

Preparation of Ferric Nitrate Modified Expandable Graphite and Its Flame Retardance for Polyethylene

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Abstract

A ferric nitrate modified expandable graphite (written as EGFe) was prepared through flake graphite intercalation reaction with H₂SO₄ as main intercalator and ferric nitrate as assistant intercalator simultaneously. The feasible mass ratio of C:KMnO₄:H₂SO₄(98 wt.%):ferric nitrate was determined as 1.0:0.27:5.0:0.17, H₂SO₄ was diluted to 75 wt.% before intercalation reaction, and the reaction lasted 40 min at 40°C. Expanded volume and initial expansion temperature of the prepared EGFe reached 533 mL·g⁻¹ (at 800°C) and 170°C respectively. X-ray diffraction spectroscopy testified the intercalation reaction and layer structure of EG, and Fourier transform infrared spectroscopy illuminated the intercalated functional groups. Flame retardance of the prepared EGFe and the referenced EG (with only H₂SO₄ as intercalator) for linear low density polyethylene (LLDPE) was also investigated. Addition of 30 wt.% the normal EG to the polymer improved the limiting oxygen index (LOI) from 17.5 to 25.5%. While, the LOI of the same amount of the prepared EGFe reached 27.5%. Furthermore, the combination of EGFe and ammonium polyphosphate (II) (APP) made the 70LLDPE/15APP/15EGFe system present a LOI of 30.5%. Assistant intercalation of ferric nitrate improved the EGFe dilatability and flame retardance.

Keywords: *Expandable graphite; Ferric nitrate; Modification; Dilatability; Polyethylene; Flame retardance*

Introduction

As a graphite intercalation compound (GIC), the expandable graphite (EG) is a good intumescent type flame retardant for its good capability of halogen-free and non-dropping [1-3]. When it exposes to flame, the EG can give a swollen multicellular char, which can protect materials from heat and oxygen. Simultaneously, EG absorbs huge heat during the instant expansion, which can decrease the burning temperature. When it is oxidized in reaction with H₂SO₄ at high temperature, the released CO₂, SO₂, H₂O gases can reduce concentration of combustible gas [4,5]. All these characteristics indicate EG is a good flame retardant.

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When EG is used as flame retardant, its dilatibility (shown as expanded volume (EV)) and thermal stability (shown as initial expansion temperature T_0) are very important parameters [6,7]. In the intercalation reaction of graphite, oxidant, intercalator, assistant intercalator and their contents, reaction temperature and reaction time can all affect GIC dilatibility. It was reported the H_2SO_4/APP (ammonium polyphosphate (APP), an assistant intercalator) intercalated EG exhibited a higher EV of $240 \text{ mL}\cdot\text{g}^{-1}$ than that of normal EG (the H_2SO_4 GIC) of $210 \text{ mL}\cdot\text{g}^{-1}$ [8]. EG with a T_0 of 310°C and EV of $270 \text{ mL}\cdot\text{g}^{-1}$ could be prepared with 85 wt.% H_2SO_4 as intercalator, $KMnO_4$ as oxidant and $FeSO_4$ as close agent [9]. The H_2SO_4 /sodium silicate intercalated EG presented a higher EV of $517 \text{ mL}\cdot\text{g}^{-1}$ and LOI of 28.7% for ethylene vinyl acetate copolymer than that of the single H_2SO_4 GIC with an EV of $433 \text{ mL}\cdot\text{g}^{-1}$ and LOI of 24.4% [10].

Linear Low-Density Polyethylene (LLDPE) possesses low machining temperature (less than 140°C) and it is very flammable, and then flame retardants are needed in order to prevent its combustion and delay the spread of fire after ignition. In view of the function of EG as a flame retardant and the influence of assistant intercalator on its dilatibility and flame retardance, the purpose of this research is to prepare a ferric nitrate modified EG (written as EG_{Fe}) with improved dilatibility. In graphite intercalation reaction, the doses of oxidant $KMnO_4$, intercalator H_2SO_4 , assistant intercalator ferric nitrate and reaction temperature, reaction time were optimized. X-ray diffraction spectroscopy (XRD) and Fourier transform infrared spectroscopy (FTIR) were employed to illuminate the layer structure and intercalation components. Flame retardance, indicated as limiting oxygen index (LOI) of the EG_{Fe} for LLDPE was also investigated.

Experimental

Materials and sample preparation

Natural flake graphite (average particle size of 0.30 mm, carbon content of 95 wt.%) was provided by Action Carbon CO. LTD, Baoding, China. LLDPE ($0.918 \text{ g}\cdot\text{cm}^{-3}$, melt index $0.2 \text{ g}\cdot\text{min}^{-1}$) and APP (II, $n>1000$) were purchased from Tianjin and Sichuan, respectively. Ferric nitrate and H_2SO_4 (98 wt.%) were all analytical agents and used as received. Firstly, the reactants were weighed according to a definite mass ratio of graphite (C): H_2SO_4 (98 wt.%): $KMnO_4$:ferric nitrate, and H_2SO_4 was diluted to a demanded weight percent with deionized water before reaction. Then, the quantified reactants were mixed in the order of diluted H_2SO_4 , C, $KMnO_4$ and ferric nitrate in beaker and stirred at a controlled temperature using a water bath. When the reaction finished, the solid phase was washed with deionized water and dipped in water for 2.0 h until pH value of the waste water reached to 6.0-7.0, then filtrated and dried at 60°C for 5.0 h.

Characterization of the samples

EV and T_0 : EV and T_0 of the prepared GICs were detected according to the reported method [7].

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

FTIR analysis: The prepared GICs 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 $4000\text{-}400 \text{ cm}^{-1}$ using FTS-40 FTIR spectrograph (America) with a resolution of 2 cm^{-1} .

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 it was chopped into slivers with size of $120.0\times 6.0\times 3.0 \text{ mm}^3$. The slivers were used to measure LOI according to GB/T2406-1993 with oxygen index instrument (Chengde, China).

Results and Discussion

Influence of reactant doses and reaction condition on EG_{Fe} dilatibility

The influence of various factors on EV of the EG_{Fe} were optimized through single-factor tests including the doses of H₂SO₄ (98 wt.%), KMnO₄, ferric nitrate, and H₂SO₄ concentration, reaction temperature, reaction time.

Influence of KMnO₄ dose on EG_{Fe} dilatibility

In order to investigate the influence of KMnO₄ dose on dilatibility, single-factor experiments were carried out by changing KMnO₄ dose in the range of 0.23-0.37 g·g⁻¹. According to the method mentioned above, they were tried under the constant mass ratio C:ferric nitrate:H₂SO₄ (98 wt.%) of 1.0:0.2:5.0. Before reaction, H₂SO₄ was diluted to 75 wt.%, and the reaction lasted 40 min at 40°C. As shown in Figure 1, the amount of KMnO₄ presents obvious influence on EV. As an oxidant, insufficiency KMnO₄ will cause an incomplete oxygenation of graphite and decrease of EV, while superfluous KMnO₄ will cause excessive oxygenation of graphite, which leads to a decrease in EG granularity and EV. When the mass ratio of KMnO₄ to C is controlled as 0.27 g·g⁻¹, the prepared EG_{Fe} possesses a higher EV of 453 mL·g⁻¹. The feasible dose of KMnO₄ is set as 0.27 g·g⁻¹.

Figure 1: Influence of KMnO₄ dose on EV.

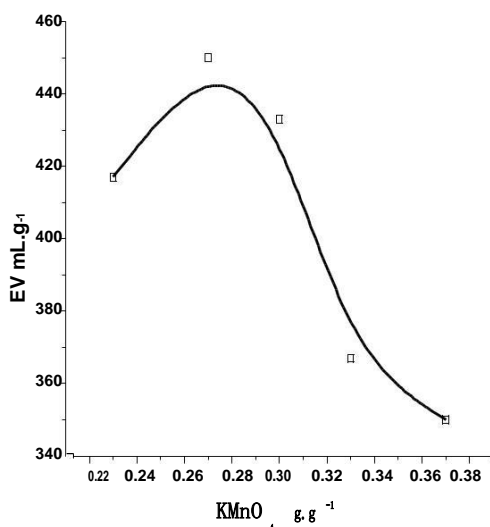
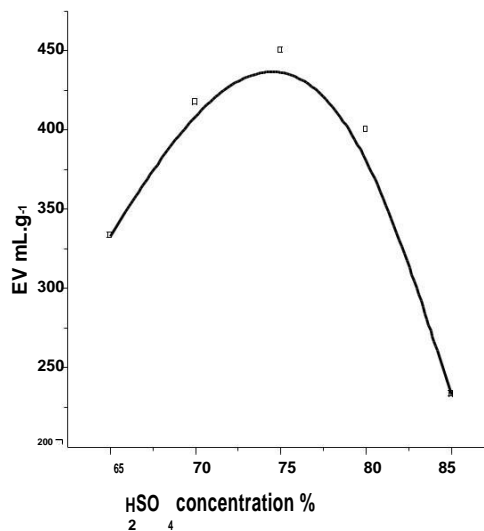


Figure 2: Influence of H₂SO₄ wt.% on EV.



Influence of H₂SO₄ concentration on EG_{Fe} dilatibility

Under the constant mass ratio C:ferric nitrate:KMnO₄:H₂SO₄ (98 wt.%) of 1.0:0.2:0.27:5.0, the reaction lasted 40 min at 40°C, influence of H₂SO₄ wt.% in the reaction was detected. Before reaction, 98 wt.% H₂SO₄ was diluted with de-ionized water to different wt.% in the range of 65%-85%. The electrode potential of MnO₄⁻/Mn²⁺ can be calculated according to equation (1). It shows there are a positive correlation between [H⁺] and the oxidation of KMnO₄. Therefore, within a certain range, the oxidation of KMnO₄ enhances with the increase of H₂SO₄ concentration, causing the intercalation reaction gradually completed and leading to the increases of dilatibility. But, with the further increase of H₂SO₄ concentration, it will cause the excessive oxidation of graphite when it over a suitable concentration (Figure 2). As shown in experiment results, the feasible H₂SO₄ concentration is 75 wt.%.

$$E_{\text{MnO}_4^-/\text{Mn}^{2+}} = E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} + (0.05916/5) \lg([\text{H}^+]^8[\text{MnO}_4^-]/[\text{Mn}^{2+}]) \quad (1)$$

Influence of H₂SO₄ dose on EG_{Fe} dilatibility

In order to investigate the influence and feasible amount, H₂SO₄ dose was changed in the range of 3.5-5.5 g·g⁻¹. Experiments were carried out under the constant mass ratio C:ferric nitrate:KMnO₄ of 1.0:0.2:0.27, the reaction lasted 40 min at 40°C, and H₂SO₄ was diluted to 75 wt.%.

Figure 3 shows the changes of EV with H₂SO₄ amount. In intercalation reaction of graphite, H₂SO₄ acts as intercalator, oxidant and providing an acidic environment for the oxidability of KMnO₄. Equation (1) indicates that insufficient H₂SO₄ will incur a poor oxidation, cause an incomplete intercalation reaction and decrease of dilatibility. With the increase of H₂SO₄ dose, the oxidation is enhanced, causing the intercalation reaction gradually completed and the increases of dilatibility. When the H₂SO₄ dose achieves a balance in three areas, the prepared EG_{Fe} will present high EV. Conversely, EV will decrease when the H₂SO₄ dosage under or over the suitable value. The feasible mass ratio of H₂SO₄ to C is 5.0 g·g⁻¹.

Figure 3: Influence of H₂SO₄ dose on EV.

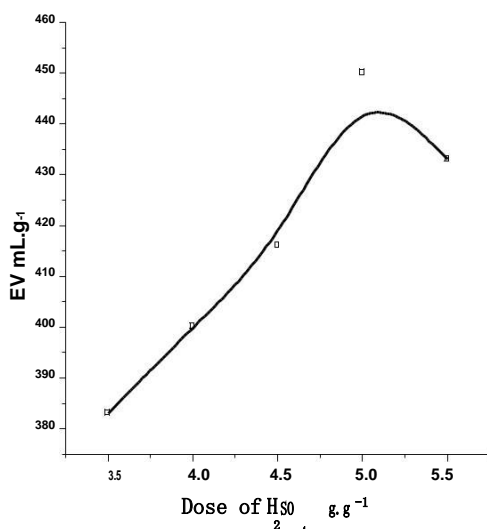
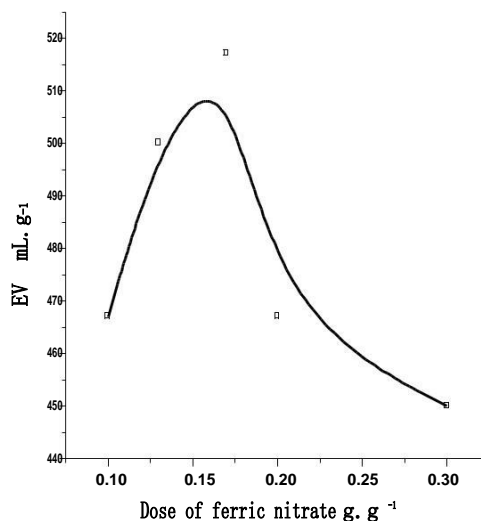


Figure 4: Influence of ferric nitrate dose on EV.



Influence of ferric nitrate dose on EG_{Fe} dilatibility

Under the constant mass ratio C:H₂SO₄(98 wt.%):KMnO₄ of 1.0:5.0:0.27, the reaction lasted 40 min at 40°C and H₂SO₄ diluted to 75 wt.%, the influence of ferric nitrate dose was detected in the range of 0.1-0.3 g·g⁻¹

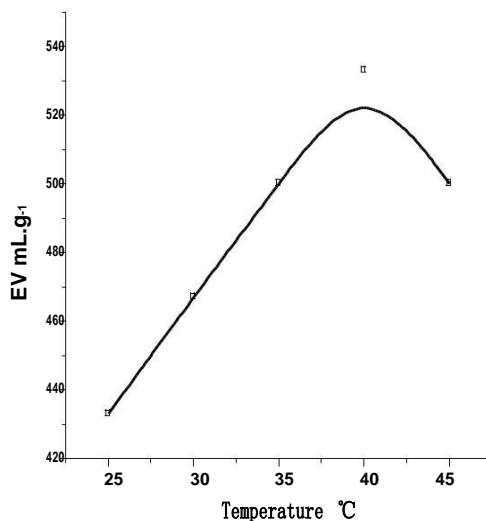
As an assistant intercalator, increase of ferric nitrate can improve EG_{Fe} dilatibility as shown in Figure 4. When the mass ratio of ferric nitrate to C is controlled as 0.17 g·g⁻¹, EG_{Fe} holds a maximum of EV. Superfluous ferric nitrate will cause the relative scarcity of KMnO₄ and incomplete oxygenation of graphite.

Influence of reaction temperature on EG_{Fe} 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 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.

Under the constant mass ratio C:H₂SO₄(98 wt.%):KMnO₄:ferric nitrate of 1.0:5.0:0.27:0.17 H₂SO₄ diluted to 75 wt.% before reaction, and reaction lasted 40 min, the influence of reaction temperature on EV was detected and shown as Figure 5. When it is less than 40°C, the increase of temperature can improve EG_{Fe} 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.

Figure 5: Influence of reaction temperature on EV.



Influence of reaction time on EG_{Fe} dilatibility

Under the constant mass ratio C:H₂SO₄(98 wt.%):KMnO₄:ferric nitrate of 1.0:5.0:0.27:0.17 H₂SO₄ diluted to 75 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_{Fe} dilatibility in the former 40 min, and then it remain the same. Therefore, reaction time can be set as 40 min.

Feasible condition of EG_{Fe} Preparation

According to the experiment results, the feasible condition of EG_{Fe} preparation was finally identified as: mass ratio of C:KMnO₄:H₂SO₄(98 wt.%):ferric nitrate was 1.0:0.27:5.0:0.17; the concentrated H₂SO₄ was diluted to 75 wt.% before reaction; intercalation reaction was totally maintained for 40 min at 40°C. T₀ and the EV maximum of the prepared EG_{Fe} are 170°C and 533 mL·g⁻¹ respectively.

Preparation of the referenced EG with single H₂SO₄ intercalation

Compared with EG_{Fe}, the referenced EG with only H₂SO₄ as intercalator was prepared at the mass ratio C:KMnO₄:H₂SO₄(98 wt.%) of 1.0:0.27:5.0 under the same condition as mentioned in the preparation of EG_{Fe}. Its T₀ and the EV maximum were detected as 180°C and 483 mL·g⁻¹ respectively. It's obvious that the assistant intercalation of ferric nitrate has significant influence on dilatibility, reflected by the improved EV and the adjustment of T₀. It can be deduced that EG_{Fe} will form thicker intumesce char than the normal EG, and then show better flame retardance.

Characterization of graphite and its GICs

XRD analysis of natural graphite and its GICs: XRD analysis for natural graphite, the EG and EG_{Fe} were performed. EG_{Fe} and the referenced EG all show the same characteristic diffraction lines like natural graphite at about 26.6° and 55° as shown in Figure 6, which indicates they all keep the layer structures. Whereas, it is worthy to note that the (002) diffraction peaks transfer to a smaller angle of 26.2° for the EG and 25.8° for EG_{Fe} respectively. At the same time, each corresponds to a big interplanar spacing of 3.40 Å for EG and 3.46 Å for EG_{Fe}. This can be explained that natural graphite is oxidized by KMnO₄ and then exhibited positive charge. Then gap between graphite layers is extended due to the repulsion, and intercalating reaction can proceed between graphite and intercalator. The positive charge of the oxidized graphite network is balanced by negatively charged acid anions and also includes acid molecules [1,11]. The XRD results confirm that intercalators have been inserted into graphite layers.

Figure 6: XRD analyses for graphite and its GICs.

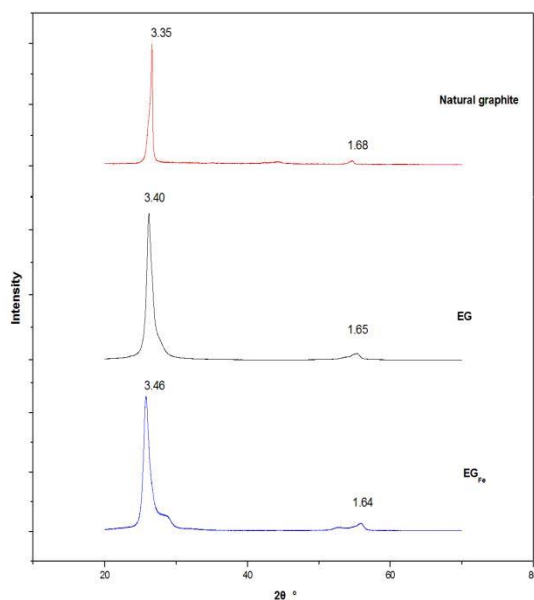
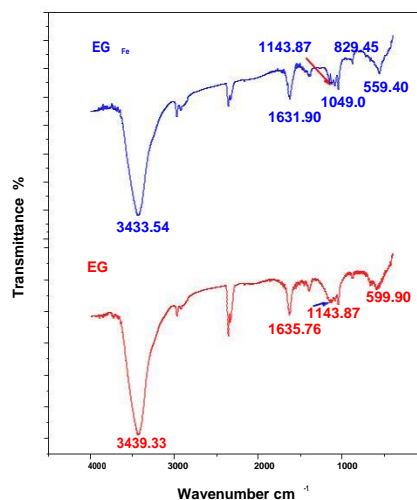


Figure 7: FTIR spectra of the EG and EG_{Fe}.



FTIR analysis

Figure 7 shows FTIR spectra of the EG and EG_{Fe}. As can be seen from the results, the two samples both show the characteristic stretching vibrations absorption peaks of -OH (about 3430 cm⁻¹) and S=O (about 1143 cm⁻¹) caused by intercalation of H₂SO₄/HSO₄⁻ [11]. At the same time, the peaks at about 1620 cm⁻¹ are the specific absorption of C=C stretching vibrations [1], originating from graphite conjugated structure. It's worth noting that the C-N characteristic stretching vibrations absorption peaks located at 1049 cm⁻¹ is observed in the FTIR spectra of the EG_{Fe} [12]. At the same time, the peak at 829.45 cm⁻¹ is the characteristic absorption of NO₃⁻, and specific absorption of the Fe-O appears at 559.40 cm⁻¹ as well. These results confirm the intercalation of ferric nitrate.

Detection of flame retardance for LLDPE

Processing temperature of LLDPE is lower than 140°C, so the prepared EG_{Fe} and EG can be used as flame retardant. The flame retarded composites were prepared as mentioned above, and the LOI of pure LLDPE, 70LLDPE/30EG, 70LLDPE/30APP, 70LLDPE/30EG_{Fe} and 70LLDPE/15APP/15EG (shown as wt.%) were detected according to the

mentioned method. Results show that LOI of pure LLDPE is only 17.5%, and its combustion accompanies with serious molten drop at the same time. Addition of 30 wt.% the EG improves LOI to 25.5%, higher than the same amount of single APP of 22.0%. Whereas, the addition of 30 wt.% the EG_{Fe} can improve LOI value to 27.5%, and no molten drop occurs. Furthermore, the combination of EG_{Fe} and APP makes the 70LLDPE/15APP/15 EG_{Fe} system present a LOI of 30.8%, and no molten drop occurs too. Therefore, the prepared EG_{Fe} is more effectual in improving the flame retardance, and there is synergistic efficiency between EG_{Fe} and APP.

Conclusions

According to the analysis of the experiment results, it is evident that the mass ratio of C:KMnO₄:H₂SO₄(98 wt.%):ferric nitrate has important influence on EG_{Fe} dilatibility, and when it is controlled as 1.0:0.27:5.0:0.17, H₂SO₄ diluted to 75 wt.% before intercalation reaction and intercalating reaction lasted 40 min at 40°C, the EV and T₀ of the prepared GIC can reach 533 mL·g⁻¹ and 170°C respectively. The intercalation reaction between graphite and H₂SO₄, ferric nitrate can be revealed by XRD and FTIR analysis of GICs. EG_{Fe} shows more effective flame retardance than the normal EG.

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