Effect of Graphene Oxide–Modified Cobalt Nickel Phosphate on Flame Retardancy of Epoxy Resin

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Synergistic effect is an effective strategy for improving the flame retardancy of epoxy resin (EP). In this work, a novel graphene oxide–cobalt nickel phosphate (GO-NiCoPO3) is successfully synthesized, which is incorporated into an EP matrix for preparing EP/GO-NiCoPO3 nanocomposites. The results show that the limiting oxygen index value of EP/GO-NiCoPO3 nanocomposites is as high as 30.3%, and UL-94 can reach V-1 rating. The results of micro-combustion calorimetry indicate that the total heat release value and peak of heat release rate of EP/GO-NiCoPO3 nanocomposites are decreased by 41.9 and 23.8% compared with those of pure EP. This is mainly due to the synergistic barrier effect of GO and NiCoPO3, which together have their own advantages. Meanwhile, EP/GO-NiCoPO3 nanocomposites can form a dense char layer during the burning process and improve the thermal stability of EP/GO-NiCoPO3 nanocomposites.

Keywords: epoxy resin, graphene oxide–cobalt nickel phosphate, thermal stability, flame retardancy, synergistic barrier effect

INTRODUCTION

Epoxy resin (EP) is well known for its excellent mechanical and chemical properties and has been used in various fields such as electronics and insulating materials. (Kong et al., 2017a; Li et al., 2018; Xu et al., 2019; Ding et al., 2020; Nie et al., 2020). However, its severe flammability with toxic gases and smoke during combustion limits its wide application (Zhang et al., 2018; Kong et al., 2019c; Yang et al., 2019). Therefore, searching for efficient and environmentally friendly flame retardants that can reduce the flammability of EP has become the pursuit of many researchers.

In recent years, transition metals and phosphorus-containing compounds have been found to have excellent ability to catalyze the formation of char and catalyze the conversion of harmful substances, arousing wide attention of researchers (Zheng et al., 2017; Sun et al., 2018; Peng et al., 2019; Kong et al., 2019a; Zhang et al., 2019; Zhou et al., 2019). A new flame retardant (P-MnMo6) was synthesized with 9,10-dihydro-9-oxa-10-phosphapentathrene-10-oxide (DOPO) with polyoxometalate and added to EP (Peng et al., 2020). The results demonstrated that the peak of heat release rate (PHRR) of EP/P-MnMo6-4 nanocomposites was reduced by 41% and the char yield increased significantly, and CO and smoke emissions were also greatly suppressed. In particular, the addition of ultra-thin layered nanomaterials can increase the viscosity of a polymer and form an insulating char layer during the combustion process, thereby slowing the oxygen flow rates and reducing the amount of combustible gas (Kong et al., 2018b, Asabina et al., 2019, Kong et al., 2019b). For example, the hybrid NiFe-LDH-MoS2 was prepared by a simple self-assembly method and blended into EP to...
prepare EP/NiFe-LDH-MoS2 nanocomposites. When 2 wt% NiFe-LDH-MoS2 was added to EP, the PHRR and total heat release (THR) values were reduced by 66 and 34%, respectively. The output of smoke and toxic gas, such as CO and CO2, was significantly reduced (Zhou et al., 2017). A multifunctional nanohybrid (Ti3C2Tx@MCA-3.0) was prepared by interacting titanium carbide nanosheets (Ti3C2Tx, MXene) with melamine cyanurate (MCA) via hydrogen bonding interactions. The significantly improved mechanical and fire-safe performances of TPU/Ti3C2Tx@MCA-3.0 were superior to those of thermoplastic polyurethane (TPU) nanocomposites filled with other nanoadditives (Shi et al., 2020). Therefore, it is possible that layered transition metal phosphide flame retardants could be prepared together with catalytic transition metals and phosphorus element, and applied to polymers, which will inevitably improve the flame retardancy of macromolecule polymers.

Graphene has attracted more and more attention in the flame retardancy of polymers due to its high specific surface area, thermal stability, and unique 2D structure (Cote et al., 2011; Yue et al., 2019). DOPO-rGO was added, the char yield and limiting oxygen index (LOI) value were increased by 81 and 30%, respectively, when only 4 wt% was added to EP, in the UL-94 tests, EP/4 GO-NiCoPO3 nanocomposites passed V-1 rating.

**EXPERIMENTAL SECTION**

**Materials**

Graphite powder (spectral pure), potassium permanganate (KMnO4, AR, ≥99.5%), cobalt(II) acetate tetrahydrate (C2H4CoO4·4H2O, AR, ≥99.5%), nickel(II) acetate tetrahydrate (C2H6NiO4·4H2O, AR, ≥98.0%), sodium pyrophosphate (Na2O·P2O5, AR, ≥99.0%), acetone (C6H12O, AR, ≥99.5%) and hydrogen peroxide (H2O2, AR, ≥30%) were purchased by Sinopharm Chemical Reagent Co., Ltd. Sodium nitrate (NaNO3, AR, ≥99.0%) and hydrogen peroxide (H2O2, AR, ≥30%) were purchased from Wuxi Jingshe Chemical Co., Ltd. Sulfuric acid (H2SO4, AR, 95–98%) was provided by Shanghai Jutai Special Reagent Co., Ltd. All chemicals were of analytical grade purity and used without any further purification.

**Preparation of NiCoPO3**

C6H6NiO4·4H2O (0.4 g), C6H6CoO4·4H2O (0.478 g), Na4O7P2·4H2O (0.839 g), and 10 ml of water were mixed together. Then, the above mixed solution was stirred at room temperature for 30 min and transferred to a 100-ml stainless steel autoclave lined with polytetrafluoroethylene heated at 180°C for 24 h. The products were washed several times with water and ethanol, and dried at 80°C for 24 h.

**Preparation of GO-NiCoPO3**

GO was prepared by a modified Hummer’s method (Yu et al., 2017). First, C6H6NiO4·4H2O (0.4 g), C6H6CoO4·4H2O (0.478 g), Na4O7P2·4H2O (0.839 g), and 15 ml (1 g/l) of GO were mixed together. Then, the above mixed solution was stirred at room temperature for 30 min and transferred to a 100-ml stainless steel autoclave lined with polytetrafluoroethylene heated at 180°C for 24 h. The black products were centrifuged and dried under vacuum at 80°C for 24 h.

**Preparation of Epoxy Resin/Graphene Oxide–Cobalt Nickel Phosphate Nanocomposites**

First, GO-NiCoPO3 was added to acetone and sonicated until completely dispersed; then, EP was added to the above solution and subjected to ultrasound. The homogenous system was stirred at 90°C, DDM was charged into the above system, and stirring was continued until DDM completely dissolved and blended vigorously for 5 min. The homogenized samples were centrifuged and cured at 110, 130, and 150°C/2 h. The preparation procedure of pure EP and EP/NiCoPO3 nanocomposites was exactly the same as the above process. The specific contents are shown in Table 1.

**Characterization**

X-ray powder diffraction (XRD) has a graphite monochromatic diffraction line of Cu Kα, λ = 1.5418 Å, an operating voltage of...
40 kV, and current of 100 mA. The diffractometer was of the Japanese Rigaku MAX-RB model. Fourier transform infrared spectra (FTIR) were tested by the KBr tableting method, and the spectral frequency ranges from 400 to 4,000 cm\(^{-1}\). It is a spectrometer of the 6700 model of Nicolet Instrument Co., Ltd. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) were used to observe the microstructures and morphology of NiCoPO\(_3\) and GO-NiCoPO\(_3\). The acceleration voltage was 100 kV, and the transmission electron microscope was of the Japanese JEOL JEM-100SX model.

Thermogravimetric (TG) analysis was carried out using a TG/DSC1 device manufactured by METTLER TOLEDO under a nitrogen atmosphere with a linear heating rate of 10°C min\(^{-1}\). LOI measurements were performed using an oxygen index model instrument (Fire Testing Technology, United Kingdom). The spline size was 130 mm\(^3\) × 6.5 mm\(^3\) × 3.2 mm\(^3\) according to ASTM D 2863-97. Based on ASTM D 3801, the vertical combustion test (UL-94) was carried out in a combustion chamber (Fire Testing Technology, United Kingdom), and the spline size was 130 mm\(^3\) × 12.7 mm\(^3\) × 3.2 mm\(^3\). Micro-combustion calorimetry (MCC) generally involved pulverizing a sample (5 mg) in a nitrogen stream (80 cm\(^3\) min\(^{-1}\)). The cleavage product was mixed with a stream of oxygen (20 cm\(^3\) min\(^{-1}\)) and then burned at 900°C. The furnace was heated to the desired temperature to obtain heat release parameters, which were measured using a MCC-2 calorimeter (Govmark, United States).

**RESULTS AND DISCUSSION**

**Structure and Performance of Graphene Oxide–Cobalt Nickel Phosphate**

The XRD is often used to investigate the lamellar structure and crystallinity of inorganic nanomaterials (Guo et al., 2020; Xue et al., 2020; Zhang et al., 2020). Figure 1A presents the XRD pattern of NiCoPO\(_3\), which reveals the characteristic peaks at 2\(\theta\) =

![Figure 1A](https://example.com/figure1a.png)

**TABLE 1 | Ingredients of EP nanocomposites.**

| Sample       | EP (wt%) | GO-NiCoPO\(_3\) (wt%) | NiCoPO\(_3\) (wt%) |
|--------------|----------|------------------------|--------------------|
| EP           | 100      | 0                      | 0                  |
| EP/10GO-NiCoPO\(_3\) | 99       | 1                      | 0                  |
| EP/2GO-NiCoPO\(_3\) | 98       | 2                      | 0                  |
| EP/4GO-NiCoPO\(_3\) | 96       | 4                      | 0                  |
| EP/6GO-NiCoPO\(_3\) | 94       | 6                      | 0                  |
| EP/8GO-NiCoPO\(_3\) | 92       | 8                      | 0                  |
| EP/4NiCoPO\(_3\) | 96       | 0                      | 4                  |

EP, epoxy resin; GO, graphene oxide; NiCoPO\(_3\), cobalt nickel phosphate.

![Figure 1B](https://example.com/figure1b.png)

![Figure 1C](https://example.com/figure1c.png)

![Figure 1D](https://example.com/figure1d.png)

**FIGURE 1 | (A) X-ray powder diffraction pattern of NiCoPO\(_3\); (B) X-ray powder diffraction pattern of GO-NiCoPO\(_3\); (C) TG curves of NiCoPO\(_3\) and GO-NiCoPO\(_3\); (D) Fourier transform infrared spectra spectra of NiCoPO\(_3\) and GO-NiCoPO\(_3\); the inset is Fourier transform infrared spectra legend of GO. Go, graphene oxide; NiCoPO\(_3\), cobalt nickel phosphate.**
13.3°, 17.9°, 26.1°, 26.7°, 26.9°, 27.4°, 29.9°, 33.8°, 38.6°, and 48.5°, corresponding to the orders of Co$_3$(PO$_4$)$_2$ on (101), (111), (102), (112), (202), (021), (012), (221), (031), and (402) planes, respectively. Simultaneously, the diffraction peaks are observed at 2θ = 17.5°, 23.5°, 26.0°, 37.2°, and 39.3°, corresponding to the position of Ni$_3$(PO$_4$)$_2$ on the (002), (102), (111), (211), and (021) (Li et al., 2017). Figure 1B shows the XRD pattern of GO-NiCoPO$_3$, and a weak characteristic diffraction peak of GO appears at 2θ = 9.8°, which may be caused by the low content of GO (Si and Samulski, 2008). GO has hydroxyl groups and carboxyl groups, and can form hydrogen bonds with the surface of NiCoPO$_3$, making the original strong diffraction peak weak. Figure 1C shows the TG curves of NiCoPO$_3$ and GO-NiCoPO$_3$. Before 200°C, due to dehydration of NiCoPO$_3$ nanosheets, NiCoPO$_3$, and GO-NiCoPO$_3$ had a little weight loss. After 200°C, NiCoPO$_3$ is decomposed into metaphosphoric acid and metal oxide, and the organic groups of GO also begin to decompose, but the weight loss of GO-NiCoPO$_3$ is less than that of NiCoPO$_3$ in the whole process (Zhao et al., 2010; Huang et al., 2016). The FTIR spectra of NiCoPO$_3$ and GO-NiCoPO$_3$ are shown in Figure 1D, and the FTIR legend of GO is embedded in the inset. The peak of 3,500 cm$^{-1}$ corresponds to the -OH stretching vibration of NiCoPO$_3$, and the characteristic peaks of the P-O structure are 1,182, 1,174, and 938 cm$^{-1}$. For GO-NiCoPO$_3$ nanosheets, the peak at 1,782 cm$^{-1}$ corresponds to the chary C=O stretching vibration peak. The peak at 1,434 cm$^{-1}$ corresponds to the epoxy group C-O, and the peak at 1,055 cm$^{-1}$ corresponds to the alkoxy C-O telescopic vibration peak. This further illustrates the successful preparation of GO-NiCoPO$_3$.

In order to understand the morphology and microstructure of the product in more detail, SEM and TEM tests were performed. The SEM image of NiCoPO$_3$ is presented in Figure 2A, which shows that NiCoPO$_3$ has an irregular layered structure of 100–200 nm. As can be seen from Figure 2B, the surface of GO is wrinkled, and the nanometer scale is about 500 nm (Stobinski et al., 2014). Figure 2C shows the SEM image of GO-NiCoPO$_3$. It can be seen that the lamellar structure is darker than NiCoPO$_3$, probably due to the addition of GO to the surface of NiCoPO$_3$. Figure 2D shows the TEM image of GO-NiCoPO$_3$. The morphology of GO-NiCoPO$_3$ is substantially smooth and flat, and the edge portion also has a typical lamellar shape.

**Thermal Stability of Epoxy Resin/Graphene Oxide–Cobalt Nickel Phosphate Nanocomposites**

TG curves were used to further study the effect of GO-NiCoPO$_3$ nanosheets on EP/GO-NiCoPO$_3$ nanocomposites. The TG curves of EP nanocomposites are shown in Figure 3, and the key data are listed in Table 2. Under the nitrogen atmosphere, pure EP begins to decompose ($T_{5\%}$) at 354°C and the 50% mass loss decomposition temperature ($T_{50\%}$) is 397°C, showing that the main thermal decomposition stage is mainly attributed to oxidation of the main C chain in EP, and the char residual is only 11.8 wt% at 700°C. The addition of GO-NiCoPO$_3$ markedly improves the thermal stability of EP.
When 1, 2, 4, 6, and 8 wt% GO-NiCoPO3 nanosheets are added to EP nanocomposites, the T5% and T50% are increased to 366, 367, 365, 360, and 400°C, 402, 402, 402, and 406°C, respectively. The amount of residual char in EP/GO-NiCoPO3 nanocomposites is also increased significantly compared with that of pure EP. Particularly, the residue of EP nanocomposites with 8 wt% GO-NiCoPO3 reaches up to 27.6 wt% at 700°C. Because of the lamellar structure of GO, it has a barrier effect and prolongs the time for the combustible gas to escape from the matrix to the surface of EP/GO-NiCoPO3 nanocomposites (Nine et al., 2017; Shi et al., 2018), so that the Ni ions and Co ions in NiCoPO3 have sufficient time to catalyze the carbonization of EP during the degradation process. The EP/4NiCoPO3 nanocomposites are used as a comparison sample to further verify that the incorporation of GO-NiCoPO3 in EP nanocomposites can improve its thermal stability. The T5% and T50% values of EP/4NiCoPO3 nanocomposites are 363 and 398°C, respectively, and the residue reaches 16.2% at 700°C. Compared to pure EP, the LOI value of EP/4NiCoPO3 nanocomposites is 27.9%, and it has no UL-94 rating, but EP/4GO-NiCoPO3 nanocomposites reach V-1 rating in UL-94 tests. The improvement in UL-94 rating is attributed to the catalytic formation of denser and richer char layer during thermal decomposition (Kong et al., 2018c).

UL-94 vertical burning tests and LOI are commonly used for evaluating the combustion properties of polymer composites. The results are shown in Table 3. The pure EP has no rating (NR) in the UL-94 test, and the LOI value is 25.7%. When 1 and 2 wt% GO-NiCoPO3 are added into the EP matrix, the LOI values of EP/GO-NiCoPO3 nanocomposites are increased to 27.1 and 28.3%, respectively. But they still have no UL-94 rating. With GO-NiCoPO3 increasing to 4 and 6 wt%, the LOI values of EP/GO-NiCoPO3 nanocomposites are increased to 30.3 and 29.7%, respectively, and 30% of 0.8s 94°C 2.4s 4.1°C 4.1°C 4.1°C

TABLE 2 | Thermogravimetric data of pure EP and EP nanocomposites.

| Sample           | T5% (°C) | T50% (°C) | Char residues at 700°C (wt%) |
|------------------|----------|-----------|------------------------------|
| Pure EP          | 354      | 397       | 11.8                         |
| EP/1GO-NiCoPO3   | 366      | 400       | 18.1                         |
| EP/2GO-NiCoPO3   | 367      | 402       | 20.4                         |
| EP/4GO-NiCoPO3   | 365      | 402       | 21.6                         |
| EP/6GO-NiCoPO3   | 369      | 402       | 22.5                         |
| EP/8GO-NiCoPO3   | 360      | 406       | 27.6                         |
| EP/4NiCoPO3      | 363      | 398       | 16.2                         |

EP, epoxy resin; Go, graphene oxide; NiCoPO3, cobalt nickel phosphate.

TABLE 3 | LOI and UL-94 results of pure EP and EP nanocomposites.

| Sample           | LOI (vol%) | Flame retardancy | UL-94 test | Rating |
|------------------|------------|------------------|------------|--------|
| Pure EP          | 25.7       | >50              | NR         |
| EP/1GO-NiCoPO3   | 27.1       | 68.5             | NR         |
| EP/2GO-NiCoPO3   | 28.3       | 54.4             | NR         |
| EP/4GO-NiCoPO3   | 30.3       | 44.0             | V-1        |
| EP/6GO-NiCoPO3   | 29.7       | 46.5             | V-1        |
| EP/8GO-NiCoPO3   | 29.1       | 51.2             | NR         |
| EP/4NiCoPO3      | 27.9       | 63.5             | NR         |

LOI, limiting oxygen index; EP, epoxy resin; Go, graphene oxide; NiCoPO3, cobalt nickel phosphate. Combustion performance of EP/GO-NiCoPO3 nanocomposites.

reaching 365 and 402°C, respectively, and the residue reaches 21.6% at 700°C. Compared with pure EP, the TG data of EP/4NiCoPO3 and EP/4GO-NiCoPO3 nanocomposites are significantly improved. The above results indicate that NiCoPO3 has excellent performance in catalyzing char formation, but the char layer is loose and weak. The layered GO can increase the viscosity of the polymer and combine the Co, Ni, and P in NiCoPO3 through covalent and non-covalent bonds (Cao et al., 2016; Xu et al., 2016), so that EP nanocomposites can be catalytic formed denser and richer char layer during thermal decomposition (Kong et al., 2018c).

UL-94 vertical burning tests and LOI are commonly used for evaluating the combustion properties of polymer composites. The results are shown in Table 3. The pure EP has no rating (NR) in the UL-94 test, and the LOI value is 25.8%. When 1 and 2 wt% GO-NiCoPO3 are added into the EP matrix, the LOI values of EP/GO-NiCoPO3 nanocomposites are increased to 27.1 and 28.3%, respectively. But they still have no UL-94 rating. With GO-NiCoPO3 increasing to 4 and 6 wt%, the LOI values of EP/GO-NiCoPO3 nanocomposites are increased to 30.3 and 29.7%, respectively, and they can reach the V-1 level in UL-94 tests. However, with the amount of GO-NiCoPO3 reaching 8 wt% in the EP matrix, the LOI value of EP/GO-NiCoPO3 nanocomposites is slightly reduced to 29.1%, and it still has no UL-94 rating. This may be caused by the excessive addition of GO-NiCoPO3, which cannot be uniformly dispersed in the EP matrix. The comparative sample EP/4NiCoPO3 nanocomposites have a LOI value of 27.9%, and it has no UL-94 rating, but EP/4GO-NiCoPO3 nanocomposites reach V-1 rating in UL-94 tests. The improvement in UL-94 rating is attributed to the catalytic formation of denser and richer char layer during thermal decomposition (Kong et al., 2018c).
rating and LOI values of EP/GO-NiCoPO3 nanocomposites is mainly attributed to the synergistic flame retardant effect of GO and NiCoPO3. On the one hand, GO containing a large number of organic groups (hydroxyl, carboxyl, epoxy, etc.) provides active sites that combine with transition metal ions in NiCoPO3, which not only play a barrier effect for protecting the unburned EP nanocomposites below but also catalytically convert toxic gases to nontoxic gases. On the other hand, the phosphate ions in NiCoPO3 are converted into metaphosphoric acid and polymetaphosphoric acid during the combustion process. Polymetaphosphoric acid has strong dehydration properties, which can dehydrate and char the polymer to form a char film to isolate the air, thereby changing the combustion process and improving the thermal stability of EP (Kong et al., 2017c; Wu et al., 2018; Guo et al., 2019).

MCC tests were performed to further verify the combustion performance of EP/GO-NiCoPO3 nanocomposites. The MCC tests were used to evaluate the potential fire hazard of EP/GO-NiCoPO3 nanocomposites by measuring the HRR, the PHRR, and the THR (Shi et al., 2019). Detailed data are listed in Table 4, and the HRR and THR curves of pure EP and EP/GO-NiCoPO3 nanocomposites are shown in Figure 4. The PHRR value of pure EP is 560.9 W/g. Compared with pure EP, when 1, 4, and 8 wt% GO-NiCoPO3 are added into the EP matrix, the PHRR values are decreased to 490.4, 458.6, and 427.1 W/g, respectively, reducing about 12.6, 18.2, and 23.9%, respectively. The THR values of EP/1GO-NiCoPO3, EP/4GO-NiCoPO3, and EP/8GO-NiCoPO3 nanocomposites are 26.2, 24, and 22.9 KJ/g, reducing about 33.5, 39.1, and 41.9%, respectively. This fully indicates that GO-NiCoPO3 can promote the formation of a dense and strong char layer on the surface of the polymer and prevent the transfer of external heat and oxygen to the EP matrix, inhibiting polymer combustion and reducing heat release. However, the PHRR value (557.8 W/g) and THR value (30.7 KJ/g) of EP/4NiCoPO3 nanocomposites are higher than those of EP/4 GO-NiCoPO3 and slightly lower than those of pure EP. This may be due to the addition of NiCoPO3: although it has a certain catalytic char formation, the char layer formed is thin and sparse, which has a poor barrier effect so that the heat release amount is not significantly reduced. When NiCoPO3 modified by GO with a rich C structure is added to the EP matrix, the viscosity of the EP/GO-NiCoPO3 polymer increases and reduces the burning rates, which provides sufficient time to catalyze the carbonization of the matrix in the polymer (Wang et al., 2017; Feng et al., 2018). The char layer, whose quantity and quality have been significantly changed, can cover the polymer surface, prevent heat from escaping, inhibit the combustion, and enhance the flame retardant performance of the composites (Zhang et al., 2016; Kong et al., 2017b).

CONCLUSIONS

In summary, NiCoPO3 nanosheets and GO-NiCoPO3 were synthesized by a simple solvothermal method. The TG results showed that the addition of GO-NiCoPO3 promoted char formation and enhanced the thermal stability of the polymer at high temperatures. The LOI and UL-94 data showed that when 4 wt% GO-NiCoPO3 was added, the LOI value was as high as 30.3%, and it reached UL-94 V-1 rating. The MCC results showed that the addition of GO-NiCoPO3 significantly reduced the PHRR and THR values of EP nanocomposites. Compared with pure EP, the THR value of EP/8GO-NiCoPO3 nanocomposites was decreased by 41.9%. These results indicated that GO-NiCoPO3 increased the flame retardancy of EP/GO-NiCoPO3 nanocomposites to some extent. This was mainly due to the fact that GO-NiCoPO3 formed dense carbonaceous protection layers to reduce heat transfer, inhibit combustion, and improve thermal stability of composites.
DATA AVAILABILITY STATEMENT

All datasets presented in this study are included in the article.

AUTHOR CONTRIBUTIONS

QK and JZ conceived and designed the study and experiment plan and wrote the manuscript. CZ drafted the manuscript. MZ and TZ analyzed the experimental results.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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