Preparation of Expandable Graphite Intercalated by Sulfuric Acid and Sodium Silicate and Its Flame Retardancy Application for Ethylene Vinyl Acetate Copolymer

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Expandable graphite intercalated by sulfuric acid and sodium silicate (Na_2SiO_3) was prepared by two step intercalation method under oxidation of $KMnO_4$. The influence of various factors on dilatability of the expandable graphite were discussed including the dosages of $KMnO_4$, H_2SO_4, $Na_2SiO_3 \cdot 9H_2O$ and H_2SO_4 concentration, pH of Na_2SiO_3 and NaOH mixed solution, reaction temperature, reaction time. Expandable graphite with an initial expansion temperature of 202 °C and expansion volume of 517 mL/g could be prepared under the mass ratio $C:KMnO_4:H_2SO_4$ (98 %):$Na_2SiO_3 \cdot 9H_2O$ of 1.0:0.22:4.0:0.8. H_2SO_4 should be diluted to mass concentration of 75 % before intercalation, Na_2SiO_3 dissolved in NaOH aqueous solution with a pH of 13 was dropwise added when the intercalation of H_2SO_4 preceded 7.5 min and the reaction was totally maintained 40 min at 40 °C. X-ray powder diffraction analysis was performed to illuminate the structure characteristics of expandable graphite and its flame retarding property for ethylene vinyl acetate copolymer (EVA) was investigated and characterized by limiting oxygen index (LOI) and scanning electron microscope. The LOI of EVA is only 19.3 %; addition of 30 % expandable graphite made the LOI of EVA/expandable graphite reaches 28.4 %, but the addition of same dosage of compared blank expandable graphite only get a LOI of 24.4 %. The excellent anti-flame capability of expandable graphite is owing to its fully endothermic expansion and formation of heat insulation swollen multicellular char.

Keywords: Expandable graphite, Silicate, Dilatability, Intumescent flame retardant, Ethylene vinyl acetate copolymer.

INTRODUCTION

Graphite is a crystal compound with graphene planes structure bonded by van der Waals force and the bond energy is only 16.7 kJ/mol. Under oxidation, many compounds can intercalate graphene planes and then graphite intercalation substances called expandable graphite can be prepared[1,2]. Expandable graphite has many uses: it has catalysis in the reaction of organic acid and alcohol[3]; Porous expanded graphite adsorbent can be prepared with expandable graphite expanding instantly at high temperature[4]. The expandable graphite is an intumescent type flame retardant, a char-forming agent, a blowing agent and smoke suppressant[5-8]. Due to its outstanding anti-flame capability, expandable graphite has been used widely in the flame retarded polymers such as poly-olefin blends[9], polylactide[10], polyurethane[11] and poly (methyl methacrylate)[12].

In its traditional preparation methods, the mainly used intercalating agent is H_2SO_4 for its dual function *i.e.*, as a donor of H^+ and intercalating agent, low-price, easy and simple to handle, high dilatability of the prepared product[13,14]. However, the use of it leads to high sulfur content in products and corrosion of storage devices caused by lixiviating vitriol. So,

it is necessary to supplement assistant intercalating agent to replace part of H_2SO_4[15,16]. The most remarkable thing is that if a traditional flame retardant is used as assistant intercalating agent, it is not only can decrease sulfur content in graphite intercalation substances, but also improve its flame retardant property. For examples, expandable graphite, intercalated by H_2SO_4 and ammonium polyphosphate (APP) by two-step method, showed higher expansion volume than the product intercalated by single H_2SO_4[17]; expandable graphite, inter-calated by H_2SO_4 and $Na_4P_2O_7$ with direct method, presented excellent dilatability and combustion limiting oxygen index than the compared single H_2SO_4 intercalation substance[18]. Silicate is a kind of well-known flame retardant with good flame retardancy for its formation of SiO_2 protective layer on composite surface[19,20]. As far as little study is reported about preparation of expansible graphite (EG) using H_2SO_4 and silicate as main intercalating agent and assistant intercalating agent, respectively.

The purpose of this research is to prepare a high dilatability and combined intumescent flame retardant expandable graphite through chemical intercalation reaction of graphite using H_2SO_4 and Na_2SiO_3 as intercalating agent. Due to the poor solubility of silicate in acid medium, Na_2SiO_3 dissolved

in NaOH aqueous solution was used. At the same time, a two-step intercalating method was performed to ensure oxidation of $KMnO_4$ and preferentially intercalation of H_2SO_4. Expansion property and structure characteristics of the prepared expandable graphite were characterized by expanded volume (EV) and initial expansion temperature. Influence of various factors on dilatability of the expandable graphite were detected including the dosages of $KMnO_4$, H_2SO_4, $Na_2SiO_3 \cdot 9H_2O$ and H_2SO_4 concentration, pH of Na_2SiO_3 and NaOH mixed solution, reaction temperature, reaction time. X-ray diffraction (XRD) was performed to characterize the crystal structure of expandable graphite. Its flame retarding property for ethylene vinyl acetate copolymer (EVA) was investigated and characterized by limiting oxygen index (LOI) and scanning electron microscope (SEM).

EXPERIMENTAL

SX3-4-13 Muffle furnace (Tientsin, China. precision of temperature ± 0.1-0.4 % °C), 101-3 Oven (Shanghai, China. precision of temperature ± 2 °C), Muller (Jiangsu, China), Y-4Q X-ray diffractometer (Dandong, China), Muller (Jiangsu, China), JF-3 Limiting oxygen index (LOI) instrument (Chengde, China) and TM3000 electron microscope (Japan) were used in this experiment.

Natural flake graphite with a carbon content of 95 % was provided by Action Carbon CO. LTD, Baoding, China; and an average flake size is 0.18 mm. Ethylene vinyl acetate copolymer was purchased from Tianjin, China. $Na_2SiO_3 \cdot 9H_2O$, H_2SO_4 (98 %), NaOH and $KMnO_4$ are all analytical agents.

Preparation of expandable graphite: At first, the quantified reactants were mixed in a 250 mL beaker in the order of diluted H_2SO_4, natural graphite C, $KMnO_4$. The mixture was stirred at a definite temperature controlled with water bath. Then mixture of Na_2SiO_3 and aqueous solution of NaOH with a certain pH was added dropwise when the intercalation of H_2SO_4 preceded a certain amount of time. Follow-up intercalation of Na_2SiO_3 was maintained some time and then the solid phase was washed with de-ionized water until pH of the waste water reached to 6.0-7.0. After dipping in water for 2 h, filtrated and dried the sample at 50-60 °C for 4-5 h, then expandable graphite was obtained.

Characterization of the samples: Expanded volume is an important factor to judge dilatability of expandable graphite and it is defined as the volume of 1.0 g expandable graphite after expansion at a certain temperature. The temperature corresponding to 1.5 times of initial volume of expandable graphite is defined as initiation expansion temperature. They were detected according to our previous work[21].

XRD pattern was obtained on a Y-4Q X-ray diffractometer operating at 40 kV, 30 mA, employing Ni-filtered CuK_α radiation with 2° ranging from 20° to 70°.

Preparation of flame retarded ethylene vinyl acetate copolymer (EVA) composites: A certain amount of flame retardant was added into melting EVA at 130 °C in Muller, the mixtures were pressed at 125 °C and 10 MPa and then chopped in slivers with a size of 120 mm × 6 mm × 3 mm.

Detection of limiting oxygen index (LOI) of retarded EVA composites: Limiting oxygen index is the minimum amount of oxygen in an oxygen-nitrogen mixture required to support combustion over 3 min. The incised slivers of retarded EVA composites were used to measure LOI according to Standard of GB/T2406-1993 with oxygen index instrument (Chengde, China).

SEM micrographs analysis of samples: To observe layer structures of natural graphite and expandable graphite and survey the combustion residues morphology of retardant compo-sites, SEM micrographs of these samples were detected with scanning electron microscope.

RESULTS AND DISCUSSION

Optimization of influence factor in the preparation of expandable graphite: Influence of various factors on dilatability of the expandable graphite were optimized through single factor tests including the dosages of $KMnO_4$, H_2SO_4, $Na_2SiO_3 \cdot 9H_2O$ and H_2SO_4 concentration, pH of Na_2SiO_3 and NaOH mixed solution, reaction temperature, reaction time.

Influence of H_2SO_4 dosage on expandable graphite dilatability: As an important intercalating agent, H_2SO_4 dosage in reaction has obvious effect on expandable graphite dilatability. To investigate this feasible dosage, it was changed in the range of 2.5-4.5 g/g. In the following experiment, the operational program was the same as mentioned above. Mass ratio of C to $KMnO_4$ was controlled as 1.0:0.2; H_2SO_4 was diluted to mass concentration of 65 %. Mixed solution of Na_2SiO_3 and NaOH containing 4 g Na_2SiO_3 and with a pH of 13 was added dropwise when the intercalation of H_2SO_4 preceded 2.5 min. The reactions maintained 40 min at 40 °C. Fig. 1 illustrate that feasible mass ratio of H_2SO_4 to graphite should be 4.0 g/g. Under this ratio, expanded volume of expandable graphite can reach 300 mL/g. Insufficiency H_2SO_4 dosage would cause an incomplete intercalation and leading to the decrease of dilatability; Superfluous H_2SO_4 would cause the relative scarcity of $KMnO_4$ and incomplete oxygenation for graphite.
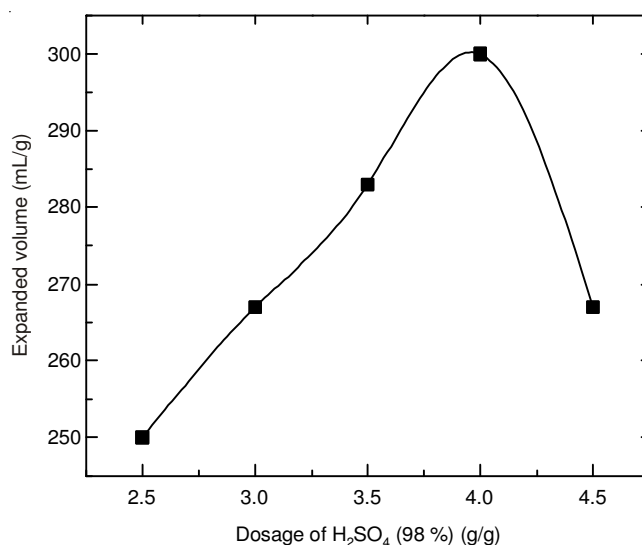

Fig. 1. Influence of H_2SO_4 dosage on expanded volume of expandable graphite

Influence of H_2SO_4 concentration on expandable graphite dilatability: Under mass ratio $C:KMnO_4:H_2SO_4$

(98 %) of 1.0:0.2:4.0, influence of H_2SO_4 mass concentration in the range of 65-85 % on expandable graphite dilatability was detected. Other conditions were controlled the same as mentioned above. As shown in Fig. 2, expanded volume of expandable graphite increases with mass concentration of H_2SO_4 at first and then decreases when it is beyond 75 %. According to eqn (1), the oxidation ability of $KMnO_4$ is affected by hydrogen ion effective concentration $[H^+]$. Too lower or too higher H_2SO_4 concentration in reaction can all lead to the decrease of $[H^+]$ and oxidation ability $KMnO_4$, then cause insufficient intercalation of H_2SO_4 and Na_2SiO_3. Feasible mass concentration of H_2SO_4 in reaction can be set as 75 %.

$$E_{MnO_4^-/Mn^{2+}} = E^\theta_{MnO_4^-/Mn^{2+}} + (0.05916/5)$$
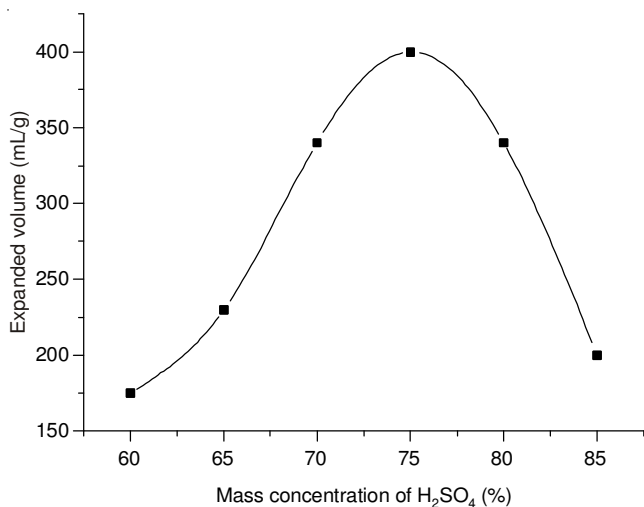$$\lg\{[H^+]^8[MnO_4^-]/[Mn^{2+}]\} \qquad (1)$$

Fig. 2.   Influence of H_2SO_4 mass concentration on expanded volume of expandable graphite

Influence of $KMnO_4$ dosage on expandable graphite dilatability: In intercalating reaction of natural graphite, $KMnO_4$ acts as an oxidant to capture electrons between graphene planes structure and then leads to the formation of the graphite carbon cations and subsequent intercalation of H_2SO_4 and Na_2SiO_3. In order to investigate its influence on dilatability in two step intercalation, single-factor experiments were carried out by changing $KMnO_4$ dosage in the range of 0.17-0.40 g/g. Experiments were carried out under the mass ratio $C:H_2SO_4$ (98 %) of 1.0:4.0, H_2SO_4 was diluted to mass concentration of 75 % and other conditions were controlled the same as mentioned above. Fig. 3 illustrate that when the mass ratio of $KMnO_4$ to graphite is controlled as 0.22 g/g, the prepared expandable graphite possesses a maximum expanded volume of 466 mL/g. Insufficiency $KMnO_4$ would cause an incomplete oxygenation of graphite and superfluous $KMnO_4$ would cause an excessive oxygenation, which would lead to a decrease of expandable graphite granularity and its expanded volume. The feasible dosage of $KMnO_4$ can be set as 0.22 g/g.

Influence of Na_2SiO_3 dosage on expandable graphite dilatability: Under mass ratio $C:KMnO_4:H_2SO_4$ (98 %) of 1.0:0.22:4.0, H_2SO_4 was diluted to mass concentration of 75 % before reaction and other conditions were controlled the same as mentioned above. The influence of $Na_2SiO_3 \cdot 9H_2O$ dosage, dissolved in 2 mL aqueous solution of NaOH with a concen-

tration of 0.1 mol/L, was detected in the range of 0-1.2 g. As an assistant intercalating agent, increase of its dosage can improve expandable graphite dilatability as shown in Fig. 4. When it is controlled as 0.8 g, expandable graphite with a maximum expanded volume of 517 mL/g can be gained. Superfluous dosage would cause the relative scarcity of $KMnO_4$ oxidation ability and incomplete oxygenation of graphite.
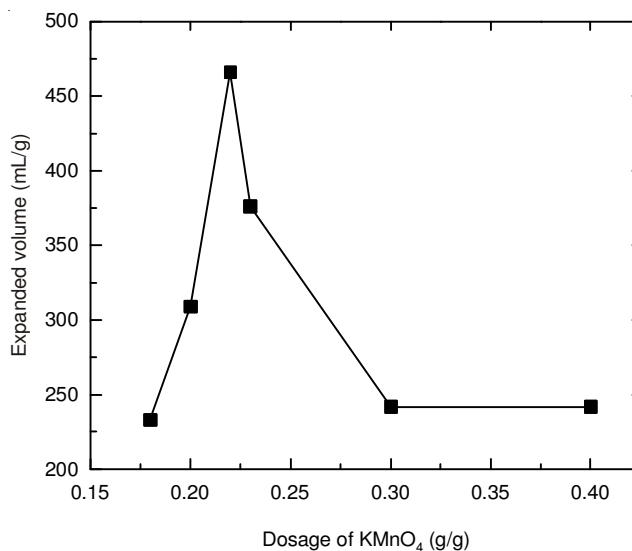

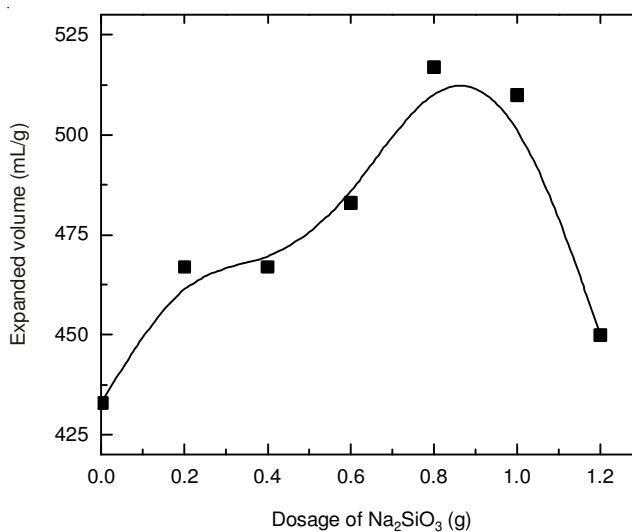Fig. 3. Influence of $KMnO_4$ dosage on expanded volume of expandable graphite

Fig. 4. Influence of Na_2SiO_3 dosage on expanded volume of expandable graphite

Influence of pH of aqueous solution of NaOH on expandable graphite dilatability: Under mass ratio $C:KMnO_4:H_2SO_4$ (98 %) of 1.0:0.22:4.0, H_2SO_4 was diluted to the mass concentration of 75 % before reaction. Mixed solution of Na_2SiO_3 and NaOH (containing 0.8 g Na_2SiO_3 in 2.0 mL NaOH aqueous solution) with different pH was added dropwise when the intercalation of H_2SO_4 preceded 2.5 min and other conditions were controlled the same as mentioned above. Influence of pH of aqueous solution of NaOH on expandable graphite dilatability was detected and shown as Fig. 5. It can be seen that pH of aqueous solution of NaOH has obvious influence

on expanded volume. When the pH is low, there are insufficient OH^- ions to neutralize the superfluous H^+ in solution, then lead to the formation of H_2SiO_3 sediment and decrease the effective intercalation of Na_2SiO_3. High pH causes the decrease of $KMnO_4$ oxidation ability and incompletely open the graphite layers and intercalate substances. In order to get a high dilatability, pH of aqueous solution of NaOH should be controlled 13.
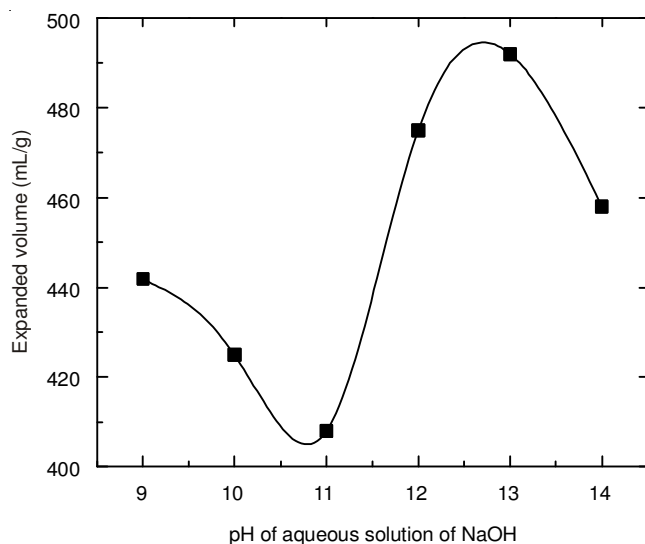

Fig. 5. Influence of pH of aqueous solution of NaOH on expanded volume of expandable graphite

Influence of the first-step reaction preceded time on expandable graphite dilatability: In view of the poor solubility of silicate in acid medium, Na_2SiO_3 dissolved in aqueous solution of NaOH was used. At the same time, a two-step intercalating method was performed to ensure $KMnO_4$ oxidation ability and preferentially intercalation of H_2SO_4. Conditions were controlled the same as mentioned above, mixed solution of Na_2SiO_3 and NaOH containing 0.8 g Na_2SiO_3 and with a pH of 13 was dropwise added when the intercalation of H_2SO_4 preceded 2.5, 5, 7.5, 10 and 15 min, respectively. Influence of the first-step reaction preceded time on expandable graphite dilatability was shown as Fig. 6.
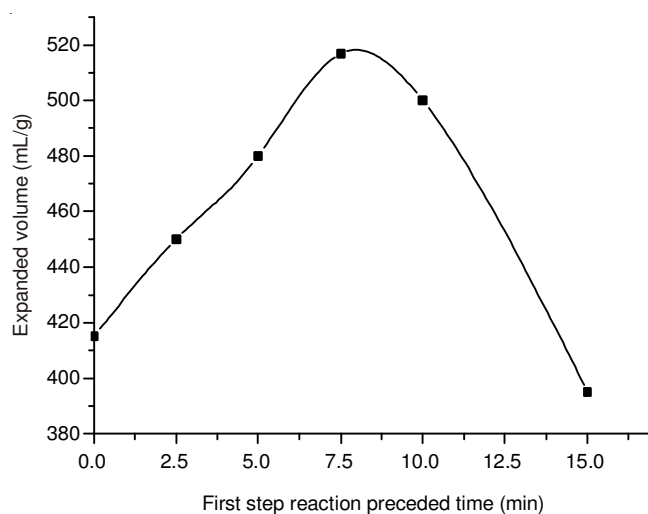
Results show that the expanded volume increases with the increase of the first-step reaction preceded time at first and then decreases with the further increase of preceded time. When mixture of Na_2SiO_3 and NaOH is added dropwise together with H_2SO_4, OH^- would consume a part of H^+, which would cause the decline of $KMnO_4$ oxidation ability and then further influence the gap between graphite layers and intercalation of H_2SO_4 and Na_2SiO_3. So a step-by-step intercalation of H_2SO_4 and Na_2SiO_3 is needed. Increase of the first-step reaction preceded time leads expanded volume increases gradually. Intercalation of graphite includes oxidation, intercalation and change of graphite layers. When the first-step reaction proceeded for a feasible time, oxidation of graphite is almost completed, the gap between graphite layers is extended, the intercalating reaction of H_2SO_4 proceeds extensively and the successive addition and intercalation of Na_2SiO_3 increase total intercalating amount in graphite layers and dilatability of expandable graphite[17]. Oxidation, intercalation and layer structure change will be finished over time, when the addition of Na_2SiO_3 is too late. The intercalation and layer change of graphite will be finished, then expanded volume will decrease. According to the experimental results, feasible preceded time of the first-step reaction should be 7.5 min.

Influence of reaction temperature on expandable graphite dilatability: Under mass ratio $C:KMnO_4:H_2SO_4$ (98 %) of 1.0:0.22:4.0; H_2SO_4 was diluted to the mass concentration of 75 % before reaction; mixed solution of Na_2SiO_3 and NaOH containing 0.8 g Na_2SiO_3 and with a pH of 13 was added dropwise when the intercalation of H_2SO_4 preceded 7.5 min; reaction totally maintains 40 min; the influence of reaction temperature on expanded volume (EV) was detected. When it is less than 40 °C, the increase of temperature can improve expandable graphite dilatability as shown in Fig. 7. Too low temperature may cause low reaction speed and insufficient intercalation. While, too high temperature can lead the exothermic reaction releasing more heat and excessive oxygenation of graphite. The feasible reaction temperature can be set as 40 °C.
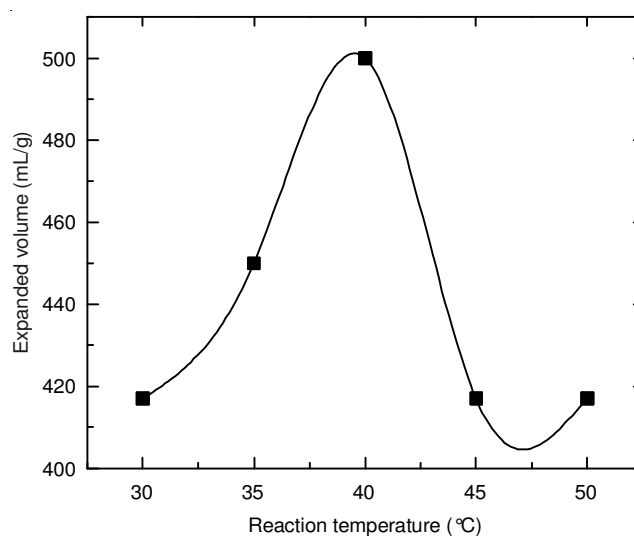

Fig. 6. Influence of the first-step preceded reaction time on expanded volume of expandable graphite

Fig. 7. Influence of reaction temperature on expanded volume of expandable graphite

Feasible condition of preparation of expandable graphite: According to the experimental results, feasible conditions to prepare expandable graphite can be set as following: mass ratio of C, $KMnO_4$ and H_2SO_4 (98 %) is 1.0:0.22:4.0; H_2SO_4 diluted to mass concentration of 75 % before reaction; mixed solution of Na_2SiO_3 and NaOH containing 0.8 g Na_2SiO_3 and with a pH of 13 is dropwise added when the intercalation of H_2SO_4 preceded 7.5 min; reaction totally maintains 40 min at 40 °C. The solid obtained through filtration is dried at 50-60 °C for 4-5 h and then expandable graphite is obtained. Its initial expansion temperature and expanded volume are detected as 202 °C and 517 mL/g (at 800 °C), respectively.

Preparation of the blank expandable graphite without Na_2SiO_3 intercalation: Compared with expandable graphite, the blank expandable graphite (EG_1) is prepared under mass ratio $C:KMnO_4:H_2SO_4$ (98 %) of 1.0:0.22:4.0, H_2SO_4 is diluted to the mass concentration of 75 % before reaction and reaction maintains 40 min at 40 °C. It's initial expansion temperature and expanded volume is detected as 235 °C and 433 mL/g (at 800 °C), respectively. It is obvious that Na_2SiO_3 obviously affect initial expansion temperature and dilatability of expandable graphite, addition of 0.8 g/g of this assistant intercalating agent in graphite intercalating reaction can cause an increase of 19 % of expanded volume. The expandable graphite shows better flame retardancy than blank expandable graphite for its good dilatability.

XRD analysis of the prepared samples: XRD analysis for natural graphite and expandable graphite were performed. As shown in Fig. 8(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 spectrum of natural graphite. While, as shown in Fig. 8(b), the characteristic peaks of expandable graphite transfer to a small angle of 26.4° and it corresponds to a big interplanar crystal spacing of 3.40 Å due to intercalation in graphene planes. Natural graphite is oxidized under oxidation of $KMnO_4$ and carried on positive charge. Due to the distortion of conjugate system and the exclusive function of positive charge, the gap between graphite layers is extended[2], the intercalating reaction can proceed extensively between graphite and intercalating agent. A new reflection peak caused by the intercalation of Na_2SiO_3 can be observed at 28.6° with a crystal spacing of 3.12 Å. Compared with standard XRD chart, it indicates that the possible existing form of Si is SiO_2 or sodium silicate. For the known flame retardancy of SiO_2 and sodium silicate, it can be forecast that expandable graphite will present better flame retardancy than the contrast blank expansible graphite.

Detection of expandable graphite anti-flame capability for EVA: Processing temperature of EVA is normally 130 °C, so the prepared expandable graphite and blank expansible graphite can be used as flame retardant and they are added to the polymer according to the proportion listed in Table-1. LOI was detected according to the mentioned method. The results show that LOI of single EVA is only 19.3 % and its combustion accompanies with molten drop at the same time. Addition of 30 % blank expansible graphite can make LOI improve to 24.4 %, no molten drop occurs. Whereas, the addition of the same amount of expandable graphite to EVA can make LOI reach 28.5 % and no molten drop occurs too. The results
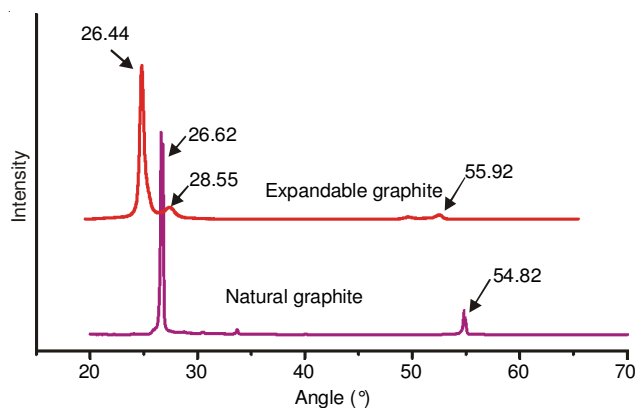
Fig. 8. XRD analysis of natural graphite and expandable graphite

indicate that the use of $Na_2SiO_3 \cdot 9H_2O$ in intercalating reaction of graphite can improve flame retardancy for EVA. Furthermore, comparing sample 3 with sample 4, it is find that the intercalated silicate is more effectual in improving the flame retardancy than the direct addition of $Na_2SiO_3 \cdot 9H_2O$.

TABLE-1 LOI OF THE FLAME RETARDED EVA COMPOSITES					
Sample	Flame retardant content (%)				LOI (%)
	EVA	Expandable graphite	Blank expandable graphite	$Na_2SiO_3 \cdot 9H_2O$	
1	100	0	0	0	19.3
2	70	0	30	0	24.4
3	70	30	0	0	28.5
4	70	0	13	17	25

SEM analysis of samples: Fig. 9 presents SEM micrographs of natural graphite, expandable graphite and the combustion residues of retardant composites. Comparing Fig. 9 (a) with Fig. 9 (b), the layers' structures of natural graphite are

(a) × 40,000   (b) × 25,000
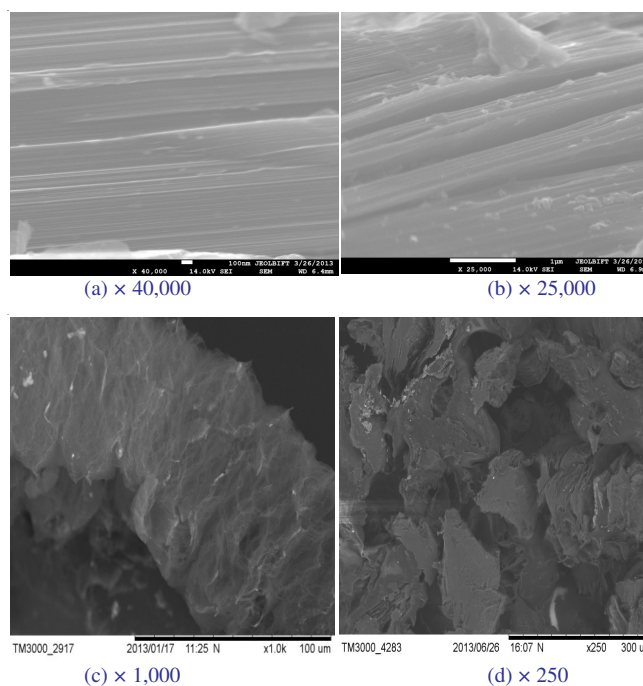
(c) × 1,000   (d) × 250

Fig. 9. SEM micrographs of samples, (a) Natural graphite (b) expandable graphite (c) Worm-like expanded graphite particle (d) Section of EVA/expandable graphite composites combustion residues

compact and the layers' distance is very small in Fig. 9 (a). After the graphite is oxidized and intercalated, the layers distance has been enlarged and the boundary layers of Fig. 9 (b) have been loosed while the forces between the layers disappear. As can be seen in Fig. 9 (c) and (d), when expandable graphite touches with fire, it absorbs heat and turns into worm-like expanded graphite particles and the inserted agents release CO_2, H_2O gas and escape from the expandable graphite. Clearly, EVA/expandable graphite composite takes place dramatically expansion and the layers of graphite protect the polymer matrix to avoid further thermal degradation. It results in the promotion of flame retardancy property of the composites.

Conclusion

Control reaction conditions as following: C, $KMnO_4$ and H_2SO_4 (98 %) is with the mass ratio of 1.0:0.22:4.0; H_2SO_4 is diluted to the mass concentration of 75 % before reaction; mixed solution of Na_2SiO_3 and NaOH containing 0.8 g Na_2SiO_3 and with a pH of 13 is dropwise added when the intercalation of H_2SO_4 preceded 7.5 min; reaction totally maintains 40 min at 40 °C. We can prepare expandable graphite flame retardant with an initial expansion temperature of 202 °C and maximum expanded volume of 517 mL/g. The intercalating silicate has obvious influence on expandable graphite dilatability and flame retardancy. Feasible intercalating dosage can increase its expanded volume and flame retardant capability. The excellent anti-flame capability of expandable graphite is contributed by the ability of absorbing enormous amount heat and forming swollen multicellular carbonaceous char. The intercalating silicate is more effectual in improving the flame retardancy than the direct addition of $Na_2SiO_3·9H_2O$.

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