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Extrudate Swell Behavior of Polypropylene Composites Filled with Microencapsulated Red Phosphorus

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ABSTRACT: The microencapsulated red phosphorus (MRP) filled polypropylene (PP) composites were prepared using a twin-screw extruder. The effects of load and temperature on the extrudate swell behavior of the PP/MRP composite melts were investigated by means of a melt flow indexer. The test temperatures and loads were varied from 180 to 205°C and from 2.16 to 12.5 kg, respectively. The results showed that the die-swell ratio (*B*) of the composite melts increased roughly linearly with increasing load while decreased slightly with a rise of test temperature. The sensitivity of the die-swell ratio of the composite melts to load was significant. When the test temperature or load was constant, the values of the *B* of the composite melts decreased slightly with increasing MRP weight fraction. The findings can provide useful information for processing of these composites. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 3497–3501, 2013

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INTRODUCTION

Extrudate swell is also called die-swell or the Barus effect and is an important phenomenon related to the melt elasticity during extrusion flow of polymeric materials, which occurs as a result of the recovery of the elastic deformation imposed. Hence, studying the melt die-swell and its affecting factors is helpful to reveal the rheological mechanisms and also provides useful guidelines of optimum processing conditions for polymer materials.[1] Since 1995, Liang et al.[2–5] have investigated the effects of extrusion conditions on the melt die-swell behavior of polyolefin blends using capillary rheometer and observed some interesting findings.

Polypropylene (PP) is a general resin with good insulation properties, small dielectric constant, good stress crack resistance, and chemical resistance.[6,7] However, PP resin has a poor flammability resistance and can continue to burn and cause flaming drips when ignited. In order to widen the applications of PP, flame retardants are usually added into this material for enhancing its flame-retarding ability. Recently, the flame retardant for PP have received increasing attention.[8–11] Aluminum hydroxide ($Al(OH)_3$) and magnesium hydroxide ($Mg(OH)_2$), the kind of halogen-free flame retardants, have been widely used in various polymers such as PP, because of its triple functions: filler, flame retardant, and smoke suppressant.[12–14] Microencapsulated red phosphorus (MRP) is a kind of synergist for flame retardant and usually used along with $Al(OH)_3$ and $Mg(OH)_2$ in producing flame retardant filled polymer composites.[15–18] More recently, Liang et al.[19] investigated the effects of extrusion conditions on the extrudate swell behavior during die flow of PP/$Al(OH)_3$/$Mg(OH)_2$ composites; the results showed that the extrudate swell ratio of the composite melts decreased linearly with an increase of the filler concentration and increased approximately linearly with increase of the particle size of the flame retardant.

There are a few of studies on the rheological properties for the PP/MRP composite melts, especially on the extrudate swell behavior. The objectives of this article are to investigate the effects of the MRP content and extrusion conditions (e.g., temperature and load) on the melt extrudate swell behavior during extrusion flow of the PP/MRP composites.

EXPERIMENTAL

Raw Materials

The PP with a trademark of CJS-700G was used as a matrix resin in the present work. This resin was supplied by

Table I. Summarization of Partial Physical Properties

Material	W_f (%)	Density (g/cm^3)	MFR (g/10 min) (230°C, 2.16 kg)
PP	0	0.91	10.00
PP/MRP	2	0.934	10.26
PP/MRP	4	0.958	10.54
PP/MRP	6	0.982	10.8
PP/MRP	8	1.006	11.00
PP/MRP	10	1.03	11.74

Guangzhou Petrochemical Works in Guangdong province (Guangzhou, China), and its densities in a solid form and melt flow rate (MFR) were 0.91 g/cm^3 and 10 g/10 min (190°C, 2.16 kg), respectively.

The MRP with trademark of FRP-950-9, produced by Guangzhou Yinsu Flame retardant Materials Co. (Guangzhou, China), was used as a filler. The mean diameter, density, and melting temperature of the MRP were about 10 μm, 1.2 g/cm^3 and 140°C, respectively.

Preparation

After the PP resin was simply mixed with the MRP, they were blended in their molten state in a twin-screw extruder supplied by Nanjing Chengmeng Machinery Ltd. (model SHJ-26, Nanjing, China) at the temperature of 165–180°C and screw speed of 200 rpm. The extrudates of the PP/MRP composites were then water granulated. The weight fractions of MRP (W_f) were 2%, 4%, 6%, 8%, and 10%, respectively. Table I lists the summarization of partial physical properties for the composites. The diameter and length to diameter ratio of the screw were 24.5 mm and 40, respectively. The prepared PP/MRP composite particles were dried for 5 h at 80°C before the rheological tests.

Apparatus and Methodology

The extrusion flow tests were performed on a melt flow indexer supplied by Kauth Scientific Technical Services (model XNR-400C, Chengde city, China) at temperatures ranging from 180 to 205°C, and loads varying from 2.16 to 12.50 kg. Three tests were conducted, and the average was reported for each load and temperature. The die diameter (D) and the die length (L) were 2.095 mm and 8.000 mm, respectively. The entry angle was 180°. In general, the extrudate swell degree is usually expressed by die-swell ratio (B), which was defined as the ratio of the extrudate diameter (D_e) to the die diameter (D). That is,

$$B = \frac{D_e}{D} \quad (1)$$

where the extrudate diameter was measured using an electronic digital caliper after full cooling and relaxation.

RESULTS AND DISCUSSION

Dependence of Die-Swell Ratio on Load

Figure 1 illustrates the dependence of the die-swell ratio on loads for the composite melt with the MRP weight fraction of 8% under different test temperatures. It may be observed that the die-swell ratio of the composite melts increases roughly linearly with increasing loads when the test temperature is constant. As the load is fixed, the value of the B of the composite melts decreases with a rise of the test temperature.

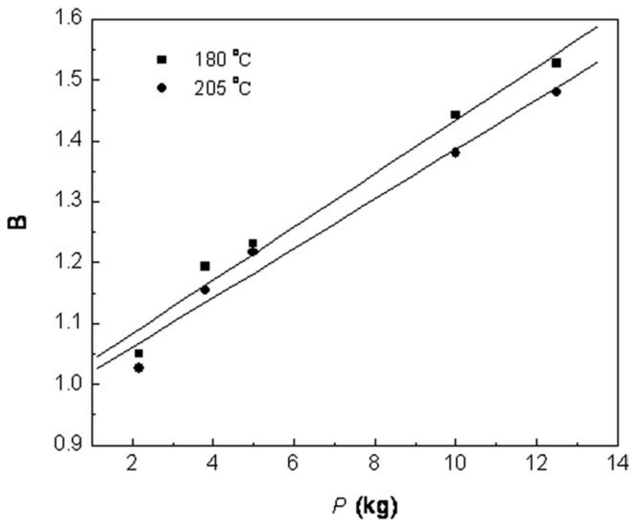

Figure 1. Dependence of die-swell ratio on load of PP/MRP composite melt ($W_f = 8\%$).

Figure 2 shows the dependence of the die-swell ratio on loads for the composite melts with the MRP weight fraction of 8% under different filler contents and test temperature of 185°C. Similarly, the die-swell ratio of the composite melts also increases roughly linearly with an increase of the loads, while it decreases with an addition of the filler content.

During extrusion flow of polymer, the melts are subjected with the shear stress by flow field, and the shear deformation is generated correspondingly. In this case, the extrudate swell is partly attributed as the elastic recovery of the shear deformation as the melt leaves from the die. In generally, the shear stress subjected by polymer melt in extrusion flow increases with increasing

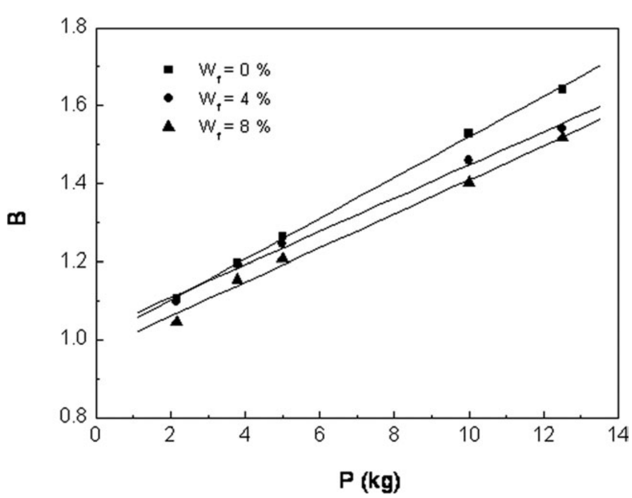

Figure 2. Dependence of die-swell ratio on load of PP/MRP composite melt at 185°C.

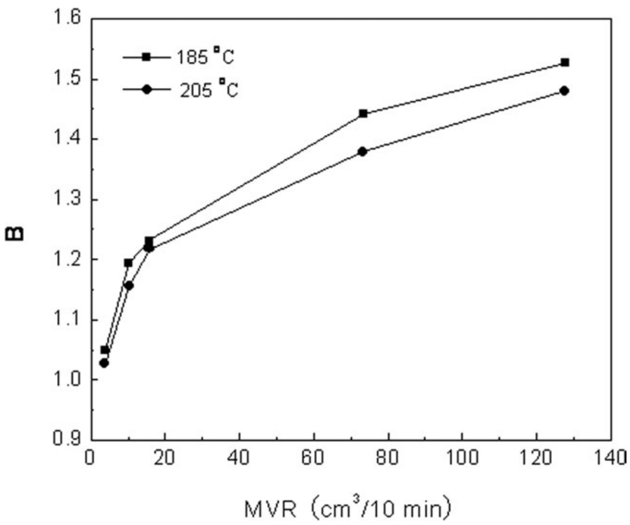

Figure 3. Dependence of die-swell ratio on MVR of PP/MRP composite melt ($W_f = 8\%$).

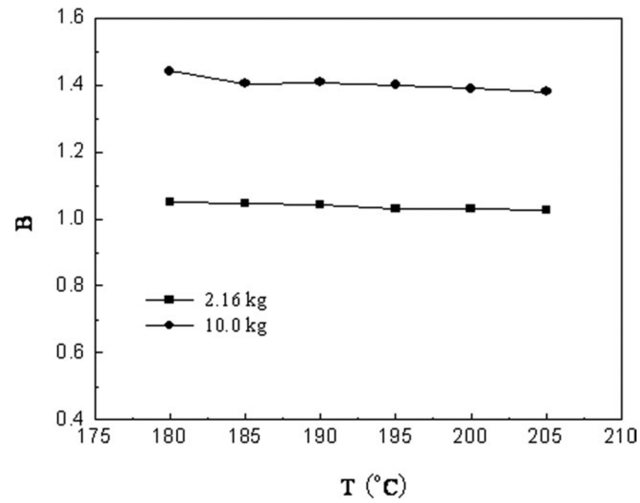

Figure 5. Dependence of die-swell ratio on temperature of PP/MRP composite melt ($W_f = 8\%$).

load as temperature is fixed, and the relationship between the load and shear stress at the channel wall (τ_w) may be expressed roughly as follows[20]:

$$\tau_w = \frac{FR}{2\pi R_p^2 L} \qquad (2)$$

where L is the die length.

Influence of Flow Rate on Die-Swell Ratio

Figure 3 illustrates the influence of melt volume flow rate (MVR) on the melt die-swell ratio for the PP/MRP composites with the MRP weight fraction of 8% at different temperatures. It may be found that the value of B of the composite melt increases nonlinearly with increasing MVR when the test temperature is constant, and the sensitivity of the B to MVR will be weakened as the MVR is more than 20 cm^3/10 min. It can also be seen from Figure 3 that the value of B of the PP/MRP composite melts decreases with a rise in temperature under given the MVR. Figure 4 displays the dependence of the die-swell ratio on the MVR for the unfilled PP (i.e., filler weight fraction $W_f = 0$) and the PP/MRP composite melts with different filler contents at test temperature of 185°C. Similarly, the value of B of the unfilled PP and the PP/MRP composite melts increases nonlinearly with increasing MVR when the filler content is constant, and the sensitivity of the value of B to MVR for the composite melts decreases as the MVR is more than 20 cm^3/10 min. Moreover, the sensitivity of the value of B to MVR for the composite melts decreases with increasing filler weight fraction when the MVR is fixed.

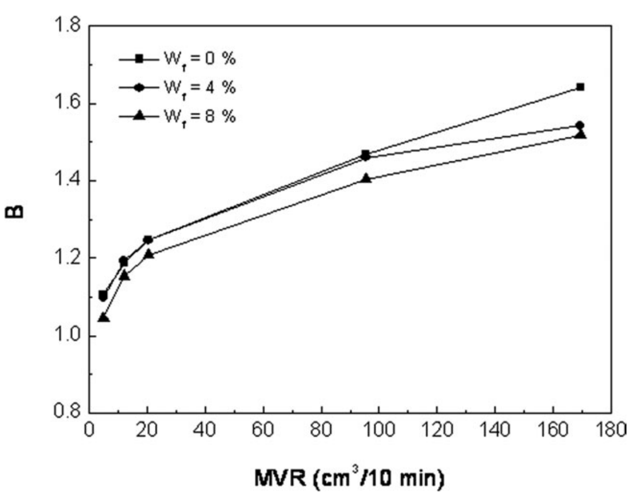

Figure 4. Dependence of die-swell ratio on MVR of PP/MRP composite melt at 185°C.

In general, shear rate increases with an increase of flow rate, the resident time of polymer melt in a channel during extrusion flow will be shortened, and the elastic recovery effect will be enhanced after the melt leaves from the die, leading to increase of the die-swell ratio. It was found that the melt die-swell ratio of polymeric materials was closely related to residence time, the total pressure and entry pressure losses, the channel length–diameter ratio, the melt shear modulus, the melt relaxation time, etc.[21] In addition, the MVR is the linear function of apparent shear rate under given conditions. Consequently, the melt die-swell ratio of the PP/MRP composites increases with increasing MVR.

Dependence of Melt Die-Swell Ratio on Temperature

Figure 5 illustrates the dependence of the melt die-swell ratio on the test temperature for the PP/MRP composite with the filler weight fraction of 8% at two different loads. When the load is kept constant, the melt die-swell ratio of the composites decreases slightly with increasing temperature, improving insignificantly the effect of test temperature on the melt die-swell ratio for the composites. When the test temperature is constant, the value of the B of the composite melts increases with an increase of the load. Figure 6 displays the dependence of the melt die-swell ratio on the test temperature at a load of 12.5 kg for the unfilled PP and the PP/MRP composites when the filler weight fractions are 4% and 8%, respectively. With a rise of test

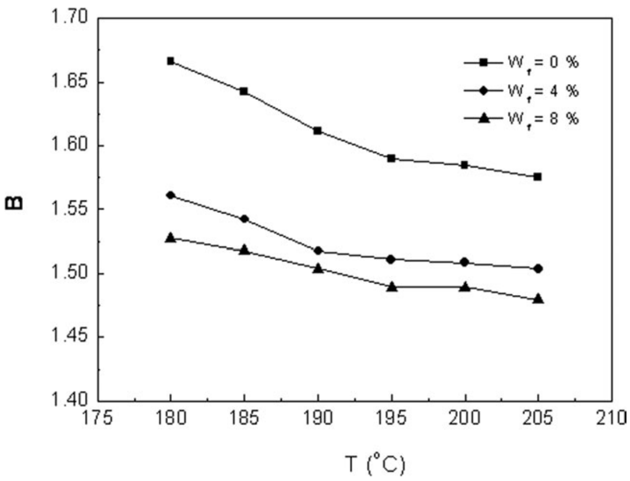

Figure 6. Dependence of die-swell ratio on temperature of PP/MRP composite melt at a load of 12.5 kg.

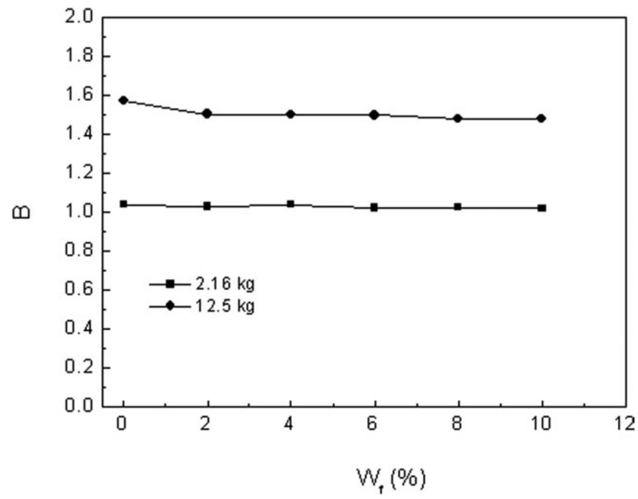

Figure 7. Relationship between die-swell ratio and filler weight fraction of PP/MRP composite melts at 205°C.

temperature the melt die-swell ratio of the unfilled PP and the composites decreases nonlinearly. Relatively, the sensitivity of the melt die-swell ratio to temperature for the unfilled PP is higher than that for the composites. In addition, the value of the *B* of the melts decreases with addition of the filler content.

In general, the activities or transition ability of the macromolecular chain of the resin increase as the temperature raises; meanwhile, the melt viscosity decreases, leading to quickening of relaxation process. In this case, the viscous dissipation of the deformation energy stored in extrusion flow increases, and the ability of the elastic recovery of the deformation is weakened relevantly, resulting in the reduction of extrusion swell of the composite melts. On the other hand, the activities or transition ability of the macromolecular chain of the resin will be blocked to some extent by the inclusions, and the elastic recovery of the deformation for the extrudate will be weakened, leading to a decrease in the sensitivity of the melt die-swell ratio to temperature and die-swell ratio for the composites with increasing filler content.

Relationship between Melt Die-Swell Ratio and MRP Content

Figure 7 shows the relationship between the melt die-swell ratio and the MRP weight fraction for the PP/MRP composites and the unfilled PP under two different loads and at test temperature of 205°C. The melt die-swell ratio of the composites decreases slightly with increasing MRP weight fraction for the both loads except for individual data point. Figure 8 displays the correlation between the melt die-swell ratio and the MRP weight fraction for the PP/MRP composites under two different test temperatures and at a load of 12.5 kg. Similarly, the melt die-swell ratio of the composites decreases slightly with increasing W_f. This phenomenon should be attributed to the microencapsulated resin around the red phosphorus, because the microencapsulated resin improves the melt flow properties of the PP (see Table I) and decreases the melt elasticity of the filled systems, resulting in the reduction of the extrudate swell with increasing MRP concentration. In addition, the melt die-swell ratio of the composite with W_f of 6% decreases obviously at 185°C. It should be that the stability for the melt flow might be weakened during extrusion of the PP/MRP blends under lower temperature, leading to the extrudate swell being easy to fluctuate. It can also be seen in Table I that the MFR of the PP/MRP composites slightly increases with an increase of the MRP weight fraction; it indicates that the melt flow property of the filled systems is somewhat improved.

When molten polymer flows through a die, molecular chains will deviate from equilibrium conformations and orient along the flow direction due to the applied shear and extension from the flow field. As melt leaves from the die, molecular chains tend to recoil in the flow direction and grow in the normal direction, leading to extrudate swell. Polymer melt is a kind of typical mater with viscoelasticity, and extrudate swell is one of the important characterizations during extrusion flow. In general, the extrudate swell is affected by many factors, such as the shear rate or shear stress, temperature, channel geometry (e.g., die length/diameter ratio), as well as polymer melt

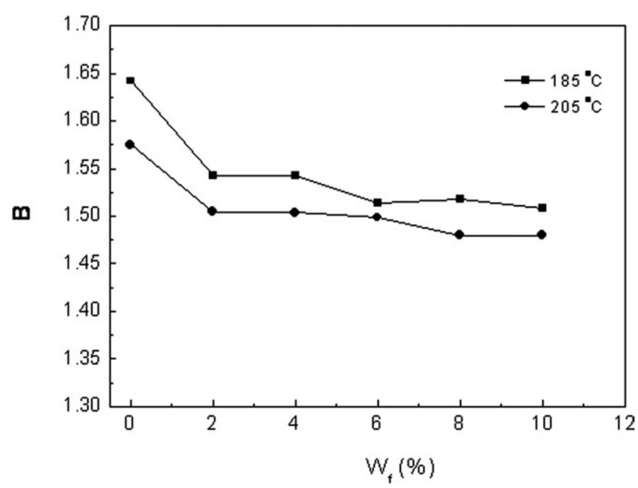

Figure 8. Relationship between die-swell ratio and filler weight fraction of PP/MRP composite melts at a load of 12.5 kg.

viscoelasticity. For example, with increasing load or MFR, the deformation energy stored in the melt increases, while the remaining time of the melt in the channel is shortened, leading to increase of the extrudate swell of the composite melts (see Figures 1–4). With a rise in test temperature, the activities or transition ability of the macromolecular chains of the resin increase, the melt viscosity decreases, and the relaxation process is quickened. In this case, the viscous dissipation of the deformation energy stored in extrusion flow increases, and the ability of the elastic recovery of the deformation is weakened relevantly, resulting in the reduction of die-swell ratio of the PP/MRP composite melts (see Figures 5 and 6).

From a viewpoint of macroscopic rheology, the extrudate swell is the elastic recovery of the shear and extension deformation generated in die flow of polymer melt when it leaves from the channel. For polymer composites, the die-swell is related to the size, content of the filler, and its dispersion uniformity in the matrix, as well as the difference in the viscoelasticity of the components in addition of the factors stated above. In general, the resin in the composites will be reduced with an addition of the filler. In this case, the elastic energy stored during extrusion flow of the composite melts will be decreased correspondingly. Furthermore, the elastic recovery of the shear and elongation deformation are obstructed with increasing filler concentration. Consequently, the melt die-swell ratio of the PP/MRP composites decreases with an increase of the MRP weight fraction under given experimental conditions (see Figures 7 and 8).

Hristov and Vlachopoulos[22] observed the surface tearing and wall slip phenomena in capillary extrusion flow of highly filled high density polyethylene (HDPE) wood flour composites; they found that with increasing shear rate the slip velocity sharply increased, leading to plug-like flow in the case of 60% and 70% filled HDPE. It was also observed that the surface of the extrudates became smoother with increasing shear rate and wood flour content and rougher with increasing die diameter at constant aspect ratio ($L/D = 16$) of the dies. The current investigation suggested that surface irregularities observed during extrusion of wood plastic composites were reduced or eliminated by wall slip. In this study, the flow rate is relatively low, and the surface tearing and wall slip phenomena in die extrusion flow of the PP/MRP composites could not be observed.

CONCLUSIONS

The dependence of the melt die-swell ratio (B) of the PP/MRP composites on the experimental conditions was significant. The B of the composites increased roughly linearly with increasing load when the temperature was held constant and increased nonlinearly with increasing temperature for fixed load, because the elastic deformation energy stored in extrusion flow of the composite melts increased owing to the increase of load or flow rate but decreased due to a rise in temperature. When the constant temperature and load were constant, the B of the composite melts decreased slightly with an increase of the MRP weight fraction. It might be attributed to the reduction of the elastic deformation energy stored in extrusion flow of the composite melts due to the addition of the microencapsulated resin around the red phosphorus with increasing MRP concentration. The findings can provide useful information for processing of these composites.

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