



(Proceedings of 2011 Shanghai International Nanotechnology Cooperation Symposium, SINCS 2011, Published online 10 January 2012)

# Study on the Preparation and Synergistic Flame Retardancy of Organic Modified Montmorillonite

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**Abstract:** Organic modified layered silicate montmorillonite was prepared by solution intercalating with cetyltrimethylammonium bromide, which was characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Modified montmorillonite was added to linear low density polyethylene (LLDPE) with intumescent flame retardant, their flame retardant properties were evaluated by Limiting Oxygen Index (LOI) and Thermogravimetric Analysis (TGA), and mechanical properties were tested simultaneously. The results showed that montmorillonite could not only improve the flame retardant effect, reduce the additive dosage of intumescent flame retardant, but also increase the mechanical properties of LLDPE.

**Keywords:** Montmorillonite; Organic modified; Linear low density polyethylene; Synergistic flame retardancy

**Citation:** Yuanyuan Meng, Weiguang Gong and Baicun Zheng, "Study on the Preparation and Synergistic Flame Retardancy of Organic Modified Montmorillonite", Proceedings of Shanghai International Nanotechnology Cooperation Symposium, 99-104 (2011). <http://dx.doi.org/10.3786/sincs2011.24>

## Introduction

Linear low density polyethylene (LLDPE) is one of the most important polyolefins, but its bad inherent flammability has put limits on its practical applications. Therefore, improving its flame retardancy has become very important. Recently, the addition of halogen-free flame retardant has received much attention for their environmentally friendly properties [1-3]. However, the high loading leads to the processing difficulties and poor mechanical properties of the materials. Montmorillonite is a layered clay mineral composed of one aluminium-oxide octahedral layer between two silicon-oxide tetrahedral layers, which has wide applications after surface modifications [4]. Synergistic flame retardants comprised of montmorillonite and other halogen-free flame retardants, such as magnesium hydroxide can give better flame retardant effect for LLDPE [5,6], but synergistic flame retardancy of montmorillonite and intumescent flame retardant (IFR) have not been reported. Intumescent flame retardant systems consist of

a precursor of carbonization catalyst, such as ammonium polyphosphate (APP), and a carbonization agent such as polyol and a blowing agent (melamine phosphate) [7,8], which are efficient in polyolefin and widely used as environmentally friendly, halogen-free additives [9]. In this study, we choose intumescent flame retardants and montmorillonite as flame retardant to evaluate their flame retardant and mechanical properties of LLDPE.

## Experimental

### Materials

LLDPE (DFDA7042) was supplied as pellets by Yangzi Petrochemical Co. (China). Intumescent flame retardant was supplied by Shanghai Xusen non-halogen flame retardant and smoke Co., Ltd. The pristine MMT (CEC 90mequiv/100g) was kindly provided by Zhejiang Fenghong Clay Chemical Co., Ltd. Cetyltrimethylammonium bromide was acquired from British Norwich

Chemical Co., Ltd. Xiamen.

### Preparation of the Samples

The organic montmorillonite was prepared in the ion-exchange reaction. Montmorillonite powder (5 g) was dispersed in 200 ml of deionised water at room temperature by mixing for 1 h. The quaternary ammonium bromides were dissolved in 200 ml of water at 40°C and slowly added to the montmorillonite dispersion. The suspension was mixed at 80°C for 2 h and filtered by leaching. The modified montmorillonite was washed several times with about 3-4 dm<sup>3</sup> of redistilled water until no bromide ions were detected by AgNO<sub>3</sub> solution. The obtained organic montmorillonite was resuspended in water and centrifuged. The obtained pellet was dried at 100°C and ground into powder.

Before mixing, LLDPE, IFR and OMMT were dried in an oven at 100°C for 2 h and then cooled to room temperature. In this study, the composites were prepared in a single step. The organophilic montmorillonite was blended with LLDPE into a blender, and then the blender was run at a high speed for about 5 min. The mixed powder was added to a twin-screw extruder (KS-20, Jiangshu Kunshan Kexin Plastic Machinery Co., Ltd.). The compounds in the twin-screw extruder were carried out at 180-200°C and at a screw speed of 30 rpm, and then the composites were obtained. After that, the dried IFR was added to the LLDPE/OMMT composites and extruded with a twin-screw extruder with the aforementioned method. The pellets will be quelled into tablet shape with the vulcanizing machine of tablet, and the samples were cut into standard specimens spline as required with a universal sample machine for limiting oxygen index (LOI) test and the mechanical properties test.

### Characterization and measurement

The X-ray studies were performed using the powder diffraction technique. The analysis was conducted using a Japan Rigaku D/max-2550 V diffractometer. The source of X-ray radiation was a sealed tube with the copper anode and Ni filter ( $\lambda=0.154178$  nm); supplied using the TUR M62 (40 kV, 200 mA) generator. Diffraction measurements were conducted within the  $2\theta$  angle of 1.2-10°, at the scanning rate of 0.002°/min.

The Fourier transform infrared (FTIR) spectra were recorded in the range 7800~50 cm<sup>-1</sup> in a Nicolet 6700 infrared fourier transform spectrometer, using the KBr pellet technique (about 1 mg of sample and 300 mg of KBr were used in the preparation of the pellets). For each spectrum scans were taken with the resolution of 0.01 cm<sup>-1</sup>.

The flammability was characterized with limiting oxygen index (LOI) test. All the samples (10 cm×0.65

cm×0.3 cm) were based on ASTM D 2863-77. The experiments were repeated three to six times, and the results were reproducible to within ±10%.

A Shimadzu SDT Q600 device was employed to perform the thermo gravimetric analysis (TGA) and derivative thermo gravimetric (DTG) in air atmosphere and at a heating rate of 20°C/min from 25°C to 700°C.

## Results and discussion

### X-ray diffraction of the organophilic montmorillonite

Figure 1 presented the XRD patterns of the pristine MMT and the organic modified MMT. According to Bragg formula  $n\lambda = 2d\sin\theta$ , the  $d_{001}$  peak of pristine MMT at  $2\theta=5.8^\circ$  corresponded to 1.51 nm of interlayer spacing. The  $d_{001}$  peak of the OMMT was observed at a lower angle than that of the pristine MMT, which indicated the increase of the basal spacing. The  $d_{001}$  peak of the OMMT modified by cetyltrimethylammonium bromide (C16) at  $2\theta = 2.22^\circ$  corresponded to 3.98 nm of interlayer spacing. The interlayer spacing had been significantly increased, which indicated that the cetyltrimethylammonium bromide (C16) had been intercalated into silicate layers [10].

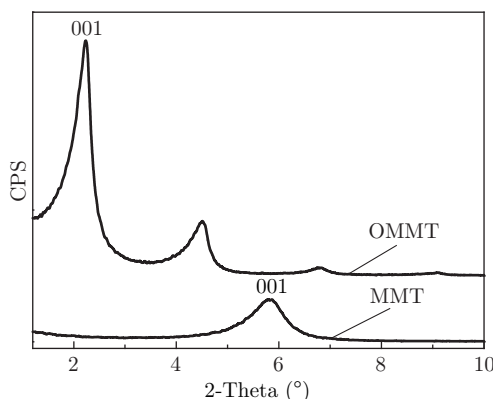


Fig. 1 The XRD patterns of MMT and OMMT.

### FT-IR of the organic montmorillonite

The unmodified montmorillonite was characterized by the bands (Si-O stretching and bending as well as -OH bending). Figure 2 performed the FTIR spectrums of montmorillonite and organic modified montmorillonite, and the vibration peaks of the main groups were shown in Table 1.

These -OH stretching bands are present in the IR spectra of modified samples were at 3628 cm<sup>-1</sup> and 3421 cm<sup>-1</sup>, and the pristine MMT were at 3616 cm<sup>-1</sup> and 3446 cm<sup>-1</sup>. There were the results of the adsorbed water between the layers. The figure also showed that at 1637 cm<sup>-1</sup> both the pristine MMT and the organic

**Table 1** Vibration peaks of main groups ( $\text{cm}^{-1}$ )

Groups	Si-O-Mg	Mg-Al-OH	Si-O	-OH vibration absorption	C-CH <sub>2</sub> -C	-OH stretching vibration
pristine MMT	519	797	1036	1637	none	3446, 3616
modified MMT	519	798	1037	1637	2918, 2850	3421, 3628

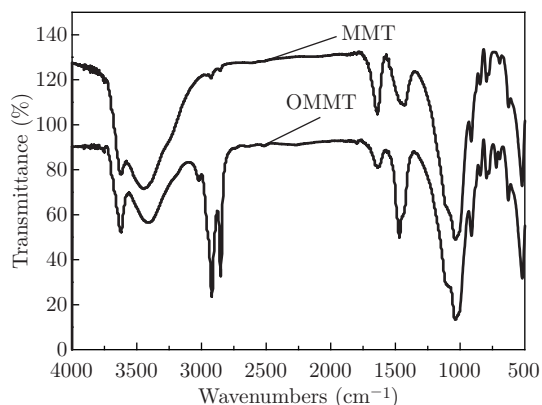


Fig. 2 FTIR spectrum of montmorillonite and organophilic montmorillonite.

modified MMT had a -OH bond vibration absorption peak, compared with the pristine MMT, the strength of the -OH bond vibration absorption peak of the organic modified MMT was relatively weak and the peak shape was more smooth. This confirmed that the content of the absorbed water in the organic MMT layers decreased, which might be resulted from the introduction of organic ions by hydrophobic interaction, with no change in crystal water. At the vicinity of  $1037 \text{ cm}^{-1}$ ,  $797 \text{ cm}^{-1}$  and  $519 \text{ cm}^{-1}$  both the pristine MMT and the organic modified MMT had the vibration peaks of Si-O, Mg-Al-OH and Si-O-Mg bonds, which indicated that the skeleton of the layer silicate structure of the MMT had not been destroyed after modified [11].

Figure 2 also showed that at  $2918 \text{ cm}^{-1}$  and  $2850 \text{ cm}^{-1}$ , the organic modified MMT had the typical stretching vibration peaks of the -CH<sub>2</sub>- bond, which further confirmed that the organic ions had entered into the interlayer of the montmorillonite. So the hydrophilic montmorillonite had been changed to be the hydrophobic clay, improving its dispersion in the organic matrix.

### Flammability properties

MMT could not be used as flame retardant alone. As could be observed in Table 2, the limit oxygen index (LOI) values of LLDPE was 17.6% and the LLDPE/OMMT composites were just 18.5% approximately. MMT could inhibit the combustion by preventing oxygen reaching the surface of the burning composites. At the same time, the heat was kept around the composites, thus heat was accumulated to support the

combustion again [12]. Although polymer chains can be intercalated into the interlayer of layered silicate to form polymer/clay nanocomposites making them effective flame-retardant materials, sometimes it is difficult to meet the requirements of new standards or regulations related to the evaluation of fire hazards. It is necessary, therefore, to develop a novel synergistic flame-retardant system with high efficiency and acceptable environmental impact [13]. Thereby, the IFR was chose to collaborate with montmorillonite as synergistic flame retardant.

**Table 2** The flame retardant properties of the LLDPE/OMMT.

Samples	LOI(%)	Burning behaviour
LLDPE=100	17.6	Dripping
LLDPE/OMMT=100/1	18.1	Dripping
LLDPE/OMMT=100/2	18.2	Dripping
LLDPE/OMMT=100/3	18.4	Dripping
LLDPE/OMMT=100/4	18.5	Dripping
LLDPE/OMMT=100/5	18.5	Dripping

It was interesting to note that the addition of the intumescent flame retardant (IFR) can effectively inhibit the occurrence of melt dripping. When OMMT and IFR were used as flame retardant together, the flame retardant properties of LLDPE increased and the LOI value was greater than OMMT or IFR used as flame retardant alone (Table 3). When the mass fraction of the OMMT was 2wt%, the LOI value increased from 23.1% to 25.2%, it was the result of the synergistic flame retardancy effect between MMT and IFR. In this study, when the mass fraction of OMMT exceeded 2wt%, the

**Table 3** The flame retardant properties and mechanical properties of LLDPE/IFR/OMMT.

LLDPE/ IFR/OMMT	LOI (%)	Burning behaviour	Tensile Strength (MPa)
70/30/0	23.1	No dripping	8.48
70/30/1	24.2	No dripping	8.60
70/30/2	25.2	No dripping	9.16
70/30/3	25.1	No dripping	9.00
70/30/4	25.0	No dripping	8.71
70/30/5	24.6	No dripping	8.50

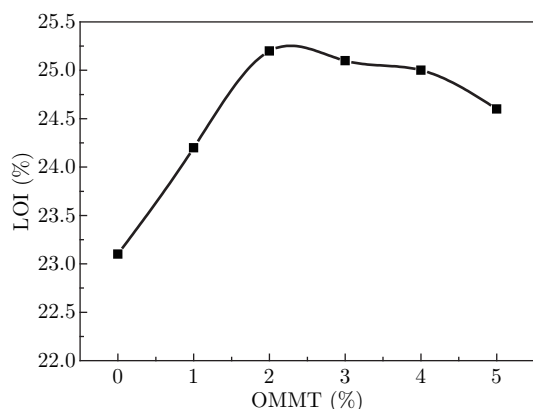


Fig. 3 The synergistic flame retardancy of IFR and OMMT.

LOI value of the system decreased, which indicated that when the mass fraction of the clay was greater than a certain amount, the MMT and IFR showed the anti-synergy effect. The reason was that the layered structure of the excessive MMT would impede the escaping of the water vapor and the production of non-flammable gases from the IFR, which was not conducive to the expansion of foam of the system, thus affecting the flame-retardant effect [12].

The mechanisms for synergistic flame retardancy of OMMT and IFR may be more complex. In intumescent flame retardant systems, APP was used as the acid source, forming polyphosphoric acid as an acid catalyst on heating. It took part in the dehydration of the carbonic compounds to form carbon char and, finally, the blowing agent decomposed to form gaseous products. This caused the char to swell, and the char could effectively prohibit the burning of the materials. Moreover, when IFR was added to LLDPE/OMMT composites, APP reacted with OMMT to form an aluminophosphate structure and a ceramic-like structure in the 310–560°C temperature range [14,15]. These aluminophosphate species may thermally stabilize and lead to good fire performance in this temperature range. On the other hand, there was a catalytic role played by the layered silicates deriving from the Hoffman reaction of quaternary ammonium salt. The decomposition of the silicate modifier produced a strong acid catalytic site that may further favor the oxidative dehydrogenation-crosslinking-charring process and increase the char yield in the charring process [12]. Moreover, during combustion, an ablative reassembling of the silicate layers may occur on the surface of a burning nanocomposite, creating a physical protective barrier on the surface of the material. The physical process of layers reassembling acted as a protective barrier in addition to the intumescent shield and could limit the oxygen diffusion to the substrate or gave a low volatilization rate [16–20].

As shown in Fig. 3, when the mass fraction of OMMT exceeded 2wt%, the synergistic effect decreased. The

main reason for this phenomenon may be that during the combustion process, the silicate layers have the positive and negative roles. The silicate layers could limit the oxygen diffusion to the substrate or gave a low volatilization rate, which produced a positive effect on the fire properties. At the same time, an ablative reassembling of the silicate layers could hinder  $\text{NH}_3$  from swelling, and this led to a negative effect on the fire properties.  $\text{NH}_3$  was the main gaseous product, it volatilized and made the mixture of the carbonaceous residue and phospho carbonaceous materials swell, leading to the formation of the intumescent residue char. In particular, when the mass of OMMT was increased, the negative effect may exceed the positive effect on the fire properties [21].

### Mechanical properties of the compounds

The addition of OMMT could also improve the mechanical properties of the composites (Table 3). When the mass fraction of OMMT was 2wt%, tensile strength of the system increased from 8.48 MPa to 9.16 MPa, increased by 8.02%. However, when the mass fraction of OMMT exceeded 2wt%, the tensile strength of the compounds decreased. Because the organic modified MMT could act as polymeric compatibilizers, which could increase the strength of interface bond, leading to improved mechanical properties of the system. When the mass fraction of OMMT exceeded a certain amount, it was prone to agglomeration and resulted in stress concentration and decreased mechanical properties of the system.

### Thermal degradation behavior of compound materials

Since the majority of polymer composite materials were applied in air, the research of the thermal degradation behavior of the materials in air atmosphere will be more of practical significance.

The TGA and DTG curves of pure LLDPE, LLDPE/IFR blend and LLDPE/IFR/OMMT composites in air atmosphere were shown in Fig. 4. The corresponding temperature of the particular stage degradation of the polymer materials were presented in Table 4. The initial decomposition of all the compounds is earlier than that of pure LLDPE. Because the small molecular gas in IFR began to break down earlier.

It was observed that the degradation temperature (weight loss 10wt%) of pure LLDPE was 354°C. The temperature of the maximum of the mass loss rate ( $T_{\text{max}}$ ) appeared at about 410°C, and the end of the degradation of pure LLDPE occurred at 570°C. As the degradation products of pure LLDPE are ethylene, hexene and other small gas molecules, hence there was very few final residues of the quality. Table 4 showed the



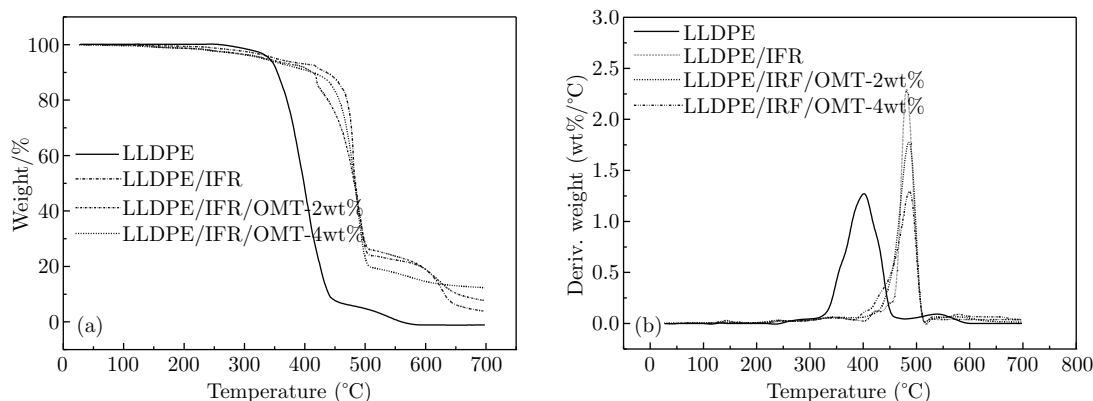


Fig. 4 TGA and DTG curves for LLDPE, LLDPE/IFR and LLDPE/IFR/OMMT composites in air. (a) TGA curves; (b) DTG curves.

**Table 4** The TGA and DTG results under air atmosphere for pure LLDPE and its composites.

Samples	$T_{0.1}/^{\circ}\text{C}$	$T_{0.5}/^{\circ}\text{C}$	$T_{\max}/^{\circ}\text{C}$	Carbon residue content/wt%
PE0-LLDPE	354	398	410	0
PE1-LLDPE/IFR	435	483	482	3.93
PE2-LLDPE/IFR/ OMMT-2wt%	412	482	492	7.72
PE2-LLDPE/IFR/ OMMT-4wt%	413	483	494	12.3

10wt% weight loss decomposition temperature of the IFR/LLDPE composite was higher than that of pure LLDPE by about 81°C. Because the carbon layer had the inhibitory effect on the thermal degradation of the composite materials, which can significantly improve the thermal stability of the compounds. The protective effect of the carbon layer to the matrix resin could be confirmed from the DTG curves of the Fig. 4b. The figure showed that the  $T_{\max}$  of the retardant LLDPE were significantly higher than pure LLDPE, and the  $T_{\max}$  values of PE1, PE2 and PE3 improved from 410°C of PE0 to 482°C, 492°C and 494°C respectively. It indicated that the IFR could significantly increase the decomposition temperature of the retardant LLDPE. The addition of organic clay further enhanced the thermal stability of the composites materials, and the increase of thermal stability was more significant with the mass fraction of OMMT increased in the test range.

It's worth noting that, the presence of OMMT could make the residual carbon content of the PE2 and PE3 increased from 3.93wt% of the PE1 to about 7.72wt% and 12.3wt%. It was to say that the organic clay could play a facilitating role in charring behavior of the retardant LLDPE in the heating process. Thereby the clay could effectively improve the flame retardant properties of the compounds.

## Conclusions

The presence of the quaternary ammonium bromides in the interlayer space were confirmed by XRD and FTIR. The changes in the basal spacing suggested the quaternary ammonium bromides had been intercalated into silicate layers and it was manifested by the appearance of band corresponding to -OH stretching and C-H vibrations.

The synergistic flame retarding effect between the OMMT and IFR was investigated by means of LOI test. The addition of OMMT could produce the synergistic effect on flame-retarding. When the addition of IFR and OMMT was 30phr and 2wt% respectively, the LOI value of the compound was up to 25.2%. Through the analysis of TGA-DTG, it was proved that the barrier effect of the char layer was promoted when OMMT was added to the compounds.

The addition of OMMT could improve the mechanical properties of the compounds. When the mass fraction of OMMT was 2wt%, the tensile strength of the system increased from 8.48 MPa to 9.16 MPa, increased by 8.02%

## References

- [1] Z. Z. Wang, B. J. Qu and W. C. Fan, et al. *J. Polymer Research*, 81(1), 206 (2001).
- [2] H. M. Lim, J. Yun and M. Hyun, et al. *J. Ceramic Processing Research*, 10(4), 571 (2009).
- [3] R. Gul, A. Islam and T. Yasin, et al. *J. Polymer Research*, 121(5), 2772 (2011).
- [4] A. Okada, A. Usuki. *Macromolecular Mater & Eng*, 291(12), 1449 (2006).
- [5] T. H. Chuang, W. J. Guo and K. C. Cheng, et al. *J. Polymer Research*, 11, 169 (2004).
- [6] D. Chang, D. D. Huang and W. L. Huang, et al. *Plastics Manufacture*, 1/2, 63 (2007).
- [7] H. L. Vandersall, *J. Fire Flammability*, 2, 97 (1971).

- [8] M. Le Bras and S. Bourbigot, Fire Retardancy of Polymers-The use of intumescence, 1998: 64.
- [9] S. H. Chiu and W. K. Wang, Polymer, 39 (10), 1951 (1998).
- [10] L. Prado and C. Karthikeyan, et al. J. Non-Cryst Solids, 351 (12-13), 970 (2005).
- [11] Q. W. Mou and Tao Lin, Mater Sci, 23, 433 (2009).
- [12] Z. Chang and F. Guo, et al. Polymer, 48 (10), 2892 (2007).
- [13] H. Ma and L. Tong, et al. Appl Clay Sci, 42 (1-2), 238 (2008).
- [14] Zanetti Marco and G. C., et al. Macromolecular Rapid Commun, 22, 176 (2001).
- [15] Marco Zanetti., Kashiwagi, T., et al. Chem Mater, 14, 881 (2002).
- [16] Y. Tang and Y. Hu, et al. J. Polymer Sci Part A: Polymer Chem, 42 (23), 6163 (2004).
- [17] S. Bourbigot and M. Le Bras, et al. Fire Mater, 24, 201 (2002).
- [18] S. Bourbigot, M. Le Bras and R. Delobel, Carbon, 33, 283 (1995).
- [19] M. Bugajny, S. Bourbigot, M. Le Bras and R. Delobel, Polymer International, 48, 264 (1999).
- [20] F. Dabrowski, M. Le Bras, L. Cartier and S. J. Bourbigot, Fire Sci, 19, 219 (2001).
- [21] Y. Tang and Y. Hu, et al. Polymer International, 52 (8), 1396 (2003).