

Modified Montmorillonite and Its Application as a Flame Retardant for Polyester

Jiaoning Wang, Zhiping Mao

Key Laboratory of Science and Technology of Eco-Textiles (Ministry of Education), College of Chemistry, Chemical Engineering, and Biotechnology, Donghua University, Shanghai 201620, People's Republic of China

Correspondence to: Z. Mao (E-mail: donghuatougao@126.com)

ABSTRACT: A novel flame retardant composed of montmorillonite (MMT) and hexachlorocyclotriphosphazene (HCCP) was prepared in this study. MMT was chemically bonded with HCCP via a 3-aminopropyltriethoxysilane (KH-550) coupling agent. The structure was characterized by Fourier transform infrared spectroscopy, X-ray diffraction, and NMR. The preliminary application for improving the flame retardancy of poly(ethylene terephthalate) (PET) was investigated by means of the limited oxygen index, the vertical burning test, and thermogravimetric analysis. Scanning electron microscopy was used to investigate the morphology of the char residue. The results show that the novel flame retardant had excellent fire retardancy; that is, the sample achieved an increased UL-94 V-0 rating and limited oxygen index value of 31.5. The residue of the flame-retarded PET increased to 14.7% compared to the 6.2% value of pristine PET. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39625.

KEYWORDS: clay; flame retardance; polyesters

Received 6 December 2012; accepted 3 June 2013

DOI: 10.1002/app.39625

INTRODUCTION

As is well known, poly(ethylene terephthalate) (PET) is a very important polymer for producing high-performance engineering plastics, fibers, films, and bottles. This is because of its good mechanical properties, resistance to fatigue, high rigidity, low cost, high transparency, high processability, and moderate recyclability.¹ However, like other organic thermoplastics, the uses of PET are limited by its combustibility.^{2,3} Because PET almost totally converts to volatile fragments upon exposure to heat, providing fuel to the flame, it is a challenging task to flame-retard this polymer. Currently, the flame retardancy of PET can be improved by the addition of flame retardants, its blending with other materials, and the introduction of flame-retardant elements in its backbone. The flame-retardant systems that have been commonly used in past decades consist of a halogenated additive, most often brominated and polymeric, and an antimony source, which is the preferred synergist with halogenated flame retardants. However, their potential to corrode metal components and, more pressingly, the toxicity of the hydrogen halide formed during combustion are obvious disadvantages. These have made some governments and organizations propose restrictions on the use of halogen-containing flame retardants.^{4–6} The range of phosphorus containing flame retardants is also extremely wide, and the materials are versatile for polymers because the element exists in several oxidation states. Phosphines, phosphine oxides,

phosphonium compounds, phosphonates, elemental red phosphorus, phosphites, and phosphate are all used as flame retardants. These compounds mostly perform their flame-retardancy function in the condensed phase by increasing the amount of carbonaceous residue or char. These substances can improve the flame retardancy of PET, but their volatility and poor thermostability are their biggest drawbacks. Moreover, sometimes phosphorus flame retardants still retain some halogens, which may have synergistic effects in polymeric materials.^{7–10}

Recently, polymer/clay nanocomposites (PCNs) have attracted much attention in both scientific research and industrial exploitation.^{11,12} Numerous studies have indicated that the thermal stability of linear polymers such as PET can be improved by the introduction of layered silicate at low filler concentrations (1–5 wt %).^{11,13–17} This may be based on the fact that silicate char formed in combustion attaches to the polymer surface and protects the polymer matrix; this slows the mass loss rate of the degradation products; the layers also probably work as heat-insulating layers to impart flame retardancy to materials.^{12,18} Although clay minerals can improve the thermal stability of composites, naturally hydrophilic clay minerals are immiscible with the hydrophobic polymer matrix; therefore, other components containing flame-retardant elements should be added to improve the compatibility between clay minerals and organic polymers and further improve the flame resistance of polyester.

In this study, hexachlorocyclotriphosphazene (HCCP), with skeletal nitrogen and phosphorus atoms, was introduced to modify montmorillonite (MMT). The unusual thermal properties, including the flame retardancy and self-extinguishability, obtained when cyclotriphosphazenes are incorporated into the chain structure of thermoplastics can increase the thermal and flame resistance of the polymers.¹⁹ The extreme reactivity of the six reactive chlorine atoms in HCCP toward nucleophilic substitution can be used to introduce a number of functional groups for conversion into the required compound. To make MMT and HCCP chemically bond, a silane coupling agent (KH-550) was recommended to connect them. Together with MMT and HCCP, a novel flame retardant was prepared to impart PET with excellent flame retardancy.

EXPERIMENTAL

Materials

HCCP, which was recrystallized twice from petroleum ether before use, was provided by Zibo Lanyin Chemical Co., Ltd. (Shandong, China). Sodium montmorillonite (Na^+ -MMT) was supplied by Zhejiang Fenghong Clay Chemical Co., Ltd. (Zhejiang, China). The silane used in this research was KH-550 and was obtained from Shanghai Yuanye Biotechnology, Ltd. Pristine PET chips were supplied by Sinopec Yizheng Chemical Fiber Co., Ltd. (Jiangsu, China). Absolute ethyl alcohol, tetrahydrofuran (THF), and triethylamine (TEA) were all purchased from Shanghai Chemical Reagents Corp. (Shanghai, China).

Preparation of Modified MMT with HCCP

This preparation was divided into two steps: the first one was the preparation of the organic MMT grafted with KH-550 [organic montmorillonite (OMMT)], and the other was the preparation of the modified MMT by HCCP through a substitution reaction (OMMT-HCCP)

Preparation of OMMT.

1. MMT (3 g) was dispersed in a 200-mL mixture solution of ethanol and water (75/25) and then stirred vigorously for 2 h to make MMT disperse completely in the solvent.
2. KH-550 (2 g) was introduced into the aforementioned mixture and stirred at reflux temperature for 6 h.
3. The resulting product was washed with the mixture of ethanol and water to remove the residual KH-550 and dried overnight at 60°C in a vacuum oven. It was then ground into a fine powder (10–20 μm) to obtain the OMMT.
4. The used ethanol/water solvent was collected in a flask for recycling.

Preparation of OMMT-HCCP.

1. OMMT (3 g) was dispersed in THF solution (200 mL) and then stirred vigorously for 2 h to make it disperse completely into the solvent.
2. HCCP (2 g) and TEA (1 g), as the binding acid agent, were introduced into the aforementioned mixture and stirred at reflux temperature for 8 h.
3. The resulting product was washed with THF solvent to remove the residual HCCP and TEA and then washed with

water to remove triethylamine hydrochloride. The filtered cake was dried overnight at 60°C in a vacuum oven and then ground into a fine powder (10–20 μm) to obtain the product OMMT-HCCP. The structure is shown in Scheme 1.

4. The used solvent of THF was collected in a flask for recycling.

Preparation of PET Flame-Retardant Materials: PCNs. The samples were prepared by the mixture of the new flame retardant (OMMT-HCCP) and PET in a torque rheometer (Haake RC90, Haake Co., Germany) at a temperature of 280°C for 8 min. The amount of OMMT-HCCP used was 3% of the total quantity. The blended materials were then pressed on a miniaturized injection-molding machine (SZ-5-Q, Dehong Rubber and Plastic Machinery Co., Ltd.) at 275°C to produce sheets with various dimensions and were recorded as PET/OMMT-HCCP material, which was used in all of the tests. With the same process, two other samples were prepared from pristine PET and 3% MMT into PET for comparison and were recorded as pristine PET and PET/MMT materials, respectively.

Characterization

Fourier transform infrared (FTIR) spectra pellets of the samples (KBr) were recorded on a Varian 640 FTIR spectrometer (Agilent Technologies) at room temperature (25°C). The samples were scanned 32 times over the spectral range 4000–400 cm^{-1} with a nominal resolution of 4 cm^{-1} .

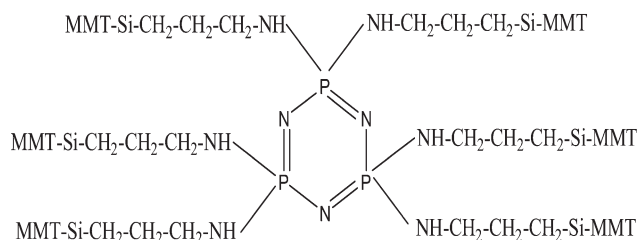
The X-ray diffraction (XRD) study was performed with a D/Max-2550 PC system diffractometer (Rigaku Corp., Japan) with Cu K α radiation under a target voltage of 40 kV and a current of 100 mA ($\lambda = 0.154 \text{ nm}$). The basal spacing (d) was calculated with the following equation:

$$d = \lambda / 2 \sin \theta$$

where λ is the wavelength of the X-ray radiation (0.154 nm for Cu) and θ is diffraction angle.

Solid-state ^{13}C -NMR and ^{31}P -NMR spectra were measured on a Bruker Avance 400 NMR spectrometer (Bruker Corp., Germany).

The thermogravimetric analysis (TGA) of MMT and the grafted products were performed on a TG 209 F1 thermobalance (Netzsch-Gerätebau GmbH) in a dry nitrogen atmosphere flow (30 mL/min). The weight of the samples was kept within 3–5 mg. The samples were heated at ambient temperature of 800°C at a heating rate of 10°C/min. The same operation was used for



Scheme 1. OMMT-HCCP.

the pristine PET, PET/MMT, and PET/OMMT-HCCP materials.

The flame retardancy of all of the samples was characterized by the limited oxygen index (LOI) and UL-94 vertical burning test. The LOI data of all of the samples were obtained at room temperature on an ATS 1004050 FAA oxygen index instrument produced by ATSSFAAR Industries (Italy) according to ISO4589-1984. LOI is a parameter for evaluating the flame retardancy and flammability of polymeric materials under the same conditions. It denotes the lowest volume concentration of oxygen sustaining the candle burning of materials in mixed gases of nitrogen and oxygen. Generally, materials with an LOI value of greater than 26 can be considered to have flame retardancy.²⁰ The vertical burning rates of all of the samples were evaluated on an XMC-2 instrument produced by Xinma Analysis Instrument Factory (Shandong, China) according to UL-94. UL-94 is another common testing method for flame retardancy; the test results are classified by burning ratings of V-0, V-1, or V-2. A V-0 rating presents the best flame retardancy of polymeric materials.

Scanning electron microscopy (SEM) analysis was carried out with a T-1000 scanning microscope (Hitachi). All of the sample surfaces studied were sprayed with gold to prevent charging under the electron beam.

Transmission electron microscopy (TEM) photographs of the composites were obtained on a JEM-2100F electron microscope (JEOL, Japan) operated at an accelerating voltage of 200 kV. The PET composites were microtomed into layers with thicknesses of about 60 nm.

The tensile strength and elastic modulus of the extruded strands were measured with a universal electronic tensile machine (Dongguan, China) at a tensile rate of 20 mm/min according to ASTM D 412. A grip length of 50 mm, and a full-scale load of 1000 N were set.

RESULTS AND DISCUSSION

FTIR Analysis

Successful synthesis was evident in the IR spectra, as shown in Figure 1. Figure 1(A)(a–c) corresponds to MMT, OMMT, and OMMT-HCCP, respectively. In a comparison of Figure 1(A)(a) and Figure 1(A)(b), the two new peaks at 2933 and 2886 cm^{-1} in curve b correspond to the $-\text{CH}_2-$ asymmetric and symmetric stretching vibrations, respectively, from KH-550; this implies that KH-550 was successfully grafted onto MMT. Similarly, from the characteristic peaks at 1208 and 886 cm^{-1} , appearing in Figure 1(A)(c) and corresponding to the $-\text{P}=\text{N}-$ and $-\text{P}-\text{N}-$, respectively, we reasonably assumed that the reaction between HCCP and OMMT was successfully accomplished. Furthermore, the characteristic absorption peaks of MMT, such as the peak at 1034 cm^{-1} corresponding to the stretching vibration of Si–O bonds and the peaks between 600 to 400 cm^{-1} corresponding to the bending vibrations of Si–O and Al–O bonds showed no change in the spectra. This phenomenon also showed that the grafting reaction did not change the MMT's characteristic groups. The method used here for synthesizing organic MMT not only successfully grafted small organic mole-

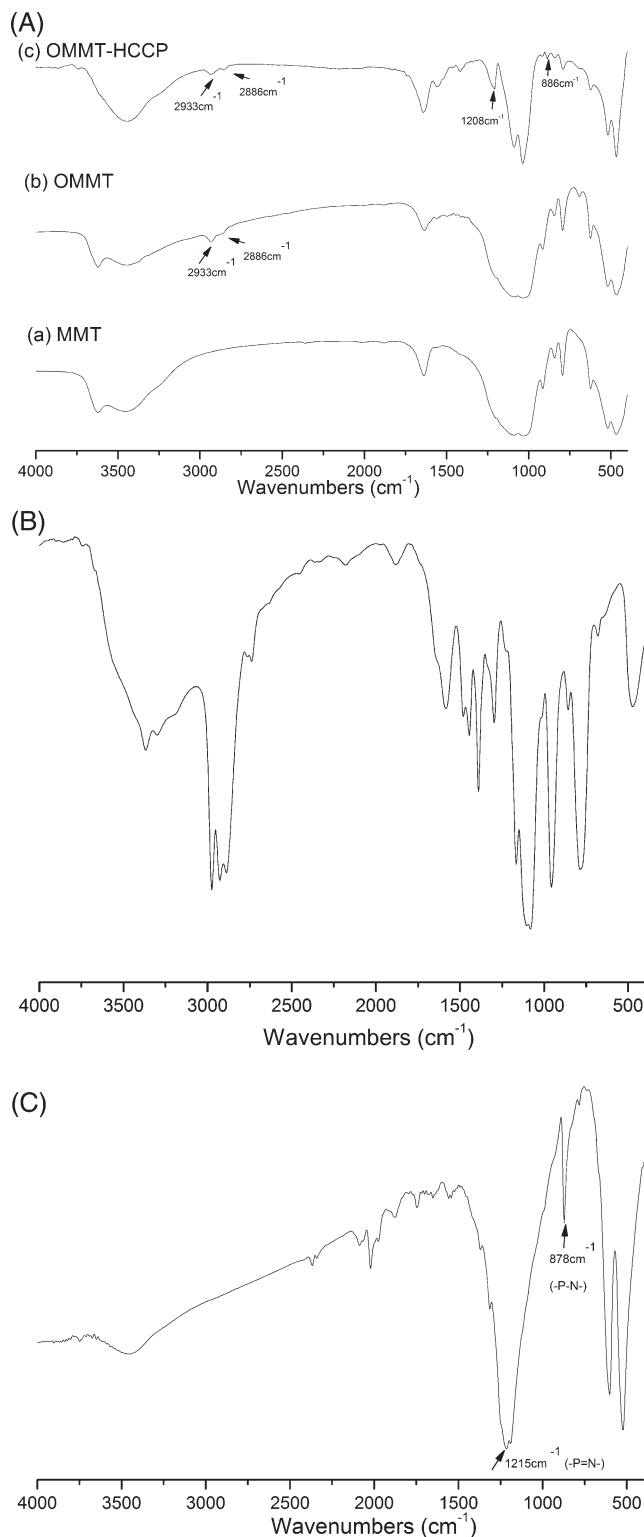


Figure 1. FTIR spectra of the (A) MMT, (b) OMMT, and (c) OMMT-HCCP and (B) KH-550 and (C) twice-recrystallized HCCP.

cules onto MMT but also reserved the intrinsic properties of MMT. For comparison purposes, the FTIR spectra of KH-550 and twice-recrystallized HCCP are given in Figure 1(B) and Figure 1(C), respectively.

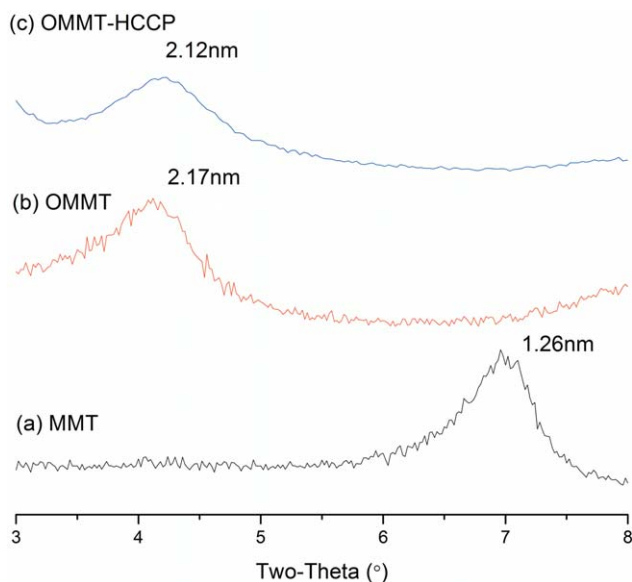


Figure 2. XRD patterns of the (a) MMT, (b) OMMT, and (c) OMMT-HCCP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

XRD Study

With the grafting of silane onto MMT, the expansion of the interlayer space was demonstrated by XRD. The XRD patterns of the MMT before and after grafting are shown in Figure 2. The basal spacing of $d(001)$ for Na^+ -MMT was 1.26 nm; this is the characteristic $d(001)$ value of Na^+ -MMT as reported in literature.^{21,22} From the figure, it was evident that in the presence of KH-550, d of the KH-550-grafted MMT was obviously bigger than that of MMT. After the grafting reaction, $d(001)$ increased from 1.26 to 2.17 nm; this indicated that the silane was also intercalated into the interlayer space. In combination with the FTIR analysis, we concluded that under these conditions, not only did KH-550 graft onto MMT, but it was also intercalated into MMT's interlayer spaces. The layered structure of MMT swelled in the solvent;^{23–25} thus, KH-550 easily dissolved into the solvent, entered into the interlayer or surface of MMT, and was adsorbed in it. It then reacted with the hydroxyl groups in the layers; thus d increased significantly. The test also showed that $d(001)$ before and after the reaction with HCCP showed almost no change, probably because the small-molecule phosphazene could not increase it further. The increase in d was a favorable condition for the next material blending.

NMR Study

To further confirm that the silane coupling agent KH-550, containing carbon, was successfully grafted onto MMT, solid-state ^{13}C -NMR spectra were obtained for MMT and OMMT. There was no signal for carbon in the spectrogram of the MMT sample, but we gladly found that there were three peaks at 43.6, 23.2, and 12.0 ppm, respectively, in the spectrogram of the OMMT sample [Figure 3(A)]. The results further illustrate that the KH-550 was successfully grafted onto MMT.

Similarly, HCCP was successfully bonded with OMMT, as judged from the solid-state ^{31}P -NMR spectra test of OMMT

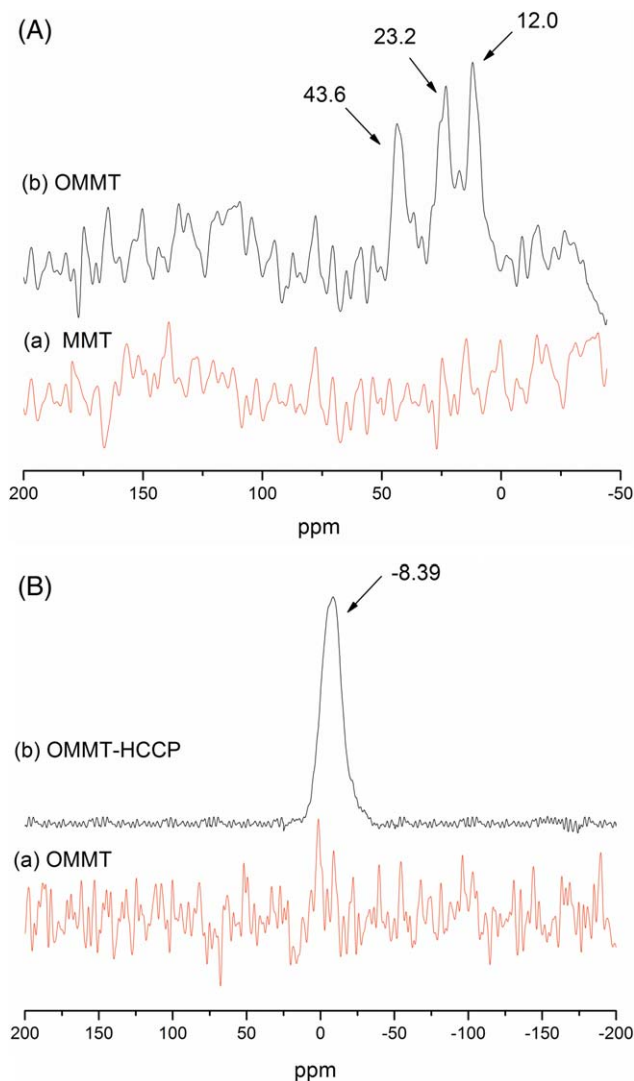


Figure 3. (A) ^{13}C -NMR spectra of the MMT and OMMT and (B) ^{31}P -NMR spectra of the OMMT and OMMT-HCCP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and OMMT-HCCP. The results show that there was no peak in the OMMT spectrogram, but a new peak at -8.39 ppm appeared in the OMMT-HCCP spectrogram [Figure 3(B)]. As it is well known, the chemical shift of phosphorus in HCCP was near 20 ppm. The change in the chemical shift for phosphorus proved that the substitution reaction took place smoothly, and the flame-retardant OMMT-HCCP was successfully synthesized.²⁶

TGA of MMT, OMMT, and OMMT-HCCP

TGA was used as a simple method for judging the thermal stability of the products and measuring the contents of silanes, physisorbed water, and HCCP.²⁷ The thermal stability of MMT, OMMT, and OMMT-HCCP is graphically shown in Figure 4.

For MMT [Figure 4(a)], the thermal degradation process was separated into two steps: One step was the first mass loss in the thermograms before 100°C , which was the exhaustion of the physisorbed water in the interlayer space of MMT; the other

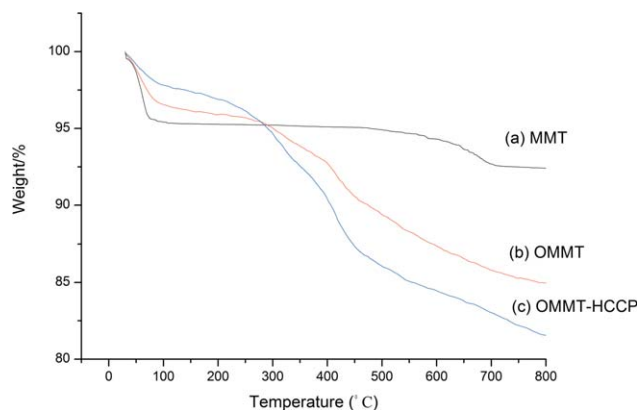


Figure 4. TGA thermograms of the (a) MMT, (b) OMMT, and (c) OMMT-HCCP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

step was the second mass loss in the thermograms from 460 to 700°C, which was the thermal degradation of the —OH group in the crystal layer of MMT. The amount of physisorbed water was calculated from the curve, and the value was about 5%.

Through a comparison of Figure 4(b,c) with Figure 4(a), we found that there were significant differences in the thermal properties between MMT, OMMT, and OMMT-HCCP. The first mass loss in the thermograms before 100°C, which was the exhaustion of the physisorbed water in the interlayer space, was about 3% for OMMT and about 2% for OMMT-HCCP. The reason for the reduction of physisorbed water was probably because part of KH-550 or HCCP entered the galleries of MMT and expelled the interlayer space water there. Above all, attention had to be paid to the second step from 100 to 460°C in the thermograms (curves b and c); these were not reflected in the degradation process of MMT. In this process, the mass loss increased dramatically for OMMT and OMMT-HCCP compared to MMT; this indicated that KH-550 was grafted onto MMT and also that HCCP was grafted onto OMMT. In addition, the physisorbed water was largely excluded; this illustrated that the hydrophobic agents mainly entered the galleries of MMT and expelled the interlayer space water there. The increase in *d* obtained from the XRD study was the best proof for this viewpoint. The third step, which was from 460 to 800°C in the thermograms, was also different from MMT in mass loss because the thermal degradation of small organic molecules still happened in this step. From the graph, it was clear that the residue of OMMT-HCCP was about 81.5%.

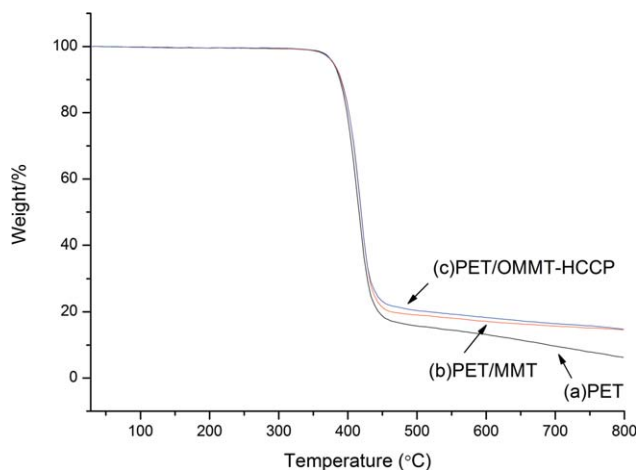


Figure 5. TGA curves of the (a) pristine PET, (b) PET/MMT, and (c) PET/OMMT-HCCP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Flame Retardancy of PET Materials Blended with MMT and OMMT-HCCP

Table I gives the LOI and UL-94 data of the PET flame-retardant materials blended with MMT and OMMT-HCCP, respectively. In a comparison of samples 2 and 1, the LOI value increased from 24 to 28.5 and achieved a V-2 rating in the UL-94 test. This phenomenon demonstrated that the clay mineral could improve the thermal stability of the polymers and slow burning because of a barrier layer formed by MMT, which hindered the diffusion of gases.²⁸ As shown in Table I, OMMT-HCCP played an important role in improving the flame retardancy of PET. A small content of OMMT-HCCP greatly increased their LOI values to more than 30. Furthermore, Table I indicates that OMMT-HCCP also improved the UL-94 rate of PET. The PET sample with an OMMT-HCCP content of 3% exhibited a scarcely dripping behavior during flame ignition and reached a UL-94 V-0 rating. A worthy point of attention from this research was the flame combustion time of our samples, whereby the flame combustion time for almost all of the samples containing additives was 3 s, particularly in the PET blends with 3% OMMT-HCCP. The excellent flame retardancy of OMMT-HCCP originated from its flame-retardant synergy effect of phosphorus and nitrogen and the unique nature of MMT. Here, phosphorus and nitrogen worked as flame-retardant elements to dilute the concentration of flammable gas

Table I. Flame Retardancy of the PET Materials Blended with Different Additives

Sample	Materials	LOI (%)	UL-94 test					UL-94 rating
			First ignition (s) ^a	Was the cotton ignited?	Second ignition (s) ^a	Was the cotton ignited?	Did it burn out?	
1	Pristine PET	24.0	—	Yes	—	—	Yes	—
2	PET/MMT	28.5	3.0	Yes	3.0	Yes	No	V-2
3	PET/OMMT-HCCP	31.5	3.0	No	1.0	No	No	V-0

^a Time to self-extinguishing after ignition.

Table II. TGA Data for All of the Material Samples

Sample	Materials	Temperature (°C)			Residue (%)		
		T_5	T_{50}	T_{max}	450°C	600°C	800°C
1	Pristine PET	379.0	416.0	414.1	18.8	13.1	6.2
2	PET/MMT	379.8	419.1	417.5	21.4	17.1	14.4
3	PET/OMMT-HCCP	378.7	419.3	419.5	23.1	18.3	14.7

produced during the combustion process and decreased the heat release of the composite. MMT worked as a heat-insulating layer to impart flame retardancy to the materials. Together, they improved the thermal stability of the materials.

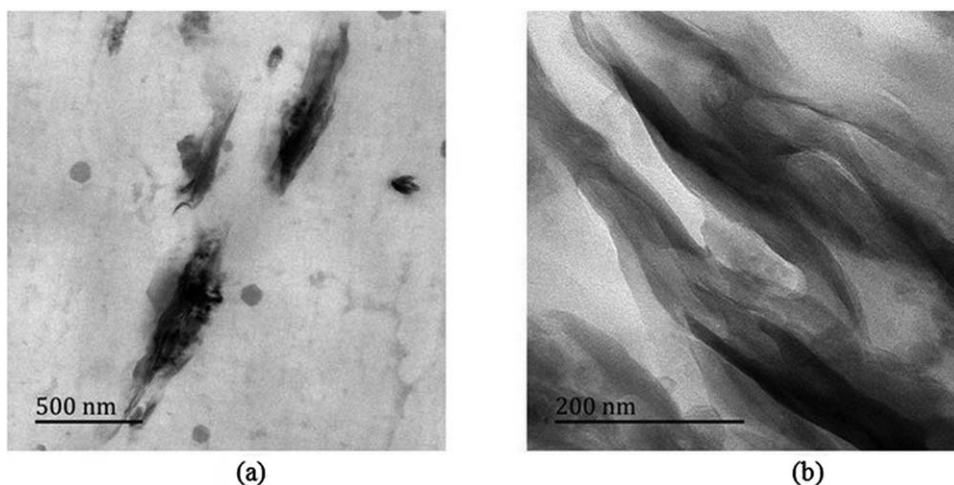
Comparison of the TGAs of PET Materials Blended with MMT and OMMT-HCCP with the TGA of Pristine PET

TGA was also used to investigate the thermal stability of the materials. The results are shown in Figure 5 and Table II. Here, T_5 and T_{50} are defined as the temperatures at which 5 and 50% weight loss occurred, respectively, and T_{max} is the temperature at maximum weight loss rate. From the results shown in Figure 5, we found that pristine PET started decomposing around 379°C (T_5), and 18.8% was left when it was heated to 450°C. Its residual mass was 6.2% when it was heated to 800°C. The thermal degradation process of PET was very complicated and was studied previously.^{29,30} Figure 5 shows that the TGA curve of PET/MMT or PET/OMMT-HCCP was similar to that of PET. It was found, from Table II, that among the three samples, T_5 showed only a little change. The thermal behavior of the composites in a nitrogen atmosphere indicated that the addition of MMT or OMMT-HCCP did not change the initial thermal degradation process of the polyester because of the catalysis effect of water in MMT (bound or from dehydroxylation) and hydroxyl groups on the clay mineral platelets.^{13,31–33} Then, as the temperature increased, the weight loss rate also increased rapidly. Here, the weight loss range of 50% and T_{max} was selected to calculate the degradation reaction rate. The degradation reaction rates of the PET/MMT and PET/OMMT-HCCP composites were slower than that of pristine PET because of the

clay mineral barrier effect. Similar results were reported by Xu et al.³⁴ In particular, we were delighted to find that a high amount of residue for the PET/MMT and PET/OMMT-HCCP composites was obtained in the experiment. The amount of residue was as high as 14.7% for the PET/OMMT-HCCP composites when the temperature reached 800°C and only 6.2% for pristine PET. With the residual amount of MMT in the composite deducted, the char residue was about 12.3%. At this point, the clay mineral layers played an important role in hindering the diffusion of volatile degradation products on PET degradation and contributed to the enhancement of the thermal stability of the composites.^{35,36} The result that almost the same amount of residue of the PET/MMT and PET/OMMT-HCCP materials was obtained under the condition of the same amount of MMT in the materials illustrated this point. It is worth noting that HCCP played an important role in improving the LOI value and UL-94 rating, as confirmed earlier.

TEM Results for the Prepared Composites

TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization. The dispersion state of OMMT-HCCP inside the PET matrix was observed via TEM, as shown in Figure 6. The light gray areas are the PET matrix, and the darker regions are made up of dispersed OMMT-HCCP layers. Figure 6(a) shows that the agglomeration of clay still existed, but in most cases, their width was about 50–150 nm. At a higher magnification, it was clear that a black filamentous structure, namely, intercalated silicate layers, was present, as shown in Figure 6(b). This indicated the

**Figure 6.** TEM micrographs of the composites at different magnification levels.

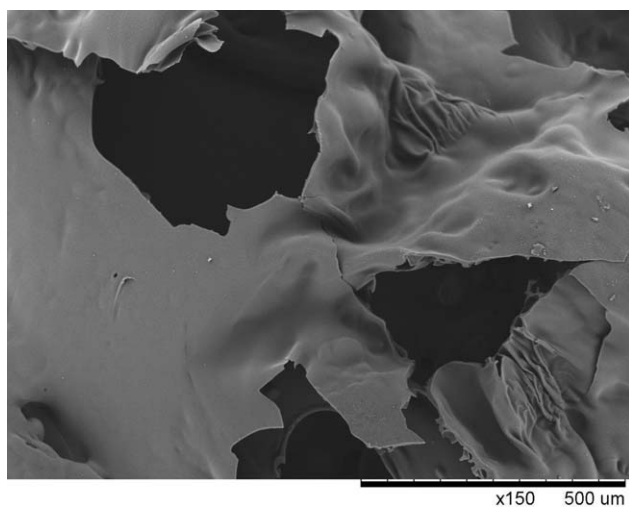


Figure 7. SEM images of the pristine PET char crusts.

intercalation of PET molecular chains into the layered silicate structure. Combined with XRD analysis, the TEM results suggested that melt blending could be used in the preparation of intercalating-type PCNs.

SEM Analysis of the Char Residues

Figure 7 shows that the charred surface layer of the pure PET was very thin, and the holes were all large, with diameters in the range 150–500 μm . Compared with that of pure PET, the char layer structure of PET/OMMT–HCCP was not similar; it was more consistent, and the char crust was very thick [Figure 8(a,b)]. The holes had diameters of 20 μm or less. This char crust not only reduced the rates of formation of volatile gases but also provided a barrier to heat and flame penetration into the inner layers of the material; thereby, it resisted the initiation and spreading of the fire. In general, OMMT–HCCP in a PET matrix played a more active role in retarding condensed-phase flames and in this way inhibited flame propagation.³⁷

Mechanical Properties of the Prepared Composites

Finally, to investigate whether the mechanical properties of the PET composites were greatly changed, stress–strain curves of the pristine PET and PET/OMMT–HCCP composite were researched. The tensile strength and elastic modulus of the composites were measured, and the results are shown in Table III.

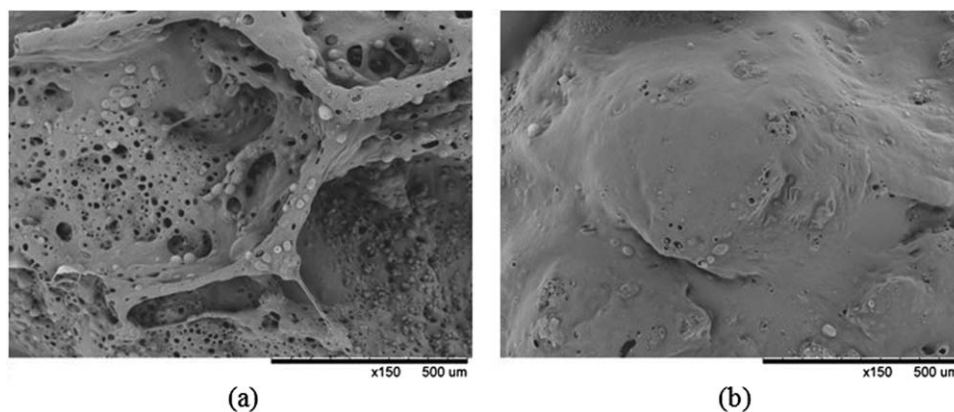


Figure 8. SEM images of the PET/OMMT–HCCP char crusts: (a) inner and (b) outer.

Table III. Tensile Strength and Elastic Modulus Values of the PET and PET/OMMT–HCCP Composites

Materials	Tensile strength (MPa)	Elastic modulus (MPa)
Pristine PET	29.3	755.0
PET/OMMT–HCCP	28.8	785.0

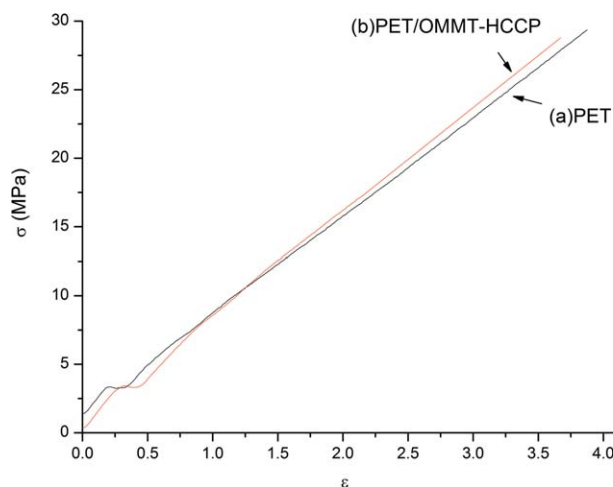


Figure 9. Stress (σ)–strain (ε) curves of the (a) pristine PET and (b) PET/OMMT–HCCP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The data in the table are the averages of five parallel tests. One of the curves is shown in Figure 9. We found that the tensile strength and elastic modulus values of the prepared composites were close to those of the pristine PET. That is, the mechanical properties of the prepared composites were stable, despite the additives.

CONCLUSIONS

In this article, we presented a new method for modifying MMT by HCCP, whereby MMT was chemically bound with HCCP via a silane 3-aminopropyltriethoxysilane (KH-550) coupling agent. The OMMT–HCCP product was obtained, and its application as a flame retardant for PET polyester was preliminarily

researched. PET containing 3% flame retardant had excellent flame retardancy; that is, it achieved a UL-94 V-0 rating and an LOI value of 31.5. The residue was up to 14.7% when the temperature reached 800°C. This study confirmed that MMT modified by phosphazene was an effective flame retardant for polyester. Future work will focus on the investigation of the flame-retardant mechanism and the effect on other properties of the flame-retardant materials.

REFERENCES

1. Bikiaris, D. *Thermochim. Acta* **2011**, 523, 25.
2. Wang, Y. Z.; Chen, X. T.; Tang, X. D.; Du, X. H. *J. Mater. Chem.* **2003**, 13, 1248.
3. Ban, D. M.; Wang, Y. Z.; Yang, B.; Zhao, G. M. *Eur. Polym. J.* **2004**, 40, 1909.
4. Nelson, G. L. *The Fire Retardant Chemicals Association (FRCA)* **1994**, 135.
5. Stevens, G. C.; Mann, A. H. Department of Trade and Industry (DTI) Report; London, **1999**.
6. Li, S. M.; Yuan, H.; Yu, T.; Yuan, W. Z.; Ren, J. *Polym. Adv. Technol.* **2009**, 20, 1114.
7. Annakutty, K. S.; Kishore, K. *J. Sci. Ind. Res.* **1989**, 48, 479.
8. Edward, D. W.; Sergei, V. L.; Maney, R.; Zhu, W. M. *Phosphorus Sulfur* **1994**, 144, 17.
9. Joseph, G. *J. Fire Sci.* **1994**, 12, 388.
10. Wu, Q.; Lu, J. P.; Qu, B. *J. Polym. Int.* **2003**, 42, 1326.
11. Giannelis, E. P. *Adv. Mater.* **1996**, 8, 29.
12. Suprakas, S. R.; Massami, O. *Prog. Polym. Sci.* **2003**, 28, 1539.
13. Qin, H. L.; Su, Q. S.; Zhang, S. M.; Zhao, B.; Yang, M. S. *Polymer* **2003**, 44, 7533.
14. David, J. C.; Arquetina, A. L. *Chem. Mater.* **2005**, 17, 13.
15. Alexander, B. M. *Polym. Adv. Technol.* **2006**, 17, 206.
16. Nazaré, S.; Kandola, B. K.; Horrocks, A. R. *Polym. Adv. Technol.* **2006**, 17, 294.
17. Pluta, M.; Jeszka, J. K.; Boiteux, G. *Eur. Polym. J.* **2007**, 43, 2819.
18. Si, M. Y.; Vladimir, Z.; Michael, G.; Anatoly, F.; Dennis, G. P.; Edward, W.; Jonathan, C. S.; Miriam, H. R. *Polym. Degrad. Stab.* **2007**, 92, 86.
19. Roger, D. J.; Mario, G. *Prog. Polym. Sci.* **1998**, 23, 179.
20. Cullis, C. F.; Hirschler, M. M. *Eur. Polym. J.* **1984**, 20, 53.
21. He, H. P.; Jannick, D.; Jocelyne, G.; Jean, F. G. *J. Colloid Interface Sci.* **2005**, 288, 171.
22. Ray, L. F.; Llew, R. *Appl. Clay Sci.* **1996**, 11, 171.
23. Karaborni, S.; Smit, B.; Heidug, W. *Science* **1996**, 271, 1102.
24. David, E. S. *Langmuir* **1998**, 14, 5959.
25. Ahmed, R.; Nehal, S. *Mater. Sci. Eng. A* **2005**, 399, 368.
26. Alexey, S. B.; Paul, H.; Paul, G. H. *J. Inorg. Organomet. Polym.* **2010**, 20, 395.
27. Satu, E. K.; Andrew, R.; Marko, P.; Lauri, N. *Thermochim. Acta* **2001**, 379, 201.
28. Alexander, B. M. *Polym. Adv. Technol.* **2006**, 17, 206.
29. Dzieciol, M.; Trzeczczynski, J. *J. Appl. Polym. Sci.* **1998**, 69, 2377.
30. Saha, B.; Maiti, A. K.; Ghoshal, A. K. *Thermochim. Acta* **2006**, 444, 46.
31. Rick, D. D.; Jeffery, W. G.; David, L. V. *Polym. Degrad. Stab.* **2003**, 79, 111.
32. Xie, W.; Gao, Z. M.; Pan, W. P.; Hunter, D.; Singh, A.; Vaia, R. *Chem. Mater.* **2001**, 13, 2979.
33. Qin, H. L.; Zhang, Z. G.; Feng, M.; Gong, F. L.; Zhang, S. M.; Yang, M. S. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, 42, 3006.
34. Xu, X. F.; Ding, Y. F.; Wang, F.; Wen, B.; Zhang, J. H.; Zhang, S. M.; Yang, M. S. *Polym. Compos.* **2010**, 31, 825.
35. Qin, H. L.; Zhang, S. M.; Zhao, C. G.; Hu, G. G.; Yang, M. S. *Polymer* **2005**, 46, 8386.
36. Xu, X. F.; Ding, F. F.; Qian, Z. Z.; Wang, F.; Wen, B.; Zhou, H.; Zhang, S. M.; Yang, M. S. *Polym. Degrad. Stab.* **2009**, 94, 113.
37. Zhang, J. J.; Ji, Q.; Zhang, P.; Xia, Y. Z.; Kong, Q. S. *Polym. Degrad. Stab.* **2010**, 95, 1211.