Predication of Critical Distance of Wall-Slip Phenomenon During Extrusion of Carbon Black–Filled Natural Rubber/*cis*-Polybutadiene Rubber Compound

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ABSTRACT: The wall-slip phenomenon during extrusion of polymer fluids is an important characteristic of viscoelasticity. The wall-slip behavior and the factors affecting it for natural rubber (NR)/*cis*-polybutadiene rubber (BR) filled with carbon black compound were investigated by using a Monsanto processability tester in a temperature range of 90–130°C and at shear rates that varied from 50 to 10^3 s^{-1}. Under simplified supposition conditions, a mathematical model for description of the relationship between pressure variation, polymeric properties, and extrusion operation parameters when wall-slip phenomenon occurs was established by using a tensor analysis method. On the basis of this model, an equation for estimation of critical slip distance (or position) was derived. The results showed that the measured critical pressure drop, when wall-slip begins to occur, was consistent with the theoretical predictions. The wall-slip phenomenon of the sample happened near the exit of the die. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3239–3243, 2004

Key words: rubber compound; extrusion; wall-slip; pressure drop; modeling

INTRODUCTION

When a viscoelastic fluid flows through a duct, the flow may be accompanied by slip-stick motion at the channel wall at particular conditions (e.g., the flow rate exceeds certain limit), in addition to extensional flow and shear flow. In this case, the extrudate appears to have an irregular shape, and pressure fluctuation will be produced. This is designated the wall-slip phenomenon. Wall-slip is an important elasticity characteristic of polymer fluids. It influences not only the outward appearance and quality of the extrudate to some extent, but also the melt flow stability in die extrusion of polymers. Consequently, it has received much interest in the past three decades.[1–14] Recently, the quantification of the wall-slip phenomena, the shear thinning effect[15] and the stick-slip phenomenon[16] during die flow of linear polyethylene melts, have been extensively studied. It is generally believed that the wall-slip phenomenon occurs when the wall shear stress exceeds a critical value during extrusion of polymer fluids. Cohen and Metzner[3] investigated the wall-slip phenomenon and its influence on extrusion during small duct flow of viscoelastic solutions. The results showed that the effective slip velocity increased with the wall shear stress. For polyethylene melts, the critical shear stress is about 0.1–0.4 MPa, and the critical shear stress is relatively insensitive to molecular characteristics (molecular weight and chain branching).[4]

Slip velocity is an important characteristic of wall-slip behavior of viscoelastic fluids, which is usually determined by using the classical Mooney method. Mourniac et al.[11] found that the Mooney method was impossible to apply to their experiments on styrene–butadiene–rubber compounds. They developed a new characterization method for both capillary and slit die experiments. The dependency of slip velocity on shear stress can be described by using the power law during capillary extrusion of filled rubber compounds.[13] Usually, the wall-slip phenomenon occurs at the duct exit in extrusion of viscoelastic fluids, and the adhesion between the fluid and channel wall is an important factor affecting wall-slip behavior. Hatzikiriakos[14] pointed out that both it and slip promoters eliminated surface defects by decreasing the stretching rate of polymer melt at the exit region of the die. In previous work, the author[17] investigated the influences of extrusion conditions on the flow instability of a carbon black–filled rubber compound.

It is very important, for polymer rheology and polymer processing engineering, that the critical conditions and the position of the onset of the wall-slip phenomenon are predicted in channel flow of polymer fluids. Uhland[2] proposed some mathematical models for description of the wall-slip in die flow of viscous

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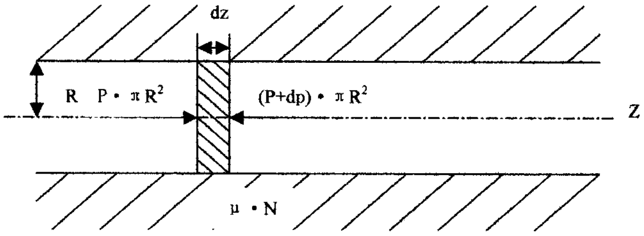

Figure 1 Mechanical analysis of the melt element in extrusion.

fluids in 1976. The objective in this article was to investigate the effects of temperature and die diameter on the pressure fluctuation behavior and the critical conditions and the position of the onset of the wall-slip phenomenon during capillary extrusion of carbon black–filled rubber compounds.

THEORY

In this article, a cylindrical coordinate system was used to analyze rubber compound flow in capillary extrusion. This analysis was based on the following hypotheses: (i) the fluid was incompressible; (ii) the flow was steady laminar and had axial symmetry flow at constant temperature; and (iii) the influence of surface tension, gravity, and inertia on the flow can be neglected. In this case, the velocity component during capillary flow of the fluid is given by

$$V(0,\ 0,\ V_Z) \tag{1}$$

where Z stands for the flow direction and r stands for the longitudinal direction. Thus, the deformation rate tensor D can be expressed as

$$D = \begin{bmatrix} 0 & 0 & \dfrac{dV_Z}{dt} \\ 0 & 0 & 0 \\ \dfrac{dV_Z}{dt} & 0 & 0 \end{bmatrix} \tag{2}$$

and the stress tensor S is given by

$$S = \begin{bmatrix} \tau_{rr} & 0 & \tau_{rz} \\ 0 & \tau_{\vartheta\vartheta} & 0 \\ \tau_{zr} & 0 & \tau_{zz} \end{bmatrix} \tag{3}$$

By substituting eqs. (1)–(3) into the motion equation, one obtains

$$\tau_{rz} = \frac{r}{2}\frac{\partial P}{\partial Z} \tag{4}$$

According to the force balance in the Z direction (see Fig. 1), we have

$$\frac{\partial P}{\partial Z} = \frac{2\mu P}{R} \tag{5}$$

By integrating eq. (5), one obtains

$$\Delta P_Z = \Delta P_L \exp\left[-\frac{2\mu}{R}(L - Z)\right] \tag{6}$$

where ΔP_L is the total pressure drop of the die, ΔP_Z is the pressure drop at distance Z, and μ is the friction coefficient between channel and fluid. If the wall-slip motion of the fluid occurs at Z_1, then the critical pressure drop ΔP_{Z_1} can be estimated by the following equation:

$$\Delta P_{Z_1} = \Delta P_L \exp\left[-\frac{2\mu}{R}(L - Z_1)\right] \tag{7}$$

and the critical wall-slip distance (or position) Z_1 can be expressed according to eqs. (4)–(6) (see Fig. 2):

$$Z_1 = L + \frac{R}{2\mu}\ln\left(\frac{\tau_{RZ}}{\mu \Delta P_L}\right) \tag{8}$$

where τ_{RZ} is the shear stress at the wall.

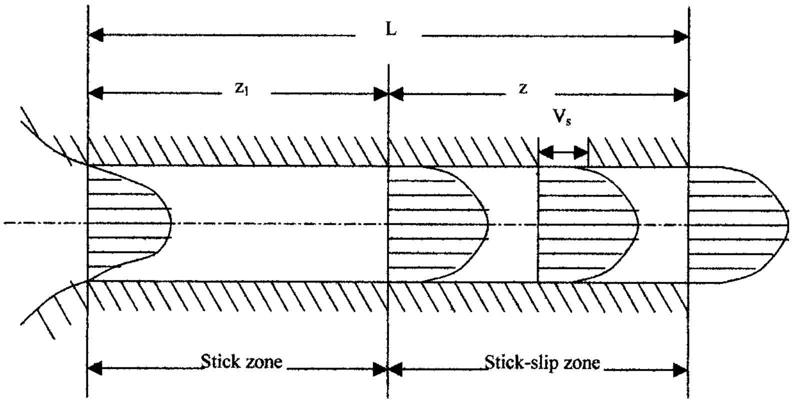

Figure 2 Diagram of the extrusion flow when wall-slip occurs.

EXPERIMENTAL

Sample material

The sample material used in this work was an industrial rubber compound. It was a masterbatch rubber by blending natural rubber (NR) with *cis*-polybutadiene rubber (BR) filled with 30% weight fraction of carbon black and other additives. The blending ratio of NR/BR was 70/30.

Methodology

The experiments were conducted by using a Monsanto processability tester. A set of capillary dies with different diameters and lengths was selected. The rheological properties of the samples were measured under test conditions: temperature range of 90–130°C and shear rates varied from 50 to 10^3 s^{-1}, parameters that were close to those of practical extrusion technology. In these tests, the pressure change was recorded and the outward appearance of the extrudate was observed.

RESULTS AND DISCUSSION

Effects of wall-slip on extrusion flow

During die extrusion flow of polymeric materials, the melt at the channel wall will be subjected to the effects of the shear force and the wall friction force (adhesion force) attributed to the pressure difference back and forth in the channel and the velocity difference between melt layers during extrusion. A dynamic balance relationship among them will be formed under given conditions (see Fig. 1). With the increase of extrusion rates, the melt will slip forward as a whole (small section channel) or slip at the side of the wall at some moment (large section channel) when the shear force subjected to the melt exceeds the adhesive force between the melt and the wall. In this case, the pressure decreases suddenly and the stress relaxes. Consequently, the melt sticks on the channel wall again, whereas the outer layer of melt still moves in the direction of shear flow to a new balance state. With the shear stress increasing gradually, the pressure increases proportionately, and the melt may produce a wall-slip phenomenon.

It is known from eq. (4) that shear stress is proportional to the pressure gradient. Therefore, the pressure will vary cyclically as long as the melt undergoes the slip-stick motion, called pressure oscillation. In this case, it will influence the flow pattern of the fluid in the duct and the extrudate will appear to have a "sharkskin-like" surface. When the situation becomes critical, it will induce unsteady flow and result in cyclic distortion, giving a bamboo-like joint shape to the extrudate.

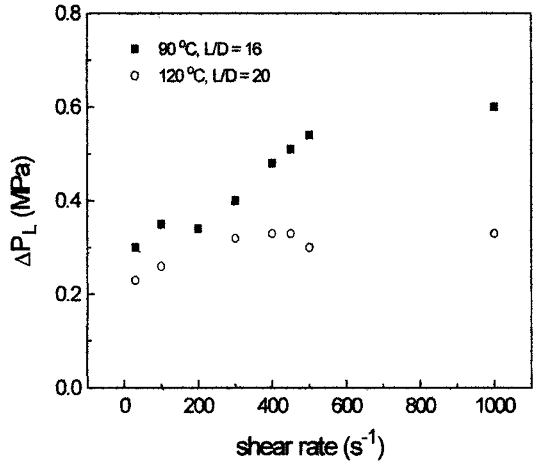

Figure 3 Plot of the dependency of pressure drop on shear rates.

Analysis of factors affecting wall-slip

In general, the shear force and friction force or adhesive force supported by polymer melts are a function of pressure, shear rate, temperature, and materials or composition. Hence, the generation of the wall-slip phenomenon during extrusion of polymer melts is also affected by the above factors. Figure 3 shows the dependency of pressure change on the wall shear rates ($\dot{\gamma}_w$) and temperature (T) for the sample in extrusion. It can be seen that the lower temperature is, the lower is the critical shear rate, resulting in pressure fluctuation at a lower extrusion rate. In other words, the wall-slip phenomenon easily occurs at a lower flow rate. Here, $\dot{\gamma}_w$ is given by

$$\dot{\gamma}_w = \frac{3n+1}{4n}\dot{\gamma}_a \tag{9}$$

and the apparent shear rate is defined as

$$\dot{\gamma}_a = \frac{32Q}{\pi \bar{D}^3} \tag{10}$$

where n is the flow behavior index and Q is the volumetric flow rate.

For a given extrusion die, pressure fluctuation is mainly a function of the friction coefficient (μ) between the melt and the channel wall [see eq. (7)], whereas μ depends on temperature, wall roughness, and composition, for example. Thus, development of the wall-slip phenomenon is intimately related to the change of temperature under given conditions. Figure 4 demonstrates the dependency of the friction coefficients between several types of rubber materials and metal surface on temperature.[18] It can be seen that μ increases with an increase of temperature (T). Gregory[19] measured the friction coefficients between several

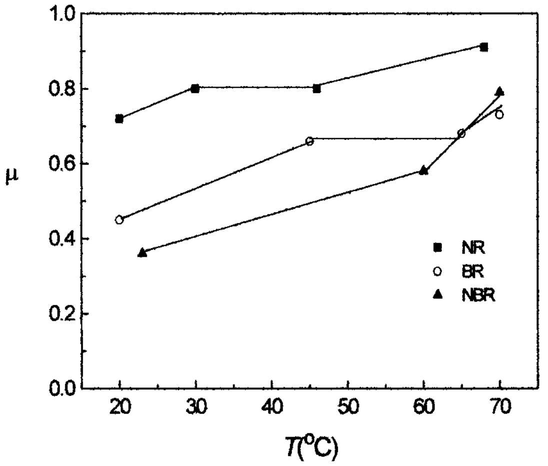

Figure 4 Relationship between friction coefficient and temperatures for rubber materials.

types of polymer materials and metal surface under different temperature conditions. The results showed that μ increases or decreases with an increase of T, and achieved a maximum at some temperature. For example, the value of μ for LDPE (low-density polyethylene) was the highest when metal temperature was 110°C. For high-density polyethylene (HDPE), μ had higher values in a temperature range of 149–220°C. For ABS, the situation was similar to HDPE. Under given operation conditions (e.g., extrusion rate or flow rate), the flow properties of polymer materials are improved and the elasticity effect is weakened with an increase of temperature, leading to an obvious reduction of pressure and a corresponding increase of the critical extrusion rate (see Fig. 3). Furthermore, when a lubricant is added into polymer fluids, the extrusion pressure can be effectively decreased, resulting in a pronounced increase in the critical shear rates at which wall-slip occurs.

For given polymer materials and extrusion operation conditions, the critical pressure drop will decrease exponentially with an increase of the channel radius (R) [see eq. (7)]. Table I lists the values of critical extrusion rates (V_c) and critical pressure drop (ΔP_{Lc}) when wall-slip occurs during extrusion of the sample. It may be observed that, at the same test temperature, V_c increases, whereas ΔP_{Lc} decreases with increasing die diameter (D). The major reasons for the onset of the above phenomenon are as follows: (1) The flow resistance reduces with increasing D, and energy losses correspondingly decrease, leading to a reduction of the critical pressure drop. (2) The diameter ratio (D_R/D) of the reservoir to the die decreases with increasing D, the entry converging degree is weakened, and the melt elastic effect is also weakened. In this case, the elastic energy stored in the melt is reduced, whereas the flow stability is increased. (3) The value of Z_1 decreases with the increase of D, resulting in an increase of the value of ($L - Z_1$) [see eqs. (7) and (8)].

TABLE I
Critical Extrusion Conditions for the Sample (L = 30 mm)

T (°C)	D (mm)	V_c (mm/s)	Δ_{Lc} (MPa)
90	1.00	0.028	0.412
	1.50	0.093	0.300
	2.00	0.138	0.243
120	1.00	0.173	0.572
	1.50	0.350	0.348
	2.00	0.440	0.234

TABLE II
Comparison Between Measured and Predicted ΔP_{Z_1}

T (ΔC)	$\dot{\gamma}_a$ (s^{-1})	ΔP_{Z_1p} (kPa)	ΔP_{Z_1m} (kPa)	Z_1 (mm)
90	200	3688.8	3571.4	31.66
105	400	3654.4	3614.4	31.54
120	600	3585.4	3243.2	31.47
135	800	3516.4	3157.9	31.46

It is generally believed that the wall-slip phenomenon often occurs at the exit of the duct during extrusion flow of viscoelastic fluids (see Fig. 2). For a die with constant diameter, the value of ($L - Z_1$) can be increased by increasing its length, but the ΔP_L also correspondingly increases. Therefore, the influence of L on the critical pressure drop is not significant like that of D.

Preliminary verification

Equation (7) describes the relationship among the processing parameters, die geometry, melt properties, and pressure drop during extrusion of polymer melts when wall-slip occurs. As stated above, the factors affecting the friction coefficient are numerous and complicated, thus making determination of the friction coefficient of polymer blends difficult. Combining the results reported in Gregory[19] and Leblane,[20] and according to these test conditions, we chose a μ value ranging between 0.5 and 0.9. By substituting the known conditions and measured data into eq. (8), the critical wall-slip distance Z_1 can be calculated. We then substituted it into eq. (7) to estimate the relevant pressure drop ΔP_{Z_1}, the results of which are listed in Table II, where D = 2 mm, L/D = 16, and ΔP_{Z_1m} and ΔP_{Z_1p} represent the measured and predicted critical pressure drop, respectively.

It can be seen in Table II that the values of Z_1 are close to L, indicating that the wall-slip phenomenon of the sample occurs around the exit of the die, and the distance Z_1 is <1 mm. This is consistent with the results reported in most of the literature. In addition, good agreement is shown between the measured ΔP_{Z_1} and the predictions by using eq. (7), and the maximal relative error is 10.2%. The factors relating to these errors are numerous. Among them, the main factor should be the determination of μ. This is because accurate measurement of μ for polymeric materials is very difficult under practical extrusion conditions. Second, the accurate measurement of the pressure drop at Z_1 is also difficult during capillary extrusion of viscoelastic fluids. In this article, considering that the wall-slip phenomenon of the sample occurs at the die exit, ΔP_{Z_1} is taken to be approximately ΔP_{Lc}.

CONCLUSIONS

Wall-slip behavior is an important characteristic of viscoelastic properties in extrusion flow of polymeric materials. In this study, the presence of pressure fluctuation and surface roughness (e.g., sharkskin) of the extrudate were considered. From the perspective of macrorheology, the main factors affecting the wall-slip behavior are temperature, flow rate, channel geometry and surface roughness of the wall, and the composition of the materials processed. It was found, from the experiments on rubber compound filled with carbon black, that the critical pressure drop for onset of the wall-slip phenomenon for the sample decreased, whereas the critical shear rate (or extrusion rate) increased with an increase of temperature. When the temperature was fixed, the critical extrusion rate increased, whereas the critical pressure drop decreased with increasing die diameter. Furthermore, the wall-slip phenomenon of the sample occurred around the duct exit.

In general, development of the wall-slip phenomenon for polymer melts can be controlled effectively by modification of extrusion conditions, such as appropriately increasing operation temperature, improving surface smoothness of the channel, optimizing the channel geometry as much as possible, and adding lubricant. In such cases, the extrusion rate and flow stability will be increased. Furthermore, the position for onset of the wall-slip phenomenon during die extrusion flow of polymer melts can be estimated by using eq. (8).

References

1. Boger, D. V.; Williams, H. L. Polym Eng Sci 1972, 12, 309.
2. Uhlang, E. Rheol Acta 1976, 15, 30.
3. Cohen, Y.; Metzner, A. B. J Rheol 1985, 29, 67.
4. Ramamurthy, A. V. J Rheol 1986, 30, 337.
5. Kalika, D. S.; Denn, M. M. J Rheol 1987, 31, 815.
6. Thien, N. P. J Non-Newton Fluid Mech 1988, 26, 327.
7. Schowalter, W. R. J Non-Newtonian Fluid Mech 1988, 29, 25.
8. Yilmazer, U.; Kalyon, D. M. J Rheol 1989, 33, 1197.
9. De Vargas, L.; Manero, O. Polym Eng Sci 1989, 29, 1232.
10. Liang, J. Z. Acta Mech Sinica 1990, 22, 79.
11. Mourniac, Ph.; Agassant, J. F.; Vergnes, B. Rheol Acta 1992, 31, 565.
12. Larson, R. G. Rheol Acta 1992, 31, 213.
13. Malkin, A. Ya.; Baranov, A. V.; Vickulenkova, M. E. Rheol Acta 1993, 32, 50.
14. Hatzikiriakos, S. G. Polym Eng Sci 1994, 34, 1441.
15. Perez-Gonzalez, J.; De Vargas, L. Polym Eng Sci 2002, 42, 1231.
16. Vargas, D.; Carreau, P. J.; Lafleur, P. G.; et al. Polym Eng Sci 2003, 43, 78.
17. Liang, J. Z. J Mater Process Technol 1997, 66, 97.
18. Liang, J. Z.; Tang, G. J.; Huang, Z. C. J South China Univ Technol 1994, 22, 120.
19. Gregory, R. B. Soc Plast Eng 1969, 25, 55.
20. Leblane, J. L. Plast Rubber Compos Process Appl 1989, 11, 53.