Preparation of expandable graphite composite under the auxiliary intercalation of Zinc sulfate and its flame retardancy for ethylene/vinyl acetate copolymer

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Abstract : By investigation the influence of various factors, such as the amount of oxidant $KMnO_4$, inserting reagent H_2SO_4, the assistant intercalating agent $ZnSO_4 \cdot 7H_2O$, weight concentration of H_2SO_4, reaction temperature and time, on dilatability of graphite intercalation compound, the feasible mass ratio of reactants was detected. Expandable graphite composite (EG) with an initial expansion temperature of 190°C and expansion volume of 500 mL/g was prepared, and its flame retardancy for EVA was also investigated. The flame retarded EVA composites were characterized by means of limiting oxygen index (LOI), thermal gravimetric (TG) and differential thermal analysis (DTA). The results show that the influence of EG on EVA combustion property is significantly; addition of 30% EG can improve the LOI from 19.3% to 27.5%, while 20% EG together with 10% Ammonium polyphosphate (APP II) improve the LOI to 32.5%. Thermal stability and char layer denseness are the fundamental to achieve efficient flame retardance.
Key words: Expandable graphite, Zinc sulfate, chemical oxidation, Dilatability, Ethylene/vinyl acetate copolymer.

Introduction

Graphite is a crystal substance with graphene planes structure bonded by Van Der Waals force, thereby, many compounds can insert into the graphene planes and form graphite intercalating compound (GIC) called expandable graphite[1]. Expandable graphite possesses a series of functions such as catalyst in the esterification reaction[2]; porous expanded graphite adsorbent can be prepared through the instant expansion of GIC at a high temperature[3]. What's more, expandable graphite is a good intumescent type flame retardant for its good capability of halogen-free, non-dropping, low-smoke and low pollution potential[4, 5]. When touched with flame source, expandable graphite will instantly expand and turn into swollen multicellular worms, which can retard the transfer of heat, oxygen and improve thermal stability of the polymer. Meanwhile, CO_2, H_2O released in expansion of GIC, can dilute the concentration of the volatile flammable compositions, thereby enhancing char formation. Furthermore, expansion of GIC will consume an enormous amount of heat, which is helpful to decrease the combustion temperature and rate.

Due to its outstanding anti-flame capability, GIC has been used in the anti-flame of polystyrene foamed materials[6], Ethylene/vinyl acetate copolymer (EVA)[7] and particularly in polyurethane and polyurethane coatings[8, 9]. In these reports, the used GIC was commercial product, and the researches were mainly focused on its anti-flame property and synergistic effect with other retardants. Usual GIC was prepared with single intercalating reagent, and it often possessed lower dilatability and flame retardance[10]. Therefore, it is necessary to supplement some assistant intercalating agents, especially, a traditional flame retardant used as assistant intercalating agent, which can not only increase GIC dilatability, but can also improve its flame retarding property.

$ZnSO_4 \cdot 7H_2O$ is easily lost most of the crystal water under lower temperature, and lose all crystal water at 280°C. Then $Zn_3O(SO_4)_2$, and ZnO will produce before 680°C and 930°C, respectively[11]. As a result, an enormous amount of heat would be consumed and a large amount of vapor produced. Thereby, $ZnSO_4$ is an excellent flame retardant. $ZnSO_4$ together with ammonium polyphosphate (APP) and di-pentaerythritol, could obviously improve polypropylene limiting oxygen index (LOI), and the vertical combustion could reach a grade of V-0 due to the formation of char layer with a high denseness[12].

Herein, in this work, a coupled expandable graphite composite (EG) with high dilatability was prepared via intercalation reaction of material graphite using H_2SO_4 and $ZnSO_4 \cdot 7H_2O$ as intercalating and assistant intercalating agents. The dosages of $KMnO_4$, H_2SO_4, $ZnSO_4 \cdot 7H_2O$, H_2SO_4 weight concentration (wt), reaction temperature and time were optimized through single-factor experiment, and EG expansion properties were characterized by expandable volume (EV) and initial expansion temperature. X-ray diffraction spectroscopy (XRD) were used to characterize the structure of EG and confirm EG has been prepared successfully. Flame retardancy of EG for EVA and its synergistic effect with APP were all tested. LOI, thermal gravimetric (TG) and differential thermal analysis (DTA) were performed to investigate the thermal and the flame retarding performance. Electron microscope was applied to observe the residual char morphology of EVA composites.

Experimental Procedure

Materials

$ZnSO_4 \cdot 7H_2O$, H_2SO_4 (98, wt%), $KMnO_4$ are all analytical reagents. Material graphite (C, 5092) was provided by Action Carbon CO. LTD, Baoding, China. Ammonium polyphosphate APP (type II, n>1000) and EVA was purchased from Sichuan and Tianjin, China, respectively.

Method

Preparation of the EG flame retardant

In the intercalation reaction of material graphite, the reactants were weighted according to a definite mass ratio of C : H_2SO_4 (98%) : $KMnO_4$: $ZnSO_4 \cdot 7H_2O$, and the H_2SO_4 was diluted with deionized water before reaction. Then, the quantified reactants were mixed and stirred in the order of diluted H_2SO_4, $ZnSO_4 \cdot 7H_2O$, C and $KMnO_4$ in a 250mL beaker, under various reaction temperature and time. After reaction, the solid phase was washed with deionized water and dipped in water for 2.0 h until pH of the waste water reached to 6.0-7.0, then EG was obtained after filtration and drying at 60-70°C for about 5.0 h.

Preparation of flame retarded EVA samples

A certain amount of flame retardant was added into melting EVA at less than 130°C in Muller (Jiangsu, China), the mixtures were pressed at 125°C and 10MPa, and then chopped in slivers with a size of 120 mm ×6 mm×3 mm.

Characterization of the samples

X-ray powder diffraction (XRD) analysis for natural graphite and the prepared EG were performed with a Y-4Q X-ray diffractometer (Dandong, China) employing Ni-filtered Cu Kα $_{1, 2}$ radiation with 2θ ranging from 10° to 70°.

The incised slivers of flame retarded EVA were used to measure the LOI according to Standard of GB/T2406-

1993 with oxygen index instrument (Chengde, China). TG and DTG analysis were carried out by using a STA 449 C thermal gravimetric analyzer (Germany). A sample of about 10 mg for test was put on a porcelain crucible, and the heating rate, N_2 flux were 10K/min and 25 mL/min, respectively; and the DTA analysis condition was set as follows: N_2 flux was controlled as 25 mL/min, Al_2O_3 was used as reference compound, and a heating rate was 10K/min.

Results and discussion

Optimization of influence factors in the preparation of EG

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, $ZnSO_4 \cdot 7H_2O$, H_2SO_4 weight concentration, reaction temperature and time. According to the experiment results (shown in Fig. 1), the feasible conditions to prepare EG were finally detected as: mass ratio $C:KMnO_4:H_2SO_4(98\%): ZnSO_4 \cdot 7H_2O$ is 1.0:0.35:5.0:0.4, H_2SO_4 was diluted to 80 wt % before reaction, and reaction lasted 40 min at 30°C. Initiation expansion temperature and the maximum EV of the prepared EG are 190°C and 500 mL/g, respectively.

Preparation of EG_1 with no $ZnSO_4 \cdot 7H_2O$ intercalation

Compared with EG, EG1 was prepared under the mass ratio $C:KMnO_4:H_2SO_4(98\%)$ of 1.0:0.35:5.0, H_2SO_4 was diluted to 80 wt % before reaction, and reaction lasted 40 min at 30°C. EV of EG1 was detected as 370 mL/g. It is obvious that $ZnSO_4 \cdot 7H_2O$ affect dilatability of EG. Addition of 0.4 g/g of $ZnSO_4 \cdot 7H_2O$ in graphite intercalating reaction can cause an increase of 35% of EV.

XRD analysis of natural graphite and the EG

XRD analysis for natural graphite and EG were performed and shown in Fig. 2. Sharp diffraction peaks at 26.6° and 26.3° appear in natural graphite and EG, respectively. It is suggested that in the preparation of EG, the layered structure of the flake graphite is not changed by oxidation and intercalation, but the distance between the layers changes from 0.334 nm to 0.339 nm. Although the structure of the flake graphite is not changed in GIC broadly, the surface structure changed a little; which wakens the diffraction peak at 55.8°. This can be explained that 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 [13], and then intercalation reaction can be proceed extensively between graphite and intercalating agent.

Flammability properties of composites

The processing temperature of EVA is normally lower than 130°C, so the prepared EG can be used as flame retardant, and they are added into EVA according to the percentage listed in Table 1. As shown in Table 1, LOI of single EVA is only 19.3%, but the LOI values of EVA composites are all higher than that of pure EVA. Addition of 30% APP (II) or EG_1 or EG can improve LOI to 20.3%, 26.0% and 27.5%, respectively. Furthermore, addition of 20% EG together with 10% APP (II) exhibits a LOI of 30.5%, which is obviously higher than the LOI of 25.1%, calculated according to the single EG and APP (II) percent and LOI. Therefore, the results show synergistic efficiency between EG and APP (II)[14].

TG analysis of flame retarded EVA composites

Fig. 3 and Fig. 4 show the TG and DTG analysis results of 70EVA/10APP/20EG and 70EVA/30EG specimens, the related data are listed in Table 2. It is known that pure EVA is thermally stable under 300°C[15], however, it nearly thoroughly decomposes when the temperature is above 500°C. The temperature T_1 corresponding to a 1% weight loss and temperature T_5 corresponding to a 5% weight loss of EVA are 319°C and 446°C respectively. It is noticed that the addition of EG/APP can affect its weight loss property, the T_1 and T_5 of 70EVA/10APP/20EG and 70EVA/30EG specimens are 191°C, 323°C and 127°C, 195°C, respectively, which indicate that the addition of EG/APP caused the decrease of EVA thermal stability at lower temperature due to the expansion or decomposition of EG and APP. However, a higher thermal stability and residual char are observed at higher temperature due to the formation of "expanded graphite worm" residual char, which can slow down heat and mass transfer between gas and condensed phase. Furthermore, the 70EVA/10APP/20EG composite exhibits a

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higher thermal stability than the70EVA/30EG composite, even at a lower residual char mass than the latter. This suggests that the influence of APP/EG mixture on the formation of a thermally stable material is better than single EG. The increase of thermal stability can be explained that existence and decomposition of APP leads to a cohesive and dense charry structure, which can effectively limit transfer of heat and mass, and it is beneficial to improving flame retardancy[16].
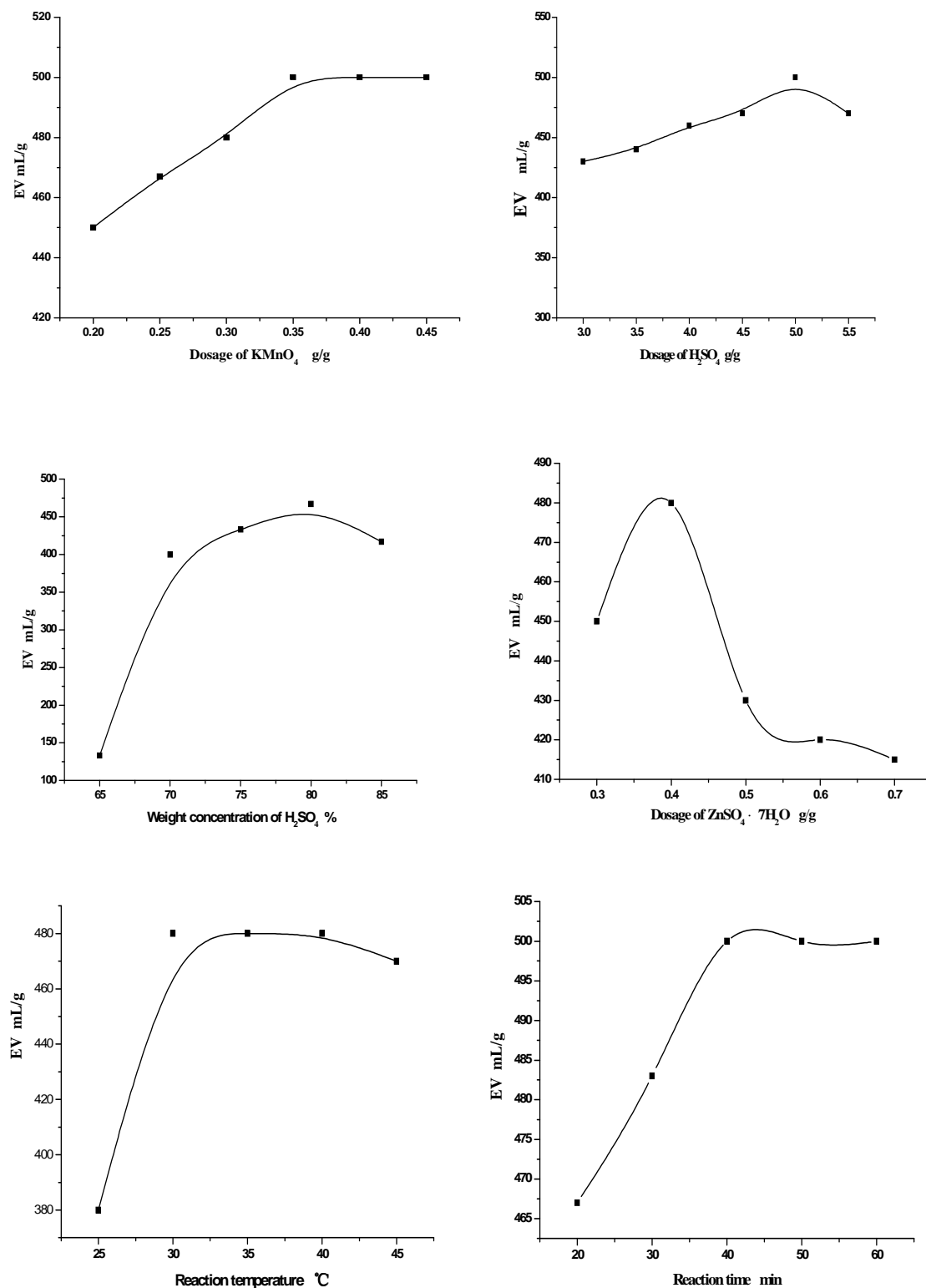

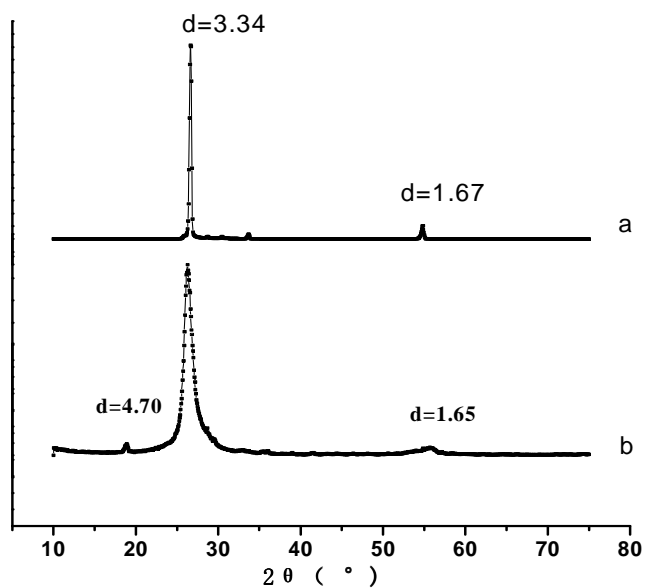
Fig. 1 Influence of experimental factors on EV of EG

Fig. 2 XRD of nature graphite and EG
(a) natural graphite   (b) EG

Table 1 LOI of the EVA flame retarding samples

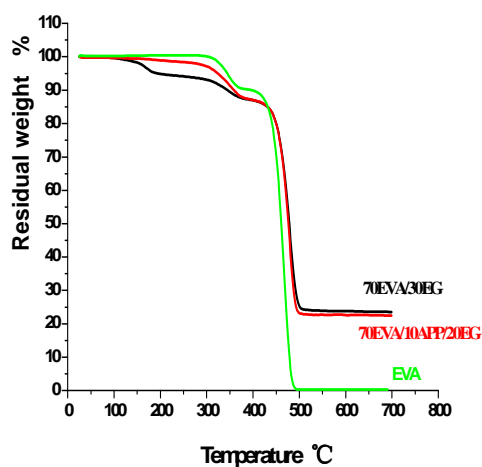| EVA/%	EG/%	EG$_1$/%	APP (II)/%	LOI/%
100	0	0	0	19.3
70	0	0	30	20.3
70	30	0	0	27.5
70	0	30	0	26.0
70	20	0	10	32.5

**Fig. 3 TG curve of EVA composites   Fig. 4 DTG curve of EVA composites**
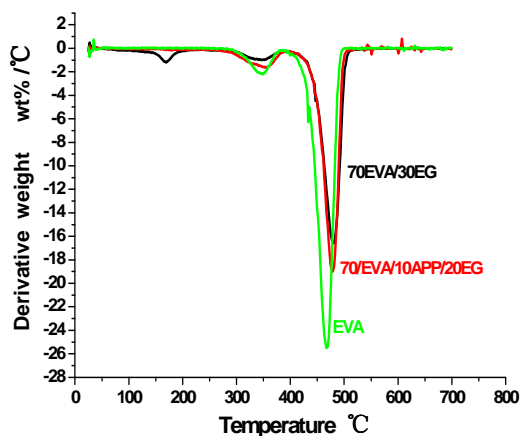
Table 2 Thermal data of 70EVA/10APP/20EG and 70EVA/30EG composites*

Specimens	T_1	T_5	T_{max}	Residual char at 700°C
	/°C	/°C	/°C	/%
EVA	319	344	446	0
70EVA/30EG	127	195	482	23.52
70EVA/10APP/20EG	191	323	481	22.46

*T_1: temperatures corresponding to a 1% weight loss;

T_5: temperatures corresponding to a 5% weight loss;

T_{max}: temperatures corresponding to a maximum weight loss rate
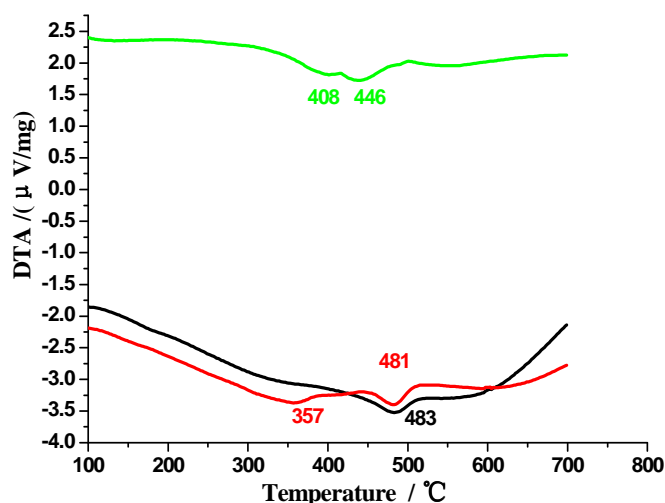
Fig. 5 The DTA curve of flame retarded EVA composites

Thermal property of EVA composites—DTA analysis

Heat will be consumed during melt, decomposition and expansion of EVA composites as shown in Fig. 5. It is noticed that there are differences in location of those specific endothermic peaks. In the DTA curve of EVA, peaks at 408°C and 446°C are corresponding to EVA decomposition and release of acetic acid at the first stage, and further decomposition of the unsaturated crosslinked backbone, respectively. For 70EVA/30EG composite, the addition of EG leads to a decrease of EVA decomposing temperature in the first step, but it improve to 483°C in the second stage. While, for 70EVA/10APP/20EG composite, the addition of EG and APP lead to a change of EVA decomposing temperature which decrease to 357°C in the first step, but improve to 481°C in the second stage. That is to say, the thermal stability of EVA is decreased by addition of APP/EG at first stage but increased at the second stage.

Microstructures of the char residue

It is well known that an effective protective char layer can improve flame retardancy. Fig. 6 shows the incision section microstructures of the residues of 70EVA/30EG and 70EVA/10APP/20EG composites after their LOI tests. Fig. 6 (a) shows that the residual char of 70EVA/30EG composite after combustion 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 (1)[17]. Finally, discontinuity and low mechanical strength of the residue make the EVA/EG system show a decrease in its thermal stability and flame retarding property. As for 70EVA/10APP/

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20EG composite, the residue incision section in Fig. 6 (b) 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. Precisely the continuous and compact residual make 70EVA/10APP/20EG composite hold higher LOI value and thermal stability than 70EVA/30EG composite.
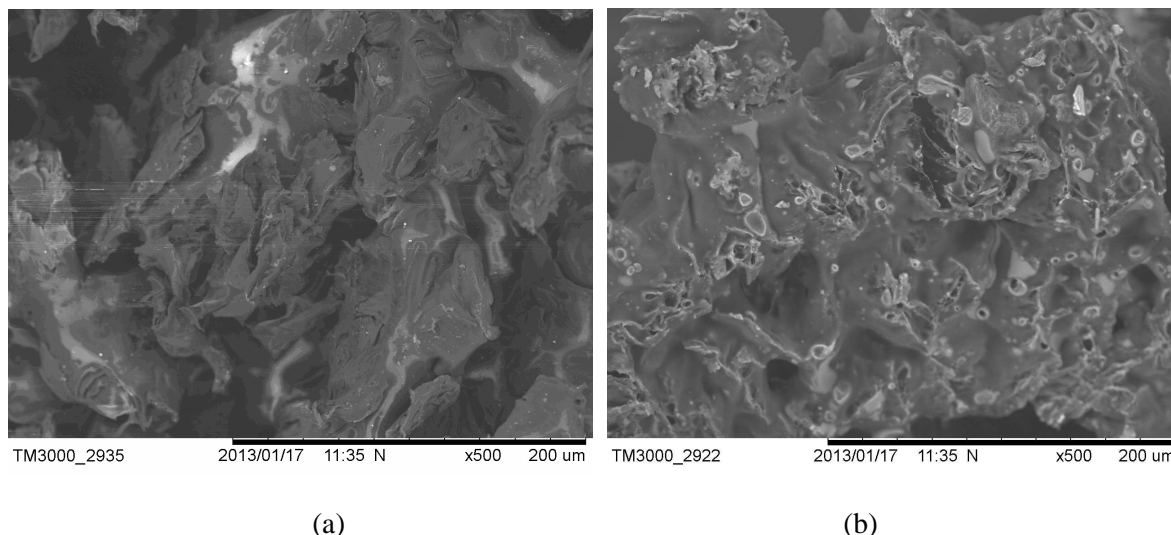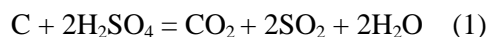
$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O \quad (1)$$

| TM3000_2935 | 2013/01/17 11:35 N | x500 200 um | TM3000_2922 | 2013/01/17 11:35 N | x500 200 um |

(a)   (b)

Fig. 6 SEM analysis of flame retarded EVA

(a) 70EVA/30EG (b) 70EVA/10APP/20EG

Conclusions

The combined intumescent flame retardant EG can be prepared under the condition of C : $KMnO_4$: H_2SO_4 (98 wt%): $ZnSO_4 \cdot 7H_2O$ = 1.0 : 0.35 : 5.0 : 0.4 (mass ratio), H_2SO_4 is dilute to 80 wt%, and reaction is maintained for 40 min at 30°C. $ZnSO_4 \cdot 7H_2O$ can improve EG dilatability and flame retardancy. The excellent anti-flame capability of EG is owing to its absorbing an enormous amount of heat and forming multicellular carbonaceous char. The coexistence of APP can improve the compactness of the multicellular char, which plays a more important role in retarding the transfer of heat, oxygen and improving thermal stability of the flame retarded EVA composite.

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