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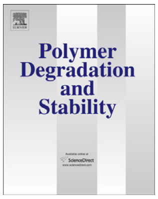

Synthesis of a novel phosphorus-containing epoxy curing agent and the thermal, mechanical and flame-retardant properties of the cured products

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ABSTRACT

A novel α, ω-dicarboxyl aromatic polyphosphonate (HP-1001-COOH) was synthesized and characterized. It was used as a reactive flame retardant for diglycidyl ether of bisphenol A (DGEBA)/methyl tetrahydrophthalic anhydride (MeTHPA) cured system. The thermal, mechanical and flame retardant properties of the cured epoxy resins were examined. The glass transition temperature (T_g) of the cured epoxy resins decrease with the increasing of the HP-1001-COOH content. The mechanical properties of cured films were slightly affected, although the crosslinking density decreases with the incorporation of HP-1001-COOH. The onset decomposition temperatures and the maximum-rate decomposition temperatures decrease, while the char yields increase with the increase of the phosphorus content. When the mass fraction of HP-1001-COOH is 30 wt%, the epoxy thermosets reaches a LOI value of 32.4% and successfully pass UL-94 V-0 rating. The heat release rate (HRR), peak heat release rate (P-HRR), total heat release (THR), average of effective heat of combustion (AvEHC) and total smoke production (TSP) of the flame retardant epoxy resins decrease significantly compared with neat epoxy resin. The macro-morphology and micro-morphology of the residues after cone calorimeter tests show that the flame retardant epoxy thermosets compact char layers are formed to prevent the transmission of heat and gases during combustion process, and the main structure in the char residues of the phosphorus-containing epoxy resins are polyaromatic carbons and phosphate esters.

1. Introduction

Epoxy resins have many outstanding characteristics such as high heat, solvent and chemical resistance, low moisture absorption, good mechanical and electrical properties, excellent dimensional stability and strong adherence to many substrates. Therefore, they have already caught attentions, and have been applied in adhesive, surface coating materials, painting materials, laminates, semi-conductive, electronic devices and so on [1,2]. Unfortunately, conventional epoxy resins are flammable, thus they failed to meet the flame retardant standards required in many high technology electronic industrial products, in order to reduce or to avoid the potential fire threats [3,4]. To improve the flame resistance of epoxy resins, halogen containing compounds were widely used to improve the flame resistance of epoxy resins in the past decades. Although this strategy succeeded in solving the flammable shortage in traditional epoxy resins, a large amount of toxic and corrosive gases such as dioxin are generated from the combustion of these halogen-containing epoxy resins, which are not only environmentally unfriendly but also potential health threatening [5–8].

Nowadays, many researchers focus their attention on the halogen free flame retardants to improve the flame resistance of epoxy resins. Among which, phosphorus-containing compounds are considered as an effective agent, thanks to its notable flame retardant efficiency [9–11]. Epoxy resins can be turned into flame resistance by either adding additive phosphorus-containing flame retardants or incorporating reactive phosphorus-containing flame retardants [12,13]. The additive phosphorus-containing flame retardants, such as widely used triphenyl phosphate (TPP), were generally directly incorporated into polymers by physical means, which offered a fast and relatively cost-effective method. However,

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a variety of problems like poor compatibility, leaching over time and deterioration in mechanical properties occurred [14]. Therefore, more studies have been attributed to incorporating phosphorus-containing flame units into the macromolecular backbone and side chains [15], which is a much more effective way to introduce a sustainable flame resistance as well as maintain the original physical properties of the epoxy resins [16,17]. For example, 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide(DOPO) has been widely investigated, since P–H bonds in the DOPO can react with some functional groups such as epoxide group, C═N and C═C groups etc. [18–20]. Gu et al. synthesized two novel DOPO-containing curing agents, which performed excellent flame resistance with 0.73 wt% phosphorus content [21]. Sun et al. synthesized three new DOPO derivative flame-retardants, which were reported to achieve the UL-94 V-0 for the cured epoxy resin with 1.0 wt% of phosphorus content [22]. Xu et al. successfully synthesized a DOPO-based flame retardant and the results revealed that the epoxy thermosets exhibited excellent flame behavior and passed UL-94 V-0 rating, when the phosphorus content was only 0.5 wt% [23].

Aromatic polyphosphonates as flame retardant are superior to non-polymeric ones, because they possess lower volatility, lower extractability and better compatibility with epoxy resins. It can introduce more phosphorus element into epoxy resin matrix. Carja et al. prepared a new phosphorus flame retardant (13.5 wt% phosphorus) with a bisphenol-A based epoxy polymer [24]. Thermo-gravimetric data showed that the flame retardant significantly increased the char yield and thermal stability of epoxy resins. In addition, it has been reported that the incorporation of aromatic moieties would also enhance the flame resistance [22]. In this paper, a novel epoxy hardener with aromatic polyphosphonate structure was synthesized and characterized by chemical titration, GPC, FTIR, ^{1}H NMR and ^{31}P NMR. The structure, fire retardant, thermal and mechanical properties of the cured epoxy resins were studied by DSC, DMA, TGA, SEM and cone calorimetry etc.

2. Experimental

2.1. Materials

Propylene oxide (PO, CP), phosphoric acid (CP) and potassium hydroxide (KOH, CP) were purchased from Shanghai Lingfeng Reagent Co., Ltd., and were used as received. Diatomaceous earth (99%, Aladdin) was used as received. Succinic anhydride (SA) was purchased from Sinopharm Chemical Reagent Co., Ltd. 1-methylimidazole was supplied by Changzhou City Key Chemical Co., Ltd, China. α, ω-phenol terminated aromatic polyphosphonate (Nofia® OL1001), hydroxyl number (OH_V) = 80 mg KOH/g, M_n = 1400 g mol^{-1}, was supplied by FRX polymers, Inc. Diglycidyl ether of bisphenol A (DGEBA) with the epoxide equivalent weight of 196 g/equiv. was kindly provided by Blue Star New Chemical Materials Co., China. Methyl tetrahydrophthalic anhydride (MeTHPA) was supplied by Puyang Hui Cheng Electronic Material Co., Ltd. Tris(dimethylaminomethyl) phenol (DMP-30) was provided by Greg Chemical Materials Co., Ltd. n-hexane, 1, 4-Dioxane, anhydrous diethyl ether and tetrahydrofuran (THF) had been redistilled prior to use.

2.2. Synthesis of α, ω-hydroxypropyl aromatic polyphosphonate (HP-1001)

The oxyalkylation reactions were carried out in a stainless steel autoclave equipped with stirring, heating, and pressure sensor. OL1001 (700 g, 0.5 mol) and KOH (0.96 g, 0.1 wt%) were dissolved in THF (500 mL) first. This solution was then transferred into a high-pressure autoclave (2 L) with digital control of stirring rate (300 rpm), and heated to 110 °C under argon. Then PO (260 g, 4.5 mol) was added into the reactor slowly. The pressure and temperature in the reactor were kept at 0.3–0.5 MPa and 130 °C, respectively. After the addition of PO, the reaction was continued for another 2 h at 130 °C. Once the reaction was finished, the mixture was cooled down to ambient temperature. THF (250 mL), stoichiometric amount of phosphoric acid (1.17 g) and diatomaceous earth (15 g) were charged to remove KOH and decolor. Afterwards, the insoluble solid was filtered off, and THF was removed under vacuum to give a viscous yellow liquid. Finally, the yellow liquid was precipitated by n-hexane for several times and dried in vacuum at 80 °C for 24 h to obtain a yellow solid (HP-1001, 856 g), and the yield was about 98% (Scheme 1).

2.3. Synthesis of α, ω-dicarboxyl aromatic polyphosphonate (HP-1001-COOH)

HP-1001 (435 g, 0.25 mol), SA (55 g, 0.55mol), 1,4-dioxane (490 mL) and 1-methylimidazole (0.49 g, 0.1 wt%) as catalyst were charged into a 1000 mL three necked round-bottom flask equipped with mechanical stirrer, thermometer and nitrogen inlet. The reaction was kept at 50 °C for 12 h under nitrogen atmosphere. The obtained product was concentrated by rotary evaporation, precipitated by anhydrous ethyl ether for several times and dried in vacuum at 70 °C for 24 h to give 436 g yellow solid (HP-1001-COOH), and the yield was about 90% (Scheme 1).

2.4. Preparation of the cured epoxy resins

According to Table 1, stoichiometric amount of HP-1001-COOH and DGEBA were charged to a 500 mL three-neck round bottom flask equipped with mechanical stirrer, thermometer and nitrogen inlet. The mixture was heated to 100 °C and stirred until HP-1001-COOH was completely dissolved. MeTHPA and DMP-30 were then added into the mixture, stirred for 2–3 min at 100 °C, degassed for 5 min under vacuum, and poured into a preheated steel mold. The mixture was cured at 100 °C for 5 h and then 150 °C for 15 h. Six kinds of cured epoxy resins were prepared with different content of HP-1001-COOH, as shown in Table 1.

2.5. Characterization

Acid value (A_V) of each sample was measured according to ASTM D974-2004. Hydroxyl value (OH_V) of each sample was measured according to GB/T 12008.3–2009.

GPC measurements were conducted on a gel permeation chromatographic system, equipped with a Waters 1515 isocratic HPLC pump and a Waters 2414 refractive index detector. The molecular weight and molecular weight distributions (PDI) were calibrated against polystyrene (PS) standards at 40 °C, with THF as the eluent at a flow rate of 1.0 mL min^{-1}.

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 5700 FTIR spectrometer at frequencies ranging from 4000 to 400 cm^{-1}. Samples were mixed with KBr and pressed into pellets.

^{1}H NMR and ^{31}P NMR spectra were obtained at room temperature on a Bruker AVANCE 400MHz spectrometer with $CDCl_3$ as the solvent.

The elemental analysis was performed with a Vario EL III elemental analyzer.

Thermal transitions of the samples were measured on a DSC2910 (TA Instruments). Samples (8–10 mg) were put into aluminum pans and heated from room temperature to 200 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere with a flow rate of 40 ml min^{-1}.