Synthesis of the Zinc Borate Modified Expanded Graphite and Its Influence on Polyurethane Foam Properties

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Abstract

In order to get the graphite intercalation compound with low sulfur content, high expansibility and fire resistance, the synthetic method of expandable graphite modified by zinc borate (EG_{Zn}) was investigated, and its influence on rigid polyurethane foam (RPUF) structure, compress strength and flame retardancy was also carried out. The feasible preparing condition of EG_{Zn} was determined to be: mass ratio of graphite C, $KMnO_4$, H_2SO_4 (98 wt%) and $2ZnO·3B_2O_3·3.5H_2O$ was 1.0:0.25:4.5:0.3, the used H_2SO_4 should be diluted to 75 wt% before reaction, and the reaction lasts 40min at 50 ℃. Expansion properties, X-ray powder diffractiometer and Fourier transform infrared spectroscopy testified the existence of EG_{Zn}. Addition of EG_{Zn} is not conducive to the formation of the cell structure, which causes an increase in foam density and a decrease in compressive strength. However, addition of EG_{Zn} at a 30 wt% can increase the limiting oxygen index of RPUF to 26.9%, and increased by 31.2%. The vertical burning level increases to V-0. The flame retardation is come from form protection of "worm-like" expanded graphite residues. At the same time, the expansion process absorbs a large amount of heat and release CO_2, H_2O and SO_2 gases.

Keywords —*expandable graphite, zinc borate, flame retardancy, rigid polyurethane foam, structure and property*

I. INTRODUCTION

In order to prevent combustion and delay fire spread, flame retardants (FRs) are commonly used in polymers [1, 2]. Expandable graphite (EG) is an intumescent flame retardant with good capability of halogen-free, non-dropping and low-smoke [3, 4]. It is because of its excellent performance, EG is widely used as FR for polymer materials such as polyolefin [5], ethylene vinyl acetate (EVA) [6], epoxy resin [7], acrylonitrile butadiene styrene (ABS) [8].

Rigid polyurethane foam (RPUF) is widely used in insulation and space filler due to its excellent properties [9, 10]. However, the flammability restricts its widespread application. EG has been used to retard RPUF not only because of its high efficiency, but also because its expansion temperature

can match the decomposition temperature of RPUF [11, 12]. However, when EG is prepared with H_2SO_4 as intercalator, the combustion will release more SO_2 gas [13, 14]. In graphite intercalating reaction, in addition to H_2SO_4, the embedding of the assistant intercalator can not only reduce the relative content of sulfur, but also improve the flame retardancy [15, 16]. Borate is a kind of well-known FR with remarkable flame retardancy. Its decomposition cannot only absorb heat and lose crystal water, but also dilute the concentration of the volatile oxidizable pyrolysis production in the flame zone; thereby an enhanced char formation can be obtained. Furthermore, the residual B_2O_3 can form a glassy coat on the surface of polymer to limit the transfer of heat and mass, as well as oxygen diffusion, and then block the combustion [17]. In the anti-flame test of linear low density polyethylene, the addition of zinc borate ($2ZnO·3B_2O_3·3.5H_2O$) could improve the thermal stability and substantially enhance the residue carbon [18].

As a result, the purpose of this research was to combine the EG and borate together, and prepare expandable graphite modified by zinc borate (EG_{Zn}) through one-step graphite intercalating reaction. In this reaction, zinc borate was used as assistant intercalating reagent, $KMnO_4$, H_2SO_4 were used as oxidation reagent, main intercalator, respectively. The dosages of $KMnO_4$, H_2SO_4, $2ZnO·3B_2O_3·3.5H_2O$ were optimized through single-factor experiment. The obtained samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and its influence on RPUF structure, compress strength and flame retardancy was further investigated.

II. EXPERIMENT

A. Reagents and materials

$2ZnO·3B_2O_3·3.5H_2O$, H_2SO_4 (98 wt%), $KMnO_4$ were all analytical reagents and obtained from the local vendors. Natural graphite (C, 5092) was provided by Qingdao Xite Carbon CO. LTD, China.

The polyether polyol (YD–4110) supplied by Hebei Yadong Chemical Company of China holds a hydroxyl value of 460±15 mg/g KOH and a viscosity of 4300±500 mPa/s at 25 °C. Polymethylene polyphenylene isocyanate (PM-200) with a NCO

content of 31.3 wt % and a viscosity of 197 mPa/s at 25 °C was provided by Yantai Wanhua Chemical Group Co. Ltd of China. The industry grade foam stabilizer silicone oil -178 was available from Jiangsu Mei Maysta Chemical Co. Ltd of China. The triethylene diamine (A-33) solution with a 33 wt % and N,N,N',N',N'' -pentamethyldiethylenetriamine (PC-5) were all industry grade and provided by US Air Products Company. The industry grade foaming agent dichlorofluoroethane (141B-1) was supplied by Zhejiang Sanmei Chemical Co. Ltd of China.

B. Methods

Preparation of the EG_{Zn}

In the intercalating reaction of graphite, the reactants were quantified according to a definite mass ratio of C : H_2SO_4 (98%) : $KMnO_4$: $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$, and the H_2SO_4 was diluted with deionized water before reaction. Then, the quantified reactants were mixed and stirred in the order of diluted H_2SO_4, $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$, C and $KMnO_4$ in a 250 mL beaker under 50 °C. After 40 min, 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_{Zn} was obtained after filtration and drying at 60-80 °C for about 6.0 h.

Preparation of pure RPUF and its flame retarded composites

Pure RPUF was prepared by an oneshot, free rise procedure according to the reported method [19]. FR was added at a certain wt % of the total component I and component II during the preparation of component I. Other preparing conditions of the flame retarded foams were the same as pure RPUF.

C. Instruments and analysis

XRD data of the prepared graphite intercalating compounds (GICs) were collected by an Y2000 X-ray diffractometer (BRUKER-AXS, Germany) employing Ni-filtered (wavelength λ=0.15418 nm) Cu Kα radiation with 40 kV, 30 mA and 2θ ranging from 20° to 70°. The interlayer spacing was obtained based on the angle at which the corresponding peak was diffracted. The FTIR spectra data were recorded between 4000-400 cm^{-1} using a spectrometer (FTS-40FTIR, America) with a resolution of 2 cm^{-1}.

RPUF apparent density was surveyed according to ASTM D1622M-2014, and the compression strength at 10% strain in the direction parallel to foam growth was detected according to ASTM D 1621-94 using an electronic universal testing machine under ambient condition. The movement rate of crosshead was fixed at 2.0 mm/min for each sample with a size of $50 \times 50 \times 50$ mm^3, and the preload was set to 1 N. The RPUF pore structure and the morphologies of the composite combustion residues were investigated by Scanning electron microscope (SEM).

The limiting oxygen index (LOI) value was detected using an oxygen index instrument (Suzhou of China) according to ASTM D 2863-97 on sheets with a size of $127 \times 10 \times 10$ mm^3. Vertical burning test was performed using a PX-01-005 vertical burning instrument (Suzhou of China) according to ASTM D 3801-96 on $127 \times 13 \times 10$ mm^3 sized sheet.

III. RESULTS AND DISCUSSION

A. Optimization of EG_{Zn} preparing conditions

The good flame retardancy of EG depends on its high expandable volume (EV). Therefore, dosages of H_2SO_4, $KMnO_4$ and $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$, H_2SO_4 wt% concentration were optimized through one-factor experiments at 50 °C and kept 40 min. In the intercalating reaction of graphite, $KMnO_4$ acts as oxidant to capture the electrons between graphene planes, and H_2SO_4 serves as oxidant and main intercalator. As shown in Fig. 1 and Fig. 2, low or high $KMnO_4$ and H_2SO_4 dosages can cause the EV decrease. H_2SO_4 concentration affects the solubility of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$. Too low H_2SO_4 wt% make $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ harden, while too high concentration cause it a gelatinous state, which further affects the numbers intercalated in graphite layers, and then affects the EG dilatability. Fig. 3 shows the impact of H_2SO_4 wt% on EV in the range of 65 wt% to 85 wt%. EV increases with the increasing of H_2SO_4 concentration, and when it reaches 75 wt%, the EV gives about 500 mL/g. But when the concentration further increases, an excessive oxygenation of graphite will occur, which leads to a decrease in EV. The influence of assistant intercalator $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ was detected in the range of 0.1~0.5 g/g. Increase of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ dosage can improve EG dilatability as shown in Fig. 4. When the mass ratio is controlled as 0.3 g/g, EV reaches a maximum of 517 mL/g. Superfluous $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ cause the relative scarcity of $KMnO_4$ and incomplete oxygenation of graphite.

Based on the above experiments, the feasible preparing condition of EG_{Zn} was determined to be: mass ratio of graphite C, $KMnO_4$, H_2SO_4 (98 wt%) and $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ was 1.0:0.25:4.5:0.3, the used H_2SO_4 should be diluted to 75 wt% before reaction, and the reaction lasts 40 min at 50 °C. Initiation expansion temperature and the maximum EV of the prepared EG_{Zn} are 183 °C and 517 mL/g (at 800 °C), respectively.
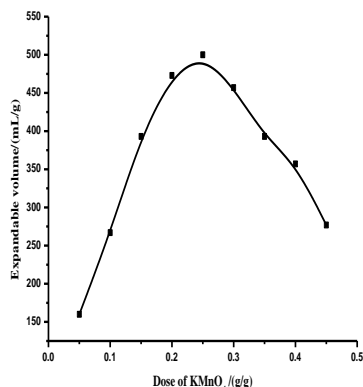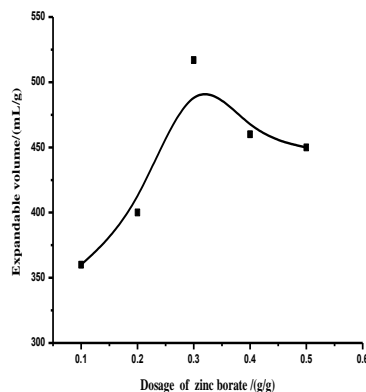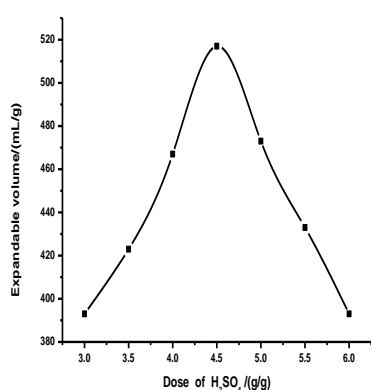
Fig 1. Influence of KMnO₄ dosage on EV

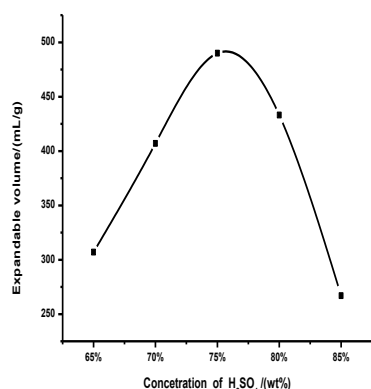**Fig 2. Influence of H₂SO₄ dosage on EV**

Fig 3. Influence of H₂SO₄ wt% on EV

B. Preparation of the referenced expandable graphite (EG₀)

Compared with EG_{Zn}, EG_0 was prepared under the mass ratio C : KMnO₄ : H₂SO₄ (98%) of 1.0:0.25:4.5, H₂SO₄ was diluted to 75 wt % before reaction, and reaction lasted 40 min at 50°C. The initial expansion temperature and EV of EG_0 was detected as 190°C and 500 mL/g, respectively.

Fig 4. Influence of zinc borate dose on EV

C. Characterizations of graphite and its GICs

XRD analysis of the prepared samples

XRD analysis for material graphite, EG_{Zn} and EG_0 were performed. As shown in Fig. 5, the two peaks with the interplanar crystal spacing of 0.3354 nm and 0.167 nm corresponding to diffraction angle of 26.6°, 54.8° are the characteristic spectrum of natural graphite. While, the characteristic peaks corresponding to 002 crystal spacing of EG_{Zn} and EG_0 transfer to a smaller angle of 25.8° and 26.0°, respectively. Each peak corresponds to a big interplanar crystal spacing of 0.3423 nm and 0.3420 nm due to intercalation in graphene planes. Under the oxidation of KMnO₄, the non-carbonaceous reactant can be easily inserted into the graphene planes, leading to the increase of interplanar crystal spacing. Owing to adequate intercalation reaction, EG_{Zn} gets bigger interplanar crystal spacing than EG, and it possesses higher dilatability.
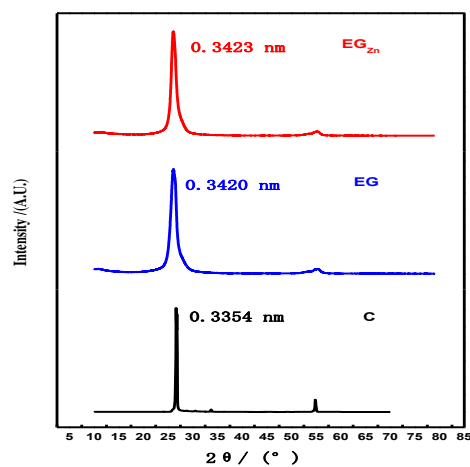

Fig 5. XRD analysis of graphite, EG and EG$_{Zn}$

FTIR analysis of EG$_{Zn}$

Fig. 6 is the FTIR of EG_{Zn}. It gives the characteristic absorption peaks of -OH (3432 cm^{-1}) and sulfate (1080-1000 cm^{-1}) caused by the intercalation of H_2SO_4/HSO_4^-, which indicates the intercalation of H_2SO_4/HSO_4^- [20]. Peaks around 1730 cm^{-1} is the adsorption band of C=O [21]. At the same time, absorption at about 1627 cm^{-1} are the specific peak of C=C [22]. The peak in the range of 1100-1460 cm^{-1} is the stretching vibration of the three-coordinate B-O bond. Among them, the absorption peak at 1289 cm^{-1} is generated by the in-plane bending vibration of the B-O-H bond, and the peak at 1394 cm^{-1} is the characteristic peak of BO_3 [23], which verifies the existence of borate.
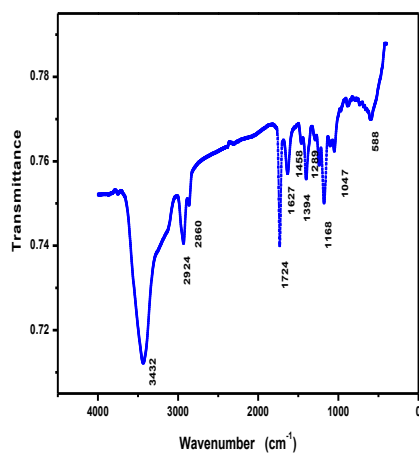

Fig 6. FTIR of the EG_{Zn}

D. Characterizations of RPUFs

Influence of the GICs on RPUF density and compression strength

Density and compression strength of RPUF mainly depends on the type and amount of foaming agent and FRs [24]. Results listed in Table 1 indicate that the addition of EG and EG_{Zn} can increase the foam density. However, it shows a negative effect on compression strength, and the value reduces by about 68%. So, in order to maintain the strength of the RPUF while maintaining its flame retardancy, it is necessary to add a reinforcing agent, such as APP [25].

TABLE I
Influence of the GICs on RPUF density and compression strength

Samples	Compression strength (MPa)	Density (kg/m^3)
100RPUF	0.1178	29.8
70RPUF/30EG$_0$	0.0369	32.0
70RPUF/30EG$_{Zn}$	0.0373	32.5

Influence of the GICs on RPUF pore structure

To further discuss the results of foam compression strength, the influence of GICs on foam pore structure was investigated by SEM. As shown in Fig. 7, holes of the pure RPUF are rich and closed with the diameter ranging from 50 μm to 250 μm (Fig. 7(a)). Addition of EG_{Zn} and the EG_0 can damage the cellular structure in the direction parallel to foam growth, and then cause tearing, collapsing and colliding of pores (Fig. 7(b), Fig. 7(c)). So they directly reduce the closed cell numbers and the foam compression strength.

Influence on RPUF combustion behaviors

The influence of EG_{Zn} and the EG_0 on RPUF combustion LOI and vertical burning level were investigated in the form of comparison. As shown in Table 2, pure RPUF is very flammable; the cellular structure makes it hold high level of radiant flux and large surface areas. Addition of EG_{Zn} and the EG_0 can improve the LOI value. This is because when graphite reacts with the intercalated H_2SO_4/HSO_4^- at high temperature, it cannot only consume a lot of calories and then cause the burning temperature decrease, but also release CO_2, SO_2 and H_2O gases. These evolved gases can dilute the concentration of oxygen near the flame zone, which causes the improved LOI. The high vertical burning level should be attributed to the excellent char forming property of the GICs. EG_{Zn} shows better flame retardancy than the referenced EG_0, caused by its more excellent expansion performance due to the modification. The larger the EV is, the thicker the residue layer, and the better the flame retardancy.

TABLE II
Results of LOI and vertical burning level of RPUFs

Samples	Vertical burning level	LOI /%
100RPUF	-	20.5
70RPUF/30EG$_0$	V-1	25.8
70RPUF/30EG$_{Zn}$	V-0	26.9

Structures of combustion residues

The digital camera and SEM images of vertical burning residues of pure RPUF (a, a'), 80RPUF/30EG$_{Zn}$ (b, b') were presented in Fig. 8. The char layer of pure RPUF is very less, and it contains

numerous open holes caused by the released CO, CO_2, HCN, NO, HCOH gases [26]. By contrast, residue of $80RPUF/30EG_{Zn}$ is thicker and puffier. The matrix
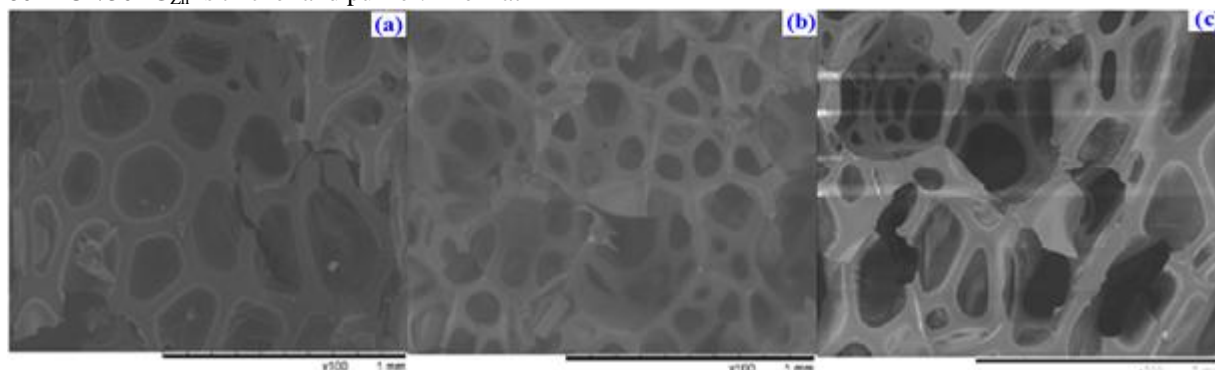

Fig 7. The SEM morphologies of pure RPUF (a), $70RPUF/30EG_{Zn}$ (b), $80RPUF/30EG_0$ (c)
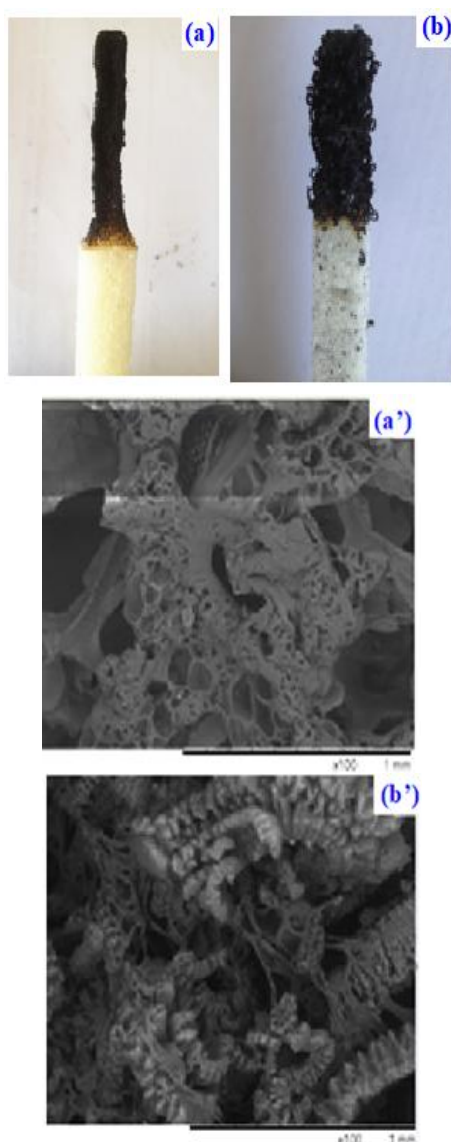

Fig 8. Residual micrographies of pure RPUF (a), $80RPUF/30EG_{Zn}$ (b) by digital camera and RPUF (a'), $80RPUF/30EG_{Zn}$ (b') by SEM

surface is completely covered with "worm-like" particles due to the expansion of EG_{Zn}. It also shows

"popcorn effect" due to the weak cohesiveness between graphite particles and RPUF.

IV. CONCLUSIONS

Adjusting the dosage of H_2SO_4, $KMnO_4$ and $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ can affect dilatability of GIC. To get GIC with high EV, the feasible mass ratio of graphite C, $KMnO_4$, H_2SO_4 (98 wt%) and $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ was determined as 1.0:0.25:4.5:0.3, the used H_2SO_4 should be diluted to 75 wt% before reaction, and the reaction lasts 40min at 50℃. Under this condition, the prepared EG_{Zn} possessed a maximum EV of 517 mL/g. EG_{Zn} showed better dilatability and flame retardancy than the normal EG_0. Its excellent flame retardancy was attributed to the ability of absorbing enormous amount heat and forming swollen multicellular carbonaceous char. Addition of the FRs increased the foam density but decreased its compress strength.

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