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Preparation of tripolyphosphate modified graphite intercalation compound and its influence on polyethylene combustion characteristics

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ABSTRACT

A tripolyphosphate modified expandable graphite (written as EG_p) was prepared through flake graphite intercalation reaction with H_2SO_4 as main intercalator and sodium tripolyphosphate as assistant intercalator simultaneously. The dilatability, main intercalated function group, crystal structure of the products were detected, and its influence on combustion characteristics of linear low density polyethylene (LLDPE) were investigated. Results show that EG_p exhibits higher dilatability and flame retardancy for LLDPE than the referenced single H_2SO_4 intercalation compound (written as EG). Addition of EG_p can obviously improve LLDPE flame retardance. The limiting oxygen index (LOI) of $70LLDPE/30EG_p$ can reach 28.4%, which is obviously higher than that of pure matrix of 17.5%. Whereas, the same dose of the referenced EG only improve the LOI of 70LLDPE/30EG to 25.1%. Furthermore, the combination of EG_p and ammonium polyphosphate (II) (APP) makes the $70LLDPE/10APP/20EG_p$ system present a LOI of 31.9%, and its UL 94 level reaches V-0.

KEYWORDS

Modified expandable graphite;
Polyphosphate;
Flame retardance;
Polyolefin.

INTRODUCTION

Flame retardants (FRs), which are chemicals added to materials in order to prevent combustion and delay the spread of fire after ignition, are used in polymers since the 1960s[1]. The halogenated flame retardants (HFRs) show excellent efficiency in suppressing ignition and slowing the spread of the flame[2]. However, the use of some of these HFRs is restrictive in recent years owing to their emitting toxic gases and smoke that can choke the people and damage equipment by corrosion[3, 4]. As typical halogen-free flame retardants (HFFRs), metal hydroxides[5-7], layered double hydroxides[8], phosphorus-nitrogen FRs[9], hosphorus-silicon FRs and so on[10], have been extensively used as smoke and toxic-free additives.

Phosphorus flame retardants (PFRs) are proposed alternatives for HFRs, which was responsible for 20% of the FRs consumption in 2006 in Europe. It can be divided in three main groups[11], inorganic (such as red phosphorus and ammonium polyphosphate (APP)), organic (such as organophosphate esters, phosphonates and phosphinates) and halogen containing (such as tris(chloropropyl)phosphate and tris (2-chloroethyl)phosphate) PFRs. The single addition of PFR, especially the inorganic PFR, normally can't get satisfied combustion limiting oxygen index (LOI) value or UL 94 level. So, they often jointly used with others in the manner of simple mixture[12-15]. However, the improvement of the flame retarded efficiency is still limited due to the insufficient mix between PFR and matrix.

Among these HFFRs, intumescent flame retardants (IFRs) have attracted great attention in recent years for their better environmental friendliness. Especially, the graphite intercalation compound (GIC), named expandable graphite (EG), is known as a new generation of IFR with good capability of halogen-free, non-dropping and low-smoke. When it's used as FR, EG plays multiple roles such as char-forming agent, blowing agent and smoke suppressant[16, 17]. Due to its outstanding capability, EG has been used in the flame retardance of polymer materials such as polyurethane (PU) or PU coatings[18,19], polyolefin[16, 20], acrylonitrile-butadiene-styrene (ABS)[21, 22], ethylene vinyl acetate (EVA) and so on[23, 24].

In the above mentioned researches, the used EG was industry product, usually prepared with H_2SO_4 as intercalation agent and H+ donor simultaneously[25, 26]. However, the high sulfur content coming from H_2SO_4 would affect its application when applied in some special area[17], and more SO_2 will release during combustion. At the same time, due to its limited efficiency, a more than 20 wt.% dosage is needed in order to achieve satisfying effect, which leads to obvious deterioration of the mechanical properties owing to the existed "popcorn effect" in the single EG system[16].

Measures have been attempted. Addition of EG together with other FRs such as phosphonate[9], polyphosphate[14], phosphorus[12], metal hydroxide[7], layered double hydroxide[13], silica[27] and so on had been tested, and normally get an improved efficiency. Surface treatments of EG is another feasible way to improve its miscibility with matrix. For example, a kind of EG modified with silane coupling agent and boric acid was prepared and used for PU[28], and results indicated thermal stability and flame retardance were all higher than that of the normal EG system. Moreover, Hong reported EG treated with phosphoric acid and silane presented an obvious increase of volume expansion ratio[22], and its addition in ABS significantly enhanced the fire performance.

Whereas, the improvement by joint addition or EG modification is usually very limited, especially the simple mix of EG with other FRs[29]. The main reason should be the insufficient mix caused by the inconsistence of particle size, density, polarity and dose between these FRs and matrix.

In the intercalating reaction of graphite, besides H_2SO_4, the assistant intercalation of the second non-carbon substance (called assistant intercalator) can normally improve the dilatability of GICs. It was reported the H_2SO_4/APP (APP as an assistant intercalator) intercalated EG, prepared through two-step method, exhibited a higher expansion volume (EV) of 240 mL‡g^{-1} than that of normal EG (the H_2SO_4 GIC) of 210 mL‡g^{-1}[30]. H_2SO_4/acetic acid intercalated EG indicated an EV of 460 mL‡g^{-1} and LOI of 28.1% for linear low density polyethylene (LLDPE)[31]. Moreover, the H_2SO_4/sodium silicate intercalated EG presented a higher EV of 517 mL/g and LOI of 28.7% for ethylene vinyl acetate copolymer (EVA) than that of the single H_2SO_4 GIC with an EV of 433 mL‡g^{-1} and LOI of 24.4%[32].

In view of the function of PFRs, EG and the influence of assistant intercalator on EG dilatability and flame retardancy, the purpose of this research is to prepare a tripolyphosphate (STPP) modified EG (written as EG_p) with low sulfur content and improved dilatability. The preparation method of EG_p was founded, X-ray diffraction spectroscopy (XRD) and Fourier transform infrared spectroscopy (FTIR) were employed to characterize the structure and main functional group. Meanwhile, the flame retardancy of EG_p and the referenced EG (intercalated with only H_2SO_4) for LLDPE matrix were all tested. Furthermore, to improve the efficiency and suppress the existed "popcorn effect" simultaneously, APP was added together in view of the reported synergistic effect between these two FRs[33, 34]. LOI level and vertical combustion UL-94 level were performed to investigate the flame retarded performance. Digital photos were applied to observe residual char morphology. Besides, to our best knowledge, there are few studies on polyphosphate modification GIC and its combining flame retardance with APP for LLDPE so far reported in the literature.

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 (7042, 0.918 g‡cm^{-3}, melt index 0.2 g‡min^{-1}) and APP (II, n>1000) were purchased from Tianjin and Sichuan, respectively. STPP 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.%):$KMnO_4$:STPP, 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, STPP, C and $KMnO_4$ 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 50-60°C for 5.0 h. The influence of various factors on dilatability of the EG_P were optimized through single-factor tests including the dose of H_2SO_4 (98 wt.%), $KMnO_4$, STPP and H_2SO_4 concentration, reaction temperature and time. Feasible conditions of EG_P preparation were finally identified as: mass ratio of C:$KMnO_4$:H_2SO_4(98 wt.%):STPP was 1.0:0.18:5.0:0.7; the concentrated H_2SO_4 was diluted to 80 wt.% before reaction; intercalation reaction was totally maintained for 40 min at 40°C. Initiation expansion temperature (temperature when the volume of GIC expanded to 1.5 times of its initial value, detected with DHG-9075A oven (temperature precision ±0.1°C, Shanghai, China) and volumetric cylinder) and the EV maximum (detected with SX3-4-13 Muffle furnace, temperature precision ±0.1-0.4%°C, Tientsin, China) of the prepared EG_P are 146°C and 630 mL‡g^{-1}, respectively.

Compared with EG_P, the referenced EG with only H_2SO_4 as intercalator was prepared at the mass ratio C:$KMnO_4$:H_2SO_4(98 wt.%) of 1.0:0.18:5.0 under the same condition as mentioned in the preparation of EG_P. Its initial expansion temperature and EV were detected as 205°C and 450 mL‡g^{-1}, respectively. It's obvious that the assistant intercalation of STPP has significant influence on dilatability, reflected by the increase of EV and change of initial expansion temperature. It can be deduced that EG_P will form thicker intumesce char than the normal EG, and then show better flame retardance.

A certain amount of FRs were added into melted LLDPE at 120°C in Muller, the mixtures were pressed at 125°C and 10 MPa, and then chopped into slivers with two different sizes of 120.0×6.0×3.0 mm^3 and 127.0×13.0×3.0 mm^3.

Measurements and characterization

The FTIR spectra of the prepared EG_P and EG were recorded between 4000-400 cm^{-1} using a FTIR spectrometer (Nicolet 380, America Thermo Electron Corporation) with a resolution of 2 cm^{-1}.

XRD pattern was obtained with an Y2000 X-ray diffractometer (Dandong, China) under the operation condition of 40 kV, 30 mA, employing Ni-filtered Cu K_α radiation with 2θ ranging from 15° to 70°. The interlayer spacing was obtained from the angle at which the corresponding peak was diffracted (Bragg's law: $2d\sin\theta=n\lambda$)[35].

Combustion property

LOI test was used to evaluate the combustion property of the flame retarded LLDPE composites with a size of 120.0×6.0×3.0 mm^3, and it was detected using a JF-3 LOI instrument (Chengde, China) according to Standard of GB/T2406-1993. At the same time, vertical burning test was performed using a HC-3 vertical burning instrument (Tientsin, China) on sheets of size 127.0×13.0×3.0 mm^3 as per the standard UL 94-1996.

RESULTS AND DISCUSSION

Characterizations of graphite and its GICs: FTIR analysis

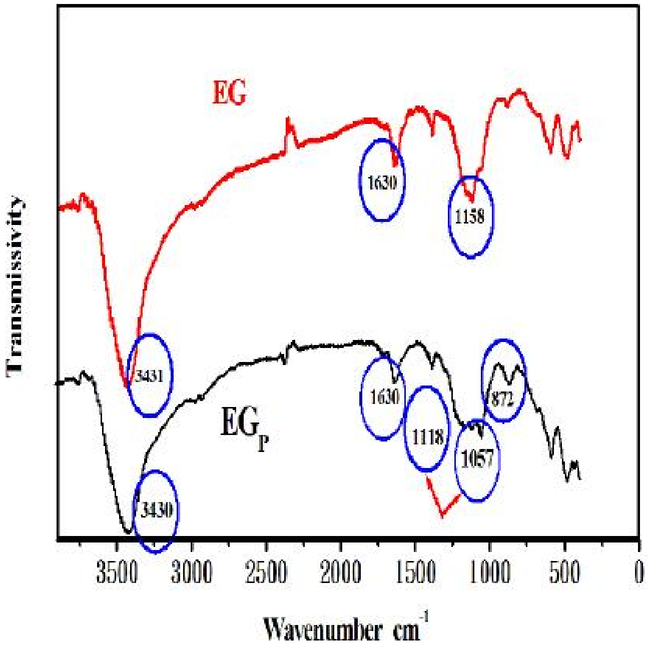

Figure 1 FTIR analysis of the referenced EG and EG_P

Figure 1 shows FTIR spectra of the prepared EG_P and the referenced EG. As can be seen from the results, two samples both show the characteristic stretching vibrations absorption peaks of -OH (3430 cm^{-1}), caused by intercalation of H_2SO_4/HSO_4^-. At the same time, the peaks at about 1620 cm^{-1} are the specific absorption of C=C stretching vibrations[25], originating from graphite conjugated structure. The strong stretching vibration absorption peak of sulphate is observed in EG (1158 cm^{-1})[11], but there are obvious superimposed peaks at 1118 cm^{-1} and 1057 cm^{-1} in the FTIR of EG_P, it is because the absorption peaks of S=O and P=O are both appear in the range of 1180-1100 cm^{-1} as reported[36]. Furthermore, peak at 872 cm^{-1} in EG_P is the same as STPP standard spectrum in the range of 1000-800 cm^{-1}[37]. The results confirm the intercalation of these two intercalators.

Characterizations of graphite and its GICs: XRD analysis

XRD analysis for natural graphite and its GICs were performed, EG_P and the referenced EG all show the same characteristic diffraction lines like natural graphite at about 26° and 55° as shown in Figure 2, which indicate they all keep the layer structures. Whereas, it is worthy to note that the (002) diffraction peaks transfer to a smaller angle of 26.4° for EG and 26.1° for EG_P respectively. At the same time, each corresponds to a big interplanar spacing of 3.37 Å for EG and 3.41 Å for EG_P. This can be explained that natural graphite is oxidized by $KMnO_4$ 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[11, 38]. The XRD results confirm that intercalators have been inserted into graphite layers.

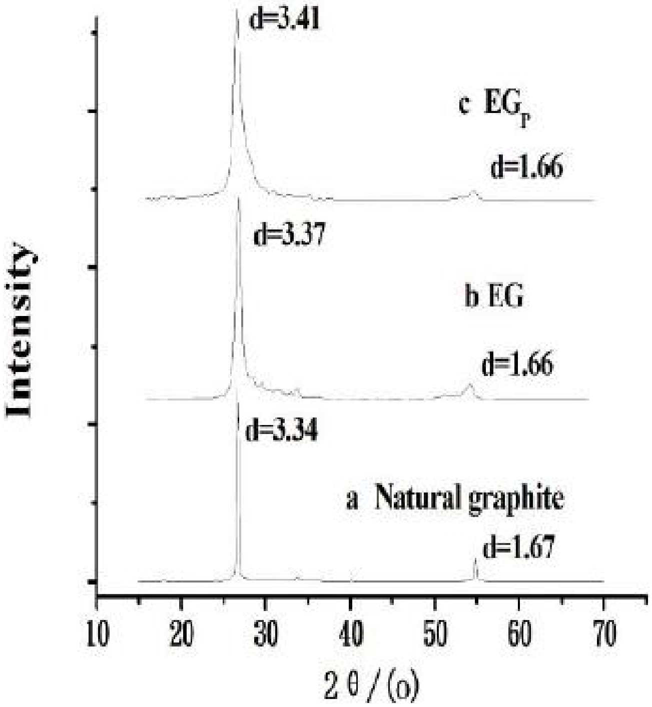

Figure 2 : XRD analysis of natural graphite (a), EG (b) and EG_P (c)

Combustion characteristics of the flame retarded LLDPE

The processing temperature of LLDPE is about 120°C, so the prepared GICs can be used to suppress this polymer combustion. The flame retarded LLDPE specimens were prepared following the above mentioned method, weight percent of FRs and matrix was listed in TABLE 1. LOI detection and vertical combustion tests were carried out to evaluate flame retardance and observe ignition, expansion-extinguishing process and melt-dripping phenomenon. The results were also listed in TABLE 1.

TABLE 1 : Specimens combustion characteristics

Specimens	LOI %		UL 94 level	Melt dripping
	LOI$_{exp}$	LOI$_{cal}$		
100LLDPE	17.5	-	-	Yes
70LLDPE/30EG	25.6	-	-	Yes
70LLDPE/30EG$_P$	28.4	-	V-2	Yes
70LLDPE/30APP	19.8	-	-	Yes
70LLDPE/10APP/20EG$_P$	31.9	25.5	V-0	No
70LLDPE/15APP/15EG$_P$	31.4	24.1	V-0	No
70LLDPE/20APP/10EG$_P$	29.7	22.7	V-0	No

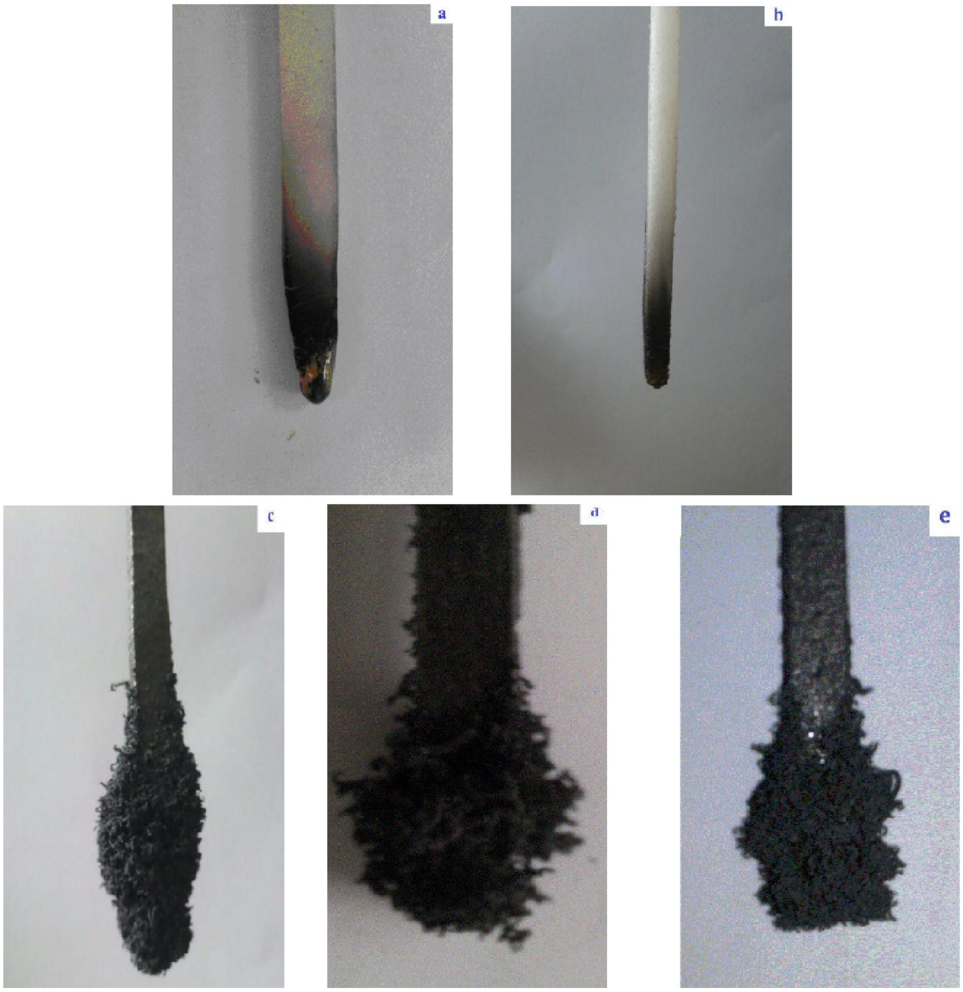

Figure 3 The combustion morphology of LLDPE specimens in vertical flame tests LLDPE (a); 70LLDPE/30APP (b); 70LLDPE/30EG (c); 70LLDPE/30EG$_p$ (d); 70LLDPE/10APP/20EG$_p$ (e)

As shown in TABLE 1, LLDPE is very flammable with a LOI of 17.5%, and additionally, the combustion accompanies with serious melt-dripping (as shown in Figure 3a). While, the addition of the tested FRs can all affect combustion process. Addition of the referenced EG at 30 wt.% leads LOI of 70LLDPE/30EG composite improved to 25.6%, but the melt-dripping and ignition still occurs and gets no UL 94 level. Noticeably, addition of the same amount of EG$_p$ improves the LOI to 28.4% and the vertical combustion level to V-2. These results indicate the assistant intercalation of STPP ameliorates flame retardance of EG_P for LLDPE. The addition of the prepared GICs can all reduce the dripping phenomena, which should be attributed to the protective intumescent carbonaceous char (as shown in Figure 3c and 3d) formed on polymer surface by EG or EG_p expansion[39, 40].

Moreover, the efficiency of APP for LLDPE and its synergetic efficiency with EG_P were also investigated. When it is solely added at 30 wt.%, LOI of the 70LLDPE/30APP specimen is only 19.8%, and accompanied by melt-dripping and ignition as shown in Figure 3b. While, additions of EG_P and APP at different wt.% can not only increase LOI value, but also all improve the UL 94 level to V-0 level simultaneously as shown in Figure 3e. Meanwhile, these LOI values are all obviously higher than the theoritical calculated LOI_{cal} according to their single wt.%, and LOI values[32]. Therefore, it can be inferred that there is synergistic efficiency between these two FRs. Meanwhile, the APP/EG_P ratio has an important influence on flame retardancy, and the tested optimum mass ratio is 10:20 as shown in 70LLDPE/10APP/20EG_P specimen, the LOI and UL 94 level are 31.9% and V-0 respectively.

Possible flame retardant mechanism

According to the LOI, UL 94 results and residual morphology of the flame retarded LLDPE composites, it can be indicated that:

When contacting with flame source, GIC will instantly expand and turn into swollen multicellular “graphite worms” covering on the matrix surface, which is in favor of slowing down the heat and mass transfer and interrupting the degradation of polymer. Moreover, expansion of GIC will consume an enormous amount of heat, which is helpful to decrease the combustion temperature and rate. Furthermore, oxidation reaction between graphite and H_2SO_4 releases CO_2, H_2O and SO_2 and it reduces combustible gas concentration; thereby char formation has been enhanced. The intervention of STPP and APP are active in the solid phase of burning materials based on char forming[39].

CONCLUSIONS

STPP modified expandable graphite EG_P was successfully prepared with H_2SO_4 and STPP as intercalator and assistant intercalator with chemical oxidation intercalation method. Compared with the referenced EG, EG_P possessed a better dilatability and flame retardance. FTIR and XRD confirmed that the oxidation and intercalation reaction between natural graphite and intercalators could take place. As for the flame retarded efficiency for LLDPE, EG_P exhibited a higher LOI value and UL 94 level than the normal EG. Moreover, the combination of EG_P with APP indicated synergistic efficiency between these two FRs.

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