Flame-Retardant Performance of Epoxy Resin Composites with SiO$_2$ Nanoparticles and Phenethyl-Bridged DOPO Derivative

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ABSTRACT: Flame retardancy of epoxy resin (EP) plays a vital role in its applications. When inorganic nanomaterials form inorganic/organic nanocomposites, they exhibit special flame-retardant effects. In this study, EP nanocomposites were prepared by the incorporation of SiO$_2$ nanoparticles and phenethyl-bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivative (DiDOPO), and the synergistic effects of SiO$_2$ nanoparticles and DiDOPO on the flame-retardant performance of EP were discussed. Results indicated that the introduction of only 15 wt % SiO$_2$ and 5 wt % DiDOPO in EP leads to the increase in the limiting oxygen index from 21.8 to 30.2%, and the nanocomposites achieve the UL-94 V-0 rating. Thermogravimetric analysis revealed that char yield increases with the increase in the SiO$_2$ content of the nanocomposites and that an increased amount of thermally stable carbonaceous char is formed. SiO$_2$ nanoparticles can improve the thermal stability and mechanical performance of EP; hence, the nanoparticles can serve as an efficient adjuvant for the DiDOPO/EP flame-retardant system.

INTRODUCTION

Epoxy resin (EP) is used in structural laminates, adhesives, and electrical devices. However, EP exhibits significant safety hazards due to its flammability when it is used in an application that requires good flame resistance. Therefore, it is crucial to improve the flame retardancy of EP composites in several fields. Currently, this is being done by the introduction of a functional group that contains a flame-retardant element (e.g., halogen element) and physical addition of a widely used flame retardant into the EP matrix. Although flame retardancy of EP composites is improved, halogen-containing flame retardants are deleterious to the environment. Besides, a high amount of additive flame retardants can effectively reduce the heat release rate and mechanical properties of flame-retardant EP composites.

Recently, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have attracted widespread attention, and several studies on DOPO derivatives, including triazine, phenethyl, diphenosphonate, silsesquioxane, and bismaleimide, have been reported. Their activities are mainly related to the PO· radical, produced by a gaseous-phase mechanism, and its interaction with the decomposing polymer, inducing charring in the condensed phase. Although DOPO derivatives exhibit good flame-retardant effects, they are typically added in high amounts. Hence, it is challenging to reduce their addition amount as well as costs associated with their use. Currently, the addition of synergists has become a facile and versatile strategy.

Inorganic synergists have been frequently used in the flame-retardant EP, exhibiting key characteristics of good dispersion and strong interfacial interaction. Several types of particles, such as titania, zinc oxide, carbon fillers, and phosphates, have been widely used in flame-retardant systems. As synergists, nanoparticles have attracted widespread attention due to their nanoscale effects. Owing to the high stability of silica at high temperatures, EP/SiO$_2$ nanocomposites exhibit increased thermal stability due to the strong linkage between EP and SiO$_2$. Besides, the effect of SiO$_2$ on the
mechanical performance of EP/SiO₂ has been discussed, and the SiO₂ content has been reported to exhibit different effects on the tensile modulus and fracture toughness of nanocomposites.²⁴ Zhang and co-workers used polysiloxane flame retardants together with DOPO to prepare a flame-retardant system for EP and found the synergistic effect between DOPO and polysiloxane.²⁵ Vu and co-workers extracted silica from rice husk and researched the effects of modified DOPO on the flammability and mechanical properties of an EP/silica system.²⁶ Although SiO₂-containing phosphorus EP nanocomposites have been researched, the content of DOPO and inorganic materials is higher, and the synergistic effect of colloidal nanosilica with DOPO derivatives (DiDOPO) on flame retardancy and char formation has not been investigated. In this study, SiO₂ with a diameter less than 50 nm combined with a phenethyl-bridged DOPO derivative (DiDOPO) was introduced in EP to improve its mechanical performance of EP/SiO₂ has been discussed, and the SiO₂ content has been reported to exhibit different effects on the tensile modulus and fracture toughness of nanocomposites.²⁴ Zhang and co-workers used polysiloxane flame retardants together with DOPO to prepare a flame-retardant system for EP and found the synergistic effect between DOPO and polysiloxane.²⁵ Vu and co-workers extracted silica from rice husk and researched the effects of modified DOPO on the flammability and mechanical properties of an EP/silica system.²⁶ Although SiO₂-containing phosphorus EP nanocomposites have been researched, the content of DOPO and inorganic materials is higher, and the synergistic effect of colloidal nanosilica with DOPO derivatives (DiDOPO) on flame retardancy and char formation has not been investigated. In this study, SiO₂ with a diameter less than 50 nm combined with a phenethyl-bridged DOPO derivative (DiDOPO) was introduced in EP to improve its flame retardancy; the DiDOPO was designed and synthesized by our laboratory, and the synergistic effect of SiO₂ and DiDOPO on the EP flame-retardant system was investigated. Scanning electron microscopy (SEM) was employed to observe the morphology and structure of SiO₂ nanoparticles and the char layer of EP/DiDOPO/SiO₂ nanocomposites. The cone calorimeter test (CCT), limiting oxygen index (LOI) method, and vertical UL-94 tests were employed to analyze the flame-retardant performance of EP/DiDOPO/SiO₂ nanocomposites, and 3D TG-FTIR was employed for the chemical analysis of EP nanocomposites. In addition, thermal stability and mechanical properties of EP and EP/DiDOPO/SiO₂ nanocomposites were investigated.

2. RESULTS AND DISCUSSION

2.1. Organic Modification of SiO₂ Nanoparticles. Figure 1a shows the morphology of raw SiO₂ nanoparticles: raw SiO₂ tends to from aggregates due to nanoscale effects, and nanoparticles do not exhibit a regular spherical shape. The statistical distribution in Figure 1b revealed that the diameter of SiO₂ nanoparticles is 33.58 ± 3.58 nm. To reduce the aggregation of SiO₂ nanoparticles and further improve their compatibility with EP in acetone, SiO₂ was treated with diluted HCl and CG-570 to prepare organic-modified nanoparticles. SEM results indicated that there is almost no change in the diameter and morphology of SiO₂ nanoparticles before and after modification because the molecular weight and content of the modifier is relatively small. From the FTIR curves shown in Figure 1c, a broad absorption peak at 3410 cm⁻¹ corresponded to the antisymmetric stretching vibration and symmetric stretching vibration of the −OH group, and the wide absorption band at 1061 cm⁻¹ corresponded to the antisymmetric stretching vibration absorption of the Si−O−Si bond. After organic modification, stretching vibration peaks of the alkane CH bond were observed at 2980 cm⁻¹ (−CH₃), 2922 cm⁻¹ (−CH₂), and 2854 cm⁻¹ (−CH). In addition, absorption peaks observed at 2359 and 2340 cm⁻¹ corresponded to CO₂ and the absorption peak observed at 1625 cm⁻¹ corresponded to H₂O in the environment. FTIR results indicated that SiO₂ is successfully modified by the silane coupling agent. Furthermore, TGA results (Figure 1d) are consistent with the FTIR results: neither raw SiO₂ nor modified SiO₂ contained hydroxyl water and coordination water, and modified SiO₂ was extremely stable at a temperature of less than ~400 °C. Besides, after organic modification with CG-570, the mass loss of SiO₂ increased, further indicating that SiO₂ is successfully modified with CG-570.

2.2. Flame Retardancy of EP Composites. After organic modification, SiO₂ was applied with DiDOPO to investigate the synergistic effect on the EP flame-retardant system. Table 5 lists the results for the LOI values and UL-94 grade of EP and EP/DiDOPO/SiO₂ nanocomposites. The results revealed that the LOI value of EP is 21.8, with no UL-94 rating. However, after the incorporation of 5 wt % DiDOPO and a certain amount of SiO₂, the LOI value increased, and the LOI values for EP/DiDOPO/SiO₂, EP/DiDOPO/SiO₂5, EP/DiDOPO/SiO₂10, and EP/DiDOPO/SiO₂15 were 25.6, 27.7, 28.1, and 30.2, respectively. In addition, EP/DiDOPO/SiO₂5 exhibited a V-0 rating. The results indicated that EP and modified SiO₂
exhibit good compatibility, and that SiO2 can help to improve the flame retardancy of the EP system. Figure 2 shows the heat release rate (HRR) and total heat release (THR) curves of EP and EP/DiDOPO/SiO2 nanocomposites evaluated by CCT. The results in Figure 2a revealed that a peak heat release rate (pHRR) of pure EP is 1101.7 kW/m². After the incorporation of 5 wt % DiDOPO and a certain amount of SiO2, pHRR values for EP/DiDOPO/SiO22, EP/DiDOPO/SiO25, EP/DiDOPO/SiO210, and EP/DiDOPO/SiO215 were 1093.6, 1059.1, 801.5, and 644.1 kW/m², respectively, and pHRR decreased by 0.7, 3.9, 27.2, and 41.5%, respectively. These results thankfully form protective residue layers. Table 1 summarizes CCT data, including the time to ignition (TTI), pHRR divided by TPhrr (FGI), and pHRR divided by TTI (FPI). The THR value of EP/DiDOPO/SiO2 decreased by 4.4 and 5.4% after incorporating 2 and 10 wt % SiO2, respectively. For EP/DiDOPO/SiO215, the slightly increased THR value is attributed to the longer burning time. The TSR value is increased due to more incomplete combustion. Furthermore, a high value of TSR/av-EHC indicates the formation of an increased number of noncombustible components in the gas phase. Results revealed that EP nanocomposites exhibit a higher value of TSR/av-EHC than that of pure EP, indicating that an increased number of organic structures retained in the condensed phase participate in carbonization.27−30 Furthermore, the flame-retardant performance was quantitatively evaluated according to the following equation

\[ FRI = \frac{\text{THR} \times \left( \frac{\text{pHRR}}{\text{TTI}} \right)_{\text{heat polymer}}}{\text{THR} \times \left( \frac{\text{pHRR}}{\text{TTI}} \right)_{\text{composite}}} \]  

where FRI is the “flame-retardancy index”. pHRR, THR, and TTI were estimated by CCT. Table 1 lists the calculation results. The results revealed FRI values of 1.05, 1.16, 1.42, and 1.86 for the four composites. Previous studies have reported that “poor,” “good,” and “excellent” fire-retardancy features correspond to FRI values of <1, 1−10, and >10, respectively. Hence, EP/DiDOPO/SiO2 nanocomposites retain a “good” flame-retardant performance in comparison with that of pure EP.

2.3. Thermal Stability of EP Nanocomposites. Figure 3a,b shows the TG and DTG curves of EP and EP/DiDOPO/SiO2 nanocomposites under N2 at a heating rate of 10 °C/min.
SiO₂, the residual char became denser, and the holes were the incorporation of 5 wt % DiDOPO and a certain amount of exhibited a badly broken carbon layer structure. However, after residual char. The residue char of pure EP (Figure 5a) the formation of residual carbon in the condensed phase. temperature char formation and that SiO₂ nanoparticles promote an activity, the protective barrier produced from the expanded low-temperature decomposition slightly promotes high-temperature char surface may cover the inorganic SiO₂ complex and the barrier. As a result, the protective barrier is formed. The content of O was greater than that of EP. The radicals and that it exerts a quenching effect in the gas phase. In summary, the results suggested that gas- and condensed-phase working modes exist during the combustion of EP/ DiDOPO/SiO₂ nanocomposites.

XPS was employed to examine the chemical components in residual char of EP and EP/DiDOPO/SiO₂ nanocomposites after CCT. In the XPS spectrum of EP/DiDOPO/SiO₂ in Figure 6 and Table 3, the peaks at 134, 103, and 400 eV corresponded to P 2p, Si 2p, and N 1s, respectively. Peaks located at 284.8 eV corresponded to C—H and C—C bonds in aliphatic and aromatic species, respectively, and the peak at 532.8 eV corresponded to —O— in C—O—C, C—O—P, and/or C—OH groups. With the addition in DiDOPO and SiO₂, the C and N contents were considerably less than that of EP, and the content of O was greater than that of EP. The nanoparticles tended to migrate to the polymer surface during combustion, which can form an effective char layer and delay the transformation of heat and oxygen.

In Figure 7a–e shows the 3D TG-FTIR spectra of the gas phase induced by the thermal degradation of EP composites. FTIR spectra of pyrolysis products at different reaction times were obtained, as shown in Figure 7d–f. The primary products of EP composites obtained by thermal decomposition were defined as: H₂O (4000–3400, 2000–1500 cm⁻¹), aliphatic C—H (2970, 2760 cm⁻¹), CO₂ (2366, 2334 cm⁻¹), C—C (1506 cm⁻¹), C—H of bisphenol-A (1241, 1125 cm⁻¹), and RC=CH₂ (833 cm⁻¹). In Figure 7, most peaks corresponded to the bisphenol-A part with the EP component. Besides, different EP composites were obtained, as shown in Figure 7d–f. The primary products of EP composites obtained by thermal decomposition were defined as: H₂O (4000–3400, 2000–1500 cm⁻¹), aliphatic C—H (2970, 2760 cm⁻¹), CO₂ (2366, 2334 cm⁻¹), C—C (1506 cm⁻¹), C—H of bisphenol-A (1241, 1125 cm⁻¹), and RC=CH₂ (833 cm⁻¹). In Figure 7, most peaks corresponded to the bisphenol-A part with the EP component. Besides, different EP composites were obtained, as shown in Figure 7d–f. The primary products of EP composites obtained by thermal decomposition were defined as: H₂O (4000–3400, 2000–1500 cm⁻¹), aliphatic C—H (2970, 2760 cm⁻¹), CO₂ (2366, 2334 cm⁻¹), C—C (1506 cm⁻¹), C—H of bisphenol-A (1241, 1125 cm⁻¹), and RC=CH₂ (833 cm⁻¹). In Figure 7, most peaks corresponded to the bisphenol-A part with the EP component.
exhibited different peak ratios. As SiO₂ and DiDOPO did not generate any novel peaks or shoulders with noticeable heights, furthermore, any increase in the peak height may be related to the overlapping of the additional peak with the peaks originating from EP. The released amount of CO₂ from EP composites was greater than that of pure EP, indicating that phosphorus is released into the gaseous phase with some minor additional changes in the number of products. The release of phosphorus led to the flame inhibition of the EP/DiDOPO/SiO₂ nanocomposites. Figure 8 shows the schematic of flame-retardant mechanism of EP/DiDOPO/SiO₂ nano-

Table 3. XPS Results for the Residue Char in EP and EP/DiDOPO/SiO₂ Nanocomposites

| Name   | EP | EP/DiDOPO/SiO₂ | EP/DiDOPO/SiO₂ | EP/DiDOPO/SiO₂ |
|--------|----|----------------|----------------|----------------|
|        | B.E. (eV) | atom (%) | B.E. (eV) | atom (%) | B.E. (eV) | atom (%) |
| C 1s   | 284.8     | 85.57   | 284.8     | 48.27   | 284.8     | 60.38   |
| N 1s   | 400.39    | 3.71    | 400.39    | 2.15    | 400.39    | 1.81    |
| O 1s   | 532.73    | 10.72   | 532.83    | 35.37   | 532.95    | 27      |
| P 2p   | 134       | 0.5     | 134       | 0.5     | 134       | 0.65    |
| Si 2p  | 103.42    | 13.71   | 103.42    | 13.71   | 103.52    | 10.16   |
0.31 GPa and 3.44 ± 0.48%, and 2.60 ± 0.30 GPa and 3.16 ± 0.43%, respectively (Table 4). The results revealed that modified SiO2 can effectively increase the elastic modulus of EP but slightly reduce its elongation at break.

3. CONCLUSIONS

In this study, SiO2 nanoparticles and phenethyl-bridged DOPO derivative (DiDOPO) were used to prepare EP nanocomposites, and the synergistic effects of SiO2 and DiDOPO on the flame-retardant performance, thermal stability, and the flame-retardant mechanism of the EP system were discussed. With the increase in the SiO2 content from 2 to 15 wt %, the UL-94 result changed from N.R. to V0 rating, the LOI value increased from 21.8 to 30.2%, and pHRR decreased from 1101.7 to 644.1 kW/m² in comparison to pure EP. FRI results indicated that compared to pure EP, nanocomposites retain a “good” flame-retardancy performance. In addition, SEM results revealed that the residual char becomes more continuous and compact with the increase in the SiO2 content. Besides, elemental analysis indicated that flame fillers were transferred to the matrix surface during combustion to form an effective char layer and delay the permeation of heat and toxic gases. This work revealed that the EP/DiDOPO/SiO2 nanocomposites exhibit gas- and condensed-phase flame-retardant effects, which may provide a new route to improve the flame retardancy and thermal stability of the EP system.

4. EXPERIMENTAL SECTION

4.1. Materials. SiO2 nanoparticles were purchased from Beijing Anbiqi Biological Technology Co., Ltd., China, and its morphology and diameter were measured by SEM. A silane coupler CG-570 (≥98%) with a density of ~1.070 g/cm³ and a refractive index of ~1.425 at 25 °C was purchased from Nanjing Chengong Silicone Material Co., Ltd., China. The flame-retardant phenethyl-bridged DOPO derivative (DiDOPO) was synthesized in our laboratory, according to a previously reported method. Figure 10 shows the chemical structure of EP, D230, CG-570, and DiDOPO. Diglycidyl ether of bisphenol-A (DGEBA, EP: epoxide value of 0.48–0.52

Table 4. Tensile Performance of EP and EP/DiDOPO/SiO2 Nanocomposites

| sample designation | strength (GPa) | elongation at break (%) |
|---------------------|---------------|------------------------|
| EP                  | 1.70 ± 0.21   | 4.72 ± 0.61            |
| EP/DiDOPO/SiO22     | 1.94 ± 0.27   | 4.42 ± 0.58            |
| EP/DiDOPO/SiO25     | 2.07 ± 0.25   | 4.25 ± 0.51            |
| EP/DiDOPO/SiO210    | 2.53 ± 0.31   | 3.44 ± 0.48            |
| EP/DiDOPO/SiO215    | 2.60 ± 0.30   | 3.16 ± 0.43            |

Figure 7. (a–c) 3D TG-FTIR profiles and (d–f) FTIR curves of the pyrolysis products obtained for EP, EP/DiDOPO/SiO2, and EP/DiDOPO/SiO215, respectively.

Figure 8. Schematic of the flame-retardant mechanism of EP/DiDOPO/SiO2 nanocomposites.

Figure 9. Typical stress/strain curves of EP and EP/DiDOPO/SiO2 nanocomposites.
mol/100 g) was purchased from Laizhou Baichen Insulation Materials Co., Ltd., China. O,O′-Bis(2-amino propyl)-polypropylene glycol (D230; 98%) was purchased from Beijing Huawei Ruike Chemical Co., Ltd., China. Ultrapure water (Millipore Milli-Q grade) with a resistivity of 18.0 MΩ was used in all experiments. All chemicals were used as received without further purification.

4.2. Organic Modification of SiO2 Nanoparticles. SiO2 nanoparticles were modified by a conventional strategy with modifications according to our previous study.41 The detailed experimental procedure was as follows: first, SiO2 was washed three times with ultrapure water and dried at 60 °C for 12 h, followed by the addition of dried SiO2 to HCl/H2O (v/v 1:7) and stirring at room temperature for 1 h. After the reaction was continued for 24 h, the mixture was washed three to five times with ultrapure water, followed by drying at 60 °C for 12 h to prepare acidiﬁed SiO2. Second, the silane coupler CG-570 was dissolved in ethanol/H2O (v/v 18:1), and the solution pH was adjusted to 4–6 with formic acid. Finally, the CG-570 solution was added to an acidiﬁed SiO2 aqueous solution with 8 wt % of CG-570 relative to SiO2 and subsequently stirred at 60 °C for 5 h. Purification of the final products by centrifugation and drying afforded organic-modiﬁed SiO2 nanoparticles.

4.3. Preparation of Flame-Retardant EP Composites. The flame-retardant EP/DiDOPO/SiO2 nanocomposites were prepared by a modiﬁed method according to that reported by our group, and the corresponding preparation routes were almost similar, just replacing the inorganic materials OLDH with SiO2 nanoparticles.40 Typically, modiﬁed SiO2 was ﬁrst dispersed in acetone (1 g/mL) by ultrasonication at room temperature for 1 h. Then, EP was added to the solution, and the mixture was stirred at 80 °C for 3 h. Next, the mixture was transferred to an oil bath and continuously stirred at 130 °C for 1 h to evaporate the excess acetone, followed by the addition of DiDOPO to the mixture and stirring for 0.5 h. Then, the solution was cooled to 50 °C, and the curing agent D230 was added to the solution. The ﬁnal homogeneous solution was degassed in a vacuum oven at 50 °C for 15 min. Next, the solution was poured into preheated molds and cured at 80 °C for 1 h and then at 140 °C for 2 h. In addition, all samples were prepared using the same strategy. Table 5 lists the designated samples and corresponding content of each component.

4.4. Characterization. Field-emission SEM (FEI Quanta 250 FEG, FEI Inc.) under high vacuum at a voltage of 20 kV was employed to observe morphologies of all testing samples. FTIR spectroscopy (Nicolet IS50, Thermo Fisher Scientiﬁc Inc.) was employed to characterize raw and modiﬁed SiO2. The resolution was 4 cm−1, the number of scans was 32, and the test range was 400–4000 cm−1. A TG 219 F3 thermal analyzer (Netzsch Instruments Co., Ltd., Germany) was utilized at a constant scanning rate of 10 °C/min under nitrogen at temperatures ranging from 50 to 800 °C to evaluate the thermal stability of all testing materials. UL-94 tests (CZF-2, Jiangning, China; dimensions of 130 mm × 13 mm × 3.2 mm) were performed as per ASTM D3801. LOI (according to ASTM D2863-77) was measured using a JF-3 oxygen index meter (Jiangning, China), with a sample size of 100 mm × 6.5 mm × 3.2 mm. CCT (FTT, U.K.) was conducted as per ASTM E1354/ISO 5660. Specimens with dimensions of 100 mm × 100 mm × 6 mm and an external heat ﬂux of 50 kW/m2 were selected. A TG-FTIR instrument comprised a TG 219 F3 system (Netzsch Instruments Co., Ltd., Germany), an FTIR spectrometer (Nicolet IS50, Thermo Fisher Scientiﬁc Inc.), and a transfer tube with an inner diameter of 1 mm connected to the TG and IR cells. Measurements were conducted from 30 to 600 °C at a linear heating rate of 20 °C/min under a nitrogen ﬂow of 30 mL/min. X-ray photoelectron spectroscopy (XPS) proﬁles of the char residue were recorded on a Thermo Escalab 250Xi system (Thermo Fisher Scientiﬁc Inc.) using Al Kα excitation radiation (hv = 1253.6 eV). CMT6104 (MTS, Tianjin, China) was utilized to conduct tensile performance tests (sample size: 75 mm × 5 mm × 1.88 mm).

| Table 5. Formulations and Flame-Retardant Results for EP and EP/DiDOPO/SiO2 Nanocomposites |
|---|---|---|---|---|---|
| sample designation | EP | DiDOPO | SiO2 | LOI (%) | UL-94 |
| EP | 100 | 0 | 0 | 21.8 | N.R. |
| EP/DiDOPO/SiO2-2 | 100 | 5 | 2 | 25.6 | V1 |
| EP/DiDOPO/SiO2-5 | 100 | 5 | 5 | 27.7 | V0 |
| EP/DiDOPO/SiO2-10 | 100 | 5 | 10 | 28.1 | V0 |
| EP/DiDOPO/SiO2-15 | 100 | 5 | 15 | 30.2 | V0 |

![Figure 10. Chemical structures of (a) EP, (b) D230, (c) CG-570, and (d) DiDOPO.](image)
Notes
The authors declare no competing financial interest.

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