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Synthesis of a novel flame retardant based on cyclotriphosphazene and DOPO groups and its application in epoxy resins

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ABSTRACT

A novel flame retardant additive with phosphazene and phosphaphenanthrene groups hexa-[4-(*p*-hydroxyanilino-phosphaphenanthrene-methyl)-phenoxyl]-cyclotriphosphazene defined as CTP-DOPO was successfully synthesized from hexachlorocyclotriphosphazene, *p*-hydroxybenzaldehyde, 4-aminophenol and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO). Its chemical structure was well characterized by Fourier transform infrared (FTIR) spectroscopy, ^{1}H nuclear magnetic resonance (^{1}H NMR) and ^{31}P nuclear magnetic resonance (^{31}P NMR). The prepared flame retardant additive CTP-DOPO was incorporated into diglycidyl ether of bisphenol-A (DGEBA) to prepare flame retardant epoxy resins thermosets. The flame retardant properties, thermal degradation behavior and combustion behavior of the DGEBA thermosets cured by 4, 4′ -Diamino-diphenyl sulfone (DDS) were investigated by limiting oxygen index (LOI), vertical burning test (UL-94), thermogravimetric analysis/infrared spectrometry (TG-IR) and cone calorimeter tests. The structure and surface morphology of the char residues after cone calorimeter tests was measured by FTIR and scanning electron microscopy (SEM). The results revealed that DGEBA/CTP-DOPO thermosets successfully passed UL-94 V-0 flammability rating and its LOI value dramatically increased from 21.7% for cured pure DGEBA to 36.6% when the loading amount of CTP-DOPO was 10.6 wt % and the phosphorus content was only 1.1 wt % in thermosets, which indicated that the prepared CTP-DOPO possessed excellent flame retardancy for DGEBA thermoset. The TG-IR results indicated that the introduction of CTP-DOPO stimulated epoxy resins matrix decomposed and char forming ahead of time, which led to a higher residual char and thermal stability for epoxy resins thermosets at high temperature. The cone calorimeter tests revealed that the incorporation of CTP-DOPO effectively reduced the combustion parameters of DGEBA thermosets, such as heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and total heat production (TSP), and so on. The SEM results showed that the phosphazene and phosphaphenanthrene groups in CTP-DOPO obviously stimulated the formation of the intumescent, compact and strong char layer, which enhanced the flame retardany of the DGEBA matrix during combustion. Therefore, the underlying materials were protected from further degradation and combustion and resulted in the efficient flame retardancy for EDGEBA thermoset.

1. Introduction

Epoxy resins are important thermosetting materials in modern industry and have been widely used as advanced composite matrices in various areas for its outstanding properties of good mechanical properties, chemical resistance, high intensity, excellent electric insulating property and low manufacturing cost [1,2]. However, the flammability of epoxy resins lead to fire disaster inevitably, which severely limits their functional applications. Therefore, the epoxy resins are subjected to various mandatory controls for safety reasons [3].

Traditionally, bromine containing reactive compounds are used as co-monomers for epoxy resins to obtain fire-retardant materials. However, the flame retardant epoxy resins materials containing bromine may release super-toxic halogenated dibenzodioxins and dibenzofurans with deleterious effects on the environment and human health [4]. Recently, in consideration of environmental

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problems, researches for halogen-free fire retardant epoxy resins have attracted a great deal of attention. Organo-phosphorus molecules are efficient radical scavengers and flame quenching materials, and combustion processes are essentially exothermic free radical reactions, so the existence of radical stabilizers impedes combustion by the quenching mechanism [5]. On the other hand, the nitrogen-containing compounds can release the inert gaseous by-products to form a highly porous char that provides thermal insulation and prevents the combustion from spreading [6,7]. There are lots of works reported about the molecular design and synthesis of flame retardant epoxy resins as well as a reactive flame-retardant additives by incorporating phosphorus-containing flame retarding units such as phosphine oxide, phosphates, and the other phosphorylated and phosphonylated derivatives [8–10]. However, these phosphorus-containing epoxy resins have some disadvantages, such as low weight fraction of phosphorus, which resulting in a low degree of flame retardancy [11,12]. 9, 10-dihydro-9-oxa-10- phosphaphenanthrene-10-oxide (DOPO) and its derivatives have been widely used for their high reactivity, applicability and flame retardancy on epoxy resins [13–17]. But the mechanical properties of the flame retardant epoxy resins prepared by above methods is obviously decreased and the flame retardant epoxy resins based on DOPO reach UL-94 V-0 flammability rating still need a higher adding ratio of DOPO or its derivatives for their low phosphorus content [18,19].

Currently, many researchers have reported the phosphazene-based family of materials because they not only possess a wide range of thermal and chemical stabilities, but also can provide improved thermal and flame retardant properties to polymers and their composites [20–22]. Hexachlorocyclotriphosphazene is a versatile starting oligomer for the synthesis of phosphazene-based polymers as there are two chlorine groups attaching to each phosphorus atom in cyclotriphosphazenes, which are active to be substituted by different nucleophiles. Multiple functions can be realized by replacing the chlorine groups with various functional substituents [23–25]. When cyclotriphosphazenes are incorporated into the network of thermoset polymers, they exhibit unusual properties such as flame retardancy and self-extinguishability due to phosphorous and nitrogen flame retardant synergistic effect. The phosphazene-based polymers present more effective flame retardancy than other flame-retardants, which make them a new focus [26–30]. So we attempt to construct a novel molecule with multifunctional groups of amino, phenolic hydroxyl, phosphazene and DOPO groups for preparing the DGEBA thermosets with excellent comprehensive properties as well as the efficient flame retardancy.

In this work, the compound with phosphazene and DOPO groups hexa-[4-(*p*-hydroxyanilino-phosphaphenanthrene-methyl)-phenoxyl]-cyclotriphosphazene defined as CTP-DOPO was successfully synthesized and used as flame retardant additive for epoxy resins. Its chemical structure was well characterized by FTIR, ^{1}H NMR and ^{31}P NMR. The obtained flame retardant CTP-DOPO was blended with DGEBA and then cured with 4, 4′ -Diamino-diphenyl sulfone (DDS) to prepare the flame retardant DGEBA thermosets. The flame retardancy, thermal decomposition and combustion behaviors for the prepared DGEBA thermosets were characterized and disclosed.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP), 4-hydroxybenzaldehyde and 4-aminophenol and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) were purchased from Wuhan Yuancheng Chemical Co. Ltd., China. Tetrahydrofuran (THF), alcohol, 1,4-dioxane, triethylamine (TEA) and ethyl acetates (EA) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd., China. Diamino diphenyl sulfone (DDS) and 4-aminophenol were purchased from Aladdin reagent (Shanghai) Co. Ltd., China. Diglycidyl ether of bisphenol-A (DGEBA) (E-44, epoxide equivalent weights = 213 g/epoxide) of technical grade was supplied by Guangzhou Fude Chemicals Industry Co. Ltd., China.

2.2. Synthesis of CTP-DOPO

The hexa-[4-(*p*-hydroxyanilino-phosphaphenanthrene-methyl)-phenoxyl]-cyclotriphosphazene defined as CTP-DOPO was synthesized according to the following steps and the synthetic routes are shown in Scheme 1. Firstly, according to the previously reported works of our laboratory [31], in a 200 mL four necked flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet, 14 g (0.04 mol) hexachlorocyclotriphosphazene (HCCP), 35 g (0.28 mol) 4-hydroxybenzaldehyde and 50 mL dry THF was added at room temperature. The reaction mixture was heated to reflux temperature with stirring and maintained for 24 h at that temperature under nitrogen atmosphere. 28 g (0.28 mol) TEA used as deacid reagent was added dropwise into the mixture. After reaction, the mixture was concentrated by rotary evaporator to remove part of the solvent and then poured into a large amount of water to precipitate the crude product. The compound HAPCP was recrystallized and purified by ethyl acetates and 31.6 g HAPCP was obtained with the yield of 92%.

The obtained intermediate product HAPCP (17.2 g, 0.02 mol) and 100 mL 1,4-dioxane was added in a four-necked-flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet. After the HAPCP was completely dissolved in 1,4-dioxane with stirring, 4-aminophenol (15 g, 0.14 mol) was added in the reaction mixture and then the mixture was heated to reflux temperature and maintained for 12 h. After that, DOPO (30 g, 0.14 mol) was added into the reaction system and reacted for another 12 h at refluxed temperature. After reaction, most of the solvent was removed by rotary evaporator and the concentrated reaction mixture was poured into the cold alcohol, a great deal of precipitates appeared in alcohol solution. Finally, the light yellow solids was obtained by filtrated and respectively washed three times with hot water and cold alcohol, and then dried at 105 °C in a drying oven to constant weight. Finally, 52.4 g light yellow product was obtained with the yield of 97%.

2.3. Preparation of the cured epoxy resins

In order to prepare the flame retardant epoxy resins thermosets with various content of CTP-DOPO, the flame retardant additive, epoxy resins and the curing agent of DDS were mixed homogeneously in an epoxide/N–H equivalent ration of 1/1 by mechanical stirrer at 120 °C. The prepared CTP-DOPO containing secondary amines can not be acted as a hardener for epoxy resins due to the large steric hindrance existed in the surrounding of N–H bonds. Then the liquid mixture was poured into the prepared moulds and cured in a convection oven at 150 °C for 2 h followed by 180 °C for 2 h. Thereafter, all samples were cooled slowly to room temperature in order to avoid cracking, and then carried out the performance testing.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were characterized on potassium bromide discs and Perkin Elmer 400 spectrometer (USA). Nuclear magnetic resonance (NMR) spectra were obtained