

Die-Swell Behavior of Glass Bead-Filled Low-Density Polyethylene Composite Melts at High Extrusion Rates

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ABSTRACT: The extrudate swell behavior of glass bead-filled low-density polyethylene (LDPE) composite melts was investigated using a constant rate type of capillary rheometer at high extrusion rates and test temperatures varied from 140 to 170°C. The results show that the die swell ratio (B) of the melts increases nonlinearly with increasing apparent shear rates for the system filled with the surface of glass beads pretreated with a silane coupling agent, while the B for the system filled with uncoated particles remains almost constant when the true wall shear rate is greater than 2000 s^{-1} at a constant temperature. The values of B for both the pure LDPE and the filled systems decreases linearly with an increase of the temperature and an increase of the die diameter at fixed shear rates, and the sensitivity of B on the die diameter and temperature for the former is higher than that of the latter. Furthermore, the effect of the filler content on B is insignificant, while the values of B decreases, obviously, with an increasing glass bead diameter (d) when d is smaller than 50 μm ; then B varies slightly with d . © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 419–424, 2000

Key words: low-density polyethylene; glass bead; composite melt; die swell; capillary extrusion

INTRODUCTION

To improve the mechanical strength and impact toughness of polymeric materials and to reduce their production cost, polymer blends and composites are extensively used in industry. Apart from the use performance of the materials, the rheological properties of their melts should be

understood in order to design or choose suitable processing machinery and technological conditions. Low-density polyethylene (LDPE) is a thermoplastic resin with branched molecular chains and shows distinctive viscoelastic properties in the entry/exit flow of a channel, compared with linear polymers, such as high-density polyethylene (HDPE).¹ Generally, the factors affecting the melt rheological behavior of polymer melts are more complex, especially for polymeric composite melts. There have been a number of studies on the measurement and characterization of the

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melt-flow properties of polymeric composites, and several empirical or semiempirical expressions describing the relationship between shear viscosity and the volume fraction of the fillers have been presented in the past two decades.^{2–11} Faulkner and Schmid³ measured the rheological and mechanical properties of glass bead-filled polypropylene composites and found that the relative viscosity decreased with increasing shear rate, and the melt zero shear-rate viscosity was in very good agreement with the Guth–Gold equation.¹²

Die swell (extrudate swell) is also called the Barus effect, which is an important parameter for characterizing polymer melt elasticity in an extrusion flow and is related to the quality of the products. Some studies on the extrudate swell behavior of polymeric composite melts have been done.^{13–17} White and Crowder¹³ investigated the die-swell behavior of carbon black-filled polybutadiene and the butadiene–styrene copolymer at a low shear rate and found that the die-swell ratio (B) decreased with increasing carbon black content and the die length–diameter ratio. Similarly, the B of HDPE filled with a titanium dioxide (TiO_2) composite melt decreases nonlinearly with the volume fraction of TiO_2 at a low shear rate.¹⁴ For polymeric liquids, including solutions and melts, many equations predicting the die-swell ratio have been proposed^{18–20} since the 1960s. Relatively speaking, a quantitative description of the die swell for polymeric composite melts is relatively rare. The objective of this article was to investigate the effects of filler content, size, and surface treatment as well as temperature on the die-swell behavior of glass bead-filled LDPE composite melts at high extrusion rates.

EXPERIMENTAL

Materials and Preparation

The LDPE used in this test was Cosmothene LDPE G812 (Polyolefin Co., Singapore). The density at the solid state and the melt-flow index (2.16 kg, 190°C) were 0.917 g cm⁻³ and 35 g (10 min)⁻¹, respectively. Two A-glass beads (GB) (the surface of which was pretreated with the silane coupling agent CP-01 was 3000 and the uncoated was 3000U) were chosen as the fillers. They were small solid spheres (Spheriglass®, Potters Industries Inc., USA) with a mean diameter of 35 μm and a density of 2.5 g cm⁻³.

After the LDPE was mixed with the glass beads, they were put into a twin-screw extruder (Brabender PL 2000) with a screw length–diameter ratio of 42 : 7 for blending further at a temperature that varied from 160 to 180°C and a screw speed of 20 rpm to produce the composites. The blending ratios (LDPE/GB) by weight were 100/0, 90/10, 80/20, 70/30, and 60/40. Finally, the extrudates were pelleted using a pelletizer and packed.

Apparatus and Methodology

The melt-extrusion flow experiments were conducted under the test conditions of temperature varied from 140 to 170°C and piston speed (V) from 5 to 240 mm/min (corresponding apparent shear rates were from 150 to 7200 s⁻¹) using a constant rate type of capillary rheometer with twin bores (reservoirs or cylinders) supplied by Rosand Precision Ltd. The diameter (D_R) of the bores of the rheometer was 15 mm. A long die and a short die with a diameter of 1 mm were selected in order to make the Rabinowitsch correction. The length–diameter ratios of these dies were 16 and 1, respectively. The extrudate diameter (D_e) of the composite melts was measured under these test conditions using a laser scanning device installed at the exit of the dies. The die-swell ratio is given by

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

In this test, the apparent shear rate (γ_a) at the wall is expressed as follows:

$$\gamma_a = \frac{32Q}{\pi D^3} = 30V \quad (2)$$

where Q is the volumetric flow rate.

RESULTS AND DISCUSSION

Dependence of B on Shear Rates

Figure 1 shows the dependence of the B of the pure LDPE and the LDPE 3000U system on the apparent shear rates (γ_a) at 150°C. When γ_a is lower than 2000 s⁻¹, B increases sharply with increasing γ_a and then it varies slightly. Under the same shear rate, the values of B for the composite melts are lower than those of the pure

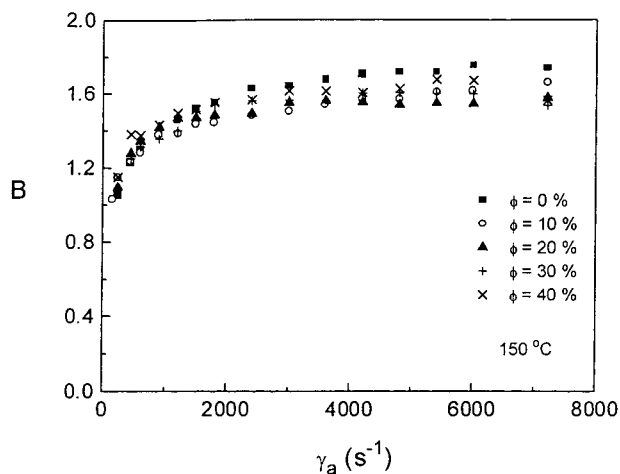


Figure 1 B as a function of γ_a .

LDPE, but the variation of B with the filler content is not too obvious. From the viewpoint of microrheology, the flow occurs when polymer molecules slide past each other. The molecular chains extend, orient, and arrange along the flow direction under the action of an outside shear field. Therefore, the melt viscosity decreases with increasing shear rates within a given range owing to the shear-thinning effect of thermoplastics. On the other hand, the elastic energy stored in the melts increases correspondingly with increasing shear rates. When the melt leaves the die exit, the extended and oriented molecular chains exhibit elastic recovery and return to their original random state, and the elastic energy is released due to the disappearance of an outside force field. Consequently, the diameter of the melt extrudate increases correspondingly with increasing flow rates. However, in the case of high shear rates, the entanglement of the molecular chains is completely deentangled and oriented. Thus, the die-swell does not evidently vary with increase of the shear rates.

Influence of Extrusion Conditions on B

For given a polymer, the effects of the flow conditions, including operation parameters and channel geometry, on the rheological behavior of the melt are significant. Figure 2 displays the influence of the die diameter on the die-swell ratios of the pure LDPE and the composite with $\phi = 20\%$ melts. It can be seen that B decreases linearly with increasing D , and the linear line slope of the B - D curve for the pure LDPE melt is greater than that of the composite melt, suggesting that

the sensitivity of the extrudate swell on the die diameter for the pure LDPE melt is more significant than that of the composite melt, especially at a lower shear rate. In other words, the addition of glass beads into LDPE is beneficial to decrease the sensitivity of the die swell of the melt to the channel geometry. When the bore diameter is fixed, the contraction ratio of the extrusion channel decreases with an increasing die diameter, and the entry converging flow of the polymer melts is weakened in this case. The elongational deformation and orientation as well as the elastic energy stored in the melts during the inlet flow decrease relevantly. The extrudate swell ratio of the melts, therefore, decreases with an increasing die diameter. Furthermore, the addition of glass beads into the LDPE results in a decrease of the dependence of die-swell on the die diameter.

Figure 3 illustrates the relationship between the test temperatures (T) and the die-swell ratios of the pure LDPE melt and the composite melt with $\phi = 20\%$. Similarly, B decreases linearly with an increase of temperature, and the linear line slope of the B - T curve of the pure LDPE melt is greater than that of the composite melt, meaning that the temperature sensitivity of the extrudate swell of the pure LDPE melt is also more obvious than that of the composite melt. In other words, the addition of glass beads into LDPE is also beneficial to decrease the sensitivity of the die swell of the melt to the temperature. It is generally believed that the stress-relaxation process is quickened and the motion ability of the polymer molecule chains is increased with an increase of temperature. In this case, the recovered elastic deformation and the released elastic en-

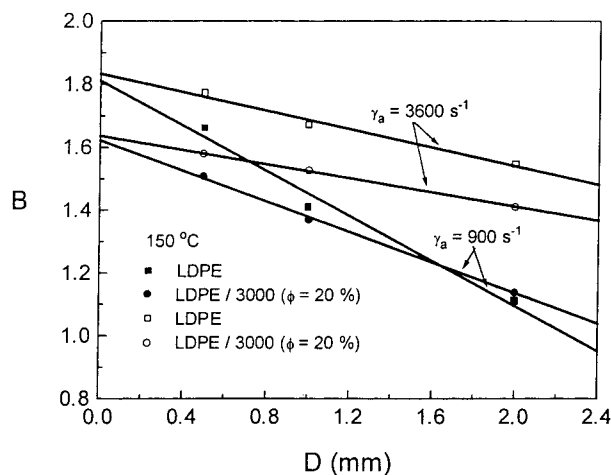


Figure 2 B versus D .

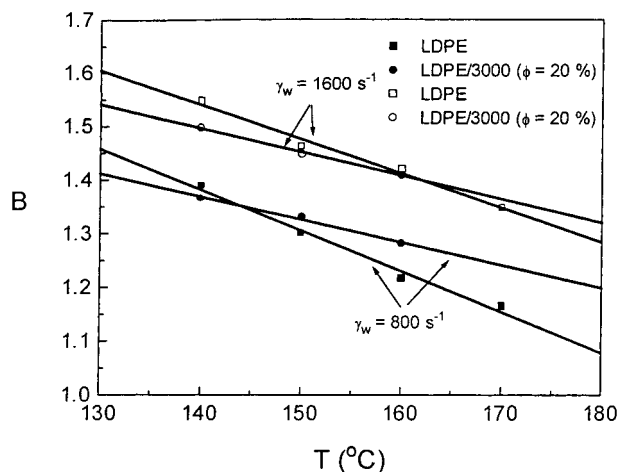


Figure 3 Dependence of B on temperature.

ergy in the melts at the die exit are decreased correspondingly. Consequently, the degree of the extrudate swell decreases.

Effect of Filler Surface Treatment on B

Figure 4 shows the effect of the surface of glass beads pretreated with the silane coupling agent on the die-swell ratios of the filled systems with $\phi = 20\%$ when the temperature is constant ($T = 20^\circ\text{C}$). It can be seen that when the true wall shear rate (γ_w) is greater than 2000 s^{-1} the B of the LDPE/3000 system melt increases linearly while the value of the B of the LDPE/3000U system melt remains almost constant with increasing γ_w , where γ_w is defined as follows:

$$\gamma_w = \frac{3n + 1}{4n} \gamma_a \quad (3)$$

where n is the melt-flow behavior index.

For the LDPE/3000U system, the interfacial bonding between the glass beads and the LDPE matrix is relatively poor; thus, the small spheres can slide and roll relative to the melt. That is the so-called bear effect. In this case, the stored energy release and elastic recovery of deformation of the melt are relatively free when it leaves the channel. As stated above, the molecular chain orientation and stored elastic energy of the melt remain basically constant at a high flow rate. The extrudate swell, therefore, varies gently with the shear rates. For the LDPE/3000 system, the interfacial adhesion between the LDPE matrix and the fillers is enhanced due to the pretreatment of the surface of the glass beads with the silane

coupling agent. In this case, the relative motion between the inclusions and the matrix is somewhat blocked. In other words, the bear effect is weakened in the extrusion flow. Thus, the elastic energy stored in the melt increases with increasing flow rate. Furthermore, the stress relaxation is somewhat limited during the extrusion flow of the composite melt. These factors result in increasing the elastic deformation to be recovered and the elastic energy stored in the melt when the melt leaves the channel exit. The extrudate swell, therefore, increases with increasing shear rates even though at a high level of the flow rate.

It can be also seen in Figure 4 that some plateaus appear at the curves of B against the γ_w of these composite melts when γ_w is greater than 1000 s^{-1} , indicating that the melt flow results in a wall-slip phenomenon at higher shear rates, that is, the melt moves as a form of stick-slip in the die flow. In this case, the elastic energy stored in the melt can be released and the stresses supported by the melt can be relaxed partially at this moment. The extrudate swell, therefore, does not vary with increasing shear rates to produce some plateaus at a relevant level of the shear rate at the curves. For the LDPE/3000 system, the first plateau appears at $\gamma_w = 2400\text{ s}^{-1}$, while for the LDPE/3000U system, the first plateau appears at $\gamma_w = 1800\text{ s}^{-1}$, meaning that the surface treatment of the glass beads is helpful to improve the flow stability of the composite melt.

Influence of Filler Content and Size on B

Figure 5 shows the correlation between B and the fraction by weight of the glass beads of the melts

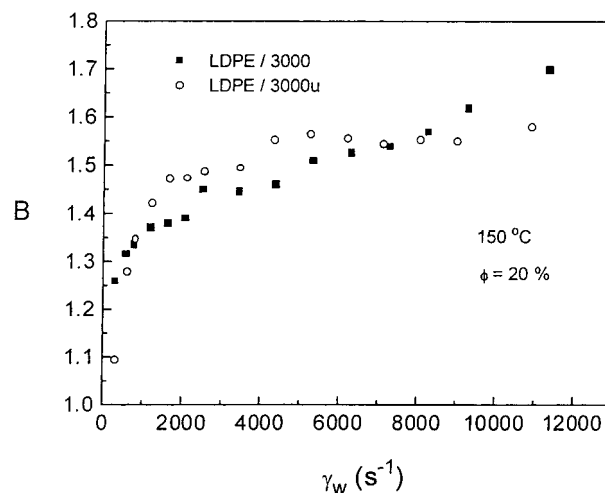


Figure 4 Effect of filler surface treatment on B .

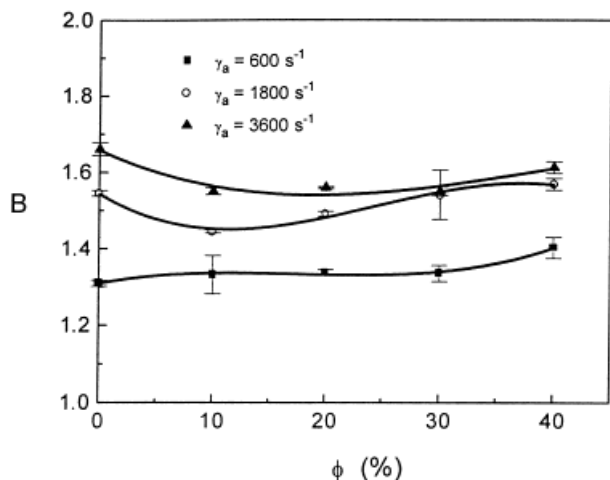


Figure 5 B versus ϕ .

at different apparent shear rates and 150°C. It can be seen that the B values of the composite melts are close to those of the pure LDPE melt, that is, the values of B vary gently with the filler content. It is different from the results measured by Faulkner and Schmid³ for glass bead-filled polypropylene composites, White and Crowder¹³ for carbon black-filled rubber compounds, and Minagawa and White¹⁴ for TiO₂-filled polyolefin composites at low shear rates. They found that the end correction factor (characterizing the stored energy) and die-swell ratios decrease with increase of the filler content. This is because the polymer and its composite melts show different rheological behavior at low and high flow rates, respectively, owing to the melt viscoelasticity themselves. As discussed above, the molecular chains are completely oriented and the melt viscosity reaches the minimum and does not change with increasing shear rates any more. In this case, the glass beads more easily move relative to the melt. In other words, the effect of the fillers on the viscoelastic properties of the melt is further weakened. Thus, the sensitivity of the extrudate swell of the composite melts to the concentration of the inclusions decreases correspondingly.

Figure 6 displays the influence of the filler size on the extrudate swell of the melts also at different apparent shear rates and 150°C. When the glass bead diameter (d) is smaller than 50 μm and $\gamma_a < 2000 \text{ s}^{-1}$, B decreases with increasing d ; then, it remains approximately constant. When the apparent shear rate is 3600 s^{-1} and $d < 50 \mu\text{m}$, B also decreases with the increase of d ; then, it increases slightly with increasing d . Generally, the addition of bigger particles may in-

crease the melt-flow resistance to lead to increasing the viscous dissipation while decreasing the stored energy in the die flow. Consequently, the extrudate swell decreases with increasing filler size within limits.

On the other hand, the melt flow easily results in an unsteady flow or melt fracture phenomenon at high shear rate. In this case, the measurement of the die-swell will produce an error because of the irregular shape or torsion of the extrudates. The measured values of B , therefore, may deviate toward large ones.

CONCLUSIONS

The effects of the filler content and its surface treatment on the extrudate swell behavior of glass bead-filled LDPE hybrid composites at high extrusion rates and test temperatures that varied from 140 to 170°C were investigated using a Rosand capillary rheometer. The results show that the effect of the surface treatment of the glass beads (coated with a silane coupling agent) on the extrudate swell is significant, especially at a high shear rate. The die-swell ratio (B) of the melts increases nonlinearly with increasing true wall shear rates (γ_w) for the LDPE/3000 system (coated), while the B for LDPE/3000U (uncoated) remains almost constant when γ_w is greater than 2000 s^{-1} at a constant temperature.

The values of B for both the filled system and the pure LDPE melts decrease linearly with an increase of temperature and increase of the die diameter at fixed shear rates, and the sensitivity of the extrudate swell of the composite melt to the

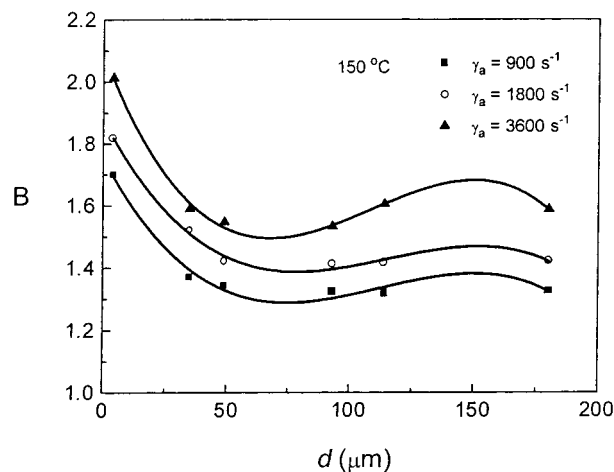


Figure 6 Influence of filler size on B .

temperature and the die diameter is lower than that of the pure LDPE melt. The effect of the filler content on B is insignificant, while the values of B decrease, obviously, with increase of the glass bead diameter (d) when d is smaller than $50\ \mu\text{m}$; then, they vary slightly with d .

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