

PREPARATION OF SULFUR-FREE EXPANDABLE GRAPHITE AND ITS FLAME RETARDANT PROPERTY OF HDPE COMPOSITES

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Abstract

This study employs phosphoric acid (H_3PO_4) as the intercalating agent, and potassium permanganate ($KMnO_4$) and nitric acid (HNO_3) as the oxidizing agent. The hydrothermal method was used to prepare a novel, sulfur-free EG, which is then added to high-density polyethylene (HDPE) to improve the flammability and the dripping property of the composites. Subsequently, the success of the EG preparation was examined using a powder X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results from the thermogravimetric analyzer indicated that the EG composite possessed superior thermal stability. Furthermore, at 30 wt%, the limiting oxygen index value reached 30, and the flammability standard UL94 reached the V0 level.

1. Introduction

High-density polyethylene (HDPE) is a widely-used polymer substrate that is a common commercially-sold thermoplastic material. Increasingly used worldwide [1-6], HDPE is frequently employed in packaging film, healthcare, construction, vehicles, agriculture, instrument, and electronics. Polyethylene (PE) is a type of semi-crystalline polymer and a non-polar, thermoplastic resin that is formed from copolymerization of ethylene polymer. It is extensively used in industries and composite materials. Thermoplastic PE is commonly adopted because it features characteristics such as being lightweight and having low thermal conductivity, high toughness, great impact strength, resistance to abrasion and corrosion, excellent mechanical properties; in addition, it is easy to process (i.e., simple processing methods can be applied on PE to manufacture a variety of products) [7-8]. Despite these advantages, one critical shortcoming of PE is its flammability; this poses many restrictions on various uses in products or industries. Consequently the adoption of a halogen flame retardant with PE is required. The retardant is extremely effective — a small quantity achieves superior flame-retardant effect. However, halogen flame retardant was recently found to produce toxic gases during pyrolysis combustion at high temperatures. These toxic gases are harmful to the environment and to health; thus, to protect these, the European Union (EU) adopted the Restriction of Hazardous Substances Directive (RoHS) and the Waste Electrical and Electronic Equipment Directive (WEEE) regulations to prohibit the use of hazardous substances (including halogen flame retardant) [9-12]. Subsequently, elements such as

aluminum, boron, sulfur, nitrogen, phosphorous, and silicon are used in flame retardants as halogen replacements. In this study, to comply with regulations, expandable graphite (EG) was prepared from halogen-free flame retardant.

In previous studies, sulfuric acid (H_2SO_4) was typically used as an intercalating agent for the preparation of EG; however, the use of this intercalating agent is restricted in certain industries. In addition, combustion of H_2SO_4 generates sulfur dioxide, which creates pollution in the environment and causes corrosion when used in machines [13-15]. Hence, this study employed phosphoric acid (H_3PO_4) instead of H_2SO_4 as the intercalating agent to develop sulfur-free EG because H_3PO_4 can significantly retard flame; therefore, adding this compound enhances the flame retardation of the EG.

In response to international trends, a green, halogen-free, sulfur-free, EG was prepared from an expandable flame retardant that comprises three constituent elements: acid, carbon, and gas. Furthermore, various methods were used to prepare EG by adding an equal concentration of polyethylene. Finally, a powder X-ray diffractometer (XRD), an UL94 vertical burn test instrument, the limiting oxygen index (LOI), and scanning electron microscopy (SEM) were used to examine, analyze, and investigate the structure and flame-retardant properties of the HPDE/sulfur-free EG composite.

2. Experimental

2.1 Materials

Natural flake graphite (NG) was supplied by Inter. Carbide Tech. Co., Taiwan. Flake graphite of carbon content with the purity is 99 wt. %, and an average flake size is 193 μm . Nitric acid (70.0 wt. %) and concentrated sulfuric acid (95.0 wt. %) were purchased from Union Chemical Works Ltd., Taiwan. Phosphoric acid (85.0 wt. %) and potassium permanganate ($KMnO_4$) were supplied by TEDIA, Co Ltd, Japan. The high density polyethylene (HDPE) with M.W. 135,700 was supplied as pellets by Chi-Mei Plastics Company.

2.2 Preparation of expandable graphite

At first, NG with 5 g was immersed into 15 ml mixed acid solution ($H_3PO_4/HNO_3=3/1$, v/v) with mechanical stirring for 5 min at room temperature, and then 1g $KMnO_4$ was put into the mixture with mechanical stirring for 80 min. Then they were placed into a teflon-lined autoclave. The autoclave was sealed and quickly heated to the desired temperature (typically at 80°C within 30 min), where it was maintained for 2 hour before it was cooled to room temperature naturally. After heating, the graphite mixture was washed to neutrality with water, dehydrated, put in the air for 24 hr; and placed in the oven for 1 hour at 60 °C, the EG was prepared, and then expanded at 1000 °C for 30 seconds to obtain the expanded graphite. The expanded volume was determined by expanding 1.0 g of the EG and its volume was measured by graduated cylinder. Meanwhile, we use ultrasound irradiation (600 W) method and normal hydrothermal method to compare with the H_3PO_4 -hydrothermal method to prepare EG. The addition of the acid mixture into NG is the same process as hydrothermal method. Then they were placed in the ultrasound irradiation bath with 600 W at room temperature for 1 hour. The graphite mixture was washed to neutrality with water, dehydrated, put in the air for 24 hr; and placed in the oven for 1 hour at 60 °C, the EG from ultrasound irradiation method was prepared. EG prepared from the hydrothermal method was called as HEG and that prepared from ultrasound irradiation process was defined as UEG. EG fabricated from the H_3PO_4 -

hydrothermal method was named as PEG. The convectional liquid phase synthesis means natural flake graphite was dipped into mixed acids without ultrasound irradiation and heat treatment, which was defined as CEG.

2.3 Preparation of HDPE /EG composites

All samples were mixed as 50 g batches of HDPE with the desired amounts of EG for 8 min at 150°C using Brabender mixer. The resulting mixtures were then compression molded at 130 °C into sheets (3 mm thickness) under a pressure of 9 MPa for 10 min. The sheets were cut into suitable size specimens for fire testing.

2.4 Measurements

X-ray diffraction (XRD) pattern was obtained on a D8-Advance Bruker X-Ray operating at 40 kV, 30 mA, using Ni-filtered Cu Ka radiation.

The morphology of the fractured surface of the NG and composites was examined using a scanning electron microscope (SEM) (JEOL JSM 840A, Japan).

Thermal degradation of composite was investigated by a thermogravimetric analyzer (TGA) (Perkin Elmer TGA 7) from room temperature to 800°C with various heating rates under nitrogen atmosphere. The measurements were conducted using 6-10mg samples. Weight-loss/temperature curves were recorded.

The limiting oxygen index (LOI) is defined as the minimum fraction of O₂ in a mixture of O₂ and N₂ that will just support flaming combustion. The LOI test was conducted according to the ASTM D 2836 Oxygen Index Method, using a test specimen bar that was 7-15 cm long, 6.5 ± 0.5 mm wide and 3.0 ± 0.5 mm thick. The sample bars were suspended vertically and ignited by a Bunsen burner. The flame was removed and the timer was started. The concentration of oxygen was increased if the flame on the specimen was extinguished before it had burned for 3 min or it had burned away 5 cm of the bar. The oxygen content was adjusted until the limiting concentration was determined.

The vertical burning test was done inside a fume hood. Samples were held vertically with tongs at one end and burned from the free end. Samples were exposed to ignition source for 10 s then they were allowed to burn above a cotton wool until both sample and cotton wool extinguished. Observable parameters were recorded to assess fire retardancy. The UL 94 test classifies the materials as V-0, V-1 and V-2 according to the time period needed before self-extinction and the occurrence of flaming dripping after removing the ignition source. V-0 is the most ambitious and desired classification.

3. Results and Discussion

3.1. The Effects of Different Preparation Methods on the Expansion Volume

Fig. 1 presents an image of differently-processed graphite after thermal shock at 1000 oC. PEG refers to the EG that was prepared using H₃PO₄ as the intercalating agent; CEG represents the EG that was prepared through conventional liquid phase synthesis; UEG denotes the EG that was prepared using ultrasonication; and HEG was the EG that was formed through the hydrothermal method. According to the image, the expansion volume of PEGD (180 mL/g) is larger than that of NG (3 mL/g), CEGD (40 mL/g), UEGD (50 mL/g), and HEGD (78 mL/g) primarily because the distance between the natural flake graphite (NG) layers increased after effective oxidation with potassium permanganate (KMnO₄). Following

oxidation with the second nitric acid (HNO₃) oxidizing agent, more intercalating agent could be added, which could therefore react effectively during the hydrothermal process at high temperature. Thus, the use of H₃PO₄ with the hydrothermal method (hereafter known as the H₃PO₄-hydrothermal method) is an effective approach for preparing EG.

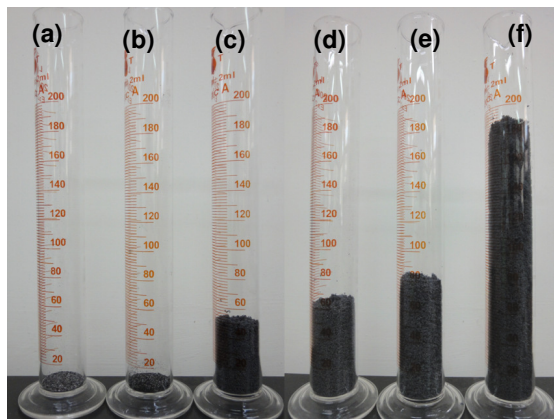


Figure 1 Expansion behavior of EG (a) NG (3ml/g) (b) PEG (3ml/g) (c) CEGD (40ml/g) (d) UEGD (50ml/g) (e) HEGD (78ml/g) (f) P-EGD (180ml/g).

3.2 XRD

In this study, halogen-free, sulfur-free EG was prepared. To determine the distance between the NG layers and the EG (prepared after the intercalation process), the XRD technique was employed as the examination tool. The XRD patterns for the EG (before and after expansion) are presented in Fig. 2. A stronger intensity indicates that the graphite structure is increasingly intact. Based on Fig. 2(a), NG has the most perfect crystalline structure, and two sharp absorption peaks that are characteristic of graphite were identified at $2\Theta=26.50^\circ$ and $2\Theta=25.70^\circ$. At $2\Theta=26.50^\circ$, the absorption peak for NG is characteristically narrow, because NG possess layer-like structures and the van der Waals force is present between the layers. Consequently, the structure of NG is regularly arranged and has a high degree of crystallization, therefore producing extremely sharp (or narrow) absorption peaks. Two distinct peaks at $2\Theta=26.07^\circ$ and $2\Theta=28.07^\circ$ were observed for UEG (Fig. 2c), because numerous high peaks appeared at $2\Theta=28.07^\circ$. This phenomenon indicates that layered structures are formed as a result of thermal destruction, explaining the presence of two distinct peaks [16]. Fig. 2(d) shows the XRD results for HEG. The displacement angle shifted distinctly because NG became EG through high-pressure autoclaving, and the heat and pressure used in the hydrothermal method do not change the layered structure of NG. Furthermore, the thermal cycle during high-pressure autoclaving possess a superior oxidation capability, which enables more intercalating agent to enter into the NG layers. Consequently, graphite with better expandability was formed. In Fig. 2(e), the H₃PO₄-hydrothermal method was adopted to prepare EG. The results showed that the use of KMnO₄ effectively broadened the distance between the graphite layers, thereby enabling more H₃PO₄ to intercalate between the layers. In addition, the displacement angle for PEG presented the largest transition, shifting from $2\Theta=26.50^\circ$ to the left $2\Theta=25.44^\circ$. This indicates that the graphite layers contained the largest amount of H₃PO₄ intercalating agent, further implying that the H₃PO₄-hydrothermal method can produce EG with outstanding expandability. After the EG undergoes thermal expansion, the PEGD (Fig. 2f) expands at high temperature and

subsequently releases water. The displacement angle increased ($2\Theta=26.63^\circ$), which suggests that the distance between the layers decreased.

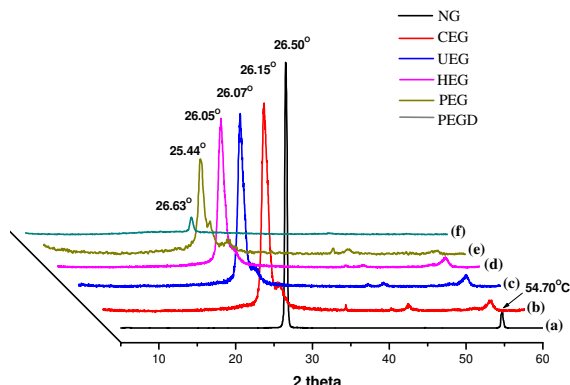


Figure 2 XRD patterns of (a) NG (b) CEG (c) UEG (d) HEG (e) PEG (f) PEGD.

3.3 Morphology of EG

The SEM photographs of the NG processed after H_3PO_4 intercalation are shown in Fig. 3. The SEM technique allows researchers to microscopically observe whether intercalation with NG succeeded and to determine the differences in morphology between NG and the EG. First, in Fig. 3(a), NG is characterized by flaky structures that are formed as a result of layers stacking closely on top of each other. Following oxidation with a strong oxidizing agent and after processing using the hydrothermal method (which facilitated the acidic intercalation reaction), the morphology of the resultant NG demonstrated an irregular arrangement. This is because H_3PO_4 and HNO_3 intercalated between the NG layers at a ratio of 3:1, thus damaging and loosening (i.e., becoming less cohesive) the layered structures.

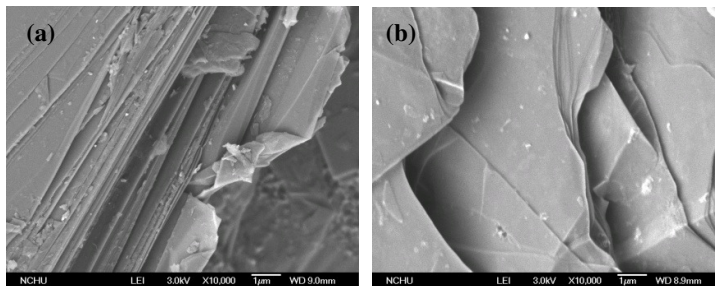


Figure 3 SEM micrographs of (a) flake graphite ($\times 10,000$) (b) EG ($\times 10,000$).

3.4 Thermogravimetric Analysis

In this study, the TGA technique was adopted to analyze the thermal property of graphite by using the char yield to examine the thermal stability of the graphite composite. The TGA curves are shown in Fig. 4. The char yield of pure HDPE at $800^\circ C$ approximates zero, which indicates poor thermal stability (Fig. 4). The HDPE/NG 40 wt% composite has the lowest char yield of 10.95 wt%, because NG does not contain intercalating agent. Thus, when NG is heated, it cannot expand, thereby forming a barrier that causes the polymer

substrate (i.e., HDPE) to decompose completely. After the addition of the EG that was prepared using different methods, the char yield increased noticeably. The PEG composite has the highest char yield of 36.5 wt%. When intercalating agent was added with the graphite, decomposition occurred at 200 °C. However, this phenomenon was not observed in NG because after intercalation, the EG releases sulfate ions and expands to protect the substrate. Consequently, when EG composites that were prepared using different methods are added to the polymer substrate, the decomposition temperature decreased slightly.

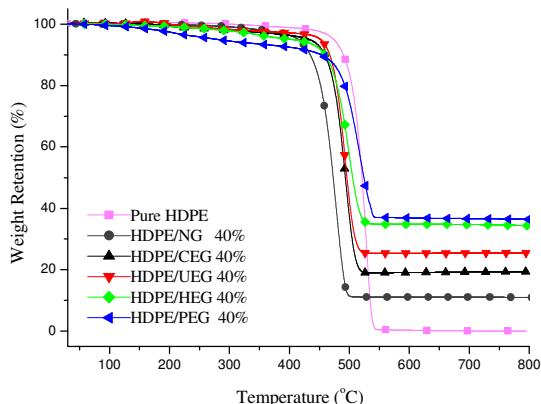


Figure 4 TGA of HDPE composites with different preparation methods.

3.5 Flame retardant property of the composites

Different preparation methods and flame retardant added in different volumes to the HDPE were used to investigate the flame-retardant property of graphite. The limiting oxygen index (LOI) is the most commonly-used indicator for testing the flame-retardant property to determine whether the anti-dripping effect or a certain level of flame retardation is achieved. Currently, industries are using the UL94 standards as a basis for examining the flame-retardant property of materials. According to Table 1, after the addition of 40 wt% NG to HDPE, the LOI value was only 24, meaning that NG features a self-extinguishing characteristic. However, the UL94 test failed because NG (unlike EG) cannot expand, and therefore it cannot form a barrier layer to protect the internal substrate. Conversely, the LOI values increased as the concentrations of CEG, UEG, and HEG added to HDPE increased, and the LOI value exceeded 26 at 30%. Thus, the flame-retardant effect was achieved, but almost all the UL94 tests failed. When 20 wt% of PEG was added, the LOI was 26 (flammability) and the UL94 test obtained a V1 anti-dripping level. Further increasing the concentration to 30 wt% caused the LOI to reach 30 (flammability) and the UL94 test to achieve a V0 level. In summary, these results confirmed that the EG of this experiment, prepared with H₃PO₄ intercalating agent, can effectively acquire flame-retardant properties.

Table 1 The LOI of flame retarded HDPE composites.

	NG		CEG		UEG		HEG		PEG	
Content	LOI	UL-94	LOI	UL-94	LOI	UL-94	LOI	UL-94	LOI	UL-94
		rating		rating		rating		rating		rating

10%	19	fail	19	fail	19	fail	22	fail	23	fail
20%	21	fail	22	fail	22	fail	24	fail	26	V-1
30%	24	fail	26	fail	27	fail	27	fail	30	V-0
40%	24	fail	27	fail	29	fail	31	V-1	34	V-0

4. Conclusions

This study successfully prepared EG by using H₃PO₄ (instead of H₂O₄) as the intercalating agent through hydrothermal process. Comparing CEG, UEG, HEG, and PEG, the expansion effect of the EG produced from employing the H₃PO₄ intercalating agent was superior to that prepared using other acidic mixtures at the same concentration. Furthermore, H₃PO₄ was able to effectively increase the size of the expansion. The success of EG preparation was verified using XRD and SEM. The results of this study indicated that the improvement of thermal stability was attained and that the thermal decomposition rate was reduced and caused the char yield to increase. The UL94 test and the LOI indicator showed that the flame-retardant and anti-dripping effects were efficiently enhanced; therefore, the HDPE/PEG composite possessed an outstanding flame-retardant capability.

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