



Polyethyleneimine modified ammonium polyphosphate toward polyamine-hardener for epoxy resin: Thermal stability, flame retardance and smoke suppression



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ABSTRACT

To expand the application of ammonium polyphosphate (APP) in epoxy resin (EP), hyperbranched polyethyleneimines (PEI) were selected to modify it via cation exchange reaction. Then, a highly-efficient flame-retardant hardener with poly-functionalities for EP was successfully prepared and named as PEI-APP. After curing, PEI-APP endowed the EP samples with good flame retardance and smoke suppression performance. Results suggested the total heat release (THR) and total smoke production (TSP) decreased 76.1% and 70.5% respectively. Thermogravimetric analyses (TGA) of the PEI-APP cured EPs displayed a slight improvement in the high temperature region compared with the reference sample (PEI/EP). Dynamic mechanical analysis (DMA) demonstrated that the glass transition temperature (T_g) of PEI-APP/EP also slightly increased compared with PEI/EP. Fourier transform infrared spectra (FTIR) was used to analyse the condensed products of PEI-APP/EP samples at different temperatures to investigate the flame-retardant mechanism. All the aforementioned results distinctly confirmed that PEI-APP did not only act as an effective flame-retardant hardener for EP, but also brought a good thermal stability and improved the smoke suppression to the system. This polyamine hardener provided a new platform for intumescent flame-retardant application in EP.

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1. Introduction

As one of the well-received thermosets, epoxy resin (EP) attracted most attention for decades, due to good heat and solvent resistance, satisfactory electrical and mechanical properties, remarkable adhesive strength, etc. [1,2] However, the flammability, as its main drawback, largely restricted the further application of EPs [3–5]. It is very urgent and significant to improve the flame retardance of EP materials. To circumvent this limitation, many efforts have been made recently, including the developments of flame-retardant additives [6–9], the design and preparation of functional monomers [10–13] or hardeners [14–17].

Hyperbranched polymers (HBP) are a common and typical materials, which can be used as effective polymer modifiers for

thermosets because (1) their high degree of branching makes them less viscous than their linear counterparts with a similar molecular weight and (2) they possess a high concentration of surface groups that can be modified to fine tune their physical compatibility with the matrix or make possible for their covalent linkage to the matrix [18]. Among them, branched or hyperbranched poly(ethyleneimine)s (PEI) received more attentions, because their potential application as hardeners [18,19] or tougheners for thermosets [20,21]. F. N. Nguyen and J. C. Berg [20] found that when PEI was incorporated into EP networks, it reacted with the epoxy/hardener networks and swelled as the networks absorbed the strain/crack energy. As a result, both fracture toughness and stiffness were enhanced. C. Acebo et al. [19] synthesized a kind of multi-armed polymers, with a PEI core and poly(ϵ -caprolactone) (PCL) arms end-capped with acetyl groups. Among the polymers, some residual amine groups potentially reacted with the epoxy groups, resulting an improvement up to 130% on impact strength and a reduction in the thermal stresses up to 55%. David Santiago et al. [22] applied commercially available hyperbranched PEI as the hardener for EP. Results suggested that, compared with a low

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molecular weight aliphatic amine hardener, diethylenetriamine (DETA) for instance, hyperbranched PEI were more densely cross-linked than DETA/EP because of the pre-existing internal hyperbranched structures of the PEI. Moreover, thermogravimetric analysis (TGA) illustrated the maximum rate of mass loss of the hyperbranched PEI cured sample was lower than that of the reference. Besides, Xavier Fernández-Francos et al. [18] also reported that hyperbranched PEI (commercial code as LP2000) was capable of curing EP with or without 1-methylimidazole (MI) as the initiator. Compared to the aliphatic amines with lower molecular weight, the initial decomposition temperature of LP2000 cured sample was as high as 350 °C, and could also be further increased with the addition of MI, suggesting that an excellent thermal stability of the cured resin was obtained.

In our previous studies [23,24], derived from the cation exchange reaction between ammonium polyphosphate (APP) and organo-amines, two kinds of hybrids as the mono-component flame-retardant hardeners of EP, named DETA-APP (from aliphatic diethylenetriamine, DETA) and PAz-APP (from alicyclic piperazine, PAz) respectively, were designed and prepared. Cured with these unique flame-retardant hardeners, the samples exhibited both excellent flame retardance and efficient smoke suppression performance. However, compared with the reference samples cured by the relevant organo-amines, the thermal stabilities of flame-retardant samples were slightly deteriorated.

As reported, the initial decomposition temperature of EP cured by PEI was 350 °C [18], much higher than the one cured by DETA [23] or PAz [24]. Concerning this, in this article, a novel flame-retardant hardener for EP, named PEI-APP, was designed and prepared through the cation exchange reaction between APP and PEI adapting from our previous studies [23,24]. Thermal stability, flame retardance, combustion behavior and dynamic mechanical behavior were investigated in detail. Based on the FTIR spectra of the condensed products of the decomposed PEI-APP/EP samples collected at different temperatures, a potential flame-retardant mechanism was also proposed.

2. Experimental section

2.1. Materials

Commercial APP (form II) was supplied by Changfeng Fire Retardants Co., Ltd. (Sichuan, China). Branched polyethyleneimine (PEI, AR, 99.0%) was supplied by Aladdin Ind. Co. (Shanghai, China). Ethanol (AR, 99.7%) and imidazole (AR, 99.0%) were purchased from Chengdu Kelong Chemicals Ind. Co. (Sichuan, China). Diglycidyl ether of biphenol A (E-44) was provided by Lanxing Resin Co., Ltd (Lanzhou, China) and used as received.

2.2. Preparation of PEI-APP

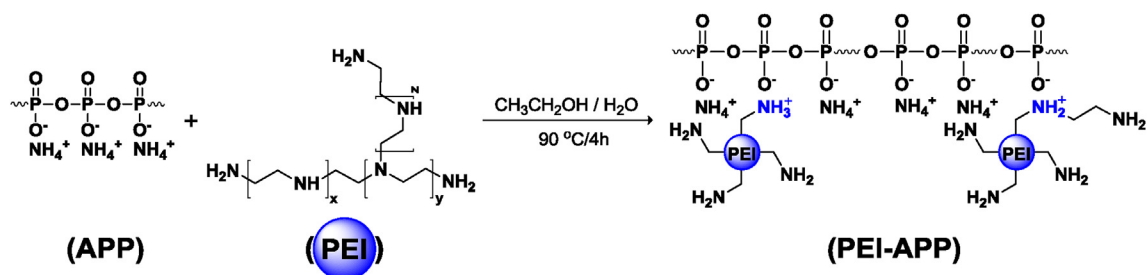
The procedure to prepare PEI-APP was illustrated as Scheme 1, adapting from our previous literatures [23,24]. Four kinds of PEI-APP with different modified ratios (named PEI-APP-1, PEI-APP-2, PEI-APP-3, and PEI-APP-4 respectively) were prepared as follows. A certain ratio of ethanol (210 mL) and water (10 mL) were transferred into a three-neck flask and stirred under nitrogen atmosphere. Then PEI (detailed data shown in Table 1) was added into the flask with stirring. Over half an hour later, APP (10 g) was added sequentially. After 4 h reaction at 90 °C in N₂ atmosphere with continuously stirring, the mixture was cooled down to room temperature and filtrated to remove the solvent. Then, the white products were dried overnight in a vacuum oven at 80 °C after washed with excessive ethanol. The achieved yields of these reactions were also listed in Table 1.

2.3 Preparation of the cured EPs

The cured EP samples were all obtained through traditionally thermal curing process. The reference sample was prepared with following steps. EP was steadily stirred at 100 °C in vacuum until no bubbles emerged. Then PEI with imidazole as the accelerator were added with discontinuous stirring. When the mixture became homogenous, it was rapidly poured into a pre-heated mould. After cooling down to room temperature, detailed curing steps (80 °C/4 h + 115 °C/2 h + 155 °C/2 h) were conducted. Addition of PEI in the reference sample was according to the calculation of PEI content in PEI-APP 15/EP.

The curing steps of the flame-retardant samples were similar to the reference sample. A certain mass ratio of EP and the prepared PEI-APP, as presented in Table 2, were mixed in a one-neck flask. Then the blend was steadily stirred at 145 °C in vacuum until no bubbles emerged. And then imidazole was mixed as the curing accelerator. When the viscous liquid became homogenous, it should be transferred quickly into a preheated mould (145 °C). After the curing process (145 °C/14–16 h + 165 °C/5 h), the corresponding flame-retardant samples were obtained.

In the curing reaction between PEI-APP and EP, imidazole was used as the curing accelerator, suggesting that the curing reactivity of the flame-retardant hardener was low. Meanwhile, the relatively very long curing process also confirmed the low reactivity. Actually, the content of PEI structure introduced in PEI-APP was very low. Getting rid of the ionic bonded amines, the content of the residual



Scheme 1. Synthesis route of PEI-APP.

Table 1
The yield of PEI-APP with different additions of PEI.

	PEI-APP-1	PEI-APP-2	PEI-APP-3	PEI-APP-4
PEI/g	5	6	7	8
yield/%	76.7	71.9	65.9	61.1

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