# Properties of epoxy resin composites containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide

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**Abstract**Flame-retardant epoxy resin composites were prepared via in situ polymerization of diglycidyl ether of bisphenol A epoxy monomer and 4,4'-diaminodiphenyl methane, using 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide as additives. The thermal and flame-retardant properties of cured samples were investigated by differential scanning calorimetry, thermogravimetric analysis, limiting oxygen index (LOI), UL–94 vertical burning test, and cone calorimetry. Evaluation of thermal properties demonstrated that the resulting composites achieved high thermal stability with high char yields. Results indicated that the increase in LOI and UL-94 rating was not obvious. The peak of heat release rate of epoxy resin composite containing 15wt.% DOPO was 57.6% less than that of neat epoxy resin. Meanwhile, other flame-retardant parameters were also improved. Scanning electron microscopy was used to study flame retardancy mechanism.

## Introduction

Epoxy resin is one of the most widely used materials in modern industrial areas because of its excellent mechanical and chemical properties [1–3]. However, its inherent flammability limits its specific applications. Thus, improving the flame retardancy of epoxy resin can lead to its more widespread applications.Some scholars have done some research on the flame retardancy of epoxy resin [4–8] Concerning the flame retardancy of epoxy resin, halogenated compounds meet flame-retardant requirements. However, halogen-containing compounds produce corrosive and poisonous smoke during burning, thereby harming human health and posing risks to environment safety. Therefore, researchers from both scientific and industrial fields introduce halogen-free flame retardants into epoxy resin to obtain flame-retardant epoxy resin composites.

In recent years, phosphorus-containing compounds have shown extensive application as halogen-free flame retardants in epoxy resin. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a type of cyclic phosphate with a diphenyl structure, which can react with epoxy resin monomer. As reported in previous studies, DOPO and its derivatives can significantly improve the flame retardancy and thermal properties of epoxy resin.

In this study, DOPO was used to prepare the flame-retardant epoxy resin composites. The influence of flame retardants on thermal properties of epoxy resins was investigated by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The flame retardancy of the epoxy resins was estimated by the limiting oxygen index (LOI), UL–94 vertical burning test, and cone calorimeter.

## Materials and Metholds

### Materials

The system was based on diglycidyl ether of bisphenol-A (DGEBA), with epoxide equivalent weight of 185, was purchased from Wuxi Resin Co. The curing agent 4,4'-diamino diphenylmethane (DDM) was supplied by Sinopharm Chemical Reagent Co., Ltd. DOPO was purchased from Eutec Trading (Shanghai) Co., Ltd.. Other reagents and solvents were used as received.

### Preparation of samples

DOPO was dispersed in epoxy monomer (i.e., DGEBA) by mechanical stirring at 120 °C until a homogenous system was obtained. Thereafter, a stoichiometric amount of curing agent (i.e., DDM) with respect to epoxide groups was incorporated into the above system with continuous stirring. The resulting mixtures were transferred to aluminum molds coated with the release agent for curing. All samples were cured at 80 °C for 3 h and then at 130 °C for another 3 h. After the mold slowly cooled, samples were taken out for testing.

 

## Results and Discussion

### Thermal behavior

$T_g$ is an important parameter for various applications of epoxy resin. Fig.1 shows the DSC curves of the samples. As an additive, DOPO obviously lowers the $T_g$ values of epoxy resin. Moreover, $T_g$ values decrease with increased DOPO contents. This phenomenon results from the incorporation of reactive DOPO, leading to a lower crosslinking density. Nevertheless, the epoxy resin composites achieve a high thermal resistance because of $T_g$ values over 145 °C.

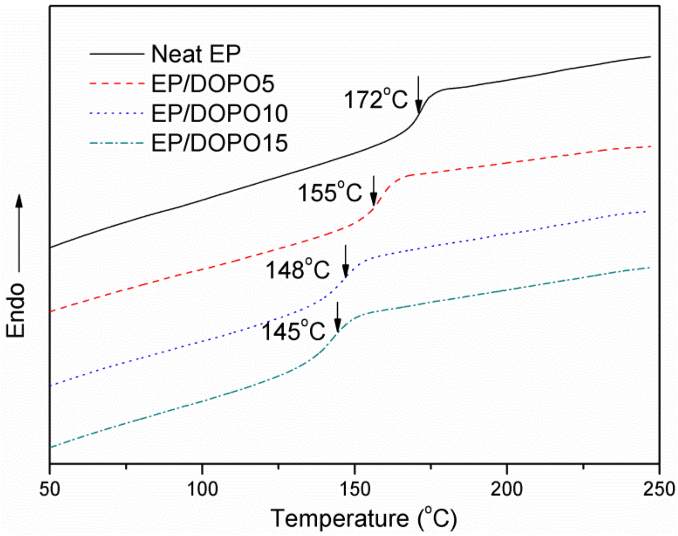


Fig.1 DSC curves of cured epoxy resin samples

Fig.2 shows the TGA curves under nitrogen atmosphere. The results indicate the thermal degradation of the epoxy thermosets, and the detailed data are summarized in Table 1. A one-step degradation process for control epoxy resin and its composites is clearly shown in Fig. 2. This finding obviously indicates that DOPO does not change the thermal decomposition mechanism of epoxy resin matrix. The thermal decomposition temperature of epoxy/DOPO composites shifts to a slightly lower temperature range than the neat epoxy resin, which can be attributed to the less stable DOPO additive. The temperatures corresponding to 5 wt.%, 50 wt.% ($T_{5wt.\%}$, $T_{50wt.\%}$) are essential for evaluating the decomposition of the epoxy resin composites. Table 1 shows that $T_{5wt.\%}$, $T_{50wt.\%}$ gradually decrease with increased DOPO content. Another important thermal characteristic parameter corresponding to the maximum rate of weight loss ($T_{max}$) also decreases with increased DOPO content. Furthermore, the char yields of epoxy resin composites are much higher than those of the neat epoxy resin, indicating that DOPO can promote char formation during thermal degradation [9-12].

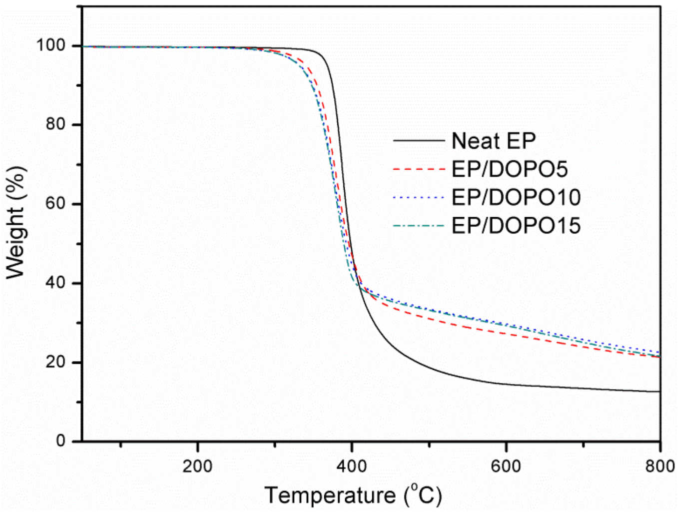


Fig. 2 TGA curves of cured epoxy resin samples

Table 1 Thermal properties of cured epoxy resin samples

| Samples | $T_{5wt.\%}$(°C ) | $T_{50wt.\%}$(°C ) | $T_{Max}$(°C ) | Residues at 800 °C (wt%) |
|---|---|---|---|---|
| Neat EP | 368 | 398 | 389 | 12.4 |
| EP/DODO5 | 346 | 397 | 380 | 21.6 |
| EP/DODO10 | 336 | 394 | 378 | 22.8 |
| EP/DODO15 | 332 | 390 | 380 | 22.1 |

## Fire behavior

To investigate the flame retardancy of the cured epoxy resins, LOI and UL-94 tests were carried out. As listed in Table 2, the LOI values increase with the increase of DOPO loadings and the highest value corresponding to EP/DOPO15 reaches approximately 28.2. The UL-94 vertical burning test is widely used to obtain information about the combustion rate and anti-dripping properties. In the case of neat EP, after the first 10 s of ignition, the sample burns continuously, and no char layer formed at the end of the burnt samples. Compared with the neat EP, the incorporation of DOPO is more beneficial for the improvement of the UL-94 rating of epoxy resin.

Table 2 Combustion parameters obtained from LOI and UL-94 tests

| Samples | LOI(%) | UL-94(3.2mm) | Dripping |
|---|---|---|---|
| Neat EP | 22.6 | No rating | Yes |
| EP/DODO5 | 24.5 | V-2 | No |
| EP/DODO10 | 26.6 | V-2 | No |
| EP/DODO15 | 28.2 | V-1 | No |

The cone calorimeter is one of most useful bench-scale tests and provides substantial abundant information under simulated real-world fire conditions. The concerned combustion parameters, including time to ignition (TTI), heat release rate (HRR), peak of HRR (PHRR), mean HRR, and total heat release (THR) are summarized in Table 3.

Table 3 Combustion parameters obtained from cone calorimetry

| Samples | TTI (s) | PHRR ($kWm^2$) | Mean HRR ($kWm^2$) | THR ($MJm^2$) | Average MLR (gs) |
|---|---|---|---|---|---|
| Neat EP | 59 | 1321 | 292 | 157 | 0.091 |
| EP/DODO5 | 53 | 1026 | 268 | 145 | 0.082 |
| EP/DODO10 | 52 | 707 | 227 | 123 | 0.079 |
| EP/DODO15 | 49 | 560 | 194 | 105 | 0.073 |

The HRR versus time for the samples are presented in Fig. 3. The neat epoxy resin rapidly burns after ignition, and HRR reaches a sharp peak with a PHRR of 1105 $kW/m^2$. The PHRR of the composites decreases with the incorporation of DOPO. Specifically, for the composites containing 10 and 15 wt.% DOPO, the PHRR decreases to 578 and 505 $kW/m^2$ , respectively, which is much lower than that of neat EP. Meanwhile, the mean HRR also decreases with increased DOPO content.

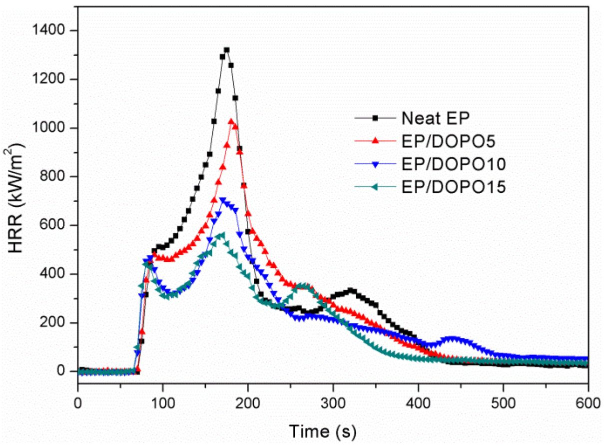


Fig.3 HRR curves of cured epoxy resin samples

The curves of THR with combustion time are shown in Fig. 4. As shown in Table 3, the THR of neat EP was 114 $MJ/m^2$. With the incorporation of flame retardants, the THR of EP/DOPO10 and EP/DOPO15 reduced to 78 and 81 $MJ/m^2$, respectively. These decrements in the heat release intensity with DOPO loadings are expected. DOPO can evidently decrease the heat release intensity with higher efficiency during combustion. In other words, DOPO can serve as an efficient flame retardant for epoxy resin.

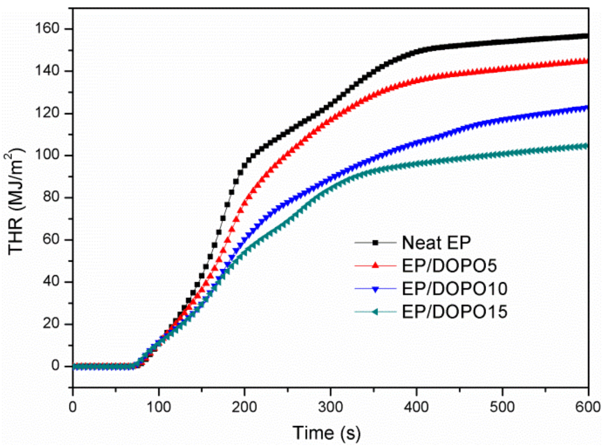


Fig.4 THR curves of cured epoxy resins

## Char structure analysis

The morphology and structure of the residual chars after cone calorimetry test were studied, which could help further understand the flame-retardant effect of the additives on epoxy thermosets [13-16]. Fig. 5 shows the SEM photographs obtained from the interior chars of the cured epoxy resins. For neat EP, the chars were continuous, but uneven and weak, and many cracks and holes were observed. Such a char structure cannot be thermostable. For EP/DOPO15, a strong char structure was observed, which presented a continuous and rugged structure, with few cracks and small pores. The morphologies of residual chars became compact with the addition of DOPO. This phenomenon was consistent with the results of LOI and UL-94 tests.

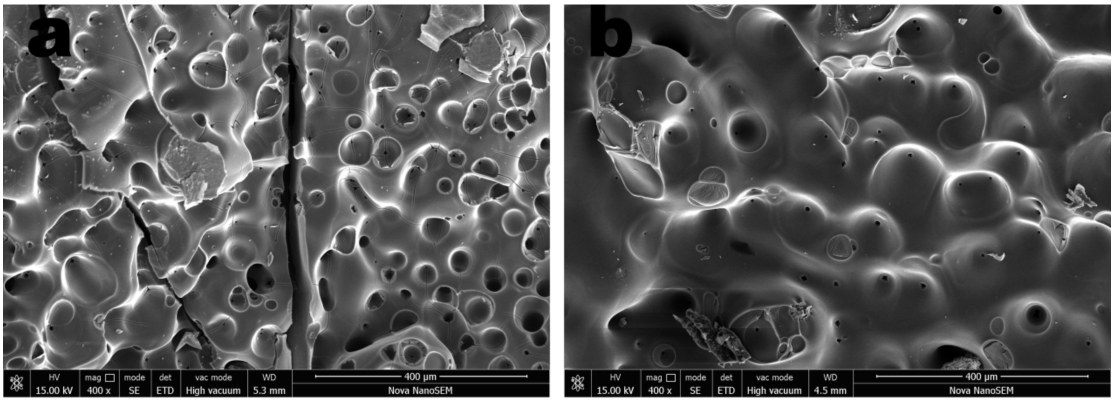


Fig.5 SEM micrographs of the inside structures of residual chars after the cone calorimetry test: (a) neat EP, (b) EP/DOPO/15

## Conclusions

High thermal resistance epoxy composites were developed and characterized for measurement of differential scanning calorimetry and thermogravimetric analysis. The important conclusions drawn are reported as follows.

(1) The containing DOPO achieve a high thermal resistance because $T_g$ values higher than 145 °C, as well as good thermal stability with high char yields.

(2) The composites can reach a UL–94 V–1 rating.

(3) The heat release intensity is dramatically reduced during combustion with the incorporation of DOPO.

The over all results suggested that addition of 15wt.% is very beneficial to improving the flame retardant effects of epoxy. Meanwhile, other flame-retardant parameters were also improved.

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