Rheological Properties of Glass Bead-Filled Low-Density Polyethylene Composite Melts in Capillary Extrusion

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ABSTRACT: The melt flow of glass bead-filled low-density polyethylene composites in extrusion have been observed by using a capillary rheometer to investigate the effects of temperature, shear rate, and filler content on the rheological properties of the melts. The results show that the melt shear flow obeys a power law, and the dependence of the apparent shear viscosity, $\eta_{\rm app}$, on temperature is in accord with an Arrhenius equation. At the same temperature and shear rate, $\eta_{\rm app}$ increases slightly with increasing the volume fraction of glass beads, but the flow behavior index decreases with increasing filler content. In addition, the first normal stress difference of the melts linearly increases with increasing wall shear stress. Good agreement is shown with the N_1 calculated with the equation presented in this article and the pressured data from the sample melts. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1451–1456, 1999

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

INTRODUCTION

Plastics filled with rigid inorganic particles (RIP) are widely used in industry to modify the final performance of thermoplastic materials, such as stiffness and toughness, etc. But the processability (e.g., flow property) of the materials may suffer due to the added particles. Polymers filled with glass beads have good processability, small and relatively well-distributed internal stress in the products, and good dimensional stability of the products and service performances owing to the smooth spherical surface of the fillers, com-

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 $r_{\rm ress}$ insuch as die swell, melt fracture, and wall slip of
glass bead-filled high-density polyethylene
(HDPE) composites, and found that the shape of
flow curves is similar to the unfilled system.
Faulkner and Schmidt² studied the rheological
and mechanical properties of glass bead-filled
polypropylene (PP) composites, and pointed out
that the relative viscosity decreased with increas-
ing shear rate, and the zero shear-rate data were
in very good agreement with the Guth-Gold equa-
tion.³ Lepez et al.⁴ examined the thermorheologi-

paring them with other RIPs. Viscoelasticity is a key parameter indicating the use properties and processability of these materials. It is very impor-

tant to understand the rheological properties of

polymer melts for processing and equipment or

mold design. Rheological properties of glass bead-

filled polymers have been documented for the past

20 years.¹⁻¹¹ Lim¹ observed viscoelastic behavior

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cal properties of glass bead-filled HDPE and polystyrene (PS) melts, and proposed a new empirical model, allowing the prediction of complex viscosity of a glass bead-filled thermoplastic melt providing only four parameters: the average maximum packing volume fraction characteristic of the filler geometry and size distribution, the flow activation energy, the shear-thinning parameter, and an adjustable parameter. The results, conducted by Friedrich et al.,⁵ showed that the thermorheological properties of polystyrene melts filled with grafted and ungrafted glass beads follow the WLF behavior. Kataoka et al.⁶ measured the viscosities of LDPE and PS filled with glass beads and sisals, respectively, at low shear rates with a cone-plate rheometer. Apart from the relative viscosity (η_r) being in accord with the equations derived by Maron and Pierce or by Mooney, the particle size distribution had an effect on η_{r} . The rheological analysis of LDPE/stainless steel spherical powder composites showed that the dynamic viscosity decreased with increasing frequency but increased with the filler content.⁷ LDPE is a long chain-branched polyethylene with rheological behavior (e.g., entry flow pattern, die swell) being quite different from linear thermoplastic, such as HDPE.¹²

Capillary extrusion tests are close to the technological conditions of practical die extrusion and injection processing of polymers. The objectives in the present article are to investigate the effects of the filler content, shear rate, and temperature on the rheological behavior of glass bead-filled LDPE composite melts in capillary extrusion.

EXPERIMENTAL

Materials and Preparation

The LDPE used in this work was an injection grade granular material (LDPE G812, Polyolefin Co., Singapore). The density at solid state and the melt index measured at standard conditions were 0.917 g/cm³ and 35 g/10 min, respectively. The glass beads (GB), pretreated with a coupling agent (CP-01), were small solid globes (Potters Indust. Inc., USA), and the density and the mean diameter were 2.5 g/cm³ and 49 μ m, respectively. Both the LDPE and the glass beads were blended in a twin-screw extruder at temperatures varying from 160 to 180°C to produce the composite. The mixing ratios by weight (LDPE/GB) were 100/0, 80/20, 70/30, and 60/40.

Apparatus and Methodology

The extrusion flow tests were conducted by using a capillary rheometer (Rheograph 2003, Gottfert[®], Germany) in a temperature range from 130 to 170°C, and apparent shear rate varied from 10^{0} s⁻¹ to 10^{3} s⁻¹ to measure the melt flow curves (relationship between shear stress and shear rate), apparent shear viscosity (η_{app}), and the first normal stress difference (a load shell and a pressure transducer were installed at the top of the piston and the die inlet, respectively). The reservoir diameter was 12 mm, die angle was 180°, and the diameter (*D*) and the length (*L*) of the capillary die were 1 mm and 30 mm, respectively. η_{app} is defined as follows:

$$\eta_{\rm app} = \tau_{w} / \gamma_{\rm app} \tag{1}$$

where γ_{app} is the apparent shear rate, and τ_w the wall shear stress, which are expressed by:

$$\tau_w = \frac{(\Delta P - \Delta P_{\rm end})D}{4L} \tag{2}$$

and

$$\gamma_{\rm app} = \frac{32Q}{\pi D^3} \tag{3}$$

where ΔP and ΔP_{end} are the total pressure drop and the end pressure drop in capillary extrusion of polymer melts, respectively, and Q the volumetric rate.

It is generally believed that the entry pressure drop tends to a constant when L/D is greater than 16-20.¹³ For a long die extrusion of polymer melts, therefore, the influence of inlet pressure losses on melt flow can be neglected because of the small ration of the inlet to the total pressure drop. In this work, the capillary used is a long die (L/D= 30); thus, an entry correction is not necessary.

RESULTS AND DISCUSSION

Flow Curves

Figure 1 shows the melt flow curves of the composites at 160°C. It can be seen that the wall shear stress irregularly increases with increasing apparent shear rate (γ_{app}) when γ_{app} is lower than 60 s⁻¹; it can be considered that a stick-slip phenomenon occurs according to Lim's results,¹ al-



Figure 1 Flow curves of the melts .

though the relationship between τ_w and γ_{app} is linear in a double logarithm coordinate system when γ_{app} is greater than 60 s⁻¹. This suggests that the melt shear flow (shear stress–shear rate relationship) basically obeys a power law relationship except individual data points, that is

$$\tau_w = K \gamma_{\rm app}^n \tag{4}$$

where K is the consistency and n the flow behavior index.

It can be also observed from Figure 1 that at the same shear rate the values of τ_w for the composite melts are higher than that of the pure LDPE melt. This means that the flow resistance increases, resulting from the LDPE filled with glass beads leading to a rise in pressure. Figure 2 shows the flow curves of the melt with the weight fraction of glass beads (ϕ) of 20% measured at various temperatures. It can be seen that the shear stress-shear rate relationship is also basically linear in a double logarithm coordinate system except for a few data points. With a rise of temperature, the value of wall shear stress decreases, especially at lower apparent shear rate.

Dependence of *n* and *K* on ϕ

K and n in eq. (4) can be determined by using a numerical analysis method, and n is given by:

$$n = \frac{d \log \tau_w}{d \log \gamma_{\rm app}} \tag{5}$$

Figure 3 displays the dependence of *K* and *n* for



Figure 2 Flow curves of the melt ($\phi = 20\%$).

the melts as a function of the weight fraction (ϕ) of glass beads at a test temperature of 160°C. When ϕ is smaller than 20%, the value of *n* decreases slightly with increasing the ϕ . But when ϕ is greater than 20%, the value of *n* decreases significantly with increasing the ϕ . This illustrates that the non-Newtonian properties of the composite melts will be outstandingly enhanced at higher concentration of the inclusions. Conversely, the value of *K* increases with increasing the ϕ . This is because the flow resistance in the extrusion of the composites melts increases with increasing the concentration of the glass beads.

Effect of Filler Content and Shear Rate on Melt Viscosity

Figure 4 illustrates the correlation between the apparent shear viscosity of the melts, η_{app} , and



Figure 3 *K* and *n* as a function of ϕ .



Figure 4 Relationship between η_{app} and γ_{app} .

apparent shear rate at a test temperature of 160°C. It can be seen that η_{app} decreases rapidly with an increase of γ_{app} when γ_{app} is lower than 100 s⁻¹; but when γ_{app} is greater than 100 s⁻¹, η_{app} gently decreases with increasing the γ_{app} . In addition, the values of η_{app} for the composite melts are somewhat higher than that of the pure LDPE melt at the same γ_{app} . Under given apparent shear rates, the dependence of η_{app} on the volume fraction of glass beads, ϕ_f , is shown in Figure 5. At higher apparent shear rates, η_{app} slightly increases with increasing the ϕ_f at lower γ_{app} . In other words, the dependence of the apparent shear viscosity of the composite melts on the filler concentration is closely related to shear rates.

From the molecular level, the flow occurs when polymer molecules slide past each other. There-



Figure 5 Dependence of η_{app} on ϕ_{f} .



fore, the ease of melt flow depends upon the mobility of the molecular chains and the forces or entanglements holding the molecules together. When a thermoplastic is filled with rigid inorganic particles, the flow resistance in the melt will increase more or less. The slide between intermolecule layers will be suffered, especially at higher filler content. Thus, the melt viscosity will increase correspondingly.

Influence of Temperature on η_{app}

It is well known that viscosity of polymer melts or solutions decreases with a rise of temperature, and the relationship between them is in accord with the Arrhrnius expression, which is give by:

$$\eta(T) = \eta(T_o) \exp\left[\beta\left(\frac{1}{T} - \frac{1}{T_o}\right)\right]$$
(6)

where $\eta(T)$ and $\eta(T_o)$ are the viscosity measured at absolute temperature (T) and reference temperature (T_o) , respectively. β is the constant characterizing the sensitivity of viscosity on temperatures.

Figure 6 shows the relationship between $\ln \eta_{app}$ and 1/T of the pure LDPE melt and LDPE/GB composite melt with a ϕ of 20%. It can be observed that $\ln \eta_{app}$ for both melts increases linearly with increasing the 1/T. This suggests that this relationship can be described by using a form of the Arrhenius equation. For describing conveniently, eq. (6) can be simplified as follows:

$$\eta_{\rm app} = \alpha \, \exp(\beta/T) \tag{7}$$



Figure 7 N_1 as a function of τ_w .

where α is the constant related to the melt viscosity, $\beta = E'/R$, is a parameter characterizing the sensitivity of the melt viscosity to temperature, R is the universal gas constant, and E' is the activation energy of viscous flow. The values of α and β can be determined by using a linear regression analysis method from the experimental data. For LDPE/GB composite melts with a ϕ equal to 20%, the value of β is 2.9651, and 3.5261 for the pure LDPE melt in these test conditions. This means that the value of E' of the composite is smaller than that of the pure LDPE, because R is a constant. In other words, the sensitivity of shear viscosity of LDPE melt can be weakened, to some extent, by filling a suitable content of the glass beads. It is generally believed that polymer melt flow is realized in the form of the transition of molecular chains. With a rise of temperature, therefore, the transition ability of the polymer molecular chains will enhance correspondingly.

The First Normal Stress Difference

The first normal stress difference, N_1 , is an important parameter characterizing the viscoelastity of the polymer melt. Figure 7 displays the correlation between the measured values of N_1 of the melts and the wall shear stress at 160°C. N_1 basically increases linearly with the increase of τ_w , and the effect of glass bead content on N_1 is insignificant. These results illustrates that the $N_1-\tau_w$ relationship can be described by employing the following linear form of expression:

$$N_1 = A_0 + A_1 \tau_w \tag{8}$$

where A_0 and A_1 are the constants.

 A_0 and A_1 can be also determined by employing a numerical method, such as the linear regression analysis method. It can be observed from Figure 7 that the slope of the curves of N_1 vs. τ_w is close to each other. The results of calculation from the experimental data show that the values of A_1 are about 3.1 for the composite melts and 2.9 for the pure LDPE melt, respectively. Extrudate swell (i.e., Barus effect) is an important characteristic of the elasticity of polymer melts. The first normal stress difference is usually related with die swell ratio B (for the circular die $B = D_e/D$, D_e is the extrudate diameter).¹⁴ For long dies and from nonlinear viscoelastic fluid theory, Tanner¹⁵ presented a formula as follows:

$$B = 0.1 + \left[1 + \frac{1}{2} \left(\frac{N_1}{2\tau_w}\right)^2\right]^{1/6}$$
(9)

In previous work, the author proposed the following expression: $^{16}\,$

$$B = \left[\left(\frac{\Delta P_{\rm ENT}}{E} + \frac{N_1}{2\tau_w} \right) \exp(-t_R/\lambda) + 1 \right]^{1/2} \quad (8)$$

where $\Delta P_{\rm ENT}$ is the entry pressure loses, and E the extensional elasticity modulus, and t_R and λ are the resident time of the melt in the die and the relaxation time of the melt, respectively. Clearly, under given conditions the greater the N_1 , the more significant the die swell is. These results show that the influence of the glass bead content on N_1 is not obvious.

From Philippoff and Gaskins' work¹⁷ and the assumption that material melt obeys Hooke's law in shear, an expression describing the relationship between N_1 and ΔP can be derived:

$$N_1 = 2\Delta P[\xi - n_c(1 - \xi)D/2L]$$
(9)

where $\xi = \Delta P_{en} / \Delta P$, n_c is the Conutte correction factor, which is about 1.5–2 for polymer melts.¹⁸

Santamaria and Guzman¹⁹ pointed out that the ξ is about 0.17 for polymer melts. In this case, the N_1 values of the composite melts can be predicted with eq. (9) under the extrusion conditions. Figure 8 displays the correlation between the first normal stress difference and the total pressure drops of the composite melts at 160°C. It can be seen that the N_1 increases linearly with increasing the ΔP , and the measured N_1 data are close to



the theoretical calculated values (solid line) with eq. (9).

CONCLUSION

The rheological properties of melts are very important for predicting the processing of polymer materials including polymer alloys (polyblends) and polymer composites, and design of processing and shaping equipment and molds. The effects of temperature, shear rate, and filler content on the rheological properties of the glass bead-filled low-density polyethylene composite melts have been investigated by employing a capillary rheometer. The results show that the melt flow basically obeys a power law relationship, and the dependence of apparent shear viscosity, η_{app} , on the temperature is in accord with the Arrhenius equation.

At the same temperature and shear rate, $\eta_{\rm app}$ slightly increases with increasing the volume fraction of the glass beads. But the flow behavior index of the melts and the sensitivity of $\eta_{\rm app}$ on temperature decrease with an increase of the filler content. In addition, the first normal stress

difference of the melts basically linearly increases with an increase of wall shear stress. On the basis of a predecessor's work, an equation describing the relationship between the N_1 and pressure losses in extrusion of the polymer melts is presented. Good agreement is shown between the predicted N_1 and the measured values from the sample melts.

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