

PREPARATION OF TITANIUM DIOXIDE MODIFIED EXPANDABLE GRAPHITE WITH OXIDATION INTERCALATION AND HYDROLYSIS PRECIPITATION METHOD AND ITS FLAME RETARDANCY FOR POLYETHYLENE

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ABSTRACT

A type of expandable graphite (EG_{T1}) modified by titanium dioxide was stepwise prepared through chemical oxidation and hydrolysis precipitation reaction, and the synthesizing method was established through single-factor experiment. The EG_{T1} dilatibility, crystal structure, main functional groups and flame retardation for Liner low density polyethylene (LLDPE) were all characterized. The optimal conditions for preparation are as follows: mass ratio of TiCl₄ to normal expandable graphite (EG) prepared in advance with chemical oxidation method is 0.35:1, dosage of NH₃·H₂O with a wt% of 25% is controlled as 0.32 g/g. The prepared EG_{T1} keeps a layer structure just like natural graphite, and the hydrolysis product of TiCl₄ is TiO₂ after high temperature roasting. EG_{T1} indicates better flame retardancy for LLDPE than the normal EG, pure TiO₂, EG_{T2} prepared with chemical oxidation intercalation method with TiCl₄ as assistant intercalator, binary-mixture of EG and TiO₂. Furthermore, there is synergistic effect between ammonium polyphosphate (APP) and EG_{T1}, the combination makes the 70LLDPE/20EG_{T1}/10APP composite show a better LOI of 31.3%.

Keywords: *Modified Expandable Graphite, TiO₂, Oxidation Intercalation Reaction, Hydrolysis Precipitation, Flame Retardancy*

INTRODUCTION

Graphite is a crystal compound with graphene planes structure bonded by the weak Van Der Waals force. 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 (Ma, 1993; Pang and Sun, 2014). EG has showed catalysis for the esterification between organic acid and alcohol (Lin *et al.*, 2013), and its high temperature expansion product named expanded graphite is a kind of adsorbent with well adsorption capability for floating oil and other pollutants (Pang *et al.*, 2009; Toyoda *et al.*, 2000). Furthermore, EG is an intumescent type flame retardant (FR) with functions of char-formation and smoke suppressing. Due to its outstanding flame retardation, expandable graphite has been widely used as FR of polyolefin (Xie and Qu, 2001), ethylene-vinyl acetate (Pang *et al.*, 2015), polyurethane (Pang *et al.*, 2002) and so on.

In the preparation of EG, H₂SO₄ is a commonly used intercalator due to its strong oxidizability, low-price and well dilatibility of the obtained product (Shioyam and Fujii, 1987). However, the use of H₂SO₄ normally leads to high sulfur content in GIC and corrosion for storage devices. Besides, more SO₂ 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 (Shornikova *et al.*, 2006), some assistant intercalators such as nitric acid, oxalic acid, acetic anhydride can replace a part of H₂SO₄ (Song *et al.*, 1993; Song *et al.*, 1996). EG intercalated by H₂SO₄/acetic acid indicated an expandable volume (EV) of 460 mL/g and limited oxygen index (LOI) value of 28.1% for Liner low density polyethylene (LLDPE) (Pang *et al.*, 2013). It was higher than that of the single H₂SO₄ intercalated EG with an EV of 390 mL/g and LOI value of 24.0% respectively. The EG intercalated by H₂SO₄ and H₃BO₃ with direct method presented excellent dilatibility and LOI than the compared independent H₂SO₄ intercalated product (Zhao *et al.*, 2016). Through outside surface modification by chemical bonding or sol-gel hydrolysis precipitation methods, EG can also get

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excellent property. The titanium dioxide (TiO_2) nanocrystals in EG could be prepared using organically modified silicate as a binder (Ramanathan *et al.*, 1997). The EG prepared using chemical bonding method with silane coupling agent and boric acid presented improved flame retardancy for rigid polyurethane foam (Xu *et al.*, 2013). An expanded graphite loading anatase TiO_2 was prepared through sol-gel process with TiO_2 gel introduced to EG surface (Lai *et al.*, 2010).

TiO_2 is a good FR attributing to prolonging ignition time and slowing combustion speed (Mosurkal *et al.*, 2008). In addition, as one of transition metal oxides, TiO_2 has obvious impact on the thermal decomposition process of ammonium polyphosphate (APP) (Zhou *et al.*, 2013), it can accelerate the release of NH_3 and H_2O in the earlier period, and increase the high temperature residues in the later period due to the formation of metallic phosphate. In view of the independent flame retardation of EG, APP, TiO_2 , and acceleration decomposition of TiO_2 for APP, the purpose of this research was to prepare a TiO_2 modified GIC (written as EG_{T1}) through hydrolysis precipitation reaction between TiCl_4 and EG synthesized by chemical oxidation method in advance. A preparation method of the EG_{T1} was found with natural graphite (C), KMnO_4 , H_2SO_4 , titanium tetrachloride (TiCl_4 , precursor of TiO_2 by hydrolysis reaction), $\text{NH}_3\cdot\text{H}_2\text{O}$ as materials, and its flame retardancy for LLDPE was compared with the normal EG, TiO_2 , EG_{T2} (synthesized through chemical oxidation intercalation reaction with titanium tetrachloride as assistant-intercalator (Pang *et al.*, 2009)), binary mixture of TiO_2 and EG. Furthermore, the combined flame retardation of these FRs including APP for LLDPE was discussed also. Scanning electron microscope (SEM), X-ray diffraction spectroscopy (XRD) and Fourier transform infrared spectroscopy (FTIR) were employed to characterize morphology and structure of the prepared TiO_2 modified EG. The flame retardant performance was characterized in the LOI and vertical combustion tests of LLDPE.

MATERIALS AND METHODS

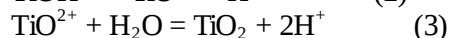
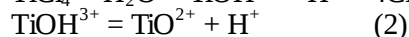
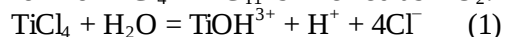
Natural flake graphite (average particle size of 0.30 mm, carbon content of 96 wt%) was provided by Xite Carbon CO. LTD, Qingdao, China. LLDPE (920NT(EGF-34), melt index 0.2 g/min) was purchased from Sinopec Sabic Tianjin Petrochemical. KMnO_4 , $\text{NH}_3\cdot\text{H}_2\text{O}$ (25 wt%), H_2SO_4 (98 wt%) and TiCl_4 were all analytical agents and used as received.

Preparation of the EG_{T1}

Firstly, the normal EG was synthesized through chemical oxidation intercalation reaction with KMnO_4 as oxidant and H_2SO_4 as intercalator (Pang, 2012) as per the mass ratio graphite (C): H_2SO_4 (75 wt%): KMnO_4 of 1.0:6.67:0.15. The obtained EG showed an EV of 400 mL/g at 800°C. Then, reactants with definite mass were added into beaker in the order of deionized water, the EG, $\text{NH}_3\cdot\text{H}_2\text{O}$ and TiCl_4 . The hydrolysis reaction time maintained 2.0 h with continuous agitation at room temperature. After stewing 3.0 h, the solids were filtrated and dried at 100°C until it kept a constant mass, and then EG_{T1} obtained. The influence of $\text{NH}_3\cdot\text{H}_2\text{O}$ and TiCl_4 dosages on the EG_{T1} dilatibility and flame retardancy for LLDPE labeled as LOI were optimized through single-factor experiments.

Check Test: Preparation of the EG_{T2} through Chemical Oxidation Intercalation Reaction

According to the reported method and its further optimization (Pang *et al.*, 2009), EG_{T2} was synthesized through chemical oxidation intercalation reaction between graphite and KMnO_4 , H_2SO_4 , TiCl_4 following the mass ratio C: H_2SO_4 (98 wt%): KMnO_4 : TiCl_4 of 1:4.8:0.28:0.23. The obtained EG_{T2} showed an EV of 400 mL/g at 800°C. It has been testified TiO_2 can be prepared through the hydrolysis of TiCl_4 under the strong acidic condition as shown in equation (1), (2) and (3) (Zhang *et al.*, 2000). Therefore, the existence form of TiCl_4 in EG_{T1} is inferred as TiO_2 .



Preparation of the Flame Retarded LLDPE Composites

FRs were added into the 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.

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Characterization of the Samples

A TM3000 SEM (Japan) was applied to observe structure and morphology of the prepared GICs. The XRD pattern was obtained on a Y-4Q X-ray diffractometer operating at 40 kV, 30 mA, employing Ni-filtered Cu K α radiation with 2θ 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} .

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.

RESULTS AND DISCUSSION

Optimization of Influence Factor in the Preparation of EG_{Ti}

Influence of various factors on EG_{Ti} dilatibility and combustion LOI for LLDPE were optimized through single-factor experiments.

Influence of NH₃·H₂O dosage on EV of the EG_{Ti}

With dosage of the EG controlled as 1.0 g, mass ratio of TiCl₄ to EG set as 0.35 g/g, the influence of NH₃·H₂O dosage with mass concentration of 25 wt % on EV was tested and showed in Figure 1. In the tested concentration range, the influence is very slight, and the maximum EV is obtained when the dosage is controlled as 0.32 g/g. In this condition, the hydrolysis of TiCl₄ is completed, and the generated precipitation mass almost keeps constant.

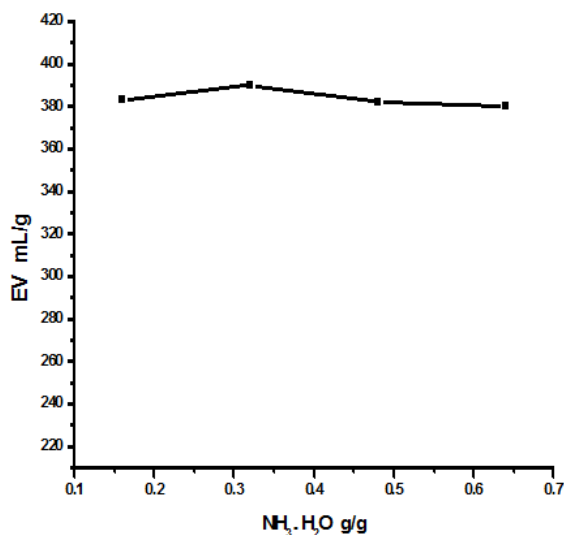


Figure 1 Influence of NH₃·H₂O on EV

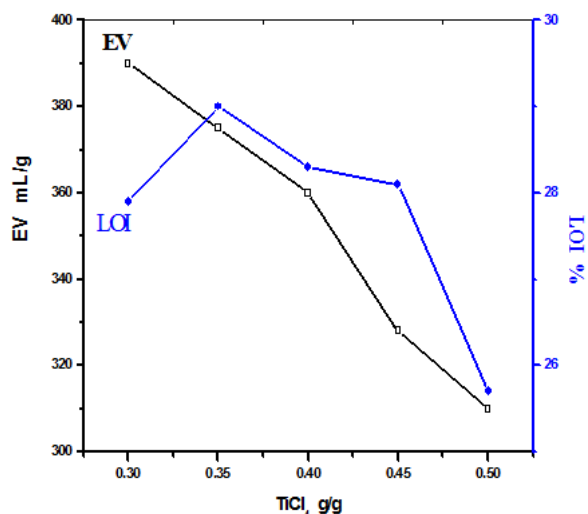


Figure 2 Influence of TiCl₄ on EV and LOI

Influence of TiCl₄ Dosage on EV of EG_{Ti} and LOI of the Flame Retarded LLDPE

With mass of the EG and NH₃·H₂O set as 1.0 g and 0.32 g respectively, the influence of TiCl₄ dosage on EV of EG_{Ti} and LOI of the flame retarded LLDPE was tested and showed in Figure 2 respectively. As showed in Figure 2, the EV sharply decreases with the increasing TiCl₄ mass. This is because the generated precipitation mass on EG surface increases with the increasing TiCl₄ mass, which would reduce the heat utilized for EG expansion. However, its influence on LOI of the flame retarded LLDPE is totally different. There is a maximum LOI value of 29.0% when it's controlled as 0.35g. The above results indicate the flame retardancy of the prepared EG_{Ti} for LLDPE based on both its EV and the hydrolysis

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precipitation mass. Normally, as for the independent influence of EV of GICs or TiO_2 dosage on LOI, the bigger value means the better LOI due to the achieving thick residual char layer. As for the EG_{T1} , loading of precipitation would decrease its EV. Therefore, there is an optimum precipitation adsorbance or TiCl_4 dosage, and the value is 0.35 g/g of TiCl_4 .

Base on the above experiment results, the feasible synthesis method of EG_{T1} is described as: mass ratio of TiCl_4 to EG is 0.35 g/g, dosage of $\text{NH}_3 \cdot \text{H}_2\text{O}$ with a 25 wt% is controlled as 0.32 g/g, hydrolysis reaction maintains 2.0 h with continuous agitation at room temperature. After stewing 3.0 h, the solids are filtrated and dried at 100°C until it keeps a constant mass. The obtained EG_{T1} shows an EV of 390 mL/g at 800°C .

Characteristics of the Prepared GICs

SEM Analysis

As a comparison, Figure 3 presents SEM morphology of the EG_{T1} and the referenced EG_{T2} taking from different angle. As showed in Figure 3a of the EG_{T1} , some white particles can be seen covering on the outside surface of EG cause by the hydrolysis precipitation reaction of TiCl_4 , and the distribution presents uniform cracks caused by the magnetic stirring effect. It's relatively smooth for the EG_{T2} as presented in Figure 3c. As for the profile showed in Figure 3b and Figure 3d, they both show the layer structures just like natural graphite, but the layers distances are enlarged caused by the intercalation reaction, so they can show excellent dilatability.

Compared Figure 3a with Figure 3b of the EG_{T1} , it shows that white particles mainly cover on the EG outside surface, and no particle is found between the layers, which indicates the hydrolysis precipitation reaction mainly occurs on the outer surface of EG.

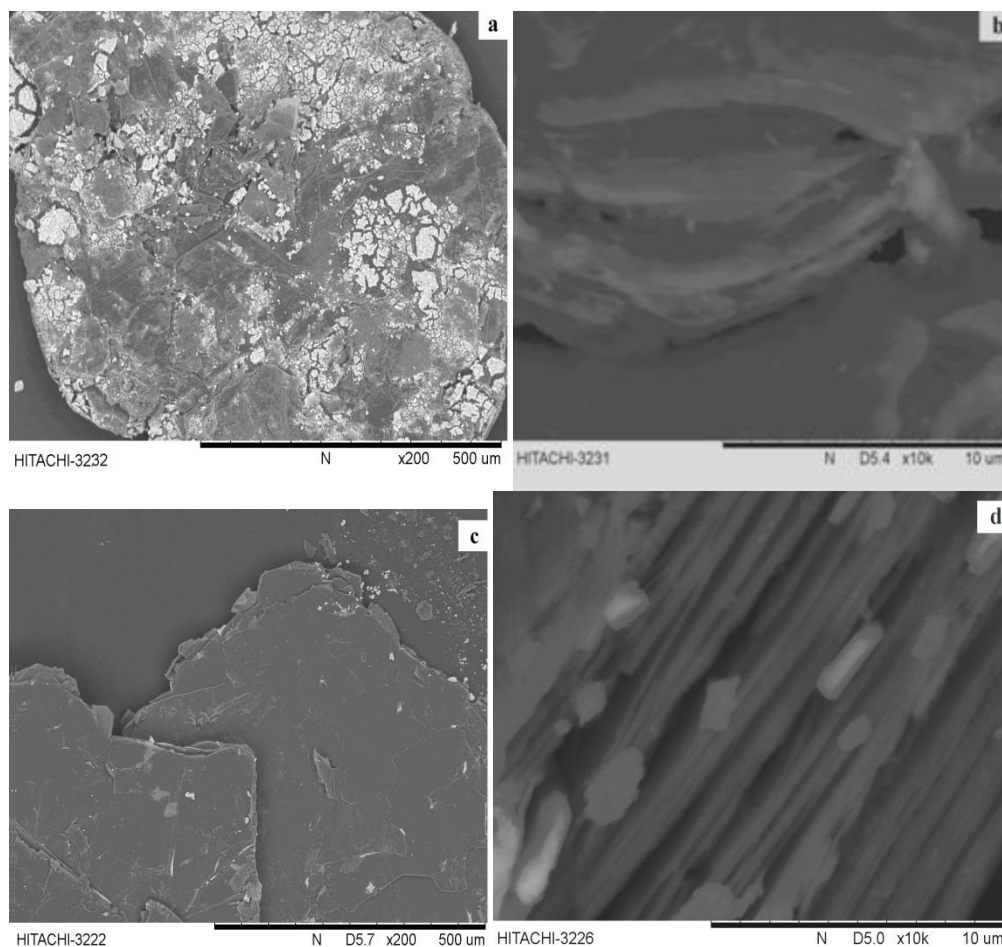


Figure 3: Outside Surface and Profile Morphologies of EG_{T1} (a), (b) and EG_{T2} (c), (d)

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FTIR Analysis

Figure 4 shows FTIR spectrums of the prepared EG, EG_{T1} and EG_{T2}. The three samples show the characteristic stretching vibrations absorption peaks of -OH (round 3440 - 3460 cm⁻¹) and S=O (round 1120 cm⁻¹) caused by intercalation of H₂SO₄/HSO₄⁻ (Shioyam and Fujii, 1987). 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 stretching vibration absorptions of Ti-O is observed at 619 cm⁻¹ and 466 cm⁻¹ in the spectrum of EG_{T1} and EG_{T2} (Weng *et al.*, 2008; Lu *et al.*, 2015).

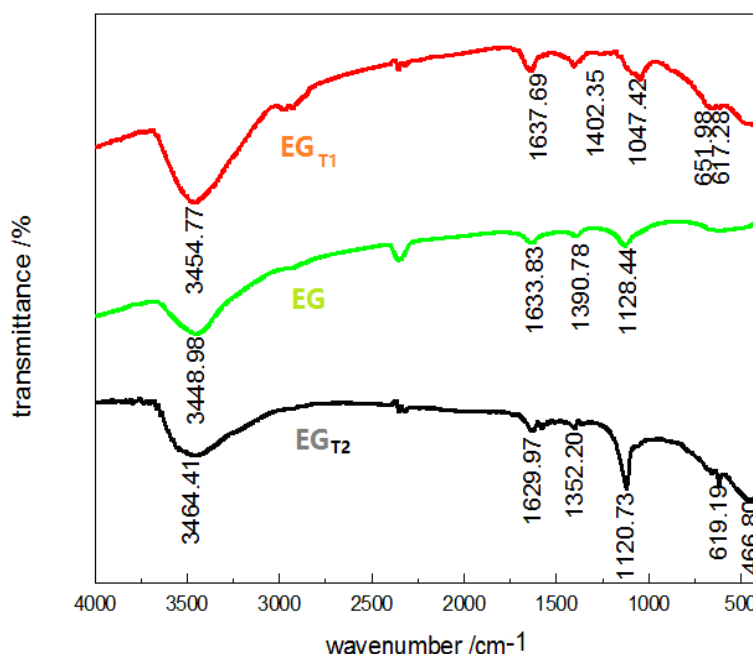


Figure 4: The FTIR Spectra of EG, EG_{T1} and EG_{T2}

XRD Analysis

XRD analysis was carried out for natural graphite, the expansion products of EG_{T1} and EG_{T2} at 800°C. As shown in Figure 5, they all show the specific diffraction peaks of natural graphite round 26.6° and 54.8°. The spectrogram differences present that the 001 diffraction peak strength of the expansion product is weak, and new reflection peaks appear at the same time, which is in accordance with the characteristic peaks of rutile TiO₂ caused by the hydrolysis or assistant intercalation reaction of TiCl₄ (Weng *et al.*, 2008). Based on the results of SEM, FTIR and XRD, it can be suggested hydrolysis precipitation reaction between EG and TiCl₄ produces the EG_{T1}. The difference between the EG_{T1} and EG_{T2} is the hydrolysis product covering on the outside surface of EG, and it's in the graphene layers for EG_{T2}.

Application to the Flame Retardance of LLDPE

The combustion behavior of LLDPE loading with the prepared EG_{T1} was evaluated in LOI and vertical combustion UL-94 tests, and the results listed in Table 1 are contrasted with other FRs such as APP, EG, pure TiO₂, EG_{T2}, and three groups of binary-mixture of TiO₂ and EG, APP and EG_{T1}, APP and EG_{T2}. Pure LLDPE is very flammable, and the combustion companies serious melt-dropping. When mixed LLDPE with FRs at a total 30 wt% dosage, they can all improve the LOI value.

The efficiencies are compared between these FRs, and EG_{T1} shows the better flame retardancy for 70 LLDPE/30EG_{T1} than the others. It improves the LOI from 17.6% to 28.0%, and UL-94 level from the not detected (N.D.) to V-0. As for the addition of binary-mixture, the LOI and UL-94 level are all higher than the single FR system, which indicates there is synergistic effect between TiO₂ and EG, APP and EG_{T1}, APP and EG_{T2}. The combination makes the 70LLDPE/20EG_{T1}/10APP composite show the best LOI of 31.3%.

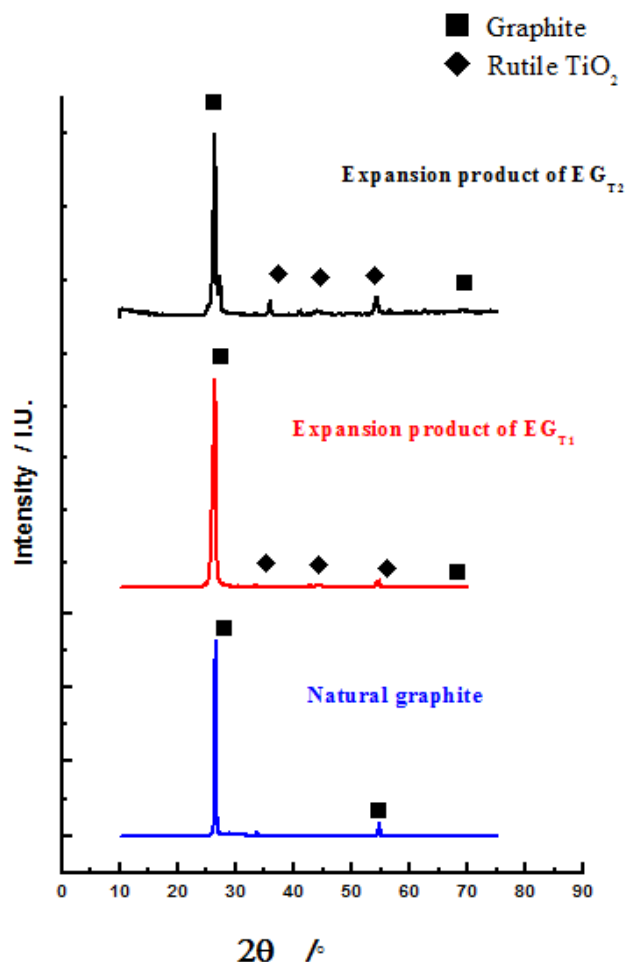


Figure 5: XRD Analysis of Natural Graphite, Expansion Product of EG_{T1} and EG_{T2}

Table 1: The LOI Results of LLDPE Composites

Specimens	LOI /%	UL-94 Level
100LLDPE	17.6	N.D.
70LLDPE/30APP	19.9	N.D.
70LLDPE/30EG	25.0	V-1
70LLDPE/30TiO ₂	23.4	N.D.
70LLDPE/30EG _{T1}	28.0	V-0
70LLDPE/30EG _{T2}	26.8	V-0
70LLDPE/20EG _{T1} /10APP	31.3	V-0
70LLDPE/25.6EG/4.4 TiO ₂	26.6	V-1
70LLDPE/20EG _{T2} /10APP	30.4	V-0

Conclusion

The EG_{T1} was stepwise prepared with chemical oxidation and hydrolysis precipitation method. SEM, FTIR and XRD results confirmed the oxidation intercalation reaction and hydrolysis precipitation of TiCl₄. Compared EG_{T1} with the normal EG, TiO₂, EG_{T2} prepared with chemical oxidation intercalation method, binary-mixture of EG and TiO₂, it indicated better flame retardancy for LLDPE. There is synergistic effect between APP and EG_{T1}, the combination makes the 70LLDPE/20EG_{T1}/10APP composite show the best LOI of 31.3%.

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