

# Using PA6 as a Charring Agent in Intumescent Polypropylene Formulations Based on Carboxylated Polypropylene Compatibilizer and Nano-Montmorillonite Synergistic Agent

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**ABSTRACT:** The intumescent fire retardant polypropylene (IFP/PP) filled with ammonium polyphosphate (APP), melamine (M), and PA6 (charring agent) is discussed. Intumescent degree (ID) and the char yield were determined. Only when the three main components of IFR coexist at appropriate proportions, it has optimal ID and higher char yield. The appropriate proportion is PA6 : APP : M = 10 : 10 : 5. A new compatibilizer, carboxylated polypropylene (EPP), was added to PP/PA-6 blend. Flow tests indicated that the apparent viscosity increased with the addition of EPP, thermal characterization suggested that EPP has reacted with PA6, PA6-g-EPP cocrystallized with PA6, and EPP-g-PA6 cocrystallized with PP; SEM micrographs illustrated that the presence of EPP improved the compatibility of PP and PA6. All the investigations showed

that EPP was an excellent compatibilizer, and it was a true coupling agent for PP/PA6 blends. Using PA6 as a charring agent resulted in the IFR/PP dripping, which deteriorated the flammability properties. The addition of nano-montmorillonite (nano-MMT) as a synergistic agent of IFR enabled to overcome the shortcoming. The tensile test testified that the addition of nano-MMT enhanced the mechanical strength by 44.3%. SEM showed that nano-MMT improved the compatibility of the composites. It was concluded that the intumescent system with nano-MMT was an effective flame retardant in improving combustion properties of polypropylene. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 739–746, 2006

**Key words:** intumescent fire retardant; polypropylene; nano-MMT; nylon 6; carboxylated polypropylene

## INTRODUCTION

Polypropylene (PP) is used in many industrial applications because of its low cost and easy processing. However, its poor fire properties and, in particular, dripping observed during its combustion limits its wide use. Thus, flame-retardant (FR) additives are incorporated into PP to get fire performance. Research and development activities are now mostly directed toward halogen free fire retardants, among which much attention is paid to intumescent systems. On heating, intumescent materials form a foamed surface cellular charred layer, which protects the underlying material from the charred layer acting as a physical barrier, which slows down heat and mass transfer between gas and condensed phase. Three ingredients are generally needed in an intumescent system: a carbonific or char former, an acidic char promoter, and a “foaming” of gas-generating and inflating agent.

Camino et al. considered that special chemical structure, especially spirostructure formation in the charred layer during the ignition, improved flame retardancy.<sup>1</sup> Ma and Zhao have proposed the influence of melt visco-elastic behavior of the intumescent charred layer as an important factor.<sup>2</sup> Study results of Bourbigot and coworker's have shown that the increased melt viscosity reduces the melt dripping susceptibility, while the improved plasticity of intumescent char increases the barrier properties, thereby resulting in improved flame retardancy.<sup>3–5</sup>

The intumescent fire retardant (IFR), composed of ammonium polyphosphate (APP), pentaerythritol (PT), and melamine (M) has best flame retardancy in PP, in accordance with the structure and visco-elastic demands of flame retardancy mechanism. In the literature, it was found that IFR deteriorates the mechanical properties of PP, especially, the PT melts at the processing temperature, which affects the processing properties of the composites.<sup>6</sup> Some studies have shown that PA6 has synergistic flame retardancy with APP<sup>7,8</sup> and that the intumescent mixtures of the additives APP and PA6 have been developed for use in PP. Also, PA6 plays the role of both a polymeric matrix and a carbonization agent, because of its unique me-

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chanical properties and processability. PA6, instead of pentaerythriol, can improve the mechanical properties of the IFR/PP composites. On the other hand, APP, M, and PA6 are incompatible with PP, because of their different polarities. In our laboratory, the carboxylated polypropylene (EPP) was successfully added to PP/IFR blend as compatibilizer,<sup>6</sup> and now its effect on PA6 and PP is studied.

In fire retardant tests in air, the PA6 shows nonsatisfactory behavior because of intensive inflammable dripping,<sup>9</sup> which deteriorated the flame retardancy. Inorganic filler can increase the melt viscosity of the intumescent char, and increase the barrier properties, and these resulted in improved flame retardancy.<sup>10,11</sup> Polymer/nano-montmorillonite (nano-MMT) composites have received a great deal of attention since their first demonstration by the Toyota group in 1987. These nanocomposites exhibit superior properties such as higher tensile strength, modulus, heat resistance, light weight, and less permeability to gas at a lower level of loading relative to conventionally scaled composites. Many researchers reported the use of nano-MMT for compatibility.<sup>10</sup> Hao et al.<sup>12</sup> have showed that nano-MMT not only solved the problem of dripping in PA6, but also increased the char yield, thereby increasing both mechanical properties and flame retardancy. Hence, we have studied nano-MMT as a synergistic agent of IFR, with the aim of improving the compatibilization, overcoming the shortcoming of dripping, and retaining or increasing the flame retardancy of the composites.

## EXPERIMENTAL

### Materials

PP [type T30S,  $d = 0.901 \text{ g/cm}^3$ , melt flow index (230°C/2.16 kg) = 3.88 g/10 min, tacticity = 96.6%] was supplied by Tian-Jin united Chemical Co. (Tianjin, China). PA6 was supplied by Chemical factory of -BoYe (HeBei, China), and it was dried in vacuum for 10 h at 60°C before use. Carboxylated polypropylene (EPP), prepared by us,<sup>6</sup> had an acid no. of 0.23 mg KOH/g. APP was supplied by Changfeng Chemical factory (HeBei, China); melamine (M) was purchased from Gaocheng chemical factory (HeBei, China). Cetyl trimethyl ammonium bromide organic-modified nano-MMT was supplied by Institute of Process Engineering, Chinese Academy of Sciences(Beijing, China).

### Preparation of blends

#### Preparation of PP/PA6/EPP blends

First, PA6 and EPP were mixed by an XJ-20 extruder (Jilin, China), with the temperatures set at 210, 225, and 240°C and with a screw speed of 12 rpm. The PA6/EPP blends were then mixed with PP at the same

conditions, followed by further mixing at 180–190°C in an XKR-160 two-roll mill (Zhanjiang, China) for 10 min, and a final compression in an XLB-D400 electric-heat pressing machine (Shangqiu, China) at 185°C for 5 min at 16 MPa. Finally, the composites were cooled to room temperature by cool pressing.

#### Preparation of PP/IFR/PA6/EPP/nano-MMT blends

First, PA6, nano-MMT, and EPP were mixed by an XJ-20 extruder, with the temperatures set at 210, 225, and 240°C and with a screw speed of 12 rpm. The PA6/nano-MMT/EPP blends were then mixed with PP at the same conditions, followed by mixing the PP/PA6/EPP/nano-MMT blends with APP and M at 180–190°C in a two-roll mill for 10 min, and a final compression in an electric-heat pressing machine for 5 min at 16 MPa and 180°C. Finally, the composites were cooled to room temperature by cool pressing.

#### Characterization of blends

An LJ-3000 N tensile tester measured the tensile strengths at room temperature, following the GB 1843 Standard, and the extension rate was found to be 10 mm/min.

Melt flow properties of the samples were measured on a capillary rheometer of XLY-II (Jilin, China), with a length/diameter ratio of 40, the temperature fixed at 180°C, and the experimental loads of 40, 60, 80, 100, 120, and 140 kg/cm<sup>2</sup>.

The morphology of the sample was observed with a Ammry 1000B scanning electron microscope (SEM), after being coated with gold.

DSC analysis was made on a CDR-4P apparatus (Shanghai, China), with the sample weight of about 7.08 mg. All the operations were carried out under a nitrogen environment. The temperature and melting enthalpy were calibrated with standard indium. First, the samples were heated to 240°C at a rate of 20°C/min, with programmed temperature controller, and held in the molten state for 5 min so as to eliminate the influence of thermal history and the samples were then cooled to 80°C at 20°C/min. The exothermic crystallization peak was recorded as a function of temperature.

#### Measurement of flame retardancy

0.2–0.5g of IFR was weighed accurately and held at 500°C for 10 min in a muffle furnace. By measuring the variation in the volume and mass before and after being heated, the intumescent degree (ID) and char yield could be calculated using the following equation:

TABLE I  
The Component of IFR

APP/PA6		M (g)			
$W_{APP}:W_{PA6}$	W (g)	A	B	C	D
0:10	3	0	0.5	1.0	1.5
1:9	3	0	0.5	1.0	1.5
2:8	3	0	0.5	1.0	1.5
3:7	3	0	0.5	1.0	1.5
4:6	3	0	0.5	1.0	1.5
5:5	3	0	0.5	1.0	1.5
6:4	3	0	0.5	1.0	1.5
7:3	3	0	0.5	1.0	1.5
8:2	3	0	0.5	1.0	1.5
9:1	3	0	0.5	1.0	1.5
10:0	3	0	0.5	1.0	1.5

ID = Volume changes  $\Delta V$  (cm<sup>3</sup>)/Sample mass (g)

Char yield = [Char mass (g)/Sample mass (g)]  
× 100%

The ease of ignition of the PP was studied according to GB 2408–80 horizontal Standard, using samples with dimensions  $127 \times 12.7 \times 3.5$  mm<sup>3</sup>. With the Bunsen burner being ignited, the ignition time, flame spread rate, and extinguish time were recorded.

## RESULTS AND DISCUSSION

### Intumescent fire retardant (IFR)

Intumescent is an essential property for a compound to be used as an IFR. So the intumescent property of IFR at different compositions has been studied.

Table I shows the components of IFR and Figures 1

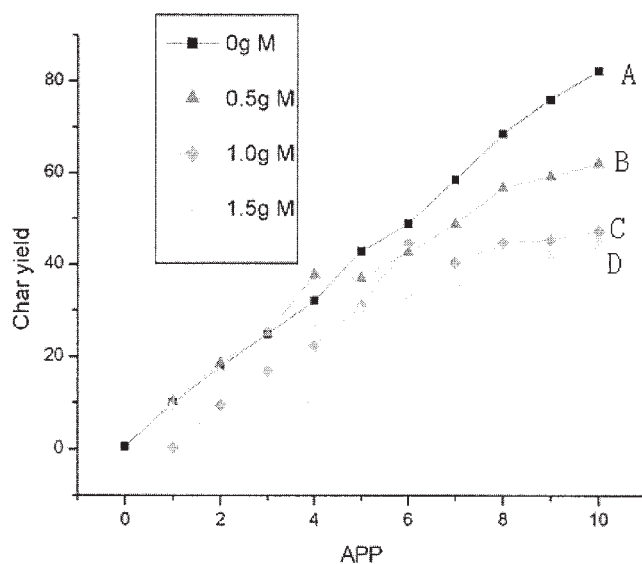


Figure 1 The Char yield of IFR.

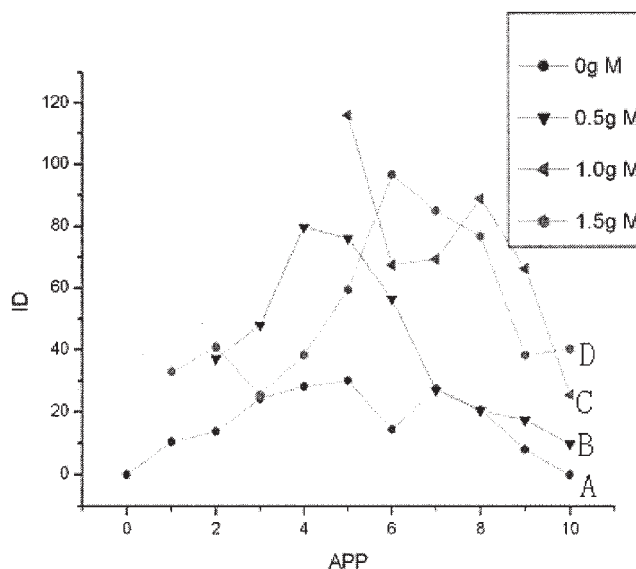


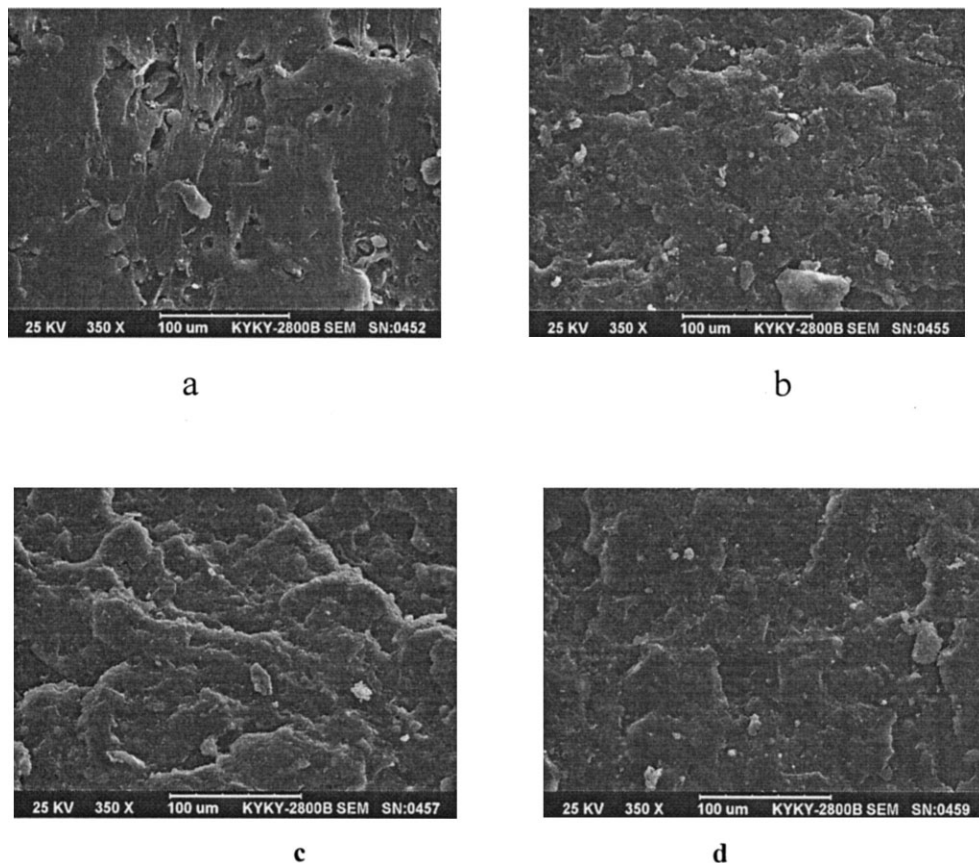
Figure 2 The ID of IFR.

and 2 represent the char yield and ID of the IFR, respectively. It can be seen from Figure 1 that as APP content increases, the char yield increases, and upon the addition M, char yield decreased a little. From Figure 2 we can see that with the addition of gas source M, the ID increased obviously; with no change in M and the APP content increasing, the ID first increased, then remained steady up to a certain level, and then decreased rapidly. Experiments show that only when the three main components of IFR coexists at appropriate proportions, it has optimal ID and higher char yield. The appropriate proportions are PA6 : APP = 4–6 : 6–4 and  $(W_{APP} + W_{PA6}) : W_M = 3 : 0.5$ . Here, the one composed of PA6 : APP : M = 10 : 10 : 5 was selected as IFR.

### Compatibility of EPP for PP/PA6 blend

In recent decades, the properties of physical mixtures of PP/PA6 have been studied. The mechanical properties of this immiscible blend, with poor interfacial adhesion and high interfacial tension between the dispersed and continuous phases, can be changed with the addition of a compatibilizer agent.

In PA6 molecule, the presence of amine end-groups offers sites for specific interactions, which has been widely used to compatibilize PA6 with other polymers, especially polymer containing acid groups. For instance, maleic anhydride grafted PP (PP-g-MA) can compatibilize or partially compatibilize with PA6 during melt blending through the formation of PP-g-PA6 graft copolymer, since maleic anhydride groups of PP-g-MA can react with amine end-groups of PA6. But the grafting reaction of PP-g-MA will deteriorate the mechanical properties, and the grafting efficiency is



**Figure 3** SEM of impact strength test fracture surfaces. (a) PP/PA6/EPP = 90/10/0; (b) PP/PA6/EPP = 84/10/6; (c) PP/PA6/EPP = 82/10/8; and (d) PP/PA6/EPP = 80/10/10.

very low; in addition, adding excessive grafted monomer will cause environmental problems. So it is significant to seek a commercial product with the virtue of good applicability and being environmental friendly and as compatibilizer for PP/PA6 blends.

In our recent work, a new compatibilizer—EPP—was used for intumescent fire retardant polypropylene successfully.<sup>6</sup> In this work, the EPP was applied to PP/PA6 blend as compatibilizer.

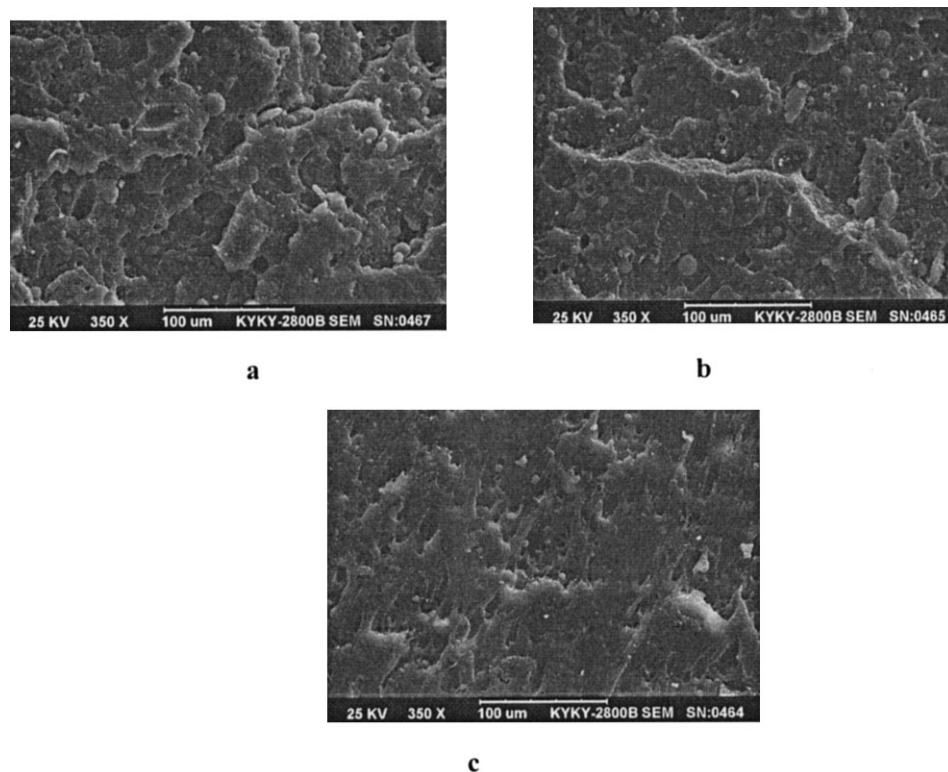
### Morphology

SEM observation was made on the fractured surface of the PP/PA6 = 90/10 blends with varying content of EPP to examine the morphology of the compatibilized blend. The blend without EPP shows the typical characteristics of an immiscible blend [Figs. 3(a) and 4(a)], indicating a very broad size distribution. The interface between the PP matrix and the PA6 is smooth and clear, suggesting a poor adhesion between the two phases.

Great difference was observed in the morphology of the samples containing EPP. When 6% EPP was added, the interface between the PP and PA6 became rough [Figs. 3(b) and 4(b)], indicating an enhanced

compatibility and interfacial adhesion. When the EPP content reached 8%, the interfacial adhesion between the two phases improved further.

The fracture surfaces of the sample were polished first, and then immersed in 18mol/L sulfuric acid, which is a solvent for PA6 and a nonsolvent for PP. Five hours later, the surfaces were rinsed with water and alcohol and dried at room temperature. After being coated with gold, the morphology of the surfaces of the blends were observed with an Ammry 1000B scanning electron microscope, and the SEM micrographs are shown in Figure 5. PA6 is seen as small holes because it was dissolved. Figure 5(a) shows a binary blend, i.e., the blend prepared without any compatibilizer, and the micrograph clearly shows that the PA6 phase was dispersed in the PP matrix as both spherical and fiber-shaped domains having a diameter between  $\sim 3$  and  $30 \mu\text{m}$ , indicating a very broad size distribution, and the PA6 phase borders are clear and easy to observe, suggesting a poor adhesion between PA6 and PP matrix. When 6% EPP was added [Fig. 5(b)], the average size of the PA6 domains decreased greatly and dispersed homogeneously, and the phase borders



**Figure 4** SEM of tensile strength test fracture surfaces. (a) PP/PA6/EPP = 90/10/0; (b) PP/PA6/EPP = 84/10/6; and (c) PP/PA6/EPP = 82/10/8.

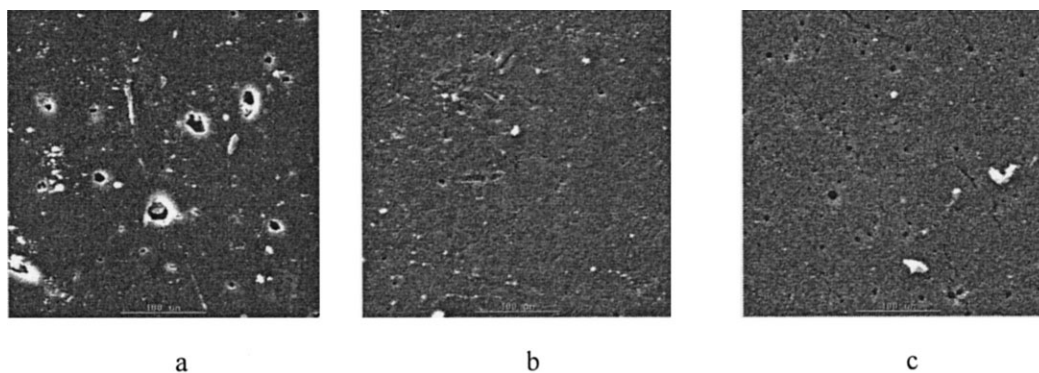
became rough, indicating an enhanced compatibility on the blend.

#### Rheological behavior

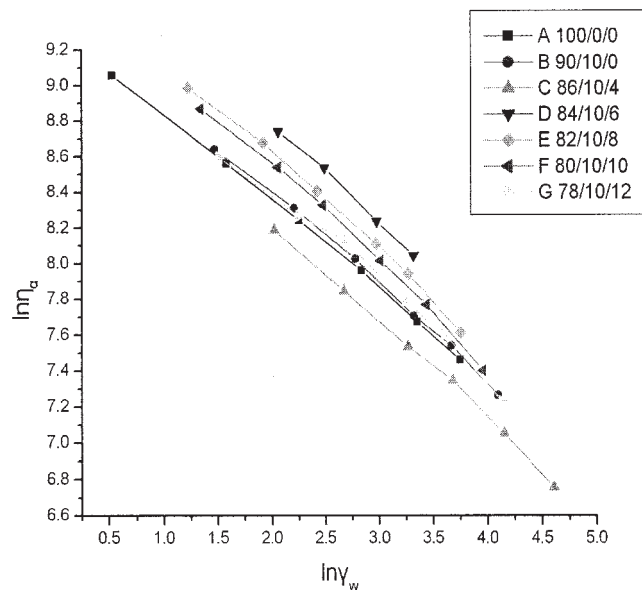
As can be seen from Figures 6 and 7, the apparent viscosity ( $\eta_a$ ) of PP/PA6/EPP blends was varied with the increase in EPP. Compared with that of the pure PP, the apparent viscosity of PP/PA6 (blend B) decreased, because PA6 destroyed the helix of PP and influenced the rheological behavior of PP. As EPP content increased to 6%, the apparent viscosity of

PP/PA6/EPP (blend D) increased markedly; the high apparent viscosity could be the result of the reaction between the  $-\text{COOH}$  of EPP and the  $-\text{NH}_2$  of PA6, or the formation of hydrogen bond. But the apparent viscosity of blends C, E, F, and G decreased lightly, because the oxidizing reaction decreased the molecular weight of PP, which decreased the viscosity of the blends. In conclusion, EPP reinforced the interaction between PP and PA6 significantly.

In addition, Figure 6 shows that the PP/PA6/EPP melt was a pseudoplastic liquid, which indicated that the blends had a favorable processing.



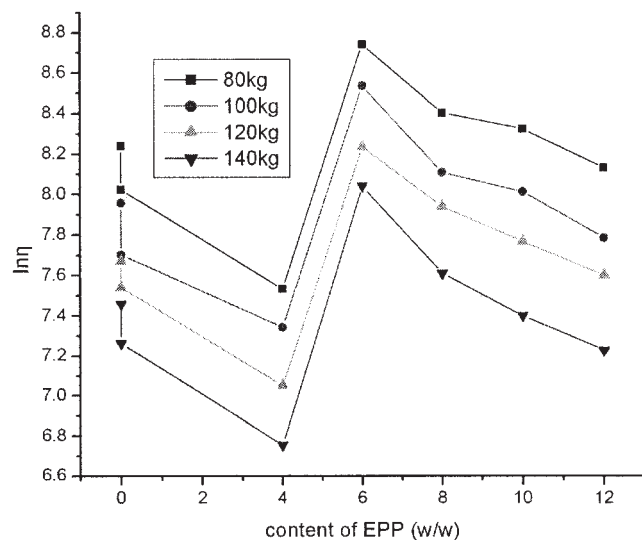
**Figure 5** The SEM of PP/PA6/EPP blends. (a) PP/PA6/EPP = 90/10/0; (b) PP/PA6/EPP = 80/10/10; and (c) PP/PA6/EPP = 76/10/14.



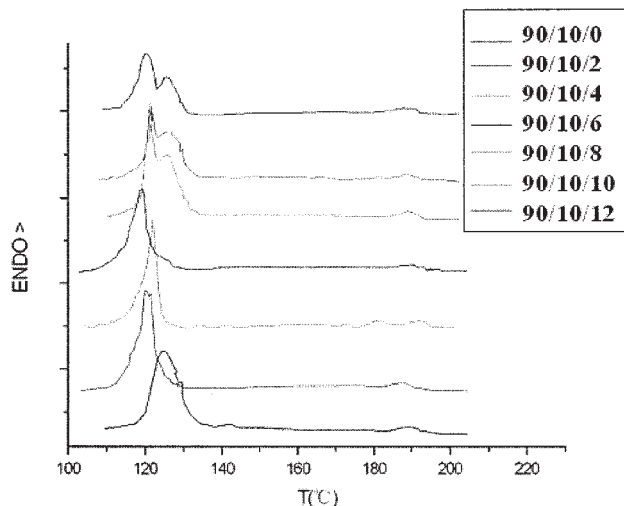
**Figure 6** The rheological behavior of PP/PA-6/EPP blends (180°C).

#### Thermal characterization

A comparison of DSC cooling curves for the blends is presented in Figure 8, and the corresponding crystallization enthalpies were determined. The results from these measurements are presented in Table II. PP/PA6 blend shows crystallization exotherms at 125.3 and 189.6°C, corresponding to PP and PA6, respectively. With the addition of EPP,  $T_c$  and  $\Delta H_c$  values changed. With blend PP/PA6/EPP = 86/10/4, exothermic peak corresponding to crystallization of PA6 split into two peaks, and with EPP content  $\geq 8\%$ , it was a single peak again, but the exothermic peak corresponding to



**Figure 7** The apparent viscosity of PP/PA-6 blends with different content of EPP (180°C).



**Figure 8** DSC curves for PP/PA6/EPP (wt %) at cooling rate 20 K/min.

crystallization of PP split into two.  $\Delta H_c$  data show that when EPP was added, the PP crystallization enthalpies increased, and the crystallization enthalpies of PA6 decreased. The PP/PA6/EPP (86/10/4) was an exception; the crystallization enthalpies of PA6 also increased. This can be explained by the reaction of EPP with PA6. When EPP content was lower, PA6-g-EPP cocrystallized with PA6, and when it was higher, EPP-g-PA6 cocrystallized with PP. At PP crystallization temperature, PA6 had already crystallized, and as PA-6 being the nucleus of PP, the crystallinity of PP also increased. It seems to support the idea that the EPP enhanced the interfacial adhesion of PP/PA6 blends, and it was an efficient interface modifier of the heterogeneous materials, which was in agreement with the increasing viscosity.

When EPP was added to PP/PA6 blends, it enhanced the interfacial adhesion between PP and PA6 and increased the viscosity of the blends. As EPP improved the compatibility and the interactions of PP and PA6, it was a true coupling agent for PP/PA6 blends.

**TABLE II**  
Parameters of Sample During Nonisothermal Crystallization Process

PP/PA6/EPP	$T_c$		$\Delta H_c$ ( $J g^{-1}$ )	
	PA6	PP	PA6	PP
90/10/0	189.6	125.3	2.41	56.36
88/10/2	187.6	120.5	2.06	68.85
86/10/4	192.1	123.4	181.8	71.41
84/10/6	190.6	120	1.38	63.58
82/10/8	189.6	126.3	114.8	81.43
80/10/10	189.1	126.3	113.8	65.08
78/10/12	188.6	125.8	120.5	1.93

**TABLE III**  
The Flame Retardancy and Tensile Strength of PP/IFR/Nano-MMT Blends

Sample	PP/IFR*/EPP/ NANO-MMT	Tensile strength (MPa/m <sup>2</sup> )	Flame retardancy		
			Ignition time (s)	Flame stability	Extinguish time (s)
A	100/0/0/0	36.0	12	Burn and dripping	
B	75/25/0/0	23.5	14	Burn and dripping	
C	60/25/10/0	28.5	15	Burn	
D	60/25/10/2	32.4	18	Unstable flame	
E	60/25/10/4	33.9	20	Extinguish	67
F	60/25/10/6	32	22	Extinguish	44
G	60/25/10/8	31	28	Extinguish	39

IFR\* = APP/PA6/M = 10/10/5

### Nano-MMT reinforced IFR/PP

#### Properties test

Because of the poor compatibility of PP and IFR, it is nearly impossible to prepare the IFR/PP composites with good mechanical properties. As seen in Table III (composite B), addition of 25 g of IFR to 75 g of PP drastically decreased the tensile strength to 23.5 MPa. To improve the compatibility, part of the PP of the composites was substituted by EPP. In composite C, addition of 10% EPP produced a significant improvement in the mechanical properties, and the tensile strength increased to 28.5 MPa, but the flame retardancy does not. From the flame retardancy of the composites D, E, F, and G we can note that upon addition of 4 wt % nano-MMT, the composites can self-extinguish. Meanwhile, the tensile strength increases by 44.3% than that in the composite without nano-MMT. But as the nano-MMT content was continuously increased, the tensile strength decreased.

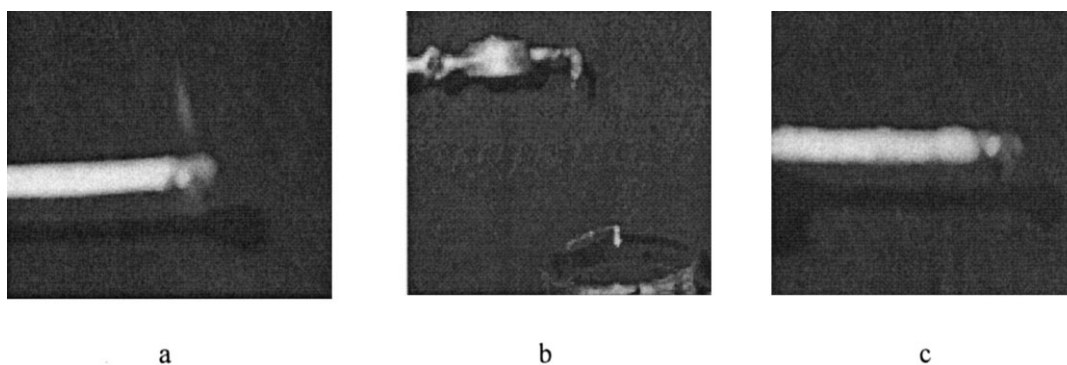
To obtain the desired mechanical and flammability properties, the appropriate nano-MMT content required is 4 wt %. The superior mechanical property is attributed to the nano-MMT uniformly distributed in the matrix, and forms a favorable interfacial adhesion.

#### Flame retardancy test

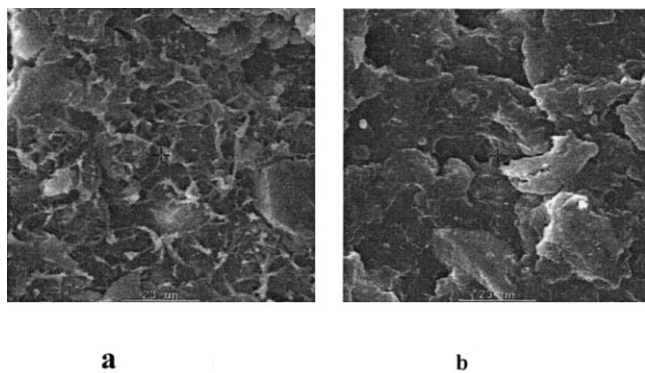
Figure 9 presents the flame retardancy test. It can be seen from Figure 9(a) and Table III that the composite without nano-MMT has the shortest ignition time, burning and dripping, and flame stability. Addition of 4 wt % nano-MMT prolonged the ignition time of composite E to 18 s, and it could also self-extinguish. As the nano-MMT content was increased, the composite had a longer ignition time, shorter self-extinguishing time, and a lower flame spread rate. When the tensile strength was considered, 4 wt % MMT content was favorable. Flame retardancy test showed that nano-MMT accelerated char yield of IFR/PP, enhanced char density, and improved the flame retardancy of the composite.

#### Morphology

Figure 10 shows the SEM of tensile test fracture of PP/IFR/nano-MMT composites. It can be seen from Figure 10(a) that upon addition of EPP, the system's compatibility improved to a certain extent; however, smooth fracture surface existed, implying that the break took place at the interface between the IFR and the matrix. Figure 10(b) shows that the fracture surface



**Figure 9** Photos of GB2408–80 test. (a) composite C, (b) composite D, and (c) composite E.



**Figure 10** The SEM of PP/IFR/nano-MMT blends. (a) composite C and (b) composite E.

became rough and had distinct slide and fold, suggesting that the tough fracture makes the system a continuous phase. The addition of nano-MMT increased the interior interface adhesion of the system.

### CONCLUSIONS

1. Only when the three main components of IFR coexist at appropriate proportions, it has optimal ID and higher char yield. The appropriate proportion is PA6 : APP : M = 10 : 10 : 5.
2. Morphology analysis, rheological behavior study, and thermal characterization showed that EPP enhanced the interfacial adhesion between PP and PA6, increased the viscosity of PP/PA6 blend, and improved the compatibility and the interactions of PP and PA6.
3. Using PA6 as carbonization agent resulted in the IFR/PP dripping, which deteriorated the flammability properties. Addition of 4 wt % nano-MMT accelerated char yield and enhanced char density of IFR/PP, improved the flame retardancy of the composite, and made the composite self-extinguish. Nano-MMT also improved the compatibility of the blends. It was concluded that the intumescent system with nano-MMT was an effective flame retardant in improving combustion properties of PP.

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