

Chemical Modification of Expandable Graphite by Boric Acid and Its Flame Retarded Application in Polyethylene

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Abstract

The aim of this research is to get the graphite intercalation compound with high thermal stability and fire resistance. Firstly, the normal expandable graphite (EG) was prepared with potassium permanganate (KMnO₄) as oxidant and sulfuric acid (H₂SO₄) as intercalator, respectively. Then, with (3-Aminopropyl)-trimethoxysilane (KH-550) as coupling agent, the boric acid (H₃BO₃) modified EG (EG_B) was prepared by silane grafting method through H₃BO₃ bonded with EG. The analysis of X-ray powder diffractometer and Fourier transform infrared spectroscopy testified the existence of EG_B. EG_B showed better thermal stability and flame retardancy for linear low density polyethylene (LLDPE) than the referenced EG. Addition of 13.0 wt% of EG_B improved the limiting oxygen index (LOI) of 87.0LLDPE/13.0EG_B to 24.6%, which was obviously higher than that of pure matrix of 17.5%. Whereas, the LOI of 87.0LLDPE/13EG was 22.7%. Furthermore, when EG_B combined with ammonium polyphosphate (APP), the LOI and UL-94 level of 87.0LLDPE/8.7EG_B/4.3APP reached 27.1% and V-0, respectively.

Keywords: Expandable graphite; Modification; Boric acid; Silane grafting; Flame retardancy.



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1. Introduction

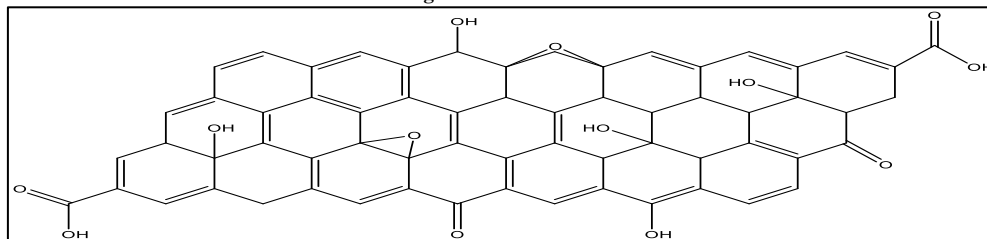
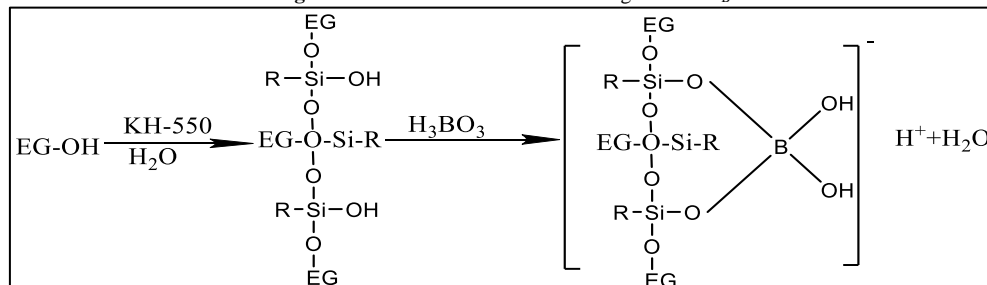
Flame retardants (FRs) are widely used to protect materials from combustion [1, 2]. Expandable graphite (EG) is a graphite intercalation compound (GIC), which is prepared by natural graphite through electrochemical or chemical oxidation method. EG belongs to an intumescent type FR with good capability of halogen-free, non-dropping and low-smoke [3, 4]. Its flame retardant mechanism is shown in equation (1). When EG is heated or burned, the interacted H₂SO₄ will react with graphite, and rapidly expand to form “worm like” expanded graphite residue which can prevent the entry of air [5]. In addition, the released H₂O, CO₂ and SO₂ can play the role of dilution O₂ to achieve flame retardant effect. It is because of its excellent performance, EG is widely used as FR for polymer materials such as polyolefin [6], ethylene vinyl acetate (EVA) [7], epoxy resin [8].



However, there are still some shortcomings. The function of slowing or inhibiting the decomposition of materials is mainly based on residual layer produced in thermal expansion. There is almost no chemical reaction between the material and EG. Due to the poor compactness of the residue with matrix, it is easy to be damaged in heat convection and even fall off into “fly ash”, which reduces the abilities of the thermal insulation and oxygen insulation, and further worsens the flame retardant performance. In addition, the “popcorn effect” makes the formed “worm like” residue very loose and easy collapse [9].

Modification or coordination addition with other FRs is an effective way to improve EG flame retardancy. In the laboratory or industrial, H₂SO₄ is normally used as oxidant and intercalator, the structure of the prepared EG is shown in Figure 1. There are some functional groups of C-OH, C=O and C(O)O on EG surface [10], which will provide basis for its surface modification. The hydrolysis of KH-550 can generate -Si-OH functional group which can further react with C-OH and C(O)O or carry out polycondensation reaction, or react with H₃BO₃ to form a complex of EG. The formation mechanism of H₃BO₃ modified EG (EG_B) is shown in Figure 2 [10].

Figure-1. EG structure

Figure-2. The formation mechanism diagram of EG_B

Polyethylene is widely used in daily life, such as film, plastic bags, daily necessities, pipe, wire and cable. However, polyethylene emits black smoke and poisonous gas during combustion. Therefore, it needs to add one or more FRs to improve its flame retardancy. However, if a larger amount of FRs is added, the mechanical properties of materials will greatly reduce. The aim of this study is to improve flame retardancy and compatibility of EG to linear low density polyethylene (LLDPE) through chemical modification. In addition, the flame retardant efficiency can be guaranteed by a small amount of FR, and the influence on the mechanical properties of the material can be reduced as much as possible. Therefore, the boric acid (H₃BO₃) modified EG (EG_B) was prepared by silane grafting method through H₃BO₃ bonded with EG. EG_B influence and synergistic effect with ammonium polyphosphate (APP) on LLDPE flame retardancy were investigated by comparison [11].

2. Experimental

2.1. Materials and Sample Preparation

Natural graphite with an average particle size of 0.30 mm and carbon content of 96 wt% was provided by Xite Carbon CO. LTD, Qingdao, China. LLDPE (7042, 0.918 g/cm³, melt index 2.0 g/10 min) was purchased from Zhongsha Petrochemical Co. Ltd, Tianjin, PRC. APP (II, polymerization degree n>1000) was provided by Shifang Changfeng Chemical Ltd., Chengdu, PRC. KMnO₄, H₃BO₃, KH-550, ethanol and H₂SO₄ (98 wt%) were all analytical agents and used as received.

2.2. Preparation of the EG

Natural graphite C, KMnO₄ and H₂SO₄ (75%) were weighed at a mass ratio of 1:0.15:5.0. Then, C and KMnO₄ were added to the cooled H₂SO₄, and then the mixture was placed in a 30 °C water bath and stirred for 30 minutes. After the reaction completed, the reaction system was washed with water, and then soaked for 2h until the pH of the impregnation solution approached to 7.0. Finally, the mixture was baked in an oven at about 60 °C for 7h, and then got the EG.

2.3. Preparation of EG_B

Weighed 45.0 g of 90 % ethanol solution, 20.0 g of EG, 0.4g of KH-550, 2.0g of H₃BO₃, respectively. Then mixed and stirred for 1 h at room temperature to ensure completely react. Finally, filtration and drying at 85°C for 7h to get the product.

2.4. Preparation of the Flame Retarded LLDPE

In mixing mill, LLDPE and FRs were mixed at a 30 wt% ratio in a molten state at 120°C, then the mixtures were pressed at 125°C and 10 MPa, and chopped into slivers with two different sizes of 120.0×6.0×3.0 mm³ and 127.0×13.0×3.0 mm³ for the evaluation of LOI and vertically burning UL-94 level.

2.5. Characterization of the Samples

2.5.1. Analysis of Chemical Structure of the GICs

The chemical structures of EG and EG_B were analyzed by Fourier transform infrared (FTIR) spectrometer (Bruker) from the scanning range of 4000 cm⁻¹ to 400 cm⁻¹ at a scanning frequency of 2 cm⁻¹. The KBr was mixed with the sample at a ratio of about 100:1.

2.5.2. Analysis of Crystal Structure of the GICs

The structure information of EG and EG_B were analyzed by X-ray diffraction (XRD) in the range of 10°-70° with a step width of 0.06°. The scanning process uses Ni-filtered Cu K α radiation with a tube voltage of 40 kV and a tube current of 15 mA.

2.5.3. Analysis of Morphology

The morphology of EG and EG_B was analyzed by TM3000 platform scanning electron microscope (SEM) of Japan Hitachi High-Technologies Corporation.

2.5.4. Thermal Stability Analysis of the GICs

In thermal thermogravimetry (TG) analysis (STA 449C, Germany), about 3~10 mg sample was measured in porcelain crucible under N₂ atmosphere with a flux of 30 mL/min. It was heated in the range of 30-800 °C at a heating rate of 10 °C/min. Changes of sample weight as temperature were recorded.

2.5.5. Analysis of Combustion Performance

LOI is the volume fraction of O₂ that can support the polymer to combust in a mixed gas of O₂ and N₂. Polymers are combustible with a LOI value bigger than 22%; polymers are flammable with the LOI value in 22%~27%; and polymers are non-flammable with a LOI value bigger than 27%. The sample with a size of 120.0×6.0×3.0 mm³ was used to measure LOI value according to standard of GB/T2406-1993 with oxygen index instrument (Chengde, China). While, the UL-94 level test was performed using a HC-3 vertical burning instrument (Tientsin, China) on sheet with a size of 127.0×13.0×3.0 mm³.

3. Results and Discussion

3.1. Characterizations of the GICs

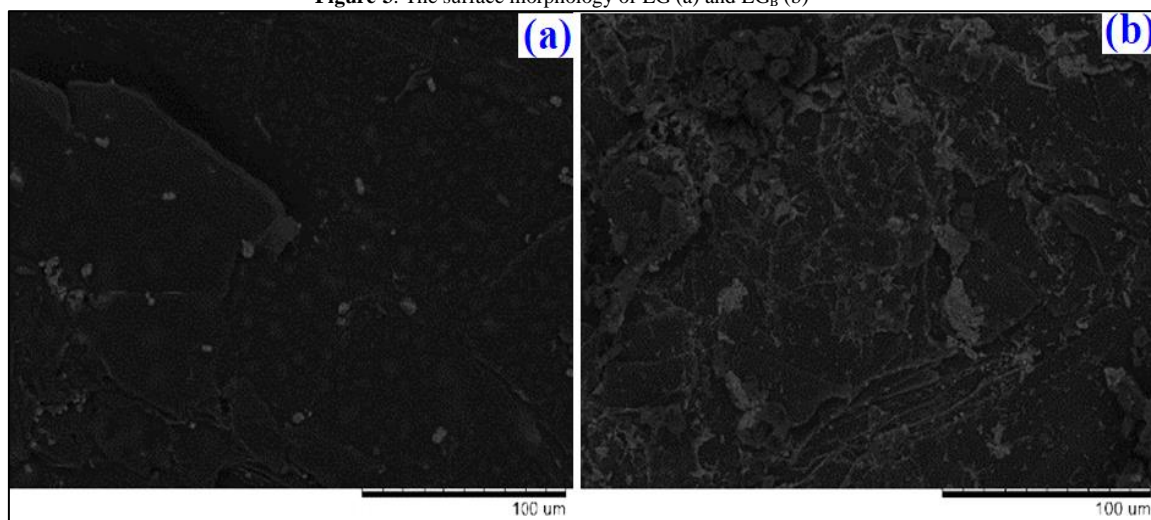
3.1.1. Characterizations of Expansion Properties

The initial expansion temperature and expandable volume of EG was detected as 197 °C and 467 mL/g at 800 °C, respectively [5]. As for the EG_B, it presented an initial expansion temperature of 175 °C and an expandable volume of 376 mL/g at 800 °C and 480 mL/g at 900 °C.

3.1.2. SEM Analysis of the GICs

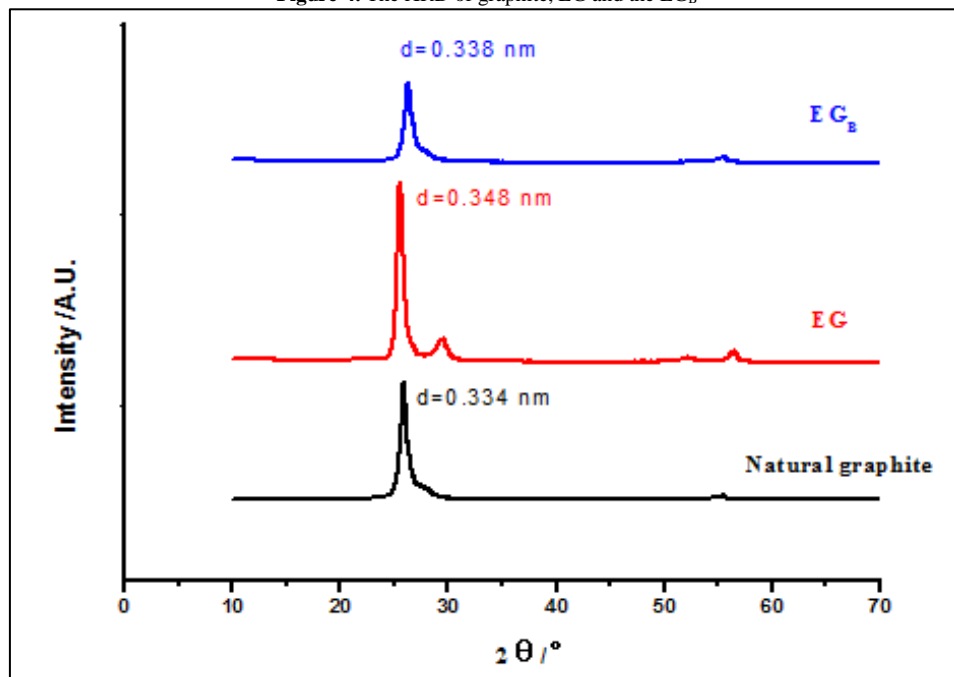
The EG and EG_B were analyzed by SEM to compare their surface morphology. As shown in Figure 3, the surface of EG is relatively smooth. While, EG_B shows a large amount of white and translucent markings, which uniformly distributes on the surface. It is presumed that the white or translucent material on the surface is the ceramic precursors of borosilicate with different thickness.

Figure-3. The surface morphology of EG (a) and EG_B (b)



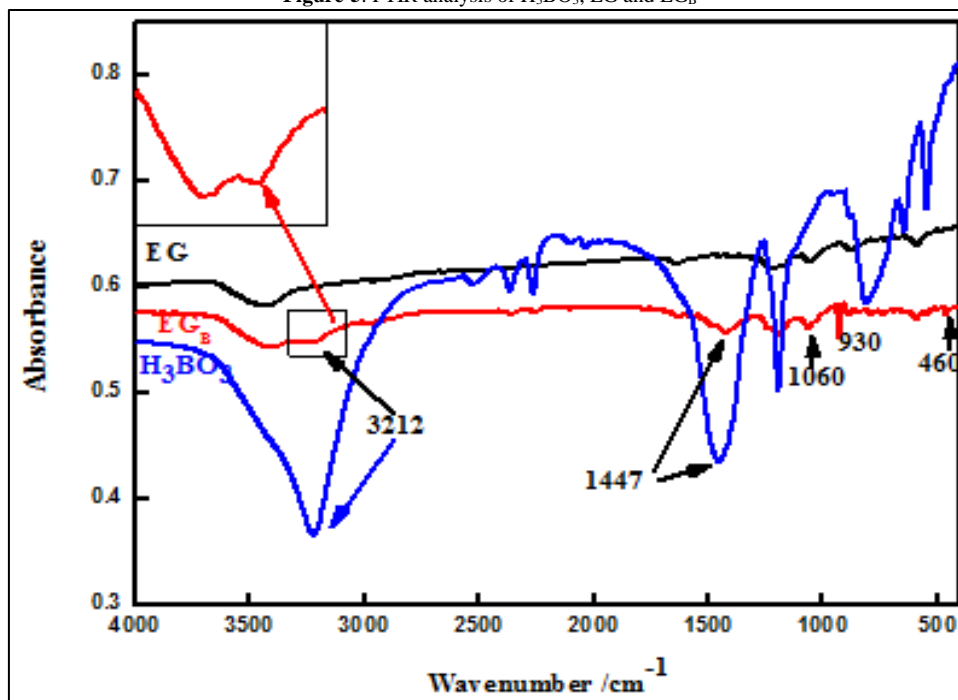
3.1.3. XRD Analysis of the GICs

In order to compare the crystal structures of graphite, EG and the EG_B, XRD analysis was carried out for each of them. It can be seen from the Figure 4 that the natural graphite shows the characteristic peak of 002 interplanar at 26.6° with an interplanar spacing of 0.334 nm. EG and EG_B give the same characteristic peaks around 26°, indicating that they still maintain the same layer structure as natural graphite. However, their 002 interplanar diffraction angles transfer to small values of 25.6° and 26.3°, respectively. At the same time, EG and EG_B hold a big interplanar spacing of 0.348 nm and 0.338 nm respectively, which indicates the oxidation and intercalation of graphite. However, the interplanar distance of EG_B is lower than the EG, indicating that H₃BO₃ is not intercalated into the interlayers but only bonded or adsorbed on the surface or the edge of EG_B.

Figure-4. The XRD of graphite, EG and the EG_B

3.1.4. FTIR Analysis of H₃BO₃, EG and EG_B

Figure 5 shows the results of FTIR analysis of H₃BO₃, EG and EG_B. Compared with EG, EG_B exhibits characteristic absorptions of H₃BO₃ at 1447 cm⁻¹ (O-H) and 3212 cm⁻¹ (B-O). At the same time, EG_B increases the characteristic absorption peak of 1065cm⁻¹, 930 cm⁻¹ and 460cm⁻¹, which indicates there is -Si-OH polymerization product and B-O-Si groups [12]. All this indicates that EG_B was modified successfully.

Figure-5. FTIR analysis of H₃BO₃, EG and EG_B

3.1.5. TG/DTG Analysis of EG and EG_B

Table 1 show the TG data of EG and EG_B. The two samples present the similar one stage weight loss tendency, and the obvious mass loss occurs in the range of 300~400 °C. However, there still exist some differences. EG_B shows higher thermal stability than the referenced EG, reflected by the higher T₅ of temperature corresponding to a 5% weight loss and residue yield at 800 °C.

Table-1. TG/DTG data of EG and EG_B

Samples	T ₅ /°C	Residue yield/%
EG	242.1	84.74
EG _B	335.8	86.17

3.2. The Flame Retardant Application for LLDPEs

The decomposition temperature of EG, EG_B and APP are higher than the mixing temperature of LLDPE, so they can be used as FRs. In order to compare the flame retardant effect and investigate the synergistic effect between different FRs, the EG, EG_B, H₃BO₃, APP, mixture of EG_B and APP at different mass ratio were compared keeping the total FRs dosage as 13.0 wt%. The experimental measurement results of LOI (LOI_{exp}) and UL-94 level of LLDPE composites were shown in Table 2.

Table-2. Results of LOI and vertical burning UL-94 level

Samples	LOI/%		UL-94
	LOI _{exp}	LOI _{the}	
100LLDPE	19.2	-	-
87.0LLDPE/13.0APP	20.3	-	-
87.0LLDPE/13.0EG	22.7	-	-
87.0LLDPE/13.0H ₃ BO ₃	19.5	-	-
87.0LLDPE/13.0EG _B	24.6	-	-
87.0LLDPE/8.7EG _B /4.3APP	27.1	23.1	V-0
87.0LLDPE/6.5EG _B /6.5APP	27.0	22.45	-
87.0LLDPE/4.3EG _B /8.7APP	25.3	21.7	-

-: Indicates not detected or not calculated

As can be seen from Table 2, LLDPE presents a low LOI value and with no UL-94 level. As for the single flame retarded LLDPE composites, 87.0LLDPE/13.0EG_B shows the biggest LOI_{exp}. It's obviously higher than that of the 87.0LLDPE/13.0H₃BO₃, 87.0LLDPE/13.0APP and 87.0LLDPE/13.0EG. The flame retardancy of EG_B is better than the referenced EG. This is because the bonded H₃BO₃ on EG_B surface can not only absorb heat, but also release H₂O during its decomposition, and the B₂O₃ produced by the decomposition can adhere to the surface of the material play a role of insulation [13]. However, 87.0LLDPE/13.0EG_B still cannot inhibit melting and dripping. The 13.0 wt% EG_B cannot achieve the industrial flame retardant standard.

It can be seen that the LOI_{exp} values of LLDPEs adding the mixture EG_B and APP are higher than the single flame retarded system. Especially, their LOI_{exp} values are also higher than the theoretical calculated LOI results (LOI_{cal}), counted according to each 87.0LLDPE/13.0EG_B and 87.0LLDPE/13.0APP LOI_{exp} value and the FR mass fraction [14]. In addition, the ratio of EG_B to APP has obvious effect on the synergy. Here, EG_B plays an important role in increasing mass of residual char. While, APP plays an important role in improving the carbon density [13, 15]. The feasible mass ratio of EG_B to APP is 2:1. The LOI_{exp} and UL-94 of 87.0LLDPE/8.7EG_B/4.3APP have reached the industrial flame retardant standard.

4. Conclusions

EG_B can be prepared by silane grafting method through H₃BO₃ bonded with EG. XRD and FTIR results testify the existence of EG_B. EG_B presents higher thermal stability and flame retardancy for LLDPE than the referenced EG. Especially, combination of EG_B with APP obviously improves the LLDPE flame retardancy. The LOI and UL-94 level of 87LLDPE/8.7EG_B/4.3APP reach 27.1% and V-0, respectively. It has reached the industrial flame retardant standard.

Acknowledgements

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