Effects of Diatomite on Extrudate Swell Behavior of Polypropylene Composite Melts

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ABSTRACT: Extrudate swell (i.e., die swell) is an important parameter for characterization of melt elasticity during extrusion of polymeric melts, and die swell ratio (*B*) is usually used to describe quantitatively the melt swell degree. The *B* of the polypropylene (PP) composites filled with diatomite particles was measured by means of a melt flow rate instrument to investigate the effects of the filler content and size on the die swell behavior of the composite system melts under the experimental conditions with temperature from 210 to 230°C and load varying from 1.2 to 7.5 kg. The particle diameters were 5, 7, and 13 μm, and the filler volume fractions were 5, 10, and 15%, respectively. The results showed that the *B* of the composites decreased nonlinearly with an increase of the filler volume fraction, whereas it increased as a quadratic function with an increase of the particle diameter when the load and temperature were fixed. It might be attributed to the interaction between the inclusions and the matrix, leading to blocking the recovery of the elastic deformation as the composite melts left from the die exit. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 385–389, 2010

Key words: polypropylene; diatomite; composite; extrudate swell

INTRODUCTION

Polypropylene (PP) is one of the thermoplastics used widely in industry and daily life owing to its good performance in processing and practical applications as well as low price. However, the application range is somewhat limited to expand further because of its poor impact toughness, especially at/under room temperature. Therefore, the toughening of PP resin has become one of the research focuses since 1980s. In polymeric industry, PP is usually filled with organic or inorganic particles to improve their mechanical properties and reduce cost, such as wood and flour,[1] talc,[2] mica,[3] glass bead,[4–6] and calcium carbonate ($CaCO_3$).[2,7,8] To prepare some kind of functional composite materials, PP is filled with metal powders, such as alumina,[9] iron,[10] and hollow microspheres.[11] As to inorganic fillers, $CaCO_3$ is one of the most extensive fillers used in plastics industry because of its low cost. Recently, the structure/property relationship of nanometer $CaCO_3$-filled PP composites has been paid extensive attention.[8]

Diatomite is a kind of silicate materials; it is a nonmetal deposit that is produced from the remains of diatoms living in ocean or lakes by action in natural circumstances. Diatomite has some specific properties such as good stability and dispersive property, acid proof and heat proof, low density, wear proof, large surface area, and high value of absorbing oil.[12] It is, therefore, a new kind of filler or reinforcing additive extensively used in polymer composites, coat and paint, catalyst carrier, adsorbent carrier, surface activator, and so on. Recently, diatomite is used extensively more and more in sound insulation materials, construct materials, and heat insulation materials.[13,14]

Extrudate swell (or die swell) is an important parameter for characterization of elastic properties during die extrusion of polymeric melts, and the swell degree is usually expressed by die swell ratio (*B*). For a given material system, the factors affecting extrudate swell behavior of polymeric melts are complicated, such as channel geometry (e.g., die entrance angle, channel contraction ratio), temperature, and flow rate.[15–17] The objectives of this work are to investigate the effects of the diatomite content and particle size on the extrudate swell behavior of PP/diatomite composite melts during capillary extrusion flow.

EXPERIMENTAL

Raw materials

The polypropylene with trade mark of CJS-700G was used as a matrix resin in this work. This resin was

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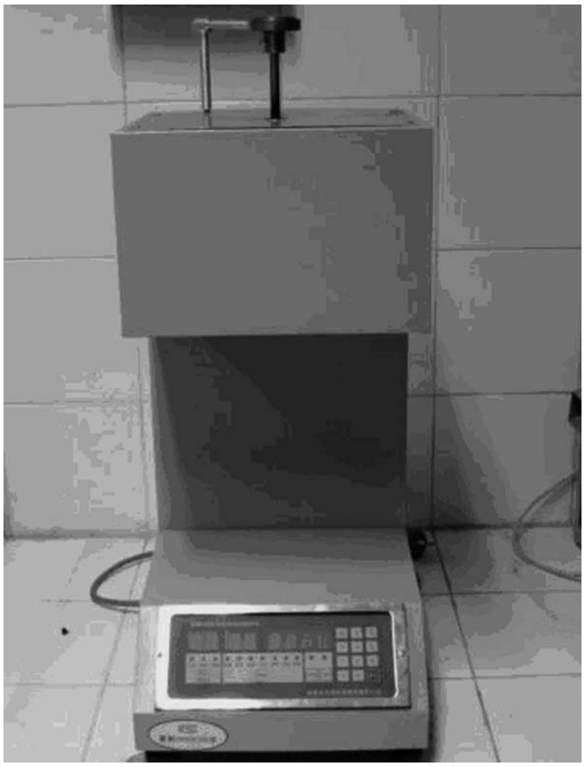

Figure 1 Melt flow indexer (Model XNR-400).

supplied by Guangzhou Petrochemical Works in Guangdong province (P.R. China), and its density in solid state and melt flow rate (2.16 kg, 230°C) were 910 kg/m^3 and 10 g/10 min, respectively.

The diatomite with different particle size supplied by Dewei Chemical in Guangzhou (P.R. China) was used as filler in this test. The filler density was 230 kg/m^3, the trade mark was 700, 499, and 281, and the relevant mean particle diameter was 5, 7, and 13 μm, respectively.

Fabrication

The surface of diatomite particles was first treated with a silane coupling agent, and then they were blended with PP in a high-speed mixer. The silane coupling agent with trade mark of KH-143 was supplied by the Xiangfei Institute of Chemistry in Nanjing, P.R. China. The filler volume fractions were 5, 10, and 15%. The PP/diatomite blends were extruded in the resin melt state by means of a twin-screw extruder, and the extrudate was granulated to produce PP/diatomite composites. Finally, these granular composites were dried for 5 h at 90°C before rheological 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 in Chengde city, P.R. China, which is as shown in Figure 1. Several loads and different temperature were selected to measure the melt die swell diameter (D_0) of the composite systems by using a photograph method under experimental conditions. Figure 2 shows the sketch of measuring *principium* for extrudate swell ratio of polymeric melts using photographing method. The extrudate photograph was input to a computer and was treated with an image software to determine the D_0; five tests were conducted, and the average was reported for each composition experimental condition.

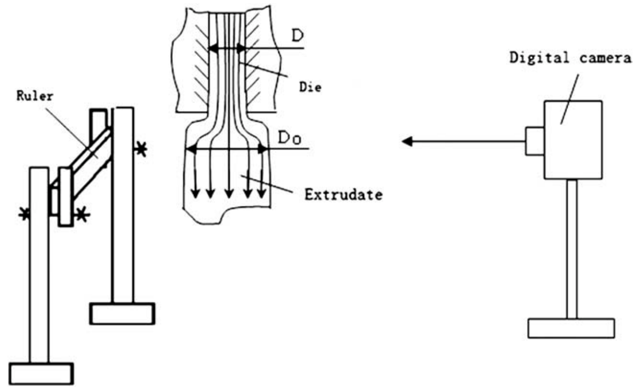

Figure 2 Sketch of taking picture measuring extrudate swell.

The length and diameter (D) of the die used in this work were 8.000 and 2.095 mm, respectively. The test temperature was from 210 to 230°C, and the load was varied from 1.2 to 7.5 kg. In this case, the die swell ratio is defined as follows:

$$B = D_o/D \tag{1}$$

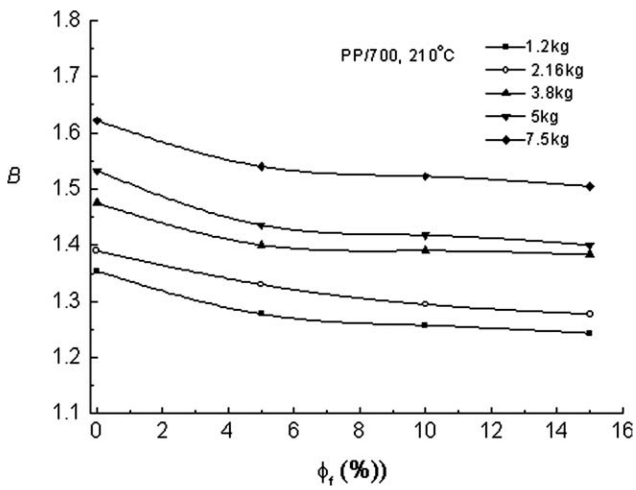

Figure 3 Die swell ratio versus diatomite volume fraction of PP/700 composite system.

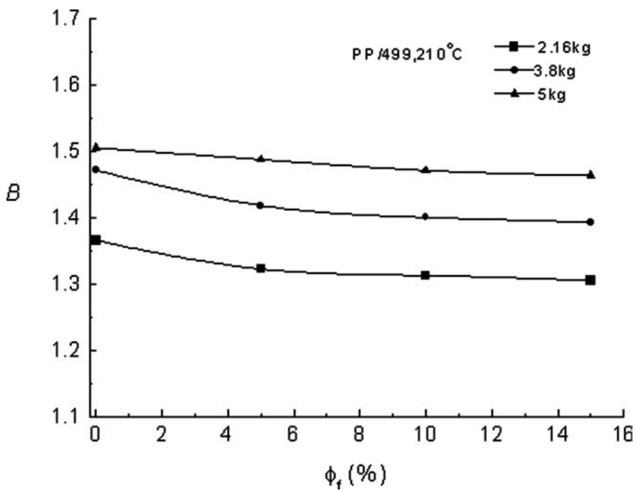

Figure 4 Die swell ratio versus diatomite volume fraction of PP/499 composite system.

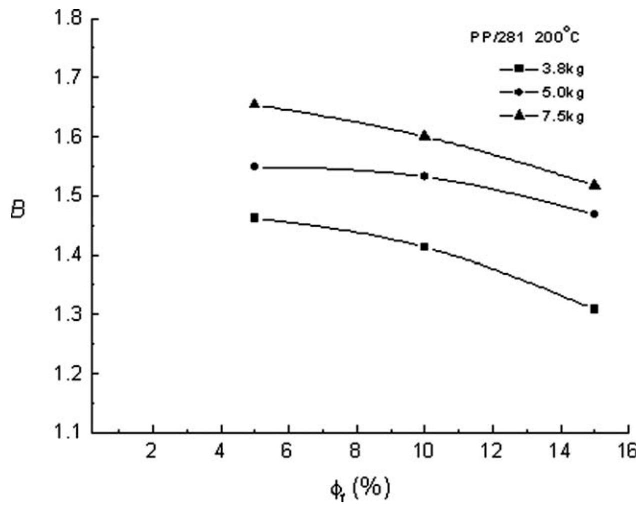

Figure 5 Die swell ratio versus diatomite volume fraction of PP/281 system.

RESULTS AND DISCUSSION

Relationship between die swell ratio and diatomite content

Figure 3 shows the relationship between the die swell ratio of the PP/700 composite melt and filler volume fraction (ϕ_f) under various loads and at temperature of 210°C. It can be seen that the *B* of the composite melt decreases nonlinearly with an addition of ϕ_f under the same load. In addition, in a case of higher ϕ_f, the increase extent of the *B* reduces. With further increasing ϕ_f, the interaction among the particles as well as between the filler and matrix is enhanced to result from increasing the stress around the inclusions and relevant deformation as well as stored energy, leading to the change of total die swell ratio tending to gentle reduction with an increase of ϕ_f.

From a viewpoint of phenomenal (morphological) rheology, the die swell might be attributed to the elasticity recovery of the deformation generated during extrusion flow of polymer melt. The filler particles in the resin matrix will block the molecular movement and the elasticity recovery, and this hindering will increase with increasing the filler concentration. On the other hand, the resin phase in the composite systems decreases with an increase of the filler volume fraction, and the elastic recovery of the deformation produced in the melt extrusion is weakened, leading to reduction of the melt die swell ratio as the melt leaves from the die exit.

Figure 4 displays the relationship between the die swell ratio of the PP/499 composite melt and filler volume fraction under various loads and at temperature of 210°C. Similarly, the *B* of the composite melt decreases nonlinearly with an addition of ϕ_f under the same load. Furthermore, the reduction of the *B* tends to gently with further increasing ϕ_f. Figure 5 illustrates the relationship between the die swell ratio of the PP/281 composite melt and filler volume fraction under various loads and at temperature of 210°C. It can be observed that the *B* of the composite melt decreases nonlinearly with an addition of ϕ_f when load is constant. The difference from the PP/700 and PP/499 composite systems is that the reduction of the *B* does not tend to gently with an increase of ϕ_f. This indicates that the sensitivity of

TABLE I
The Value of B_o, δ, and ξ of PP/Diatomite Systems at 200°C

Composites	Load (kg)	B_o	δ	ξ	Correlation coefficient (R^2)
PP/700	1.20	1.1717	0.0004	1.6666	0.9308
PP/700	2.16	3.06457	1.80084	0.01953	0.9476
PP/700	3.80	1.27886	0.00012	1.91776	0.9615
PP/700	5.00	2.53864	1.19487	0.01994	0.9578
PP/700	7.50	1.41577	0.00166	1.27631	0.9817
PP/281	2.16	1.17469	0.00242	1.07625	0.9999
PP/281	3.80	1.305	0.0032	1.0000	1.0000
PP/281	5.00	1.279	0.0009	1.1124	0.98544

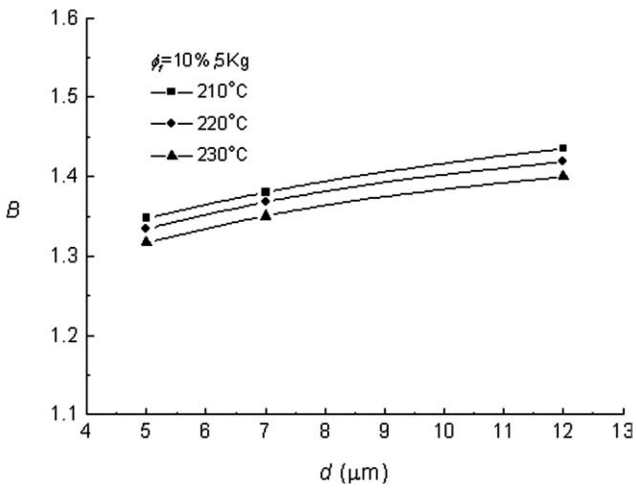

Figure 6 Dependence of die swell ratio on filler particle diameter of PP/diatomite system.

the die swell ratio to ϕ_f for the PP composite melts filled with big particle size diatomite is different from that of the PP composite melts filled with small particle diameter diatomite. In other words, the mechanisms of the influence of big particle diameter diatomite on the die swell of the filled PP composite systems are different from the composite systems filled with small particle diameter diatomite. The reason of this phenomenon might be that the number of big particle diameter diatomite is quite less than small particle diameter diatomite at the same filler content; the interaction among the filler particles is weaker than that of the latter. Consequently, the relevant deformation and stored energy during extrusion of the composite melts are less than those of the latter.

It is known by further analyzing that the B of the PP/diatomite composites decreases nonlinearly with an increases of ϕ_f, and the relationship between them may be described by the following equation:

$$B = B_o - \delta\phi_f^{\xi} \tag{2}$$

where B_o, δ, and ξ are the coefficients related to melt elasticity. The values of B_o, δ, and ξ may be determined by using a curve fitting method under experimental conditions. Table I lists the values of B_o, δ, and ξ of the PP/700 and PP/281 composite systems at 200°C.

It can be seen from Table I that the values of B_o, δ, and ξ of these composite systems are different at various loads, and the correlation coefficient (R^2) is more than 0.93. This means that eq. (2) may be used to describe the relationship between the melt die swell ratio and filler volume fraction for these composites under the experimental conditions. It is known that ξ in eq. (2) presents the sensitivity of B to ϕ_f of the PP/diatomite composite systems. The greater the ξ, the more change of B with an increase of ϕ_f is. It can also be seen from Figures 3 and 4 that a relationship between ξ and load is close to each other for two composite systems.

Dependence of die swell ratio on diatomite particle size

Figure 6 shows the dependence of the die swell ratio of the PP/diatomite composite systems on the particle diameter (d) when $\phi_f = 10\%$ and load is 5 kg. It can be observed that the B increases nonlinearly with an increase of d, and then the increasing rate of the B reduces gradually. In general, the filler particle number reduces with an increase of the particle diameter when the filler volume fraction is constant, and the specific area of the particles decreases relevantly. The interaction among the inclusions as well as between the fillers and the resin matrix will weaken in this case. Consequently, the blocking effect of the elastic recovery for the deformation generated in extrusion flow of the composite melts decreases with an increase of the particle size, resulting in increasing the die swell ratio correspondingly. It can also be seen in Figure 6 that a relationship between the B and d is roughly consistent with a quadratic function under the conditions with fixed load and particle content. That is

$$B = B_m(e_0 + e_1 d + e_2 d^2) \tag{3}$$

where B_m is the resin melt die swell ratio, e_0, e_1, and e_2 are the constants related to the melt elasticity. Similarly, the values of e_0, e_1, and e_2 may be determined by using a curve fitting method under experimental conditions. Table II lists the values of e_0, e_1, and e_2 of the PP/diatomite composite systems at load of 5 kg and different temperatures.

TABLE II
The Value of e_0, e_1, and e_2 of PP/Diameter Systems Under Load of 5 kg

Temperature (°C)	e_0	e_1	e_2	Correlation coefficient (R^2)
210	0.92207	5.46186E − 4	−2.03122E − 6	1
220	0.91003	5.39052E − 4	−2.00469E − 6	1
230	0.89798	5.31919E − 4	−1.97816E − 6	1

It can be observed from Table II that the absolute values of e_0, e_1, and e_2 decrease with a rise of temperature. It is known from eq. (3) that e_2 presents the sensitivity of the melt die swell behavior to the filler particle diameter for diatomite-filled PP composite systems. It illustrates that this sensitivity of the melt die swell behavior to the filler particle diameter of the diatomite-filled PP composite systems is related closely to temperature. In addition, the correlation coefficient is equal to 1.

CONCLUSIONS

Under the experimental conditions with temperature from 210 to 230°C and load varying from 1.2 to 7.5 kg, the effects of the diatomite content and diameter on the melt die swell behavior during extrusion of the diatomite-filled PP composite systems were quite significantly.

When the load and temperature were constant, the melt die swell ratio of the diatomite-filled PP composite systems decreased nonlinearly with an increase of the filler volume fraction, whereas increased nonlinearly with an addition of the diatomite particle diameter, and the relationship between them was a quadratic function. It might be attributed to the interaction between the inclusions and the matrix, leading to blocking the recovery of the elastic deformation as the composite melts left from the die exit.

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