



Study on synthesis of novel phosphorus-containing flame retardant epoxy curing agents from renewable resources and the comprehensive properties of their combined cured products

Xuejuan Yang^{a,b,c,d}, Chunpeng Wang^{a,b,c,d,e}, Jianling Xia^{a,b,c,d,e}, Wei Mao^{a,b,c,d}, Shouhai Li^{a,b,c,d,e,*}

^a Institute of Chemical Industry of Forestry Products, CAF, China

^b Key Lab. of Biomass Energy and Material, Jiangsu Province, China

^c National Engineering Lab. for Biomass Chemical Utilization, China

^d Key and Lab. on Forest Chemical Engineering, SFA, Nanjing 210042, China

^e Institute of Forest New Technology, CAF, Beijing 100091, China

ARTICLE INFO

Article history:

Received 13 April 2016

Received in revised form 4 October 2016

Accepted 16 January 2017

Keywords:

Myrcene

Castor oil

Epoxy curing agent

Organophosphorus

Flame retardant

Mechanical property balance

ABSTRACT

Two bio-based organophosphorus-containing epoxy curing agents (MMDOPO and MAPDGR) with different rigid or flexible characteristics were synthesized from myrcene and castor oil, respectively. Their molecular structures were characterized by Fourier transform infrared spectroscopy (FTIR), ¹H and ³¹P nuclear magnetic resonance (¹HNMR). Then they were mixed at different weight ratios to form new curing agents for epoxy resin (E-51). Results show the tensile and flexural strength of the cured epoxy materials first increase and then decrease with the increase of MMDOPO content. Dynamic mechanical analysis (DMA) shows the glass transition temperature (T_g) rises significantly with the increase of MMDOPO content. The material's thermal stability and flame retardant properties were also investigated. The initial decomposition temperature (T_i) and limiting oxygen index (LOI) both are elevated while the residue decreases with the increase of MMDOPO content. When the MMDOPO/MAPDGR weight ratio is 25/75, the mechanical properties are relatively balanced with a high elongation at break of 160.8% and a moderate tensile strength of 9.95 MPa, and bending test indicates that the sample exhibits a flexible failure behavior with a yielding point.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

As a traditional thermosetting polymer, epoxy resins are widely applied in adhesives, surface coatings, semiconductor encapsulations, laminates, insulating materials for electric devices, and polymer composites due to their excellent adhesive, mechanical and electrical properties, low cure shrinkage, and high moisture and chemical resistances [1–3]. However, further applications of conventional epoxy cured materials are limited by inherent brittleness, low elongation upon curing, and high flammability (LOI only 19.8 [4]). Therefore, great efforts have been made to enhance the toughness and flame resistance of epoxy cured materials [5,6].

Several methods have been proposed to chemically or physically improve the toughness of epoxy resins, including elastomer modification, particulate modification, and thermoplastic modification [7,8]. Chemical toughening could improve mechanical and thermal properties due to the formation of strong covalent bonds, but physical blending only depends on the marginal toughening effect. Thus, considerable efforts have been made to design suitable molecular structure of epoxy or synthesize flexible curing agents to improve the toughness of epoxy resins [9]. For example, a novel amine with flexible polyoxypropylene (AFPE) chain was synthesized and the AFPEs with different molecular weight were used as curing agent for diglycidyl ether of bisphenol A (DGEBA) [10]. A kind of novel aromatic amine bis(4-nonyl-2,5-diamine-penoxyl) alkylate (RA_n) as curing agents for epoxy resins were prepared through three steps of reactions using nonyl phenol and dibromoalkylate as materials [11]. Polyesters prepared by direct polycondensation from bisphenol A and aliphatic dicarboxylic acids (adipic acid, sebacic acid and dodecanoic acid) also have been used to improve

* Corresponding authors at: Institute of Chemical Industry of Forestry Products, CAF, China.

E-mail address: lishouhai1979@163.com (S. Li).

thoughness of DGEBA [12]. A polyurethane (PU) prepolymer was synthesized based on hydroxyl-terminated polyester resin and was used as a modifier for epoxy resin at different concentrations [13]. Besides, three type of polyurethane (namely, polycarbonate-type PU, polyether-type PU, and polycarbonate–polyether-type PU) prepolymers were employed to modify epoxy resin [14]. Chunhua Lou synthesized a series of imidazole(MI) blocked 2,4-toluene diisocyanate (TDI) with polyethylene glycol (PEG-400) as soft segment (PEG-MI-b-TDI) for toughening and curing the bisphenol A type epoxy resin (E-44). The toughness of E-44 cured by PEG-MI-b-TDI was effectively improved without sacrificing the tensile shear strength [15]. Shouhai Li synthesized a polymerized fatty acid (PFA) epoxy curing agent from epoxy fatty acid methyl ester (EFAME), then the curing agent was used to prepare toughened epoxy asphalt materials. Mechanical tests showed that the prepared toughened epoxy asphalt materials had excellent flexible tensile properties [16].

In addition, the flame retardant properties of epoxy resins can be improved by adding flame retardants or by incorporating reactive flame retardants. The reactive type of flame retardants is of great interest because of their more stable flame retardance and less gas emission during processing or burning. Meanwhile, the reactive type has less impact on the physical and mechanical properties of the polymer [17,18]. Among the flame retardant compounds, reactive organic phosphorus and some organophosphorus compounds that can effectively improve the flame retardancy attract more attention [19]. Organophosphorus compounds can quench flammable radicals like H^{\bullet} or OH^{\bullet} and reduce the flame energy [17]. Moreover, the organophosphorus functional groups in the solid phase are converted by thermal decomposition to phosphoric acid. The polyphosphoric acid esterifies and dehydrates the polymer to form a protective carbonaceous layer. This protective layer is high-temperature-resistant, and shields the underlying polymer from attacks by oxygen and radiant heat [17].

In recent years, polymer materials derived from sustainable resources have drawn growing attention owing to their environmental friendliness and low price [20]. Besides the epoxy, many biobased epoxy curing agents were also prepared. For example, a novel vegetable oil-based polyamine (AGSO) issued from grapessed oil (GSO) was prepared using cysteamine chloride by thiol-ene coupling, and then AGSO was employed as a novel curing agent for bio-based epoxy resin [21]. Two rosin-based curing agents containing imide groups were synthesized, and for comparison, an imide-diacid derived from trimellitic anhydride was also prepared. The glass transition temperature, tensile and dynamic mechanical properties of cured epoxy resins were significantly improved than an imide-diacid cured epoxy resin [22]. A light-color cardanol-based epoxy curing agent was synthesized with markedly improved toughness and shear strength [23]. In this work, we prepared a organophosphorus-containing castor-oil-derived diacid from the reaction of ricinoleic acid with epichlorohydrin, dibutyl phosphate and maleic anhydride. The castor-oil-derived

diacid was used as a curing agent for epoxy resin (E-51). Because of the presence of long aliphatic chain in the ricinoleic acid, however, the glass transition temperature and mechanical properties of the cured epoxy resin are very unsatisfactory, which limits the industrial application of this cured material. To solve this problem, we prepared another organophosphorus-containing myrcene-derived curing agent from the reaction of myrcene with maleic anhydride and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The anhydride curing agent has many alicyclic structures, which endow the cured resin with higher modulus, hardness, and brittleness. Thus, we mixed the two curing agents at different ratios to form the new curing agent for epoxy resin (E-51), with a balance between strength and toughness. The dynamic mechanical property, thermostability, and flame resistance of the cured epoxy materials were also studied.

2. Experimental

2.1. Materials and chemicals

Ricinoleic acid (>97%) was purchased from Aladdin Industrial Corporation. Myrcene was purchased from Jiangxi Kaiyuan spices Co., Ltd, contains about 75% of myrcene. Maleic anhydride (stabilized, 99.5%), benzyltriethylammonium chloride($\geq 98.0\%$) were purchased from the Group chemical reagent Co.,Ltd. Epichlorohydrin ($\geq 99.0\%$), sodium hydroxide($\geq 98.0\%$), calcium oxide (99.5%), triphenyl phosphine were purchased from Shanghai Lingfeng chemical reagent Co., Ltd. Dibutyl phosphate(97%) was purchased from 9 Ding Chemistry(Shanghai) Co., Ltd. 2,4,6-Tris(dimethylaminomethyl)phenol and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide(DOPO) were purchased from Aladdin Industrial Corporation. Ethyl acetate(Boiling range 60–90 °C), petroleum ether ($\geq 98.0\%$) were purchased from Shanghai Titan Scientific Co.Ltd. Epoxy resin E-51 was provided by Nanjing science and technology development corporation of institute of chemical industry of forestry products.

2.2. Synthesis

2.2.1. Synthesis of maleinized organophosphorus – containing castor oil-derived diacid (MAPDGR)

150.00 g of ricinoleic acid, 465.00 g of epichlorohydrin and 2.29 g of benzyltriethylammonium chloride were charged to a 1000-mL flask equipped with a magnetic stirrer, a thermometer and a reflux condenser. The temperature was raised to 117 °C and continued to react for 2 h. Then after the mixture cooled to 60 °C, 20.10 g sodium hydroxide and 28.15 g calcium oxide were added under stirring at this temperature for 3 h. At last the product was filtered with celite and the filtrate was collected. Then the excess of epichlorohydrin was distilled via rotary vacuum evaporation, and a light yellowish liquid, viz. diglycidyl ester of ricinoleic acid (DGR)was obtained.

200 g of DGR and 0.5 g of triphenyl phosphine were added to a flask equipped with a magnetic stirrer, a thermometer, a dropping

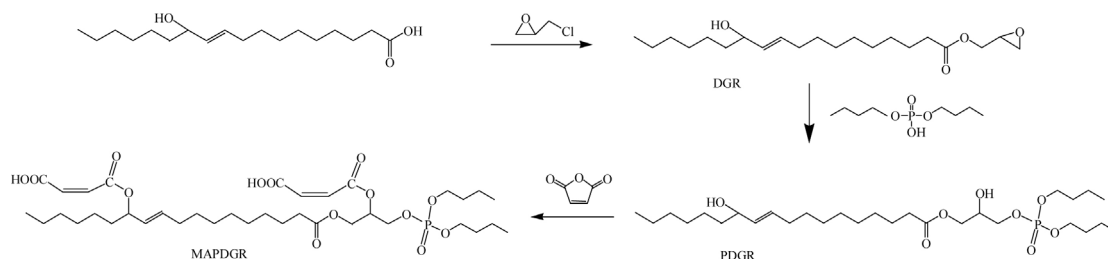


Fig. 1. The synthesis route of MAPDGR.

Download English Version:

<https://daneshyari.com/en/article/4999230>

Download Persian Version:

<https://daneshyari.com/article/4999230>

[Daneshyari.com](https://daneshyari.com)