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An intumescent flame retardant - expandable graphite: Preparation, characteristics and flame retardance for polyethylene

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ABSTRACT

A combined intumescent flame retardant expandable graphite (EG), with an initial expansion temperature of 155°C and expansion volume of 515 mL g^{-1}, was successfully prepared based on a chemical intercalation method of material graphite under oxidation of $KMnO_4$, intercalation of H_2SO_4 and $Na_4B_2O_7 \cdot 10H_2O$ at the mass ratio C : $KMnO_4$: H_2SO_4 (98%) : $Na_4B_2O_7 \cdot 10H_2O$ of 1.0 : 0.4 : 5.5 : 0.6 (H_2SO_4 diluted to a mass concentration of 80-wt. % before reaction), and characterized by expansion volume (EV), initial expansion temperature, X-ray diffraction (XRD). The flame retarding and thermal properties of LLDPE/EG and LLDPE/EG/APP composites (LLDPE-Linear low density polyethylene; APP-ammonium polyphosphate) were investigated and characterized by limiting oxygen index (LOI), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric (TG) and differential thermal analysis (DTA). The results showed that addition of EG (30-wt. %) increased the LOI of 70LLDPE/30EG composite to 28.4 %. Even more, the synergistic effect of 20% EG together with 10% APP improved the LOI of 70LLDPE/20EG/10APP composite to 30.5%. At the same time, temperatures corresponding to a 1% weight loss and a maximum weight loss rate increased at about 50°C and 2°C, respectively. The 70LLDPE/10APP/20EG composite exhibited higher flame retardancy even at a lower residual chars than 70LLDPE/30EG specimen. Cohesive and dense char layer caused by swollen expanded graphite and decomposing products of APP played a more important role in improving thermal stability and flame retardancy than weight of residual carbon. The intercalated borate was more effectual in improving the flame retardancy than the direct additive of $Na_4B_2O_7 \cdot 10H_2O$.

Keywords: Borate; expandable graphite; intumescent flame retardant; polyethylene; synergistic efficiency.

INTRODUCTION

Graphite is a crystalline compound with graphene planes structure bonded by Van Der Waals force. Under oxidation, the graphite intercalating substance called expandable graphite could be prepared by chemical or electrochemical reaction inserting non-carbonaceous reactants into graphene planes (Avdeev *et al.*, 1992a,1992b; Li, 1993; Xue *et al.*, 2002; Kuan *et al.*, 2012). Expandable graphite has been used as an intumescent type flame retardant for its good capability of halogen-free, non-dropping, low-smoke and low pollution potential (Thirumal *et al*., 2008; Pang *et al*., 2012). When exposed to flame source, expandable graphite would form voluminous swollen multicellular char layers, which could protect materials from the heat of combustion, limit the diffusion of oxygen into the polymer, and reduce the production of smoke. Simultaneously, expandable graphite could absorb an enormous amount of heat during instant expansion, which could decrease the burning temperature. In addition, when graphite was oxidized by H_2SO_4 at high temperature, the releasing gases such as CO_2, H_2O could reduce the concentration of oxygen (Thirumal *et al*., 2008).

Due to its outstanding anti-flame capability, expandable graphite has been used widely in improving the flame retardancy of polyolefins (Xie & Qu, 2001a and 2001b), high-density PUF, polyurethane-poly-isocyanurate foam (Modesti *et al*., 2002, Modesti & Lorenzetti, 2002a, 2002b and 2003; Duquesne *et al*., 2002; Shi *et al*., 2006; Bian *et al*., 2007), poly (methyl methacrylate) (Ye *et al*., 2009). In the above mentioned reports, the conventional expandable graphite flame retardant was usually a commercial product. In particular, multi-complexes of expandable graphite together with ammonium polyphosphate (APP), zinc borate, phosphorous nitrogen or micro-capsulated red phosphorus were used to improve anti-flame efficiency (Zhu *et al*., 2011).

Linear low density Polyethylene (LLDPE) is one of the most widely used polyolefin due to its balanced mechanical properties, chemical resistance, and ease of processing advantages. However, its inherent flammability has limited its applications in some fields where good flame retardancy is required. To solve this problem, many flame retardants have been applied in improving its flame retardancy, such as magnesium hydroxide (Wang *et al*., 2003), complex containing phosphorus, nitrogen (Gao *et al*., 2011), zinc borate (Li *et al*., 2010), antimony trioxide (Zhang *et al*., 2010), triazine containing flame retardant hyperbranched polyamines (Mahapatra & Karak, 2007), and their synergistic effects (Genovese & Shanks, 2007; Ramazani *et al*., 2008). It is well known that borate is one kind of important flame retardant with remarkable flame retardancy. Boric acid and hydrated borates hold low melting temperature, and they can absorb heat and lose water of crystallization. The water vapor caused by material decomposition may provide a dual function: it not only absorbs an enormous amount of heat, but also dilutes the concentration of the volatile oxidizable pyrolysis production in the flame zone, thereby enhanceing residual char formation. Furthermore, the residual boric oxide can form a glassy coating on the surface of polymer, limiting the transfer of heat and mass, as well as oxygen diffusion, and then retarding further combustion (Xue & Zeng, 1988). In the anti-flame test of LLDPE, the addition of zinc borate could improve the thermal stability and substantially enhance the residue carbon of APP-PER-LLDPE system [PER- pentaerythritol] (Wu *et al*., 2008). Addition of the synthesized netlike nano-zinc borate $2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$ into polyethylene resulted in an increasing of residual char (Li *et al*., 2010). Whereas, in these reported literatures, either borate together with other synergistic retardants or fine borate prepared with complex and costly methods was used in order to improve flame retardancy.

It is known that non-carbonaceous reactants can be inserted into graphene planes using chemical or electrochemical reaction, and the dilatability of expandable graphite can be affected by oxidant, intercalating agent and assistant intercalating agent. For examples, with graphite, $KMnO_4$, HNO_3 and $HBrO_3$ used as reactant, expandable graphite with an initial expansion temperature of 130°C and expandable volume (EV) of 350 mL g^{-1} was prepared (Wang *et al.*, 2009). Expandable graphite with an initial expansion temperature of 300°C and EV of 360 mL g^{-1} could be prepared using 50% H_2SO_4 and $KMnO_4$ reacting for 30 min at 45°C (Pang *et al.*, 2011), and its addition of 30-wt. % into ethylene vinyl acetate copolymer (EVA) could improve the limiting oxygen index (LOI) to 28.1%.

As a result, the purpose of this research was to prepare a combined intumescent flame retardant consisting of expandable graphite (EG) and borate in graphite intercalating reaction. To our best knowledge, no study on this method and the EG flame retarding property for LLDPE has so far been reported in the literature. In intercalating reaction of material graphite, $KMnO_4$, H_2SO_4 and sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) were used as oxidant (Pang *et al.*, 2011 and 2012), intercalating and assistant intercalating agent, respectively. The method of preparing EG fitting for flame retardancy of LLDPE was found, and its expansion property, structure characteristics were characterized by EV, initial expansion temperature and X-ray diffraction (XRD). The flame retardancy of LLDPE/EG and LLDPE/EG/APP composites were characterized by LOI. Fourier transform infrared spectroscopy (FTIR), thermal gravimetric (TG) and differential thermal analysis (DTA) were applied to illuminate thermal property and anti-flame mechanism.

EXPERIMENTAL PROCEDURE

Instruments and materials

SX3-4-13 muffle furnace (Tientsin, China, precision of temperature ± 0.1%–0.4%°C); Y-4Q X-ray diffractometer (XRD) (Dandong, China); Muller (Jiangsu, China); Instrument of limiting oxygen index (LOI) (Chengde, China); TM3000 electron microscope (Japan); STA 449C thermal gravimetric (TG) and differential thermal analysis (DTA) (Germany) FTS-40 fourier transform infrared (FTIR) spectrograph (America Biorad) were used in this experiment.

Natural flake graphite was provided by Action Carbon CO. LTD, Baoding, China. Carbon content of flake graphite was 95 wt%, and an average flake size was 0.3 mm. $Na_2B_4O_7 \cdot 10H_2O$, H_2SO_4 (98 wt%), $KMnO_4$ were all analytical agents and bought from China. APP (I, n>50) was purchased from Sichuan, China. LLDPE 7540 was purchased from Daqing, China.

Preparation of the EG

Reactants were weighed and mixed in the order of diluted H_2SO_4, $Na_2B_4O_7 \cdot 10H_2O$, material graphite C and $KMnO_4$ in a 250 mL beaker and stirred at a controlled temperature using a water bath. After maintaining for 40 min, the solid phase was washed with de-ionized water until pH of the waste water reached to 6.0–7.0. Solid product was dipped in water for 2 h, then filtrated and dried at 60-70°C for 6 h, and EG was obtained. The effects of various factors on dilatability of the EG were optimized through single factor tests including the dosages of $KMnO_4$, H_2SO_4, $Na_2B_4O_7 \cdot 10H_2O$, H_2SO_4 concentration, reaction temperature and time. It was noticed that, $KMnO_4$ dosage and H_2SO_4 concentration had important influence on intercalation of graphite. Too higher $KMnO_4$ dosage and H_2SO_4 concentration would cause excessive oxygenation of material, which could lead to a decrease in EG granularity and dilatability. For examples: with H_2SO_4 diluted to 80-wt. % and dosage of $KMnO_4$ increased from 0.4 g g^{-1} to 0.6 g g^{-1}, EV of the EG decreased from 515 mL g^{-1} to 330 mL g^{-1}, while, keeping the $KMnO_4$ dosage as 0.4 g g^{-1} and H_2SO_4 concentration increased from 80-wt. % to 85-wt. %, EV of the EG would decrease from 515 mL g^{-1} to 450 mL g^{-1}. Finally, preparation conditions of EG with high dilatability and low expansion temperature were determined as follows: mass ratio of C: $KMnO_4$: H_2SO_4(98%) : $Na_2B_4O_7 \cdot 10H_2O$ was controlled as 1.0:0.4:5.5:0.6, H_2SO_4 was diluted to 80 wt%, and the reaction maintained for 40 min at 40°C, then EG with an initial expansion temperature of 155°C and maximum EV of 515 mL g^{-1} obtained. The expansion temperature curve of the EG was detected and shown in Figure 1. When temperature was among 600-900°C, EV of EG was all above 400 mL g^{-1}.

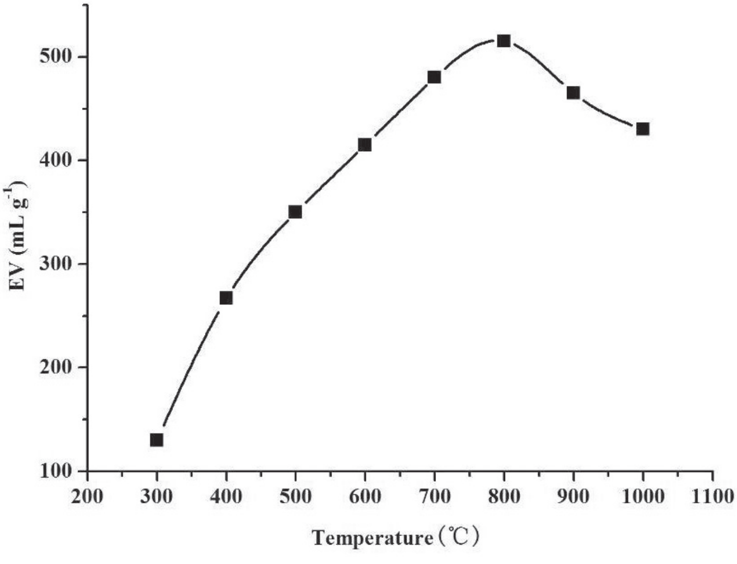


Fig. 1. Expansion curve of EG
(EV is the volume of 1.0 g EG after expansion at a definite oven temperature)

Preparation of contrast EG_1 prepared with no $Na_2B_4O_7 \cdot 10H_2O$ reactant

Compared with EG, EG_1 was prepared under the mass ratio C:$KMnO_4$: H_2SO_4 (98%) of 1.0:0.4:5.5, H_2SO_4 was diluted to 80-wt. %, and the reaction maintained for 40 min at 40°C. The initial expansion temperature and maximum EV of EG_1 was 265°C and 330 mL g^{-1}, respectively. Obviously, $Na_2B_4O_7 \cdot 10H_2O$ significantly influenced EG dilatability, and then it could be forecast that EG should show better flame retardancy than EG_1.

Preparation of flame retarded LLDPE composites

A certain amount of flame retardant was added into melting LLDPE at lower than 120°C, the mixtures were pressed at 140°C and 10 MPa to form sheets of 120 mm ×50 mm×3 mm, and then chopped in slice of 120 mm ×6 mm×3 mm.

Measurements and characterization

XRD pattern was obtained under the operation condition of 40 kV, 30 mA, employing Ni-filtered Cu K_α radiation with 2θ ranging from 10° to 70°.

LOI is the minimum amount of oxygen in an oxygen-nitrogen mixture required to support combustion over 3 min. The LOI method is a simple, fast, and effective method of studying the flame retardancy of plastic materials. In this study, the flame retardancy of composites was measured by using the LOI values according to Standard of GB/T2406-1993 with oxygen index instrument.

Thermal analysis of the samples were carried out by TG with N_2 flux of 25 mL min^{-1} and 10 mg of the sample was placed in porcelain crucible, then it was heated to 900°C at a heating rate of 10°C min^{-1}. Changes of sample weight with increasing temperature were recorded. DTA was carried under N_2 ambience with a flux of 25 mL min^{-1}. Al_2O_3 was used as reference compound, and the heating rate was set as 10°C min^{-1}.

Residue morphology of flame retarding composites, formed after combustion, was investigated by electron microscope. The combusting residua were analyzed with FTIR spectroscopy with a resolution ratio of 2 cm^{-1} at the ranges of 400~4000 cm^{-1}.

RESULTS AND DISCUSSION

XRD analysis of the prepared samples

XRD analysis results for material graphite, EG and EG_1 were shown in Figure 2 (a), (b) and (c). As shown in (a), the two peaks with the interplanar crystal spacing of 3.34 Å and 1.67 Å corresponding to diffraction angle of 26.6°, 54.8° are the characteristic pattern of graphite. While, as shown in (b) and (c), the characteristic peaks of EG and EG_1 shift to a small angle of 25.7° and 26.0°, respectively. Each corresponds to a bigger interplanar crystal spacing of 3.46 Å and 3.43 Å due to intercalation in graphene planes. More importantly, it is easily found that there is a new peak with the interplanar crystal spacing of 3.16 Å at 28.1° in (b). This can be explained that natural graphite is oxidized by oxidants and then exhibited positive charge (Avdeev *et al.*, 1992a and 1992b; Zhu *et al.*, 1998, Kuan *et al.*, 2012). Due to the repulsion, the gap between graphite layers is extended, and intercalating reaction can proceed between graphite and intercalating agent. As shown in (b) and (c), EG holds bigger interplanar crystal spacing than EG_1 due to full intercalation reaction, so as to EG possess higher dilatability. As for the new diffraction presented at 28.1°, compared with standard XRD pattern, it should be sodium borate or sodium metaborate. For the known flame retardancy of borate and metaborate, it could be forecast that EG would present better flame retardancy than the contrast EG_1.

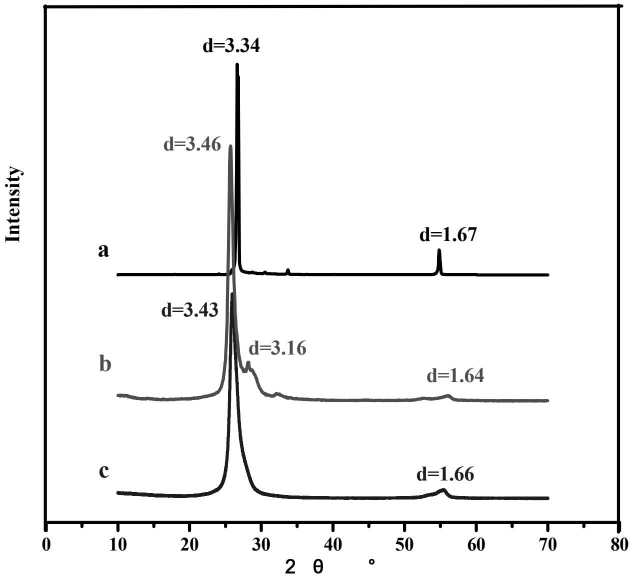


Fig. 2. XRD analysis of material graphite and the prepared products
(a) Material graphite; (b) EG; (c) EG_1

Flame retardancy of LLDPE composites

The processing temperature of LLDPE is lower than 140°C, so the prepared EG and EG_1 can be used as retardant. Flame retardants were added into LLDPE according to the proportion listed in Table 1, and LOI of composites were detected. The results showed that addition of 30-wt. % EG improved LOI to 28.4%. But addition of the same amount of EG_1 or commercial expandable graphite into LLDPE improved the

LOI to 26% and 23% (Yan *et al.*, 2006), respectively. These results indicated that the use of $Na_2B_4O_7\cdot 10H_2O$ in intercalating reaction of graphite improved flame retardancy of EG for LLDPE, and the prepared EG and EG_1 were more effectual than commercial expandable graphite. When the ordinary APP (I) was added as retardant, the LOI was only 19.3% at a 30% dosage. But as for sample 4 of 70LLDPE/10APP/20EG, the LOI improved to 30.5% when 20% EG together with 10% APP (I) were used. The value was obviously higher than the calculated LOI of 25.3% according to the single EG and APP (I) percent and LOI. Therefore, it may be inferred that there is synergistic efficiency between EG and APP.

In order to judge the retardance validity, the flame retardant efficiency (EFF) and the synergistic efficiency (SE) (Menachem, 2001) were calculated according to Equation (1) and (2), respectively.

$$EFF = \Delta LOI/FR(\%) \tag{1}$$

Where ΔLOI is the change in the *LOI*, and *FR* is the flame retardant content. The higher the *EFF*, the greater the efficiency of the flame retardant is.

$$SE=EFF_1 / EFF_2 \tag{2}$$

Where EFF_1 is the flame retardant efficiency of the synergistic system, and EFF_2 is the flame retardant efficiency of a single flame retardant. *SE* is used to evaluate the synergistic efficiency of two or more flame retardants.

Table 1. Retardant effectiveness for flame retarded LLDPE composite[a]

Samples	**Flame retardant content (%)**				**LOI (%)**	**EFF**	**SE_{EG}**	**SE_{APP}**
	EG	**EG_1**	**$Na_2B_4O_7\cdot 10H_2O$**	**APP(I)**				
1	0	0	0	0	17.1	—	—	—
2	0	0	0	30	19.3	0.073	—	—
3	10	0	0	20	28.6	0.38	1.67	5.20
4	20	0	0	10	30.5	0.45	1.78	6.16
5	30	0	0	0	28.4	0.38	—	—
6	0	30	0	0	26.0	0.30	—	—
7	0	15	15	0	25.5	0.28	—	—

[a] EG_1: the contrast expandable graphite ; APP (I): n>50;

The calculated SE_{EG} and SE_{APP} are relative to EG and APP, respectively;

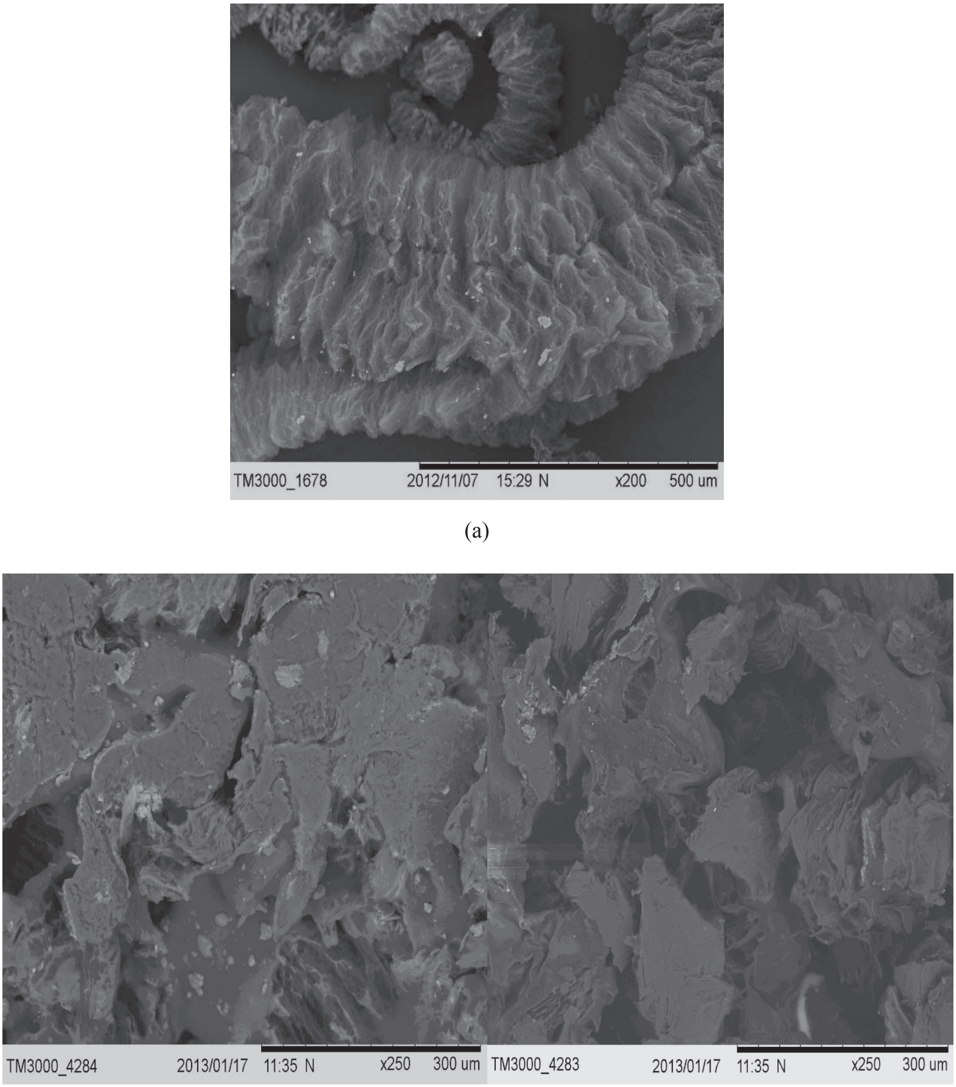
Sample 7: a 15% EG_1 together with 15% $Na_2B_4O_7\cdot 10H_2O$ were directly mixed with 70% melted LLDPE.

As listed in Table 1, EG is a highly effective flame retardant for LLDPE. Furthermore, comparing sample 5 with sample 6 and 7, it is found that the intercalating hydrated borate is more effectual in improving the flame retardancy than the direct addition of $Na_2B_4O_7{\cdot}10H_2O$. There is good synergism between EG and APP (I).

At high temperature, EG expands instantly and turns into swollen "worm-like" expanded graphite char, which can slow down heat and mass transfer between gas and condensed phase. At the same time, expansion of EG can consume an enormous amount of heat and release nonflammable gases of CO_2, H_2O as shown in equation (3) (Lu *et al.*, 2011; Thirumal *et al.*, 2008). Therefore, EG shows excellent flame retardancy for LLDPE. When EG and APP are added simultaneously, the decomposition of APP can not only release NH_3, H_2O, but can also lead to the production of metaphosphoric acid, polyphosphoric acid and diphosphoric acid, which can make the expanded graphite form a cohesive and dense charry structure (Yan *et al.*, 2006), and effectively limit transfer of heat and mass. So the 70LLDPE/10APP/20EG composite shows higher flame retardency than that of 70LLDPE/30EG specimen, even at a lower EG ratio. Besides, the results of LOI, EFF and SE are all in consistent.

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O \tag{3}$$

It is known that an effective char layer can improve flame retardants performance. In order to further investigate the effect of EG, APP on the char formation of LLDPE/EG and LLDPE /APP/EG composites, the morphologies of the specimens after the LOI tests were characterized by electron microscope and were shown in Figure 3, (a), (b) and (c). As can be seen, EG changes to "graphite worm" on the surface of LLDPE (a), and the swollen multicellular char forms a heat insulation layer. Figure 3 (b) shows the incision section of 70LLDPE/10APP/20EG composite, the residue incision section is continuous and compact due to the conglutination of APP decomposing products; this structure provides a shield that insulates the substrate from radiant heat, and avoids the direct contact between substrate and flame. As for the 70EVA/30EG composite as shown in Figure 3 (c), the incision section is discontinuous with some small holes, originating from blowing gases in redox reaction between residual H_2SO_4 and the graphite according to the reaction (3). Finally, discontinuity and low mechanical strength of the residue cause the LLDPE/EG system a decrease in flame retardancy (Yan *et al.*, 2006; Zhu *et al.*, 2011).



(a)

(b) (c)

Fig. 3. SEM micrographs of carbonaceous chars

(a)"worm like" expanded graphite (b) 70 LLDPE/10 APP/20EG (c) 70LLDPE/30EG

FTIR analysis of flame retarded LLDPE composites

To get the combustion residues and do the further analysis of FTIR, sample 4-6 adequately burned in Muffle furnace and maintained for 1 h at 800°C, then the residues and $Na_2B_4O_7\cdot 10H_2O$ agent were all analyzed with FTIR spectrograph, respectively. As shown in Figure 4, the appearance of specific absorption peak at 2924 cm^{-1} (corresponding to CH_3, CH_2 groups) in 70LLDPE/10APP/20EG and 70 LLDPE/30EG proved that the addition of EG and APP was in favor of the formation of CH_3, CH_2 groups, improving thermal stability and retarding the further degradation of LLDPE. The peak strength of 70LLDPE/10APP/20EG was higher than that of 70LLDPE/30EG due to the synergism of EG and APP (I) (Han *et al.*, 2012). Peaks at 1171 cm^{-1} and 1035 cm^{-1} in 70LLDPE/10APP/20EG are the characteristic peaks of P-O and P=O caused by APP (I) decomposition. As for the characteristic peaks of BO_3, although they are not obvious due to the little inserting dosage, they still can be observed in 70LLDPE/10APP/20EG and 70LLDPE/30EG composites. Peaks at 700-400 cm^{-1} are normally the asymmetric stretching and bending of trigonal of BO_3. Combining these results with XRD analysis of EG, it could be deduced that the possible form of B in EG was borate. For the known anti-flame property, the existence of the inserted borate could improve the flame retardancy of EG flame retardant.

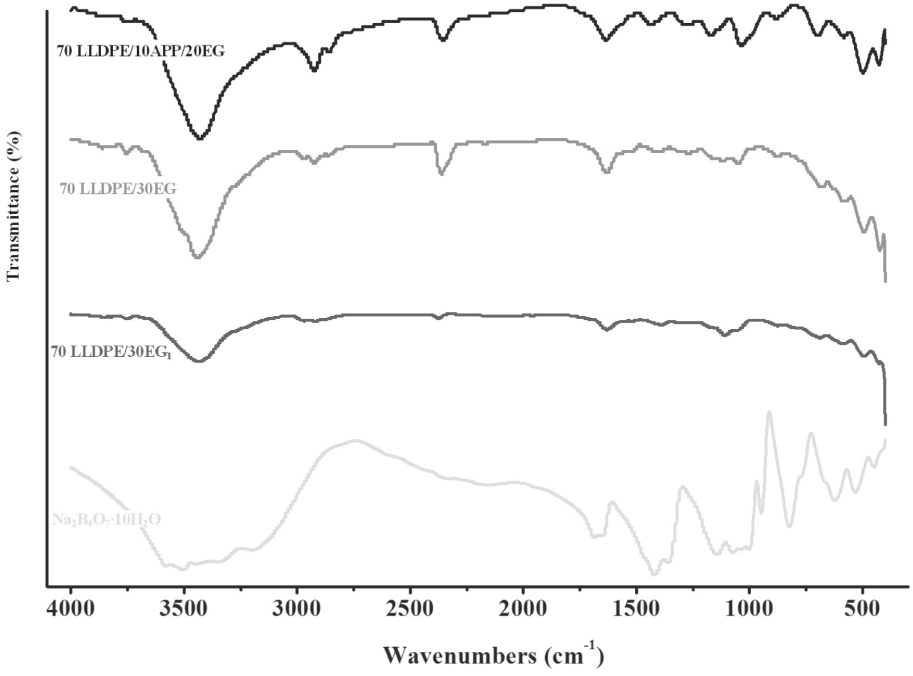


Fig. 4. The FTIR for 70LLDPE/10APP/20EG, 70LLDPE/30EG, 70LLDPE/30EG_1 composites and $Na_2B_4O_7 \cdot 10H_2O$

TG Analysis of flame retarded LLDPE composites

Figure 5 shows TG results of sample 4 of 70LLDPE/10APP/20EG composite and sample 5 of 70LLDPE/30EG specimen. The weight loss of these composites can be divided into two stages. The obvious weight loss occurs among 380-500°C. Among 100-380°C, weight loss is very slight, which is caused by the initial expansion of EG and decomposition APP (I). Temperature T_1 corresponding to a 1% weight loss are 260°C for sample 4 and 207°C for sample 5, respectively. It can be seen that the addition of APP (I) leads to a higher T_1 increased at about 50°C, which indicates sample 4 possesses higher thermal stability than sample 5. When temperature increases above 150°C, initial expansion of EG and decomposition of APP (I) occur, and the swollen EG worm can be felt together by the decomposing products of APP (I) and form into a compact multicellular carbonaceous char, retarding the transfer of heat and oxygen (Liu *et al*., 2007). A 65%−70% weight loss occurs among the second stage of 380-500°C, caused by the full expansion of EG and combustion of LLDPE. For the well formation of multicellular carbonaceous char among 380-500°C, further combustion is obviously retarded, and then the weight loss above 500°C is very slight. The final residual carbon is 21.09% for sample 4 and 28.68% for sample 5, respectively. For 70LLDPE/10APP/20EG composite, in spite of a lower residual carbon than 70LLDPE/30EG specimen, it exhibits a higher flame retardancy indicated by T_1 and LOI. This is because the swollen EG worm can form a compacter carbonaceous char layer due to the conglutination of APP (I) decomposing products. Compared with residual carbon weight, the carbonaceous char compaction should play a more important role in improving thermal stability and flame retardancy.

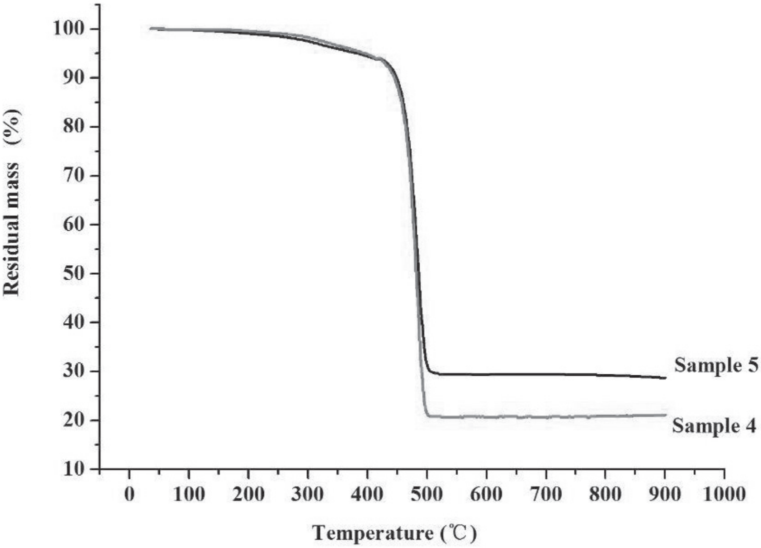


Fig. 5. TG analysis of flame retarding LLDPE composites
sample 4, 70LLDPE/10APP/20EG; sample 5, 70LLDPE/30EG

DTA analysis of flame retarded LLDPE composites

DTA curves can reveal the physical and chemical change of retardant composites along with the increasing temperature. Heat would be consumed during melt of LLDPE, decomposition of APP (I) and expansion of EG, which resulted in the decrease of combustion temperature. As shown in Figure 6, peaks corresponding to 113°C in sample 4 and sample 5 are melting specific peak of LLDPE, and peaks corresponding to 486°C and 484°C should be two strong decalescence peaks corresponding to EG expansion and LLDPE decomposition. The higher decomposing temperature of 486°C than 484°C shows that the addition of APP can improve thermal stability of sample 4 due to the formation of cohesive and dense char layer. Peaks corresponding to about 600°C maybe the melting decalescence peak of borate (Liu *et al*., 2011), and the generated boric oxide is to benefit form a glassy coating on polymer surface, limiting the transfer of heat and mass, as well as oxygen.

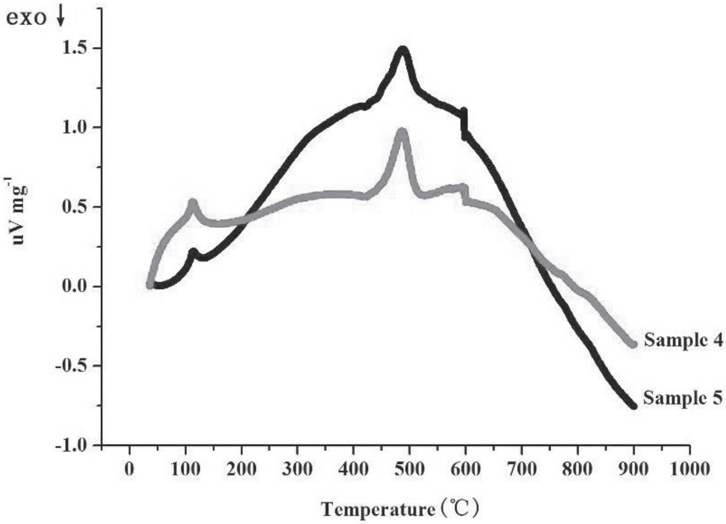


Fig. 6. DTA analysis of flame retarding LLDPE composites
sample 4, 70LLDPE/10APP/20EG; sample 5, 70LLDPE/30EG

Discussion of anti-flame mechanism

According to the results of LOI, FTIR, TG and DTA, the anti-flame mechanism of LLDPE/EG/APP composite was proposed as follows: when touched with flame source, EG instantly expanded and turned into swollen multicellular worms. The fleecy graphite worm was felt and fixed on the polymer surface by the decomposing products of APP (I) in early combustion stage. Formation of the cohesive and dense char layer was very important in retarding the transfer of heat, oxygen and improving thermal stability of the composite. The nonflammable gases of CO_2, H_2O and NH_3, released during expansion and decomposition of EG, APP (I) and hydrated borate, diluted the concentration of the volatile oxidizable pyrolysis production in the flame zone, and then enhanced carbonaceous char formation. Simultaneously, expansion and decomposition of these retardants consumed an enormous amount of heat and led to a decrease of combustion temperature.

CONCLUSIONS

The combined intumescent flame retardant EG could be prepared under the condition of C : $KMnO_4$: H_2SO_4(98%) : $Na_2B_4O_7\cdot 10H_2O$ =1.0:0.4:5.5:0.6 (mass ratio), H_2SO_4 was diluted to 80 wt%, and the reaction maintained for 40 min at 40°C. $Na_2B_4O_7\cdot 10H_2O$ could affect EG dilatability and increase its interplanar crystal spacing. The excellent anti-flame capability of EG was owing to its excellent absorbability for heat and forming swollen multicellular carbonaceous char. The coexistence of APP improved the compactness of the multicellular char, which played a more important role in retarding the transfer of heat, oxygen and improving thermal stability of the flame retarding LLDPE composite. Borate had obvious positive influence on EG flame retardancy. The intercalating hydrated borate was more effectual in improving the flame retardancy than the direct addition of $Na_2B_4O_7\cdot 10H_2O$.

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مثبطات اللهب المنتفخة - جرافيت قابل للتوسع: تحضير، خصائص وتثبيط اللهب للبولي ايثيلين

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خلاصة

تم بنجاح تحضير منتخفات لمتراكبات من الجرافت القابل للتوسع (EG) كمثبطات للهب، مع التوسع الأولي عند درجة حرارة ($155^{o}C$) وحجم توسع ($515mL\ g^{1-}$). وقد تم ذلك بنجاح بالإدراج الكيميائي لمادة الجرافيت تحت ظروف الأكسدة بواسطة $KMnO_4$، في وجود H_2SO_4 و NaB_2O_7. $10H_2O$ بنسبة كتلة C: $KMnO_4$: (98%) H_2SO_4: $Na4B_2O_7$. $10H_2O$ 1.0: 0.4 : 5.5 : 0.6 (H_2SO_4 خففل تركيز 80% بالوزن قبل التفاعل) وقد تم تمييز حجم التوسع (EV)، ودرجة الحرارة التوسع الأولية وحيود الأشعة السينية (XRD).

تم اختبار وتمييز تثبيط اللهب، والخواص الحرارية للمتراكبات من EG/LLDPE و EG/LLDPE/ APP(LLDPE-Linear low density polyethylene; APP-ammonium polyphosphate) باستخدام حد مؤشر الأوكسجين (LOI)، طيف الأشعة تحت الحمراء (FTIR)، الوزني الحراري (TG) والتحليل الحراري التفاضلي (DTA). وقد أظهرت النتائج أن إضافة EG (وزن 30٪) زادت حد مؤشر الأكسجين (LOI) لمتراكب 70LLDPE/20EG/10APP إلى 284%. أكثر من ذلك، حديث تاثير متناغم لوجود 20% EG جنباً إلى جنب مع 10% APP وذلك بتحسين LOI لمتراكب 70LLDPE/20EG/10APP إلى 30.5%. في الوقت نفسه، وجد أن درجات الحرارة المقابلة لفقد 1% من الوزن والحد الأقصى لمعدل فقدان الوزن زاد عند نحو $50^{o}C$ و $2^{o}C$، على التوالي. وقد وجد أن المتراطب 70LLDPE/20EG/10APP له تثبيط أعلى للهب حتى في أقل تفحم متبقي من عينة 70LLDPE/20EG. وقد لعبت ماسك وكثافة الطبقة الناجمة عن تورم الجرافيت المنتفخ والمنتجات المتحللة من APP دوراً أكثر أهمية في تحسين الاستقرار الحراري وتثبيط اللهب من وزن الكربون المتبقي. وكانت البورات المقحمة أكثر فعالية في تحسين تثبيط اللهب من الإضافة المباشرة لـ $Na_2B_2O_7$. $10H_2O$.

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