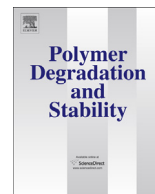




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Unsaturated polyester resins modified with phosphorus-containing groups: Effects on thermal properties and flammability

Kang Dai^{a,b,c}, Lei Song^a, Saihua Jiang^{a,b,c}, Bin Yu^{a,b,c}, Wei Yang^a, Richard K.K. Yuen^{b,**}, Yuan Hu^{a,c,*}

^a State Key Laboratory of Fire Science, University of Science and Technology of China and USTC-CityU Joint Advanced Research Centre, Suzhou, PR China

^b Department of Civil and Architectural Engineering, City University of Hong Kong and USTC-CityU Joint Advanced Research Centre, Suzhou, PR China

^c Suzhou Key Laboratory of Urban Public Safety, Suzhou Institute of University of Science and Technology of China, Suzhou, PR China

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ABSTRACT

A novel reactive phosphorus-containing monomer [1-oxo-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane-methyl diallyl phosphate, PDAP] was synthesized, and various amounts of PDAP were combined with unsaturated polyester by radical bulk polymerization. The resulting flame-retardant unsaturated polyester resin (FR-UPR) samples were investigated by thermogravimetric analysis (TGA), microscale combustion calorimetry (MCC), and limiting oxygen index (LOI) tests. Due to the relatively high phosphorus content of PDAP (18.2 wt%), incorporation of this monomer into unsaturated polyester resin (UPR) led to a marked decrease in the heat release capacity (HRC), the total heat release (THR), an increase in the LOI and the char yield upon combustion. In order to elaborate the interactions between the UPR and PDAP in degradation, differences between the experimental and theoretical mass losses of a FR-UPR sample were evaluated. Furthermore, thermogravimetry-Fourier transform infrared (TG-FTIR) and real-time Fourier transform infrared (RTIR) spectroscopy were employed to investigate the degradation behavior of UPRs, providing insight into the degradation mechanism.

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1. Introduction

As representative thermosetting materials with prominent processability and low cost, unsaturated polyester resins (UPRs) have been extensively employed as the polymer matrices to produce fiber-reinforced composites and substitute for traditional materials in many modern engineering applications [1,2]. Generally, UPRs processing are based on a radical polymerization between unsaturated polyester chains and styrene. During the reaction, styrene plays a versatile role both as a diluent and a cross-linking agent. The rather high intrinsic flammability of styrene as well as the high content (ca. 35–40 wt %), however, gives rise to high fire risks in UPRs. Consequently, the drawback limits the application of UPRs to a great extent and must be overcome to reach these polymer materials' full potential. To meet this challenge, amounts of flame retardants were utilized to enhance the

fire resistance of UPRs, and substantial progress has been achieved by a variety of additive or reactive approaches over the past decades [3–8]. While adding flame retardants into a polymer is a facile way, the unfavorable matrix-additive interfacial relationship will deteriorate the other properties of the polymer, in particular inducing a severe degradation of the mechanical properties [9]. In contrast, reactive flame retardant molecules demonstrate desirable characteristics of tailoring the properties of the material and optimizing its overall performance. Based on these conceptions, improved fire behavior as well as other properties in polystyrene [10,11], polyurethane [12], and epoxy resin [13–16] was reported in the literatures. From a sustainably developmental perspective, developing halogen-free flame retardants is a promising trend in both academic and industrial fields. Among numerous candidates, phosphorus-containing compounds have been the subject of intense research in recent years [17–22], owing to the environmental friendliness and efficacy in flame retardancy. Particularly, reactive phosphorus-containing flame retardants exhibit little or no compromise of the matrices' intrinsic properties in addition to a low required composition to achieve prominent nonflammability. Furthermore, for oxygen-containing polymers, the chemically incorporated phosphorus-containing moieties can convert matrices fuel into carbonaceous char rather than

* Corresponding author. State Key Laboratory of Fire Science, University of Science and Technology of China and USTC-CityU Joint Advanced Research Centre, Suzhou, PR China. Tel./fax: +86 551 3601664.

** Corresponding author. Tel.: +86 852 2788 7621.

E-mail addresses: Richard.Yuen@cityu.edu.hk (R.K.K. Yuen), yuanhu@ustc.edu.cn (Y. Hu).

pyrolyzed products during decomposition [12,23]. Thus many studies have reported the introducing phosphorus-containing groups into the chemical backbone of polyester and UPRs, which leads to dramatic improvements in limiting oxygen index (LOI) value and decreases in peak heat release rate (pHRR) [24–27].

In phosphorus-containing flame retardants, high phosphorus content is one of the major aims of research. As there is high phosphorus content for the flame retardants, their molecular structure should be with few trivial chains. Allyl is the functional group $-\text{CH}_2-\text{CH}=\text{CH}_2$. This substituent with a concise structure can be used for the preparation of flame retardants containing unsaturated bonds. While monoallyl derivatives predominantly undergo chain transfer during polymerization, the diallyl ether functional monomers can be employed to form a cross-linked structure [28]. Hence diallyl monomers have been widely used to prepare copolymers with improved performance [29–32].

In our previous studies a diallyl ester, DASPP, was successfully incorporated into unsaturated polyester to produce flame-retardant unsaturated polyester resins (FR-UPRs) [33]. Results indicated that the char formation was significantly promoted by phosphates, and the resulting carbonaceous char played a crucial role in protecting the substrate from degradation. Thus reactive flame retardants with higher phosphorus content are expected to demonstrate better performance in UPRs.

Inspired by previous work, in this study, we synthesized a novel reactive flame-retardant monomer, PDAP, and then introduced into resin to prepare FR-UPRs. The phosphorus content of the monomer reaches 18.2 wt%, substantially higher than that of other monomers reported before. Much enhanced flame retardancy, charring properties, and thermal behavior were observed in UPRs after incorporation of PDAP. Further, the influences of the monomer on char formation and thermal degradation of UPRs were investigated, shedding light on the mechanisms for further study.

2. Experimental

2.1. Materials

Unsaturated polyester (commercial name 196) with a styrene content of 38 wt % was supplied by Hefei Chaoyu Chemical Co. Ltd. Phosphorus oxychloride was obtained from Shanghai HuaYi Group HuaYuan Chemical Industry Co. Ltd (Shanghai, China) and was distilled before further use. Allyl alcohol was generously provided by Yangzhou Weide Chemical Raw Material Co. Ltd (Shanghai, China). Triethylamine (TEA), dioxane, acetonitrile, and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and dried over 4-Å molecular sieves. Benzoyl peroxide (BPO) was purified by recrystallization from methanol. Other reagents were used as received.

2.2. Synthesis of 2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane-4-methanol (PEPA)

PEPA was prepared as described in previous literature [34]. In one three-necked flask equipped with a stir bar, a reflux condenser, and a N_2 inlet, pentaerythritol (68.075 g, 0.5 mol) was dissolved in 250 mL dioxane. The mixture was stirred vigorously under dry N_2 and heated. When the reaction temperature was 80 °C, phosphorus oxychloride (76.665 g, 0.5 mol) was added dropwise within 1 h. After that, the resulting mixture was heated to 110 °C gradually and stirred until no HCl was detected. Subsequently, the raw product was filtered off and washed once with 100 mL dioxane and twice with 200 mL hexane, yielding a white powder. The powder was dried under a vacuum at 70 °C overnight (67.3 g, 75% yield, mp 210–212 °C). ^1H NMR (DMSO- d_6), δ (ppm): 4.56–4.60 (6H, intra-

annular $\text{P}-\text{O}-\text{CH}_2$), 3.27–3.29 (2H, exocyclic $\text{C}-\text{CH}_2-\text{O}$); ^{31}P NMR (DMSO- d_6), δ (ppm): –7.4 (singlet peak).

2.3. Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane-methyl diallyl phosphate (PDAP)

In a typical procedure, phosphorus oxychloride (10.733 g, 0.07 mol) dissolved in 80 mL of acetonitrile was charged into a three-necked flask equipped with a stir bar, a reflux condenser, and a N_2 inlet. The reaction mixture was stirred vigorously and cooled to –10 °C under dry N_2 . Then TEA (22.264 g, 0.22 mol) diluted with acetonitrile (20 mL) was added to the solution as a proton scavenger. After 10 min, allyl alcohol (8.132 g, 0.14 mol) in 80 mL acetonitrile were added dropwise for 2 h and maintained at this temperature for an additional 2 h. Subsequently, CuCl (0.023 g) was added, and the mixture was heated to reflux. After this, PEPA (12.607 g, 0.07 mol) was added, and the reaction was maintained at a constant temperature for an additional 4 h. After cooling, the solvent was evaporated, and the residue was dissolved in THF followed by filtration to remove precipitated triethylamine hydrochloride. The mixture was concentrated by rotary evaporation and then washed with distilled water, extracted with chloroform, and dried over MgSO_4 , giving a brown viscous liquid (18.6 g, 78% yield). ^1H NMR (DMSO- d_6), δ (ppm): 5.75–5.93 (2H, $\text{CH}=\text{CH}_2$), 5.46–5.55 (2H, $\text{CH}=\text{CH}_2$, trans), 5.38–5.45 (2H, $\text{CH}=\text{CH}_2$, cis), 4.52–4.59 (6H, intra-annular $\text{P}-\text{O}-\text{CH}_2$), 3.80–3.86 (4H, CH_2-CH), 3.22–3.25 (2H, exocyclic $\text{C}-\text{CH}_2-\text{O}$); ^{31}P NMR (DMSO- d_6), δ (ppm): –1.0 (exocyclic), –7.0 (intra-annular).

The synthetic procedures for PEPA and PDAP are illustrated in Scheme 1.

2.4. Preparation of UPR samples

UPR samples were prepared by blending unsaturated polyester with different contents of PDAP, combined with BPO at a concentration of 2 wt % as an initiator. Each sample was prepared in a 100 mL beaker with adequate stirring. In order to remove bubbles, the samples were placed in an ultrasonic bath (VGT-2013QT, Ningbo Haishudasheng Instrument) for 10 min. Then all homogenized samples were cast into polytetrafluoroethylene molds, cured at 70 °C for 3 h, and postcured at 120 °C for 2 h. In conformity with the concentration of PDAP in the resin, the cured UPR samples are referred to hereafter as PDAP0, PDAP10, PDAP15, and PDAP20.

2.5. Characterization

Fourier Transform Infrared (FTIR) spectrum was collected on a Nicolet 6700 FTIR spectrometer. ^1H NMR and ^{31}P NMR spectra were recorded on an AVANCE 300 Bruker spectrometer and referenced to the solvent (^1H NMR, DMSO- d_6 = 2.42 ppm). The microscale combustion calorimetry (MCC) tests were obtained from an MCC-2 (Govmark Inc, USA). In the measurements, polymer samples of approximate 5 mg were heated from 50 to 650 °C at 1 K/s heating rate under nitrogen, and subsequently the pyrolysis products were mixed with O_2 (20 cm^3/min) prior to entering a 900 °C combustion furnace. Each sample was run in triplicate and the heat of combustion of the pyrolysis products were measured by the oxygen consumption principle. Limiting oxygen index (LOI) measurements were carried out on an HC-2 oxygen index meter (Jiangning Analysis Instrument Co.) with sample dimensions $10 \times 6.7 \times 3 \text{ mm}^3$, in accordance with standard ASTM D2863-2010. Thermogravimetric analysis (TGA) was conducted on a Q5000 IR thermogravimetric analyzer (TA Instruments/Waters) under N_2 or air atmosphere, using a heating rate of 20 °C/min from room temperature to 800 °C, and all samples were maintained within 3–5 mg. Thermogravimetry-Fourier

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