Co-Effect Flame Retardation of Co$_3$O$_4$-Loaded Titania Nanotubes and $\alpha$-Zirconium Phosphate in the Epoxy Matrix

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**ABSTRACT:** Like most macromolecule polymers, epoxy resin (EP) is easy to burn, and there are great fire safety hazards in the process of use. Therefore, how to improve the fire safety of EP becomes one of the problems to be considered in the application of EP. In this study, tricobalt tetraoxide (Co$_3$O$_4$)-loaded TiO$_2$ nanotube (TNT) (Co$_3$O$_4$-TNT) hybrid material was prepared by the co-precipitation method, and organophilic $\alpha$-ZrP (OZrP) was obtained by hexadecyl trimethyl ammonium bromide-intercalated $\alpha$-zirconium phosphate ($\alpha$-ZrP) which was prepared by the hydrothermal synthesis method. Then, a series of nanocomposites were obtained by adding the synthesized nanomaterials to the EP at a certain ratio. The structure and morphology characterization indicated that Co$_3$O$_4$-TNTs and OZrP were synthesized successfully. The results of thermogravimetric analysis showed that the co-addition of Co$_3$O$_4$-TNTs and OZrP could further enhance the thermal stability of EP. The results of a cone calorimeter showed that EP/OZrP/Co$_3$O$_4$-TNTs had the lowest peak heat release rate and total heat release, which decreased by 36.2 and 35.4%, respectively, compared with the pure EP. This indicates that Co$_3$O$_4$-TNTs and OZrP had a good synergetic flame retardant effect and could effectively enhance the flame retardancy of EP.

1. **INTRODUCTION**

Epoxy resin (EP) is one member of thermosetting resins. Driven by the remarkable physical, mechanical, and electrical insulating properties, EP is widely utilized in our production and daily life, such as composites, adhesives, coatings, and so on. However, similar to most high-molecular polymers, the high flammability of EP immensely brings about potential safety hazards in the process of use. Therefore, the modification of epoxy in order to improve the fire safety of EP is an important issue which needs to be addressed.

In recent years, more and more nanoparticles have been used in flame retardancy, and the combination of different nanoparticles to prepare multicomponent polymer composites has also attracted widespread attention. Among these combinations, the combination of two-dimensional layered nanoparticles with other nanoparticles is the most common type which can exhibit extraordinary synergy in certain properties. Fang’s group once incorporated one-dimensional carbon nanotubes and three typical two-dimensional layered materials (graphene oxide, clay, and layered double hydroxide) into polypropylene, ABS resin, and polypropylene respectively. All the tests of flame retardancy show that the coexistence of two-dimensional layered materials and carbon nanotubes in nanocomposites can form a more effective network structure for enhancing physical barriers. In addition, the research of Pan et al. showed that there was an obvious complementary effect between two-dimensional nanosheet layer and one-dimensional nanotube, which could permeate each other to make the network structure more compact and better protect the polymer matrix during combustion.

Therefore, the incorporation of two-dimensional and one-dimensional nanomaterials as flame retardants seems to be a good choice for improving the flame retardant properties of polymer matrices. $\alpha$-Zirconium phosphate [$\alpha$-Zr(HPO$_4$)$_2$·H$_2$O, called $\alpha$-ZrP] is a typical layered nanostructure compound with excellent thermal stability, mechanical properties, and chemical properties, which have aroused great interest of researchers. In the field of the flame retardant, adding $\alpha$-ZrP to the polymer matrix can play an excellent role in flame retardancy. On the one hand, the unique two-dimensional laminar structure of $\alpha$-ZrP serves as a thermal insulating barrier that could effectively inhibit the mass and the heat transfer between the matrix and the surroundings. On the other hand, $\alpha$-ZrP can also act as the Lewis acid and play a catalytic role in the formation of the residue of carbon. The study of the fire performance of the $\alpha$-ZrP serves as a thermal insulating barrier that could effectively inhibit the mass and the heat transfer between the matrix and the surroundings. On the other hand, $\alpha$-ZrP can also act as the Lewis acid and play a catalytic role in the formation of the residue of carbon.
ZrP/polymer nanocomposites including poly(ethylene terephthalate), poly(vinyl alcohol), and poly(lactic acid) revealed that the catalytic carbonization and barrier effect of α-ZrP can reduce the heat release rate (HRR) and total heat release (THR) of the polymer during the combustion. In addition, the protons between layers of α-ZrP can exchange with many cations. Yang et al. indicated that the hexadecyl trimethyl ammonium bromide (CTAB) intercalated α-ZrP (OZrP) could stabilize the carbon skeleton of the PP and increase char residue through promoting an early cross-linking reaction of the PP carbon chain.

Nowadays, titanate nanotubes (TNTs) have attracted growing interest owing to the highly specific surface area and ion exchangeable and photocatalytic abilities. TNTs have also been widely studied for the applications in improving the thermal stability and flame retardant properties of polymers. The tubular structure of TNTs has a large specific surface area which can support some metal oxide nanoparticles, such as Co$_3$O$_4$. It has high thermal stability and good catalytic activity, so it has been widely used in the acceleration of oxygen reduction reaction, organic volatilization, and oxidation of carbon monoxide. TNTs and the supporting metal nanoparticles can be used as effective flame retardants.

In this work, the Co$_3$O$_4$-loaded TNTs (Co$_3$O$_4$-TNTs) and organophilic α-ZrP (OZrP) were co-incorporated into the EP matrix. Thermogravimetric analysis (TGA) and a cone calorimeter were used to evaluate thermal stability and combustion properties. Moreover, the effects of the combination between Co$_3$O$_4$-TNTs and OZrP on the flame retardant of EP composites were studied. This work attempts to provide a promising strategy for constructing a novel nanoparticle combination so as to reduce the fire hazards of materials.

2. RESULTS AND DISCUSSION

2.1. Structure and Morphology of Co$_3$O$_4$-TNTs. The crystalline structures of the TNTs and Co$_3$O$_4$-TNTs were analyzed by X-ray diffraction (XRD) (Figure 1a). By comparison with TNTs, the new characteristic peaks of Co$_3$O$_4$-TNTs at 2θ = 19.0, 31.2, 36.8, 44.9, 59.4, and 65.4° are corresponding to the (111), (220), (311), (400), (511), and (440) diffraction peaks of Co$_3$O$_4$, which is well matched to the standard diffraction pattern of Co$_3$O$_4$ (JCPDS: 43-1003).

In order to determine the elemental composition of Co$_3$O$_4$-TNTs, the X-ray photoelectron spectroscopy (XPS) tests are performed and the results are shown in Figure 1b. It can be observed from Figure 1b, as the TNTs surface is loaded with...
Co$_3$O$_4$, the XPS spectrum of Co$_3$O$_4$-TNTs shows the characteristic peak of Co at 780.1 eV, and the ratio of O to Ti increases significantly. These results indicate the successful precipitation preparation method.

Microstructures of TNTs and Co$_3$O$_4$-TNTs were studied by transmission electron microscopy (TEM) (Figure 2). Figure 2a reveals that TNTs have typical morphology of nanotubes with multilayered walls and their diameters are about 10 nm. At low magnification (Figure 2b), a large number of TNTs with a rough surface can be seen in the field of vision. After further enlargement (Figure 2c), it can be observed that many particles attached to the surface of tubular TNTs. These particles are Co$_3$O$_4$ particles, which is strong evidence that Co$_3$O$_4$ were successfully loaded on the surface of TNTs.

2.2. Structure of α-ZrP and OZrP. Figure 3 shows XRD patterns of the α-ZrP and OZrP. In the XRD pattern of α-ZrP (Figure 3a), the peaks at 11.6, 19.8, and 25.1° can be ascribed to (002), (110), and (112) crystal planes of α-ZrP. Figure 3b shows the small-angle XRD pattern of OZrP, the maximum peaks correspond to the (002) crystal plane reflection of phosphate. The d$_{002}$ peak of OZrP at 2θ = 2.9° corresponds to 3.04 nm interlayer spacing, which indicates that the (002) peak of OZrP is observed at a lower angle than that of α-ZrP (2θ = 11.6°), and the interlayer spacing is significantly higher than that of α-ZrP (0.76 nm). The results clearly signify the molecules of the CTAB intercalate into the gallery of the α-ZrP interlayer.

2.3. Microscopic Morphology of EP and Its Nanocomposites. To understand the interface interaction between the nanoparticles and EP resin, scanning electron microscopy (SEM) was used to study the microstructures of freeze-fractured surfaces of EP composites, and the result is shown in Figure 4. In general, the fracture surface roughness of the material exhibits the interfacial interactions. For the pure EP (Figure 4a), a smooth and clean surface can be observed. With the addition of nanoparticles, the fracture surfaces of EP composites are much rougher and several irregular wrinkles are found relatively (Figure 4b-g), which shows that there is a good interaction force between the nanoparticles and the EP, which can prevent the fracture of the EP composite and enhance the mechanical properties. In particular, after the addition of OZrP and Co$_3$O$_4$-TNTs together, the fracture surface of the EP/OZrP/Co$_3$O$_4$-TNTs sample is the roughest (Figure 4f-g), indicating good compatibility.

2.4. Thermal Stability. The TGA was used to study the thermal stability of EP and its nanocomposites. Figure 5 shows the thermogravimetric (TG) curves (a) and derivative of the thermogravimetric (DTG) curves (b) of each sample under a nitrogen atmosphere. The corresponding data are listed in Table 1. The temperature where the weight loss exhibits 5 wt % is defined as the initial decomposition temperature ($T_{5\%}$), $T_{50\%}$, and $T_{max}$ represent the temperature at which 50 wt % and the maximum weight loss rate occurred, respectively. From Figure 5a, it can be seen that the thermal degradation of pure EP (EP-0) with only one stage which occurs in the range of 350–500 °C, correspond to the degradation of macromolecule chains of EP. The thermal degradation of EP nanocomposites is similar to that of EP-0. As for the $T_{5\%}$ EP/TNTs is very close to EP-0, while EP/OZrP and EP/Co$_3$O$_4$-TNTs show early decomposition, and the $T_{5\%}$ of EP/OZrP/Co$_3$O$_4$-TNTs is the lowest. The reason for the early decomposition of EP/OZrP is the Hofman degradation of the alkyl chain of CTAB inserted between the layers of OZrP. The reason for the early decomposition of EP/Co$_3$O$_4$-TNTs may be because of the catalysis of Co$_3$O$_4$ on the degradation of polymer materials. Moreover, because of the coexistence of OZrP and Co$_3$O$_4$-TNTs, the EP/OZrP/Co$_3$O$_4$-TNTs decompose further in advance and exhibit the lowest initial decomposition temperature. Judging from the amount of carbon residue, the introduction of nanomaterials significantly increased the residual carbon content at 700 °C of EP. The residual carbon content of EP/TNTs, EP/Co$_3$O$_4$-TNTs, and EP/OZrP are 18.1, 19.4, and 18.5%, respectively, which are higher than that of pure EP (14.4%), indicating that the nanomaterials have the effect of catalytic carbon formation on EP. Moreover, the addition of Co$_3$O$_4$-TNTs and OZrP in EP resulted in the significant improvement in the amount of residual carbon compared to single-component nanocomposites, reaching 21.2%. This is due to the fact that tubular structure of Co$_3$O$_4$-TNTs and layered structure of OZrP are evenly distributed within the matrix and penetrate each other, forming a denser and stable physical barrier compared to the single component and exerting better barriers during the exchange of mass. Moreover, both Co$_3$O$_4$ and OZrP have the effect of catalyzing char formation, and the simultaneous existence of the two results in further increase of carbon generation. A stable carbon layer is formed on the surface of the polymer in the initial stage of combustion, which protects the substrate, delays the combustion process, and further increases the carbon content. From the DTG curve in Figure 5b, the maximum mass loss rate of EP/OZrP/Co$_3$O$_4$-TNTs is lower than that of other samples, indicating that the cross-network structure of Co$_3$O$_4$-TNTs and layer structure of OZrP can synergistically form a good physical barrier layer in the EP matrix, inhibit the mass loss in the thermal degradation process, and improve the thermal stability of the EP.
2.5. Flame Retardant Properties. A cone calorimeter can be used to simulate the combustion of the sample at the scene of the fire, and its test environment is close to the real combustion environment of the fire material. It is an ideal test instrument for investigating the combustion properties of polymer materials. Many important parameters to evaluate the potential fire hazard of a material, such as HRR and THR, can be investigated by a cone calorimeter. Figure 6 is the HRR and THR curves of EP and its nanocomposites. It can be seen that the HRR curve of EP-0 consists of a sharp peak, the corresponding PHRR is 1164.0 kW/m². The PHRR decreased after adding TNTs and dropped to 1031 kW/m². This is due to the fact that TNTs form a cross-linked, net-like barrier layer in the EP and inhibit the release of heat. After addition of Co₃O₄-TNTs, the PHRR of the EP nanocomposites was reduced to 840 kW/m² with a decrease of 27.8%, which is due to the catalytic charring of Co₃O₄. Similarly, the PHRR of EP/OZrP decreased by 17.0% compared with EP-0. This is because when the nanocomposite is burned, OZrP will release crystalline water when heated, reducing the concentration of combustible in the gas-phase combustion zone and absorbing a lot of heat. When OZrP and Co₃O₄-TNTs were introduced together into the EP matrix, the PHRR of the EP/OZrP/Co₃O₄-TNTs had the largest reduction, reaching 36.2%, which indicate that OZrP and Co₃O₄-TNTs play a synergistic flame retardant effect and exhibit their own flame retardant effects. The possible reason is the synergistic effect of the tubular nanoparticles and the layered nanoparticles. The Co₃O₄-TNTs and the OZrP are filled with each other’s gaps in the EP matrix, which makes the barrier layer more complete, thus significantly delaying the release of heat during the combustion process. In addition, the presence of Co₃O₄ and OZrP promotes the formation of the carbon layer on the surface of EP during combustion owing to the effect of catalytic carbonation. With the combustion of nanocomposites, the carbonized layer is gradually strengthened and thickened. The dispersed phosphate sheets in the nanocomposites have a catalytic carbonization effect on the degradation products of the polymer, and also fixate and enhance the carbonization layer. The carbon layer on the surface of the substrate also has a good protective effect, blocking heat radiation, preventing the release of the combustible gas, and inhibiting the combustion of the substrate. The THR curves of EP and its nanocomposites are shown in Figure 6b. By adding the nanoadditives, all of the values of THR were lowered. Moreover, among the nanocomposites, EP/OZrP/Co₃O₄-TNTs showed the lowest THR (35.4% lower than that of EP-0), which also implies the synergistic effect between OZrP and Co₃O₄-TNTs and significantly reduce the THR of the matrix during combustion. It may be ascribed to the excellent adsorption properties of TNTs. These TNTs uniformly distributed in the gaps between OZrP layers can adsorb small molecules and free radicals of flammable gases, further improving the catalytic carbonization ability of OZrP and Co₃O₄ and more flammable material is converted to the carbon residue, thereby reducing the THR.

### Table 1. TGA Data for EP and its Nanocomposites

| sample name                  | \( T_{-5\%} \) (°C) | \( T_{-50\%} \) (°C) | \( T_{\text{max}} \) (°C) | residue of carbon at 700 °C (%) |
|------------------------------|----------------------|----------------------|---------------------------|---------------------------------|
| EP-0                         | 380                  | 417                  | 397                       | 14.4                            |
| EP/Co₃O₄-TNTs                | 355                  | 398                  | 378                       | 19.4                            |
| EP/TNTs                      | 376                  | 413                  | 397                       | 18.1                            |
| EP/OZrP                      | 357                  | 413                  | 398                       | 18.5                            |
| EP/OZrP/Co₃O₄-TNTs           | 347                  | 399                  | 381                       | 21.2                            |

Figure 6. HRR (a) and THR (b) curves of EP and its nanocomposites.
Table 2 shows the fire growth rate index (FIGRA) of each sample. Comparing the data in the table, it is not difficult to

find that the addition of nanomaterials can effectively reduce the FIGRA value of EP. Among them, the EP/OZrP/Co3O4-
TNTs has the lowest FIGRA value, showing the best fire safety performance, indicating that the synergistic use of OZrP and
Co3O4-TNTs has a good flame retardant effect, giving the EP excellent flame retardant performance.

2.6. Char Residue Analysis. Generally speaking, the compact and continuous carbon layers are considered to be
great barriers for protecting the underlying polymers, as well as hindering the exchange of degradation products.36,37 Figure 7
presents the char residue photographs of EP and its nanocomposites after undergoing the cone calorimeter experi-
ments. There was very little residue which remained after the progress of EP-0 thermal decomposition. However, the
incorporation of nanoparticles leads to the remarkable improvement of the char yield. The surface of EP/TNT char
residue adheres with white TNTs and EP/Co3O4-TNTs with gray Co3O4. Because of the addition of OZrP, EP/OZrP, and
EP/OZrP/Co3O4-TNTs are demonstrating an excellent intumescent effect. The intumescent char can insulate the
heat transformation and the dispersion of oxygen into underlying polymeric substrate to prevent thermo-oxidative
reactions.38 The char residue of EP/OZrP/Co3O4-TNTs is superior to other samples in terms of the residual amount and
intumescent effect, which is due to the OZrP. In addition to the barrier effect of layered compounds, the OZrP contains
Lewis acid points and Bronsted acid points between the layers and has a synergistic effect when used with Co3O4, promoting
the charring effect of EP. Furthermore, the carbon layer

formed by the material is nonflammable, so the combustion process slows down, which explains why EP/OZrP/Co3O4-
TNTs exhibit the best flame retardancy in the cone test. The flame retarding mechanism of the EP/OZrP/Co3O4-TNTs
nanocomposites is shown in Figure 8.

3. CONCLUSIONS
In this work, Co3O4-TNTs and OZrP had been successfully synthesized and co-incorporated into the EP matrix. Thermal
stability of EP and its composites had been studied and the Co3O4-TNTs and OZrP could act as mass-transport barrier
during the thermal degradation, and enhanced the char yield dramatically. According to PHHR and THR values, the
enhanced flame retardance of EP/OZrP/Co3O4-TNTs may be due to the good synergistic flame retardation between
Co3O4-TNTs and OZrP, which involves the dense laminar barrier formed by the mutual filling of tubular nanoparticles
and layered nanomaterials, and the catalytic carbonization of OZrP and Co3O4. Thus, we can draw a conclusion that the
cooperation of OZrP and Co3O4-TNTs is an effective method to improve the fire safety of EP, which provides a new idea for
developing new environmentally friendly flame-retardant EPs.

4. EXPERIMENTAL SECTION
4.1. Materials. Titanium dioxide (anatase), sodium
hydroxide (NaOH), hydrochloric acid (HCl, 36−38%), 4,4'-

Table 2. FIGRA of EP and its Nanocomposites

| Sample Name      | PHRR (kW/m²) | Time to PHRR (s) | FIGRA (kW m⁻² s⁻¹) |
|------------------|--------------|-----------------|---------------------|
| EP-0             | 1164         | 58              | 20.1                |
| EP/TNTs          | 1031         | 61              | 16.9                |
| EP/Co3O4-TNTs    | 840          | 56              | 15.0                |
| EP/OZrP          | 966          | 51              | 18.9                |
| EP/OZrP/Co3O4-TNTs | 742      | 55              | 13.5                |
diaminodiphenyl methane (DDM), chloroform, cobaltous nitrate hexahydrate (Co(NO₃)₂·6H₂O), ammonium hydroxide(NH₄H₂O₂, 25–28%), zirconium oxychloride (ZrOCl₂·8H₂O, 98%), phosphoric acid (H₃PO₄), ethylamine, and CTAB were all provided by Sinopharm Chemical Reagent Co., Ltd. Deionized water (commercial name E-44) was purchased from Shandong Yousuo Chemical Technology Co., Ltd. Deionized water with a resistance of 18.2 MΩ was used for all experiments.

4.2. Synthesis of TNTs and Co₃O₄-TNTs. TiO₂ nanotubes (TNTs) were synthesized by a hydrothermal approach. First, 2 g of TiO₂ powder was mixed with 40 mL of 10 M NaOH solution and then transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 150 °C for 48 h and afterward allowed to be cooled to room temperature naturally. Afterward, the product was treated with 0.1 M HCl solution and deionized water. Then, the precipitate was dispersed in 1 M HCl solution and stirred for 15 h. Finally, the product was washed several times with deionized water until the pH value of the supernatant was near neutral, and dried in an oven for 24 h at 80 °C.

Co₃O₄-TNTs were synthesized by a wet-chemical deposition precipitation method. Co(NO₃)₂·6H₂O (5.93 g) was dissolved in 300 mL of deionized water and mixed with 2 g of TNTs to form a stable suspension. After that, the diluted aqueous ammonia was dropwise added under vigorous stirring to adjust the pH to about 9. The mixture was stirred for 4 h and then aged for 2 h at room temperature. After washing with deionized water to a pH near neutral, and dried in an oven at 60 °C for 24 h.

4.3. Synthesis of α-ZrP and OZrP. ZrOCl₂·8H₂O (40 g) was dissolved in 114 mL of deionized water to form a uniform and stable solution. Then, 286 mL of H₃PO₄ was dropwise added into the solution above and sonicated to introduce the CTAB molecular chain into the α-ZrP sheet, followed by repeated centrifugal washing with hot water to remove residual CTAB until no bromide ion was detected in the supernatant. The resulting product was dried at 60 °C to obtain OZrP.

4.4. Preparation of EP Nanocomposites. The preparation of EP/Co₃O₄-TNT nanocomposites was as follows: Co₃O₄-TNTs (1 g) were blended with EP (40.21 g) by ultrasonic treatment for 30 min (chloroform as a dispersant, stirring at 100 °C for 3 h to remove chloroform solvent). Subsequently, DDM (8.78 g) was melted and mixed with the above mixture under stirring for 5 min. After that, the mixture was poured quickly into a preheated mold. Finally, this blending was cured at 100 °C for 2 h and then postcured at 150 °C for 2 h. Similarly, EP/TNTs and EP/OZrP nanocomposites were also prepared through the above steps except for adding the different nanoparticles.

Preparation of EP/OZrP/Co₃O₄-TNT nanocomposites: OZrP (0.5 g) was dispersed into a chloroform solvent and blended with EP (40.21 g) by ultrasonic treatment. After that, 0.5 g of Co₃O₄-TNTs dispersed in the chloroform solvent was added to the above solution. After sonication for 2 h, the mixture was stirred at 100 °C for 3 h to remove the chloroform solvent. Subsequently, DDM (8.78 g) was melted and mixed with the above mixture under stirring for 5 min. After that, the mixture was poured quickly into a preheated mold. Finally, this blending was cured at 100 °C for 2 h and then postcured at 150 °C for 2 h. The preparation of the EP/OZrP/Co₃O₄-TNT nanocomposites is shown in Scheme 1. Moreover, the formula of EP nanocomposites is shown in Table 3.

4.5. Characterization. The morphology of the Co₃O₄-TNTs was analyzed by TEM using a JEOL JEM-100SX transmission electron microscope with an acceleration voltage of 100 kV.

XRD measurements were implemented on a Japan Rigaku D/Max-Ra X-ray diffractometer, using Cu Kα radiation (λ = 0.1542 nm) at 40 kV and 200 mA. A scan rate of 1°/min was used.
XPS was used to analyze the elemental composition of the sample with an ESCALAB Mark II spectrometer from Al Kα rays ($hv = 1486.6$ eV).

The TGA of samples under a nitrogen atmosphere were examined on a TGA-Q5000 apparatus (TA Company, USA) from 50 to 700 °C at a heating rate of 20 °C/min.

The combustion properties of samples were investigated by a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660 standard procedures, with $100 \times 100 \times 3$ mm specimens. Each specimen was exposed horizontally to $35$ kW/m$^2$ external heat flux.

SEM was performed on the cross section of EP nanocomposites using a Hitachi SU8010 scanning electron microscope. The samples were coated with a layer of gold prior to observation.

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**Notes**

The authors declare no competing financial interest.

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