PREPARATION OF HIGH DILATABILITY EXPANDABLE GRAPHITE AND ITS FLAME RETARDANCY FOR LLDPE

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(Received: March 1, 2012 - Accepted: June 12, 2012)

ABSTRACT

To prepare expandable graphite (EG) with high anti-flame property for Linear low density polyethylene (LLDPE), dosages of oxidant KMnO_4 , intercalation reagent H_2SO_4 and ancillary intercalation reagent $\text{Na}_4\text{P}_2\text{O}_7$ were optimized during oxidation intercalation reaction of natural graphite. EG with an initiation expansion temperature of $148 \pm 2^\circ\text{C}$ and expansion volume of 550 mL/g can be prepared according to the mass ratio of $\text{C}:\text{KMnO}_4:\text{H}_2\text{SO}_4(98\%):\text{Na}_4\text{P}_2\text{O}_7 = 1.0:0.4:5.0:0.6$ (H_2SO_4 should be diluted to the mass concentration of 80% before intercalation reaction), the reaction time is 40 min at constant 40°C . Addition of 30% of the prepared EG to LLDPE can improve its limiting oxygen index LOI from 17.5% to 29.4%, and the synergistic anti-flame LOI of 20% EG with 10 polyphosphate (APP II) can reach to 31.2%. TG and DTA analysis were completed to discuss the anti-flame mechanism. 70%LLDPE/10%APP(II)/20%EG synergistic anti-flame system can cause higher residual carbon and lower material surface temperature.

Key words: Expandable graphite, Dilatability, Sodium pyrophosphate, Flame retardancy, LLDPE, Mechanism

INTRODUCTION

It's the drawbacks of lower oxygen index, flammability, fusion and dripping that limit the extensive use of Polyethylene PE^{1,2}. So flame retardant FR additives are needed, among which halogenated compounds are the most widely used, and brominated additives are the main fire retardants FR³. But during the combustion of flame retarding polymer based on these retardants, halogen acids are evolved⁴, people would be exposed to these irritants and potential corrosion damage to equipment would occur⁵. So much work has been done on halogen-free FRs. Intumescent additives⁶ provide an effectively way to impact burning performance of polymeric materials. Once exposed to a heat source⁷, intumescent systems develop a voluminous, stable carbonaceous layer on the surface of the material. This layer limits heat and mass transfer, as well as oxygen diffusion, between the heat source and the polymer thus interrupting the self-sustained combustion of the polymer.

Expandable graphite EG is prepared when non-carbonaceous reactants are inserted into the layers of graphite through chemical or electrochemical reaction^{8,9}. When EG is heated, it will become expanded graphite with porous structure and high expanded volume¹⁰. So EG is a good intumescent type flame-retardant for its good capability of halogen-free, non-dropping, low-smoke and low pollution potential^{11,12}.

The anti-flame mechanisms of EG might be explained as: 1. when EG exposes to flame, it gives a swollen multicellular char, which may protect materials from the heat of combustion, limit the access of oxygen to the polymer, and reduce the production of smoke, so it is capable of protecting the underlying material from the action of the flame. 2. During the instant expansion of EG, it absorbs huge heat, which can decrease the burning temperature. 3. At high temperatures, EG gets oxidized on reaction with H_2SO_4 (equation 1). The evolved gases cause the expansion of the material; this expanded volume suffocates the flame and acts as physical barrier for heat and mass transfer.

Both initiation expansion temperature and expansion volume EV are two important characteristics of EG¹³. If its initiation expansion temperature is lower than materials' machining temperature, it will decompose during material machining, then cause void flame retardancy. While, too high initiation expansion temperature will cause EG doesn't work in the flaming early stage. In the preparation of EG, its initiation expansion temperature and expansion volume are affected by oxidant, intercalation reagent, ancillary intercalation reagent, reaction time and reaction temperature. Wang¹⁴ prepared an EG with an initiation expansion temperature of 130°C and expansion volume of 350 mL/g through $\text{HNO}_3/\text{HBrO}_3/\text{KMnO}_4$ oxidation intercalation system. With 85% H_2SO_4 as inserting reagent and KMnO_4 as oxidant, through oxidation, insertion, closedown and laid process, Wang^[13] prepared an EG with an initiation expansion temperature of 310°C and expansion volume of 270 mL/g.

Phosphorus-containing flame retardant¹⁵⁻¹⁷ is important flame retardants with good flame retardancy for its accelerating formation of charring layer and releasing $\text{PO}\cdot$, which can catch free radical such as $\text{H}\cdot$, $\text{HO}\cdot$ and then stop combustion. In this research, $\text{Na}_4\text{P}_2\text{O}_7$ is used as phosphorus-containing

ancillary intercalation reagent in the intercalation reaction of graphite, through optimizing the dosage of oxidant KMnO_4 , intercalating reagent H_2SO_4 , ancillary intercalation reagent $\text{Na}_4\text{P}_2\text{O}_7$, reaction time and reaction temperature, to provide a suitable EG flame retardant or synergistic flame retardant for Linear Low-Density Polyethylene LLDPE possessing low machining temperature (less than 140°C) and burning temperature.

MATERIALS AND METHOD

Instruments and materials

SX3-4-13 Muffle furnace (Tientsin, precision of temperature $\pm 0.1\%$ - 0.4% $^\circ\text{C}$), 101-3 Oven (Shanghai, precision of temperature $\pm 2^\circ\text{C}$), Muller (Jiangsu), Instrument of limiting oxygen index LOI (Chengde), KYKY-2800B scanning electron microscope (Peking), Y-4Q X-ray diffractometer (Dandong), STA 449C TG/MS (Germany) and WCT-2 DTA (Shimadzu Japan) are used in this experiment.

Natural graphite (C, 5092) is provided by Action Carbon CO. LTD, Baoding. Acetic acid, H_2SO_4 (96%-98%), KMnO_4 , Ammonium polyphosphate gls-APP(II) are all analytical reagents. LLDPE 7540 is purchased from Daqing.

Preparation of EG

First, the reactants are quantified according to a definite mass ratio of $\text{C}:\text{KMnO}_4:\text{H}_2\text{SO}_4(98\%):\text{Na}_4\text{P}_2\text{O}_7$, and H_2SO_4 need to dilute to the required mass concentration. Then, under a constant temperature controlled with water bath, the quantified natural graphite is mixed with H_2SO_4 , KMnO_4 and $\text{Na}_4\text{P}_2\text{O}_7$ in a 250 mL beaker, reaction lasts the required time. After reaction, the mixture is washed with de-ionized water and dipping 2.0 h until pH of waste-water reaches to 6.0 ~ 7.0, then filtrated and dried at $50\sim 60^\circ\text{C}$ for about 6h, EG products are gained.

Character of EG

Detection of initiation expansion temperature

0.3000 g of the prepared EG is spread on evaporating dish, then the dish is placed in oven (when the controlled temperature is lower than 300°C) or Muffle furnace (when the temperature is higher than 300°C), which has been set as a constant temperature. After a definite time, take the sample out and measure its volume with a 5.0 mL graduated flask. In experiment, the temperature corresponding to 1.5 times of EGs' initiation volume is defined as EGs' initiation expansion temperature.

Detection of expansion volume

EV is an important factor to judge of the anti-flame properties. Ten EG samples with the mass of 0.3000 g are prepared, and they are heated at 100°C , 200°C , 300°C , 400°C , 500°C , 600°C , 700°C , 800°C , 900°C , 1000°C , respectively, then the volume is detected. Expansion time corresponding to different expansion temperature is listed in Table 1, and the higher the expansion temperature is, the shorter expansion time is selected. Curve of EV versus expansion temperature can be draw according to the experimental results. Temperature corresponding to intersection of the curvilinear tangent with temperature axis is treated as EG' initiation expansion temperature. The results are almost the same as the temperature corresponding to 1.5 times of EG initiation volume.

Table 1. Expansion time used corresponding to different expansion temperature.

T / °C	100	200	300	400	500	600	700	800	900	1000
Expansion time	30 Min	30 Min	5 Min	1 Min	12S	12S	12S	5S	5S	5S

X-ray diffraction

The X-ray diffraction spectra were recorded with an Y-4Q X-ray spectrometer using the Cu K α $_{1,2}$ radiation in the range $5^\circ < 2\theta < 70^\circ$.

Measurement of EG flame retardancy

As flame retardant, a definite quantity of EG is added into LLDPE. After mix, extrusion, press and chop into sliver at 140 °C and 10 MPa, the slivers are used to measure anti-flame properties.

Detection of LOI

LOI is detected according to Standard of GB/T2406-1993 with oxygen index instrument.

Thermal Gravimetric TG analysis

Under N $_2$ ambience with a flux of 25 mL/min, 10 mg of the detected sample is laid in porcelain crucible, and then it is heated to 800 °C at a heating rate of 10 °C/min. Changes of sample weight with temperature are recorded.

Differential thermal analysis DTA

DTA is carried under atmosphere ambience with a flux of 60 mL/min. Al $_2$ O $_3$ is used as reference compound, and heating rate of 5, 10, 15, 20 °C/min are used.

RESULTS AND DISCUSSION

According to the former research^{18,19}, influence of mass ratio of graphite to KMnO $_4$, Na $_4$ P $_2$ O $_7$, H $_2$ SO $_4$ and its concentration, reaction time and reaction temperature on EG characteristics of initiation expansion temperature and EV are tested and discussed.

Influence of KMnO $_4$ dosage on EG characteristics

In the range of 0.2~0.6 g/g, the influence of KMnO $_4$ dosage is detected at the mass ratio of C:H $_2$ SO $_4$ (98%):Na $_4$ P $_2$ O $_7$ = 1.0:5.0:0.6 (g/g) at 40 °C reacting for 1.0 h, and H $_2$ SO $_4$ should be diluted to the mass concentration of 80% before reaction. Results showed in Figure 1 illustrate that when the mass ratio of KMnO $_4$ to C is controlled as 0.4:1.0, the prepared EG possessing lower initiation expansion temperature of 160°C and maximum EV of 550 mL/g. Insufficiency KMnO $_4$ would cause a incomplete oxygenation of graphite and decrease of product EV; Superfluous KMnO $_4$ would cause excessive oxygenation of graphite, it could lead to decrease of EG granularity and then reduce EV. In the tested dosage, increase of KMnO $_4$ would cause the increase of initiation expansion temperature. The feasible dosage of KMnO $_4$ can be set as 0.4 g/g.

Figure 1. Influence of KMnO $_4$ dosage on initiation expansion temperature and EV.**Influence of H $_2$ SO $_4$ dosage on EG characteristics**

In the range of 3.0 ~ 6.0 g/g, the influence of H $_2$ SO $_4$ dosage with a mass concentration of 98% is detected at the mass ratio of C:KMnO $_4$:Na $_4$ P $_2$ O $_7$ = 1.0:0.4:0.6 (g/g) at 40 °C reacting for 1.0 h, and H $_2$ SO $_4$ is diluted to the mass concentration of 80% before reaction. Results showed in Figure 2 illustrate that when the mass ratio of H $_2$ SO $_4$ to C is controlled as 5.0:1.0, we can get EG with lowest initiation expansion temperature of 165°C and maximum EV of 550 mL/g. Insufficiency H $_2$ SO $_4$ would cause a incomplete intercalation reaction and leading to the decrease of dilatability; Superfluous H $_2$ SO $_4$ would cause the relative scarcity of KMnO $_4$ and incomplete oxygenation of graphite. In the tested dosage, increase of H $_2$ SO $_4$ can cause V type changes of initiation expansion temperature; lowest initiation expansion temperature of 165°C can be gained when EG possessing maximum expansion volume. The feasible dosage of H $_2$ SO $_4$ can be set as 5.0 g/g.

Figure 2. Influence of H $_2$ SO $_4$ dosage on initiation expansion temperature and EV.**Influence of H $_2$ SO $_4$ concentration on EG characteristics**

By fixing the mass ratio of C:KMnO $_4$:H $_2$ SO $_4$ (98%):Na $_4$ P $_2$ O $_7$ at 1.0:0.4:5.0:0.6 (g/g) and reacting for 1.0 h at 40 °C, influence of H $_2$ SO $_4$ mass concentration in the reaction is detected. Before reaction, it is diluted with de-ionized water to the mass concentration of 65%, 70%, 75%, 80%, 85%, respectively. Results showed in Figure 3 illustrate that EV increases with the increase of H $_2$ SO $_4$ concentration when it is controlled at lower value. When it reaches to 80%, we can get EG with lowest initiation expansion temperature of 165°C and maximum EV of 550 mL/g. Too high H $_2$ SO $_4$ concentration would cause an excessive oxygenation of graphite, and it lead to decrease of EV and increase of initiation expansion temperature. Feasible mass concentration of H $_2$ SO $_4$ can be set as 80%.

Influence of Na $_4$ P $_2$ O $_7$ dosage on EG characteristics

In the range of 0.2 ~ 0.8 g/g, the influence of Na $_4$ P $_2$ O $_7$ dosage is detected at the mass ratio of C:KMnO $_4$:H $_2$ SO $_4$ (98%) = 1.0:0.4:5.0 (g/g) at 40 °C reacting for 1.0 h, and H $_2$ SO $_4$ is diluted to the mass concentration of 80% before reaction. As an ancillary intercalation reagent, increase of Na $_4$ P $_2$ O $_7$ dosage can improve EG dilatability and reduce initiation expansion temperature as showed in Figure 4. When the mass ratio of Na $_4$ P $_2$ O $_7$ to C is controlled as 0.6:1.0, we can get EG with initiation expansion temperature of 160 °C and EV of 550 mL/g. Superfluous Na $_4$ P $_2$ O $_7$ would cause the relative scarcity of KMnO $_4$ and incomplete oxygenation of graphite. The feasible dosage of Na $_4$ P $_2$ O $_7$ can be set as 0.6 g/g.

Figure 3. Influence of H₂SO₄ mass concentration on initiation expansion temperature and EV.

Figure 4. Influence of Na₄P₂O₇ dosage on initiation expansion temperature and EV.

Influence of reaction time on EG characteristics

By fixing the mass ratio of C:KMnO₄:H₂SO₄(98%):Na₄P₂O₇ at 1.0:0.4:5.0:0.6 (g/g), H₂SO₄ is diluted to 80%, and reaction temperature controlled at 40 °C, influence of reaction time on initiation expansion temperature and EV is detected. The increase of time can improve EG dilatability before the former 40 min as showed in Figure 5, and then its influence on initiation expansion temperature and EV can be ignored. The feasible reaction time can be set as 40 min.

Influence of reaction temperature on EG characteristics

By fixing the mass ratio of C:KMnO₄:H₂SO₄(98%):Na₄P₂O₇ at 1.0:0.4:5.0:0.6 (g/g), H₂SO₄ is diluted to 80%, and reacting 40 min, influence of reaction temperature on initiation expansion temperature and EV is detected. When it is less than 40 °C, the increase of temperature can improve EG dilatability as showed in Figure 6. While, too high temperature can lead to tempestuously exothermic reaction and excessive oxygenation of graphite. So the feasible reaction temperature can be set as 40 °C.

Figure 5. Influence of reaction time on initiation expansion temperature and EV.

Figure 6. Influence of reaction temperature on initiation expansion temperature and EV.

Feasible condition to prepare EG

According to the experiment results, feasible conditions to prepare EG are: mass ratio of C:KMnO₄:H₂SO₄(98%):Na₄P₂O₇=1.0:0.4:5.0:0.6 (H₂SO₄ diluted to mass concentration of 80% before intercalation reaction), the reaction time is 40 min at 40 °C. initiation expansion temperature and EV of the prepared EG are 148 ± 2 °C and 550 mL/g, respectively. Expansion curve of the gained EG is detected as Figure 7. EV can reach 267 mL/g at 400 °C, and the maximum EV of 550 mL/g get at 800 °C.

Preparation of EG₁ with no assistant inserting reagent Na₄P₂O₇

EG₁ is prepared under the condition of C:KMnO₄:H₂SO₄(98%)=1.0:0.4:5.0 for 40 min at 40 °C and H₂SO₄ diluted to mass concentration of 80%, no Na₄P₂O₇ is added during reaction. EV of EG₁ is detected as 330 mL/g.

XRD analysis of EG

XRD Analysis results for material graphite and the EG are showed in Figure 8. The two diffraction peaks of 3.34 Å and 1.67 Å are the characteristic spectrum of material graphite. Because it has the plane structure of sandwich, the peak of 3.34 Å is strengthened during XRD detection. In the XRD analysis of EG, the characteristic peak of 3.34 Å is replaced with a new peak of 3.39 Å. The displacement of diffraction peak to big angle show the layer space is bigger than the material graphite, and new substance has inserted into sandwich of graphite.

Figure 7. Expansion curve of EG.

(a) Material graphite

(b) EG

Figure 8. XRD of material graphite and the EG.

The anti-flame capability of EG for LLDPE

LLDPE is kinds of plastic with characteristics of flammability and low processing temperature less than 140 °C. So we can select the prepared EG as flame retardant. Flame retardants are added to LLDPE according to the proportion listed in Table 2. After mixing, pressing into piece and cutting into strip, the LOC is detected and the results are listed in Table 2. The addition of 30% EG can improve LOC up to 29.4%. But the addition of the same amount of EG₁ or purchase EG to LLDPE can only get a LOC of 26.8% and 23%²⁰, respectively. So the addition of assistant inserting reagent Na₄P₂O₇ can improve EG dilatibility and flame retardancy. LOC is only 19.8% with single 30% APP (II) as flame retardant, and the addition of 20% EG together with 10% APP (II) can improve LOC to 31.2%, it show the synergistic anti-flame of EG with APP (II). After combustion of the anti- flame LLDPE, EG changes to graphite worm on the surface of LLDPE (Figure 9), and the swollen multicellular char can limit heat and mass transfer, as well as oxygen diffusion, thus interrupting the self-sustained combustion of LLDPE.

Table 2. Results of LOI.

LLDPE/%	EG/%	EG ₁ /%	APP(II)/%	LOI/%
100	0	0	0	17.5
70	0	0	30	19.8
70	10	0	20	25.5
70	20	0	10	31.2
70	30	0	0	29.4
70	0	30	0	26.8

Figure 9. The SEM of 70%LLDPE/10%APP(II)/20%EG after combustion.

TG analysis

TG analysis results for samples of 70%LLDPE/10%APP(II)/20%EG and 70%LLDPE/30%EG are showed as Figure 10. Mass loss of these anti-flame systems among 100 ~ 400 °C is less than 5%, which is caused by incomplete decomposition of APP(II) and expansion of EG. The loss of weight is near to 10% when temperature increases to 450 °C. 60% of loss of weight occurs among 450 ~ 520 °C, EG already shows high dilatibility under this temperature (showed as Figure 7). Compare 70%LLDPE/10%APP(II)/20%EG sample to 70%LLDPE/30%EG sample, the former give higher residual carbon of 25% than the latter of 19%, that testify the synergistic anti-flame of EG with APP (II).

Figure 10. TG of 70%LLDPE/10%APP/20%EG and 70%LLDPE/30%EG
1. 70%LLDPE/10%APP/20%EG 2. 70%.

DTA analysis

During decomposition of APP(II) and expansion of EG, they will consume huge heat, and then reduce material temperature. Compare 70%LLDPE/10%APP(II)/20%EG sample to 70%LLDPE/30%EG sample showed as Figure 11, the former give lower surface temperature, especially in the range of 100~300 °C, and it is much more fit for the flame retardancy in fire early stage. During the expansion of EG, the existing and decomposing of APP(II) might cause compacter multicellular char, which can limit heat and mass transfer, then retard combustion.

Figure 11. DTA of 70%LLDPE/10%APP/20%EG and 70%LLDPE/30%EG
1. 70%LLDPE/10%APP/20%EG 2. 70%LLDPE/30%EG.

Analysis of anti-flame mechanism

Combine experiment data and TG DTA results, we can deduce that: When EG exposes to flame, it gives a swollen multicellular char, which limits heat and mass transfer, as well as oxygen diffusion. Instantaneous expansion of EG can absorb huge heat and releases CO₂. Coexistence of EG and APP(II) can give more residual carbon and induce lower surface temperature, that cause an effect of synergistic flame retardancy.

CONCLUSIONS

Adjustment of KMnO₄, H₂SO₄ and Na₂P₂O₇ dosages can influence EGs' initiation expansion temperature and EV. The feasible condition

to get EG with low initiation expansion temperature and high EV is: C:KMnO₄:H₂SO₄(98%):Na₂P₂O₇ =1.0:0.4:5.0:0.6 (mass ratio), the reaction lasts 40 min at 40 °C, and H₂SO₄ need to be diluted to a mass concentration of 80%. Under this condition, EG with an initiation expansion temperature of 148 ± 2 °C and expansion volume of 550 mL/g can be gained.

EG possess well anti-flame capability for its absorbing huge heat and expansion giving birth to swollen multicellular char, which acts as physical barrier for heat and mass transfer. Addition of 30% EG to LLDPE can improve LOI up to 29.4% from 17.5%. Addition of 20% EG to LLDPE together with 10% APP (II) can improve LOI up to 31.2%. There is synergistic flame retardancy between EG and APP(II).

ACKNOWLEDGEMENTS

This study was supported Doctor Foundation of Hebei province Education Office (China, No.B2004402). We gratefully acknowledge their support during the study.

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