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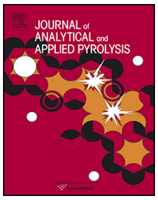

Investigation on flame retardancy, combustion and pyrolysis behavior of flame retarded unsaturated polyester resin with a star-shaped phosphorus-containing compound

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ABSTRACT

The phosphorus-containing star-shaped flame retardant (TRIPOD-DOPO) was synthesized, while the flame retardant unsaturated polyester resins (FR-UPRs) composites with various amounts of TRIPOD-DOPO were prepared. The thermogravimetric analysis (TGA) and oxygen index (OI) results showed that the incorporation of TRIPOD-DOPO improves the thermal stability and flame retardancy of UPR. The combustion properties of composites were evaluated by microscale combustion calorimeter (MCC), and the results indicated that TRIPOD-DOPO decreased the peak heat release rate (pHRR) and total heat release (THR) of UPR. Fourier transform infrared coupled with the thermogravimetric analyzer (TG–IR) revealed that UPR and TRIPOD-DOPO decomposed independently of each other. Flame inhibition was expected to occur in the gas phase. Under the air condition, TRIPOD-DOPO showed a more obviously condensed phase interaction increasing charring from the TG results. The SEM results showed that the residual char of composites were more compact and continuous, which could prevent mass and thermal transfer.

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1. Introduction

Unsaturated polyester resin (UPR) are prepared by reaction of aliphatic diols with unsaturated and saturated diacids, and diluted with unsaturated co-reactant diluents like styrene [1]. UPR are widely used as resin components in composites for the building industry, transportation sector, and electrical industry, in boats and others, because of their low cost, easy processability, low densities, good corrosion resistance, and high strength-to-weight ratios. The cross-linking reactions of unsaturated polyesters include radical polymerizations between a pre-polymer that contains unsaturated groups and styrene [2,3]. Unfortunately, due to their intrinsic chemical composition and molecular structures, typical unsaturated polyester resins are highly flammable, and produce large quantities of smoke and toxic gases when burnt.

Although halogen atoms (such as bromine and chlorine) form the most widely applied flame retardant materials, the European Community (EC) has proposed to restrict the use of halogen flame retardants because highly toxic smoke and severe environmental pollution may be produced during combustion [4]. Consequently, in order to protect the environment and human's health, researchers have focused on exploiting environmental friendly halogen-free flame retardants for UPR. It is reported that UPR can be modified with hydroxide [5], ammonium polyphosphate, melamine pyrophosphate [6], layer double hydroxide [7], and montmorillonite [8] to enhance their flame retardancy.

Recently, phosphorus-containing compounds, as halogen-free flame retardant, have received considerable attention [9–11]. Thus 9,10-dihydro-9-oxa-10-phosphaphe-nanthrene-10-oxide (DOPO) has became one of the most important flame retardants in this field, now used in several modification as a reactive or additive compound [12–14]. DOPO can either act only in the gas phase (via flame inhibition), or in the gas phase and in the condensed phase (via char formation) at the same time [15,16]. Moreover, nitrogen compounds have also been known for their good flame-retardant properties combined with excellent thermal and chemical

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properties such as high thermal-oxidative resistance, low toxicity, etc. [17,18]. Although the oligomeric star-shaped DOPO based flame retardants have been used as effective flame retardants for epoxy [19–21], little attention has been focused on the application for UPR.

In this work, the phosphorus-containing star-shaped flame retardant TRIPOD-DOPO was synthesized, and the flame retardant UPR composites with TRIPOD-DOPO were prepared. The focus of this study lies on the influence of TRIPOD-DOPO on the flame retardant properties, on the pyrolysis analysis and on the combustion properties of thermosets were investigated.

2. Experimental

2.1. Materials

Unsaturated polyester resin (commercial grade, type $196^{\#}$) was kindly supplied by Heifei Chaoyu Chemical Co. Ltd (Anhui, China). Cyanuric chloride was supplied by Alfa-Aesar Chemistry Industry Co. Ltd. 9,10-Dihydro-9-oxa-10-phosphaphenanth-re-ne-10-oxide (DOPO) was provided by Shandong Mingshan Fine Chemical Industry Co. Ltd (Shandong, China). 4-Hydroxybenzaldehyde (p-HBD), sodium carbonate anhydrous (Na_2CO_3), sodium sulfate anhydrous (Na_2SO_4), benzoyl peroxide (BPO), benzene, ethyl acetate and toluene were all reagent grade and purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). BPO was purified by recrystalizaiton, and other reagents used directly without purifying.

2.2. Synthesis of 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine (TRIPOD)

The TRIPOD was synthesized by the method described in the previous report [22]. The synthesis route is shown in Scheme 1. A 500 ml three-neck and round-bottom glass flask equipped with a mechanical stirrer, a circumference condenser and thermometer was charged with 50 g of Na_2CO_3 and 250 ml of benzene. Then 8.0 g p-hydroxybenzaldehyde and 3.0 g cyanuric chloride were added to the above suspension. The mixture was refluxed at 80 °C for 24 h. The reaction mixture was then cooled and the solid was removed by filtration and washed with hot ethyl acetate twice. The filtrate was extracted with 10% Na_2CO_3 twice and H_2O once. The organic layer was dried with anhydrous Na_2SO_4 and then concentrated. The white powder was recrystallized from ethyl acetate to obtain a white fluffy precipitate.

2.3. Synthesis of TRIPOD-DOPO

11.03 g TRIPOD, 16.20 g DOPO and 300 ml of toluene were charged into a 500 ml round-bottom flask. The mixture was stirred and heated at 110 °C for 5 h under the protection of nitrogen. Thereafter, the product was obtained by the filtration and the filtered precipitant was washed with toluene. Finally, the product was dried in vacuum at 60 °C to give a white powder.

2.4. Preparation of UPR/TRIPOD-DOPO composites

UPR and required amounts of TRIPOD-DOPO were charged into a 100 ml three-necked round bottom flask equipped with a mechanical stirrer. The mixture was stirred thoroughly until a homogeneous mixture was obtained at room temperature. Thereafter, 2 wt% radical initiator BPO as UPR amount was added and used to initiate the curing reaction with vigorous stirring for another 20 min. After the mixture was de-aerated under vacuum for 5 min, the casting composition was poured into Teflon molds. The reaction mixtures were cured at 70 °C for 4 h and post-cured at 120 °C for 3 h. Finally, samples were cooled to room temperature. The formulation of UPR/TRIPOD-DOPO composites was listed in Table 1.

2.5. Measurements

2.5.1. Structural characterization of TRIPOD-DOPO

All ^{1}H NMR spectra were performed on a Bruker AV400 NMR spectrometer (400 MHz) operating in the Fourier transform mode using DMSO-d_6 and $CDCl_3$ as solvent.

The Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 6700 spectrophotometer in KBr pellets. Spectra in the optical range of 500–4000 cm^{-1} were obtained by averaging 16 scans at a resolution of 4 cm^{-1}.

Molecular weight of TRIPOD-DOPO was determined by mass spectrometer of EXPASY/Protein Prospector in DMSO.

2.5.2. Thermogravimetric analysis (TGA)

The TGA was carried out on a TGA Q5000 IR thermalgravimetric analyzer (TA Instruments). About 5 mg of sample was heated from room temperature to 800 °C at a heating rate of 10 °C/min under both nitrogen and air condition. The temperature reproducibility of the instrument is ±1 °C, while the mass reproducibility is ±0.2 wt%.

2.5.3. Thermogravimetric analysis/infrared spectrometry (TG–IR)

The TG–IR of the cured sample was carried out by using the TGA Q5000 IR thermogravimetric analyzer, which was interfaced to the Nicolet 6700 FTIR spectrophotometer. About 5.0 mg of the sample was put in an alumina crucible and heated from room temperature to 700 °C at the heating rate of 20 °C/min in nitrogen atmosphere.

2.5.4. Microscale combustion calorimetry (MCC)

The MCC tests were carried out on a Govmark MCC-2 microscale combustion calorimeter, which was used to investigate the combustion of the cured samples. According to the standard of ASTM D7309-07, about 4 mg cured samples were heated to 700 °C at a heating rate of 1 °C/min and in a stream of nitrogen flowing at 80 cm^3/min. Next, the pyrolysis products were mixed with oxygen (20 ml/min) entering a 900 °C combustion furnace and the heat of combustion of the pyrolysis products were measured by the oxygen consumption principle. The experimental error is ±3%.

2.5.5. The oxygen index (OI)

The OI values were measured on a HC-2 oxygen index meter (Jiangning Analysis Instrument Co., China). According to ISO 4589-2, the specimens used for the test were of dimensions 100 mm × 6.5 mm × 3 mm. The specimens belonged to the form IV type material sample in the standard, and they were ignited using top surface ignition method. It should be taken into account that OI test is under the controlled laboratory conditions, and the results obtained are dependent upon the shape, orientation of the test specimen and the ignition mode, which cannot used to describe or appraise the fire hazard under actual fire condition.

2.5.6. Underwriter Laboratories 94 vertical burning test (UL-94)

The UL-94 was performed using vertical burning instrument (CFZ-2-type, Jiangning Analysis Instrument Company, China) and the specimens for test were of dimensions of 130 mm × 13 mm × 3 mm. In the measurement, the samples were vertically exposed to a Bunsen burner flame for 10 s. If the samples were self-extinguished, another 10 s was employed. The classification of the samples was defined according to ISO 1210.

2.5.7. Morphology of residual char

Scanning electron microscopy (SEM) images were obtained with a Hitachi X650.

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