Polym. Bull. (2011) 66:289–299
DOI 10.1007/s00289-010-0331-9

ORIGINAL PAPER

Heat resistant properties of PP/$Al(OH)_3$/$Mg(OH)_2$ flame retardant composites

J. Z. Liang · Y. J. Zhang · X. H. Jiang

Received: 19 November 2009 / Revised: 13 June 2010 / Accepted: 22 June 2010 /

Abstract Vicat softening point temperature (T_V) and heat deflection temperature (T_d) are important parameters for characterization of heat resistant properties of polymeric materials. PP/$Al(OH)_3$/$Mg(OH)_2$ flame retardant composites were prepared using a twin-screw extruder, and the T_V and T_d of the composites were measured. The results showed that the T_V and T_d increased nonlinearly with an addition of the weight percentage of the flame retardant additives except for individual data points, while the T_V and T_d decreased with increasing the filler particle size when the content of flame retardant additives was constant. Under the same conditions, filling small amount of zinc borate into the composites might improve the heat resistant properties of the composite systems. Moreover, the morphology of the impact fracture surface of the specimens was observed by means of scanning electron microscope to understand the dispersion and distribution of the filler particles in the PP matrix.

Keywords Polypropylene · Flame retardant composite · Heat resistant property

Introduction

Polymeric materials are used extensively more and more in industry, agriculture and daily life owing to their good mechanical properties, processing properties, as well as chemical stability. However, their applications are limited to a certain extent because most of them are flammable materials. It is, therefore, the flame retardant of polymeric materials has been paid widely attention [1–4]. Bobovitch et al. [1] proposed a new approach to flame retardants about thermal polymerization on fillers. Chiu and Wang

---

J. Z. Liang (✉) · Y. J. Zhang · X. H. Jiang
School of Mechanical and Automobile Engineering, South China University of Technology,
Guangzhou 510640, People's Republic of China
e-mail: scutjzl@sohu.com

[2] studied the dynamic flame redundancy of polypropylene (PP) filled with ammonium polyphosphate. Chen et al. [3] investigated the effect of component ratio on the performance of intumescent flame retardant master batch synthesized through twin-screw reactively extruding technology. Recently, Levchik and Weil [4] reviewed the advances in the flame retardant of thermoplastic polyesters.

Aluminum hydroxide ($Al(OH)_3$) and magnesium hydroxide ($Mg(OH)_2$) in polymeric materials have triple functions: filler, flame retardant and smoke suppressant [5–9]. It is found that the metal to fabricate flame retardant PP composites without halogen are major $Al(OH)_3$ and $Mg(OH)_2$, they are more than 80% in inorganic flame retardant additives. Titelman and Gonen [7] studied the discoloration of PP-based compounds containing magnesium hydroxide. Jiao and Chen [9] investigated the flame retardant synergism of hydroxy silicone oil and $Al(OH)_3$ in ethylene/vinylacetate (EVA) composites. Zinc borate (ZB) is usually used as a flame retardant synergist [10–13]. Bourbigot et al. [11] reviewed the recent advances in the use of zinc borates in flame retardancy of EVA.

Polypropylene (PP) is a general resin with good insulating and processing properties, small dielectric constant, as well as good stress crack resistance and chemical resistance [14]. However, PP resin is restricted to applications in fields such as electronic, electric, traffic and decorating materials because it belongs to flammable material. In order to widen the application fields of PP resin and to overcome the disadvantages that PP can cause molten drops and easy flame propagation when it is burning, compounding with flame retardants was adopted to modify PP so as to improve its flame-retarding ability.

Polymer materials will generate a series of physical and chemical variations, including softening, melting, oxidation, degradation, crosslink and heat resolution, and so on, with a rise of temperature. All of these variations will result in reduction of the mechanical properties of the materials and will lose their utility. It is, therefore, meaningful for theory and application that the heat resistant and its mechanisms of polymer materials are studied in depth. Vicat softening point temperature and heat deflection temperature are important parameters for the characterization of the heat resistant properties of polymeric materials, but there is no any theoretical correlation between them [15–17].

In the obvious work, the authors [18] prepared the $PP/Al(OH)_3/Mg(OH)_2$ flame retardant composites and measured the flame retardant properties, such as the oxygen index, the horizontal burning velocity and the smoke density rank. The objectives in this article are to measure the Vicat softening point temperature and heat deflection temperature of these composites, and investigate the effects of the content and particle size of the flame retardant agents on the heat resistant properties.

Experimental

Raw materials

A PP with trade mark of CJS-700G was used as a matrix resin in this study. This resin was supplied by Guangzhou Petrochemical Works in Guangdong province

(P.R. China), and its density in solid state and melt flow rate were 910 kg/m^3 and 10 g/10 min, respectively.

Aluminum hydroxide ($Al(OH)_3$) and magnesium hydroxide ($Mg(OH)_2$) were used as the flame retardant additives in this article. They were delivered in the form of white powder, and each additive was supplied having four different mean diameters: 1.25, 2.7, 5 and 9 μm. The density of $Al(OH)_3$ was 2420 kg/m^3 and the density of $Mg(OH)_2$ was 2390 kg/m^3. A zinc borate (ZB) used in this article was as a flame retardant synergist, the density and melting point temperature were 2800 kg/m^3 and 980 °C, respectively. All flame retardant additives were supplied by Foshan Jinge fire-fighting materials Co. Ltd, China. The surface pretreatment of these flame retardant particles was made by the supplier with surface active agent.

Fabrication

The flame retardant particles were blended with PP in a high speed mixer (model CH-10DY), and then the blends were extruded in PP melt state by means of a co-rotating twin-screw extruder (model TSE-35A). The screw diameter was 35.6 mm, and the length diameter ratio was 40. Finally, the extrudate was granulated to produce flame retardant PP composites. The fraction of PP was 100, ZB content was 4 phr (parts per hundred resin), the weight ratio between $Al(OH)_3$ and $Mg(OH)_2$ was 1:2 and the percentage weight fractions (ϕ_f) of $Al(OH)_3/Mg(OH)_2$ were 10, 20, 30, 40 and 50 phr, respectively. In addition, these granular composites were dried for 5 h at 80 °C before specimen preparation.

The specimens for heat resistant test were fabricated with a plastics injection machine (model Un120A) supplied by Yizhimi Precise Machinery Co. Ltd in Foshan, China. The injection temperature was 180 °C, the injection pressure was 7.5 MPa and the cooling time was 18 s. The size of the specimens was 13 mm × 13 mm × 6 mm.

Instrument and methodology

Heat deflection temperature

The heat deflection temperature of polymer materials is the temperature that the deformation reaches the stipulated deformation of the specimen under the given load as the temperature raises with certain speed. The CEAST automotive heat deflection-Vicat softening point tester (model P/N6921.000) supplied by Hong Kong global technology Co. Ltd was used in this study to measure the heat deflection temperature and Vicat softening point temperature of the composites. The heat deflection temperature tests were conducted according to ISO75-2 standard, the heating rate was 120 °C/h and the flexural load was 1.82 MPa. The measurement process was as follows: the rectangle specimen was put on the two fulcrums with span of 100 mm and was soaked in the conductive heat liquid, and the center of the specimen was applied the flexural load, then the liquid was heated with a constant heating rate of 120 °C/h, and the heat deflection temperature was determined as soon as the deformation at the specimen center reached the designed value according to the ISO75-2 standard.

Vicat softening point temperature

The Vicat softening point temperature of polymer materials is the temperature when a needle with cross-sectional area of 1 mm^2 inserts into the specimen up to 1 mm under the conditions of constant heating rate and load. The Vicat softening point temperature tests were carried out according to ISO306 standard, the load was 50 N and the heating rate was also 120 °C/h. The measurement process was as follows: the rectangle specimen was put on the two fulcrums with span of 100 mm and was soaked in the conductive heat liquid, and the center of the specimen was applied a needle with across area of 1 mm^2 and given load, then the liquid was heated with a constant heating rate of 120 °C/h, and the Vicat softening point temperature was determined as soon as the inserting depth of the needle into the specimen reached 1 mm.

Morphology

The impact fracture surfaces of the specimens from the experiments were examined by means of a LEO (model 1530 VP) scanning electron microscope (SEM) to observe the interfacial debonding, interlayer structure morphology and the filler dispersion or distribution in the PP matrix. The specimens were gold coated before SEM examination.

Results and discussion

Influence of flame retardant content and particle size on T_V

Figure 1 shows the relationship between the percentage weight fractions (ϕ_f) of $Al(OH)_3$/$Mg(OH)_2$ and the Vicat softening point temperature (T_V) of the composites when the mean diameter of the flame retardants is 5 μm. It can be seen that the T_V of the composites increases nonlinearly with increasing ϕ_f when ϕ_f is less than 40 phr, and then reduces somewhat. Vicat softening point temperature reflects the movement ability of molecular chains in a certain extent. The higher the T_V is the more difficulty for molecular chain movement is. The results shown in Fig. 1 indicate that molecular chain movement becomes difficulty due to addition of the flame retardant agent, leading to an increase of the Vicat softening point temperature. However, the Vicat softening point temperature decreases somewhat in a case of higher concentration of the flame retardant agent. This might be that a part of flame retardant agent is not uniform in the PP matrix and does not generate good structure state, resulting in a reduction of the Vicat softening point temperature.

Figure 2 illustrates the dependence of the Vicat softening point temperature on the particle diameter (d) of $Al(OH)_3$ and $Mg(OH)_2$ for the PP flame retardant composite systems. When ϕ_f is constant, the T_V of the PP flame retardant composites reduces with increasing d. This is because of the fact that the surface area of the filler increases with decreasing d under the same inclusion concentration,

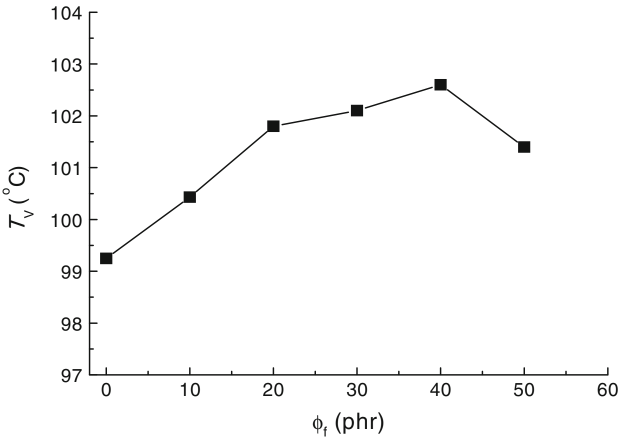


Fig. 1 Relationship between Vicat softening point temperature and flame retardant content ($d = 5$ μm)

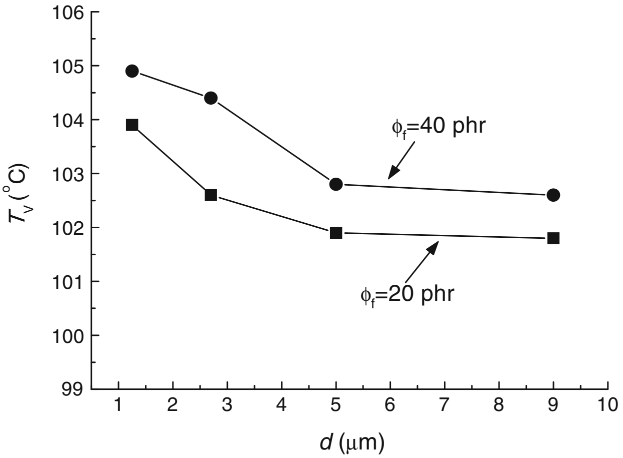


Fig. 2 Dependence of Vicat softening point temperature on flame retardant diameter

leading to enhancing the interfacial effect between the filler and matrix. In this case, the movement ability of the molecular chains reduces while the Vicat softening point temperature increases correspondingly.

Influence of flame retardant content and particle size on T_d

Figure 3 displays the relationship between the percentage weight fractions of $Al(OH)_3/Mg(OH)_2$ and the heat deflection temperature (T_d) of the composites when the mean diameter of the flame retardants is 5 μm. It may be observed that the T_d increases with an addition of ϕ_f when ϕ_f is less than 50 phr, and the T_d reaches

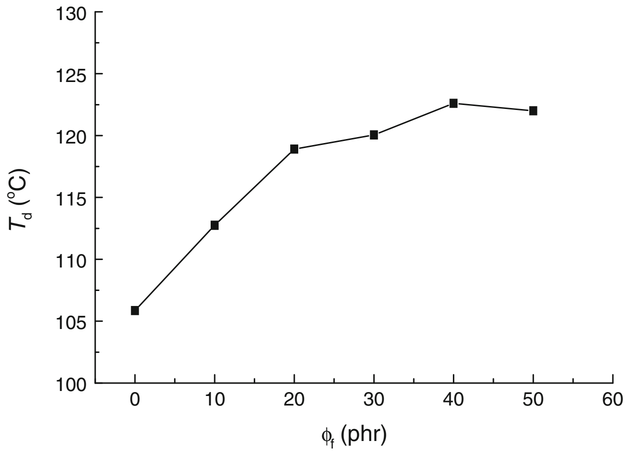


Fig. 3 Relationship between heat deflection temperature and flame retardant content ($d = 5$ μm)

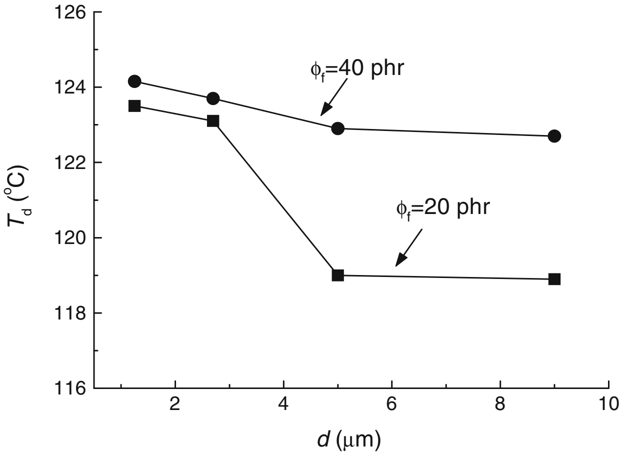


Fig. 4 Dependence of heat deflection temperature on flame retardant diameter

122.6 °C at $\phi_f = 40$ phr. Namely, the heat deflection temperature of the composites increases up to 15.82% comparing neat PP. This indicates that there is obvious effect of $Al(OH)_3$ and $Mg(OH)_2$ on increasing the heat deflection temperature of PP resin. The reason might be that the particles of $Al(OH)_3$ and $Mg(OH)_2$ have blocking action on the molecular chain movement, and this blocking action would enhance with an increase of the flame retardant content, resulting in raising the heat deflection temperature of the composite systems.

Figure 4 illustrates the dependence of the heat deflection temperature on the particle diameter of $Al(OH)_3$ and $Mg(OH)_2$ for the PP flame retardant composite systems. When ϕ_f is, respectively, 20 and 40 phr, the heat deflection temperature of the flame retardant composites decreases with increasing the d; the variation of T_d

owing to different particle diameter is up to 6% under the same ϕ_f. This indicates that the influence of the variation of the particle diameter on the heat deflection temperature is significant. As discussed above, the contacting area between the filler and matrix increases with decreasing the particle diameter under the same inclusion concentration, and the interaction effect between the filler and matrix will be enhanced, leading to reduction of the movement ability of molecular chains and increase of the heat deflection temperature of the composites.

Influence of zinc borate on heat resistant property

Figure 5 shows the relationship between the percentage weight fractions of flame retardant agent and the Vicat softening point temperature of the PP/$Al(OH)_3$/$Mg(OH)_2$ and PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composites when the mean diameter of the flame retardants is 5 μm. It can be seen that the variation of the Vicat softening point temperature with the flame retardant agent content for the two composites is similar. That is, T_V increases first when ϕ_f is varying from 0 to 40 phr and then decreases with increasing ϕ_f when ϕ_f is higher than 40 phr. However, the T_V of PP/$Al(OH)_3$/$Mg(OH)_2$/ZB system is higher than that of PP/$Al(OH)_3$/$Mg(OH)_2$ system under the same ϕ_f. This indicates that the addition of ZB is beneficial to enhance the blocking effect of the movement ability of molecular chains, resulting in increase of the Vicat softening point temperature of the composite. It can also be seen that the T_V of the two composites decreases sharply as ϕ_f is more than 40 phr, and the T_V of the PP/Al(OH)3/Mg(OH)2/ZB system lower than that of the pure PP, it might be related to the dispersion state of the filler particles in the matrix resin.

Figure 6 indicates the relationship between the percentage weight fractions of flame retardant agent and the heat deflection temperature of the PP/$Al(OH)_3$/$Mg(OH)_2$ and PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composites when the mean diameter of the flame retardants is 5 μm. It may be observed that the variation of the heat deflection

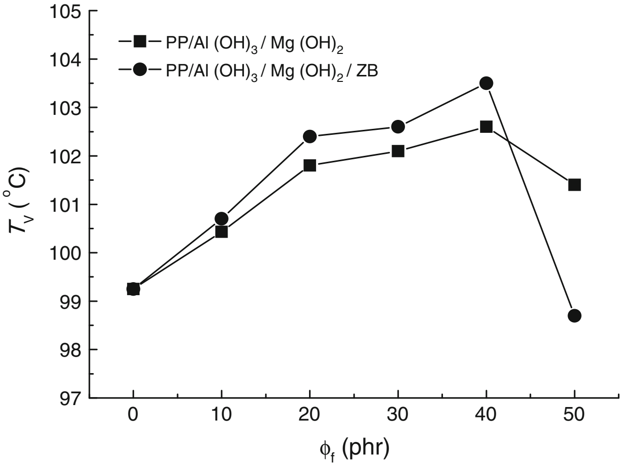


Fig. 5 Influences of zinc borate on Vicat softening point temperature ($d = 5$ μm)

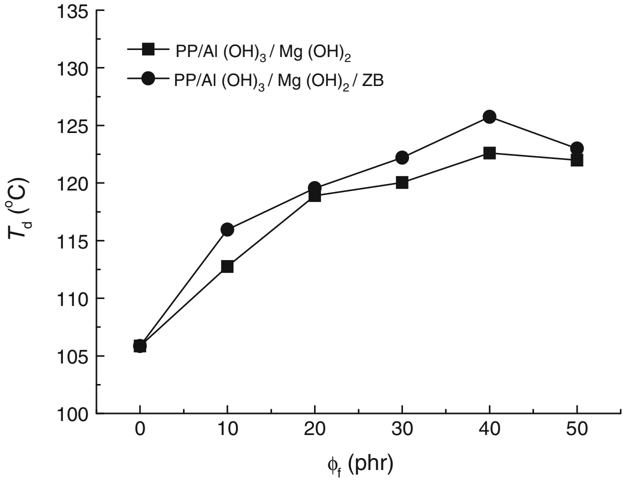


Fig. 6 Influences of zinc borate on heat deflection temperature ($d = 5$ μm)

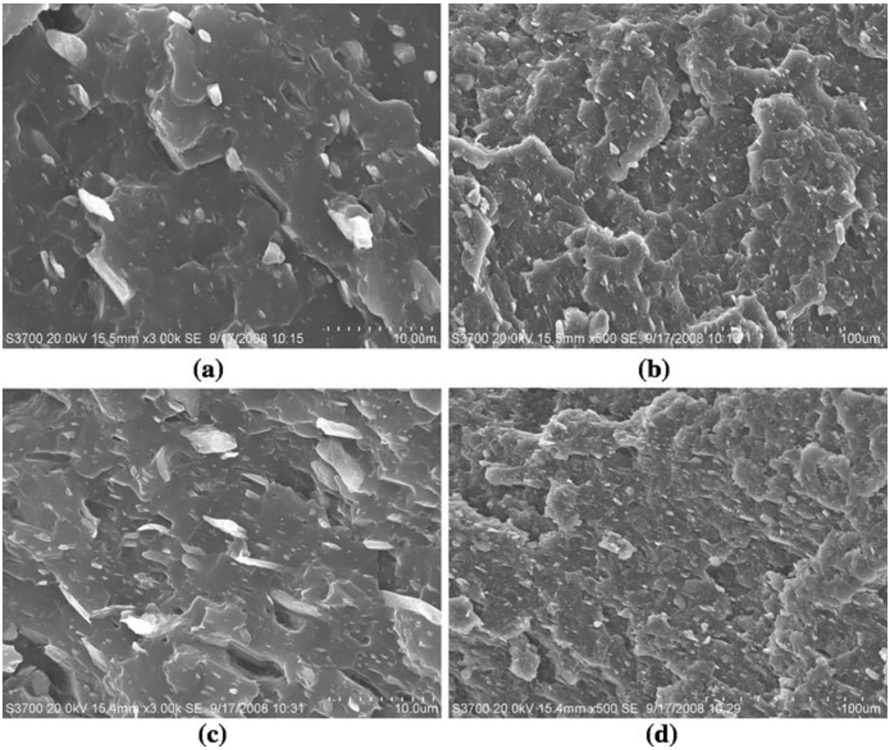
temperature with the flame retardant agent content for the two composites is similar: the T_d increases roughly linearly with increasing ϕ_f, and the T_d of PP/Al(OH)$_3$/Mg(OH)$_2$/ZB system is higher than that of PP/Al(OH)$_3$/Mg(OH)$_2$ system under the same ϕ_f. This because that the combination between Al(OH)$_3$, Mg(OH)$_2$ and ZB might change the morphological structure of the filler particles in the matrix resin, leading to increasing the blocking action to the movement ability of molecular chains. However, the increase of the heat deflection temperature is not significant owing to small concentration of the zinc borate.

Morphology analysis of fracture surface

Figure 7 illustrates the SEM photographs of the V-notched impact fracture surface of the PP/Al(OH)$_3$/Mg(OH)$_2$ composites when d is 5 μm and ϕ_f is 20 and 50 phr, respectively. Here, the magnifying multiples are 500 and 3000, respectively. It may be observed by comparing Fig. 7a–d that there is an aggregation phenomenon for part of flame retardant agent particles in the matrix at ϕ_f of 50 phr. It may be that the particles are difficult to be dispersion uniform in the matrix in the case of high filler concentration, resulting in relevant reduction of the heat deflection temperature and Vicat softening point temperature at ϕ_f of 50 phr.

In general, the type, size, shape and content of fillers as well as the distribution and dispersion state of particles in the matrix will affect significantly the heat resistant properties of the filled polymer composites. The more the dispersion uniform of the filler in the matrix is, the higher the heat resistant properties of the composites are.

In the previous study, Liang and Zhang [18] investigated the effects of the flame retardant content and the particle size on the flame retardant properties of the PP/Al(OH)$_3$/Mg(OH)$_2$ flame retardant composites. It was found that the oxygen



(a) (b)

(c) (d)

Fig. 7 Impact fracture SEM photograph of PP/Al(OH)$_3$/Mg(OH)$_2$ (d = 5 μm): **a** $\phi_f = 20$ phr, ×3000, **b** $\phi_f = 20$ phr, ×500, **c** $\phi_f = 50$ phr, ×3000, **d** $\phi_f = 50$ phr, ×500

index increased with an increase of the flame retardant content and decreased with an increase of the filler diameter. These are similar to the relationship between the T_d, T_V and the flame retardant content and size.

Conclusions

The heat resistant properties of PP flame retardant composite systems could be improved obviously by filling with Al(OH)$_3$ and Mg(OH)$_2$ particles, and a small amount of ZB might also have positive effect on the improvement of the heat resistant properties for PP/Al(OH)$_3$/Mg(OH)$_2$ flame retardant composites. It might be attributed as the blocking action of the flame retardant particles on the molecular chain movement of the matrix, and this blocking action would enhance with an increase of the flame retardant content, resulting in improvement of the heat resistant properties of the PP composite systems.

The Vicat softening point temperature and heat deflection temperature of PP/Al(OH)$_3$/Mg(OH)$_2$ composites increased with increasing the percentage weight fractions of the flame retardant agent when ϕ_f is varying from 0 to 40 phr, and then decreased as ϕ_f is more than 40 phr. It was observed by SEM that there was a aggregation phenomenon for part of flame retardant agent particles in the matrix in the case of high filler concentration (e.g. $\phi_f = 50$ phr), resulting from reduction of the heat resistant properties.

The Vicat softening point temperature and heat deflection temperature of PP/$Al(OH)_3$/$Mg(OH)_2$ composites decreased with increasing the filler particle diameter under the same content of the flame retardant agent. Moreover, the dependence of the Vicat softening point temperature and heat deflection temperature on the flame retardant agent content were similar for the two composites, and the Vicat softening point temperature and heat deflection temperature of PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composite system were higher than those of PP/$Al(OH)_3$/$Mg(OH)_2$ composite system in the case of the same ϕ_f.

Acknowledgements The authors are grateful to Foshan Fudihong Co. Ltd (in China) for their help in the tests.

References

1. Bobovitch A, Gutman E, Schenker M, Utevski L, Muskatel M (1995) New approach to flame retardants: thermal polymerization on fillers. Mater Lett 23(4–6):317–320
2. Chiu SH, Wang WK (1998) Dynamic flame redundancy of polypropylene filled with ammonium polyphosphate, pentaerythritol and melamine additives. Polymer 39(10):1951–1955
3. Chen YH, Liu Y, Wang Q, Yin HA, Aelmans N, Kierkels R (2003) Performance of intumescent flame retardant master batch synthesized through twin-screw reactively extruding technology: effect of component ratio. Polym Degrad Stab 81(2):215–224
4. Levchik SV, Weil ED (2005) Flame retardancy of thermoplastic polyesters: a review of the recent literature. Polym Int 54(1):11–35
5. Carpentier F, Bourbigot S, Le Bras M, Delobel R, Foulon M (2000) Charring of fire retarded ethylene vinyl acetate copolymer magnesium hydroxide/zinc borate formulations. Polym Degrad Stab 69: 83–92
6. Titelman GI, Gonen Y (2002) Discolouration of polypropylene-based compounds containing magnesium hydroxide. Polym Degrad Stab 77:345–352
7. Sangcheol K (2003) Flame retardancy and smoke suppression of magnesium hydroxide filled polyethylene. J Polym Sci 41(9):936–944
8. Ahmad Ramazani SA, Rahimi A, Frounchi M, Radman S (2008) Investigation of flame retardancy and physical–mechanical properties of zinc borate and aluminum hydroxide propylene composites. Mater Des 29(5):1051–1056
9. Jiao CM, Chen XL (2009) Flame retardant synergism of hydroxy silicone oil and Al(OH)3 in EVA composites. Polym Plast Technol Eng 48(6):665–670
10. Kobayashi Y, Tokoro Y, Watatani K (1998) Preparation of functionalized zinc borates and their coupling reaction with allylic acetates. Tetrahedron Lett 39:7537–7540
11. Bourbigot S, Le Bras M, Leeuwendal R, Shen KK, Schubert D (1999) Recent advances in the use of zinc borates in flame retardancy of EVA. Polym Degrad Stab 64(3):419–425
12. Garba B (1999) Effect of zinc borate as flame retardant formulation on some tropical woods. Polym Degrad Stab 64:517–522
13. Giudice CA, Benitez JC (2001) Zinc borates as flame-retardant pigments in chlorine-containing coatings. Prog Org Coat 42:82–88
14. Liang JZ (2002) Toughening and reinforcing in rigid inorganic particle filled polypropylene: a review. J Appl Polym Sci 83:1547–1555
15. Tasdemir M, Biltekin H, Caneba GT (2009) Preparation and characterization of LDPE and PP-wood fiber composites. J Appl Polym Sci 112(5):3095–3102

16. Dubnikova IL, Nizhegorodtseva EI, Lomakin SM, Krasheninnikov VG, Gorenberg AY, Kuleznev VN (2008) Preparation and characteristics of composites based on polypropylene and ultradispersed calcium carbonate. Polym Sci Ser A 50(12):1214–1225
17. Peng HQ, Wang DY, Zhou Q, Wang YZ (2008) An S- and P-containing flame retardant for polypropylene. Chin J Polym Sci 26(3):299–309
18. Liang JZ, Zhang YJ (2010) A study on flame retardant properties of PP/$Al(OH)_3$/$Mg(OH)_2$ composites. Polym Int 59:539–542