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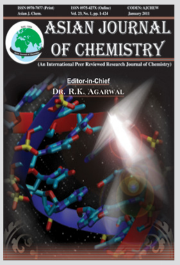

Combustion Behaviour and Morphology of Phosphonium Montmorillonite Filled Polypropylene/Magnesium Hydroxide Composites

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In order to prove the combustion behaviour of phosphonium montmorillonite (P-MMT) filled polypropylene/magnesium hydroxide (PP/MH) composites, samples of PP/MH, PP/MH/Na-MMT and PP/MH/P-MMT have been prepared by melt compounding using a co-rotating twin-screw extruder. Combustion experiments and thermogravimetric analysis were applied to determine the thermal properties of polypropylene composites, scanning electron microscope were used to study the microstructures of chars. The results show that the ignition time increased with the addition of P-MMT, but decreased with the addition of Na-MMT. SEM demonstrated that a suitable amount of P-MMT can promote formation of charred of layers in polypropylene composites.

Key Words: Phosphonium montmorillonite, Polypropylene composites, Morphology, Combustion behaviour.

INTRODUCTION

Polypropylene (PP) is now widely used in many aspects of people's life and civil production but highly combustible. Inorganic hydrates are commonly used in flame-retardant composite formulations because of their ability to undergo endothermic dehydration under fire conditions[1-3]. Flame-retardant filler often require free smoking and toxicity, no corrosive substances upon combustion. Moreover, they can be used at higher processing temperatures. Magnesium hydroxide (MH) has been frequently used in flame-retard polymer composites because of low cost and high-endothermic decomposition temperature. However, the low flame retardant efficiency and poor mechanical performance of composites due to the high dosage[4] (more than 60 wt % at required flame retarding range) hinder magnesium hydroxide as a flame-retardant filler further development. Intercalated versions of clays offer reduced flammability is growing interest this years[5-7] and a barrier effect of clay layers[8] and the role of iron in the clay[9] were suggested as possible mechanisms.

In this study, phosphonium salt intercalated montmorillonite was added into polypropylene/magnesium hydroxide (PP/MH) in order to improve the flammability property of polypropylene and decrease dosages of magnesium hydroxide. XRD has been used to study the intercalated structure of montmorillonite. Burning test has been applied to determine the thermal properties of composites. TGA and SEM provide the char constitutes and microstructures.

EXPERIMENTAL

Polypropylene was purchased from China Petroleum & Chemical Co. Ltd. (Guangzhou, China); Na-MMT with 100 meq/100 g cation-exchange capacity (CEC) was obtained from Hongyu Clay Co. Ltd. (Zhejiang, China); hexadecyl tributyl phosphonium bromide (HDTB) of CR grade was supplied by Qingte Chemical Industry Co. Ltd. (Shanghai, China); magnesium hydroxide of technical grade was purchased from Guangdong HuaLi Thai Chemical Co. Ltd. (Guangzhou, China).

The preparation of intercalated montmorillonites was carried out by the following process: 10 g montmorillonite was dispersed in 490 g deionized water, to which the HDTB was slowly added. The quantity of HDTB was at 0.5 CEC of montmorillonite. Then the mixture was stirred vigorously at 65 ºC for 6 h. The resulting compound was washed with deionized water until the reaction with 1 % $AgNO_3$ solution was negative. After dried at 65 ºC under vacuum, the layered compound was gathered with 300 mesh sieve (48 μm). The resulting compound was named as P-MMT. Polypropylene blends with magnesium hydroxide, montmorillonite (MMT) and MMT-HDTB were prepared using a Berstoff ZE25A corotating twin-screw extruder (L/D = 40, D = 35.5 mm) with a temperature profile of 200/190/200/200/220/210/200 ºC and a rotating speed of 250 rpm. The PP/MH/MMT/P-MMT/(polyamide wax) compositions for the PP1, PP2, PP3 and PP4 are 100/0/0/0/0, 53/45/0/0/2, 48/45/5/0/2, 50/45/0/3/2, respectively.

XRD patterns were recorded on a Rigaku D/Max 1200 X-ray Diffractometer, using CuK$_\alpha$ radiation ($\lambda = 0.1541$ nm) at 40 kV and 40 mA with a scan speed of 1º/min and 2θ range of 2-40º. Combustion experiments including heat release rate (HRR) were performed on a cone calorimeter at an incident heat flux of 35 kW/m^2 in accord with ISO 5660-1:2002. The char constitutes and microstructures were characterized by TGA and SEM. TGA was conducted with a thermal analyzer (SDT-Q600), 15 mg sample was heated from 40-950 ºC under N$_2$ flow at a scanning rate of 10 ºC/min. SEM photos were observed by a JSM-6330F scanning electron microscope.

RESULTS AND DISCUSSION

The XRD patterns of Na-MMT and P-MMT were graphically represented in Fig. 1. The number of peak in 2θ range 2-40º decreased from 5.96º (Na-MMT) to 2.98º for P-MMT and the basal spacing increased from 1.48 nm (Na-MMT) to 2.96 nm for P-MMT. The variation observed between the basal spacing supported the proposed configuration of phosphonium cations inside the interlayer space.

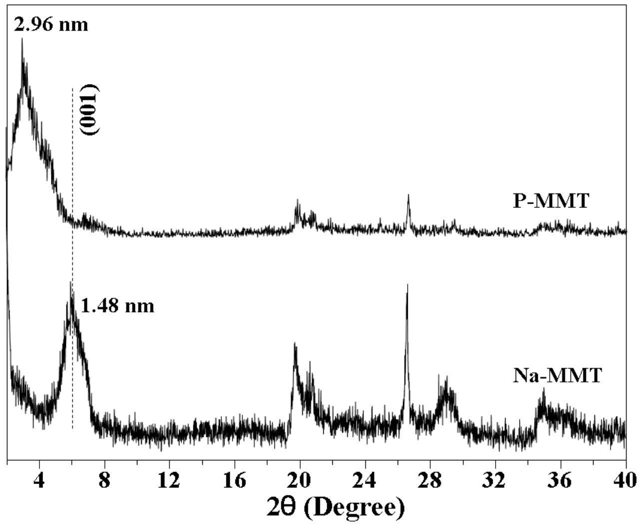

Fig. 1. X-Ray diffraction patterns of Na-MMT and P-MMT

The combustion properties of the PP/MMT composites were characterized by means of cone calorimetry. The run of heat release rate curves was shown in Fig. 2. Compared to the PP/MH system, heat release rate decreased and the ignition time reduced with the addition of 5 % Na-MMT. Qin *et al.*[10] also found that the addition of montmorillonite can accelerate the ignition of the polypropylene matrix. This is probably due to the oxidative catalysis effect of montmorillonite on the polymer. The addition of 3 % P-MMT prolonged the ignition time of PP/MH system and the heat release rate decreased further, which suggest that the thermal stability of PP/MH system was enhanced. These effects were attributed to shielding effect of clays, which migrate to the surface and form protective surface layer and/or accumulate at the surface and provide a barrier layer after the polymer burned away[11,12].

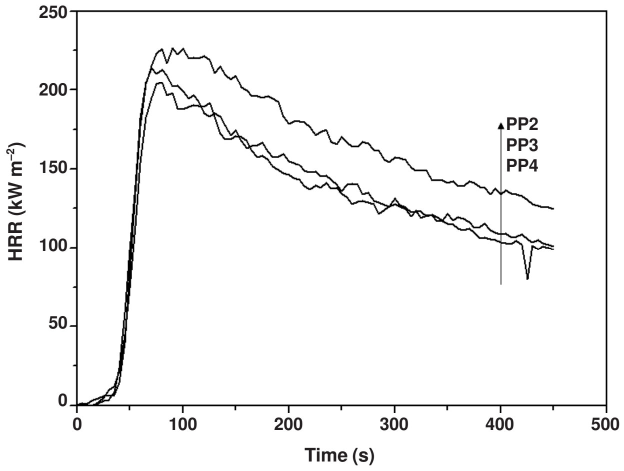

Fig. 2. Heat release rate of PP2, PP3 and PP4

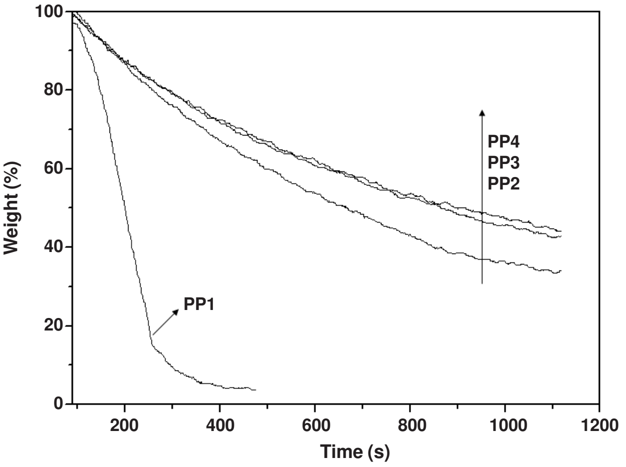

Fig. 3. TGA curves of PP1, PP2, PP3 and PP4

The mass loss plots for PP1, PP2, PP3 and PP4 were shown in Fig. 3. The mass loss for all the composites was slower than that for PP1 (pure polypropylene). The mass loss of PP2 (PP/MH) was larger than that of PP3 (PP/MH/Na-MMT) and PP4 (PP/MH/P-MMT). However, the mass loss of PP4 was slower than that of PP3, there are most residues in PP4.

The surface of PP2, PP3 and PP4 can be seen from Fig. 4. With of montmorillonite, a good carbonaceous silicate protective layer was formed in PP3 and PP4. Removing the surface layer, some black block residues were left in PP4. In contrast, without catalytic effect of P-MMT, only gray ash was left in polypropylene/magnesium hydroxide.

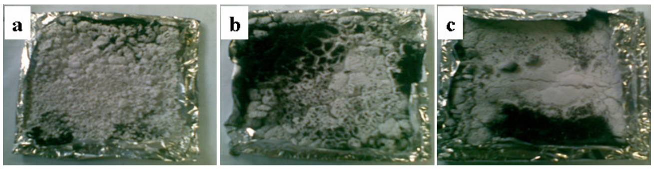

Fig. 4. Macro images of the PP2 (a), PP3 (b), PP4 (c) chars

The microstructures of the PP3, PP4 chars are shown in Fig. 5. At high magnification, the PP3 char looks like a lot of disordered flakes accumulated on the surface of the sample and the PP4 char looks slick and continuous. a ceramic-like char is formed on the surface of PP4. It shows that PP4 is more profitable for the formation of carbonaceous protective layer on the burning surface[13].

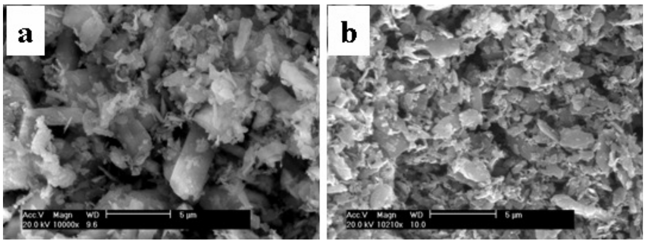

Fig. 5. Microstructures of the PP3 (a) and PP4 (b) chars

Conclusion

In this study, PP/MH, PP/MH/Na-MMT and PP/MH/P-MMT composites have been prepared by melt processing and their thermal stability and flammability have been investigated. The addition of montmorillonite can considerably reduce the heat release rate, prolong the ignition time of the composite and increase the carbon residue of the composite. The particle of combustion residue of PP/MH/P-MMT was the smallest, showed dense, scalelike, evenly distributed. With the intercalation of quaternary phosphonium salt into montmorillonite, the surface energy of montmorillonite slice layer was changed, under the burning process, the montmorillonite slice layer easier moved to the surface of the composite, cut the oxygen in air and prevents the burn of the composite[14].

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REFERENCES

1. R.N. Rothon, Magnesium Hydroxide, New Products, Processes and Polypropylene Applications, Itertech, Portland, ME (2000).
2. S. Mishra, S.H. Sonawane, R.P. Singh, A. Bendale and K. Patil, *J. Appl. Polym. Sci*., **94**, 116 (2004).
3. A. Durin-France, L. Ferry, J.-M. Lopez Cuesta and A. Crepsy, *Polym. Int*., **49**, 1101 (2000).
4. C.M. Jiao and X.L. Chen, *Polym. Eng. Sci*., **50**, 767 (2010).
5. S.S. Ray and M. Okamoto, *Prog. Polym. Sci*., **28**, 1539 (2003).
6. S. Bourbigot, J.W. Gilman and C.A. Wilkie, *Polym. Degrad. Stab*., **84**, 483 (2004).
7. B.N. Jang and C.A. Wilkie, *Polymer*, **46**, 3264 (2005).
8. J.W. Gilman and T. Kashiwagi, In eds.: T.J. Pinnavaia and G.W. Beall, Polymer-Clay Nanocomposites, Wiley, New York (2000).
9. J. Zhu, F.M. Uhl, A.B. Morgan and C.A. Wilkie, *Chem. Mater*., **13**, 4649 (2001).
10. H.L. Qin, S.M. Zhang, C.G. Zhao, M. Feng, M.S. Yang, Z.J. Shu and S.S. Yang, *Polym. Degrad. Stab*., **85**, 807 (2004).
11. A.P. Patino-Soto, S. Sanchez-Valdes and L.F. Ramos-Devalle, *J. Polym. Sci. Pol. Phys*., **46**, 190 (2008).
12. Z. Wang, X.H. Du, R.J. Song, X.Y. Meng, Z.W. Jiang and T. Tang, *Polymer*, **48**, 7301 (2007).
13. M. Modesti, A. Lorenzetti, S. Besco, D. Hrelja, S. Semenzato, R. Bertani and R.A. Michelin, *Polym. Degrad. Stab*., **93**, 2166 (2008).
14. X.F. Liu, J. Zhang and H.P. Zhang, *Acta. Polym. Sin*., **5**, 650 (2004).