Preparation and properties of polystyrene composites modified by macromolecule flame retardant DOPO-HQ

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Abstract. A macromolecular flame retardant was firstly the group reaction of DOPO-HQ. The modified polystyrene ADOPO-HQ-co-PS was prepared by copolymerization of macromolecular flame retardant and styrene. Its chemical structure was analyzed by Fourier transform infrared (FT-IR). PS composite was prepared by adding it to the experimental formula, and the cone-shaped calorimetry experiment was carried out on the material. The results show that it has a better flame retardant performance than DOPO-HQ. The smoke generation rate is very small, the highest is 0.2 m²/s, the CO production is very small, the highest is 0.007 g/s, and the mass loss is the highest is 0.14 g/s, which shows that the material is more environmentally friendly and stable during combustion.

Keywords: Macromolecular flame retardants, polymer, composite materials, combustion performance.

1. Introduction
Polymer materials are one of the three major materials that attach equal importance to ceramic materials and metal materials, and their application scope covers almost all aspects of people's work and life, from daily items to cable industry, automobile industry and construction industry, etc., which can be seen in the shadow of polymer materials [1-2]. However, the vast majority of polymer materials are polymerized with carbon as skeleton structure, and it is easy to burn in the use of open fire, which poses a serious threat to the safety of human life and property. Therefore, it is necessary to study the flame retardant properties of polymer.

The traditional flame retardant technology is mainly realized by adding a large number of small molecule flame retardants into the polymer materials. Such technology has defects such as large amount of flame retardant, poor compatibility with matrix, easy migration, easy moisture absorption, poor thermal stability, poor flame retardant effect and so on [3-5]. How to solve the flame retardant problem of polymer materials more effectively from the perspective of system is the focus and hot spot of industry research [6-8]. In recent years, reactive flame retardant, synergistic flame retardant, composite flame retardant, macromolecular flame retardant and other flame retardant technologies have been developed to a certain extent [9-12]. Zhao Wei et al. [13] conducted a series of flame retardant complex experiments with melamine tetramethylphosphine sulfate oligomer (MTMPSO) and
ammonium polyphosphate (APP), adding expansive flame retardant system (IFR) into polyethylene (PE), and explored the influence of different content of flame retardant on the flame retardant performance of PE. Xie H L [14] synthesized a new type of macromolecular expansive flame retardant (HAPN) with free radical quenching function, and mixed it with APP flame retardant polypropylene (PP). The effect of mass ratio of HAPN to APP on the flame retardant performance of PP was studied, and the mechanism of HAPN and APP synergistic flame retardant PP was discussed. Liu Y L et al. [15] prepared a composite flame retardant using APP, foaming agent (CFA) and rare earth element layered dihydroxide (LDH) as flame retardants to improve thermal stability, the flame retardancy, and smoke suppression performance of EVA matrix.

In this study, the flame retardant 10-(2,5-dihydroxyphenyl)-10-hydro-9-oxa-10-phosphenanthrene-10-oxide (DOPO-HQ) was selected for macromolecular synthesis to synthesize a new flame retardant monomer. The flame retardant polystyrene with cost characteristics was obtained by copolymerization with styrene, and its structure was characterized by FT-IR. Flame-retardant polystyrene was added into the composite formula for processing and molding, and its combustion performance were tested by cone calorimeter.

2. Experimental

2.1 Materials
Isophorone diisocyanate (IPDI) was purchased fromed Wanhua polyurethane Co., LTD. (Yantai, China). [Pentaerythritol tetrakys 3-(3,5-ditert-butyl-4-hydroxyphenyl) propionate] (Antioxidant 1010) was supplied by Shanghai Aladdin Bio-Chem Technology Co., LTD. DOPO-HQ, Hydroxyethyl acrylate (HEA), N,N-Dimethylformamide (DMF), Dibutyltin dilaurate (DBTDL), benzoyl peroxide (BPO), 1,3,5-Tris(2-hydroxyethyl)cyanuric acid (THEIC), styrene (St), sodium hydroxide(NaOH), melamine, and acacia gum powder were all supplied by Shanghai organic pharmaceutical chemical production co., LTD. Sodium chloride was purchased from Shanghai reagent No.1 factory. The processing formula is provided by Shanghai Yingke industrial co., LTD.

2.2 Preparation of macromolecular flame retardant monomer
Install a thermometer, a spherical condenser and a mechanical stirrer on a four-mouth flask, added 46g IPDI, passed nitrogen into it, start stirring, set the temperature of water bath as 36℃, dropped 18.6g HEA into the flask at a constant rate with a constant pressure funnel, and dropped a drop of DBTDL, and the reaction time was 1.5h. Dissolved 8.26g DOPO-HQ in 40mL DMF and poured it into another four-pot flask. Dropped the previous reaction product into the DOPO-HQ solution under the condition of nitrogen, water bath temperature 85℃and stirring. The reaction time was 20h, and the polymer flame retardant monomer was obtained.

2.3 Synthesis of polystyrene containing of macromolecular flame retardant monomer
Install a thermometer, a spherical condenser and a mechanical stirrer on a four-mouth flask, mixed 2.4g Arabica gum powder 10g sodium chloride and 135mL deionized water in it. Stirring and control the water bath temperature at 80℃. The 20mL St monomer was washed with 5%NaOH solution to remove the polymer inhibitor, then mixed with 0.25g BPO and macromolecular flame retardant DOPO-HQ (DOPO-HQ/St =1/2), and poured into a four-mouth flask. The water bath temperature was raised to 85℃ for 5h of copolymerization. Then the temperature rises to 90℃ and the reaction continues for another hour. Flame-retardant polystyrene (ADOPO-HQ- co-PS) was prepared.

2.4 Processing and molding of polystyrene composites
First, fly ash and aluminum titanium coupling agent were blended to improve the compatibility with the matrix material, and then the modified fly ash and PS were put into the oven for drying for 8h. Weighing the material according to the composite formula, and then adding it to the torque rheometer. The processing formula is shown in Table 1 and processing parameters are shown in Table 2.
retardants DOPO-HQ and ADOPO-HQ-co-PS are added to the formula. Flame retardant formulations are shown in Table 3. After mixing evenly, take out the material and use the plate vulcanizer to press the sheet. The heating temperature was 180°C and the tablet pressing time was 20 minutes. Then cool the pressing sheet for 10 minutes to get the polystyrene sheet. Experimental splines were prepared from the pressed polystyrene sheet for testing.

Table 1. Experimental formula of PS/coal ash composite

| Materials | coal ash | PS | HIPS | MAPS | Foaming agent |
|-----------|----------|----|------|------|---------------|
| weight/g  | 12.000   | 18.180 | 4.955 | 0.824 | 0.320         |
| Materials | White oil | Nucleating agent | Cross-linking agent | Conditioning agent | flame retardant |
| weight/g  | 0.929 | 0.723 | 0.040 | 1.6 | 0.4 |
| total/g   |        |    |     |     | 40            |

Table 2. Machining parameters of twin-screw extruder

| Name                  | Set value | Name                  | Set value |
|-----------------------|-----------|-----------------------|-----------|
| 1 zone temperature    | 180°C     | 2 zone temperature    | 180°C     |
| 3 zone temperature    | 180°C     | Machine head          | 180°C     |
| rotate speed          | 30r/min   |                       |           |

Table 3. Experimental formula of flame retardant variable

| Group | Flame retardant                      |
|-------|--------------------------------------|
| 1     | DOPO-HQ                              |
| 2     | ADOPO-HQ-co-PS                       |
| 3     | ADOPO-HQ-co-PS: THEIC=5:2            |
| 4     | ADOPO-HQ-co-PS: THEIC=2:1            |
| 5     | ADOPO-HQ-co-PS: Melamine=5:2         |

3. Results and discussion

3.1 FT-IR analysis

The FT-IR spectra of the chemical structure characterization of Adopo-HQ-co-PS are shown in Figure 1. ADOPO-HQ-co-PS was obtained by the reaction of IPDI with HEA and flame retardant DOPO-HQ. The key lies in the reaction of -NCO group and -OH group. As can be seen from the figure, the stretching vibration absorption peak of phenolic hydroxyl group is at 3454 cm⁻¹. At 1636 cm⁻¹ is the stretching vibration absorption peak of C=O double bond. The stretching vibration absorption peak of benzene ring is at 1400 cm⁻¹. However, no -NCO characteristic peak was observed at 2205-2270 cm⁻¹, and the disappearance of the characteristic peak of -NCO group indicated the completion of the reaction. The appearance of these characteristic peaks indicates that ADOPO-HQ-co-PS has been successfully prepared.
3.2 Conical calorimetric analysis of PS composites

Five groups of polystyrene composites prepared with different flame retardant formulations were tested in conical combustion. Figure 2, 3, 4, 5 and 6 respectively show the heat release rate, total heat release, smoke production rate, CO production and mass loss rate of PS composites with different formulations. It can be seen from the figure that the overall trend of each parameter is roughly the same. This can be seen in Figures 2 and 3 that the heat release increases sharply first and then decreases slowly and the total heat release curve increases gradually. The curve of group 1 is slightly higher than group 2, indicating that the ADOPO-HQ-co-PS inhibited a little more heat release than DOPO-HQ. The total heat release and heat release rate of group 3 are the lowest while group 5 is the highest. The THR of group 3 was 42MJ/s² and group 5 had a THR of 50MJ/s². That's 16% lower and the curve is flatter. As can be seen from Figure 4 and 5, at the beginning of combustion, smoke is generated faster and then slowed down, and CO is generated more and then decreased. However, both the amount of smoke and the amount of CO are very small, the highest is 0.2m²/s and 0.007g/s, indicating that this material is more environmentally friendly. Again, the group 3 has the lowest curve. The MLR curve goes up and then slowly goes down, but the loss of quality is also very small. The highest is 0.14g/s and then it goes to zero.
Figure 3. Total heat release of PS composites

Figure 4. Smoke production rate of PS composites

Figure 5. CO production of PS composites

Figure 6. Mass loss rate of PS composites

The reason for this result is that the addition of small flame retardant DOPO-HQ resulted in poor
compatibility within the material. However, the molecular structure of ADOPO-HQ-co-PS contains the PS chain segment, which is well compatible with the PS matrix, and this does not occur. Therefore, the flame retardant effect is more stable. The synergistic flame retardant effect of ADOPO-HQ-co-PS and THEIC was better than that of melamine. Composite material with mass ratio of ADOPO-HQ-co-PS and THEIC of 5:2 in flame retardant has better flame retardant effect, suggests that the synergistic flame retardant effect of phosphorus and nitrogen is better. The HRR, THR are lower, its combustion curve flattens, may be generated by the burning charcoal layer play a role of the condensed phase flame retardant, isolated oxygen and heat transfer, to protect the lower substrate by oxidation decomposition, reduced the heat release quantity, improve the flame retardant properties of polystyrene. This has better protection significance to the safety of personnel and property in fire. The low smoke volume and non-toxicity indicate that it is a relatively environmentally friendly material and the faster release of CO tends to 0 indicates that the material inhibits the release of CO faster and is more harmless to the environment. The minimal mass loss also means that it remains stable during combustion.

4. Conclusions
Polymer flame retardant was prepared and modified polystyrene ADOPO-HQ-co-PS was successfully polymerized by styrene polymerization. The structure of modified polystyrene ADOPO-HQ-co-PS was confirmed by FT-IR. In conical calorimetric analysis of the material, ADOPO-HQ-co-PS as additive has better flame retardant effect than DOPO-HQ. The composite material has less smoke, no toxic gas generation and less mass loss, which can indicate its good stability. In this study, Composite material with mass ratio of ADOPO-HQ-co-PS and THEIC of 5:2 in flame retardant has better flame retardant effect. It has lower heat release, lower smoke production, lower CO release, and less mass loss. In a word, all the above results reveal the macromolecular flame retardant has extensive potential applications in flame retardant PS composite products.

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