

Study on preparation and performance of additive flame retardant DOPO-HQ modified epoxy composite

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Abstract. An additive flame retardant was prepared from DOPO-HQ. Fourier transform infrared spectroscopy (FT-IR) was used to analyze its chemical structure. It was added to the experimental formula to prepare EP composite material, and the limiting oxygen index experiment and thermogravimetric analysis experiment were carried out on the material, and the scanning electron microscope experiment was carried out on the residual carbon after combustion. The results show that the modified epoxy resin has a limiting oxygen index of 29.5%, and there is no droplet during combustion; thermogravimetric analysis experiments show that the temperature at which the thermal weight loss is 5%wt decreases, but the residual carbon rate increases. Scanning electron microscopy (SEM) test results show that carbon layer formed by the combustion products of epoxy resin is denser..

Keywords: Additive flame retardant, epoxy resin, limiting oxygen index.

1. Introduction

As we all know, epoxy resin has a very wide range of applications in coatings, adhesives, electronic packaging materials, aerospace materials, etc. due to its excellent machinable property, bonding properties, corrosion resistance and low curing shrinkage. However, as an organic polymer material containing carbon, hydrogen, and oxygen, epoxy resin is extremely flammable, seriously threatening human life and property safety, and greatly restricts its application[1]. Therefore, the flame retardant Research and development is very necessary. Traditionally: Add-on halogen flame retardant has obvious flame retardant effect, but it will release carcinogen dioxin and toxic gas during the combustion process, and its use is restricted[2]. At present, based on people's requirements for an environmentally friendly and healthy living environment, a new type of high-efficiency, low-toxic, low-smoke, green and environmentally friendly organic flame retardant has become a research hotspot. Phosphorus-containing flame retardants catalyze and promote the formation of carbon from polymer materials during the thermal degradation process, which not only improves the flame retardant performance of the material, but also effectively reduces the emission of smoke and corrosive gases during the combustion of the material[3]. Among them, DOPO-HQ molecules have excellent thermal stability, heat resistance, flame retardant, and chemical stability have become a research trend. As a new member of the flame retardant family, silicone flame retardants have gradually attracted people's attention in the 1980s[4]. Because of their excellent flame retardant,

good processing and mechanical properties, they are environmentally friendly and have broad development prospects. Phosphorus-silicon flame retardant is not only a green flame retardant product but also has a synergistic effect. In addition, organosilicon catalyzes the degradation of organophosphorus into acid during the degradation process, and promotes the dehydration of polymer into carbon. The formed carbon layer is polymerized with lower viscosity silicon oxide, which increases the viscosity, strength, and density of the carbon layer. , Wrap the debris or gas generated by polymer degradation to form a dense insulation layer that insulates oxygen and heat transfer, and suspends or relieves the burning of polymer materials[5].

In this study, flame retardant DOPO-HQ and silane coupling agent KH-550 were selected for synthesis to synthesize a new type of phosphorous-silicon flame-retardant monomer, and its structure was characterized by FT-IR. The epoxy resin was added with flame retardant and their properties were characterized by limiting oxygen index.

2. Experimental

2.1 Materials

Isophorone diisocyanate(IPDI), analytical grade, Shanghai Organic Pharmaceutical Chemical Production Co., Ltd.; dibutyltin dilaurate (DBTDL), analytical grade, Shanghai Organic Pharmaceutical Chemical Production Co., Ltd.; N,N-dimethyl formamide (DMF), analytical

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grade, Shanghai Organic Pharmaceutical Chemical Production Co., Ltd.; flame retardant 10-(2,5-dihydroxyphenyl)-10-hydro-9-oxa-10-phosphenanthrene-10-oxide(DOPO-HQ), analytical grade, Aladdin Chemical Reagent Co., Ltd.; silane coupling agent KH-550 industrial grade, Shanghai Inco Industry Co., Ltd. ; Epoxy resin E-51, industrial grade, Guangzhou Fufei Chemical Technology Co., Ltd.; 4,4-diaminophenylsulfone, analytical grade(DDS), Jingmen Dongxin Biotechnology Co., Ltd.

2.2 Preparation of additive DOPO-HQ-IPDI-KH550

Put 20ml DMF, 6.28g DOPO-HQ into the four-necked flask, blowed in nitrogen, set the temperature to 110°C, added 4.44g IPDI and 0.1ml catalyst, reacted for 16 hours, then added 4.42g KH-550 to the mixture and reacted for 4 hours , To obtain an orange transparent liquid. After the liquid was cooled, added deionized water to precipitate the flame retardant, filtered with suction, washed several times, and put it in a 60°C blast drying oven for 4 hours to obtain 15 g of flame retardant.

2.3 Preparation of flame-retardant epoxy resin

Put 10 g of epoxy resin E-51 into a four-necked flask, heated it at 120°C for 15 minutes, added flame retardants with different proportions to it to be transparent, and then added 3.162 g of curing agent DDS to it to react 30min, poured into the preheated mold, vacuumed for 30min at 25°C, vacuumed for 30min at 120°C, and cured at 160°C for 2h to obtain the cured product of ring flame-retardant epoxy resin. The flame retardant formula is shown in Table 1:

Table 1. Experimental formula of flame retardant variable

Group	DOPO-HQ	Flame retardant
1	5%	0%
2	5%	5%
3	5%	10%
4	5%	15%
5	5%	20%

3. Results and discussion

3.1 FT-IR analysis of flame retardant

The FT-IR spectra of the chemical structure characterization of flame retardant are shown in Figure1. Flame retardant was obtained by the reaction of IPDI with KH-550 and flame retardant DOPO-HQ. The key lies in the reaction of -NCO group and -OH group. As can be seen from the figure 1, At a wavenumber of 3410cm-1, it is the phenolic hydroxyl group absorption peak, 2090cm-1 is the C=O double bond absorption peak, 1640cm-1 is the benzene ring absorption peak, 1460 cm-1 is the P=O double bond absorption peak, 1390 cm-1 It is the -CH3 absorption peak, 1140 cm-1 is the C-O-C absorption peak, 928 cm-1 is the Si-O absorption peak, 758 cm-1 is the -NH absorption peak, and there is no -NCO characteristic

at 2205-2270 cm-1.The characteristic peak of -NCO group disappears, indicating that the compound has been successfully synthesized.

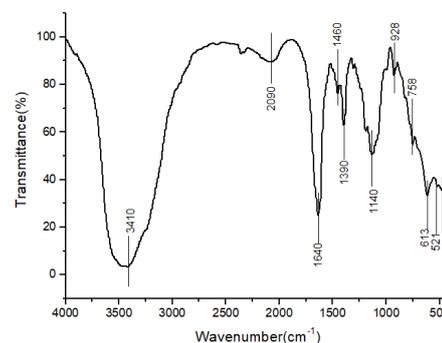


Figure 1. FT-IR spectra of DOPO-HQ-IPDI-KH550

3.2 Limiting oxygen index analysis of composite materials

The limiting oxygen index experiment was carried out on five groups of epoxy resin composites with different flame retardant formulations, and the results are shown in Figure 2: As the flame retardant content increases, the limiting oxygen index of epoxy resin increases. Compared with EP, the LOI of flame retardant/EP-5wt%, flame retardant /EP-10wt%, flame retardant /EP-15wt% and flame retardant /EP-20wt% samples increased to 25.5%, 28.5%, 29.5%, 28.5%. The epoxy cured product cannot be self-extinguished during the test, and there is a phenomenon of melting and dripping. For flame retardant modified epoxy cured products, the flame can be self-extinguished after they are evacuated from the igniter. With the increase of flame retardant content, it takes less time for the flame to self-extinguish. This may be because the organic phosphorus thermally degraded to produce phosphoric acid and other compounds to play a solidified phase flame retardant mechanism, promote the surrounding dehydration into char, and form a dense and heat insulation carbon layer, which effectively inhibits the spread of flammable gas and heat, and improves the material resistance flammability.

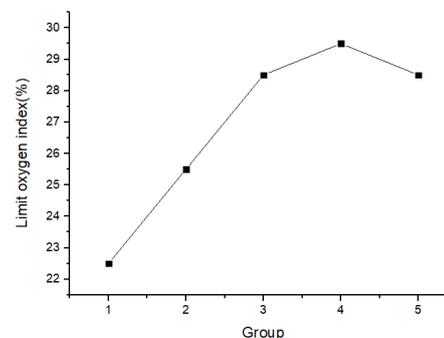


Figure 2. Limit oxygen index of epoxy resin composite

3.3 Thermogravimetric analysis test of composite materials

Thermogravimetric analysis tests were carried out on epoxy resin and epoxy resin with the highest limiting oxygen index, and the results are shown in Figure 3. The degradation of epoxy resin is one-time degradation, and the initial degradation temperature is 81.5°C. The temperature at which the thermal weight loss is 5%wt is 399.5°C. It decomposes rapidly in a narrow temperature range of 399.5°C-459.5°C, with a thermal weight loss of 76%. After the temperature rises to 484°C, the curve tends to be flat, the degradation is complete, and the carbon residue content of the compound is 16.11%. The epoxy resin with 15% flame retardant is degraded into a one-time degradation, and the initial degradation temperature is 77.5°C. The temperature at which the thermal weight loss is 5%wt is 283.36°C. It decomposes rapidly in a narrow temperature range of 346°C-400°C, and the thermal weight loss is 66%. After the temperature rises to 440°C, the curve tends to be flat, the degradation is complete, and the carbon residue content of the compound is 25.57%. This may be because the lower bond energy of organic silos in flame retardant degrades first, which promotes the degradation of organic phosphorus into acids, exerts the synergistic flame retardant effect of phosphorus - silicon interaction, forms a denser and more stable thermal insulation layer, delays or stops epoxy resin degradation.

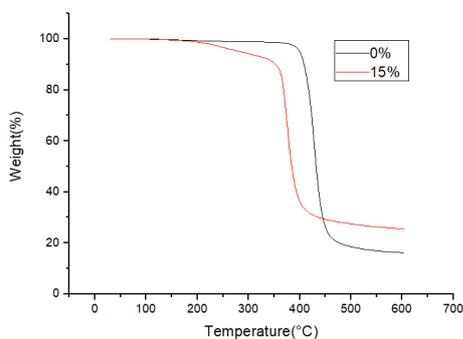


Figure 3. Thermogravimetric curve of epoxy resin composite

3.4 Scanning electron microscope analysis of residual carbon after combustion

The morphology and structure of the carbon layer formed when the material is burned is very important to the flame retardant of the material. Therefore, it is necessary to study the morphology and structure of the carbon layer formed after the epoxy curing material is burned in order to understand its flame-retardant mechanism. Figure 4 is a partial SEM picture of the residual carbon formed after the epoxy cured product is burned, where (a), (b), (c), (d) and (e) are 0%, 5%, 10%, 15%, and 20% flame retardant added. The residual carbon layer formed by 0%, 5% composite rubber has large and many pores, while the residual carbon layer formed by 10%, 15% and 20% composite rubber has almost no pores, especially the picture shown in Figure d, which has a denser structure. The ground insulates the oxygen and heat on the surface

of the material, and at the same time verifies the results shown in the limiting oxygen index.

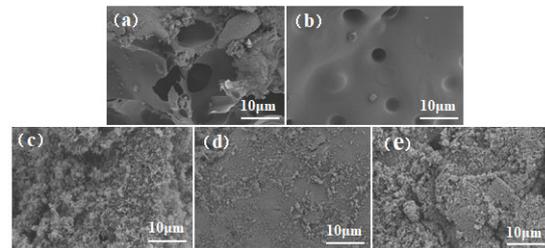


Figure 4. Scanning Electron Microscope for Residual Carbon of Epoxy Resin Composite

3.5 Tensile performance test of epoxy resin composite

Tensile performance tests were conducted on five groups of epoxy resin composites with different flame retardant content, and the results are shown in Figure 5: The tensile strength of the epoxy cured product is 19.6 MPa. When flame retardant is introduced into the cured product, its tensile strength is reduced, from 19.6 MPa of EP to 6.5 MPa. This may be because the addition of the bulky and rigid DOPO group in the flame retardant component limits the formation of macromolecular chains, which weakens the force between the three-dimensional cross-linked network structure of the cured product, which leads to the tensile strength of the cured product reduce.

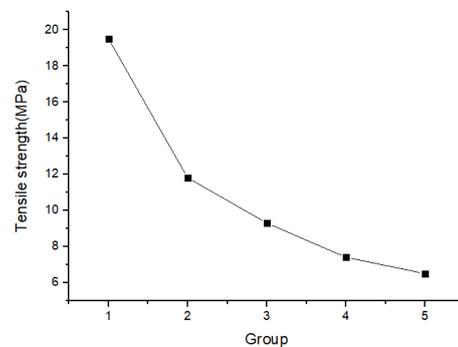


Figure 5. Tensile curve of epoxy resin composite

4. Conclusion

A phosphorus-containing additive type special agent was prepared, and a composite structural material was prepared. The structure of flame retardant was characterized by FT-IR. In the analysis of the limiting oxygen index of the material, the flame retardant has a good flame retardant effect. The composite material has no droplets, no toxic gas generation, low quality loss, and good stability. In this study, the composite material with 15% flame retardant has better flame retardant effect. It has a higher limiting oxygen index, less mass loss, and a denser carbon layer structure. In summary, it shows that flame retardant has a wide application potential in flame-retardant epoxy resin composite products.

Acknowledgments

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