



Economical and environment-friendly synthesis of a novel hyperbranched poly(aminomethylphosphine oxide-amine) as co-curing agent for simultaneous improvement of fire safety, glass transition temperature and toughness of epoxy resins



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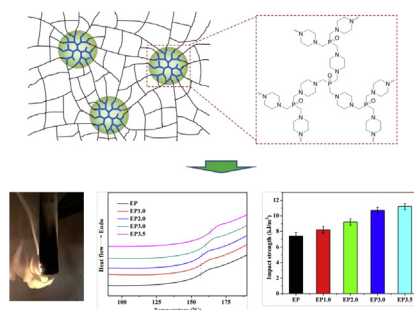
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HIGHLIGHTS

- Hyperbranched polymer was synthesized from α -aminomethylation reaction of THP.
- A novel poly(aminomethylphosphine oxide-amine) was prepared.
- Fire safety, T_g and toughness of epoxy resins were concurrently enhanced.

GRAPHICAL ABSTRACT



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ABSTRACT

Epoxy resins inherently suffer flammability and brittleness. Various approaches have been used to improve their fire safety or toughness, however, glass transition temperature (T_g) is always deteriorated concomitantly. Herein, a novel hyperbranched poly(aminomethylphosphine oxide-amine) (HPAPOA) was synthesized from α -aminomethylation reaction of trihydroxymethylphosphine (THP) with piperazine before oxidation. THP was prepared from tetrakis(hydroxymethyl)phosphonium sulfate and barium hydroxide to avoid complex purification in the synthesized process. When HPAPOA was utilized as co-curing agent for epoxy resins, T_g and impact strength of epoxy thermosets are improved due to the increased cross-linking density and the multiple toughening mechanisms. Simultaneously, fire safety include flame retardancy, smoke suppression and toxicity reduction is raised (except 1.0 wt% added). The condensed phase flame retardant mechanism is verified as increased char yield and protective and barrier effect of the formed char layer and the gas phase for release of phosphorus-containing species of HPAPOA. With as low as 3.0 wt% HPAPOA incorporated, epoxy thermoset achieved vertical burning V-0 rating with a limited oxygen index of 30.7%. The blowing-out effect for upgradation of vertical burning rating is elucidated. Moreover, the curing reactivity of epoxy systems is slightly changed and the reaction activation energy is elevated. The thermal decomposition temperature of epoxy thermoset diminishes. With 2.0 wt% HPAPOA added, tensile and flexural properties are improved and those with

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other contents are slightly depressed. The practical HPAPOA modified epoxy thermosets with obvious disadvantage conquered and higher T_g can be used in industries for high-performance applications.

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1. Introduction

Epoxy resins are widely used in areas such as coatings, adhesives, structural applications and electronics due to their thermal and chemical resistance, superior electrical properties, relatively low shrinkage and good adhesion to many substrates. However, they suffer two main drawbacks: the inherent flammability and brittleness. Epoxy resins are more combustible than similar thermosets since they have a reduced tendency to carbonize [1], while their poor impact resistance comes from the fact that they are highly cross-linked rigid thermosets [2].

At present, the efficient halogen-containing flame retardants have been restricted by legislations because that corrosive and toxic gas, such as hydrogen halide, dibenzo-p-dioxin and dibenzofuran [3], and large amount of smoke are produced during combustion. As a kind of substitute of halogen-containing flame retardants, organophosphorus compounds are of great interest for their high efficiency, low toxicity and environment-friendliness. And they are particularly effective in oxygen-rich polymers, for example, epoxy resins [4]. Organophosphorus flame retardants can influence the gas phase via radical scavenging to interrupt the burning reactions [5]. Nevertheless, it is generally accepted that they act predominantly in the condensed phase by transformation into phosphoric acid and polyphosphoric acid, which alter the rate and pathway of matrix decomposition and promote the formation of more shielding char residue [6]. The use of organophosphorus additives for flame retarded epoxy resins harbors the merit of low cost for the less change of the manufacturing process, however, they are of poor compatibility and easy to be lost by leaching. In contrast, the reactive strategy, chemically attaching organophosphorus moieties into epoxy backbones, is more attractive due to the sustainable fire resistance. Unfortunately, improving flame retardancy of epoxy resins by organophosphorus compounds is always accompanied by the deterioration of glass transition temperature (T_g) [7–11], which is a critical parameter for high-performance applications of epoxy resins. 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) derivatives exhibit good ability in maintaining or increasing T_g of epoxy thermosets [12–14] due to the hindrance of bulky rigid DOPO groups on molecular chains mobility.

As is well known, a P-C bond is more stable to hydrolysis than a P-O-C bond, thus phosphine oxides containing complete P-C bonds can maintain functions more effectively. Aryl phosphine oxides [15–18] and isobutylbis(glycidylpropylether)phosphine oxide [1,19] (IHPO-Gly) were reported to improve fire resistance of epoxy resins. The dominated gas phase flame retardant mechanism of bis(3-aminophenyl)phenylphosphine oxide in epoxy resins is demonstrated by Braun et al. [15] and various UL-94 V-0 rating epoxy thermosets were obtained with IHPO-Gly. Nevertheless, only little papers studied the flame retardant application of aminomethyl phosphine oxide. Morpholinomethylphosphine oxide, piperidinomethylphosphine oxide and bis(2-hydroxyethyl)aminomethyl phosphine oxide were prepared and used to improve the fire resistance of polyurethane [20–22]. And other aliphatic aminomethylphosphine oxides were synthesized without flame retardant application like 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane 7-oxide [23] and tris(thiomorpholinomethyl)phosphine oxide [24]. These small molecular compounds were obtained from the highly efficient α -aminomethylation reaction of trihydrox-

ymethyl phosphine (THP) and aliphatic amine in water [25] before oxidation. However, THP was prepared from tetrakis(hydroxymethyl)phosphonium chloride with sodium hydroxide or triethylamine, which brought about the removal of chloridion with organic solvent. Chen et al. synthesized trihydroxymethyl phosphine oxide (THPO) utilizing tetrakis(hydroxymethyl)phosphonium sulfate and barium hydroxide and the precipitate of barium sulfate can be simply centrifuged [26].

On the other hand, the brittleness of epoxy resins restricts their applications. As a result, tremendous efforts have been made to enhance toughness by blending them with various modifiers such as low molecular weight rubbers and functionally terminated thermoplastics [27]. Recently, hyperbranched polymers have found use as a novel class of epoxy modifiers to improve impact resistance. They don't reduce processability of epoxy resins for their tailorable compatibility with uncured resins and low viscosity-to-molecular weight ratios, which are due to a lack of restrictive interchain entanglements [28]. Furthermore, the highly functionalized nature of the shell surfaces of hyperbranched polymers enhances the interfacial adhesion of particles and matrix, which is vital for toughness improvement [29]. However, when the toughness of epoxy resins is elevated by hyperbranched polymers, their T_g are always sacrificed due to the flexible chains incorporated [27,29–33]. Several papers show that addition of epoxy-terminated hyperbranched molecules with stiff backbone can improve toughness without sacrificing T_g [34–36].

The motivation of this research is to develop practical modifiers to overcome flammability and brittleness of epoxy resins without damaging T_g . Therefore, a novel hyperbranched poly(aminomethylphosphine oxide-amine) (HPAPOA) was synthesized from the polycondensation of piperazine and THP before oxidation by hydrogen peroxide. THP was prepared from THPS and barium hydroxide to realize the synthesis of aminomethylphosphine oxide without complex purification. And the synthesis of HPAPOA is also characterized by nontoxic and environmental-friendly THPS, low-cost industrial raw materials and reaction under room temperature, in other words, it has great industrialized potential. We first utilized α -aminomethylation reaction of THP to synthesize hyperbranched polymers. With more than 1.0 wt% HPAPOA co-cured into epoxy thermosets, fire safety (flame retardancy, CO reduction and smoke suppression), T_g and toughness were concurrently optimized. To the best of our knowledge, no papers reported similar results. Moreover, the curing behavior, thermal stability and tensile and flexural properties were also investigated.

2. Experimental section

2.1. Materials

75 wt% THPS aqueous solution was purchased from Aladdin Chemistry Co. Ltd., China. Barium hydroxide octahydrate, piperazine, 30% hydrogen peroxide aqueous solution, methanol, tetrahydrofuran and 4,4'-diaminodiphenylmethane (DDM) were provided by Sinopharm Chemical Reagent Co. Ltd., China. Diglycidyl ether of bisphenol A (DGEBA, E-44, epoxy value = 0.44 mol/100 g) was bought from Hefei Jiangfeng Chemical Industry Co. Ltd., China. All chemical reagents were used without further purification.

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