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Preparation, Characterization and Flame Retardancy of Expandable Graphite Modified by Ferric Hydroxide. Part I -Preparation and Characterization

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Abstract: A type of expendable graphite (EG_{Fe}) modified by ferric hydroxide was stepwise prepared through chemical oxidation and hydrolysis precipitation reaction. Its dilatability, crystal structure, main functional groups were all characterized. The synthesizing method of the EG_{Fe} with excellent flame retardancy for linear low density polyethylene (LLDPE) was optimized through $L_9(3^4)$ orthogonal experiment. Especially, the mass ratio of FeCl₃ to normal expandable graphite (EG) prepared in advance with chemical oxidation method was 0.1:1, dosage of NH₃·H₂O with a wt% of 25% was controlled as 0.4 mL, the reaction lasted 2.5 h at room temperature, and the final drying temperature was 100°C. Characterizing results testified the EG_{Fe} kept a layer structure just like natural graphite, and the hydrolysis product of FeCl₃ was Fe(OH)₃, and it mainly covered on the outside surface of the EG. EG_{Fe} possessed a better dilatability and flame retardancy for LLDPE than the EG.

Keywords: Modified expandable graphite; Ferric trichloride; Oxidation reaction; Hydrolysis precipitation; Dilatability; Crystal structure.

1. Introduction

Graphite is a crystal compound with graphene planes structure bonded by Van Der Waals force with a small value of 16.7 kJ/mol. Therefore, many compounds can intercalate graphene layers through oxidation and intercalation reaction, and then the graphite intercalation compounds (GICs) called expandable graphite (EG) can be prepared [1, 2]. EG has showed catalysis for the esterification between organic acid and alcohol [3], and its high temperature expansion product named expanded graphite is a kind of adsorbent with well adsorbtion capability for floating oil and other pollutants [4, 5]. Furthermore, EG is an intumescent type flame retardant (FR), a char-forming agent, a blowing agent and smoke suppressant. Due to its outstanding anti-flame capability, expandable graphite has been widely used as FR for polymers such as polyolefin blends [6], polylactide [7], polyurethane [8].

In the preparation EG, H_2SO_4 is a commonly used intercalator and H^+ donor due to its low-price, strong oxidizability and well dilatability of the obtained product [9]. However, the use of it normally lead to high sulfur content in EG and corrosion for storage devices caused by lixiviating vitriol. Besides, more SO_2 gas will release in its combustion reaction. Therefore, the intercalation reaction requires improvement, or the obtained normal EG needs modification. Firstly, the wide intercalation possibilities permit graphite to possess definite properties [10], some assistant intercalators such as nitric acid, oxalic acid, acetic anhydrate can replace a part of H_2SO_4 [11, 12]. EG intercalated by H_2SO_4 /silicate indicated an expandable volume (EV) of 517 mL/g and limited oxygen index (LOI) value of 28.7% for ethylene vinyl acetate [13]. It was higher than that of the single H_2SO_4 intercalated EG with an EV of 433 mL/g and LOI value of 24.4% respectively. The EG intercalated by H_2SO_4 and H_3BO_3 with direct method presented excellent dilatability and LOI than the compared independent H_2SO_4 GIC [14]. EG can also get excellent property through its outside surface modification by chemical bonding or sol-gel hydrolysis precipition methods. The titania nanocrystals in EG could be prepared using organically modified silicate as a binder [15]. The EG prepared using chemical bonding method with silane coupling agent and boric acid presented improved flame retardancy for rigid polyurethane foam [16]. An anatase TiO₂/EG with high expansion volume was prepared through sol-gel process with titania gel introduced to EG surface [17].

As one of transition metal oxides, Fe_2O_3 can be used as FR for its smoke suppression [18]. It can also obviously impact on the thermal decomposition process of APP through accelerating the release of NH₃ and H₂O in the earlier period and increasing the high temperature residue in the later period for the formation of metallic phosphate. Basing on the reasons of (1) the independent flame retardation of EG, APP and Fe₂O₃, (2) the improvement of Fe₂O₃ for EG and APP flame retardancy and (3) the synergistic effect between APP and EG [19], the purpose of this research was to prepare a ferric hydroxide modified EG (written as EG_{Fe}) through hydrolysis precipitation $Fe(OH)_3$ on EG surface. A preparation method of the EG_{Fe} was found with natural graphite (C), KMnO₄, H₂SO₄ and ferric trichloride (FeCl₃, the precursor of Fe₂O₃, obtained through hydrolysis precipitation reaction and heating decomposition of Fe(OH)₃) as materials. Scanning electron microscope (SEM), X-ray diffraction spectroscopy (XRD) and Fourier transform infrared spectroscopy (FTIR) were employed to characterize morphology, structure and main functional groups of the prepared EG and EG_{Fe}. The flame retardant performance was characterized in the LOI and vertical combustion tests of linear low density polyethylene (LLDPE). As far as we are aware, little study is reported about preparation of EG_{Fe} by chemical oxidation and hydrolysis precipitation method.

2. Experimental

2.1. Materials and Sample Preparation

Natural flake graphite (average particle size of 0.30 mm, carbon content of 96 wt%) was provided by Xite Carbon CO. LTD, Qingdao, China. LLDPE (920NT(EGF-34), melt index 1.0 g/10 min) was purchased from Sinopec Sabic Tianjin Petrochemical. FeCl₃·6H₂O, KMnO₄, NH₃·H₂O (25 wt%) and H₂SO₄ (98 wt%) were all analytical agents and used as received.

2.2. Preparation of the EG

The EG with H_2SO_4 as intercalator was prepared with chemical oxidation method [20]. Firstly, the reactants were weighted according to the mass ratio graphite (C): H_2SO_4 (75 wt %):KMnO₄ of 1.0:6.67:0.15. Before reaction, the concentrated H_2SO_4 with a concentration of 98 wt% was diluted to 75 wt% with deionized water and cooled to room temperature before use. Then, these reactants were mixed in the order of the diluted H_2SO_4 , C and KMnO₄ in beaker, and stirred, reacted for 30 min at 30°C. 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, and the EG was prepared with an initial expansion temperature (temperature when the volume of GIC expanded to 1.5 times of its initial value) of 200°C and the EV at 800°C of 530 mL/g.

2.3. Preparation of the EG_{Fe}

Reactants with definite mass were added into beaker in the order of deionized water, the EG, NH_3 · H_2O and $FeCl_3$ · $6H_2O$. The hydrolysis precipitation reaction carried out with stir at room temperature. When the reaction finished, the solids were filtrated and dried at a certain temperature until it kept a constant mass, and then EG_{Fe} obtained. The influence of NH_3 · H_2O and $FeCl_3$ · $6H_2O$ dosages, hydrolysis precipitation reaction time and drying temperature on the EG_{Fe} dilatability and flame retardancy for LLDPE labeled as LOI were optimized through $L_9(3^4)$ orthogonal experiments. The values of the impact factors were listed in Table 1.

Factors	FeCl ₃ / g	NH ₃ ·H ₂ O / mL	Reaction time / h	Drying temperature / °C		
Value I	0.07	0.2	1.5	80		
Value II	0.1	0.3	2.0	90		
Value III	0.13	0.4	2.5	100		

Table-1. The parameter values in $L_9(3^4)$ orthogonal experiments ^a

^a The dosages of NH₃·H₂O and FeCl₃·6H₂O was based on 1.0 g EG.

2.4. Preparation of the Flame Retarded LLDPE Composites

The prepared EG_{Fe} were added into melted LLDPE at 120°C in Muller at a 30 wt% dosage, then the mixtures were pressed at 125°C and 10 MPa, and chopped into slivers with two different sizes of $120.0 \times 6.0 \times 3.0 \text{ mm}^3$ and $127.0 \times 13.0 \times 3.0 \text{ mm}^3$ for the evaluation of LOI and vertical combustion level.

2.5. Characterization of the Samples

A TM3000 SEM (Japan) was applied to observe structure and morphology of the EG and EG_{Fe}. The XRD pattern was obtained on a Y-4Q X-ray diffractometer operating at 40 kV, 30 mA, employing Ni-filtered Cu K_a radiation with 20 ranging from 20° to 70°. The FTIR spectra of the prepared GICs were recorded between 4000-400 cm⁻¹ using a FTIR spectrometer (Nicolet 380, America Thermo Electron Corporation) with a resolution of 2 cm⁻¹. Samples were prepared by mixture of the sample powder and KBr at a mass ratio of about 1:100.

The incised slivers with a size of $120.0 \times 6.0 \times 3.0 \text{ mm}^3$ were used to measure LOI according to Standard of GB/T2406-1993 with oxygen index instrument (Chengde, China). The vertical combustion test was performed using a HC-3 vertical burning instrument (Tientsin, China) on sheets with a size of $127.0 \times 13.0 \times 3.0 \text{ mm}^3$ as per the standard UL 94-1996.

3. Results and Discussion

3.1. Optimization of Influence Factor in the Preparation of Eg_{fe}

Influence of various factors on dilatability of the EG_{Fe} and LOI of flame retarded LLDPE were optimized through $L_9(3^4)$ orthogonal experiments, and the results were listed in Table 2 and Table 3 respectively.

Number		FeCl ₃ / g	NH ₃ ·H ₂ O / mL	Reaction time / h	Drying temperature / °C	EV / mL/g
1		0.07	0.2	1.5	80	487
2		0.07	0.3	2.0	90	494
3		0.07	0.4	2.5	100	537
4		0.1	0.2	2.0	100	567
5		0.1	0.3	2.5	80	574
6		0.1	0.4	1.5	90	540
7		0.13	0.2	2.5	90	512
8		0.13	0.3	1.5	100	553
9		0.13	0.4	2.0	80	523
Sum of EV	Sum _I	1518	1566	1580	1584	
	Sum _{II}	1681	1621	1584	1546	I+II+III=4787
	Sum _{III}	1588	1600	1623	1657	
R		163	55	43	111	

Table-2. L ₉ (3 ⁴) experiment results of 1	EV₿	b
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^b 1.0g of the EG was used in the experiments, and EV was detected at 800°C.

Table-3. L ₉ (3 ⁴)	experiment	results of	of LOI	with	$\mathrm{EG}_{\mathrm{Fe}}$	as	FF
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Numbe	r	FeCl ₃ / g	NH ₃ ·H ₂ O / mL	Reaction time / h	Drying temperature / °C	LOI / %
1		0.07	0.2	1.5	80	27.0
2		0.07	0.3	2.0	90	27.3
3		0.07	0.4	2.5	100	27.7
4		0.1	0.2	2.0	100	28.0
5		0.1	0.3	2.5	80	28.0
6		0.1	0.4	1.5	90	28.1
7		0.13	0.2	2.5	90	28.2
8		0.13	0.3	1.5	100	27.9
9		0.13	0.4	2.0	80	28.1
Sum of LOI	Sum _I	82	83.2	83	83.1	
	Sum _{II}	84.1	83.2	83.4	83.6	1+2+3=250.3
	Sum _{III}	84.2	83.9	83.9	83.6	
R		2.2	0.7	0.9	0.5	

3.2. Influence of FeCl₃ dosage on EV and LOI

According to the range (R) results of EV and LOI listed in Table 2 and Table 3, it can be seen that the influence of FeCl₃ dosage on EV and LOI is the most important. The maximum value of EV and LOI can almost be obtained when the dosage of FeCl₃ is controlled as 0.1 g/g. Although the 0.13 g/g does not correspond to the EV maximum value, its LOI is the best, which indicates that flame retardancy of EG_{Fe} for LLDPE is not only based on its EV, but also is connected with the hydrolysis precipitation product of FeCl₃.

3.3. Influence of NH₃·H₂O dosage on EV and LOI

The influence of NH_3 · H_2O dosage on EV and LOI is different. The maximum EV is obtained when it's controlled as 0.3 mL/g. While, LOI value slowly increases with the increasing NH_3 · H_2O dosage in the range of 0.2-0.4 mL/g. Because the flame retardancy of EG_{Fe} bases on both its EV and the hydrolysis precipitation product of FeCl₃, and NH_3 · H_2O is a weak electrolyte at the same time, a superfluous NH_3 · H_2O of 0.4 mL/g can be used in the hydrolysis reaction.

3.4. Influence of Reaction Time and Drying Temperature on EV and LOI

As showed in Table 2 and Table 3, values of EV and LOI all increase with the increasing reaction time and drying temperature. Because the influence of them is less important, 2.5 h and 100°C can be used in the large-scale preparation of EG_{Fe} .

Base on the orthogonal experiment results, the feasible synthesis method of EG_{Fe} can be described as: mass ratio of FeCl₃ to EG is 0.1:1, dosage of NH₃·H₂O with a wt% of 25% is controlled as 0.4 mL, hydrolysis precipitation

reaction lasts 2.5 h at room temperature, and the EG_{Fe} drying temperature is 100°C. The obtained EG_{Fe} shows an initial expansion temperature of 168°C and EV of 554 mL/g. The hydrolysis precipitation reaction between EG and FeCl₃ can improve the EV of EG_{Fe} .

3.5. Characteristics of the prepared graphite GICs **3.5.1.** FTIR Analysis

Figure 1 shows FTIR spectrums of the prepared EG and EG_{Fe} . The two samples both show the characteristic stretching vibrations absorption peaks of -OH (round 3430 - 3440 cm⁻¹) and S=O (round 1130 cm⁻¹) caused by intercalation of H₂SO₄/HSO₄⁻ [9]. At the same time, the peaks at about 1630 cm⁻¹ are the specific stretching vibration absorption of C=C. It's worth noting that the bending vibration absorption of Fe-O-H is observed at 890 cm⁻¹, and the stretching vibration absorptions of Fe-OH, Fe-O appear at 720 cm⁻¹ and 580 cm⁻¹ as well [21]. These results confirm that the hydrolysis precipitation product is Fe(OH)₃ showed as equation 1.

$$FeCl_3 + 3NH_3 \cdot H_2O = Fe(OH)_3 \downarrow + 3NH_4Cl$$
(1)





3.5.2. SEM Analysis

Figure 2 presents SEM morphology of the EG_{Fe} taking from different angle. Figure 2a shows that the EG_{Fe} still keeps layer structures after the oxidation and hydrolysis precipitation reaction just like natural graphite, but the layers distance is enlarged caused by the intercalation reaction [13, 14]. The surface morphology showed in Figure 2b indicates some white particles covering on the outside surface of EG, but the distribution presents uniform cracks caused by the magnetic stirring effect. Combined the results of FTIR, the white particles should be $Fe(OH)_3$.



3.5.3. XRD Analysis

XRD analysis for the EG and EG_{Fe} were performed. As shown in Figure 3, the two samples both show the specific diffraction peaks of natural graphite round 26.6° and 54.8° severally corresponding to the 002 and 001

crystal plane. What makes the spectrograms different is that the diffraction peaks strength of the EG_{Fe} is more weak than that of EG due to the loading of $Fe(OH)_3$ particles, and the interplanar crystal spacing corresponding to 002 crystal reduces to a smaller value of 3.38 Å. It's worth noting that a new reflection peak at 29.3° with a crystal spacing of 3.04 Å appears in the spectrum of EG_{Fe} caused by the loaded Fe(OH)₃ [21]. Based on the results of FTIR, SEM and XRD, it can be suggested the EG is prepared through the oxidation intercalation reaction of graphite, and hydrolysis precipitation reaction between EG and FeCl₃ produces the EG_{Fe}. The final existence form of FeCl₃ is Fe(OH)₃ covered on the outside surface of EG.

Figure-3. XRD analysis of EG and EG_{Fe}



3.5.4. Application to the Flame Retardance of LLDPE

The combustion behavior of LLDPE loading with the prepared EG and EG_{Fe} was evaluated in LOI and vertical combustion UL-94 tests. When mixed LLDPE with EG_{Fe} at a 30 wt% dosage, it can improve the LOI value from 17.6% to 28.1%, and UL-94 level to V-0. While, the same amount of the EG can only improve the LOI and UL-94 level to 25.0% and V-1 respectively. The results indicate the loaded $Fe(OH)_3$ on EG can obviously improve the flame retardancy for LLDPE caused by the combined action of EG and $Fe(OH)_3$ decomposition products. The further application and flame retardant mechanism need deep discussion.

4. Conclusions

The EG_{Fe} was stepwise prepared with chemical oxidation and hydrolysis precipitation method. Firstly, EG was synthesized through chemical oxidation reaction between graphite, H_2SO_4 and KMnO₄. Then, modification of the EG was carried out through hydrolysis reaction of FeCl₃ and precipitation of Fe(OH)₃. The SEM, FTIR and XRD detection confirmed the oxidation intercalation reaction and the loading of the Fe(OH)₃ on EG outside surface. Compared with the normal EG, EG_{Fe} possessed a better dilatability and flame retardancy for LLDPE.

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