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Synthesis and characterization of a novel cycloaliphatic epoxy resin starting from dicyclopentadiene

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Abstract

A novel tri-functional cycloaliphatic epoxy resin was synthesized starting from dicyclopentadiene. The chemical structures of the resultant epoxy resin and its precursor were characterized with FTIR spectroscopy, EEW, ^{1}H NMR and Mass spectrographic analyses. The thermal and mechanical properties of the resulting polymer were evaluated with differential scanning calorimeter (DSC), thermo-gravimetric and thermal mechanical analysis. Compared to that of the common cycloaliphatic epoxy resin ERL-4221, the cured polymer of the novel epoxy resin exhibited lower thermal degradation temperature with much higher char yield and similar thermal expansion coefficient. These excellent overall performances make it a promising packaging material.

Keywords: Cycloaliphatic epoxy resin; Dicyclopentadiene; Packaging materials

1. Introduction

Epoxy resin are known to have the combination of good thermal and dimensional stability, excellent chemical and corrosion resistance, high tensile strength and modulus, and ease of handling and processability, ensuring their wide industrial application, such as paints, coatings, matrices, etc., [1,2]. Meanwhile, epoxy resins are widely used as the primary packaging materials for printed circuit boards, because of their high glass transition temperature and acceptable dielectric properties [3]. The applications of printed circuit boards can be divided into two areas: information technology and communicates industrials. Both applications have identical technical demands for the future evolution to high-frequency appliances. As the working frequency of electronic appliances increases, signal intensity losses become more sensitive. Therefore, demand is higher in high-frequency appliance markets for small dielectric constant and low-dissipation energy substrates, and epoxy resins used for electronic encapsulation should meet higher requirements for rheological behaviors and thermal stability as well as electric insulation.

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For above purposes, some novel epoxy resins have been investigated [4–6]. Among these, cycloaliphatic epoxy resins have been considered as potential candidates for future PCB markets [7], due to their low viscosity prior to curing, and good heat and chemical resistance, superior mechanical and electrical properties after curing. Additionally, the cycloaliphatic epoxy resins, unlike the aromatic epoxy resins, do not have strong UV chromophore groups, and therefore are highly resistant to ultraviolet light and more durable for outdoor applications such as electrical insulators. Moreover, the synthesis of cycloaliphatic epoxy resins involves the peracid epoxidation of cycloaliphatic olefins rather than the condensation of epichlorohydrin with phenols so that the cycloaliphatic epoxy resins are essentially free of chloride [8,9]. For these reason, the study on the synthesis and application of novel cycloaliphatic epoxy resins is attracting considerable attention [10–15].

The objective of the present investigation was to describe the synthesis and structure of a tri-functional cycloaliphatic epoxy resin starting from dicyclopentadiene (DCPD), which was obtained as a by-product from naphtha crackers with very low cost. The differentiated reactivity between the norbornene and cyclopentene double bonds in DCPD makes it possible to conduct the addition of alcohols preferentially at the norbornenyl double bond without involvement of the markedly less reactive cyclopentene double bond. This feature of DCPD allows for the facile synthesis of monomers bearing two different functional groups [16]. Taking the adducts derived from DCPD and ethylene glycol as intermediate, the resulting epoxides would display high reactivity attributed to the high ring strain present in the epoxycyclopentyl ring system, and the resulting polymer would possess excellent rigidity, mechanical strength, and a high thermal stability. In this article, the thermal properties of the cured polymer were investigated using several methods, and compared with the common cycloaliphatic epoxy resin.

2. Experimental

2.1. Materials

Industrial product dicyclopentadiene (DCPD) and reagent grade ethylene glycol and p-hydroxylphenyl methyl ether were commercially available and used as received, phosphorous oxychloride and triethylamine were dried by molecular sieve before use. m-chloroperoxybenzoic acid (m-CPBA) were used as epoxidizing agent, and hexahydrophthalic anhydride (HHPA) as curing agent, no curing accelerator being added.

2.2. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a WQF410 spectrameter. ^{1}H NMR spectra were determined on a VarianINOVA400 NMR Spectrometer using chloroform-d$_1$(CDCl$_3$) as the solvent and tetramethylsilane (TMS) as internal standard. Differential scanning calorimeter (DSC) and thermo-gravimetric analyses (TGA) thermograms and the coefficient of thermal expansion (CTE) were obtained by using a NETZSCH-STA 449 C thermal analysis system from 50 °C to 500 °C at the heating rate of 10 °C/min under nitrogen atmosphere. Mass spectrographic analysis were performed on Finnigan LCQ-Advantage Mass spectrometer to determine the molecular weight of the cycloaliphatic epoxy resin, and epoxy equivalent weights (EEW) were determined by acid titration using the HBr-acetic acid method [17].

2.3. Synthesis of ethylene glycol monodicyclopentenyl ether (I)

49.6g (0.8 mol) of ethylene glycol, 2.5 ml of $BF_3 \cdot O(C_2H_5)_2$ (about 10 mole percent of the weight of DCPD), and 20 ml of toluene as solvent were added into a 250 ml, three-neck, round-bottomed flask equipped with a thermometer, an addition funnel, a condenser, and a magneto stirrer. The mixture was cooled in an ice-bath, and then 52.8 g (0.4 mol) of DCPD were added dropwise over 1 h. The reactive mixture was then heated to 100 °C and stirred rigorously for a further 5 h maintained at this temperature, under reflux. After cooling, the reactive mixture was washed with saturated brine, and then with 10% soda solution, and finally with deionized water to neutralization, and the organic layer was dried over anhydrous sodium sulfate, filtered, and distilled under reduced pressure. The fraction with a boiling point of 134–136 °C at 5 mmHg was collected as the product, **I**, a colorless liquid weighting 58.8 g (yield 75%).

2.4. Synthesis of tri-(dicyclopentadiene-oxyethyl)-phosphate(II)

To 14.55 g (0.075 mol) of **I** in 20 ml of toluene (dried by molecular sieve beforehand) cooled in a ice bath was added 2.3 ml (0.025 mol) of phosphorous oxychloride dropwise, following addition of 11 ml (0.080 mol) of triethylamine, while the reaction mixture was stirred and maintained at a temperature between 0 and 5 °C for 2 h. After further stirring for a period of 18 h at room temperature, the resultant mixture was washed with a solution of diluted hydrochloride acid, then with a solution of 10% soda solution, and finally with deionized water. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to give the product, **II**, a light-yellow liquid weighting 14.10 g (yield 90%).

2.5. Synthesis of epoxide of tri-(dicyclopentadiene-oxyethyl)-phosphate (III)

In a ice-cooled 250 ml, three-neck, round-bottomed flask equipped with a thermometer, an addition funnel and a magneto stirrer, 7.0 g (86% in weight) (0.03 mol) of m-CPBA were dissolved in 50 ml of dichloromethane while the mixture was stirred and maintained at a temperature of 0 °C. To this mixture was slowly added a solution of 6.26 g (0.01 mol) of **II** in 10 ml of dichloromethane, and the reaction mixture was maintained below 5 °C. At this temperature, the reaction mixture was further stirred for 12 h, then filtered. 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 6.06 g (yield 85%) of the final product, **III**, a light-yellow liquid with low viscosity, were obtained.

2.6. Preparation of cured polymers

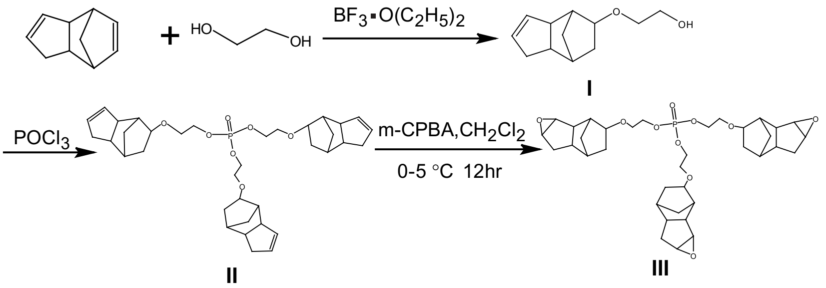
The resulting triepoxide and HHPA as a curing agent were mixed with a molar stoichiometric ratio of 1:0.8 at 80 °C. The mixture was cured first at 80 °C for 6 h, then at 150 °C for 12 h, and finally at 170 °C for 6 h. As a comparison, the commercial diepoxide ERL-4221 was also mixed with HHPA in the same ratio and cured under the same conditions mentioned previously.

3. Results and discussion

3.1. Synthesis and characterization of tri-functional cycloaliphatic epoxy resin

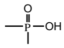
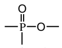
The tri-functional cycloaliphatic epoxy resin starting from DCPD was designed and prepared according to the chemical reactions outlined in Scheme 1.

As described in detail in Section 2, the overall synthesis involved three steps: (1) addition of ethylene glycol preferentially at the norbornenyl double bond in DCPD taking $BF_3 \cdot O(C_2H_5)_2$ as catalyst, (2) combination between ethylene glycol mono-dicyclopentenyl Ether **I** and phosphorous oxychloride to yield poly-functional cycloaliphatic olefin **II**, and subsequently (3) epoxidation of **II** with m-CPBA to obtain trifunctional cycloaliphatic epoxide **III**. The typical catalysts used in the first step were concentrated 95–98% sulfuric acid, p-toluenesulfonic acid or the etherates of trifluoroboron, namely, $BF_3 \cdot O(C_2H_5)_2$ or $BF_3 \cdot O(C_4H_9)_2$ [18]. In this work, $BF_3 \cdot O(C_2H_5)_2$ was the preferable choice so that the reaction could carried out at a lower temperature, 100 °C, which DCPD would not come to polymerize. According to the literature [19], the polymerization of DCPD takes place at moderate



Scheme 1. Synthesis of epoxy resin starting from DCPD.

temperature and at higher concentration. To get rid of this problem, the concentration of DCPD was kept low by adding a suitable non-polar solvent, viz. toluene during the course of reaction. Moreover, due to the difference in boiling points of toluene and other components existing in the reaction mixture, it was easily separated by fractional vacuum distillation. Consequently, 50% (based on the weight of DCPD) of toluene was added as a diluent to avoid polymerization of DCPD at higher temperatures. Meanwhile, the addition of p-hydroxyl-phenyl methyl ether also attributed to enhance the yield of **I** by inhibiting the polymerization of DCPD. With the large molar excess of ethylene glycol to DCPD (2:1) and combined with lower reaction temperature (100 °C), the optimized yield of product **I** was 75% based on DCPD. In the second step, care should be taken by adjusting the rate of addition of phosphorous oxychloride and cooling so that the reaction between **I** and phosphorous oxychloride was carried out in a molar stoichiometric ratio of 1 : 1 nearly. Poly-functional cycloaliphatic olefin **II** was subsequently epoxidized with m-CPBA in dichloromethane at 0 °C to give the desired triepoxide **III** in a yield of 85 ~ 90%.

The compounds **I**, **II**, and **III** were characterized by IR, ^{1}H NMR spectra and mass spectrographic analysis. As shown in the IR spectrum of compound **I** (see Fig. 1(a)), the original absorption signals for cyclopentene double bond in DCPD were observed at 3047,1620, and 656 cm^{-1}, besides, 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 was also observed. In the IR spectrum of product **II** (Fig. 1(b)), the absorptions of –P=O and P–O groups were observed at 1263 and 1001 cm^{-1}, respectively, while the vibration of –OH lost completely, and the absorption of  $-\overset{O}{\underset{|}{\overset{\|}{P}}}-OH$ was absent. These results indicated that –OH group in **I** was completely converted into  $-\overset{O}{\underset{|}{\overset{\|}{P}}}-O-$ to form triphosphate, **II**. In the IR spectrum of the final product **III** (Fig. 1(c)), the aforementioned absorptions of double bonds existing in **II** disappeared, while the characteristic bands of the oxirane ring fused to cyclopentane were observed at 889, 837 and 781 cm^{-1}. This result indicated the double bonds in **II** were completely converted into epoxy groups in **III**.

The chemical structures of the compounds **I**, **II**, and **III** were confirmed further by the ^{1}H NMR spectra. In the ^{1}H NMR spectrum of **I** (Fig. 2(a)), all signals corresponding to the proposed structure were observed in chloroform-d$_1$. The chemical shifts of the protons on the cyclopentene double bonds were observed at 5.67–5.43 ppm (2 H), 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 at 2.56–1.28 ppm (11H). The ^{1}H NMR spectrum of **II** (Fig. 2(b)) exhibited the chemical shifts of 17 of protons, which meant the symmetric molecular structure of **II**. As shown in Fig. 2(b), the peaks of the aliphatic ethane protons and the protons in the dicyclopentenyl ring nearest the ether bonds shifted to 4.15–3.44 ppm (5H), and the signals at 2.62–1.23 ppm involved the other 10 of protons in the dicyclopentenyl ring. In the ^{1}H NMR spectrum of **III** (Fig. 2(c)), the protons on the oxirane ring and those on ether carbon atoms were observed at 3.07–3.58 ppm, whereas the signals at 5.61–5.79 ppm for the cyclopentene double-bond protons in the compounds **I** and **II** disappeared.

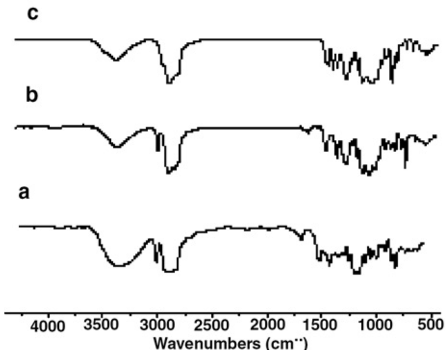


Fig. 1. IR spectra of the epoxide (**III**) and its precursors (**I** and **II**).

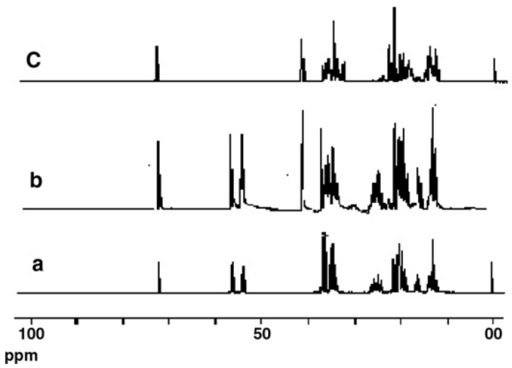


Fig. 2. ^{1}H NMR spectra of epoxide (**III**) and its precursors (**I** and **II**).

The molecular weights of **II** and **III** determined by mass spectrographic analysis were 626.2 for **II** (calcd. 626.76), and 674.3 for **III** (calcd. 674.76), respectively. The EEW value of triepoxide **III** is 226.0 ~ 230.7 g/equiv., which is close to the theoretical value of 224.7 g/equiv.

3.2. Properties of cured polymer

For practical purpose, the thermal performances of the HHPA-cured triepoxide **III** were evaluated by various means with the commercial cycloaliphatic diepoxide ERL-4221 as a comparison. Their DSC traces from dynamic scan and the thermal decomposition behaviors at a heating rate of 10 °C/min were represented in Figs. 3 and 4, and the results were summarized in Table 1. In Fig. 3, no glass transition temperature, T_g, was observed for the cured triepoxide **III**. The 5% degradation temperature for triepoxide **III** curing system was 289.2 °C and 344.8 °C for ERL-4221 curing system. Then the 10% degradation temperatures for the cured triepoxide **III** and ERL-4221 were 299.4 °C and 351.2 °C, respectively. And their temperatures of maximum rate of weight loss were 316.8 °C and 370.0 °C, respectively. Finally, triepoxide **III** reserved 20.9% char yield and 9.3% char yield for ERL-4221 at 500 °C. The results indicated that the cured triepoxide **III** exhibited higher char yield with lower degradation temperature compared to that of the cured ERL-4221. The high char yield could be due to the presence of phosphorus content in triepoxide **III** curing system. And the result with lower degradation temperature could be due to the bond strength of P–O (149 kcal/mole) from triepoxide **III** which is significantly lower than the bond strength of C–O (257 kcal/mole) from ERL-4221 [20]. TMA analysis showed that triepoxide **III** exhibited a similar CTE value with ERL-4221.

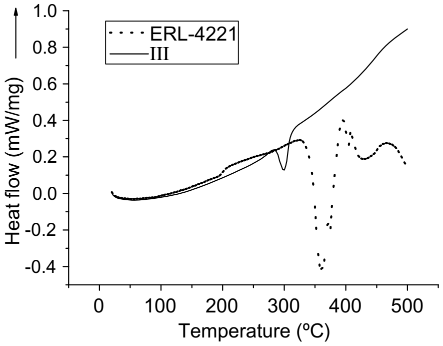


Fig. 3. DSC thermograms of cured cycloaliphatic epoxide **III** and cured ERL-4221 at a heating rate of 10 °C/min under nitrogen atmosphere.

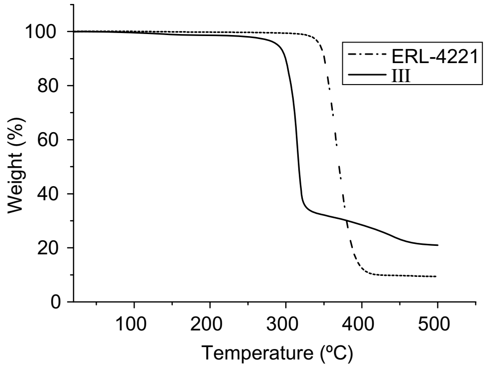


Fig. 4. TGA curves of cured cycloaliphatic epoxide **III** and cured ERL-4221 at a heating rate of 10 °C/min under nitrogen atmosphere.

4. Conclusion

DCPD is a convenient, inexpensive and versatile substrate from which new monomers and oligomers can be constructed. In this article, a novel, low-viscosity cycloaliphatic triepoxide (**III**) was successfully designed and synthesized by three steps from DCPD. The chemical structures of the triepoxide (**III**) and its precursors (**I** and **II**) were confirmed by IR, ^{1}H NMR, mass spectrographic analysis and EEW measurements. The thermal analysis results indicated that the resulting polymer from **III** exhibited a much higher residue with a lower thermal decompositiom temperature ($T_{d,5\%}$, 298.2 °C, $T_{d,10\%}$, 299.4 °C, T_p, 316.8 °C, respectively) compared to that of the cured ERL-4221. The combination of excellent thermal stability, considerably low thermal expansion coefficient and

Table 1
Thermal properties and TMA analysis of the cured polymers

Samples (10 °C/min)	T_g, DSC (°C)	$^*T_{d,5\%}$ (°C)	$^*T_{d,10\%}$ (°C)	$^*T_P$ (°C)	Char yield at 500 °C (%)	CTE (×10^{-5}/°C)
ERL-4221	201.0	344.8	351.2	370.0	9.3	7.39
III	–	289.2	299.4	316.8	20.9	7.31

$^*T_{d,5\%}$: temperature of 5% weight loss. $T_{d,10\%}$: temperature of 10% weight loss. T_p: temperature of maximum rate of weight loss.

high char yield make the resultant cycloaliphatic epoxide (**III**) a potential candidate as packaging material.

Acknowledgments

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