Research Article

Preparation and Antiflame Performance of Expandable Graphite Modified with Sodium Hexametaphosphate

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A kind of polyphosphate modified expandable graphite (EG_p) was prepared in graphite oxidation and intercalation reaction with $KMnO_4$ as oxidant, H_2SO_4 as intercalator, and sodium hexametaphosphate (SHMP) as assistant intercalator. The feasible mass ratio of C : $KMnO_4$: H_2SO_4 (98%) : SHMP was determined as 1.0 : 0.3 : 4.5 : 0.6, H_2SO_4 was diluted to 77 wt% before intercalation reaction, and the reaction lasted for 40 min at 40°C. Expanded volume and initial expansion temperature of the prepared EG_p reached 600 mL/g (at 800°C) and 151°C, respectively. X-ray diffraction spectroscopy testified the intercalation and layer structure of EG_p , and Fourier transform infrared spectroscopy illuminated the intercalated functional groups. Flame retardance of the prepared EG_p and the referenced EG (with only H_2SO_4 as intercalator) for linear low density polyethylene (LLDPE) was also investigated. Addition of 30 wt% EG_p to the polymer improved the limiting oxygen index (LOI) from 17.5 to 27.3%. On the other hand, the LOI of the same amount of the referenced EG was only 24.6%. Assistant intercalation of SHMP improved the dilatability and flame retardancy.

1. Introduction

Graphite is a kind of crystal compound with layer structure, and its intercalating compound named expandable graphite can be prepared when noncarbonaceous reactants are inserted into graphite layers through chemical or electrochemical reaction [1, 2]. Expandable graphite has many good properties: 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 nondropping [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, the released CO_2 , SO_2 , and H_2O can reduce concentration of combustible gas [9]. All these characteristics indicate expandable graphite is a good flame retardant.

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 [10], and it can be divided into three kinds: low T_0 (between 80 and 150°C), middle T_0 (between 180 and 240°C), and high T_0 (between 250 and 300°C) expandable graphite.

In the preparation of expandable graphite, reactants and their contents, such as oxidant, intercalator and assistant intercalator, and reaction temperature, reaction time can all affect its dilatability. With $KMnO_4$ as oxidant and H_2SO_4 and acetic acid as intercalator and assistant intercalator, expandable graphite with a T_0 of 160°C and EV of 460 mL g⁻¹ was prepared [11]. Expandable graphite holding a T_0 of 310°C and EV of 270 mL g⁻¹ could be prepared with 85 wt% H_2SO_4

as intercalator, KMnO_4 as oxidant, and FeSO_4 as 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 and H_2SO_4 as intercalator, and sodium hexametaphosphate (SHMP) as assistant intercalator, the phosphate modified expandable graphite (EG_p) with high dilatibility and fitting for LLDPE flame retardancy was prepared. The dosages of KMnO_4 , H_2SO_4 , and SHMP and reaction temperature and 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 EG_p for LLDPE, was also investigated.

2. Experimental

2.1. Materials and Reagents. Natural flake graphite with an average flake size of 0.3 mm and a carbon content of 92% was provided by Action Carbon Co. Ltd., Baoding, China. Analytical reagent of SHMP was obtained from Fuchen, Tianjin, China. H_2SO_4 (98%) and KMnO_4 are all analytical agents. LLDPE (7042, 0.918 g/cm^3 , melt index 2.0 g/10 min).

2.2. Experimental Method

2.2.1. EG_p Preparing Procedure and Its Optimization. In the intercalating reaction of material graphite, the reactants were quantified according to a definite mass ratio of $\text{C}:\text{H}_2\text{SO}_4$ (98%): KMnO_4 :SHMP, and H_2SO_4 was diluted with deionized water before reaction. Then, the quantified reactants were mixed and stirred in the order of the diluted H_2SO_4 , SHMP, 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 2.0 h until pH of the wastewater reached 6.0–7.0, and then EG_p is obtained after filtration and drying at $50\text{--}60^\circ\text{C}$ for about 5.0 h. Its dilatibility showing as EV and T_0 was detected according to the reported method [11].

The influences of mass ratio of graphite to KMnO_4 , SHMP, and H_2SO_4 and its concentration, reaction time, and temperature on EG_p dilatibility were tested as follows.

2.2.2. Influence of KMnO_4 Dosage on EG_p Dilatibility. In order to investigate the influence of KMnO_4 dosage on dilatibility, single-factor experiments were carried out by changing KMnO_4 dosage in the range of 0.2–0.6 g/g. According to the method mentioned above, experiments were carried out under the constant mass ratio $\text{C}:\text{SHMP}:\text{H}_2\text{SO}_4$ (98%) of 1.0:0.6:4.5. Before reaction, H_2SO_4 was diluted to 80 wt%, and the reaction lasted for 1.0 h at 40°C .

Figure 1 shows the changes of EV with the amount of KMnO_4 . As an oxidant, insufficient KMnO_4 will cause 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

FIGURE 1: Influence of KMnO_4 dosage on EV.

EV. When the mass ratio of KMnO_4 to C is controlled as 0.3 g/g, the prepared EG possesses a higher EV of 600 mL/g, and then the feasible dosage of KMnO_4 can be set as 0.3 g/g.

2.2.3. Influence of H_2SO_4 Dosage on EG Dilatibility. In order to investigate its influence and feasible dosage, H_2SO_4 dosage was changed in the range of 3.5–6.0 g/g. Experiments were carried out under the constant mass ratio $\text{C}:\text{SHMP}:\text{KMnO}_4$ of 1.0:0.6:0.3, the reaction lasted for 1 h at 40°C , and H_2SO_4 was diluted to 80 wt%.

Figure 2 shows the changes of EV with H_2SO_4 amount. In intercalation reaction of graphite, H_2SO_4 acts as intercalator and oxidant and provides an acidic environment for the oxidability of KMnO_4 . Equation (1) shows that insufficient H_2SO_4 will incur a poor oxidation of KMnO_4 and H_2SO_4 , cause an incomplete intercalation reaction, and lead to the decrease of dilatibility. 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 dilatibility. When the H_2SO_4 dosage achieves a balance in three areas, the prepared EG will present high EV. Conversely, EV will decrease when the H_2SO_4 dosage is under or over the suitable value. Results shown in Figure 2 present that the feasible mass ratio of H_2SO_4 to C is 4.5 g/g:

$$E_{\text{MnO}_4^-/\text{Mn}^{2+}} = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} + \left(\frac{0.05916}{5} \right) \log \left\{ \frac{[\text{H}^+]^8 [\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \right\} \quad (1)$$

2.2.4. Influence of H_2SO_4 Concentration on EG Dilatibility. Under the constant mass ratio $\text{C}:\text{SHMP}:\text{KMnO}_4:\text{H}_2\text{SO}_4$ (98%) of 1.0:0.6:0.3:4.5 (g/g), the reaction lasted for 1 h at 40°C , and influence of H_2SO_4 wt% in the reaction was detected and shown in Figure 3. Before reaction, 98 wt% H_2SO_4 was diluted with deionized water to different wt% in the range of 65%–85%.

Electrode potential of $\text{MnO}_4^-/\text{Mn}^{2+}$ can be calculated according to (1). It shows that there is a positive correlation

FIGURE 2: Influence of H₂SO₄ dosage on EV. FIGURE 3: Influence of H₂SO₄ wt% on EV.

between $[H^+]$ and the oxidation of $KMnO_4$. Therefore, within a certain range, the oxidation of $KMnO_4$ is enhanced with the increase of H_2SO_4 concentration, causing the intercalation reaction gradually completed and leading to the increases of dilatibility. But, with the further increase of H_2SO_4 concentration, it will cause the excessive oxidation of graphite when it is over a suitable concentration. As shown in experiment results, the feasible H_2SO_4 concentration is 77 wt%.

2.2.5. Influence of SHMP Dosage on EG Dilatibility. Under the constant mass ratio C : H_2SO_4 (98%) : $KMnO_4$ of 1.0 : 4.5 : 0.3 (g/g), the reaction lasted for 1 h at 40°C and H_2SO_4 was diluted to 77 wt%, and the influence of SHMP dosage was detected in the range of 0.4~0.8 g/g.

As an assistant intercalator, increase of SHMP dosage can improve EG dilatibility as shown in Figure 4. When the mass ratio of SHMP : C is controlled as 0.6 g/g, EG holds a maximum of EV. Superfluous SHMP will cause the relative scarcity of $KMnO_4$ and incomplete oxygenation of graphite.

FIGURE 4: Influence of SHMP dosage on EV.

2.2.6. Influence of Reaction Temperature on EG Dilatibility.

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%) : $KMnO_4$: SHMP of 1.0 : 4.5 : 0.3 : 0.6 (g/g), H_2SO_4 diluted to 77 wt% before reaction, and reaction that lasted for 1 h, the influence of reaction temperature on EV was detected. When it is less than 40°C, the increase of temperature can improve EG dilatibility. 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.

2.2.7. Influence of Reaction Time on EG Dilatibility.

Under the constant mass ratio C : H_2SO_4 (98%) : $KMnO_4$: SHMP of 1.0 : 4.5 : 0.3 : 0.6 (g/g), H_2SO_4 diluted to 77 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 dilatibility in the former 40 min, and then it remains the same. Therefore, reaction time can be set as 40 min.

2.3. Characterization of the Samples

2.3.1. 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 Cu K α radiation with 2θ ranging from 15° to 70°.

2.3.2. 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 mold, and FTIR spectra were recorded between 4000 and

400 cm^{-1} using FTS-40 FTIR spectrograph (America) with a resolution of 2 cm^{-1} .

2.3.3. Sample Processing and LOI Detection. Mixtures of flame retardant and LLDPE were melted at 140°C in Muller (Jiangsu, China) and pressed at 10 MPa, and then samples were chopped into slivers with size of 120.0 × 6.0 × 3.0 mm^3 . The slivers were used to measure LOI according to GB/T2406-1993 with oxygen index instrument (Chengde, China).

3. Results and Discussion

3.1. Feasible Condition of EG_p Preparation. According to the experiment results, feasible conditions of EG_p preparation can be set as mass ratio C : KMnO_4 : H_2SO_4 (98%) : SHMP of 1.0 : 0.3 : 4.5 : 0.6; H_2SO_4 diluted to 77 wt% before reaction; intercalation reaction that lasted for 40 min at 40°C. The EV of EG_p under different expansion temperature was detected, and it shows an increasing trend along with the increasing expansion temperature before 800°C, and then it presents a decreasing trend caused by excessive oxygenation of EG_p . T_0 and the maximum of EV are 151°C and 600 mL/g, respectively.

3.2. Preparation of the Referenced Expandable Graphite (EG). Compared with EG_p , the referenced EG was prepared under the mass ratio C : KMnO_4 : H_2SO_4 (98%) of 1.0 : 0.3 : 4.5, and other conditions were the same as EG_p . T_0 and the maximum of EV were detected as 205°C and 480 mL/g, respectively. SHMP obviously affects dilatibility of EG_p and, what is more, addition of 0.6 g/g SHMP in graphite intercalating reaction makes EV increase 25%. EG_p will show better flame retardancy than EG for its good dilatibility.

3.3. Characterization of Graphite and Its Intercalating Compounds

3.3.1. XRD Analysis of Natural Graphite and EG_p . XRD analyses for natural graphite and EG_p were performed. As shown in Figure 5 of natural graphite the two peaks with the interplanar crystal spacing of 3.34 Å and 1.67 Å corresponding to diffraction angles of 26.6° and 54.8° are the characteristic spectrum of natural graphite. As shown in Figure 5 of EG_p the peaks of 26.2° and 55.4° show that EG_p keeps the same layer structure as natural graphite. But it is worthy to note that the diffraction peak of 26.6° transfers to smaller angle of about 26.2°. At the same time, it corresponds to a big interplanar crystal spacing of 3.44 Å due to intercalation in graphene planes. It can be clearly seen that under the oxidation of KMnO_4 , the noncarbonaceous reactant can be easily inserted into the graphene planes, leading to the increase of interplanar crystal spacing.

3.3.2. FTIR Analysis of the Prepared Samples. Figure 6 shows FTIR spectra of the prepared EG_p and EG. 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 peak at 1630 cm^{-1}

FIGURE 5: XRD of natural graphite and EG_p .

FIGURE 6: FTIR analysis of EG and EG_p .

is the specific absorption peaks of C=C, originating from its conjugated structure. The absorption peaks of S=O in EG are at 1160 cm^{-1} , but there are wide superimposed peaks in the range of 1160–1110 cm^{-1} in the FTIR of EG_p , and it is because the absorption peaks of S=O and P=O both appear in the range of 1350–1100 cm^{-1} as reported [13]. Furthermore, the peaks at 1161 cm^{-1} and 901 cm^{-1} in EG_p all belong to SHMP specific absorption [14]. The results announce the intercalation of intercalator.

3.4. Detection of Flame Retardancy for LLDPE. Processing temperature of LLDPE is lower than 140°C, so the prepared EG_p and EG can be used as retardant. The flame retarding composites were prepared as mentioned above, and their LOI of pure LLDPE, 70LLDPE/30 EG_p , and 70LLDPE/30EG (shown as wt%) was detected according to the mentioned method. Results show that LOI of net LLDPE is only 17.5%,

and its combustion accompanies molten drop at the same time. Addition of 30% EG improves LOI to 24.6%, and no molten drop occurs. However, the addition of the same amount of EG_p can improve LOI to 27.3%, and no molten drop occurs too. Therefore, the intercalating STPP is more effectual in improving the flame retardancy.

4. Conclusions

According to the analysis of the experiment results, it is evident that the mass ratio of C : KMnO₄ : H₂SO₄ (98%) : SHMP has important influence on product dilatability, and when it is controlled as 1.0 : 0.3 : 4.5 : 0.6, H₂SO₄ was diluted to 77 wt% before intercalation reaction, and intercalating reaction lasted for 40 min at 40°C, the EV and T₀ of the prepared EG_p can reach 600 mL/g and 151°C, respectively. The intercalating reaction between graphite and H₂SO₄ and SHMP can be revealed by XRD and FTIR analysis of intercalation compounds. EG_p has more effective flame retardancy than the referenced EG.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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