

Pressure effect of viscosity for polymer fluids in die flow

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Abstract

Pressure effect of steady shear viscosity for viscoelastic fluids during die extrusion flow has been analyzed and discussed. On the basis of simplified conditions, an expression for estimating the pressure coefficient (β) has been proposed in the present article. The sensitivity of melt shear viscosity to pressure during the die extrusion flow of natural rubber (NR)/styrene–butadiene rubber (SBR) blend (a tread rubber), a low-density polyethylene (LDPE) and a polystyrene (PS), has been studied by using a capillary rheometer under testing conditions. The results show that values of β calculated using this equation based on the measured data from the samples are close to the values reported in literature. In addition, it is shown that β decreases with increasing extrusion flow rates and a rise in temperatures. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer fluid; Shear viscosity; Pressure effect

1. Introduction

Viscosity is an important parameter characterizing the flow properties of polymer fluids. The factors affecting the fluid shear viscosity are complex, such as temperature, pressure, shear stress or shear rate, test time etc, in addition to molecular chain structure. It is generally believed that the effect of pressure on the viscosity of polymer fluids is significant. Since the fluid viscosity depends upon the action force between molecules and the action force is related to the distance between molecules, it is not surprising that pressured fluid results in the increase of viscosity. Furthermore, the compressive property of polymer fluids at processing temperature is greater than that of fluids at normal state. It was found in experiments that the apparent shear viscosity of polystyrene (PS) increased by 135 times at a temperature of 190°C, when the pressure was increased from 0 to 124 MPa [1]. It is, therefore, necessary to understand the dependence of the viscosity of the materials to be processed on pressure for polymer processing and shaping, especially in the design of injection moldings or in the choice of injection pressure.

Since 1950s, scientists have paid more attention to the influence of pressure on polymer fluid viscosity [2–16], in addition to investigating the relationship between fluid viscosity and temperature, time, shear stress, or shear rate.

According to the Eyring hole theory of fluid, Hirai and Eyring [2] proposed an expression for describing the relationship between viscosity and pressure as follows:

$$\eta_P = \eta_{P_0} \exp [\beta(P - P_0)] \quad (1)$$

where η_P and η_{P_0} are the viscosity at pressure P and atmosphere pressure P_0 , respectively. β is the pressure coefficient which is a function of the hole volume (V_H) and absolute temperature (T). That is

$$\beta = \frac{V_H}{RT} \quad (2)$$

where R is the universal air constant.

Important work in this field was done from 1960s to 1970s. Westover [3] and Semjonow [4] measured the values of β for polymer melts using a special designed capillary rheometer. On the basis of capillary measurement, Duvdevani and Klein [5] presented an empirical equation for determining β , which is a function of shear rate and temperature. In addition, they concluded that β decreased with the increase of shear rate and a rise in temperature. Hellwege et al. [6] and Herrmann et al. [7] measured polystyrene (PS) and poly(methyl methacrylate) (PMMA) by using an apparatus designed by Semjonow, and obtained a temperature and pressure invariant plot (i.e. a master curve). Cogswell and Mc Gowan [8] provided zero-shear viscosity data of several polymers using a similar apparatus suitable for measurements in a limited shear rate range of 0.1–25 s⁻¹. Using the same apparatus, Christmann and Knappe [9]

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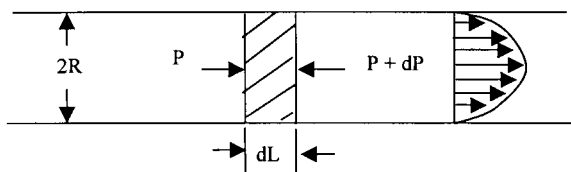


Fig. 1. Element analysis of polymer fluid in die flow.

measured low-density polyethylene (LDPE) and PMMA, and found that the zero-shear viscosity of both polymers was described by an exponential relation for pressure effect and an Arrhenius expression for temperature dependency. Christmann and Weber [10] also investigated the pressure effect on the shear viscosity for high-density polyethylene (HDPE). Lord [11] presented data for polycarbonate (PC) as measured by Westover et al. [12].

During the recent two decades, some further development and progress in this field were made. Utracki [13] presented a computation method of the pressure effect on polymer melt viscosity (η). He believed that the pressure effect on η could be determined from a single parameter function $\eta = \eta(y)$ plot, knowing the $y = y(P, T)$ relation. Huang and Shen [14] observed the pressure sensitivity of the shear viscosity in the capillary extrusion of polymer melts and obtained some data. Kadijk and Brule [15] measured the viscosity of PS, polyacrylonitrile–butadiene–styrene (ABS), and polypropylene (PP) melts in a shear rate range of five decades by using a slit viscometer, and found that the zero-shear viscosity was modeled with the generalized Arrhenius-W.L.F. relationship, incorporating a pressure dependency. Recently, Chakravorty et al. [16] proposed a simple new method to measure the pressure effect of the shear viscosity for polymer melts and examined the pressure dependence of the shear viscosity of PS melt at 200°C in capillary flow. The results show that the pressure/viscosity relationship is linear.

The objective of this article is to attempt to establish a simple expression for characterizing the pressure effect of the shear viscosity of polymer fluids in extrusion.

2. Theoretical analysis

A general expression of the relationship between pressure (P) and shear viscosity (η) is given by:

$$\eta = \eta_f \exp(\beta P) \quad (3)$$

where β is the pressure coefficient and η_f the viscosity coefficient.

If fluid shear flow obeys the power law, then η_f is expressed by the following equation:

$$\eta_f = K[\exp(-\alpha T)]\dot{\gamma}^{n-1} \quad (4)$$

where K and α are constants, T is the absolute temperature, $\dot{\gamma}$ the shear rate and n the flow behavior index.

Fig. 1 shows the flow of polymer fluid in a circular channel. Now, a mechanical analysis on a small length of fluid (dL) of the fluid in capillary flow is made. If there is no wall-slip phenomenon during the die flow of the fluid and it is a fully developing flow, then the following equation can be written according to the momentum equilibrium relationship:

$$\pi R^2 dP = 2\pi R \tau_w dL \quad (5)$$

where the wall shear stress (τ_w) is defined as:

$$\tau_w = \eta \dot{\gamma}_w \quad (6)$$

From Eq. (3), Eq. (6) can be rewritten as:

$$\tau_w = \tau_w^f \exp(\beta P) \quad (7)$$

Substituting Eq. (7) into Eq. (5) and considering the end correction (i.e. the Bagley correction), we have

$$(1 - e^{-\beta P})/\beta = 2\tau_w^f(L/R + e_B) \quad (8)$$

where e_B is the Bagley correction factor ($\tau_w = P/2[(L/R) + e_B]$), $\dot{\gamma}_w$ the true wall shear rate, τ_w^f the referent shear stress with respect to η_f , and R and L the radius and length of the die, respectively.

A set of capillaries with the same diameter but with different length, L_i ($i = 1, 2, 3$), is selected, τ_w^f and e_B are constants and P can be considered to be a function of L_i , when the operating conditions are fixed. Thus, an approximate expression for β can be derived from Eq. (8):

$$\beta = \frac{c_1 - c_2}{c_1 P_{m2} - c_2 P_{m1}} \quad (9)$$

where $c_1 = (L_1 - L_2)/(L_1 - L_3)$, $c_2 = (P_1 - P_2)/(P_1 - P_3)$, $P_{m1} = (P_1 + P_2)/2$, $P_{m2} = (P_1 + P_3)/2$. P_i ($i = 1, 2, 3$) is the pressure at channel length L_i ($i = 1, 2, 3$).

It can be seen from Eq. (3) that the β value reflects the sensitivity of the fluid shear viscosity to pressure. Because the pressure is measured easily, the pressure effect of the shear viscosity of the polymer in melting flow can be estimated conveniently using Eq. (9).

3. Experimental

3.1. Materials

The sample material used in this work included three types polymer materials: a natural rubber (NR)/styrene–butadiene rubber (SBR) blend (a tread rubber compound), a polystyrene (PS 470, Dow Chemical), and a low-density polyethylene (LDPE 160 AS, Exxon). For the tread rubber compound, the blending ratio (NR/SBR) was 70/30. In addition, this rubber compound included some additives, such as carbon black, machine oil, zinc stearate, etc.

3.2. Instruments and methodology

The rheological tests were conducted by using a capillary rheometer. A set of capillary dies with different length was

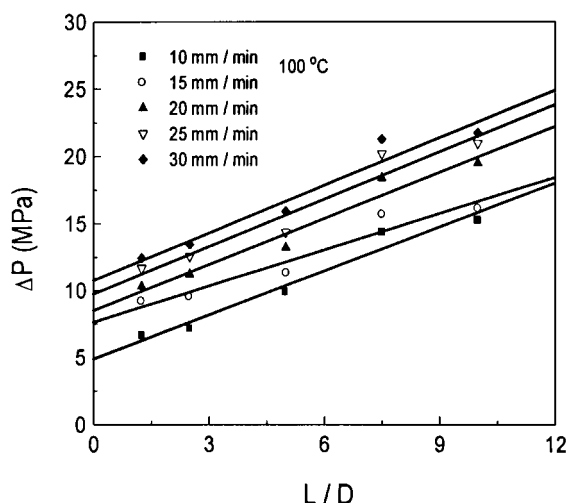


Fig. 2. Pressure drop versus L/D .

selected. The diameter (D) of these dies was 1 mm for the thermoplastic resins and 2 mm for the rubber compound, respectively. For the rubber compound, the rheological properties were measured under the test conditions of temperatures from 90 to 120°C, and the apparent shear rate ($\dot{\gamma}_a$) varying from 10 to 300 s⁻¹. For the LDPE, the rheological measurement was carried out under the testing conditions of temperature at 240°C and ($\dot{\gamma}_a$) varying from 60 to 200 s⁻¹. For PS, the experimental conditions were temperature of 260°C and ($\dot{\gamma}_a$) varying from 500 to 1000 s⁻¹. A pressure transducer was installed at the inlet of the dies to measure the pressure variation during the extrusion of the sample melts.

The relationship between $\dot{\gamma}_w$ and $\dot{\gamma}_a$ is given by:

$$\dot{\gamma}_w = \frac{3n + 1}{4n} \dot{\gamma}_a \tag{10}$$

and

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \tag{11}$$

where Q is the volumetric flow rate.

Table 1
Estimation of β for the rubber compound ($D = 2$ mm)

T_1 (°C)	$\dot{\gamma}_a$ (s ⁻¹)	P (MPa)				c_1	c_2	β (10 ⁻⁸ Pa) ⁻¹
		$L/D = 2.5$	$L/D = 5$	$L/D = 7.5$	$L/D = 10$			
100	185.65	11.210	13.227	18.384	19.505	0.500	0.179	6.699
100	232.07	12.555	14.348	20.177	20.962	0.500	0.119	5.972
100	278.48	13.452	15.918	21.298	21.747	0.500	0.077	5.452
110	139.24	8.968		15.694	17.039	0.333	0.167	4.405
110	185.65	9.977		17.823	19.281	0.333	0.157	3.998
110	232.07	10.761		18.384	19.729	0.333	0.150	3.841

Table 2
Estimation of β for the PS (260°C, $D = 1$ mm)

$\dot{\gamma}_a$ (s ⁻¹)	P (MPa)			c_1	c_2	β (10 ⁻⁸ Pa)
	$L/D = 10$	$L/D = 20$	$L/D = 30$			
519.8	4.51	7.76	11.08	0.5	0.505	0.582
626.3	4.82	8.28	11.81	0.5	0.505	0.546
716.6	5.02	8.66	12.33	0.5	0.505	0.519
920.5	5.37	9.23	13.17	0.5	0.505	0.490

4. Results and discussion

4.1. Pressure losses

Fig. 2 displays the relationship between the total pressure drop (ΔP) and the die length/diameter ratios (L/D) during the extrusion of the rubber compound at 100°C. It can be seen that ΔP increases with increasing L/D , and that the correlation between them is approximately linear. At the same value of L/D , the value of ΔP increases with the increase of the piston speed (V). The slopes of these linear lines of ΔP versus L/D are called entry pressure losses (ΔP_{en}). It can also be seen from Fig. 2 that ΔP_{en} increases with the piston speed.

4.2. Estimation of β values

Tables 1–3 list the pressure values during the die extrusion flow of the rubber compound, the PS and the LDPE melts under the operating conditions of test temperatures (T_1) and the shear rates, respectively. Substituting these measured pressure values into Eq. (9), the relevant β values can be calculated, the results are also listed in Tables 1–3, respectively. In Table 1, when T_1 is 100°C, $L_1 = 20$ mm, $L_2 = 15$ mm, and $L_3 = 10$ mm; whilst when T_1 is 110°C, $L_1 = 20$ mm, $L_2 = 15$ mm, and $L_3 = 5$ mm. In Tables 2 and 3, $L_1 = 30$ mm, $L_2 = 20$ mm, and $L_3 = 10$ mm.

Free volume and entanglement density of molecular chains are the two main factors governing polymer fluid viscosity. Either the polymer structure parameters (such as the relative molecular weight and its distribution, the branch degree of molecular chains etc.) or external conditions (e.g. temperature, pressure, stress or deformation rate, time, etc.)

Table 3
Estimation of β for the LDPE (240°C, $D = 1$ mm)

$\dot{\gamma}_a$ (s ⁻¹)	P (MPa)			c^1	c^2	β (10 ⁻⁸ Pa)
	$L/D=10$	$L/D=20$	$L/D=30$			
81.1	1.07	1.97	2.97	0.5	0.526	4.92
100.7	1.21	2.27	3.37	0.5	0.509	3.10
121.2	1.36	2.53	3.72	0.5	0.504	1.31

affect the polymer fluid viscosity through variation of the two factors stated above. It can be seen in Table 1 that the values of β decreases somewhat with increasing $\dot{\gamma}_a$ at the same temperature. Similar results can be seen also in Tables 2 and 3. This is because, an increase of $\dot{\gamma}_a$ increases the wall shear stress, leading to quickening untying entanglement and producing shear-thinning effect, thus the fluid viscosity decreases correspondingly. On the other hand, the reduction of free volume leads to weakening of the sensitivity of the viscosity to pressure.

It can also be seen from Table 1, the values of β reduces with increasing T_1 at the same $\dot{\gamma}_a$. Relatively speaking, the decrease of β values due to the increase of T_1 is greater than that of owing to the increase of $\dot{\gamma}_a$. Generally, the active ability of molecular chains is enhanced, and stress relaxation is quickened with a rise in temperature. Therefore, the fluid viscosity decreases correspondingly. Refs. [5,17] also pointed out that the effect of pressure on the melt shear viscosity decreases with a rise of temperature, and it decreases with increasing shear rate. Furthermore, the β values of several polymeric materials were listed in Ref. [17], the values of β being 0.5–4 (10⁻⁸ Pa⁻¹) for an individual resin. Agassant et al. [18] noted that the β values of polymeric materials are generally 1.2–6 (10⁻⁸ Pa⁻¹). These are of the same numeral level or order as the results predicted in the present article. Comparatively speaking, the sensitivity of the β for the LDPE to the extrusion rate is relatively significant.

5. Conclusion

The pressure coefficient, β , is an important parameter

characterizing the pressure dependence of the viscosity of polymer fluids. Eq. (9) describes the relationship between pressure, die geometry and β . The pressure effect of polymer melt shear viscosity during extrusion and injection molding flow can be conveniently estimated by using this expression.

The effect of pressure on the shear viscosity of a NR/SBR rubber compound, a polystyrene and a low-density polyethylene melts in capillary extrusion has been investigated under the experimental conditions applied. The results show that the influence of variation of extrusion speeds or shear rates and temperature on the pressure sensitivity of the sample viscosity is significant. Under constant temperature condition, the β values decrease with increasing $\dot{\gamma}_a$. When $\dot{\gamma}_a$ is fixed, the β values decreases with a rise in temperature.

References

- [1] Maxwell B, Jung A. *Mod Plast* 1957;35:174.
- [2] Hirai N, Eyring H. *J Polym Sci* 1959;37:51.
- [3] Westover RF. *Soc Plast Engng Trans J* 1961;1:14.
- [4] Semjonow VV. *Rheol Acta* 1965;4:33.
- [5] Duvdevani IJ, Klein I. *Soc Plast Engng Trans J* 1967;123(41):14.
- [6] Hellwege KH, Knappe W, Paul F, Semjonow V. *Rheol Acta* 1967;6:165.
- [7] Herrmann HD, Knappe W. *Rheol Acta* 1969;8:384.
- [8] Cogswell FM, Mc Gowan JC. *Br Polym J* 1972;4:183.
- [9] Christmann L, Knappe W. *Coll Polym Sci* 1974;252:705.
- [10] Christmann L, Weber G. *Rheol Acta* 1978;17:16.
- [11] Lord HA. *Polym Engng Sci* 1979;9:469.
- [12] Westover RF, Bearder SS. *SPE Regional Tech. Papers, Palisades, Philadelphia and Newark Sections, October 1977.*
- [13] Utracki LA. *Polym Engng Sci* 1985;25:655.
- [14] Huang JC, Shen HF. *Adv Polym Technol* 1989;9:211.
- [15] Kadijk SE, Van Den Brule BHAA. *Polym Engng Sci* 1994;34:1535.
- [16] Chakravorty S, Rides M, Allen CRG, Brown CS. *Plast Rubber Compos Process Appl* 1996;25:260.
- [17] Chengdu University of Technology. *Polymer chemistry and physics.* Beijing: Light Industry Press, 1984, 268 p.
- [18] Agassant JF, Avenas P, Sergent JP, Carreau PJ. *Polymer processing.* New York: Hanser Publishers, 1989, 366 p.