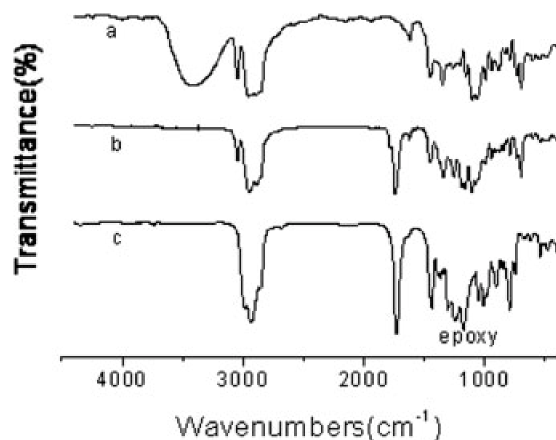


Figure 1 IR spectra of the epoxide and its precursors: (a) **1**, (b) **2**, and (c) **3**.

agent, and methyl tetrahydrophthalic anhydride (MeTHPA) was used as a curing agent, no curing accelerator being added. The commercial epoxy resin ERL-4221 was purchased from Dow Chemical Co. (Shanghai, China) and used for contrast. These materials were used as supplied without further purification.

Synthesis of ethylene glycol monodicyclopentenyl ether (1)

Ethylene glycol (74.4 g, 1.2 mol), 3.3 mL of $BF_3{\cdot}O(C_2H_5)_2$ (ca. 10 mol % of the weight of DCPD), and 20 mL of toluene as a solvent were added to a 250-mL, three-necked, round-bottom flask equipped with a thermometer, an addition funnel, a condenser, and a magneto stirrer. The mixture was cooled in an ice bath, and then 79.2 g (0.6 mol) of DCPD was added dropwise over 1 h. The reactive mixture was then heated to 100°C and stirred rigorously for another 5 h at this temperature under reflux. After cooling, the reactive mixture was washed with saturated brine, then with a 10% soda solution, and finally with deionized water to neutralization, and the organic layer was dried over anhydrous sodium sulfate, then filtered, and finally distilled under reduced pressure. The fraction with a boiling point of 134–136°C at 5 mmHg was collected as product **1**, a colorless liquid weighing 90.3 g (yield = 78%).

IR [KBr, see Fig. 1(a)]: 3413 (—OH), 3047 (C=C—H), 1620 (C=C), 1107, 1065 (C—O—C), 737, 700, 656 cm^{-1}. ^{1}H-NMR: δ = 5.68 ($1H_d$), 5.44 ($1H_e$), 3.68–3.71 ($2H_a$), 3.45–3.54 ($3H_{b,c}$), 1.22–2.58 ($11H_{others}$).

Figure 2(a) shows the ^{1}H-NMR spectrum of **1**.

Esterification of 1 with NA (2)

In a 250-mL, three-necked, round-bottom flask equipped with a trap and condenser, the esterification of **1** with NA was catalyzed by *p*-toluenesulfonic acid. The molar ratio of NA to alcohol was 1 : 2.5. The weight of the catalyst used in esterification was 0.3 wt % of NA. In a typical reaction, 16.4 g (0.1 mol) of NA, 48.5 g (0.25 mol) of **1**, and 0.05 g of *p*-toluenesulfonic acid were added to 40 mL of toluene, and the mixture was refluxed with rigorous stirring. The progress of the reaction was monitored by the collection of water in the trap. Toward the end of the esterification reaction, the acid value of the reaction mixture was determined by titration of this mixture against alcoholic KOH with phenolphthalein as an indicator. Then, the yield of **2**, calculated according to the acid value, was 89.3%.

IR [KBr; see Fig. 1(c)]: 3037 (C=C—H), 2929, 1729 (C=O), 1628 (C=C), 1436, 1203, 1155, 1093 (C—O—C), 696 cm^{-1}.

Figure 2(b) displays the ^{1}H-NMR spectrum of **2**.

Epoxidation of the esterification product (3)

In a ice-cooled, 250-mL, three-necked, round-bottom flask equipped with a thermometer, an addition funnel, and a magneto stirrer, 14.00 g (86 wt %, 0.06 mol) of *m*-CPBA was dissolved in 60 mL of CH_2Cl_2 while the mixture was stirred and maintained at a temperature of 0°C. To this mixture was slowly added a solution of 10.68 g (0.02 mol) of **2** in 30 mL of CH_2Cl_2, and the reaction mixture was maintained below 5°C. At this temperature, the reaction mixture was further stirred for 12 h, and this was followed by filtration. The filtrate was washed with a solution of 10% sodium sulfite under rigorous stirring until the solution would not turn starch–potassium iodide test paper blue, then with a solution of 10% soda solution, and finally with deionized water to neutralization. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator; then, 10.13 g (yield 87%) of the final product **3**, a light-yellow liquid with low viscosity, was obtained.

IR [KBr, see Fig. 1(d)]: 2921, 1724 (C=O), 1434, 1268, 1224, 1168, 1006, 898, 835, 788 (oxirane ring fused to cyclopentane), 538 cm^{-1}.

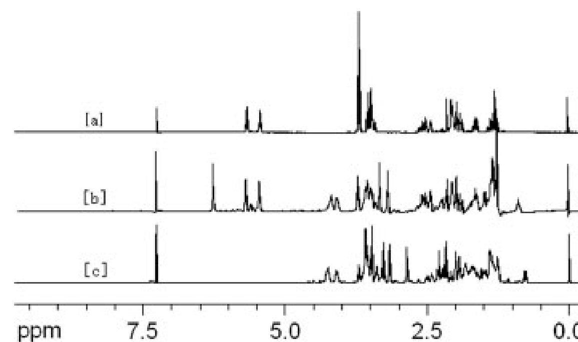


Figure 2 ^{1}H-NMR spectra of the epoxide and its precursors: (a) **1**, (b) **2**, and (c) **3**.

Figure 2(c) details the ^{1}H-NMR spectrum of **3**. The molecular weight of **3**, determined by mass spectrographic analysis, was 583.0 (M+H, calcd. 582.0).

Curing procedure of the epoxy resins

The resulting triepoxide and MeTHPA as a curing agent were mixed with a molar stoichiometric ratio of 1 : 0.80. The mixture was cured first at 80°C for 6 h, then at 150°C for 12 h, and finally at 170°C for 2 h. For comparison, the commercial diepoxide ERL-4221 was also mixed with MeTHPA in the same ratio and cured under the same conditions mentioned previously.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a WQF410 IR spectrometer (Beijing Rayleigh Analytical Instrument Corp., China). ^{1}H-NMR characterizations were carried out with a Varian Inova 400 NMR spectrometer (Palo Alto, CA) with chloroform-d_1 ($CDCl_3$) as the solvent and tetramethylsilane as an internal standard. Mass spectrographic analysis was performed on a Finnigan LCQ-Advantage mass spectrometer (San Jose, CA) to determine the molecular weight of the cycloaliphatic epoxy resin. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) thermograms were obtained with a Netzsch (Gebruder Netzsch Strasse, Germany) STA 449C thermal analysis system from 0 to 500°C at a heating rate of 10°C/min under a nitrogen atmosphere.

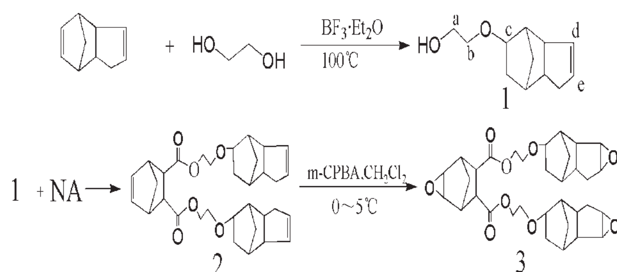
RESULTS AND DISCUSSION

Synthesis and characterization of the epoxy resins

The cycloaliphatic epoxy resin **3** was designed and prepared according to the chemical reactions outlined in Scheme 1.

The chemical structures of compounds **1**, **2**, and **3** were characterized by means of FTIR, ^{1}H-NMR, and mass spectrographic analysis. As shown in the FTIR spectra of **1** [see Fig. 1(a)], the original absorption signals for the cyclopentene double bond in DCPD were observed at 3047, 1620, and 656 cm^{-1}; in addition, the strong absorption peak at 3413 cm^{-1} corresponding to the vibration of —OH group and a strong characteristic band at 1065 cm^{-1} for the aliphatic ether linkage were observed. Compared to the FTIR spectrum of **1**, Figure 1(b,c) exhibits a series of strong characteristic bands at 1729 and 1203 cm^{-1} due to the ester functional group, whereas the vibration of —OH is lost completely; this demonstrates the esterification of **1** with NA. As a result of the epoxidation, in Figure 1(c), the aforementioned absorptions of double bonds at 3047 and 1620 cm^{-1} existing in **1** and **2** disappeared, whereas new characteristic bands of the oxirane ring fused to cyclopentane appeared at 894, 835, and 788 cm^{-1}. This result indicates that the double bonds in **2** were completely converted into epoxy groups in **3**.

The ^{1}H-NMR spectra of **1**, **2**, and **3** (see Fig. 2) confirmed further their chemical structure. In the ^{1}H-NMR spectrum of **1** [Fig. 2(a)], all signals corresponding to the proposed structure were observed. The chemical shifts of the protons on the cyclopen-



Scheme 1 Synthesis of the epoxy resin starting from DCPD, ethylene glycol, and NA.

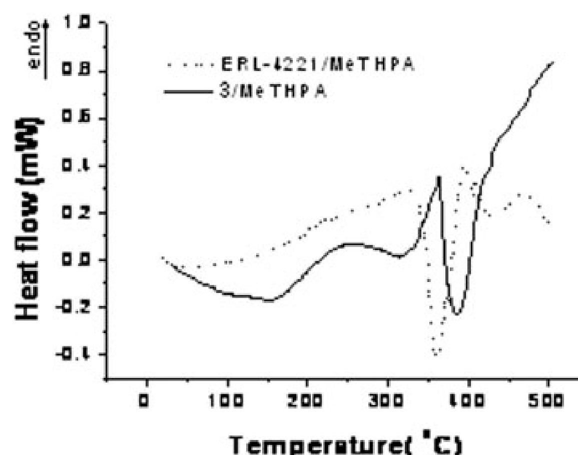


Figure 3 DSC curves of the cured polymer under nitrogen flow.

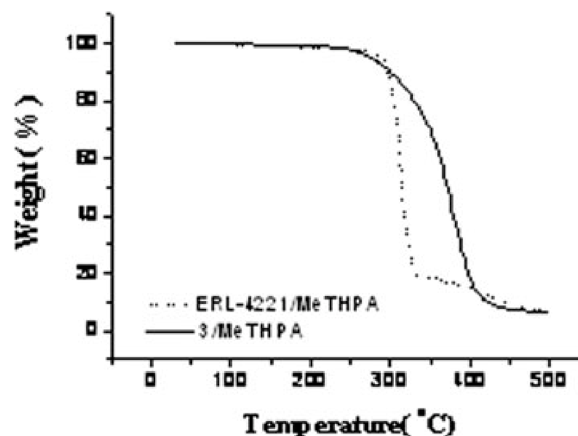


Figure 4 TGA curves of the cured polymer under nitrogen flow.

TABLE I
Thermal Analysis Data on MeTHPA-Cured Resins

Sample	$T_{g,\mathrm{DSC}}$ (°C)	Exothermic peak (°C)	$T_{d,5\%}$ (°C)	$T_{d,10\%}$ (°C)	$T_{\max}$ (°C)
ERL-4221/MeTHPA	201.2	360.2	285.5	296.0	317.5
3/MeTHPA	221.8	384.1	275.0	301.0	370.0

$T_{d,5\%}$ = temperature of 5% weight loss; $T_{d,10\%}$ = temperature of 10% weight loss; $T_{g,\mathrm{DSC}}$ = glass-transition temperature determined by differential scanning calorimetry; $T_{\max}$ = temperature of the maximum rate of weight loss.

tene double bonds were observed at 5.67–5.43 ppm (2H), both the aliphatic ethane protons and the protons in the dicyclopentenyl ring nearest the ether bonds were observed at 3.70–3.47 ppm (5H), and the other dicyclopentenyl ring protons and the proton on —OH were assigned to 2.56–1.28 ppm (11H). The ^{1}H-NMR spectrum of **2** [see Fig. 2(b)] exhibited multiplet peaks at 0.80–3.00 ppm due to the saturated protons for cycloaliphatic hydrocarbon. The chemical shifts of double-bond protons in limonenyl and in the dicyclopentenyl ring were observed at 6.26 (2H) and 5.68–5.44 ppm (4H), respectively. The signals for the protons nearest the ester bond appeared at 4.26–4.00 ppm (4H), whereas the signals for the protons nearest the ether bonds were observed at 3.70–3.47 ppm (6H). These results indicated that **1** proceeded completely to the reaction with NA. Compared to Figure 2(b), Figure 2(c) provides evidence of the epoxidation by showing the disappearance of the original signals for double-bond protons in **2** at 6.26 and 5.68–5.44 ppm and the presence of the chemical shifts of the protons both on the oxirane ring and on ether carbon atoms at 3.07–3.58 ppm (9H) in **3**.

Thermal stability

DSC is a general method for obtaining the glass-transition temperature of cured epoxy samples, and TGA traces can provide their thermal stability and thermal degradation behaviors. The DSC curves and TGA thermograms of the cured epoxy/MeTHPA systems in nitrogen gas are presented in Figures 3 and 4, respectively. Table I summarizes the results of DSC and TGA. The exothermic peak in Figure 3 implies the occurrence of the degradation process. From the DSC results, it is very obvious that the cured **3**/MeTHPA system had a higher glass-transition temperature than the ERL-4221/MeTHPA system. From the TGA results, the degradation of the cured **3**/MeTHPA system exhibited a two-stage process. Compared to that of the ERL-4221/MeTHPA system, the degradation with 5% weight loss happened at a lower temperature, 275.0°C, which was attributed to the decomposition of the unreacted epoxy or other impurity traces apart from the cured **3**/MeTHPA system. The main degradation process caused by thermal degradation of the cured network of the two cured epoxy systems happened over 300°C; the temperature of the maximum rate of weight loss was 370.0°C for the cured **3**/MeTHPA system and 317.5°C for the cured ERL-4221/MeTHPA system. These results showed that the **3**/MeTHPA system exhibited higher thermal stability than the ERL-4221/MeTHPA system, and this could be attributed to the relatively high crosslinking density of the **3**/MeTHPA system.

CONCLUSIONS

With the introduction of the cycloaliphatic moiety into the backbone, a novel trifunctional cycloaliphatic epoxy resin was successfully designed and synthesized by simple synthetic methods from inexpensive and readily available starting materials. The structure of the obtained epoxide and its precursors were confirmed by means of FTIR, ^{1}H-NMR, and mass spectroscopy. Compared with ERL-4221, the resulting polymer from the novel epoxy resin exhibited much higher thermal stability with a higher glass-transition temperature and temperature of the maximum rate of weight loss, 221.8 and 370.0°C, respectively. The results indicate that the novel cycloaliphatic epoxy resin may be a promising packaging material.

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