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## Superior flame retardancy of epoxy resin by the combined addition of graphene nanosheets and DOPO

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In this paper, the thermal stability and fire retardant behavior of epoxy resin (ER) composites filled with graphene nanosheets (GNS) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) were investigated. Addition of GNS and DOPO changed the decomposition pathway of ER. During combustion, DOPO played a key flame retardancy role in the gas phase and the char enhancement in the condensed phase, while GNS played an effect in the condensed phase. Addition of 5 wt% GNS and DOPO separated, the peak heat release rate (PHRR) of ER was reduced from 1194 kW/m<sup>2</sup> to 513.9 kW/m<sup>2</sup> and 937.1 kW/m<sup>2</sup>, respectively. With the combined addition of GNS and DOPO, the flame retardancy of ER composites was significantly improved. The PHRR was reduced to 396 kW/m<sup>2</sup> at the addition of 2.5% GNS and 2.5% DOPO. The same tendency was obtained for the total heat release (THR), showing a synergistic effect between GNS and DOPO in improving the flame retardancy of ER composites. The combined addition of GNS and DOPO extended the diffusion path for heat and combustible gas while DOPO captured the free radicals which further retarded ER degradation.

### 1. Introduction

Epoxy resin (ER) is one of the major thermosetting resins and has many attractive properties. It has been widely used as matrix for coatings, adhesives and composites in electrical industries, where flame retardant property is extremely important [1]. However, one of the major drawbacks of epoxy resin is it is flammable. There is a need to develop an ER with reduced flammability. Many researchers are working on the development of anti-flammable ER by either modifying its composition/structure or by the use of fire retardant additives [1-4]. Halogen-based flame retardants have been developed which are effective in improving the flame retardancy of ER. However, there are many concerns on their use due to the potential release of corrosive and toxic chemicals during combustion [1]. Therefore, the development of halogen-free flame retardants for epoxy resins has attracted increasing attention from both academe and industry.

One of such halogen-free alternatives is phosphorus-based flame retardant which has demonstrated excellent fire resistance for ER. Several phosphorus-containing flame retardants have been investigated [3-5]. They impart flame

retardancy to polymers by covering the outer layer of the polymers with a nonflammable coating and releasing phosphoric acid during combustion. The produced phosphoric acid reacts with the polymer matrix, providing radical-trapping ability [6]. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a highly effective phosphorus-based intumescent flame retardant, which has high thermal stability, good oxidation and water resistance. The rigid and bulky DOPO group contains an ultra-thermally stable P-O-C bond which can be attributed to the protection of O=P-O group by phenylene groups. However, DOPO with high phosphorus content can sometimes dramatically deteriorate the general properties of matrix and reduce the effectiveness of fire retardancy due to elutriation. Although DOPO has been confirmed as an effective flame retardant, there are still questions remained unanswered, such as how to combine DOPO with other flame retardants to further improve flame retardant efficiency, and what are the different mechanisms of flame retardancy in different materials [6].

Nano-additives are becoming another attractive candidate as halogen-free flame retardant. Some nano-additives have been proved not only improving flame retardancy, but also enhancing the mechanical properties of composites. Graphene nanosheet (GNS) is a new type of nano-sized filler with exceptional functional properties, high mechanical strength and chemical stability. It has drawn considerable interest in applications, such as nanoelectronics, sensors, batteries, supercapacitors, hydrogen storage and nanocomposites. In our previous work, GNS has shown the

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potential to improve the flame retardancy of ER [2]. GNS can effectively decrease melt flow and inhibit the flammable drips of ER during combustion, which means it prevents flame from spreading. A small amount of GNS can reduce the total heat release and increase the limiting oxygen index (LOI) and the amount char residues in ER composites.

In recent years, there are growing interest to incorporate small amount of novel nanoparticles into traditional flame retardants to produce highly efficient flame retardant composites with low additive contents [1, 7-12]. For example, DOPO has been grafted onto the surface of reduced graphite oxide (GO) to develop a synergistic DOPO-rGO flame retardant [8]. The addition of DOPO-rGO (up to 10 wt%) in composites improves not only the thermal stability of ER, but also the char yield and LOI. The phosphorus and GO layer cause the formation of a continuous and insulating char [8]. In another example, the flame retardant mechanism of phosphorus-silicon synergism in ER has been widely reported [7, 10-17]. Zhang, et al. indicated that DOPO and polyhedral oligomeric silsesquioxane (DOPO-POSS) can reduce the HRR of ER and accelerate the formation of char [11]. The production of char and the release of phosphorus-containing compounds drastically improve the flame retardancy of ER, which is the typical synergistic effect of phosphorus-silicon on flame retardancy of ER [10, 12]. The hexa-(phosphaphenanthrene-hydroxyl-methyl-phenoxy)-cyclotriphosphazene (HAP-DOPO) also shows a remarkable flame retardant effect in ER. During combustion, HAP-DOPO continuously release PO free radicals and *o*-phenylphenoxy free radicals, inhibiting the chain reaction of decomposition and demonstrating flame retardant effect in gas phase [14].

Since GNS and DOPO play the flame retardant role in different stages of combustion with different mechanisms, it is expected that the simultaneous addition of DOPO and GNS could combine the advantages of flame retardant effect of DOPO and the thermal stability of GNS. A low filler content and high efficiency is expected to achieve. In this paper, GNS was combined with DOPO to study their flame retardancy on ER. The possible flame retardancy reasons and the synergistic mechanisms was also explored.

## 2. Experimental methods

### 2.1. Materials

Epoxy resin (JY-256, density 1.13-1.15 g/cm<sup>3</sup>, epoxy value 0.54-0.56 mol/100g) was obtained from Jiafa Chemical Co. Ltd., Changshu, China. Poly(propylene glycol) bis (2-aminopropyl) ether (Jeffamine D230, active hydrogen equivalent 61g/eq, produced by Huntsman Co., Houston, USA.) were used as curing agents. The mass ratio of ER/curing agents equals to 100/34. 9,10-dihydro-9-oxa-10-

phosphaphenanthrene-10-oxide (DOPO, purity>99%) were supplied by Qingdao Lianmei Chemical Co. Ltd., Qingdao, China. Graphene nanosheets (JCGNP-1, density 2.25 g/cm<sup>3</sup>, purity >99.5%) was provided by Cano Technology Co. Ltd., Nanjing, China. All of the GNS was sonicated in ice bath before use. **Figure 1** illustrates the SEM images of GNS before and after sonication.

### 2.2. Preparation of ER/GNS, ER/DOPO and

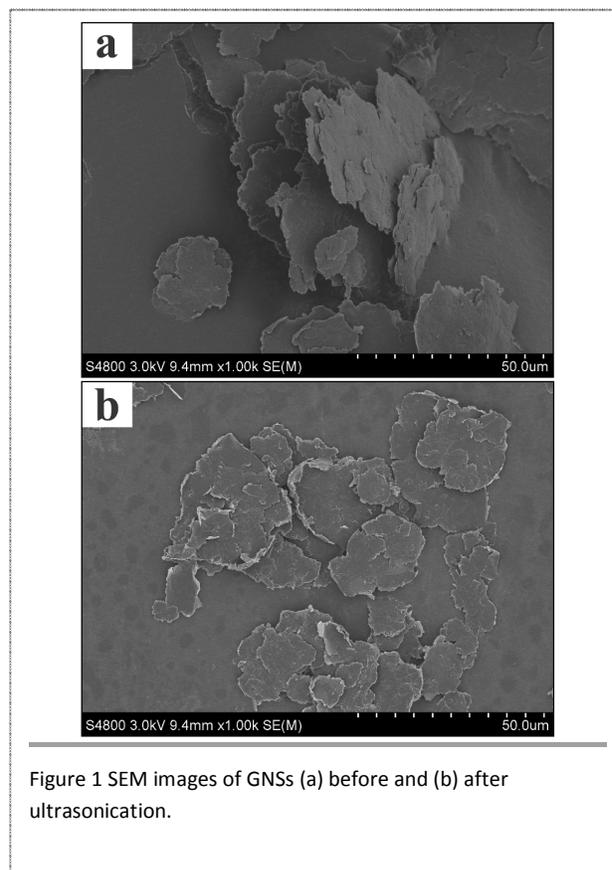


Figure 1 SEM images of GNSs (a) before and (b) after ultrasonication.

### ER/GNS/DOPO composites

The ER/GNS samples were prepared by solution polymerization. A measured amount of GNS was ultrasonically dispersed in acetone in an ice bath and stirred for 1.5 h. The epoxy monomer was added to the mixture, sonication was continued for another 1.5 h. To remove the acetone, the solution was heated to 70°C for 5 h, followed by rotary evaporation at 70°C for 1 h. Subsequently, after cooling down to room temperature, the curing agent was added into the above solution and stirred for 0.5 h. The mixture was again placed in a vacuum chamber to degas for 1 h. To carry out ER/GNS composites, the as prepared mixture was carefully poured into silicone rubber molds with a syringe, followed by pre-curing at 50°C for 5 h, and post-curing at 110°C for 2 h.

The ER/DOPO samples were prepared by in situ polymerization. A measured amount of DOPO was mixed with ER. The mixture was then heated to 130°C and stirred until DOPO was dissolved completely. After cooling to room temperature, the curing agent was added into the above solution and stirred for 0.5 h. The same curing process was followed.

To prepare the ER/GNS/DOPO composites, the uniform ER/GNS mixture and the ER/DOPO mixture obtained from the above steps was mixed and stirred for 0.5 h at 70°C, after cooling to room temperature, the curing agent was added into the above mixture and stirred for 0.5 h. The same curing process was followed.

The samples were identified as ER/GNS $x$  (mass ratio of ER/GNS=100/ $x$ ), ER/DOPO $y$  (mass ratio of ER/DOPO=100/ $y$ ) and ER/GNS $x$ /DOPO $y$  (mass ratio of ER/GNS/DOPO = 100/ $x/y$ ).

### 2.3. Characterizations

Scanning electron microscope (SEM, Hitachi S-4800) was used to observe the micro-morphology of composites. The samples were coated with a gold layer about 10 nm in thickness to improve the surface conductivity. X-ray diffraction (XRD) was applied to determine the interlayer

distances of GNS. All tests were conducted by using a Rigaku X-ray generator (Cu K $\alpha$  radiation) in the reflection mode at room temperature. Limiting oxygen index (LOI) was measured by using an HC-2 Oxygen Index Instrument (Jiangning Analyser Instrument, China) on sheets (100×6×3mm<sup>3</sup>) according to ASTM D2863-2008. Thermogravimetric analysis (TG) was carried out using a TGA 209 F1 thermal analyzer (NETZSCH, Germany). Samples were heated to 700°C at a heating rate of 20°C/min, and each specimen was examined in triplicate. The accuracy for the temperature and mass measurements were  $\pm 1^\circ\text{C}$  and  $\pm 0.1\text{wt}\%$ . Cone calorimeter measurements were performed according to ISO 5660 protocol, using a FTT0007 (Fire Testing Technology, UK). Typical results from cone calorimetry were reproducible within  $\pm 10\%$ . The parameters are the average of two measurements.

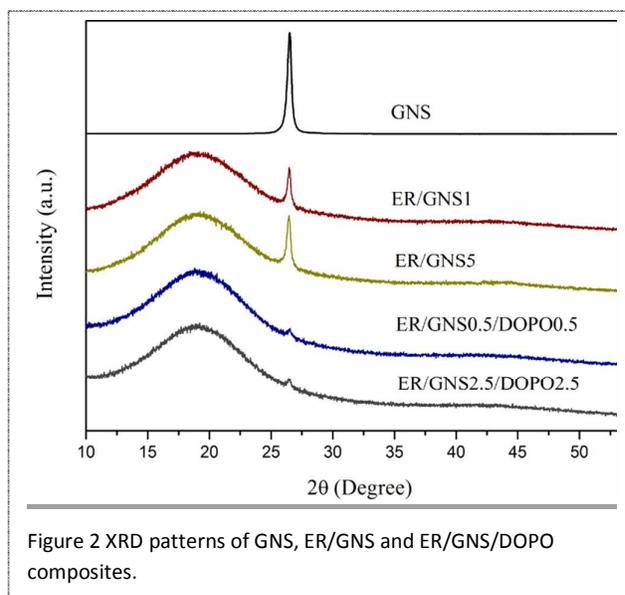


Figure 2 XRD patterns of GNS, ER/GNS and ER/GNS/DOPO composites.

## 3. Results and discussion

### 3.1. Structure and morphologies

XRD patterns of GNS, ER/GNS1, ER/GNS5, ER/GNS0.5/DOPO0.5 and ER/GNS2.5/DOPO2.5 composites are shown in **Figure 2**. The sharp diffraction peak at 26.5° in the GNS sample indicates that the original interlayer spacing of GNS is 0.34 nm. The diffraction peak of GNS in ER/GNS and ER/GNS/DOPO composites does not shift regardless of the amount of GNS added. There are still some GNS agglomerations exist. However, it is observed that the peak intensity varies with GNS content. When GNS and epoxy monomer are dispersed in acetone and ultra-sonication is applied, GNS would be exfoliated in a certain extent, as can be seen in **Figure 1**. Due to the removal of acetone, some GNS agglomerations appeared in epoxy monomer. Results from **Figure 1** and **Figure 2** indicate that the restacking and agglomeration of the GNS still exist in ER/GNS and ER/GNS/DOPO composites.

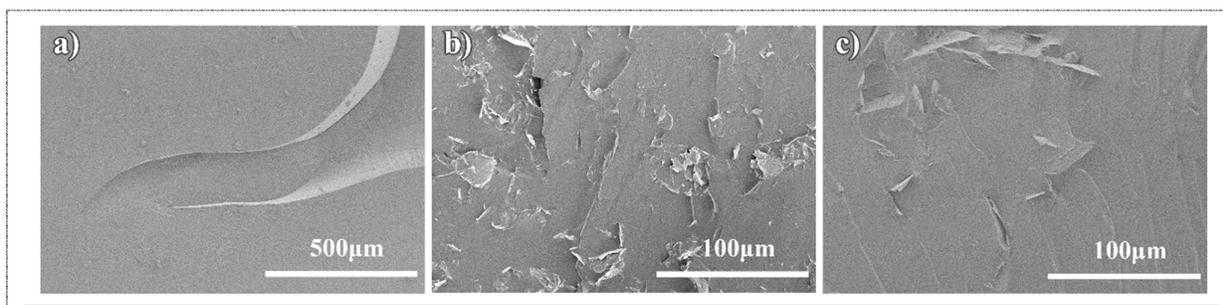
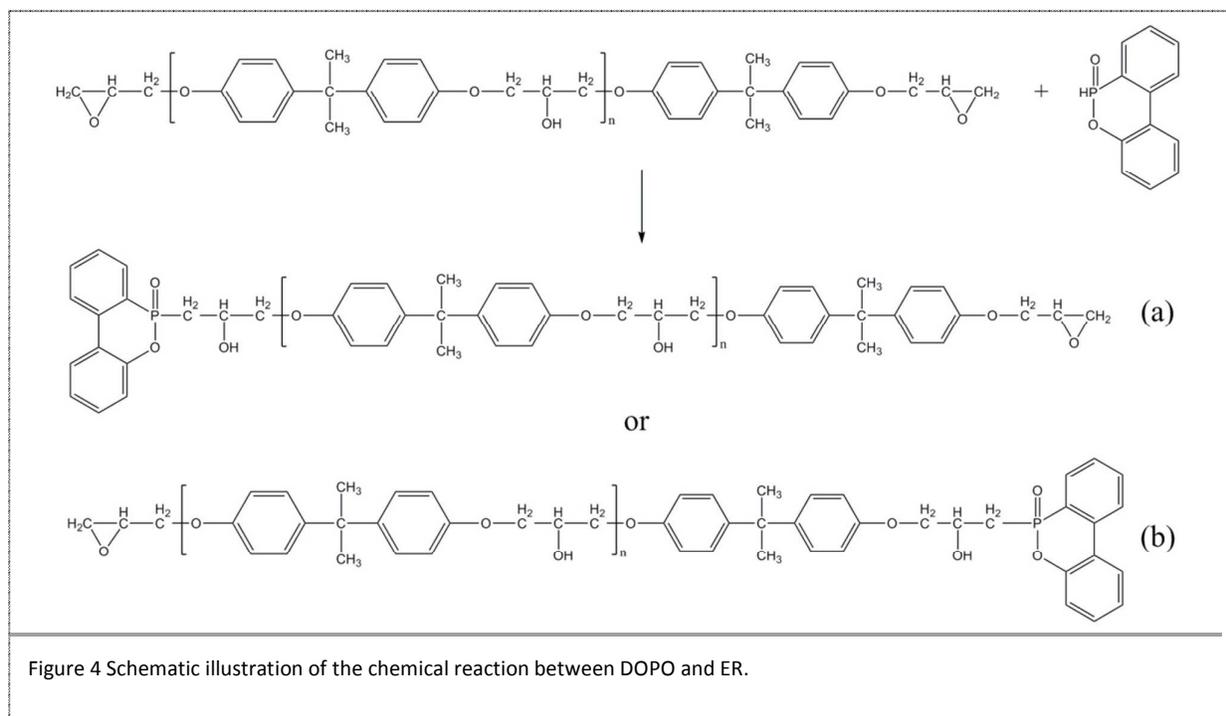


Figure 3 SEM images of (a) ER/DOPO5, (b) ER/GNS5, (c) ER/GNS2.5/DOPO2.5 composites.



To study the morphology of ER composites, the ER/DOPO5, ER/GNS5 and ER/GNS2.5/DOPO2.5 samples were frozen in liquid nitrogen and then fractured immediately. The SEM images of the fracture surface are shown in **Figure 3**. Using liquid nitrogen refrigeration, the morphologies of the additives and their distribution in matrix can be well maintained in their primary state. **Figure 3a** shows that DOPO is well compatible with ER, no phase separation was observed. This is because DOPO can react with ER by the epoxy-ring opening reaction. **Figure 4** is the schematic illustration of the chemical reaction between DOPO and ER. Two products with different structures were formed. In ER/GNS5 and ER/GNS2.5/DOPO2.5, small GNS sheet separation from matrix was observed in **Figure 3b and c**. No phase separation in ER and DOPO explains why DOPO is not appeared in **Figure 3c**. GNS is uniformly dispersed in ER matrix.

### 3.2. Thermal degradation and flame retardant properties

The TG, DTG curves of ER, DOPO and ER/DOPO composites under nitrogen atmosphere are shown in **Figure 5**. As can be seen, the degradation of DOPO occurs earlier than that of ER, with two decomposition steps, maximum mass loss rate ( $T_{max}$ ) at 317.4°C and 453.1°C respectively. About 11wt% char residues are left at 700°C. ER decomposes in a single

step with  $T_{max}$  at 388.0°C and with char residue at the end. The decomposition of ER/DOPO composites occurs earlier than that of ER due to the earlier decomposition of DOPO, and char residues are left. The char residues increase gradually with the increase of DOPO, and the  $T_{max}$  of ER/DOPO composites is decreased gradually. This is because ER/DOPO composites decompose at lower temperatures,

and during the decomposition, more phosphorus-carbon char residues cover the surface of composites, which will prevent the contact of oxygen and heat transfer between flame zone and matrix.

Synergistic effect means the enhanced performance of the mixture of two or more components compared with the simple added up of the performance if each component is added separately at the same concentration. To investigate whether there is a synergistic effect between GNS and DOPO to improve the flame retardancy of ER, the TG measurements of ER, ER/GNS1, ER/DOPO1, ER/GNS0.5/DOPO0.5 composites under nitrogen atmosphere were performed and the result are showed in **Figure 6**. The total additives in the three composite materials are kept at the same level, 1%.

As can be seen from **Figure 6**, the decomposition of ER/GNS, ER/DOPO and ER/GNS/DOPO composites occurs earlier than the pure ER. This is because that DOPO and the oxygen-containing groups on the surface of GNS are decomposed earlier than ER. However, both GNS and DOPO increase the char formation of ER, which has the flame retardant effect.

There is a slight but not significant synergistic effect of simultaneous addition of 0.5 wt% GNS and 0.5 wt% DOPO to improve the thermal stability of ER. The initial decomposition temperature and the char residues of ER/GNS0.5/DOPO0.5 are higher than ER/GNS1 and ER/DOPO1.

To evaluate the fire retardant behavior of ER, ER/GNS5, ER/DOPO5 and ER/GNS2.5/DOPO2.5 composites, cone calorimeter test was carried out to simulate real fire conditions. The cone calorimeter enables quantitative

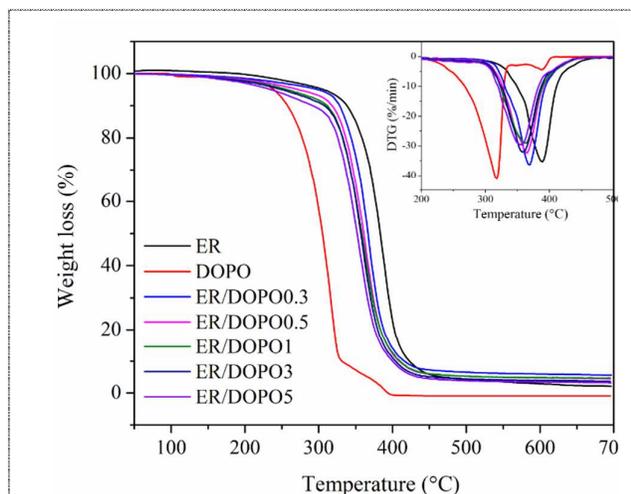


Figure 5 TG and DTG curves of ER, DOPO and ER/DOPO composites under nitrogen atmosphere.

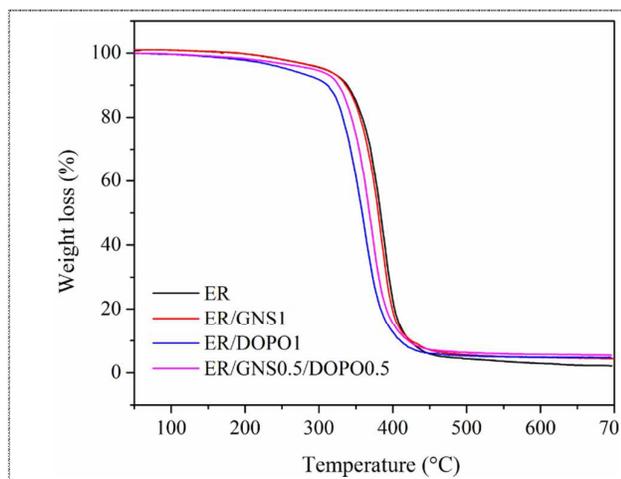


Figure 6 TG curves of ER, ER/GNS1, ER/DOPO1 and ER/GNS0.5/DOPO0.5 composites under nitrogen atmosphere.

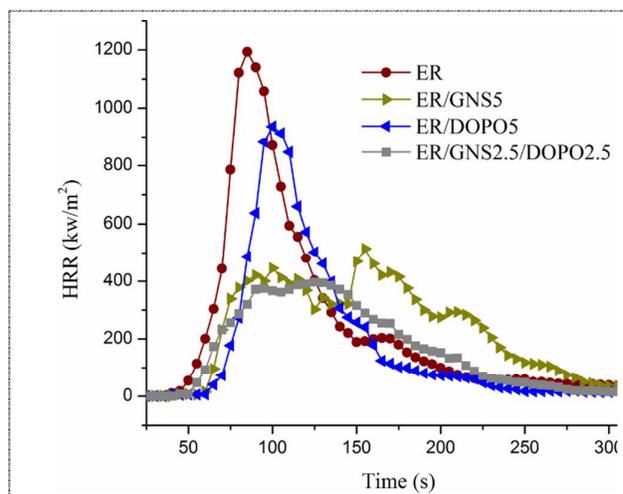


Figure 7 HRR curves of ER, ER/GNS5, ER/DOPO5 and ER/GNS2.5/DOPO2.5 composites from cone tests.

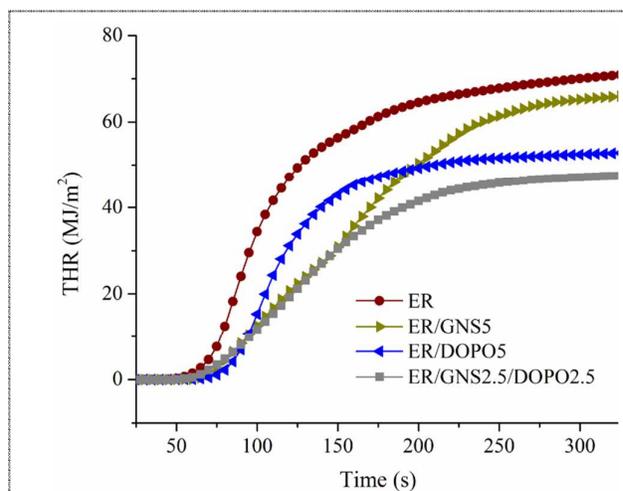


Figure 8 THR curves of ER, ER/GNS5, ER/DOPO5 and ER/GNS2.5/DOPO2.5 composites from cone tests.

analysis of the flammability using the important information received during combustion such as heat release rate (HRR), peak heat release rate (PHRR), time to ignition (TTI) and total heat released (THR). The experimental results are summarized in **Table 1** and **Figure 7-8** for all samples.

**Figure 7** shows the HRR curves of ER, ER/GNS, ER/DOPO and ER/GNS/DOPO composites. HRR and PHRR are the most important parameters to evaluate fire safety. For the pure ER, it burned rapidly after ignition and HRR shows a sharp peak with a PHRR of about  $1194 \text{ kW/m}^2$ . When ER absorbed enough heat, the temperature of sample increased rapidly and the sample started to decompose, producing a number of combustible gases which caused further combustion and released more amounts of heat. The HRR increases quickly to  $1200 \text{ kW/m}^2$  and then declines after the PHRR.

When GNS or DOPO is added into ER respectively, both of them have a significant effect on flame retardancy of ER. The addition of GNS or DOPO changes the decomposition pathway of ER composite. In ER/DOPO composite, a sharp peak of HRR still exists, however the PHRR is reduced to  $937 \text{ kW/m}^2$ . This may be because DOPO can act in either the gas phase via flame inhibition or in the condensed phase via char formation at the same time [3]. In ER/GNS composite, the changes of the HRR curve is more obvious. It is worth noting that there are two small peaks of HRR at about 100 s and 155 s respectively. The PHRR is at much lower level, about  $500 \text{ kW/m}^2$ . The improvement of HRR can be attributed to the formation of more compact and continuous ER-GNS char which protects the polymer matrix more efficiently during combustion. However, as the combustion continues, it generates more gas and can cause the char broken. When

Table 1 Some important data from cone tests.

Sample	TTI (/s)	PHRR (KW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	EHC (MJ/kg)	MLR (g/s)	TSP (m <sup>2</sup> )	CO (g/s)	CO <sub>2</sub> (g/s)
ER	34	1193.6	72.5	20.9	0.167	441.4	0.37	6.23
ER/GNS5	34	513.9	66.6	16.4	0.127	449.9	0.28	9.10
ER/DOPO5	30	937.1	53.1	25.9	0.087	404.0	0.31	4.99
ER/GNS2.5/DOPO2.5	27	396.2	48.1	18.4	0.105	502.5	0.31	6.76

the char was broken, the flammable gases and heat spread out, resulting in the increase of HRR again and forming the second HRR peak. This phenomenon was also mentioned in our previous study [2], which is the reason why we combine GNS and intumescent flame retardants to further improve the flame retardancy of ER. In ER/GNS2.5/DOPO2.5 composites, the HRR curve has the most significant change that PHRR was reduced to 396 kW/m<sup>2</sup>, which is smaller than that of both ER/GNS5 and ER/DOPO5 composites. This phenomenon indicates that there is a synergistic effect of simultaneous addition of GNS and DOPO to reduce the HRR of ER.

**Figure 8** shows the THR curves of ER, ER/GNS, ER/DOPO and ER/GNS/DOPO composites. The trend of the total heat release curves in ER and ER composites is similar. The THR of ER, ER/GNS5, ER/DOPO5 and ER/GNS2.5/DOPO2.5 composites is 72.5 MJ/m<sup>2</sup>, 66.6 MJ/m<sup>2</sup>, 53.1 MJ/m<sup>2</sup> and 48.1 MJ/m<sup>2</sup> respectively. All the THR values of the ER composites are lower than pure ER. GNS causes a more significant reduction in THR than DOPO. Simultaneous addition of GNS and DOPO is more effective than adding GNS and DOPO alone even at the same total addition level. Some synergistic effect between GNS and DOPO exists to reduce the THR of ER composites.

TTI is used to determine the influence of a flame-retardant on ignitability. Ignition occurs when the volatiles are sufficient to be ignited by a spark. As shown in **Table 1**, the TTI of pure ER is 34 s, the ER/GNS composite has the same TTI as pure ER. A decrease in TTI is detected when DOPO is added. This is because the decomposition of DOPO is before the decomposition of ER which can be seen in TG curves in

**Figure 5**. The TTI is even shorter with the simultaneous addition of GNS and DOPO.

Effective heat of combustion (EHC) refers to the combustion rate of volatile production in the gas phase during the combustion process. The EHC of pure ER is 20.9 MJ/kg while the EHC of ER/DOPO is 25.9 MJ/kg. Thus, DOPO has a flame retardant effect on ER in the gas phase to some extent. Mass loss rate (MLR) is a factor that can reflect the thermal degradation in the condensed phase during combustion process. The MLR of pure ER is 0.167 g/s. To compare, the MLR of ER/GNS5, ER/DOPO5 and ER/GNS2.5/DOPO2.5 composites are 0.127, 0.087 and 0.105 g/s respectively, which are lower than the MLR of pure ER. This indicates that both GNS and DOPO play a flame retardant effect in the condensed phase during combustion in the ER composites.

The total smoke production (TSP) is also an important parameter to investigate the flame retardant properties. The TSP of pure ER is 441.4 m<sup>2</sup> and the TSP of ER/GNS5, ER/DOPO5 and ER/GNS2.5/DOPO2.5 composites are 449.9 m<sup>2</sup>, 404.0 m<sup>2</sup> and 502.5 m<sup>2</sup> respectively. Apparently, the addition of DOPO has a smoke suppression effect in ER composites while GNS has not such an effect.

The amount of CO can be used as a reflection of the content of toxic gases during combustion. The CO release rate in pure ER is 0.37 g/s. When GNS and DOPO were added separately, both of them can effectively reduce the amount of toxic gases produced during combustion of ER. The addition of GNS and DOPO simultaneously can also decrease the CO release rates but no synergism was found between them. Besides, DOPO can reduce the amount of CO<sub>2</sub> while GNS cannot.

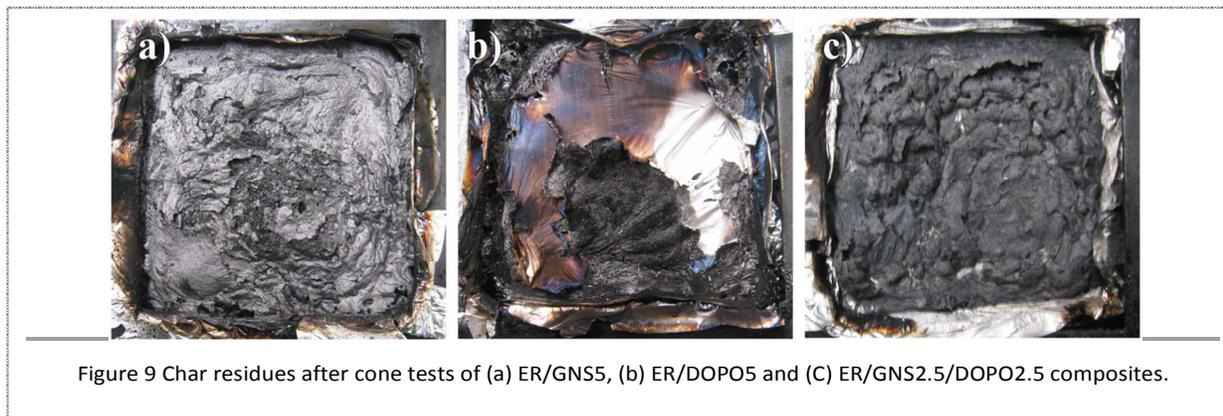


Figure 9 Char residues after cone tests of (a) ER/GNS5, (b) ER/DOPO5 and (c) ER/GNS2.5/DOPO2.5 composites.

Table 2 LOI data of ER, ER/GNS, ER/DOPO and ER/GNS/DOPO composites.

Sample	LOI
ER	15.9
ER/GNS1	19.5
ER/GNS3	21.0
ER/GNS5	21.4
ER/DOPO1	19.3
ER/DOPO3	22.8
ER/DOPO5	26.1
ER/GNS0.5/DOPO0.5	16.6
ER/GNS1.5/DOPO1.5	21.2
ER/GNS2.5/DOPO2.5	22.7

The LOI data of ER, ER/GNS, ER/DOPO and ER/GNS/DOPO composites are listed in **Table 2**. Enhanced flame retardancy appeared with the increase of GNS and DOPO loading. However, there is no synergistic effect between GNS and DOPO on the LOI in ER. This is because, ER used in this research have a low viscosity, which tends to spread flame away from a fire source by melting and producing flammable drips during combustion [2]. This is a decisive factor that affected LOI in ER composites. The melt viscosity of ER composites increases significantly during combustion when GNS and/or DOPO are added. In LOI tests, it was observed that ER was melting and formed some flammable drips during combustion while ER/GNS, ER/DOPO, ER/GNS/DOPO composites was not.

Some interesting information is found by the visual observation of char residues after cone calorimeter test. The pure ER sample is completely burned during combustion, and no obvious char residue is found, which indicates the weak thermal stability of ER. From **Figure 9**, ER/GNS5, ER/DOPO5 and ER/GNS2.5/DOPO2.5 composites have a different amount of char residue with different morphologies.

The char of ER/GNS5 presents a continuous and uniform char layer with some bubble-like structures and micro pores. This phenomenon could be attributable to the increase of the viscosity of thermal degradation products which could swell during the gas release. A small amount of char forms in ER/DOPO5 which is thin and not continuous. This may be because the nonflammable coatings from the small amount of DOPO are not enough to cover the whole matrix to protect it from heat and oxygen.

The char of ER/GNS2.5/DOPO2.5 is more complete and compact than ER/DOPO5, and the content of char residue is larger. Compared with ER/GNS 5, the char of ER/GNS2.5/DOPO2.5 is similar, but the bubble-like structure is more in the char surface. In summary, DOPO promotes the char formation, and GNS enhances the strength of the char layer. The incorporation of GNS and DOPO simultaneously into ER leads to a synergistic flame retardant effect.

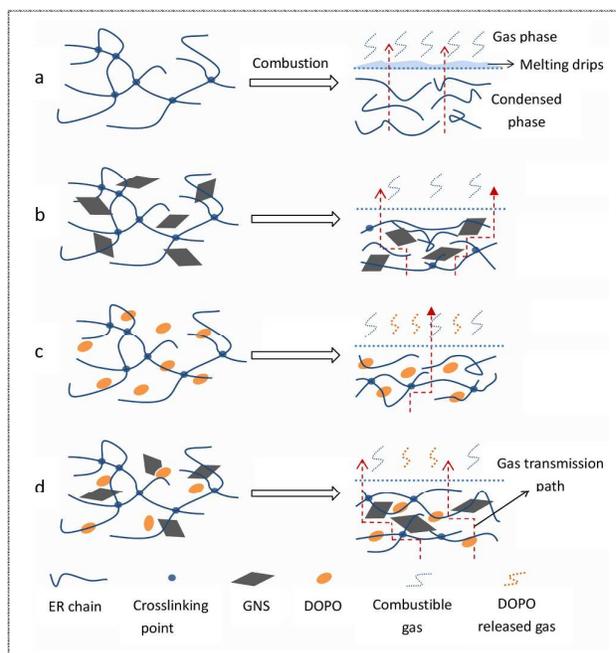


Figure 10 Schematic illustration of the flame retardancy effect of GNS and DOPO in ER combustion.

**Figure 10** is the schematic illustration of the flame retardancy effect of GNS and DOPO in ER composites. During combustion, low viscosity ER was degradation and its crosslinking points were broken. The released combustible gas and heat passed through the matrix without hindrance. ER formed some flammable drips and discontinuous char. In ER/GNS composite, the layered GNS hindered the transfer of heat and gas, hence retarded the process of combustion. Extended GNS-ER interactions increased the viscosity of the ER melt, which limited flame propagation through the inhibition of dripping. In ER/DOPO composite, DOPO released the PO radical which trapped the H and OH radicals in the gas phase, retarded polymer degradation and combustion. Meanwhile, the pyrolysis products of acid source from DOPO catalyzed the formation of carbonaceous char which protected the ER from further burning. This phenomenon was also found in other researches [3, 6]. In ER/GNS/DOPO composite, GNS mainly played the flame retardancy effect in condensed phase while DOPO played role in both condensed phase and gas phase. The combination of GNS and DOPO formed more continuous chars in ER matrix. The char and layered GNS extended the transform path for heat and gas, retarded the process of ER degradation. The effect of DOPO to capture the free radicals further retarded the process of combustion.

## 4. Conclusions

Pure ER tended to spread flame away from a fire source by melting and produced flammable drips during combustion.

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With the addition of GNS or DOPO, ER viscosity was increased and melt dripping was suppressed. GNS and DOPO changed the decomposition pathway of ER and increased the char formation. DOPO imparted flame retardancy in gas phase and condensed phase. GNS plays a key role in the condensed phase.

ER/DOPO, ER/GNS and ER/GNS/DOPO composites have lower HRR and THR compared with pure ER. There was a synergistic effect of GNS and DOPO to reduce the PHRR and THR of ER. DOPO not only improved the polymer charring, but also prevented the further oxidation of carbon monoxide to carbon dioxide. Furthermore, the addition of DOPO had a smoke suppression effect and reduced the amount of toxic gases. It is the simultaneous incorporation of GNS and DOPO in ER that generate the formation of a more firm and higher thermal stability char. In ER/GNS/DOPO composites, a low GNS and DOPO content played a high flame retardancy efficiency. The combination of GNS and DOPO could be a promising environmental friendly flame retardant for ER matrix.

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