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Flame Retardant Synergism of Bentonite and Magnesium Hydroxide in Polypropylene

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The flammability characterization and synergistic effect of bentonite with magnesium hydroxide in polypropylene have been studied in this work. A synergistic effect on flame retardancy was found when bentonite was incorporated into magnesium hydroxide/polypropylene composites. The mass ratio of magnesium hydroxide and bentonite should be 37:3 and the loading of magnesium hydroxide and bentonite should be 45-50 % to get better flame-retardant effect and mechanical properties according to the experimental results. The flame retardant synergism of bentonite and magnesium hydroxide in polypropylene is further illustrated by the horizontal burning rates. Thermogravimetric analysis revealed that the addition of magnesium hydroxide or bentonite/magnesium hydroxide improves the thermal stability of the composites. The fire performance of polypropylene and polypropylene composites was compared by cone calorimeter test, which indicated that the addition of bentonite/magnesium hydroxide in polypropylene system greatly reduced the heat release rate and mass loss rate.

Key Words: Flame retardancy, Bentonite, Magnesium hydroxide, Polypropylene, Synergistic effect.

INTRODUCTION

Halogen containing compounds, widely used as effective flame retardants for most polymeric materials, are restricted in recent years due to the environmental pollution and human hazards after burning. There has been a trend towards the development and application of halogen-free flame retardant for polymer materials. Magnesium hydroxide (MH), shown to be an effective flame retardant and smoke suppressing additive[1-7], has been extensively used as an environmentally benign flame retardant in polymers[8-11]. However, its fatal disadvantages are low flame-retardant efficiency and large usage amount, which sharply deteriorated mechanical properties of polymer materials. Some results showed that incorporations of some halogen-free flame-retardant synergistic agents with magnesium hydroxide could improve flame retardancy and reduce the high loading level of flame-retardant fillers[12-22].

There is an increasing attention on using magnesium hydroxide as effective and environmentally friendly alternative fire retardants in polypropylene (PP)[23-31]. On the other hand, effect of bentonite (BT) on the flame retardancy of intumescent flame retardant polypropylene is investigated recently[32,33]. We investigate the flame retardant synergism of bentonite and magnesium hydroxide in polypropylene composites.

EXPERIMENTAL

Organo-bentonite, GK-4, was purchased from Jiangxi Gukang new materials Co. Ltd. Nano-magnesium hydroxide with average length of 193.9 nm and specific surface area of 22.4 m^2/g was prepared using hydrothermal treatment[34]. Polypropylene, T30R, was supplied by Qilu Petrochemical Co. Ltd.

Preparation of nanocomposites: Polypropylene composites were prepared using SK-160B double mixing roller presses. The operating temperature of the roller presses was maintained at 170 ºC from hopper to die. The samples were subsequently placed in a vacuum over 24 h and the dried pellets were further prepared into standard specimens using XLB vulcanizing machine.

The limiting oxygen index (LOI) was measured with sheet dimensions of $120 \times 10 \times 4$ mm^3 using a HC-2 type instrument according to the GB/T2406 standard.

A cone calorimeter (STA449C, made in Germany) was used to measure the fire performance of the samples according to ISO5660 under an external heat flux of 35 kW/m^2 and the parameters including heat release rate were recorded simultaneously. TGA data were obtained in nitrogen at a heating rate of 10 ºC min^{-1} using a STA449C simultaneous thermal analyzer.

TABLE-1
EFFECT OF THE MASS RATIO OF MH AND BT ON PROPERTIES OF BT/MH/PP COMPOSITES

Symbol	Formulations			Properties		
	MH (mass %)	BT (mass %)	PP (mass %)	LOI (%)	Elongation at break (%)	Tensile strength (MPa)
Sa0	40	0	60	24.5	8.5	19.8
Sa1	38.5	1.5	60	24.9	27.9	21.1
Sa2	37.0	3.0	60	25.8	21.5	29.7
Sa3	35.0	5.0	60	25.4	10.9	26.5
Sa4	32.5	7.5	60	24.3	8.9	21.1
Sa5	0	3	97	18.9	51.4	25.5
Sa6	0	0	100	18.1	51.8	25.4

Tensile tests were carried out on a tensile tester, AI-7000 M, with a crosshead speed of 50 mm/min and the specimens were prepared according to GB/T 1040.3-2006.

Horizontal and vertical tests were carried out according to GB/T 2408-2008. The samples were visualized by SEM with a JSM-590OLV scanning electron microscope.

RESULTS AND DISCUSSION

Effect of the mass ratio of bentonite, magnesium hydroxide and polypropylene on properties of BT/MH/PP composites: The effect of the mass ratio of bentonite, magnesium hydroxide and polypropylene on the properties of BT/MH/PP composites was tested. The formulations of the composites and the results are presented in Table-1.

From Table-2, it can be found that the limiting oxygen index values of BT/MH/PP blends are in the range of 24.3-25.8 % when the mass fraction of polypropylene is fixed to 60 %. The increase of bentonite dosage in the composites lowered the elongation at break of BT/MH/PP blends.

TABLE-2
EFFECT OF THE LOADING OF BT/MH ON PROPERTIES OF BT/MH/PP COMPOSITES

Symbol	Formulations		Properties		
	BT/MH (mass %)	PP (mass %)	LOI (%)	Elongation at break (%)	Tensile strength (MPa)
Sc1	40	60	25.8	21.5	29.7
Sc2	45	55	27.8	19.3	29.0
Sc3	50	50	28.9	14.3	8.8
Sc4	55	45	30.2	13.9	6.0

The limiting oxygen index value showed that Sa5 (BT/PP sample) was flammable for its LOI value was only 18.9 %. The LOI value of Sa1 (MH/PP sample) was markedly increased to 24.7 % due to the addition of magnesium hydroxide. The addition of bentonite to the composites further improved the LOI data to 25.8 % and had a synergistic effect on limiting oxygen index.

The elongation at break of the composite samples increased form 8.5 % to 21.5 % and the tensile strength of the composites increased form 19.8 MPa to 29.7 MPa with the addition of bentonite. This means that improved mechanical properties were obtained in Sa2 (BT/MH/PP sample). This improvement is mainly attributed to the better dispersion of magnesium hydroxide throughout the polymer matrix. In the following sections, the mass ratio of magnesium hydroxide and bentonite is set to 37:3 considering the LOI value and the mechanical properties.

Fig. 1 compares the images of Sa0 with Sa2 observed by SEM studies. As shown in Fig. 1, uniform fracture surface are clearly seen for Sa2, which suggests that the compatibility between magnesium hydroxide and polymer matrix is increased by the addition of bentonite and results in Sa2 having enhanced mechanical properties.

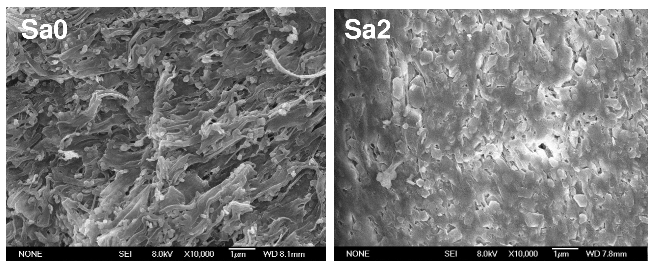

Fig. 1. SEM images of fracture surfaces after tensile tests for Sa0 (MH/PP) and Sa2 (BT/MH/PP)

Effect of the loading of BT/MH on the properties of BT/MH/PP composites: Four composites were prepared to study the loading of BT/MH on the properties of BT/MH/PP composites and the formulations of the composites are listed in Table-2. The LOI value and the mechanical properties such as the tensile strength and elongation at break of the composites have been investigated and the results are given in Table-2.

It can be seen from Table-2 that the LOI values of BT/MH/PP composites are improved from 25.8 to 30.2 % with the increase of BT/MH from 40 to 55 %. The elongations at break of BT/MH/PP blends are in the range of 13.9 %-21.5 % when the mass fraction of polypropylene decreased from 60 to 45 %. The tensile strength obviously decrease to 6.0 MPa-8.8 MPa when the mass fraction of polypropylene is smaller than 50 %. It can be concluded that the suitable value of the loading of BT/MH is 40 %-50 %.

Flammability characterization by horizontal burning test: In order to confirm further the flame retardant synergism of bentonite and magnesium hydroxide in polypropylene composites, the horizontal burning test of three composites were carried out. The formulations of the composites and the results are listed in Table-3.

It can be seen from Table-3 that 50 % filled MH/PP composite (sample S1) shows a lower burning rate than the virgin polymer (sample S0) and 50 % filled BT/MH/PP composite (sample S2) shows the lowest burning rate. This also indicates the flame retardant synergism of bentonite and magnesium hydroxide in polypropylene composites.

Thermal stability analysis: Fig. 2 shows the thermograms of S0, S1 and S2 with the thermal degradation temperatures at

TABLE-3
FORMULATIONS AND FLAMMABILITY OF THREE COMPOSITES CHARACTERIZATION BY HORIZONTAL BURNING TEST

Symbol	Formulations			Properties	
	MH (mass %)	BT (mass %)	PP (mass %)	Self-extinguishing	Horizontal burning rate (mm/min)
S0	0	0	100	No	58.16
S1	50	0	50	No	25.97
S2	46.25	3.75	50	No	21.69

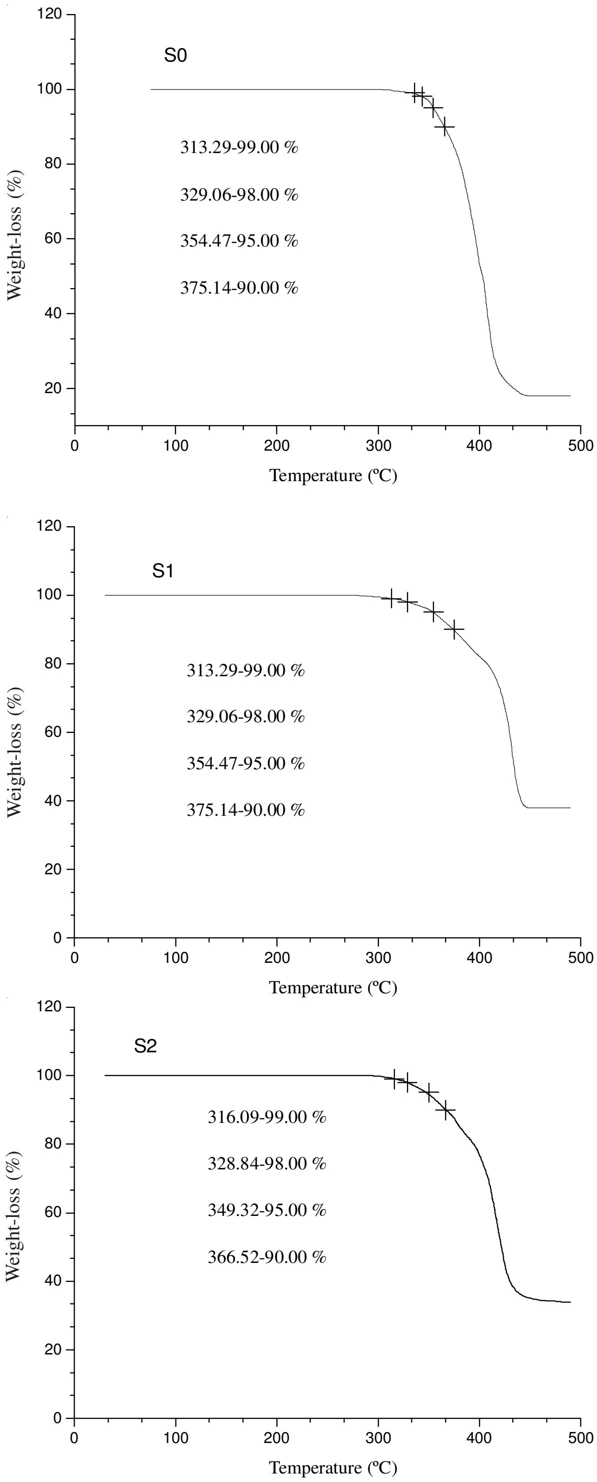

Fig. 2. Thermogravimetric analysis profiles of S0, S1 and S2 in nitrogen at a heating rate of 10 °C/min

various mass-loss percentages. The mass-loss percentages under different temperature are presented in Table-4.

TABLE-4
MASS-LOSS PERCENTAGES OF S0, S1 AND S2 UNDER DIFFERENT TEMPERATURE

	350 °C	400 °C	425 °C	450 °C
MH	8	28	29	30
S0	5	48	79	82
S1	5	24	56	66
S2	5	18	31	62

It is shown in Fig. 2 and Table-4 that, despite the initial decomposition temperature of S1 or S2 is slightly lower than that of S0, when the temperature exceeds 400 °C, the mass loss of S1 or S2 is less than that of S0 at the same temperature. The purity magnesium hydroxide completely decomposes at 400 °C for the magnesium oxide[34]. It can be found that, although the thermal stability of magnesium hydroxide is lower than that of polypropylene, the addition of magnesium hydroxide especially BT/MH improves the thermal stability of polypropylene, which further confirm the flame retardant synergism of bentonite and magnesium hydroxide in polypropylene.

Flammability characterization by cone calorimeter test: Fig. 3 shows a comparison of heat release rate curves for S0, S1 and S2. As can be seen, S0 was easier to burn and yielded a rather high peak heat release rate (PHRR) and the whole combustion process only lasted for 5 min. The peak heat release rate values of S1 and S2 were lower and the combustion times were respectively up to 13 and 16 min long, which means the addition of magnesium hydroxide or BT/MH enhanced the flame retardancy of polymeric materials. The peak heat release rate values of S2 were smaller than those of S1 and the combustion time of S2 was longer than that of S1, which is consistent with the TGA conclusion. The above observation also suggested that the incorporation of bentonite was effective to further improve the flame retardancy of MH/PP.

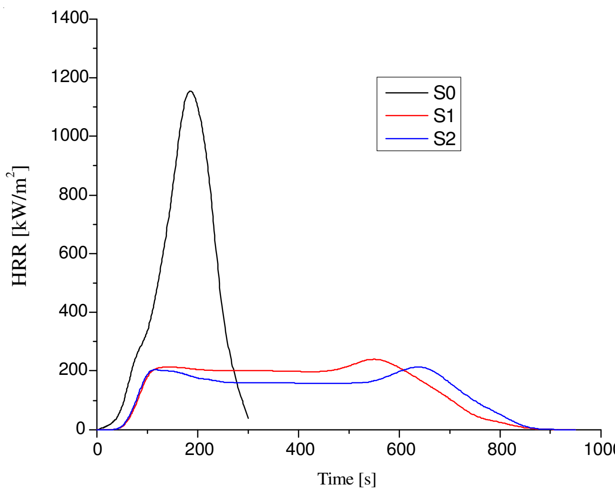

Fig. 3. Heat release rate curves of S0, S1 and S2

Total heat release calculated from the total area under the heat release rate peaks is another important parameter for flame hazard evaluation and the total heat release curves of S0, S1 and S2 are given in Fig. 4. Compared with S0, total heat release of S1 and S2 decrease, indicating the flame retardancy of the composites is improved.

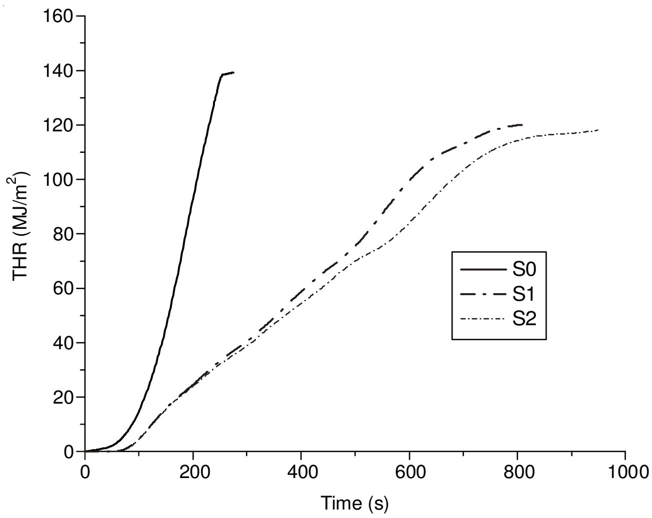

Fig. 4. Total heat release rate curves of S0, S1 and S2

It can be found from Fig. 5 that the mass loss rate (MLR) of S1 or S2 decreases remarkably to no more than 0.1 g/s while the highest mass loss rate of S0 is 0.25 g/s. This further confirms that the incorporation of BT/MH can improve the flame retardancy of polypropylene.

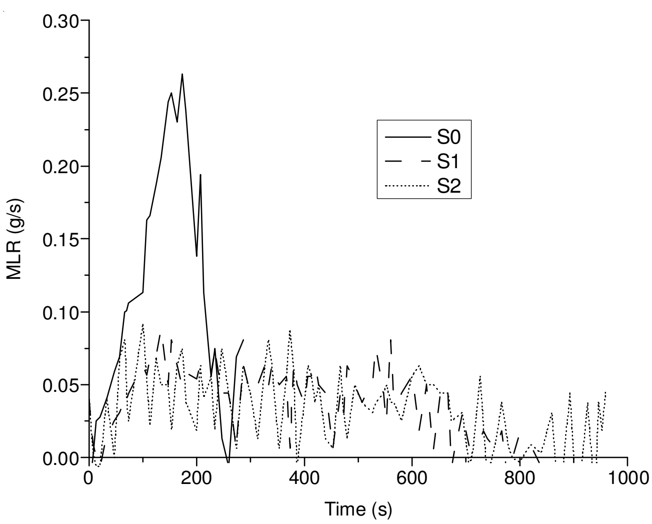

Fig. 5. Mass loss rate curves of S0, S1 and S2

Conclusion

Flame retardant BT/MH/PP composites have been prepared and it has been found that bentonite can have a synergistic effect on flame retardancy with magnesium hydroxide in polypropylene in this work. Mass ratio and loading of magnesium hydroxide and bentonite is studied to find better flame-retardant effect and mechanical properties. The significant difference in combustion behaviours of polypropylene and BT/MH/PP was observed from cone calorimeter test results. These results show that incorporation of bentonite and magnesium hydroxide to improve the flame retardancy of polypropylene has a big potential for the future studies.

REFERENCES

1. M.M. Hirschler and T.R. Thevaranjan, *Eur. Polym. J.*, **21**, 371 (1985).
2. L. Delfosse, C. Baillet, A. Brault and D. Brault, *Polym. Degrad. Stab.*, **23**, 337 (1989).
3. P.R. Hornsby and C.L. Watson, *Polym. Degrad. Stab.*, **30**, 73 (1990).
4. R.N. Rothon and P.R. Hornsby, *Polym. Degrad. Stab.*, **54**, 383 (1996).
5. H. Gui, X. Zhang, Y. Liu, W. Dong, Q. Wang, J. Gao, Z. Song, J. Lai and J. Qiao, *Compos. Sci. Technol.*, **67**, 974 (2007).
6. H. Cao, H. Zheng, J. Yin, Y. Lu, S. Wu, X. Wu and B. Li, *J. Phys. Chem. C*, **114**, 17362 (2010).
7. J. Formosa, J.M. Chimenos, A.M. Lacasta and L. Haurie, *Thermochim. Acta*, **515**, 43 (2011).
8. A.A. Sener and E. Demirhan, *Mater. Design*, **29**, 1376 (2008).
9. F. Laoutid, L. Bonnaud, M. Alexandre, J.M. Lopez-Cuesta and P. Dubois, *Mater. Sci. Eng. Reports*, **63**, 100 (2009).
10. J. Liang and Y. Zhang, *Polym. Int.*, **59**, 539 (2010).
11. T. Xu, X. Huang and Y. Zhao, *Fire Safety J.*, **46**, 330 (2011).
12. L. Ye, Q. Wu and B. Qu, *Polym. Degrad. Stab.*, **94**, 751 (2009).
13. G. Zhang, P. Ding, M. Zhang and B. Qu, *Polym. Degrad. Stab.*, **92**, 1715 (2007).
14. G. Fei, Y. Liu and Q. Wang, *Polym. Degrad. Stab.*, **93**, 1351 (2008).
15. M. Fu and B. Qu, *Polym. Degrad. Stab.*, **85**, 633 (2004).
16. Z. Li and B. Qu, *Polym. Degrad. Stab.*, **81**, 401 (2003).
17. G. Song, S. Ma, G. Tang, Z. Yin and X. Wang, *Energy*, **35**, 2179 (2010).
18. H. Gui, X. Zhang, W. Dong, Q. Wang, J. Gao, Z. Song, J. Lai, Y. Liu, F. Huang and J. Qiao, *Polymer*, **48**, 2537 (2007).
19. S. Bourbigot, S. Duquesne, Z. Sébih, S. Ségura and R. Delobel, Fire and Polymers IV, American Chemical Society, p. 200 (2005).
20. X. Chen, H. Wu, Z. Luo, B. Yang, S. Guo and J. Yu, *Polym. Eng. Sci.*, **47**, 1756 (2007).
21. Z. Wang, B. Qu, W. Fan and P. Huang, *J. Appl. Polym. Sci.*, **81**, 206 (2001).
22. F. Carpentier, S. Bourbigot, M. Le Bras, R. Delobel and M. Foulon, *Polym. Degrad. Stab.*, **69**, 83 (2000).
23. H. Dvir, M. Gottlieb, S. Daren and E. Tartakovsky, *Compos. Sci. Technol.*, **63**, 1865 (2003).
24. M. Sain, S.H. Park, F. Suhara and S. Law, *Polym. Degrad. Stab.*, **83**, 363 (2004).
25. A.B. Shehata, *Polym. Degrad. Stab.*, **85**, 577 (2004).
26. X. Chen, J. Yu and S. Guo, *J. Appl. Polym. Sci.*, **102**, 4943 (2006).
27. B.B. Marosfoi, S. Garas, B. Bodzay, F. Zubonyai and G. Marosi, *Polym. Adv. Technol.*, **19**, 693 (2008).
28. J. Yang, J.Z. Liang and C.Y. Tang, *Polym. Test.*, **28**, 907 (2009).
29. N. Suppakarn and K. Jarukumjorn, *Compos. Part. B-Eng.*, **40**, 613 (2009).
30. J.-Z. Liang, J. Yang and C.-Y. Tang, *Polym. Test.*, **29**, 624 (2010).
31. R. Gul, A. Islam, T. Yasin and S. Mir, *J. Appl. Polym. Sci.*, **121**, 2772 (2011).
32. J.B. Dahiya, M. Muller-Hagedorn, H. Bockhorn and B.K. Kandola, *Polym. Degrad. Stabil.*, **93**, 2038 (2008).
33. B. Du, Z. Guo, P. Song, H. Liu, Z. Fang and Y. Wu, *Appl. Clay. Sci.*, **45**, 178 (2009).
34. L. Tang, M. Su, J. Yang and K. Yu, *Asian. J. Chem.*, **23**, 4093 (2011).