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Preparation and Characteristics of Expandable Graphite with Sodium Tripolyphosphate Assistant Intercalation

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Expandable graphite having low initial expansion temperature and high dilatability was successfully prepared in graphite chemical oxidation and intercalating reaction with $KMnO_4$ as an oxidant, H_2SO_4 as an intercalator and sodium tripolyphosphate (STPP) as an assistant intercalator. The mass ratio of C:$KMnO_4$:H_2SO_4 (98 %):STTP was controlled as 1.0:0.18:5.0:0.7, H_2SO_4 diluted to 80 wt. % before intercalation reaction, and the reaction lasted 40 min at 40 °C. Expanded volume and initial expansion temperature of the prepared expandable graphite reached 630 mL/g (at 800 °C) and 146 °C, respectively. X-ray diffraction spectroscopy testified the intercalation and layer structure of expandable graphite, and Fourier transform infrared spectroscopy illuminated components of intercalating composite. Flame retardancy of expandable graphite for linear low density polyethylene was also investigated. Addition of 30 wt. % the expandable graphite to the polymer improved the limiting oxygen index from 17.5 to 28.4 %. On the other hand, the limiting oxygen index of the same amount of blank expandable graphite (with only H_2SO_4 as intercalator) was only 25.6 %. Assistant intercalation of sodium tripolyphosphate improved the dilatability and flame retardancy.

Keywords: Expandable graphite, Sodium tripolyphosphate, Intercalation reaction, Dilatability, Initial expansion temperature.

INTRODUCTION

Graphite is a kind of crystal compound with layer structure, and its intercalating compound named expandable graphite can be prepared when non-carbonaceous reactants are inserted into graphite layers through chemical or electrochemical reaction[1,2]. Expandable graphite has many good properties *e.g.*, it can be used as catalyst in the synthesis of organic ester[3], and when it expands at high temperature, a poriferous material called expanded graphite is prepared. Expanded graphite is a kind of effective adsorbent for heavy oil and dyes wastewater[4-6]. At the same time, expandable graphite is a good intumescent type flame-retardant for its good capability of halogen-free and non-dropping[7,8]. When expandable graphite exposes to flame, it can give a swollen multicellular char, which can protect materials from heat and oxygen. Simultaneously, expandable graphite absorbs huge heat during the instant expansion, which can decrease the burning temperature. When it is oxidized on reaction with H_2SO_4 at high temperature as shown in eqn. 1[9], the released gas can reduce concentration of combustible gas. All these characteristics indicate expandable graphite is a good flame retardant.

$$C + 2H_2SO_4 \rightarrow CO_2 \uparrow + 2SO_2 \uparrow + 2H_2O \uparrow \quad (1)$$

When expandable graphite is used as flame retardant, its dilatability [shown as expanded volume (EV)] and thermal stability (shown as initial expansion temperature T_0) are very important parameters. According to T_0, expandable graphite is classified into three kinds[10] *i.e.*, low T_0 (between 80-150 °C), middle T_0 (between 180-240 °C) and high T_0 (between 250-300 °C) expandable graphite.

In the preparation of expandable graphite, reactants and theirs contents, such as oxidant, intercalator and assistant intercalator, and reaction temperature, reaction time can all affect its dilatability. With $KMnO_4$ as an oxidant, H_2SO_4 and acetic acid as the intercalator and assistant intercalator respectively, expandable graphite with a T_0 of 160 °C and expanded volume of 460 mL g^{-1} was prepared[11]. Expandable graphite holding a T_0 of 310 °C and expanded volume of 270 mL g^{-1} could be prepared with 85 wt. % H_2SO_4 as an intercalator, $KMnO_4$ as an oxidant and $FeSO_4$ as a close agent[12].

Linear low-density polyethylene (LLDPE) possesses low machining temperature (less than 140 °C) and it is very flammable. In this research, with $KMnO_4$ as oxidant, H_2SO_4 as intercalator and sodium tripolyphosphate (STPP) as assistant intercalator, the expandable graphite (EG) with a low T_0, high dilatability and fitting for linear low-density polyethylene flame retardancy was prepared. The dosages of $KMnO_4$,

H_2SO_4, sodium tripolyphosphate 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) of the expandable graphite for linear low-density polyethylene was also investigated.

EXPERIMENTAL

Natural flake graphite with an average flake size of 0.3 mm and a carbon content of 95 % was provided by Action Carbon CO. LTD, Baoding, China. The analytical reagents sodium tripolyphosphate was obtained from Kermel CO., Tianjin, China. H_2SO_4 (98 %) and $KMnO_4$ are all analytical agents. Linear low-density polyethylene 7540 (comonomer α-butene; density 0.926 g/cm^3; tensile strength 9 kg/cm^2; MFI 0.76 g/10 min)

Preparation of the expandable graphite: In the intercalating reaction of material graphite, the reactants were quantified according to a definite mass ratio of C:H_2SO_4 (98 %):$KMnO_4$:STPP, and 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, sodium tripolyphosphate, C and $KMnO_4$ in a 250 mL beaker, controlled at a constant temperature. After reaction, the solid phase was washed with deionized water and dipped in water for 2 h until pH of the waste water reached to 6-7, then expandable graphite obtained after filtration and drying at 50-60 °C for about 5 h.

Characterization of the samples

Expanded volume: Expanded volume (EV) was an important factor to judge dilatability of expandable graphite. It is measured as follows: 0.300 g of expandable graphite was roasted for 10 sec in muffle furnace at a high temperature, and then the volume was detected and converted into expanded volume with a unit of mL/g.

Detection of T_0: A 0.300 g of the prepared expandable graphite was spread on an evaporating dish and heated in heating oven for some time, then the sample was removed and its volume was measured. When the detected volume of expandable graphite was 1.5 times of its initial volume, the oven temperature was defined as T_0.

XRD analysis: XRD analysis for material graphite and the prepared expandable graphite were performed with a Y-4Q X-ray diffractometer (Dandong, China) employing Ni-filtered $CuK_{\alpha 1,2}$ radiation with 2θ ranging from 15° to 70°.

FTIR analysis: The prepared intercalating products were 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}.

Sample processing and limiting oxygen index detection: Mixtures of flame retardant and linear low-density polyethylene 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 limiting oxygen index according to GB/T2406-1993 with oxygen index instrument (Chengde, China).

RESULTS AND DISCUSSION

Influence of reactant dosages and reaction condition on expandable graphite dilatability: Expandable graphite was prepared with $KMnO_4$ as an oxidant, H_2SO_4 as an intercalator and sodium tripolyphosphate as assistant intercalator. The influence of mass ratio of graphite to $KMnO_4$, sodium tripolyphosphate, H_2SO_4 and its concentration, reaction time and temperature on expandable graphite dilatability were tested, respectively.

Influence of $KMnO_4$ dosage on expandable graphite dilatability: In order to investigate the influence of $KMnO_4$ dosage on dilatability, single-factor experiments were carried out by changing $KMnO_4$ dosage in the range of 0.16-0.26 g/g. According to the method mentioned above, experiments were carried out under the constant mass ratio C:STPP:H_2SO_4 (98 %) of 1.0:0.7:5.0. Before reaction, H_2SO_4 was diluted to 80 wt. %, and the reaction lasted 1 h at 40 °C.

Fig. 1 shows the changes of expanded volume with the amount of $KMnO_4$. As an oxidant, less amount of $KMnO_4$ caused an incomplete oxygenation of graphite and decrease of expanded volume, while excess $KMnO_4$ will cause excessive oxygenation of graphite, which leads to a decrease in expandable graphite granularity and expanded volume. When the mass ratio of $KMnO_4$ to C is controlled as 0.18 g/g, the prepared expandable graphite possesses a maximum expanded volume of 600 mL/g. Obviously, the feasible dosage of $KMnO_4$ can be set as 0.18 g/g.

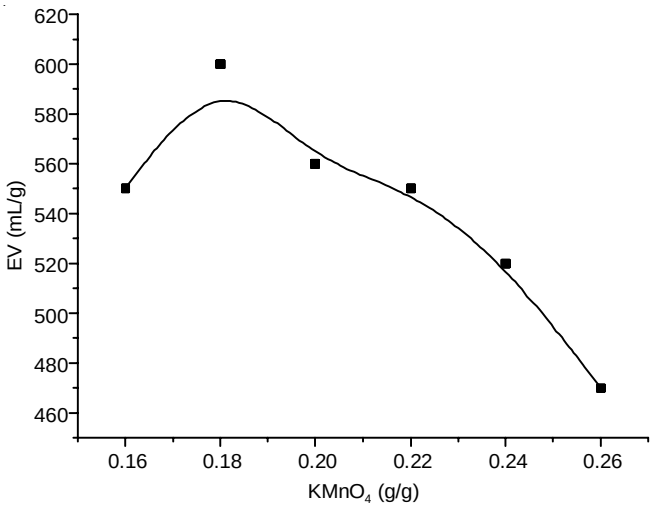

Fig. 1. Influence of $KMnO_4$ dosage on expanded volume

Influence of H_2SO_4 dosage on expandable graphite dilatability: In order to investigate its influence and feasible dosage, H_2SO_4 dosage was changed in the range of 4-6 g/g. Experiments were carried out under the constant mass ratio C:STPP:$KMnO_4$ of 1.0:0.7:0.18, the reaction lasted 1 h at 40 °C, and H_2SO_4 was diluted to 80 wt. %.

Fig. 2 shows the changes of expanded volume with H_2SO_4 amount. As a main reactant, H_2SO_4 plays three roles in this reaction: (1) as a main intercalator; (2) as an oxidant and (3) providing an acidic environment for the oxidation of $KMnO_4$. Eqn. 2 shows that insufficient H_2SO_4 will incur a poor oxidation of $KMnO_4$ and H_2SO_4, cause an incomplete intercalation

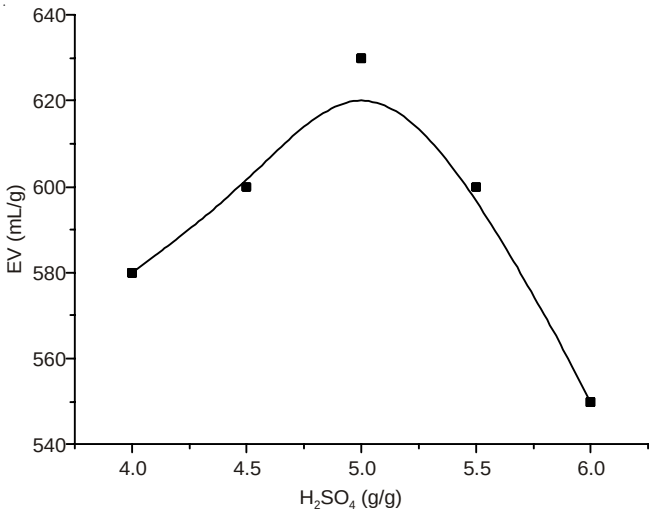

Fig. 2. Influence of H_2SO_4 dosage on expanded volume

reaction and lead to the decrease of dilatability. With the increase of H_2SO_4 dosage, the oxidation of $KMnO_4$ and H_2SO_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 in three areas, the prepared expandable graphite will have the largest expanded volume. Conversely, expanded volume will decrease when the H_2SO_4 dosage under or over the suitable value. Results shown in Fig. 2 presents the feasible mass ratio of H_2SO_4 to C is 5.0 g/g.

$$E_{MnO_4^-/Mn^{2+}} = E^\circ_{MnO_4^-/Mn^{2+}} + (0.05916/5) \lg \{[H^+]^8[MnO_4^-]/[Mn^{2+}]\} \quad (2)$$

Influence of H_2SO_4 concentration on expandable graphite dilatability: Under the constant mass ratio C:STPP:$KMnO_4$:H_2SO_4 (98 %) of 1.0:0.7:0.18:5.0 (g/g), the reaction lasted 1 h at 40 °C, influence of H_2SO_4 wt. % in the reaction was detected. Before reaction, 98 wt. % H_2SO_4 was diluted with de-ionized water to different wt. % in the range of 76-84 % as shown in Fig. 3.

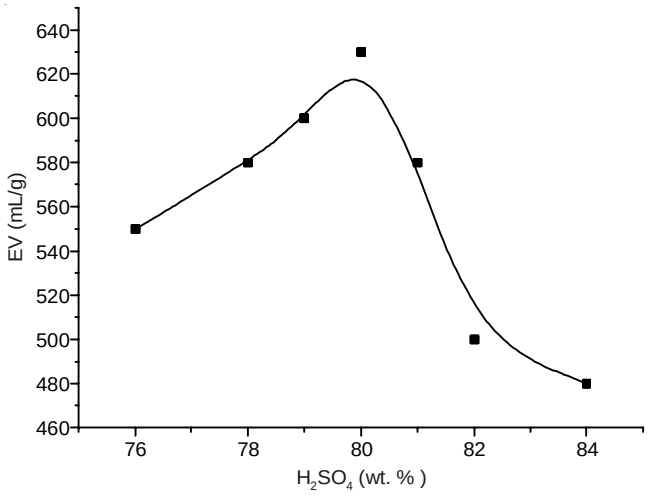

Fig. 3. Influence of concentration H_2SO_4 wt. % on expanded volume

Electrode potential of MnO_4^-/Mn^{2+} can be calculated according to eqn. 2. It shows there exists a positive correlation between $[H^+]$ and the oxidation of $KMnO_4$. Therefore, within a certain range, the oxidation of $KMnO_4$ enhances with the increase of H_2SO_4 concentration, causing the intercalation reaction gradually completed and leading 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 concentration. As shown in experiment results, the feasible H_2SO_4 concentration is 80 wt. %.

Influence of sodium tripolyphosphate dosage on expandable graphite dilatability: Under the constant mass ratio C:H_2SO_4 (98 %):$KMnO_4$ of 1.0:5.0:0.18 (g/g), the reaction lasted 1 h at 40 °C and H_2SO_4 diluted to 80 wt. %, the influence of sodium tripolyphosphate dosage was detected in the range of 0.5-0.9 g/g.

As an assistant intercalator, increase of sodium tripolyphosphate dosage can improve expandable graphite dilatability as shown in Fig. 4. When the mass ratio of sodium tripolyphosphate to C is controlled as 0.7 g/g, expandable graphite with maximum expanded volume of 630 mL/g can be gained. Superfluous sodium tripolyphosphate will cause the relative scarcity of $KMnO_4$ and incomplete oxygenation of graphite.

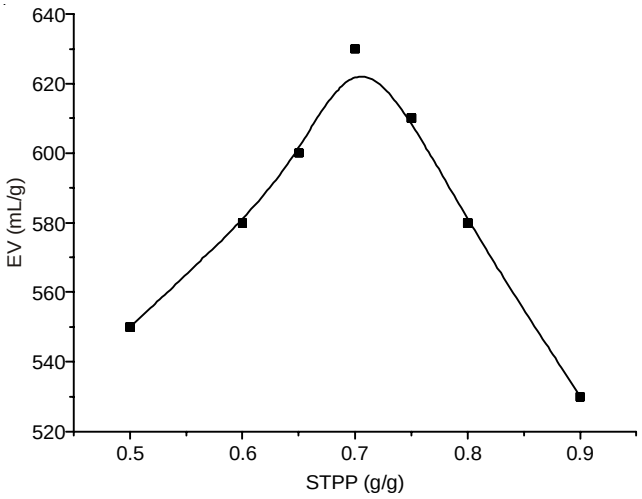

Fig. 4. Influence of sodium tripolyphosphate dosage on expanded volume

Influence of reaction temperature on expandable graphite dilatability: Influence of reaction temperature on the reaction is mainly reflected in two aspects: Reaction rate and balance direction. For the reaction rate, it is positively correlated with reaction temperature. Instead, for exothermic reaction, such as oxidation 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.

Under the constant mass ratio C:H_2SO_4 (98 %):$KMnO_4$:STTP of 1.0:5.0:0.18:0.7 (g/g), H_2SO_4 diluted to 80 wt. % before reaction, and reaction lasted 1 h, the influence of reaction temperature on expanded volume was detected. When it is less than 40 °C, the increase of temperature can improve expandable graphite dilatability. However, 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 expandable graphite dilatability: Under the constant mass ratio C:H_2SO_4 (98 %):$KMnO_4$:STPP of 1.0:5.0:0.18:0.7 (g/g), H_2SO_4 diluted to 80 wt. %

and reaction temperature controlled at 40 °C, the influence of reaction time on expanded volume was studied. Results show that extension of reaction time increases expandable graphite dilatability in the former 40 min, and then it remain the same. Therefore, reaction time can be set as 40 min.

Feasible condition of expandable graphite preparation: According to the experimental results, feasible conditions of expandable graphite (EG) preparation can be set as: (1) Mass ratio C:$KMnO_4$:H_2SO_4 (98 %):STPP of 1.0:0.18:5.0:0.7; (2) H_2SO_4 diluted to 80 wt. % before reaction; (3) Intercalation reaction lasted 40 min at 40 °C. The expanded volume of expandable graphite 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 expandable graphite. T_0 and the maximum expanded volume of the prepared expandable graphite are 146 °C and 630 mL/g, respectively.

Preparation of blank expandable graphite EG_1 with only H_2SO_4 intercalation: Compared with expandable graphite, EG_1 was prepared under the mass ratio C:$KMnO_4$:H_2SO_4 (98 %) of 1.0:0.18:5.0, other condition were the same as expandable graphite. T_0 and the maximum expanded volume of EG_1 was detected as 205 °C and 450 mL/g, respectively. Sodium tripolyphosphate obviously affect dilatability of expandable graphite, and what's more, addition of 0.7 g/g sodium tripolyphosphate in graphite intercalating reaction cause an increase of 40 % of expanded volume. expandable graphite will show better flame retardancy than EG_1 for its good dilatability.

Characterization of graphite and its intercalating compounds

XRD analysis of natural graphite and expandable graphite: XRD analysis for natural graphite and expandable graphite were performed. As shown in Fig. 5(a), the two peaks with the interplanar crystal spacing of 3.34 and 1.67 Å corresponding to diffraction angle of 26.6°, 54.8° are the characteristic spectrum of natural graphite. As shown in Fig. 5(b), the peaks at 26.16° and 55.38° show expandable graphite keeps the same layer structure as natural graphite. But it is worthy to note that the diffraction peak of 26.6° transfer to smaller angle of 26.16°. At the same time, it corresponds to a big interplanar crystal spacing of 3.41 Å 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, leading to the increase of interplanar crystal spacing.

FTIR analysis of the prepared samples: Fig. 6 shows FTIR spectra of the prepared expandable graphite and EG_1. As can be seen from the results, two samples both show the characteristic absorption peaks of -OH at 3430, caused by intercalation of H_2SO_4 or HSO_4^-. At the same time, the peaks at 1630 and 1400 cm^{-1} are the specific absorption peaks of C=O, originating from the oxidized-graphite by $KMnO_4$. The absorption peaks of S=O in EG_1 is at 1158 cm^{-1}, but there are two peaks superimposed obviously at 1118 and 1057 cm^{-1} in the FTIR of expandable graphite, it is because the absorption peaks of S=O and P=O are both appear in the range of 1350-1100 cm^{-1} as reported[13]. Furthermore, the peaks at 872 cm^{-1} in the expandable graphite belongs to sodium tripolyphosphate specific absorption[14]. The results announce the intercalation of intercalator.

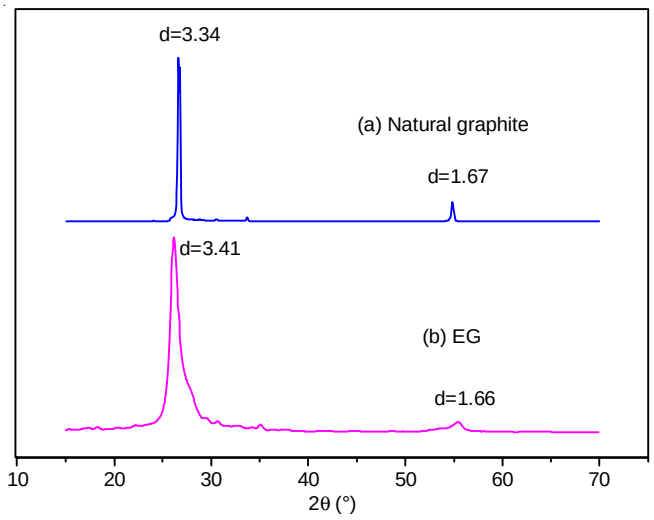

Fig. 5. XRD of natural graphite and expandable graphite (EG)

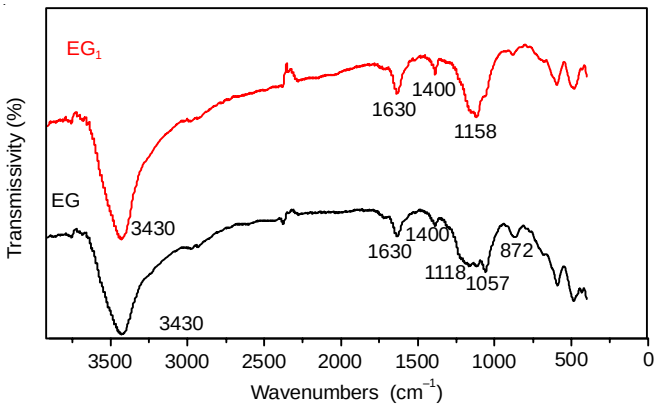

Fig. 6. FTIR analysis of EG_1 and expandable graphite (EG)

Detection of flame retardance for linear low-density polyethylene: Processing temperature of linear low-density polyethylene is lower than 140 °C, so the prepared expandable graphite and EG_1 can be used as retardant. The flame retarding composites were prepared as mentioned above, and theirs limiting oxygen index of pure linear low-density polyethylene, 70LLDPE/30EG and 70LLDPE/30EG_1 (shown as wt. %) were detected according to the mentioned method. Results show that limiting oxygen index of single linear low-density polyethylene is only 17.5 %, and its combustion accompanies with molten drop at the same time. Addition of 30 % EG_1 improves limiting oxygen index to 25.6 %, no molten drop occurs. Whereas, the addition of the same amount of expandable graphite can improve limiting oxygen index to 28.4 %, and no molten drop occurs too. Whereas, the intercalating sodium tripolyphosphate is more effectual in improving the flame retardancy.

Conclusion

According to the analysis of the experiment results, it is evident that the mass ratio of C:$KMnO_4$:H_2SO_4 (98 %):STPP has important influence on expandable graphite dilatability, and when it is controlled as 1.0:0.18:5.0:0.7, H_2SO_4 diluted to 80 wt. % before intercalation reaction and intercalating reaction lasted 40 min at 40 °C, the expanded volume and T_0 of the prepared expandable graphite can reach 630 mL/g and 146 °C,

respectively. The intercalating reaction between graphite and H_2SO_4, sodium tripolyphosphate can be revealed by XRD and FTIR analysis of intercalation compounds. Expandable graphite has more effective flame retardancy than blank EG_1.

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