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# Preparation of modified expandable graphite with boric acid as assistant intercalator

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## ABSTRACT

With $KMnO_4$ as oxidant, $H_2SO_4$ as intercalator and boric acid ($H_3BO_3$) as assistant intercalator, modified expandable graphite (written as $EG_B$) was successfully prepared in oxidizing and intercalating reaction of natural graphite. When the mass ratio of C:$KMnO_4$:$H_2SO_4$(98%):$H_3BO_3$ was controlled as 1.0:0.4:5.0:0.6 ($g \cdot g^{-1}$), $H_2SO_4$ diluted to a mass concentration of 78 wt % before intercalation reaction, and the reaction lasted 40 min at 40°C, the expanded volume and initial expansion temperature of the prepared $EG_B$ reached 570 $mL \cdot g^{-1}$ (at 800!) and 141°C, respectively. XRD pattern testified its intercalation and layer structure and FTIR spectroscopy illuminated the main functional groups of intercalating composite. Flame retardancy of $EG_B$ for linear low density polyethylene (LLDPE) was also investigated. Addition of 30 wt % the $EG_B$ to the polymer improved the limiting oxygen index (LOI) from 17.6 to 30.2%, and the UL-94 reached V-0 level. Whereas, the LOI of the same amount normal expandable graphite (EG) was only 25.1%, and the UL-94 only reached V-1 level. 

## KEYWORDS

Modified expandable graphite;
Boric acid;
Intercalator;
Dilatability;
Flame retardancy.

## INTRODUCTION

Natural graphite is a kind of crystal compound with layer structure, and its intercalating compound named expandable graphite (EG) can be prepared when non-carbonaceous reactants are inserted into graphite layers through chemical or electrochemical reaction[1, 2]. EG is known as a new generation of intumescent flame retardant for its good capability of halogen-free, low-smoke and low pollution potential[3-6]. When exposes to flame, EG expands and give a swollen multicellular char, which can protect materials from heat and oxygen. Simultaneously, the expansion will absorb huge heat, which can decrease the burning temperature. When EG is oxidized on reaction with $H_2SO_4$ at high temperature[7], the released gas such as $CO_2$, $H_2O$ and $SO_2$ can reduce concentration of combustible gas.

When EG is used as flame retardant, its expanded volume (EV) and initial expansion temperature $T_0$ are very important parameters. It's worth noting that reactants and theirs contents such as oxidant, intercalator and assistant intercalator, and reaction temperature, reaction time can all affect its dilatability. It was found that the $H_2SO_4$/APP (APP, ammonium polyphosphate, as an assistant intercalator)

EG[8], prepared through two-step method, presented a higher EV of 240 $mL \cdot g^{-1}$ than that of the single $H_2SO_4$ intercalating EG (210 $mL \cdot g^{-1}$). EG holding a $T_0$ of 310°C and EV of 270 $mL \cdot g^{-1}$ could be prepared with 85 wt % $H_2SO_4$ as intercalator, $KMnO_4$ as oxidant and $FeSO_4$ as close agent[9].

It is worth noting that if a traditional flame retardant is used as assistant intercalator, it not only improve the dilatability and flame retardancy, but also decrease sulfur content in EG. Boric acid is a well-known non-toxic, smoke suppressing and halogen-free flame retardant with good flame retardancy[10-12]. It holds lower melting point and can absorb heat and lose crystallization water, which make it has the simultaneous gas phase and condensed phase flame-retardation effect.

In this research, to obtain graphite intercalating compounds possessing high dilatability and flame retardancy, EG was modified with $H_3BO_3$. The dosages of $KMnO_4$, $H_2SO_4$, $H_3BO_3$ and reaction temperature, reaction time were optimized in graphite intercalating reaction. X-ray diffraction spectroscopy (XRD) and Fourier transform infrared spectroscopy (FTIR) were employed to illuminate the layer structure and intercalating components. Flame retardancy, indicated as limiting oxygen index (LOI) and vertical burning UL-94 rating of $H_3BO_3$ modified EG (written as $EG_B$) for LLDPE was also investigated.

## EXPERIMENTAL

### Materials and reagents

Natural flake graphite 5092 was provided by Action Carbon CO. LTD, Baoding, China. $H_3BO_3$, $H_2SO_4$ (98%) and $KMnO_4$ are all analytical agents. LLDPE 7540 obtain from Daqing.

### Preparation of the $EG_B$

In graphite intercalating reaction, reactants were quantified according to a definite mass ratio of C:$H_2SO_4$(98%):$KMnO_4$:$H_3BO_3$; $H_2SO_4$ was diluted to a definite concentration with deionized water before reaction. The quantified reactants were mixed and stirred in the order of diluted $H_2SO_4$, $H_3BO_3$, C and $KMnO_4$ in a 250mL beaker, which is controlled at a constant temperature for some time. After reaction, the solid phase was washed with deionized water and dipped in water for 2.0 h until pH of the waste water reached to 6.0-7.0, then $EG_B$ obtained after filtration and drying at 50-60°C for about 5.0 h.

### Characterization of the specimens

EV was an important factor to judge dilatability of EG. When the volume of EG increase to 1.5 times of its initial volume, the oven temperature was defined as $T_0$. EV and $T_0$ were measured following the reported method[13].

XRD analysis for material natural graphite and $EG_B$ were performed with a Y-4Q X-ray diffractometer (Dandong, China) employing Ni-filtered Cu $K\alpha_{1,2}$ radiation with 2θ ranging from 10° to 70°.

Specimen was triturated and mixed with potassium bromide at the mass ratio of about 1:100. The powder was pressed into flake in mould, and FTIR spectra were recorded between 4000-400 $cm^{-1}$ using FTS-40 FTIR spectrograph (America) with a resolution of 2 $cm^{-1}$.

Mixtures of flame retardant and LLDPE were melted at 140°C in Muller (Jiangsu, China) and pressed at 10 MPa, and then it was chopped in sliver. The slivers were used to measure LOI according to GB/T2406-1993 with oxygen index instrument (Chengde, China). At the same time, vertical burning tests were performed using a HC-3 vertical burning instrument (Tientsin, China) according to the standard UL 94-1996.

## RESULTS AND DISCUSSION

### Influence of reactants dosages and reaction condition on $EG_B$ dilatability

Modified $EG_B$ was prepared with $KMnO_4$ as oxidant, $H_2SO_4$ as intercalator and $H_3BO_3$ as assistant intercalator. The influence of mass ratio of natural graphite to $KMnO_4$, $H_3BO_3$, $H_2SO_4$ and its concentration, reaction time and reaction temperature on $EG_B$ dilatability were tested respectively.

### Influence of $KMnO_4$ dosage on $EG_B$ dilatability

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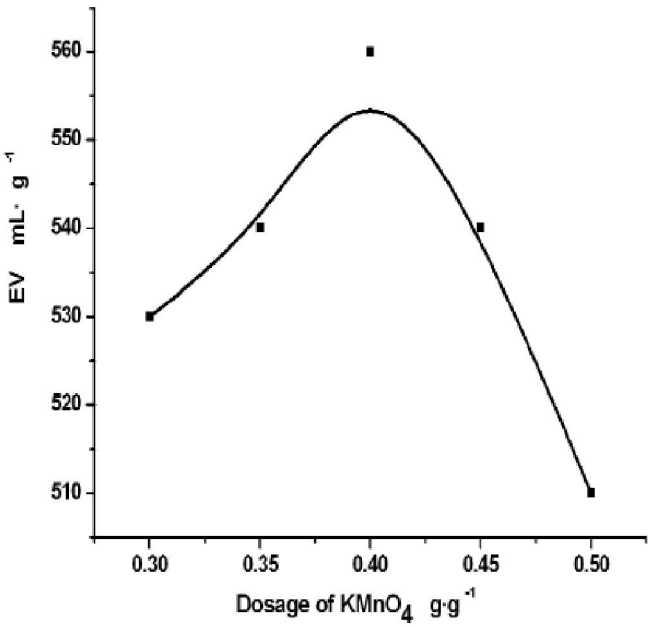


**Figure 1 : Influence of $KMnO_4$ mass on EV**

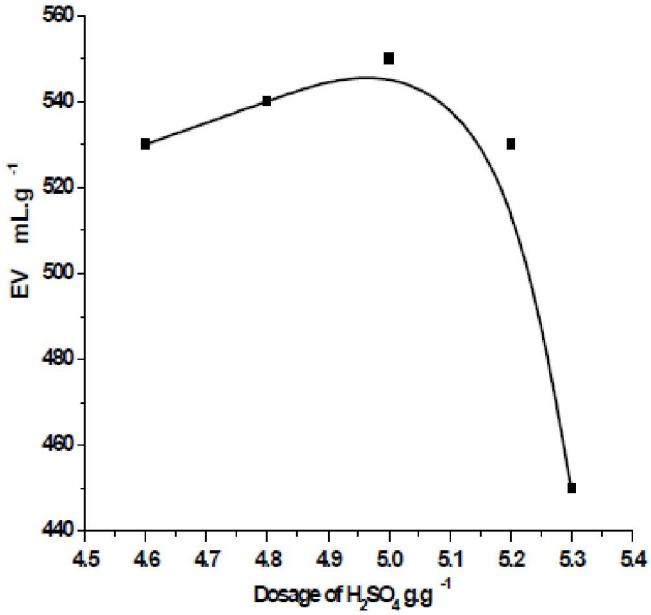


**Figure 2 Influence of $H_2SO_4$ mass on EV**

$KMnO_4$ dosage on dilatability were carried out by changing $KMnO_4$ mass in the range of 0.3-0.5 $g \cdot g^{-1}$ (with 1.0 g C as reference). According to the procedure mentioned above, experiments were carried out under the constant mass ratio C:$H_2SO_4$(98%):$H_3BO_3$ of 1.0:5.0:0.4 ($g \cdot g^{-1}$). Before reaction, $H_2SO_4$ was diluted to 78 wt %, and the reaction lasted 40 min at 40°C.

Figure 1 shows the changes of EV with the amount of $KMnO_4$. As oxidant, insufficiency $KMnO_4$ will cause an incomplete oxygenation of graphite and decrease of EV, while superfluous $KMnO_4$ will cause excessive oxygenation of graphite, which leads to a decrease in EG granularity and EV. When the mass ratio of $KMnO_4$ to C is controlled as 0.4 $g \cdot g^{-1}$, the prepared EG possesses a maximum EV of about 550 $mL \cdot g^{-1}$. So, the feasible dosage of $KMnO_4$ can be set as 0.4 $g \cdot g^{-1}$.

## Influence of $H_2SO_4$ dosage on $EG_B$ dilatability

In order to investigate the influence of $H_2SO_4$ dosage with a initial concentration of 98 wt % on dilatability, it was changed in the range of 4.6-5.3 $g \cdot g^{-1}$ and with the mass ratio C:$KMnO_4$:$H_3BO_3$ keeping as 1.0:0.4:0.4, the reaction lasted 40 min at 40°C, and $H_2SO_4$ was diluted to 78 wt %.

Figure 2 shows the changes of EV with $H_2SO_4$ mass. As a main reactant, insufficient $H_2SO_4$ will cause a poor oxidation of $KMnO_4$ and lead to an incomplete intercalation reaction and the decrease of dilatability. With the increase of $H_2SO_4$ dosage, the oxidation of $KMnO_4$ is enhanced, causing the intercalation reaction gradually completed and leading to the increases of dilatability. When the $H_2SO_4$ dosage achieves a balance, the prepared $EG_B$ will have the largest EV. Conversely, EV will decrease when the $H_2SO_4$ dosage under or over the suitable value. Results shown in Figure 2 presents the feasible mass ratio of $H_2SO_4$ to C is 5.0 $g \cdot g^{-1}$.

## Influence of $H_2SO_4$ concentration on $EG_B$ dilatability

Under the constant mass ratio C:$KMnO_4$:$H_2SO_4$(98%):$H_3BO_3$ of 1.0:0.4:5.0:0.4 ($g \cdot g^{-1}$), the reaction lasted 40 min at 40°C, influence of $H_2SO_4$ weight concentration in reaction was detected. Before reaction, 98 wt % $H_2SO_4$ was diluted with de-ionized water to the desired wt %.

The oxidation ability of $MnO_4^-/Mn^{2+}$ is related with the concentration of $[H^+]$, and there is a positive correlation. Therefore, within a certain range, the oxidation of $KMnO_4$ enhances with the increase of $H_2SO_4$ concentration, which causes the intercalation reaction gradually completed and leads to the increases of dilatability. But, with the further increase of $H_2SO_4$ concentration, it will cause the excessive oxidation of graphite when it over a suitable con-

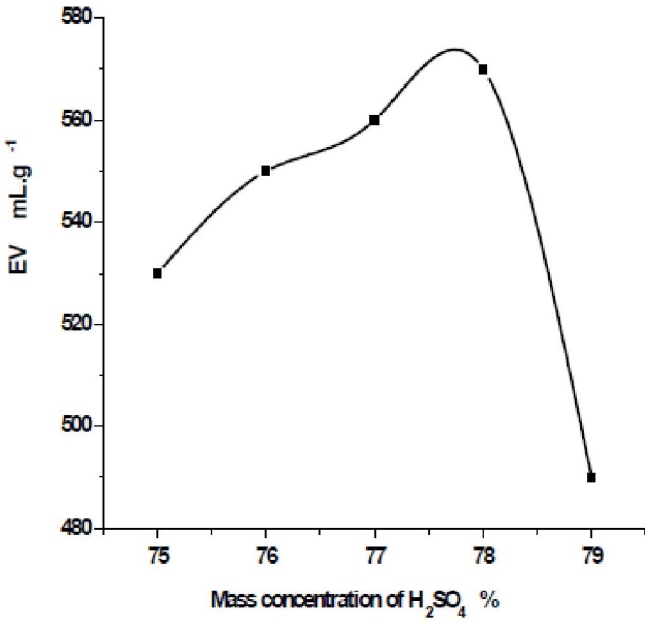


**Figure 3 : Influence of $H_2SO_4$ concentration on EV**

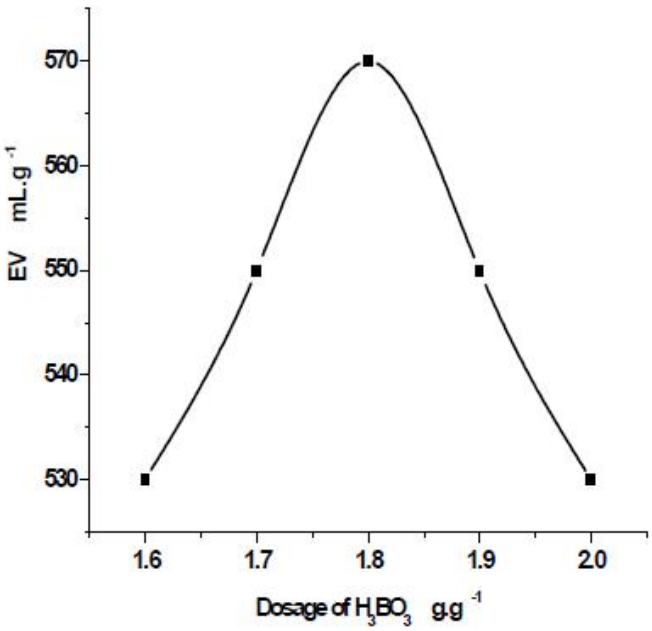


**Figure 4 Influence of $H_3BO_3$ mass on EV**

centration. As shown in experiment results, the feasible $H_2SO_4$ concentration is about 78 wt %.

### Influence of $H_3BO_3$ dosage on $EG_B$ dilatability

Under the constant mass ratio C:$H_2SO_4$(98%):$KMnO_4$ of 1.0:5.0:0.4 ($g \cdot g^{-1}$), the reaction lasted 40 min at 40°C and $H_2SO_4$ diluted to 78 wt %, the influence of $H_3BO_3$ dosage was detected in the range of 0.53-0.67 $g \cdot g^{-1}$ .

As an assistant intercalator, increase of $H_3BO_3$ dosage can improve EG dilatability as shown in Figure 4. When the mass ratio of $H_3BO_3$ to C is controlled as 0.60 $g \cdot g^{-1}$, $EG_B$ with maximum EV of 570 $mL \cdot g^{-1}$ can be gained. Superfluous $H_3BO_3$ will cause the relative scarcity of $KMnO_4$ and incomplete oxygenation of graphite.

### Influence of reaction temperature on $EG_B$ dilatability

Reaction temperature can effect reaction rate and balance direction. For exothermic reaction, such as oxidization and intercalation of graphite, the degree of reverse reaction will increase greatly with the increase temperature. So reaction temperature creates different effects on the reaction rate and direction. With C:$H_2SO_4$(98%):$KMnO_4$:$H_3BO_3$ controlled as 1.0:5.0:0.4:0.6 ($g \cdot g^{-1}$), $H_2SO_4$ diluted to 78 wt % before reaction, and reaction lasted 40 min, the influence of reaction temperature on EV was detected. When it is less than 40°C, the increase of temperature can improve EG dilatability. However, too high temperature causes the exothermic reaction releasing more heat and excessive oxygenation of graphite. So the feasible reaction temperature can be set as 40°C.

### Influence of reaction time on $EG_B$ dilatability

Under the mass ratio of C:$H_2SO_4$(98%):$KMnO_4$:$H_3BO_3$ as 1.0:5.0:0.4:0.6 ($g \cdot g^{-1}$), $H_2SO_4$ diluted to 78 wt % and reaction temperature controlled at 40°C, the influence of reaction time on EV was studied. Results show that extension of reaction time increases EG dilatability in the former 40 min, and then it has less influence on EV.

### Feasible condition of $EG_B$ Preparation

According to the above experiments, feasible conditions of $EG_B$ preparation can be set as: mass ratio C:$KMnO_4$:$H_2SO_4$(98%):$H_3BO_3$ equaling 1.0:0.4:5.0:0.6; $H_2SO_4$ diluted to 78 wt % before reaction; intercalation reaction lasted 40 min at 40°C. The EV of $EG_B$ under different expansion temperature were detected, and it shows a increasing trend along with the increasing expansion temperature before 800°C, and then it presents a decreasing trend caused by excessive oxygenation of $EG_B$. $T_0$ and the maximum EV of the prepared $EG_B$ are 141°C and

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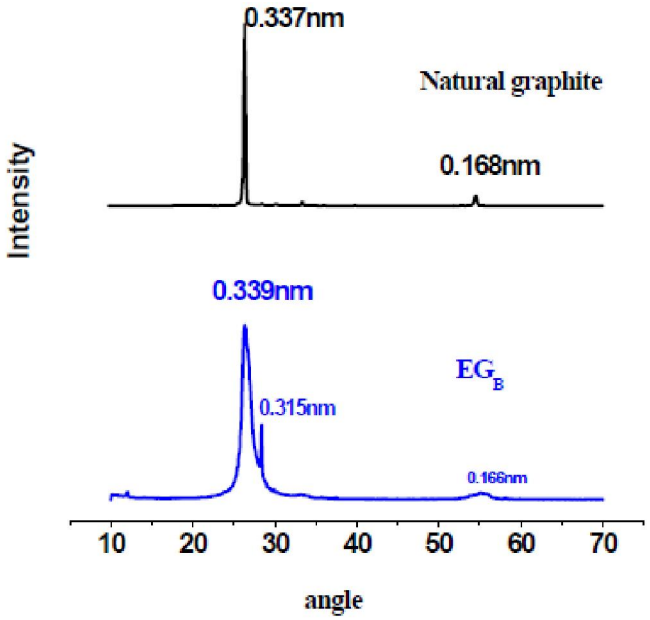


**Figure 5 : XRD of natural graphite and $EG_B$**

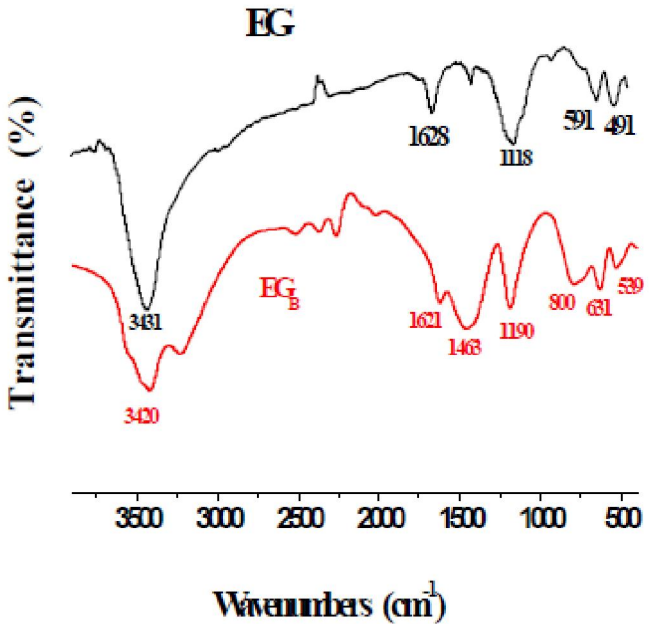


**Figure 6 : FTIR analysis of EG and $EG_B$**

570 mL·g$^{-1}$, respectively.

## Preparation of reference expandable graphite EG with only $H_2SO_4$ intercalator

Compared with $EG_B$, the reference EG was prepared under the mass ratio C:$KMnO_4$:$H_2SO_4$(98%) of 1.0:0.4:5.0 (g·g$^{-1}$), other condition were the same as $EG_B$. $T_0$ and the maximum EV of EG was detected as 150°C and 500 mL·g$^{-1}$, respectively. Therefore, $H_3BO_3$ can obviously affect dilatability, and $EG_B$ will show better flame retardancy than EG for its good dilatability.

## Characterization of graphite and its intercalating compounds

### XRD analysis of natural graphite and $EG_B$

XRD analysis for natural graphite and $EG_B$ were performed. As shown in Figure 5, the two peaks with the interplanar crystal spacing of 0.334 nm and 0.167 nm corresponding to diffraction angle of 26.4°, 55.5° are the characteristic spectrums of natural graphite. While, the peaks of 26.3° and 55.3° show $EG_B$ keeping the same layer structure as natural graphite. But it is worthy to note that the diffraction peak of 26.4° transfers to smaller angle of 26.3°. At the same time, it corresponds to a big interplanar crystal spacing of 0.339 nm due to intercalation in graphene planes. It can be clearly seen, under the oxidation of $KMnO_4$, the non-carbonaceous reactant can be easily inserted into the graphene planes, which leads to the increase of interplanar crystal spacing.

### FTIR analysis of the prepared samples

Figure 6 shows FTIR spectra of the prepared $EG_B$ and reference EG. As can be seen from the results, two samples both show the characteristic absorption peaks of -OH at about 3430 cm$^{-1}$, caused by intercalation of $H_2SO_4$ or $H_3BO_3$. At the same time, the peaks at about 1630 cm$^{-1}$ are the specific absorption peaks of C=C. The absorption peaks of S=O in EG is at 1118 cm$^{-1}$, but there are strong superimposed peaks at 1463 cm$^{-1}$ and 1190 cm$^{-1}$ in the FTIR of $EG_B$, it is because the absorption peaks of S=O and B=O are both appear in the range of 1500-1100 cm$^{-1}$ as reported[14]. Furthermore, the peaks in the range of 800-600 cm$^{-1}$ in the $EG_B$ belong to B-O specific absorption[15]. The results announce the intercalation of intercalators.

## Detection of flame retardance for LLDPE

Processing temperature of LLDPE is lower than 140°C, so the prepared $EG_B$ can be used as retardant. The flame retarding composites were prepared as mentioned above, and LOI, UL-94 level of pure LLDPE, 70LLDPE/30$EG_B$ and 70LLDPE/30EG (shown as wt %) were detected according to the mentioned methods. Results show that LOI of single LLDPE is only 17.6%, and its combustion accom-

panies with molten drop at the same time. Addition of 30% the reference EG improves LOI to 25.1%, and its UL-94 reaches V-1. Whereas, the addition of the same amount of $EG_B$ can improve LOI and UL-94 rating to 30.2% and V-0 level, respectively. Therefore, the intercalating $H_3BO_3$ is more effectual in improving the flame retardancy.

## CONCLUSIONS

According to the experiment results, it is evident that the mass ratio of $C:KMnO_4:H_2SO_4(98\%):H_3BO_3$ has important influence on $EG_B$ dilatability, and the feasible value should be controlled as 1.0:0.4:5.0:0.6 ($g \cdot g^{-1}$) At the same time, $H_2SO_4$ should be diluted to 78 wt % before intercalation reaction, and intercalating reaction lasted 40 min at 40°C, then EV and $T_0$ of the prepared $EG_B$ can reach 570 $mL \cdot g^{-1}$ and 141°C, respectively. The intercalating reaction between graphite and $H_2SO_4$, $H_3BO_3$ can be revealed by XRD and FTIR analysis. $EG_B$ presents more effective flame retardancy for LLDPE than the reference EG.

## ACKNOWLEDGEMENTS

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