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The effect of a renewable fatty acid derivatives based epoxy diluent on the curing kinetics and thermal properties of epoxy/anhydride systems

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ABSTRACT

The diglycidyl ether of dimer diol (DGEDD) was synthesized and the curing kinetics of diglycidyl ether of bisphenol-A/hexahydrophthalic anhydride/tris-(dimethylaminomethyl)phenol (DGEBA/HHPA/DMP-30) system with and without DGEDD as reactive diluent were investigated by non-isothermal DSC technique with Málek method. The dynamic mechanical properties and thermal stabilities of the cured systems with different contents of DGEDD were evaluated using DMTA and TGA, respectively. The results showed that the activation energy calculated by advanced isoconversional method for DGEBA/HHPA/DMP-30 system with DGEDD was slightly higher than that of DGEBA/HHPA/DMP-30 system without DGEDD, and Šesták-Berggren model can simulate well the curing reaction rates of both systems. DMTA showed that the storage moduli of all the cured systems were similar in glassy region and decreased with increasing DGEDD content in rubbery region, and T_g diminished with increasing DGEDD content. TGA showed that loading DGEDD had little impact on the thermal stabilities of the cured systems.
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1. Introduction

Epoxy resins have a wide range of applications as laminates, moldings, composites, electronic materials, semiconductor encapsulants, coatings, adhesives, and so on, owing to their outstanding mechanical and electrical properties, chemical resistance, adhesion, and low minimal shrinkage [1]. However, the widespread application of epoxy resins is limited in some high-performance fields because the cured epoxy resins, especially with anhydrides as curing agent, are rather rigid and brittle materials. The traditional way to improve the toughness of epoxy resin systems is its modification with various additives and fillers, such as rubber elastomers [2,3], thermoplastics [4,5], or rigid particles [6,7]. Nevertheless, it is well known that the introduction of such modifiers will increase markedly viscosities of resin mixtures and damage the technological properties and some physical mechanical properties of cured epoxy resins. Non-reactive and reactive diluents are also used to make up for this deficiency while reducing viscosity and increasing wetting action of these systems. The reactive diluents, such as diglycidyl ether of triethylene glycol (DGETEG) [8], poly(propylene glycol)diglycidyl ether (PPGDGE) [9] and diglycidyl ether of diethylene glycol (DGEG) [10], are involved in the crosslinking network, which has less influence on the integrated performance of epoxy resins than other additives [11,12].

In recent years, bio-based and eco-friendly polymers derived from renewable resources have attracted extensive attention since they can be produced in large quantities and provide a circulation of carbon in the ecological system. Epoxy resins have already been prepared from some renewable biomass, such as gallic acid [13], lignin [14,15] and rosin [16,17], whose epoxides exhibit comparable properties to those of bisphenol A type epoxy resin but tend to be rigid. Vegetable oil is one of the most important renewable resources because it is mostly inexpensive, biodegradable, easily available in large quantities and eco-friendly [18]. In general, most vegetable oil-based epoxy resins can be used as reactive modifiers or diluents for modification of epoxy resins [19–24] due to their low viscosity, high stability and good flexibility. The dimer diol (trade name Pripol 2033) is a α,ω-difunctional derivative of hydrogenated dimerized linoleic acid resulting from the dimerization and hydrogenation processes, and its molecular structure of the main component of the dimer diol has approximately the form as shown in Scheme 1. So far, Pripol 2033 is mainly used to prepare high-performance acrylate [25] and polyurethane resins [26] with good flexibility and crystalline, strong water-resistance and high weatherability because of its molecular structure including hydroxyl groups, long aliphatic alkyl chains and alicyclic group. Actually, Pripol 2033 based epoxy resin is suggested to be a novel reactive diluent combining toughening and lowering viscosity, however, there are no relative literatures reported to the best of our knowledge.

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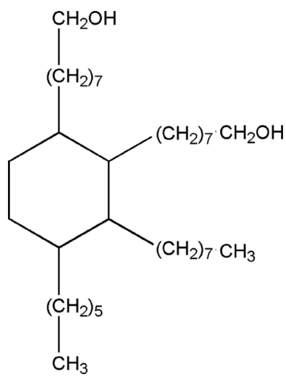

Scheme 1. The possible structure of the main component of Pripol 2033.

The influence of epoxidized vegetable oil on thermal or mechanical properties of petroleum-based epoxy systems has been investigated by some researches [19–24] but there have been few systematic overall reports regarding the effect on the curing kinetics. In this study, dimer diol Pripol 2033 was used to react with epichlorohydrin in the presence of NaOH and phase transfer catalyst to synthesize the diglycidyl ether of dimer diol (DGEDD, with viscosity about 140 mPa s at 25 °C), which was further applied as a reactive epoxy resin to dilute viscous diglycidyl ether of bisphenol-A (DGEBA). We are interested in the impact of this novel DGEDD on the curing behaviors and properties of DGEBA epoxy systems. Therefore, non isothermal DSC test was used to investigate the curing kinetics of DGEBA/DGEDD mixture resin with hexahydrophthalic anhydride (HHPA) as curing agent and tris-(dimethylaminomethyl)phenol (DMP-30) as curing accelerator. The model-free advanced isoconversional method and model-fitting Málek method were applied to calculate the curing kinetics parameters. In addition, the impact of DGEDD on the dynamic mechanical property and thermal stability of DGEBA/HHPA/DMP-30 system was also studied by DMTA and TGA respectively.

2. Experimental

2.1. Materials

DGEBA (trade name CYD128, equivalent epoxy weight 192.3 g/mol) was purchased from Epoxy Division of China Petrochemical Group Baling Petrochemical Co., Ltd.; HHPA (99.4%) was supplied by Puyang Huicheng Electronic Materials Co., Ltd.; DMP-30 was bought from Sinopharm Chemical Reagent Beijing Co., Ltd., AR; Pripol 2033 can be available by CRODA. All the raw materials were used as received. DGEDD was synthesized in our lab by means of the method mentioned by the patent [27], and the epoxy equivalent of resultant DGEDD was 351.5 g/mol analyzed by hydride chloride/acetone method.

2.2. Characterization of DGEDD

2.2.1. FT-IR measurements

The FTIR spectrum of DGEDD was recorded on a BRUKER ALPHA FTIR spectroscopy in the range of 4000–400 cm^{-1} at room temperature with a KBr pellet, and the result is given in Fig. 1. FTIR data (ν_{max}, cm^{-1}): 3047, 2923, 2853, 1457, 1373, 1339, 1252, 1109, 910 (epoxy group), 843, 762, 722.

2.2.2. ESI–MS

The sample of DGEDD was dissolved in chloroform, and the test was carried out on ESI–MS (Waters Corporation, USA). ESI–MS data: $[M+1]^+ = 649.8$, $[M+18]^+ = 666.8$, $[M+23]^+ = 671.6$, and $[2M+1]^+ = 1298.7$.

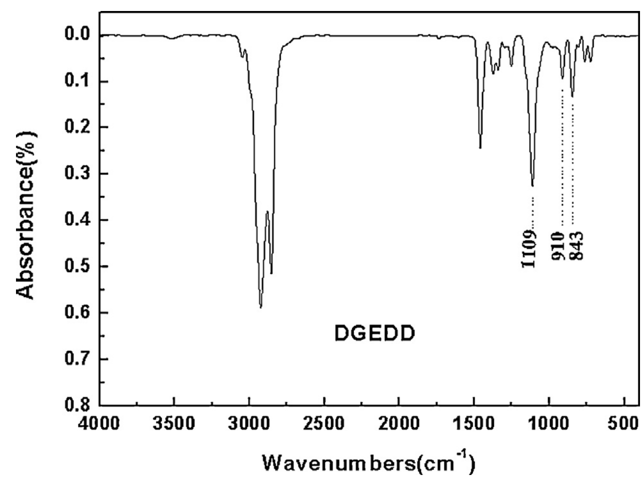

Fig. 1. FTIR spectrum of DGEDD.

2.3. DSC measurement

The curing reactions of DGEBA/DGEDD/HHPA/DMP-30 systems were manipulated by using a differential scanning calorimeter (Q20, TA Instruments) under a nitrogen flow of 50 mL/min. Formulas of DGEBA/DGEDD/HHPA/DMP-30 systems are listed in Table 1.

About 5–6 mg fresh reaction mixture was sealed in an aluminum DSC crucible, and immediately subjected to a temperature scanned from 40 to 250 °C using an empty crucible as standard reference. The heating rate was controlled at 5, 10, 15 and 20 °C/min, respectively, for systems A and D, and 10 °C/min for the others in Table 1.

2.4. DMTA measurement

The cured epoxy samples (30 mm × 6 mm × 2 mm) were tested on a dynamic mechanical analyzer (Rheometric Scientific DMTA V) under single cantilever bending mold and a frequency of 1 Hz at a heating rate 5 °C/min. The temperature ranged from −50 °C to well above the glass transition temperatures.

2.5. TGA measurement

Thermo gravimetric analysis (TGA) was performed on a TA Q500 instrument by scanning the cured epoxy resins from 25 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Table 1
Formulas of DGEBA/DGEDD/HHPA/DMP-30 systems (parts by weight).

Epoxy resin system	Epoxy resin			HHPA	DMP-30
	DGEBA	DGEDD	Viscosity (mPa s)		
A	100	0	11272	80.0	1
B	90	10	4521	76.4	1
C	80	20	3119	72.8	1
D	70	30	1267	69.1	1
E	60	40	839	65.5	1
F	50	50	689	61.9	1

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