



Synthesis of an acrylate constructed by phosphaphenanthrene and triazine-trione and its application in intrinsic flame retardant vinyl ester resin



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ABSTRACT

An intrinsic flame retardant vinyl ester TGIC-AA-DOPO constructed by phosphaphenanthrene and triazine-trione groups was successfully synthesized via the reaction between 1,3,5-triglycidyl isocyanurate (TGIC), acrylic acid and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The structure of TGIC-AA-DOPO was characterized in detail by fourier transform infrared spectroscopy (FTIR), ¹H and ³¹P nuclear magnetic resonance (NMR) and liquid chromatography-high resolution mass spectrometry (LC-HRMS). The intrinsic P-N-containing flame retardant vinyl ester resin (IFR-VER) was prepared after diluting TGIC-AA-DOPO with styrene (st) and triallyl isocyanurate (TAIC). The flame retardancy, thermal properties and combustion behavior of IFR-VER were respectively investigated by a series of tests involving limited oxygen index (LOI) measurement, UL-94 vertical burning test, cone calorimeter test, thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The results showed that the as-obtained resin system exhibited a dramatic improvement in flame retardance. In the case of 40 wt% TAIC in resin system, the LOI value achieved 31%, leading to the UL-94 V-0 rating. In addition, compared with the 901-VER, the peak heat release rate (pk-HRR), average of heat release rate (av-HRR), total heat release (THR) and average effective heat of combustion (av-EHC) of the IFR-VER containing 40% TAIC diluent were decreased by 48%, 60%, 41% and 24% respectively. The diphase flame retardant effect of the prepared IFR-VER during combustion was demonstrated by the results of Py-GC/MS, FTIR, laser raman spectroscopy and scanning electron microscope (SEM).

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1. Introduction

As a composite resin matrix, vinyl ester resin (VER) has good corrosion resistance and excellent physical and mechanical properties [1–5]. In recent years, VER have been widely applied in composite pipe, adhesives, UV-curing coatings and many other fields [6–11]. However, common VER are flammable, which greatly restricts its applications in the fields with high flame retardant requirement. The applications of traditional halogenated VER faces the great challenge from environmental reasons.

Generally, VER has been treated to enhance the flame retardant properties through incorporating phosphorus and nitrogen-

containing flame retardants because of their perceived non-pollution and nontoxicity [12–15]. A variety of star-shaped flame retardants were synthesized via Michael-addition of DOPO to tris(2-(acryloyloxy)ethyl) isocyanurate (TAEI) and pentaerythritol tetraacrylate (PETA), and their properties were thoroughly investigated [16,17]. In addition to the phosphorus-based flame retardant, taking advantages of the P-N synergistic effect [18–23], the phosphorus and nitrogen-containing flame retardant system has attracted significant attention due to its high flame-retardant efficiency and smoke inhibition performance is widely studied, which has the advantages of high flame-retardant efficiency and smoke inhibition performance due to the P-N synergistic effect. The phosphorus- and nitrogen-containing compounds synergistically act as intumescent flame retardants during the polymer burning. Phosphorus-containing parts provide acid source, which promotes the char formation in the condensed phase through extracting water from the pyrolysis substrate [24–27]. Nitrogen-containing

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parts provide a gas source and produce nonflammable and nontoxic gases at high temperature, which can dilute the oxygen concentration near the flame and form a protective layer when heating [28,29]. The formed char layers serve as superior protective barriers against heat, oxygen, or volatile products, thus preventing the polymers from further burning [30]. Therefore, compared to the phosphorus-based flame retardant, P-N flame retardants always exhibit higher flame-retardant efficiency and enhanced thermal stability [23,28,31].

Traditionally, the additive-type flame retardants are introduced into VER just through a physical blending method. Their high loadings of flame retardants often inhibit the curing process and result in severe degradation of curable resins, which deteriorates the mechanical and physical properties of the resins [32]. The additive-type flame retardants can also leach from the matrix by normal service and aging, causing an environmental threat and weakening the flame-retardant effect [33–37]. In contrast, the intrinsic flame retardant VER has good flame retardancy by itself. Consequently, there is no need to add extra flame retardants. On the basis of the analysis mentioned above, exploiting an intrinsic P-N-containing flame retardant VER is a promising avenue of research in the flame retardancy of VER.

In this paper, the intrinsic phosphorus and nitrogen-containing flame retardant vinyl ester TGIC-AA-DOPO was prepared via the reactions between triglycidyl isocyanurate (TGIC), acrylic acid and 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). On this basis, the simple and effective intrinsic P-N-containing flame retardant VER (IFR-VER) was fabricated after diluting TGIC-AA-DOPO with styrene (st) or triallyl isocyanurate (TAIC) or their mixture. The flame retardancy, thermal properties and combustion behavior of the IFR-VER were investigated and its flame-retardant mechanism thus was disclosed. The excellent flame retardancy compared to 901-VER was attributed to the synergistically effects of P, N elements in the prepared VER.

2. Experimental

2.1. Materials

Vinyl ester resin 901 (901-VER) was provided by Shang Wei (Shanghai) Fine Chemical Co., Ltd. DOPO was purchased from Huizhou Shengshi Technology Co. Ltd. TGIC was obtained from Wuhan Ranab Pharmaceutical Chemical Co., Ltd. TAIC was provided by Hunan Fangruida technology co. Ltd. Acrylic acid was purchased from National Drug Group Chemical Reagent Co., Ltd. Methylhydroquinone was purchased from Guangzhou Suno Chemical Co. Ltd. N,N-dimethylbenzylamine was purchased from aladdin reagent (Shanghai) Co., Ltd. St was purchased from Tianjin Da Mao chemical reagents factory. Benzoyl peroxide (BPO) was purchased from Shanghai mountain Chemical Co., Ltd.

2.2. Synthesis of TGIC-AA-DOPO

TGIC (47.6 g, 0.16 mol), acrylic acid (36.3 g, 0.504 mol) and methylhydroquinone (0.43 wt%) were introduced into a 250 mL, three-neck and round-bottom glass flask equipped with a mechanical stirrer, reflux condenser, thermometer. The mixture was heated to 80 °C and stirred at a constant speed. N,N-dimethylbenzylamine (0.5 wt%) was added in batches when TGIC was fully dissolved and the mixture became colorless and transparent. The mixture was further heated to 115 °C and maintained at that temperature for 3.5 h. Then DOPO (49.9 g, 0.168 mol) was added in batches. The reaction continued at 115–120 °C for 4–5 h before finished. Synthesis route of TGIC-AA-DOPO is shown in Scheme 1.

2.3. Preparation of the IFR-VER

A certain amount of TGIC-AA-DOPO together with diluent of st or TAIC or their mixture were added to the three-neck flask. The mixture was heated to 80 °C and stirred at a constant speed. The IFR-VER was obtained upon the formation of homogeneous mix. After cooling to 60 °C, 2 wt% BPO was added and dissolved completely in the mixture. Then the mixture was degassed under vacuum for 5 min and poured directly into a 70 °C preheated mold and thermally cured in an air convection oven in stages: 80 °C, 100 °C, and 140 °C for 2 h each. All the details of formula are listed in Table 1.

2.4. Measurements

Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Nicolet 6700 infrared spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets.

¹H NMR spectrum was obtained on a Bruker AV400 NMR spectrometer using CDCl₃ as the solvent. ³¹P NMR spectrum was obtained on a Bruker AV400 NMR spectrometer using DMSO-*d*₆ as the solvent.

Liquid chromatography-high resolution mass spectrometry (LC-HRMS) was carried out on a SHIMADZU UFLC-20A chromatograph with Agilent XDB-C18 column. The detection wavelength was 254 nm. The mobile phase was the mixture of methanol and water (0.1% formic acid), whose volume ratio was 70:30. The flowing rate of mobile phase was 0.2 mL/min.

The limited oxygen index (LOI) values were measured at room temperature on a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ASTM D2863 and dimensions of all samples were 100 × 6.5 × 3 mm³.

Vertical burning (UL-94) tests were carried out on the NK8017A instrument (Nklsky Instrument Co., Ltd., China) with the dimension of 130 × 13 × 3 mm³ according to the UL-94 test standard.

Cone calorimeter measurements were performed on a FTT0007 (FTT, UK) cone calorimeter according to the ISO 5660 standard under an external heat flux of 50 kW/m². The dimension of samples was 100 × 100 × 3 mm³. The measurement for each specimen was repeated for three times, and the error values of the typical cone calorimeter data were reproducible within ±5%.

Thermogravimetric analysis (TGA) was performed using NETZSCH STA449F3 (TA company, the United States) at a heating rate of 10 °C/min under nitrogen atmosphere from 40 °C to 800 °C.

The glass transition temperature (*T*_g) of the thermosets were measured by Pyris Diamond dynamic thermal mechanical analyzer (PE company, the United States).

Py-GC/MS analysis was carried out with an Agilent 7890/5975 GC/MS. The injector temperature was 250 °C, 1 min at 50 °C then the temperature was increased to 280 °C at a rate of 8 °C/min. The temperature of the GC/MS interface was 280 °C, and the cracker temperature was 500 °C.

Morphological studies on the residual chars were conducted using a JSM-IT300 scanning electron microscope (Electronics Co., Ltd., Japan) at an acceleration voltage of 20 kV.

Laser raman spectroscopy measurements were carried out at room temperature with an InVia/InVia laser Raman spectrometer (RENISHAW, Britain).

3. Results and discussion

3.1. The structure of TGIC-AA-DOPO

The chemical structure of TGIC-AA-DOPO was characterized in detail by FTIR, ¹H NMR, ³¹P NMR and LC-HRMS. The FTIR spectra of

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