Melt Density and Volume Flow Rate of Polypropylene/ $Al(OH)_3$/$Mg(OH)_2$ Flame Retardant Composites

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Received 17 July 2009; accepted 27 February 2010
DOI 10.1002/app.32370
Published online 19 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polypropylene (PP) flame retardant composites filled with aluminum hydroxide ($Al(OH)_3$), magnesium hydroxide ($Mg(OH)_2$) as well as zinc borate (ZB) were prepared with a twin-screw extruder. The melt volume flow rate (*MVR*) and density of the composites were measured by means of a melt flow rate instrument under experimental conditions with temperature of 180°C and load varying from 2.16 to 5 kg, to identify the effects of the particle size and content. The results showed that *MVR* of the composites decreased with an increase of the filler weigh fraction (ϕ_f) when ϕ_f was more than 10 phr. The *MVR* decreased first and then increased with an increase of the filler diameter (*d*). The melt density (ρ_m) of the composites increased linearly with an increase of ϕ_f and decreased linearly with the increase of *d*. In addition, the ρ_m increased with an increase of load. Under the same experimental conditions, the *MVR* decreased slightly while the ρ_m increased somewhat with addition of ZB for the PP/$Al(OH)_3$/$Mg(OH)_2$ composite systems. J Appl Polym Sci 118: 332–337, 2010

Key words: PP; $Al(OH)_3$; $Mg(OH)_2$; flow property; melt density

INTRODUCTION

Polymeric materials are used extensively in industry, agriculture, and daily life, owing to their good mechanical properties (e.g. high-specific strength), processing properties, and chemical stability. However, their applications are limited to a certain extent, because most of them are flammable materials. It is therefore that, how to improve the flame retardant of polymeric materials have 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[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 progress in the flame retardant of thermoplastic polyesters.

It is generally believed that 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[6] 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 ZBs in flame retardancy of EVA.

PP is a general thermoplastic 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 applications in some fields such as electronic, electric, traffic, and decorating materials because it belongs to flammable material. To widen the application fields of PP resin and overcome the disadvantages that PP can cause molten drops and easy flame propagation when it is burning, compounding flame retardants were adopted to modify PP with the aim to improve the flame retarding ability of PP resin.

Melt volume flow rate (*MVR*) is an important characteristics for flow properties of polymeric materials, and melt density (ρ_m) is an important parameter during polymer processing. As to flame

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retardant polymer composites, *MVR* and ρ_m are also related closely with the flame retardant functionality in addition to the processing properties. However, there have been a few studies on *MVR* and ρ_m of flame retardant polymer composites. The objectives of this article are to prepare PP/Al(OH)$_3$/Mg(OH)$_2$ composite systems and measure the *MVR* and ρ_m of these composite systems, to investigate the effects of flame retardant content, and the particle size on the flame retardant properties.

EXPERIMENTAL

Raw materials

The PP with trade mark of CJS-700G was used as the matrix resin in this work. 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.

In this article, Al(OH)$_3$ and Mg(OH)$_2$ were used as the flame retardant additives. They were white powder, and the mean diameters of both Al(OH)$_3$ and Mg(OH)$_2$ were 1.25, 2.7, 5.0, and 9.0 μm, respectively. The density of Al(OH)$_3$ was 2420 kg m^{-3} and the density of Mg(OH)$_2$ was 2390 kg m^{-3}. ZB used in this aticle was as the 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., Foshan City, China.

Material preparation

The flame retardant particles were blended with PP in a high-speed mixer (model CH-10DY), and then these 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 the flame retardant PP composites. The surface of the flame retardant particles was pretreated by the supplier. 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 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 flow property tests.

Instrument and methodology

The main experimental instrument used in this work was a melt flow indexer (Model XNR-400) supplied by Kos Scientific testing Co. (Chengde City, China). The die length and the die diameters were 8.000 mm and 2.095 mm, respectively. The die entry angle was 180°. The test temperature was 190°C, and the load was varied from 2.16 to 5.0 kg. The *MVR* of the composites was measured under these experimental conditions, five tests were conducted and the average was reported for each composition. A relationship between the *MVR* and ρ_m may be expressed as follows:

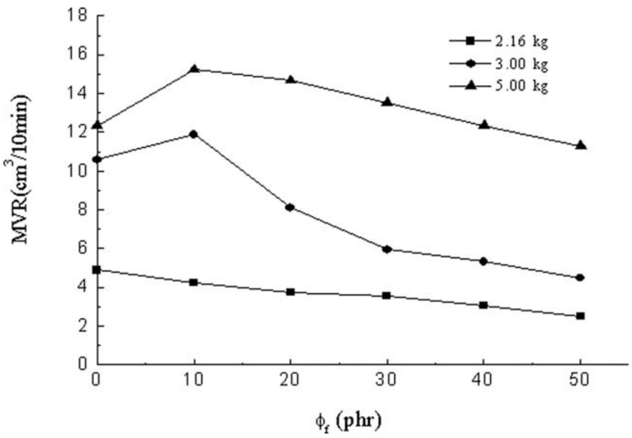

Figure 1 Relationship between *MVR* and ϕ_f of PP/Al(OH)$_3$/Mg(OH)$_2$ composite.

$$\rho = \frac{600W}{MVR \times t} \quad (1)$$

Where t is the time of the melt flowing through the capillary die, W is the extrudate weight in time t.

RESULTS AND DISCUSSION

Relationship between MVR and filler content

Figure 1 shows the relationship between the *MVR* of the PP/Al(OH)$_3$/Mg(OH)$_2$ composites and the Al(OH)$_3$/Mg(OH)$_2$ content under the conditions with different loads. When ϕ_f is $< 10\%$, the *MVR* of the composites is higher than that of the neat PP resin and then the *MVR* decreases with increasing ϕ_f under higher load level. This indicates that a small amount of the Al(OH)$_3$ and Mg(OH)$_2$ particles might reduce the melt viscosity of the PP composites in the case of higher load level, leading to increase of the *MVR*. Moreover, the *MVR* decreases roughly linearly with increasing ϕ_f when the load is < 3 kg, and the relationship between them may be expressed as follows:

$$MVR = \alpha + \beta\phi_f \quad (2)$$

Where α and β are the constants related to load and temperature.

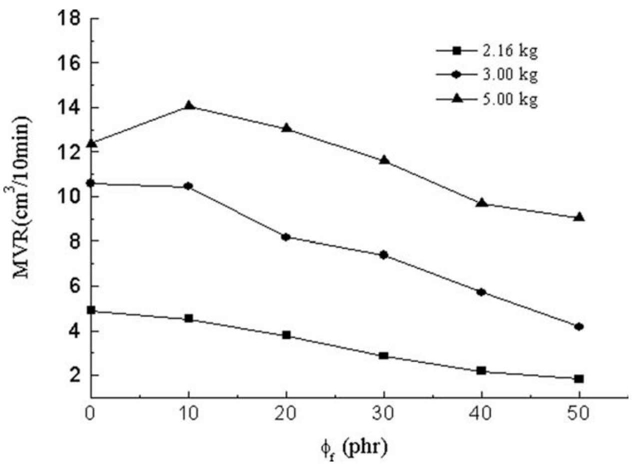

Figure 2 Relationship between *MVR* and ϕ_f of PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composite.

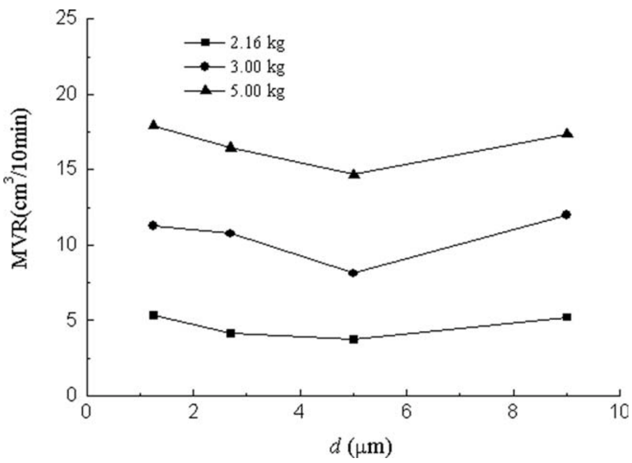

Figure 3 Dependence of *MVR* on particle diameter of PP/$Al(OH)_3$/$Mg(OH)_2$ composite ($\phi_f = 20$ phr).

Figure 2 shows the relationship between the *MVR* of PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composites and the $Al(OH)_3$/$Mg(OH)_2$ content under the conditions with different loads. It can be seen that, the relationship between the *MVR* and ϕ_f for the PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composites is similarly to the PP/$Al(OH)_3$/$Mg(OH)_2$ systems under the same experimental conditions. When the load is < 3 kg, the *MVR* decreases roughly linearly with increasing ϕ_f.

The values of the constants α and β in eq. (2) may be determined by means of a linear regression method. Table I lists the values of α and β of the PP/$Al(OH)_3$/$Mg(OH)_2$ and the PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composite melts under the experimental conditions with load of 2.16 kg and temperature of 190°C. It may be seen that the values of α and β of the PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composite are greater than those of the PP/$Al(OH)_3$/$Mg(OH)_2$ composite, and the linear correlation coefficients (R) for the two composite systems are >0.99. This indicates that there is somewhat effect of ZB on the sensitivity of the *MVR* of the composite systems to ϕ_f under these experimental conditions.

In general, the friction resistance between the neighboring melt layers in extrusion flow of polymeric composite systems will increase with an addition of inclusions, and the movement of molecular chains will be blocked correspondingly, leading to increase of the melt viscosity of the composite systems.[15] However, shear rate increases with increasing loads, when temperature is fixed. In this case, the tangle points among macromolecules and the equilibrium concentration during untangle reduce, resulting in reduction of apparent shear viscosity. However, when polymer is filled with a small amount of flame retardant, the particles might generate somewhat lubricant action in the matrix, leading to the reduction of action force between macromolecular chains. Consequently, the melt viscosity of the composites reduces or the *MVR* increases correspondingly (see Figs. 1 and 2). For the ZB, it plays a role not only a flame retardant assistant but also a compatibilizer in the composite systems, to improve the compatibility between the PP resin and the $Al(OH)_3$/$Mg(OH)_2$ particles, leading to improvement of the melt flow properties of the composite systems.

TABLE I
Values of α, β, and *R* of Composites at Loading of 2.16 Kg

Composites	α	β	R
PP/$Al(OH)_3$/$Mg(OH)_2$	4.78314	−0.04519	0.99218
PP/$Al(OH)_3$/$Mg(OH)_2$/ZB	4.999	−0.0042	0.99211

Dependence of MVR on particle size

Figure 3 displays the dependence of the *MVR* of the PP/$Al(OH)_3$/$Mg(OH)_2$ composite systems on the particle diameter (d) under different loads when ϕ_f is 20 phr. Figure 4 displays the influence of particle diameter (d) on the *MVR* of the PP/$Al(OH)_3$/$Mg(OH)_2$ composite systems under different loads when ϕ_f is 40 phr. It can be seen that, the *MVR* reduces first, then increases with increasing d as the load is constant, and it reaches the minimum at d of 5 μm. In addition, the dependence of the *MVR* on the particle diameter d is obvious with an increase of loads. It is generally believed that the factors affecting polymer melt flow properties are complicated, especially for polymer composites. For inorganic particulate-filled polymer composites, the melt flow properties depend to some extent on the state of the filler dispersion and distribution in the matrix in addition to the particle content, shape, size, and size distribution under given operation condition. In general, the number of the filler particles will

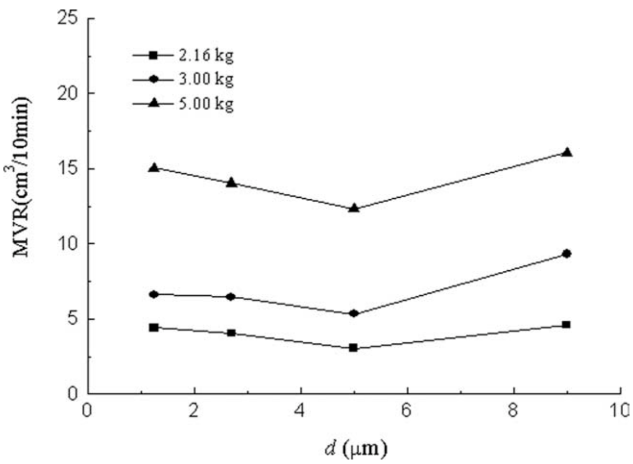

Figure 4 Dependence of *MVR* on particle diameter of $PP/Al(OH)_3/Mg(OH)_2$ composite ($\phi_f = 40$ phr).

increase with reduction of the particle diameter at the same filler concentration. However, the status of the filler dispersion and distribution in the matrix will vary with both the particle size and concentration, resulting in variation of the *MVR* of the composite.

Relationship between melt density and filler content

Figure 5 illustrates the relationship between the melt density (ρ_m) of the $PP/Al(OH)_3/Mg(OH)_2$ composites and the $Al(OH)_3/Mg(OH)_2$ content under the test conditions with different loads. With an addition of ϕ_f, the ρ_m increases roughly linearly, and the relationship between them may be expressed as

$$\rho_m = \lambda_1 + \lambda_2\phi_f \quad (3)$$

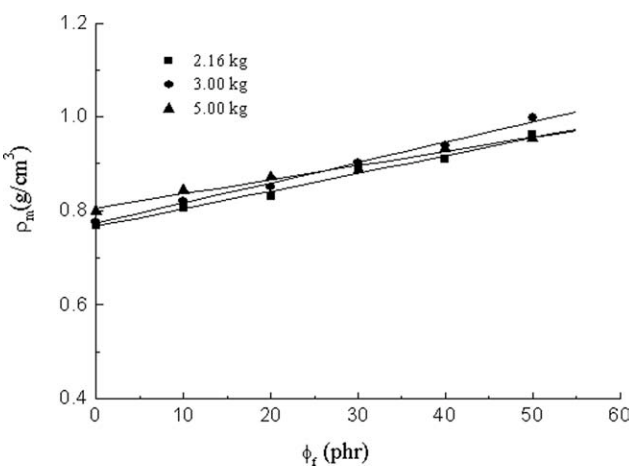

Figure 5 Relationship between ρ_m and ϕ_f of $PP/Al(OH)_3/Mg(OH)_2$ composite at different loadings.

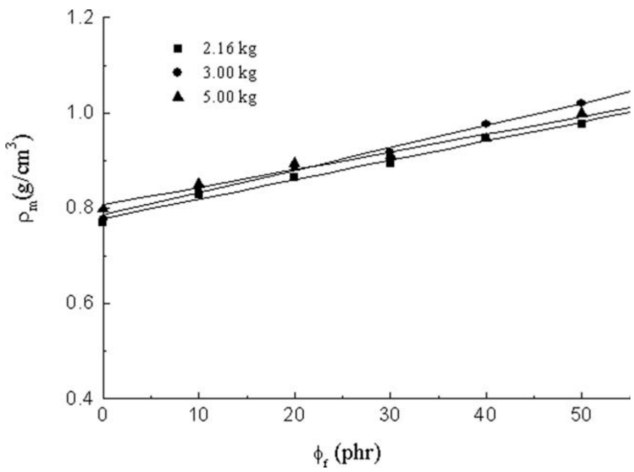

Figure 6 Relationship between ρ_m and ϕ_f of $PP/Al(OH)_3/Mg(OH)_2/ZB$ composite at different loadings.

Where λ_1 and λ_2 are the constants related to load and temperature and material property.

Figure 6 shows the relationship between the melt density of the $PP/Al(OH)_3/Mg(OH)_2/ZB$ composites and the $Al(OH)_3/Mg(OH)_2$ content under the test conditions with different loads. It can be seen that the relationship between the ρ_m and ϕ_f for the $PP/Al(OH)_3/Mg(OH)_2/ZB$ composites is similar to the $PP/Al(OH)_3/Mg(OH)_2$ under the same experimental conditions. This is because that the densities of the $Al(OH)_3$ and $Mg(OH)_2$ particles are higher than that of the PP resin, and the ρ_m of the $PP/Al(OH)_3/Mg(OH)_2$ composites increases with an increase of the filler content.

The values of constants λ_1 and λ_2 in eq. (3) may also be determined by means of linear regression. Table II lists, respectively, the values of λ_1 and λ_2 of $PP/Al(OH)_3/Mg(OH)_2$ and $PP/Al(OH)_3/Mg(OH)_2/ZB$ composite melts under the experimental conditions. It may be seen that the λ_1 increases lightly with increasing loads, and the linear correlation coefficients (R) for the composite systems are >0.99. Moreover, the values of constants λ_1 and λ_2 of the $PP/Al(OH)_3/Mg(OH)_2/ZB$ composite melt are higher than those of the $PP/Al(OH)_3/Mg(OH)_2$ composite melt, this indicates that there is a certain effect of the ZB on the melt density for the composite systems under these experimental conditions. As discussed above, the ZB plays a role not only a flame retardant assistant but also a compatibilizer in the composite systems, to improve the compatibility between the PP resin and the $Al(OH)_3/Mg(OH)_2$ particles, leading to increase of the melt density of the composites. In addition, the density of the ZB particle is higher than that $Al(OH)_3$ and $Mg(OH)_2$ particles, and the λ_1 value of the $PP/Al(OH)_3/Mg(OH)_2/ZB$ composite melt is slightly higher than that of the $PP/Al(OH)_3/Mg(OH)_2$ composite melt.

TABLE II
Values of λ_1, λ_2, and R of Composites at Different Loadings

F (kg)	λ_1	λ_2	R
(a) PP/$Al(OH)_3$/$Mg(OH)_2$ composite system			
2.16	0.76586	0.00379	0.99432
3	0.77238	0.00433	0.99617
5	0.80538	0.00301	0.99181
(b) PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composite system			
2.16	0.77838	0.00405	0.99494
3	0.78529	0.00471	0.99522
5	0.80610	0.00372	0.99020

Dependence of melt density on particle size

Figures 7 and 8 show, respectively, the dependence of the melt density of the PP/$Al(OH)_3$/$Mg(OH)_2$ composite systems on the filler particle diameter when the flame retardant content are 20 and 40 phr. It can be seen that the ρ_m decreases linearly with an increase of d. The reason generated this phenomenon might be that the number of the filler particles will increase with reduction of the particle diameter at the same filler concentration, resulting in increase of the melt density of the composite systems. In this case, the relationship between the melt density and the particle diameter may be expressed as:

$$\rho_m = \theta_1 + \theta_2 d \tag{4}$$

Where θ_1 and θ_2 are the constants related to load and temperature and material property. Similarly, the values of constants θ_1 and θ_2 in eq. (4) may be determined by means of linear regression. Table III lists, respectively, the values of θ_1 and θ_2 of the PP/$Al(OH)_3$/$Mg(OH)_2$ composite melts under the experimental conditions. It may be seen that the linear corresponding coefficients (R) for the composite systems are >0.99.

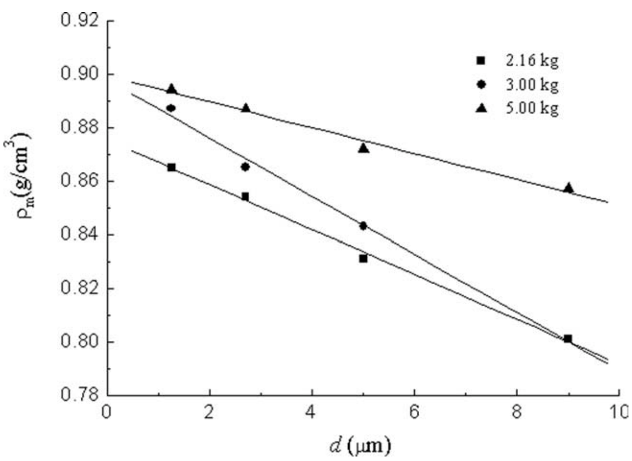

Figure 7 Dependence of ρ_m on particle diameter for PP/$Al(OH)_3$/$Mg(OH)_2$ composites at different loadings.

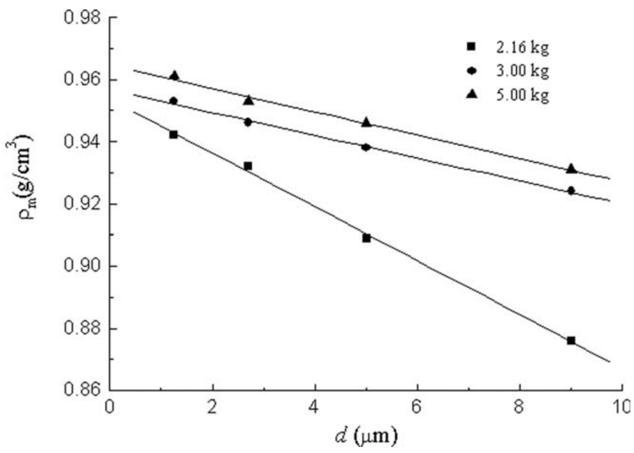

Figure 8 Dependence of ρ_m on particle diameter for PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composites at different loadings.

It may also be observed in Figures 7 and 8 that the melt density increases with an increase of loads as the other test conditions are fixed. This is because that the pressure subjected by polymer melt increases with increasing loads, and the melt volume reduces correspondingly, leading to increase of the density. In addition, the flow rate increases with increasing the loads, and PP resin is a crystalline resin, the flow-induced crystallization behavior will happen, even though at low-flow rate, resulting from variation of the melt density of the composite materials.[16]

Moreover, the effect of the ZB on the melt density of the composite systems is obvious under these experimental conditions. As stated above, it might be attributed to that the ZB plays a role not only as a flame retardant assistant but also as a compatibilizer in the composite systems, to improve the compatibility between the PP resin and the $Al(OH)_3$/$Mg(OH)_2$ particles, leading to an increase in the melt density of the composite systems.

TABLE III
Values of θ_1, θ_2, and R of Composites at Different Loadings

F (kg)	θ_1	θ_2	R
(a) $\phi_f = 20\%$			
2.16	0.95359	−0.00865	0.99817
3	0.89757	−0.01082	0.99741
5	0.89918	−0.00483	0.99239
(b) $\phi_f = 40\%$			
F(kg)	θ_1	θ_2	R
2.16	0.95359	−0.00865	0.99892
3	0.95674	−0.00367	0.99823
5	0.96460	−0.00375	0.99650

CONCLUSIONS

The influences of the content and size of the $Al(OH)_3$ and $Mg(OH)_2$ particles on the melt density and melt volume rate of the flame retardant PP composites are significant under the experimental conditions. The results showed that the *MVR* decreased roughly, linearly with increasing ϕ_f for the two flame retardant PP composites at low-load level. While the *MVR* increased first and then decreased with increasing of ϕ_f at higher load level. This might be attributed to the melt shear thinning effect during extrusion flow of the composites.

The *MVR* of the flame retardant PP composites reduced first and then increased with an increase of the filler particle diameter under the given experimental conditions. The *MVR* reached the minimum when the particle diameter was 5 μm. The melt density increased roughly linearly with an addition of ϕ_f under the conditions with the same particle diameter. However, as to the same particle diameter and filler concentration, the melt density increases with increasing loads.

Moreover, there are somewhat effects of ZB on the melt density and volume flow rate of the composite systems under these experimental conditions, and the melt density and volume flow rate of the PP/$Al(OH)_3$/$Mg(OH)_2$/ZB composite systems are higher than those of the PP/$Al(OH)_3$/$Mg(OH)_2$ composite systems. It might be attributed to that the ZB plays a role not only as a flame retardant assistant but also as a compatibilizer in the composite systems, to improve the compatibility between the PP resin and the $Al(OH)_3$/$Mg(OH)_2$ particles, leading to increasing the melt density of the composite systems.

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