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Preparation and anti-flame capability of Expandable Graphite

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Abstract: Feasible conditions to get flame retardant expandable graphite (EG) with low initiation expansion temperature and high dilatability were obtained through orthogonal test and single factor experiment. EG with initiation expansion temperature of 148 ±2 °C and expansion volume of 550 mL/g can be prepared according to the mass ratio of C : $KMnO_4$: 98% H_2SO_4 : $Na_4P_2O_7$ = 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 40 °C. Addition of 30% of the prepared EG to Liner Low-Density Polyethylene (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 was completed to discuss the anti-flame mechanism.

Introduction

Expandable graphite EG is prepared when non-carbonaceous reactant inserted into the layers of graphite through chemical or electrochemical reaction [1]. When EG is heated, it will become the so-called expanded graphite with porous structure and high expanded volume. So EG is a good intumescent type flame retardant for its good capability of halogen-free [2], non-dropping, low-smoke and low pollution potential. Both initiation expansion temperature and expansion volume EV are two important characteristics of EG, which are affected by oxidant, intercalation reagent, ancillary intercalation reagent reaction time and reaction temperature. To provide an EG flame retardant for LLDPE, dosage of oxidant $KMnO_4$, intercalating reagent H_2SO_4, ancillary intercalation reagent $Na_4P_2O_7$ reaction time and reaction temperature are optimized in the intercalation reaction of graphite. The anti-flame properties of the prepared EG are determined.

Preparation of EG

First, the reactants are quantified according to a definite mass ratio of C : $KMnO_4$: 98% H_2SO_4 : $Na_4P_2O_7$, and H_2SO_4 need to dilute to the required mass concentration. Then, under a definite temperature controlled with water bath, the quantified natural graphite is mixed with H_2SO_4, $KMnO_4$ and $Na_4P_2O_7$ in a 250mL beaker, reaction lasts the required time. After reaction, the mixture is washed with de-ionized water and marinated 2.0 h until pH of waste-water reaches to 6.0 ~7.0, then filtrated and dried at 50~60 °C for about 6h, EG products are gained.

Results and discussion

Influence of $KMnO_4$, H_2SO_4 and its concentration, $Na_4P_2O_7$, reaction time and reaction temperature on EG characteristics of initiation expansion temperature and EV are detected as Fig.1 ~ Fig. 6. Feasible conditions to prepare EG are: mass ratio of C : $KMnO_4$: 98% H_2SO_4 : $Na_4P_2O_7$ = 1.0 : 0.4 : 5.0 : 0.6 (H_2SO_4 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.

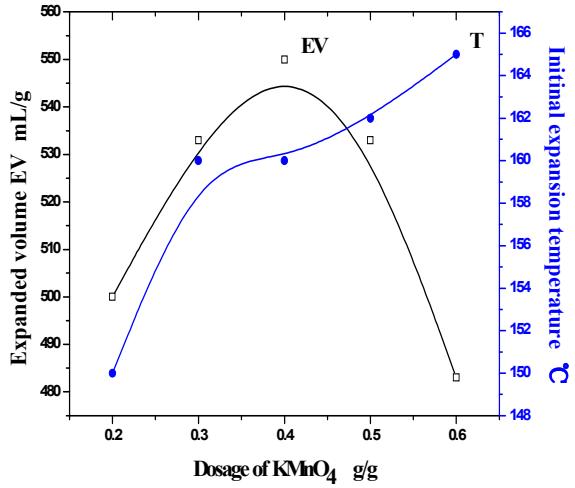

Fig. 1 Influence of $KMnO_4$ dosage on initiation expansion temperature and EV

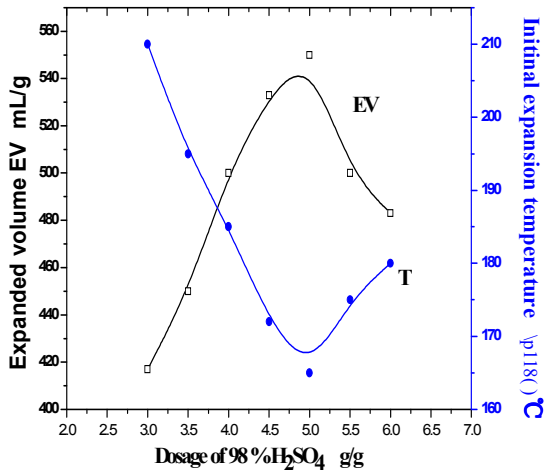

Fig. 2 Influence of H_2SO_4 dosage on initiation expansion temperature and EV

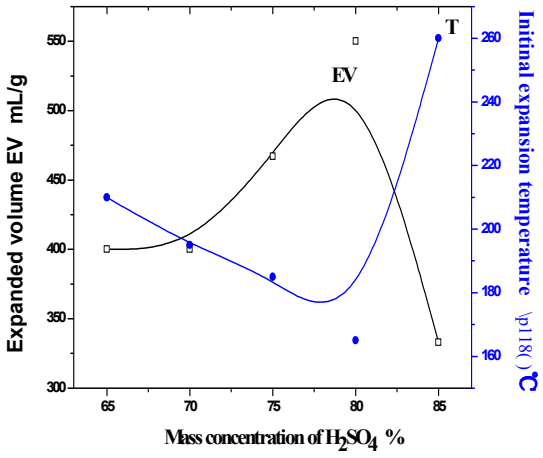

Fig. 3 Influence of H_2SO_4 mass concentration on initiation expansion temperature and EV

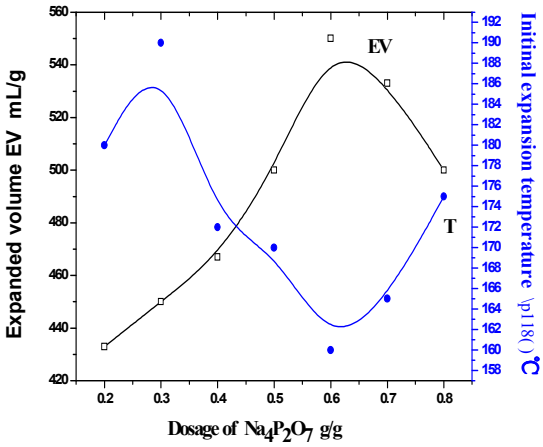

Fig. 4 Influence of $Na_4P_2O_7$ dosage on initiation expansion temperature and EV

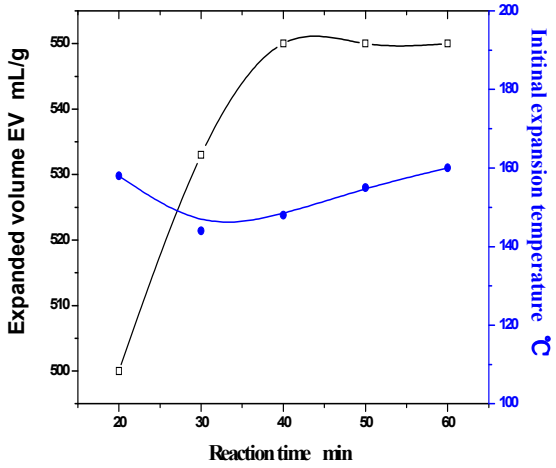

Fig. 5 Influence of reaction time on initiation expansion temperature and EV

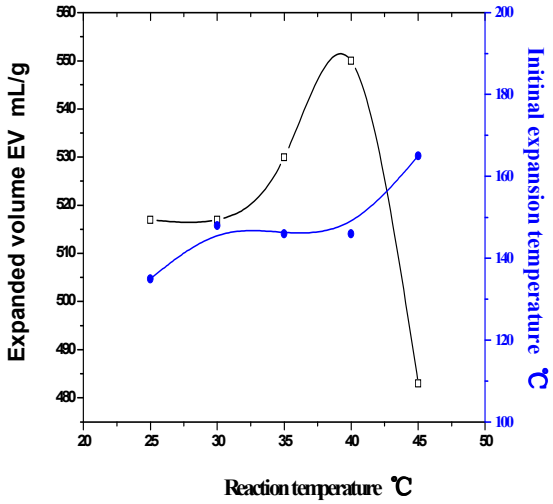

Fig. 6 Influence of reaction temperature on initiation expansion temperature and EV

The anti-flame capability of EG for LLDPE

According to the ratio listed in Table 1, EG, synergistic anti-flame reagent polyphosphate (APP II) are mixed with LLDPE. The LOI is detected and the results are listed in Table 1. The addition of 30% EG can improve LOI up to 29.4%. LOI 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 LOI to 31.2%, that 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 (Fig. 7), and the swollen multicellular char can limit heat and mass transfer, as well as oxygen diffusion.

Table 1 Results of LOI

LLDPE [%]	EG [%]	APP(II) [%]	LOI [%]
100	0	0	17.5
70	0	30	19.8
70	10	20	25.5
70	20	10	31.2
70	30	0	29.4

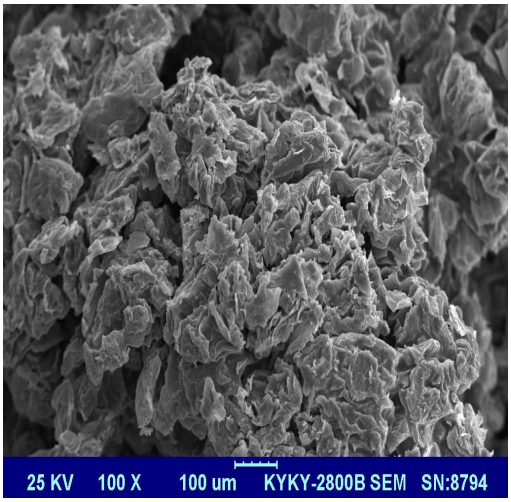

Fig. 7 SEM of 70%LLDPE/10%APP/20%EG after combustion

TG analysis

TG analysis results for samples of 70%LLDPE/10%APP(II)/20%EG and 70%LLDPE/20%EG are showed as Fig 8. 60% of loss of weight occurs among 450 ~ 520 °C. 70%LLDPE/10%APP(II)/20%EG sample give higher residual carbon of 25% than 70%LLDPE/30%EG of 19%, that testify the synergistic anti-flame of EG with APP (II).

DTA analysis

DTA analysis results for samples of 70%LLDPE/10%APP(II)/20%EG and 70%LLDPE/20%EG are showed as Fig. 9. 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/20%EG sample, 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.

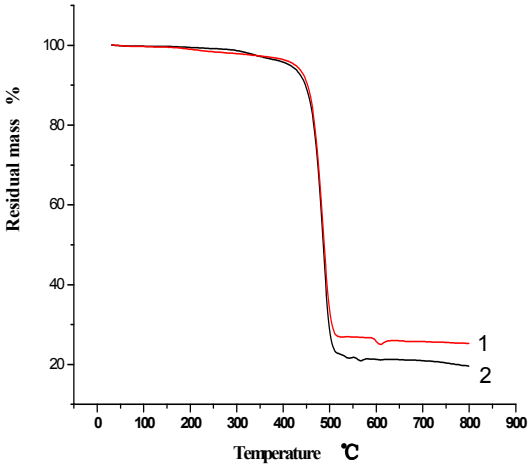

Fig. 8 TG of 70%LLDPE/10%APP/20%EG and 70%LLDPE/30%EG
1. LLDPE/APP/EG 2. LLDPE/ EG.

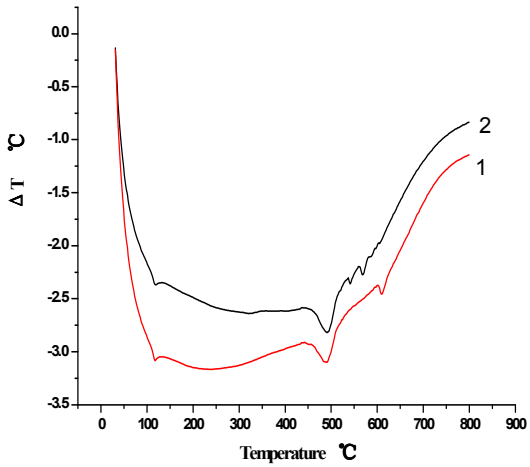

Fig. 9 DTA of 70%LLDPE/10%APP/20%EG and 70%LLDPE/30%EG
1. LLDPE/7 APP/EG 2. LLDPE/EG

Analysis of anti-flame mechanism

When EG exposes to flame, it gives a swollen multicellular char; In instant expansion, EG absorbs huge heat and releases CO_2; The synergistic anti-flame of EG and APP(II) can give more residual carbon and induce lower surface temperature.

References

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