

In Situ Synthesis and Characterization of Polypropylene/Polyvinyl Acetate-Organophilic Montmorillonite Nanocomposite

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ABSTRACT: A novel polymer-nanoclay hybrid nanocomposite based on polyvinyl acetate (PVAc)-organophilic montmorillonite (OMMT) has been reported via an *in situ* intercalated polymerization technique. The hybrid material was synthesized by one-step emulsion polymerization of vinyl acetate in the presence of OMMT using polyvinyl alcohol as the stabilizing agent. The intercalated polymerization was characterized by X-ray diffraction (XRD). The XRD patterns show that the interlayer spacing of OMMT after polymerization increased from 2.64 to 3.78 nm, indicating that the large macromolecular chain of PVAc was formed in the OMMT interlayer space. The Fourier transform infrared spectrum showed the characteristic absorption of PVAc in the OMMT particles separated from the nanocomposite, and the position of peaks shifted to high wave numbers. This showed that there was an interaction between PVAc and OMMT nanoparticles. A two-fold blend composed of PVAc-nano-OMMT/PP was prepared by the melt-blending technique. XRD and transmission

electron microscopy images of the PVAc-nano-OMMT/PP composite further confirmed the formation of a partially delaminated nanocomposite structure. Thermogravimetry results showed that the thermal stability of PVAc-nano-OMMT/PP was greater than that of either polypropylene (PP) or Nano-OMMT/PP blend. PVAc-nano-OMMT/PP had better toughness, as the mass fraction of OMMT was 5 wt %. The flame retardancy of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP composites was also studied. According to the limiting oxygen index (LOI) data and Cone calorimeter test, the addition of PVAc-OMMT resulted in higher LOI and lower heat release rate, effective heat of combustion, smoke release course, and better flame retardancy and barrier properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4107–4113, 2012

Key words: *in situ* intercalative polymerization; nanocomposite; thermal stability; mechanical property; flame retardancy

INTRODUCTION

Recently, polymer layered-silicate nanocomposites (PLSNs) have received significant attention because the mutual interactions between polymer and clay are considered to affect their properties. By comparison with conventional microcomposites, greatly improved physical and mechanical characteristics were found for hybrids based on thermoplastic matrices containing a nanoscale dispersion of layered silicates.^{1–3} High moduli,^{4–7} increased strength and heat resistance,⁸ decreased gas permeability^{9–13} and flammability,¹⁴ and increased biodegradability of biodegradable polymers can be obtained at much lower loads of the inorganic compound, hence decreasing the production costs significantly.¹⁵ In practice, the

most commonly used 2 : 1 layered silicates are: montmorillonite, hectorite, and saponite. Montmorillonite (MMT) is a hydrated alumina-silicate clay composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The silicate layers of MMT are planar, stiff, about 1 nm in thickness, and about 200 nm in length. In nature, MMT clays do not occur as isolated individual units but as crystalline structures (also known as tactoids) formed by aggregation.^{16–18}

The efficiency of the MMT dispersion in a polymer matrix depends strongly on the clay's affinity toward the macromolecular chains and, also, on the MMT tactoid sizes. The hydrophilic nature of the MMT surface impedes their homogeneous dispersion in highly hydrophobic polymer phases. One option to circumvent this drawback is to convert the silicate surface to an organophilic character, by ion-exchange reactions with cationic surfactants. The modified MMT is called organophilic montmorillonite (OMMT).

Polypropylene (PP) is an important polymer due to its low density, high water and chemical resistance,

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easy processability, and cost-effectiveness. It has been widely used in home furnishings, construction, electrical appliances, and so on. However, due to the shortcomings of its lower permeability to organic solvents, brittleness, and poor low-temperature impact resistance, as well as poor compatibility with other polar polymers and inorganic filler materials,¹⁹ its applications have been restricted to structural materials and engineering plastics. To improve the toughness of PP, it is generally blended with rubber or elastomers. These types of modified materials have greatly improved toughness; however, the simultaneous loss of rigidity of PP is much more significant. In view of excellent heat-resistance, good mechanical properties, and high barrier performances of PLSNs, it is hypothesized that the addition of PLSNs to PP can overcome the limitations of the material and broaden its applications.

In this work, we try to introduce polyvinyl acetate (PVAc) into OMMT system to improve interface compatibility between OMMT and PP matrix using good binding capacity of vinyl acetate (VAc) polar groups and OMMT. First, the intercalated polymerization of VAc into the layers of OMMT was initiated *in situ* via emulsion polymerization to prepare PVAc-OMMT hybrid, then a two-fold blend composed of PVAc-nano-OMMT/PP was prepared by the melt-blending technique. By means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), thermogravimetry analysis (TGA), and cone calorimeter (CONE), the structure and the thermal, mechanical, flame retardant properties of the obtained nanocomposites were characterized and investigated. And with the comparative studies of pure PP and Nano-OMMT/PP two systems. Thus, to provide a new thinking and trying for further research and development of new polymer/montmorillonite nanocomposites.

EXPERIMENTAL

Materials

Polypropylene (PP, T30S) was purchased from China Dalian West Pacific Petrochemical Co., and organic modified montmorillonite (OMMT, 1.44P, modifier: Dioctadecyl Dimethyl Ammonium Chloride) was provided by American Nanocor Corporation. Polyvinyl alcohol (PVA, 1750) was purchased from China Medicine Group Shanghai Chemistry Reagent Company. VAc was a commercial product obtained from China Tianjing Ruijinte Chemical Co. Sodium dodecyl sulfate (SDS) was obtained from China Shanghai QianChen Chemical Co. Ammonium persulfate (APS) was purchased from China Tianjin Yongda Chemistry Reagent Company. Antioxidant (B215) was an industrial product obtained from China Beijing JiYi Chemical Co.

Sample preparation

Preparation of PVAc-OMMT nanocomposite

OMMT (40 g) was highly dispersed in water (60 g) by vigorous stirring at 60°C for 0.5 h, then 100 g of PVA 10% solution, monomer (VAc, 50 g), and emulsifier (2.0 g SDS) were added into the OMMT-PVA suspension and stirred for 1 h at 200 rpm. Then, an initiator (0.2 g APS) was added to the suspension and polymerization was performed at 72°C for 6 h. After polymerization was completed, the reaction mixture was dried in vacuum at 80°C for 24 h and then ground. Then, PVAc-OMMT composite was obtained, in which the MMT mass fraction was 38%. The PVAc homopolymer was obtained in a similar way without OMMT.

Preparation of PVAc-nano-OMMT/PP composite

To prepare PVAc-nano-OMMT/PP composite, PP (155 g) was first added to a preheated two-roller mill and was allowed to melt at 170°C. PVAc-OMMT (23 g) and antioxidant B215 (2 g) were then added to the two-roller mill. After being mixed for 15 min, the blends were molded under compression at 180°C for 3 min and cooled to room temperature. As a control, Nano-OMMT/PP composite was also prepared following the same procedure (OMMT mass fraction: 5 wt %).

Characterization and performance testing

X-ray diffraction

The samples of OMMT, PVAc-OMMT, Nano-OMMT/PP, and PVAc-nano-OMMT/PP were fully dried and then scanned continuously with a scanning rate of 2°/min from 1° to 10° by a DMAX/III A power X-Ray diffractometer (Rigaku Corporation, Japan) using a Cu target at the tube voltage of 30 kV and tube current of 30 mA.

Fourier transform infrared spectroscopy

A Shimadzu FTIR-8400S was used for the infrared spectrometer test. The samples of PVAc, OMMT, and PVAc-OMMT were mixed and ground with KBr powder, then pressed to the tablet. The absorption peak position from infrared test spectra was used to judge the material structure and composition.

Transmission electron microscopy

TEM images of Nano-OMMT/PP and PVAc-nano-OMMT/PP were performed with a Netzsch EM400 TEM using an accelerator voltage of 120 keV. The samples were sliced with a diamond ultramicrotome

knife into 30 nm sections and analyzed without additional staining.

Thermogravimetry analysis

The TG analysis of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP was performed using a TG 209F1 thermogravimeter (Netzsch, Germany) at a heating rate of 10°C/min from 40°C to 700°C under nitrogen atmosphere.

Mechanical testing

The tensile strengths of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP samples were measured by a WAW-300 electronic universal testing machine (Guangzhou Test Instrument Factory, China) at a crosshead speed of 50 mm/min at room temperature. The tensile test was in accordance with the GB/T 1040.2—2006 standard by using samples shaped like a 4 mm-thick dumbbell. The bending strength was measured at a crosshead speed of 2 mm/min according to the GB/T 9341—2008 standard in the same machine. The notched Izod impact strength was measured by German Zwick B5113.300 Impact Tester according to the GB/T 1843—2008 standard. Five samples for each material were used for each testing and the data was presented in the form of “mean value \pm standard deviation.”

Flame retardancy testing

The flame retardancy of PP and composites was characterized by limiting oxygen index (LOI) and the combustion behavior. The LOI value was measured using samples with dimensions of 130 mm \times 6.5 mm \times 3 mm by an HC-2 LOI instrument (Jiangsu Jiangning Analysis Instrument Factory, China) according to GB/T 2406.1—2008 standard.

The combustion performance tests were performed according to ISO 5660-2 : 2002 standard procedures using a standard cone calorimeter of Fire Testing Technology Co. (UK) to obtain the heat release rate (HRR), the effective combustion heat (EHC), the total smoke production (TSP), and the smoke release rate (SPR). Each sample, with dimensions of 100 mm \times 100 mm \times 4 mm, was wrapped in aluminum foil and exposed horizontally to an external heat flux of 35 kW/m².

RESULTS AND DISCUSSION

XRD analysis

XRD analysis was used to examine the structure of OMMT nanocomposites. As shown in Figure 1, the reflection peak at $2\theta = 3.34^\circ$ corresponding to

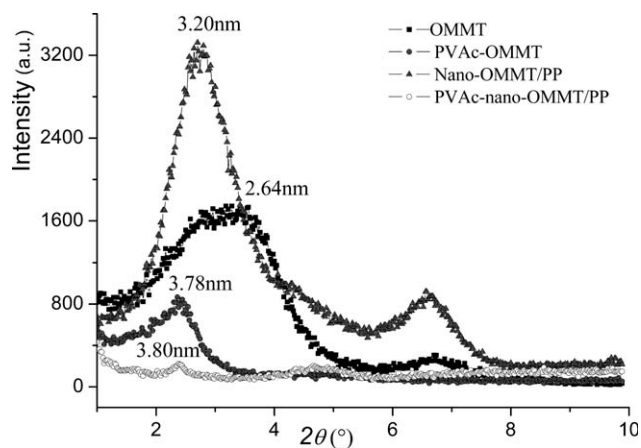


Figure 1 XRD patterns of OMMT, PVAc-OMMT (OMMT mass fraction: 38 wt %), Nano-OMMT/PP, and PVAc-nano-OMMT/PP (OMMT mass fraction: 5 wt %).

2.64 nm was the 001 interlayer spacing of OMMT. By intercalated polymerization of VAc in the layers of OMMT *in situ*, the interlayer spacing of OMMT increased by 1.14 nm to 3.78 nm, indicating that the macromolecular chains of PVAc were formed in the OMMT interlayer space.

Exploring the composite films further, we used FTIR spectroscopy to get more evidence for mutual inter-element interactions. The typical bands for the OMMT groups in the FTIR spectra were found in Figure 2, the aliphatic chain C—H vibration peak of the organic intercalation agent (3000–2800 cm^{-1} and 1452 cm^{-1}), the Si—O (1046 cm^{-1}) and Al—O (800–500 cm^{-1}) stretching, and the Si—O bending (500–400 cm^{-1}). For PVAc-OMMT (Fig. 2), one can easily recognize the peaks of the polymer: the C=O and C—O stretching vibration of PVAc at 1753–1251 cm^{-1} , and a very strong peak at 1753 cm^{-1} .²⁰ OMMT around the original 3396, 2902, 2843, and 1046 cm^{-1} had migrated to 3495, 2952, 2896, and 1058 cm^{-1} in PVAc-OMMT nanocomposite. This is because nanoparticles absorb energy in the infrared absorption spectrum and a “blue shift” phenomenon occurs. Therefore, PVAc-OMMT was characterized in the presence of nanoparticles from the side.

In Figure 1, When OMMT and PVAc-OMMT were each blended with melting PP, the peak of Nano-OMMT/PP shifted to 2.76° with an increase of interlayer spacing from 2.64 nm to 3.20 nm, which implied the part of PP chain already successfully inserted the OMMT laminar space. In comparison with PVAc-OMMT, the layer spacing of PVAc-nano-OMMT/PP was 3.80 nm; however, its XRD peak became weaker. This weakened diffraction peak implied the formation of a partially delaminated nanocomposite structure in the PVAc-nano-OMMT/PP composite, suggesting that the addition of PVAc enhanced the interface adhesion between PP and OMMT materials. Therefore, it was easy for the PP

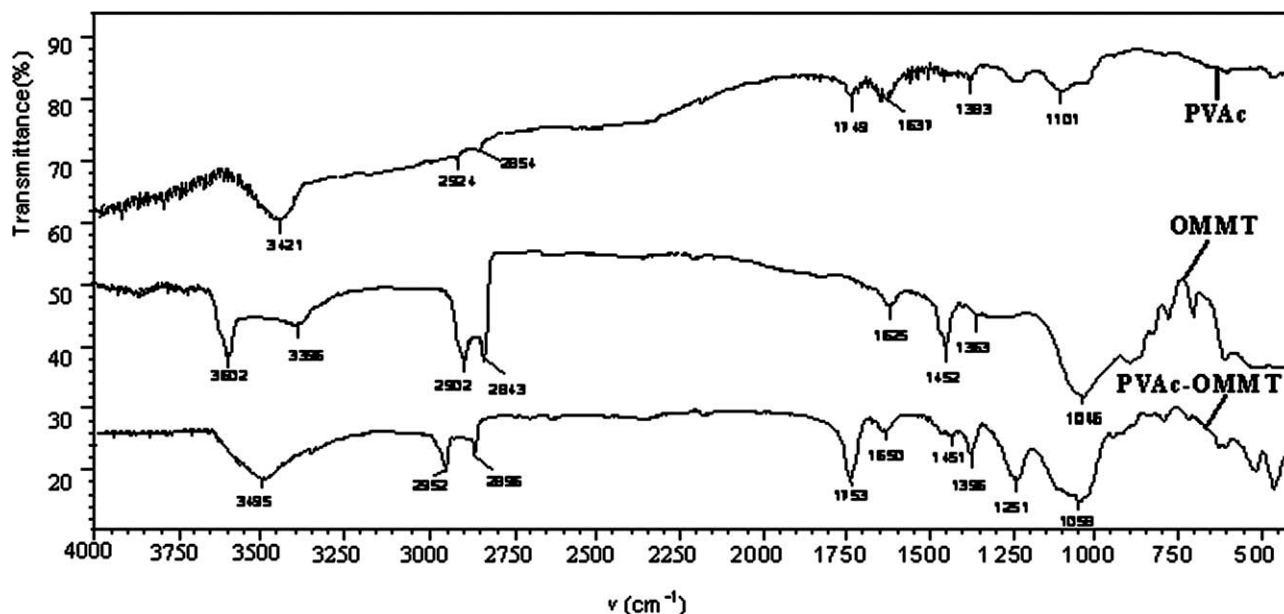


Figure 2 FTIR spectra of PVAc, OMMT, and PVAc-OMMT (OMMT mass fraction: 38 wt %).

molecular chain to intercalate in the OMMT layers, and some lamellars of OMMT were dispersed in the polymer matrix with an exfoliated form.

TEM

The morphology of the Nano-OMMT/PP and PVAc-nano-OMMT/PP composites is shown in Figure 3. It can be seen that the thickness of silicate layers in Figure 3(b) is thinner than that in Figure 3(a). It was confirmed that the clay stacks of PVAc-nano-OMMT/PP composite could be broken apart, which resulted in a reduced number of platelets per stack, and a few layers were dispersed throughout the matrix, indicating the formation of intercalated and exfoliated structure, which was consistent with the results of XRD spectra.

TG analysis

Figure 4 showed the TG curves of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP composites. Only one obvious weight-loss step was observed for the three types of systems, which rapidly lost their weights after reaching the onset weight-loss temperatures. The onset of extrapolative weight-loss temperature of PP was 416.4°C, and maximum decomposition temperature was 455.3°C. The whole weight loss was completed at 469.8°C. Nano-OMMT/PP extrapolated initial weight-loss temperature was observed at 406.6°C, an early start with little weight loss, mainly attributed to the decomposition of organic modifier in montmorillonite. The maximum decomposition temperature of Nano-OMMT/PP was 462.5°C and weight loss reached 100% at 489.2°C. Furthermore,

PVAc-nano-OMMT/PP extrapolative weight-loss temperature shifted to 423.6°C. The maximum decomposition temperature of PVAc-nano-OMMT/PP was 474.7°C, which was 19.4°C and 12.2°C higher

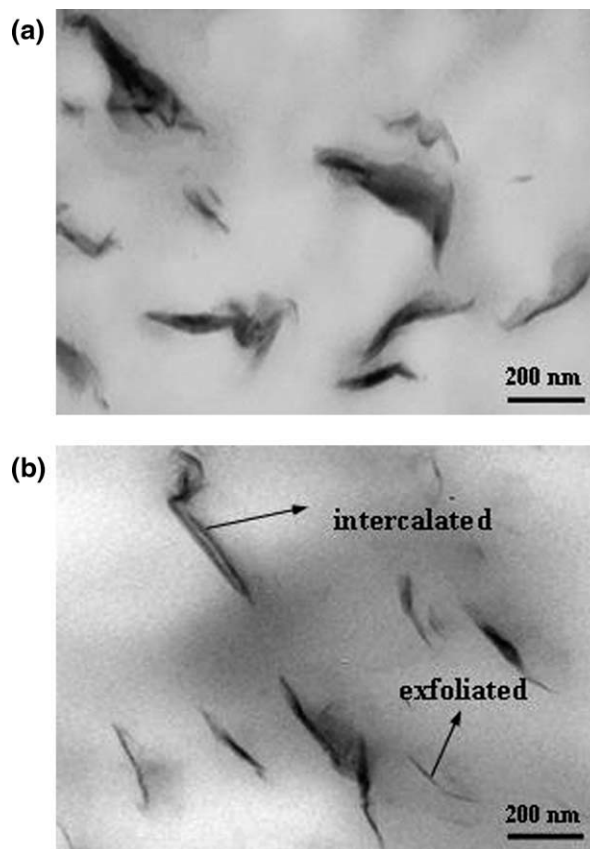


Figure 3 TEM images of (a) Nano-OMMT/PP and (b) PVAc-nano-OMMT/PP (OMMT mass fraction: 5 wt %).

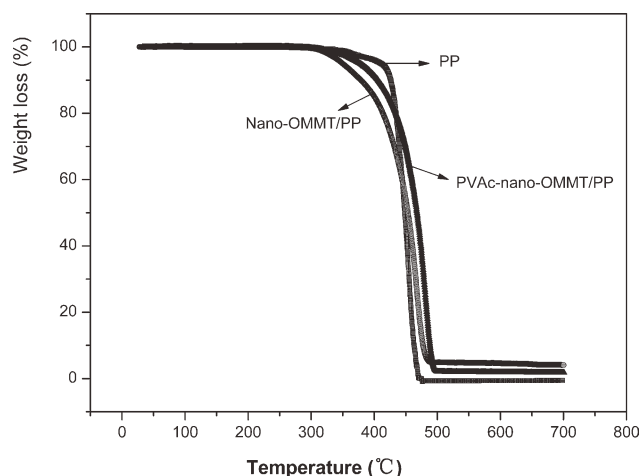


Figure 4 TG curves of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP (OMMT mass fraction: 5 wt %).

than that of PP and Nano-OMMT/PP, respectively. The weight loss of PVAc-nano-OMMT/PP was completed at 494.1°C. The enhanced decomposition temperature of PVAc-nano-OMMT/PP composite implied that PVAc-OMMT hybrid contributed to improve the thermal stability of PP.

Mechanical properties

Mechanical properties data of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP composites are listed in Table I. The addition of OMMT (5 wt %) to pristine PP resulted in a significant decrease of tensile strength from 35.6 ± 0.3 to 32.3 ± 0.4 MPa, because the addition of OMMT reduced the crystallinity and spherulite dimension of PP, which played a role in heterogeneous nucleation.^{21–23} A decrease of both PP crystallinity and spherulite dimension caused a slight decline in tensile strength,²⁴ but impact strength and bending strength had a certain significant improvement compared with those of PP, attributed to an increase of OMMT interlayer spacing. Therefore, when the material is under the impact extraneous force, the cross-section force area of OMMT layers increases, which is helpful to improve impact strength of nanocomposite, and bending strength also increases. In addition, PVAc-nano-OMMT/PP composite showed better impact

TABLE I
Mechanical Properties of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP (OMMT Mass Fraction: 5 wt %)

Sample	Tensile strength (MPa)	Impact strength (kJ/m ²)	Bending strength (MPa)
PP	35.6 ± 0.3	3.0 ± 0.2	40.2 ± 0.3
Nano-OMMT/PP	32.3 ± 0.4	3.5 ± 0.3	42.6 ± 0.4
PVAc-nano-OMMT/PP	33.7 ± 0.4	4.2 ± 0.3	43.8 ± 0.3

strength, which was significantly higher than that of Nano-OMMT/PP composite. The main reason is that PVAc enhanced interface compatibility between OMMT and PP matrix, making the interlayer spacing of OMMT increase and had better dispersion in PP matrix. In addition, because of the interaction enhancement between PP and OMMTs layers, the molecular chain did not slide easily, and the composite was more resistant to fracture than PP and Nano-OMMT/PP, resulting in the significant increase in the rigidity, and also improved tensile strength and bending strength.

Flame retardancy

LOI test

The LOI values of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP nanocomposites are listed in Table II. Compared with pure PP, the addition of OMMT and PVAc-OMMT into the polymer resulted in a small increase in the LOI values, which were 21.8% and 23.9%, respectively, when the mass fraction of OMMT was the same, showing that the flame retardancy of PVAc-OMMT with PP is better than that of OMMT with PP. In addition, the combustion phenomena of the aforementioned different systems were also different. Pure PP was easily ignited, and melt-dropping was very serious during combustion. However, the combustion phenomena of PVAc-nano-OMMT/PP and Nano-OMMT/PP were similar, i.e., they were both difficult to ignite, and melt-dropping decreased; therefore, the shape of original sample was better maintained.

Combustion behavior

The cone calorimeter is one of the most effective bench-scaled methods for studying the flammability properties of materials. Characterization of the flammability properties of a variety of polymer/clay nanocomposites using the cone calorimeter under fire-like conditions revealed the improved flammability properties.²⁵ Table III lists the peak heat release rate (PHRR), the average heat release rate (AHRR), the average effective heat of combustion (AEHC), the average specific extinction area (ASEA), the peak smoke production rate (PSPR), the TSP, and the time to ignition (TTI) of PP, Nano-OMMT/PP, and

TABLE II
LOI Values of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP (OMMT Mass Fraction: 5 wt %)

Sample	LOI value (%)
PP	18.0
Nano-OMMT/PP	21.8
PVAc-nano-OMMT/PP	23.9

TABLE III
Cone Calorimetric Data of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP (OMMT Mass Fraction: 5 wt %)

Specimen	PP	Nano-OMMT/PP	PVAc-nano-OMMT/PP
Time to ignition (TTI) (s)	35	37	38
Peak heat release rate (PHRR) (kW/m ²)	892.4	716.2	668.4
Average heat release rate (AHHR) (kW/m ²)	417.2	314.7	269.1
Average effective heat of combustion (AEHC) (MJ/kg)	40.1	38.8	36.3
Average specific extinction area (ASEA) (m ² /kg)	304.6	273.3	246.5
Peak smoke production rate (PSPR) (m ² /s)	0.083	0.068	0.062
Total smoke production (TSP) (m ²)	16.0	14.2	13.6
FPI (Fire performance index) [(m ² s)/Kw]	0.039	0.052	0.057

PVAc-nano-OMMT/PP samples when the mass fraction of OMMT was 5 wt %. These parameters are very important to evaluate fire safety.

As indicated in Table III, PHRR, AHRR, and AEHC of PVAc-nano-OMMT/PP were the lowest of the three kinds of materials. PHRR, AHRR, and AEHC of PVAc-nano-OMMT/PP decreased by 25%, 36%, and 22%, respectively, compared with those of PP. This shows that the PVAc-nano-OMMT/PP composite has good flame-retardant effect. In addition, PHRR, AHRR, and AEHC of PVAc-nano-OMMT/PP are 93%, 86%, and 85% of those of Nano-OMMT/PP, respectively. The above data suggest PVAc-nano-OMMT/PP flame-retardant efficiency is superior to that of the Nano-OMMT/PP system, which can be further confirmed from the LOI.

The HRR curves of pure PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP composites at a 35 kW/m² heat flux are illustrated in Figure 5. It can be seen that the HRR curve of pure PP rose quickly after ignition and reached a peak of 892.4 kW/m², and AHRR was 417.2 kW/m². Polymer blends with OMMT, had lower HRR and AHRR values than did PP, 716.2 and 314.7 kW/m², respectively. This result explained that the flame-retardant effect of Nano-OMMT/PP composite, proposed by Camino and coworkers,²⁶ mainly

arose from the formation of char layers obtained through the collapse of nanocomposite structure, reassembly of silicate layers, and then interaction of the charred surface layer with the reassembling silicate layers to provide a sort of ceramic-char-layered silicate. This carbonaceous silicate structure on the surface might act as an excellent insulator and mass transport barrier that retards the escape of the volatile products generated during decomposition, as well explained by Gilman et al.²⁷ On the other hand, PHRR of PVAc-nano-OMMT/PP decreased to 668.4 kW/m², possibly resulting from the addition of PVAc-OMMT improving the compatibility with PP, which makes OMMT better dispersed, even exfoliated in the polymer matrix. But exfoliated nanocomposites usually exhibit much better flame retardancy. Therefore, the PHRR of PVAc-nano-OMMT/PP composite decreased greatly during HRR test, and flame retardancy improved.

The influence of the addition of layered silicate on smoke production of the polymer blend and nanocomposite was evaluated by the ASEA and the TSP. The ASEA indicates the average value of the smoke evolved per mass unit of volatiles degraded from the sample upon burning. The TSP represents the TSP during combustion. As shown in Table III and

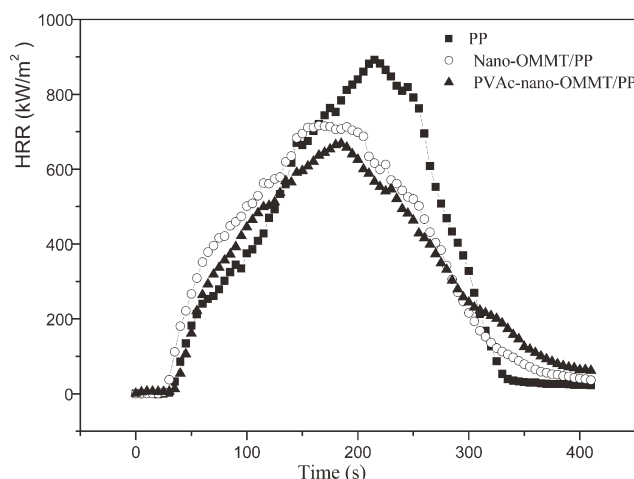


Figure 5 HRR curves of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP (OMMT mass fraction: 5 wt %).

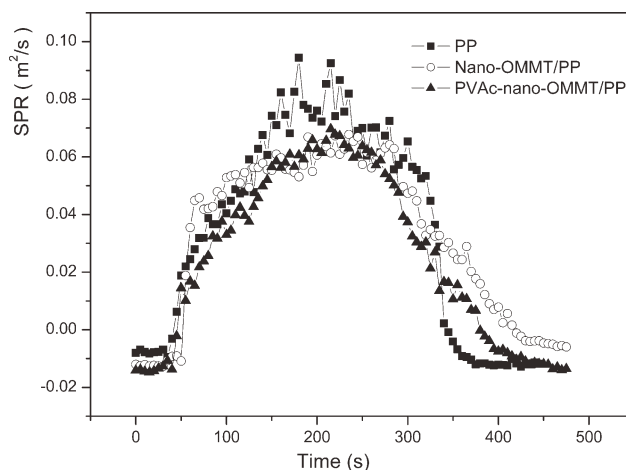


Figure 6 SPR curves of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP (OMMT mass fraction: 5 wt %).

Figure 6, the addition of PVAc-OMMT to PP slowed smoke production rate and significantly reduced the PSPR, similar to the heat release process, by 25% and 9% compared with PP and the Nano-OMMT/PP system, respectively. The Nano-OMMT/PP blend, compared with pristine PP, displayed a 10% ASEA decrease and an 11% TSP decrease. It appears that layered silicate alone has a small effect in reducing smoke evolution during combustion. However, PVAc-nano-OMMT/PP showed a reduction of the ASEA value by 19% and TSP value by 15% compared with PP, exhibiting a better smoke-suppressing effect.

Fire performance index (FPI) is the ratio of TTI to PHRR, and it has some practical significance in predicting whether fierce combustion can occur easily after the material is ignited. Because it involves both PHRR and TTI, it is better than PHRR to associate with the occurrence of fierce combustion of materials. The larger the FPI value, the lower the risk of fire and the less likely an occurrence of fierce combustion. From Table III, the magnitude of FPI values of PP, Nano-OMMT/PP, and PVAc-nano-OMMT/PP can be seen: PP < Nano-OMMT/PP < PVAc-nano-OMMT/PP. Therefore, under the same conditions, fierce combustion would occur first with PP, while PVAc-nano-OMMT/PP would exhibit the best flame resistance.

CONCLUSION

The intercalated polymerization of VAc and OMMT was initiated via *in situ* emulsion polymerization and PVAc-OMMT composite was obtained. XRD and FTIR proved that there is an interaction between PVAc and OMMT nanoparticles. When the mass fraction of OMMT was 5 wt %, PVAc-nano-OMMT/PP composite prepared by the melt-blending technique possessed overall better performance than either pure PP or Nano-OMMT/PP blend. The impact strength and bending strength were 4.2 ± 0.3 kJ/m² and 43.8 ± 0.3 MPa, and the LOI value, PHRR and PSPR are 23.9%, 668.4 kW/m², and 0.062 m²/s, respectively. XRD and TEM images of the PVAc-nano-OMMT/PP composite supported an intercalated nanocomposite with partial delamination. The TG results showed that the PVAc-nano-OMMT/PP nanocomposite presented a better protection and stabilization toward thermo-oxidation than did the pristine polymer and Nano-OMMT/PP blend. In addition, Cone test results exhibited a lower PHRR,

AHHR, AEHC, PSPR, and ASEA during combustion, indicating that the addition of PVAc-OMMT can improve the polymer's flame retardancy and decrease the destruction of materials in the fire.

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References

1. Akelah, A.; Prasad, P. N.; Mark, J. E.; Fai, T. J. *Polymer and Other Advanced Materials: Emerging Technologies and Business Opportunities*; Plenum Press: New York, 1995; p 28.
2. Giannelis, E. P. *Adv Mater* 1996, 8, 29.
3. Sinha Ray, S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
4. Giannelis, E. P.; Krishnamoorti, R.; Manias, E. *Adv Polym Sci* 1999, 138, 107.
5. LeBaron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl Clay Sci* 1999, 15, 11.
6. Vaia, R. A.; Price, G.; Ruth, P. N.; Nguyen, H. T.; Lichtenhan, J. *Appl Clay Sci* 1999, 15, 67.
7. Biswas, M.; Sinha Ray, S. *Adv Polym Sci* 2001, 155, 167.
8. Giannelis, E. P. *Appl Organomet Chem* 1998, 12, 675.
9. Xu, R.; Manias, E.; Snyder, A. J.; Runt, J. *Macromolecules* 2001, 34, 337.
10. Bharadwaj, R. K. *Macromolecules* 2001, 34, 1987.
11. Messersmith, P. B.; Giannelis, E. P. *J Polym Sci Part A: Polym Chem* 1995, 33, 1047.
12. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 2493.
13. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
14. Gilman, J. W. *Appl Clay Sci* 1999, 15, 31.
15. Sinha Ray, S.; Yamada, K.; Okamoto, M.; Ueda, K. *Nano Lett* 2002, 2, 1093.
16. Burnside, S. D.; Giannelis, E. P. *Chem Mater* 1995, 7, 1597.
17. Sikka, M.; Cerini, L. N.; Ghosh, S.; Winey, K. I. *J Polym Sci Part B: Polym Phys* 1996, 34, 1443.
18. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 1755.
19. Zheng, S. L. *Powder Surface Modification (in Chinese)*; Building Materials Industry Press: Beijing, 2003, p 54.
20. Qian, Z. M. *Plastic Performance Applications Manual*; Shanghai: Shanghai Science Press, 1985, p 117.
21. Ma Jisheng; Qi Zongneng; Li Ge; Hu Youliang. *Acta Polymerica Sinica* 2001, 44, 590 (in chinese).
22. Chen Zhonghua; Gong Kecheng; Liu Shuyin. *China Synth Resin Plast* 2000, 17, 46.
23. Ma Jisheng; Zhang Shimin; Qi Zongneng; Hu Youliang; Zhang Shufan. *Chem J Chin Univ* 2002, 23, 737.
24. Zhao, L. J.; Li, J.; Guo, S. Y.; Du, Q. *Polymer* 2006, 47, 2460.
25. Bourbigot, S.; Bras, L. M.; Dabrowski, F.; Gilman, J. W.; Kashiwagi, T. *Fire Mater* 2000, 24, 201.
26. Zanetti, M.; Kashiwagi, T.; Falqui, L.; Camino, G. *Chem Mater* 2002, 14, 881.
27. Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Harris, R., Jr. *Chem Mater* 2000, 12, 1866.