

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

Xiaohua Zhang, Zhenghua Zhang, Xinnian Xia, Zhisen Zhang,  
Weijian Xu \*, Yuanqin Xiong

*College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, PR China*  
*State Key Laboratory of ChemolBiosensing and Chemometrics, Hunan University, Changsha 410082, PR China*

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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,  $^1\text{H}$  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.

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## 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.

\* Corresponding author. Tel.: +86 731 8822286; fax: +86 731 8713642.

E-mail addresses: [guoxin512@tom.com](mailto:guoxin512@tom.com) (X. Zhang), [weijxu-59@sohu.com](mailto:weijxu-59@sohu.com) (W. Xu).

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-hydroxyphenyl 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 spectrometer.  $^1\text{H}$  NMR spectra were determined on a VarianINOVA400 NMR Spectrometer using chloroform- $d_1$  ( $\text{CDCl}_3$ ) 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  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  (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-oxethyl)-phosphate (II)

To 14.55 g (0.075 mol) of **I** in 20 ml of toluene (dried by molecular sieve beforehand) cooled in a

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