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A Rheological Interpretation of the Flow of Polymer Melts through a Circular Tube

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1. Introduction

In general, the processing of polymeric materials requires certain steps: namely, melting of solid polymers, transport of molten polymers through a reservoir section (or a calming section), and extrusion through a die section. Because of the cross section of a die being generally much smaller than that of a calming section, a pressure drop occurs at the entry to the die section. This pressure drop is considerably greater for polymer melts, than would be the case with Newtonian fluids. There is ample evidence that the viscosity of the material alone cannot explain such excessive pressure drops (1, 2, 3, 4).

When fluid enters a tube from a large reservoir the velocity profile starts to develop until a certain distance is reached beyond which flow is said to be fully developed, meaning that the velocity profile has attained either the classical parabolic form characteristic of Newtonian fluids, or the flatter than parabolic form corresponding to polymer melts. The finite length of tube required for attaining a fully developed flow profile is known as the "entrance length." Clearly, the magnitude of the entrance length is dependent upon the viscosity of the fluid, the diameter of the tube and velocity of the fluid (for Newtonian fluids), and also upon the elastic properties (for viscoelastic fluids) (5, 6, 7, 8).

The criterion for determining fully developed flow in viscoelastic fluids (e. g. polymer melts) has been a controversial subject. A conventional criterion such

as the "constant pressure gradient" in the tube, does not seem to be valid in polymer melt flow, while, of course, the same criterion has been well accepted for Newtonian fluids. Conditions other than the "constant pressure gradient" have been suggested in recent years in polymer melt flow (9). This is an important subject because, once flow is fully developed, one can write momentum balance equations to derive various expressions relating the fluid properties to flow variables (flow rate, pressure drop, etc.) and the geometry of a tube.

In the exit region of a tube, polymer melts exhibit some further unusual phenomena from the point of view of classical fluid mechanics. These are the swelling of extrudate (10, 11, 12) and the "exit pressure" (13, 14, 15, 16, 17). The former phenomenon, die swell, is the expansion of the extrudate giving rise to a ratio of the extrudate diameter to tube diameter greater than unity, and this ratio is found to be a function of the throughput rate for a specific tube and a given polymer. The latter phenomenon, exit pressure, is the pressure exerted on the polymer melt as it leaves the tube exit, giving rise to values above the ambient pressure. Its magnitude also depends on the throughput rate for a specific tube and a given polymer.

These unusual phenomena in the entrance and exit regions have been the subject of intensive research during the past several years, in order to establish a better understanding of the elastic nature of polymer melt flow. In the present paper we shall discuss the rheological implications of the anomalous behavior associated with the flow of polymer melts in both the entrance and exit regions of a tube of circular

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cross section.

2. Fully Developed Region

For a steady, fully developed flow, the equations of motion with cylindrical coordinates may be written as

$$-\frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{zr}) = 0 \quad (1)$$

$$-\frac{\partial p}{\partial r} + \frac{\partial \tau_{rr}}{\partial r} + \frac{s_{rr} - s_{\theta\theta}}{r} = 0 \quad (2)$$

$$-\frac{\partial p}{\partial \theta} = 0 \quad (3)$$

in which

$$\begin{pmatrix} s_{zz} & s_{zr} & s_{z\theta} \\ s_{zr} & s_{rr} & s_{r\theta} \\ s_{z\theta} & s_{r\theta} & s_{\theta\theta} \end{pmatrix} = - \begin{pmatrix} P & O & O \\ O & P & O \\ O & O & P \end{pmatrix} + \begin{pmatrix} \tau_{zz} & \tau_{zr} & 0 \\ \tau_{zr} & \tau_{rr} & 0 \\ 0 & 0 & \tau_{\theta\theta} \end{pmatrix} \quad (4)$$

For a sufficiently long tube with cross section radius R and length L , integration of Eq. (1) gives

$$\tau_{zr} = \left(\frac{-\partial p}{\partial z} \right) \frac{r}{2} \quad (5)$$

where $\frac{-\partial p}{\partial z}$ is the pressure gradient. The wall shear stress τ_w is then obtained from

$$\tau_w = \left(\frac{-\partial p}{\partial z} \right) \frac{R}{2} \quad (6)$$

When a Newtonian liquid is forced to flow from a reservoir through a circular tube with radius R and length L , one can define the following quantity as the shear rate ϕ

$$\phi = \frac{4Q}{\pi R^3} = \frac{8\bar{V}}{D} \quad (7)$$

in which Q is the volumetric flow rate, \bar{V} is the average velocity of the fluid in the tube and D is the diameter of the tube. In general, the volumetric flow rate Q is obtained from the velocity profiles $V_z(r)$ in the tube, thus

$$Q = 2\pi \int_0^R v_z(r) r dr \quad (8)$$

Assuming that there is no slippage at the wall, i. e.,

$V_z(R)=0$, integrating Eq. (8) by parts, gives

$$Q = -\pi \int_0^R r^2 dv_z \quad (9)$$

Combination of Eqs. (5) and (6) gives

$$r = \frac{R}{\tau_w} \tau_{zr} \quad (10)$$

For constant shear rate $\dot{\gamma}$ we have

$$\frac{dv_z}{dr} = \dot{\gamma} \quad (11)$$

or

$$dv_z = \dot{\gamma} dr \quad (12)$$

Use of Eqs. (10) and (12) in Eq. (9) gives

$$\frac{\tau_w^3 Q}{\pi R^3} = - \int_0^{\tau_w} \dot{\gamma} \tau_{zr}^2 d\tau_{zr} \quad (13)$$

Differentiating both sides of Eq. (13) with respect to τ_w and using Leibnitz's rule, we obtain

$$\frac{1}{\pi R^3} \left[\tau_w \frac{dQ}{d\tau_w} + 3Q \right] = -\dot{\gamma}_w \quad (14)$$

in which $\dot{\gamma}_w$ is the wall shear rate. Use of Eq. (7) in Eq. (14) gives

$$\frac{\phi}{4} \left(3 + \frac{d \ln \phi}{d \ln \tau_w} \right) = -\dot{\gamma}_w \quad (15)$$

which is known as the Rabinowitch-Mooney equation. Eq. (15) is commonly used to calculate the wall shear rate for non-Newtonian liquids.

On the other hand, it has been found experimentally that for many polymeric materials a plot of τ_w versus ϕ on logarithmic coordinate gives a constant slope over a wide range of ϕ values, as shown in Fig. 1. Then one can write an empirical equation as follows.

$$\tau_w = K' \phi^n \quad (16)$$

in which n is the slope of the log τ_w vs. log ϕ plot, that is

$$n = \frac{d \ln \tau_w}{d \ln \phi} \quad (17)$$

Eq. (15) may be rewritten by use of Eq. (17)

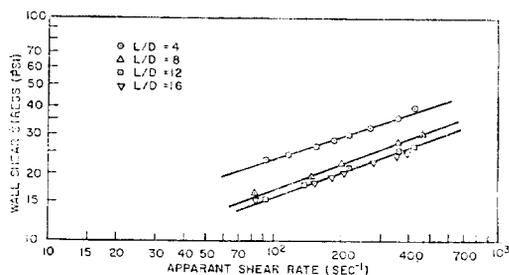


Fig. 1 Apparent wall shear rate versus apparent shear rate for high density polyethylene at 180°C

$$\left(\frac{3n+1}{4n}\right)\phi = -\dot{\gamma}_w \quad (18)$$

Use of Eq. (18) in Eq. (16) gives further

$$\tau_w = K(-\dot{\gamma}_w)^n \quad (19)$$

in which

$$K = K^1 \left(\frac{4n}{3n+1}\right)^n \quad (20)$$

Note that for $n=1$, Eq. (19) reduces to

$$\tau_w = K^1\phi \quad (21)$$

which is the well known representation for Newtonian fluids. K^1 in Eq. (21) represents the Newtonian viscosity in this case. Therefore it can be surmised that values of n different from unity describe the deviation from Newtonian fluids. In the case of polymer melts, n is usually equal to or less than unity (see Figure 1). Eq. (19) is known as the Oswald-de Wale power law relation. Therefore, we shall define the power law fluid as that fluid whose wall shear stress and true shear rate can be represented by Eq. (19).

Now, one can derive the expression for the velocity distribution in a tube for power law fluids. Integrating Eq. (12) gives

$$V_z(r) = \int_R^r \dot{\gamma} dr \quad (22)$$

in which $V_z(R)=0$ is assumed, that is, no slippage at the wall. Using Eqs. (10) and (16) in Eq. (22) and integrating the resulting equation gives

$$V_z(r) = \bar{V} \left(\frac{3n+1}{n+1}\right) \left[1 - \left(\frac{r}{R}\right)^{\frac{n+1}{n}}\right] \quad (23)$$

where \bar{V} is the average velocity of the fluid. The velocity profile of power law fluids for different values of n is shown in Figure 2.

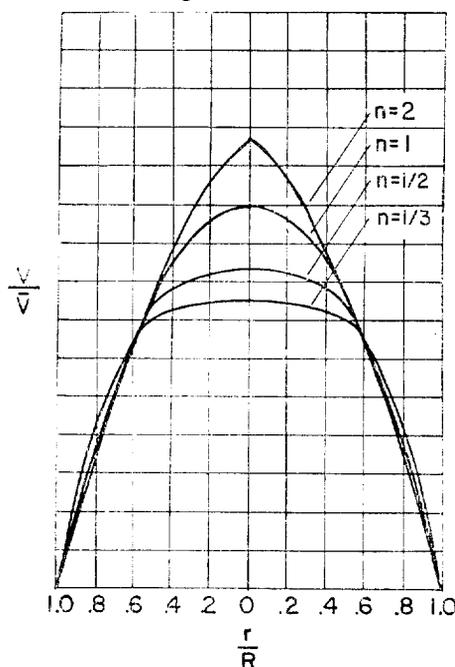


Fig. 2 Velocity profiles for the power-law fluid

3. Entrance Region

In view of the complexity of flow conditions there, theoretical treatments of the pressure drop in the entrance region of a tube are approximate in nature and are limited to certain types of entrance geometries. Consequently, it is frequently necessary to evaluate entrance pressure drops experimentally. This is particularly true in the case of highly viscous polymers where entrance effects are large. If, in fact, the excess pressure drop may be thought of as occur-

ring in an imaginary increment to the actual tube length, a plot of pressure versus capillary length-to-diameter ratio (L/D) at a given shear rate will be linear (1). Extrapolation of such a linear plot to zero pressure gives the ratio of the fictitious length to the tube diameter for that particular shear rate. In view of the work required to overcome elastic forces, it

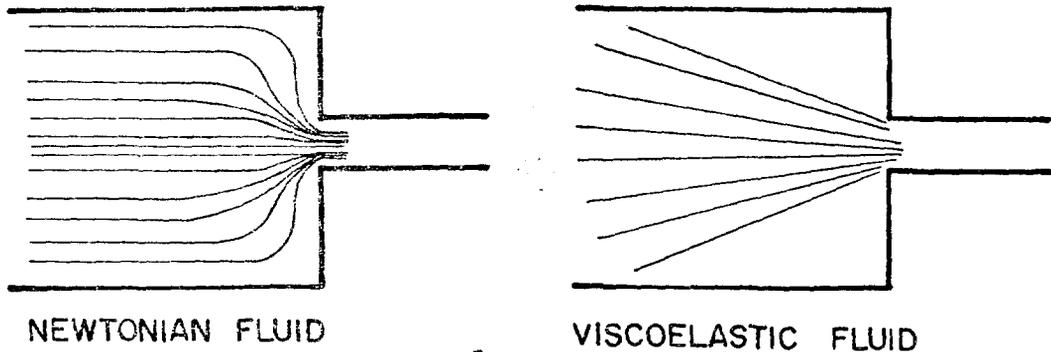


Fig. 3 Sketch of the streamlines in the reservoir

is to be expected that the entrance length and the pressure drop in the entrance region would be much greater for an elastic material than for an inelastic fluid under the same flow geometry. Observe converging streamlines in the entrance region for both Newtonian and viscoelastic fluids, sketched in Figure 3.

Now consider the situation in which pressure drop is measured from somewhere in the reservoir to the end of the capillary. For this, Eq. (6) must be modified by taking into account the pressure losses that arise in the reservoir. In the case of a Newtonian liquid these pressure losses in the reservoir are considered to be the viscous losses encountered by the liquid as a result of velocity gradients near the capillary entrance. As may be seen from Fig. 3, the streamlines in the reservoir converge at the inlet of the capillary before they reach it and thus one is inclined to consider an additional fictitious length $n_B R$ to the actual capillary length, so that the true shear stress at the wall can be written as

$$\tau_{rw} = \frac{\Delta P}{2 \left(\frac{L}{R} + n_B \right)} \quad (24)$$

The additional term n_B in the denominator of Eq. (24) is called "End Correction." n_B is reported to be $0.06 N_{Re}$ for a Newtonian liquid, where N_{Re} denotes the Reynolds number defined by

$$N_{Re} = \rho D \bar{V} / \mu \quad (25)$$

ρ is the density of the fluid, D is the tube diameter,

\bar{V} is the average velocity and μ is the viscosity of the fluid.

Bagley (1) in 1957 reported a very interesting observation from the extrusion of polyethylene melt. He found that the value of the entrance correction for such a fluid is much larger than that for Newtonian fluids, and furthermore it is a strong function of shear rate. Then, he suggested the following procedure for correcting the entrance effects: (a) plot the flow curve of $\log \dot{\gamma}_w$ versus $\log \Delta P$, for a series of $\left(\frac{L}{R} \right)$ values (see Fig. 4); (b) from the plot of $\log \dot{\gamma}_w$ versus $\log \Delta P$ and choosing an arbitrary shear rate, find the pressure ΔP corresponding to this shear rate for various capillaries of different (L/R) values. Then obtain the value of entrance length n_B from the extrapolation of the ΔP vs. L/R plots to $\Delta P=0$ (see Figure 5); (c) using the appropriate entrance corrections replot the curves of Fig. 4, using Eq. (24) to calculate the true shear stresses. This plot shown in Fig. 6 becomes a single curve independent of the capillary dimensions used to obtain the data.

Note that for polymer melts, in general, the value of n_B in Equation (24) is larger than that of Newto-

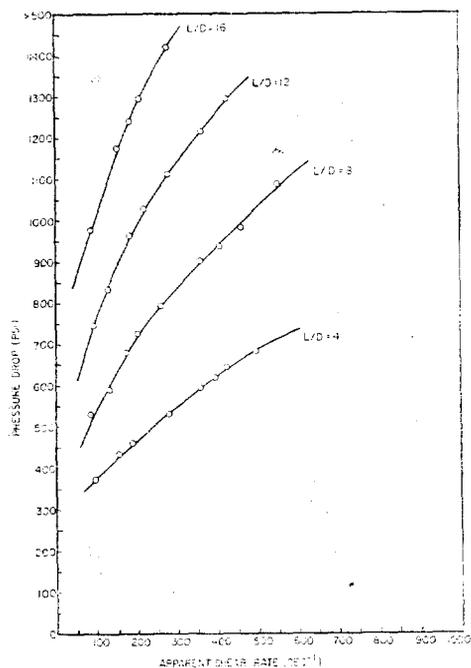


Fig. 4 Total pressure drop versus apparent shear rate for high density polyethylene at 180°C

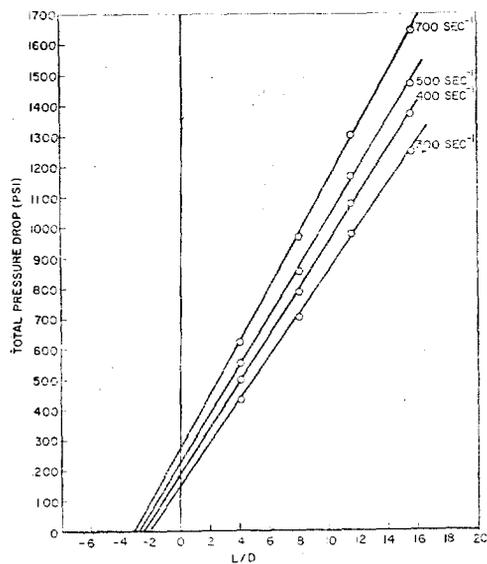


Fig. 5 Total pressure drop versus L/D ratio (Bagley plots) for high density polyethylene at 180°C

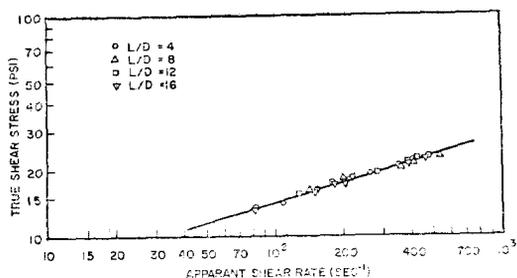


Fig. 6 True wall shear stress versus apparent shear rate for high density polyethylene at 180°C

nian liquids, The qualitative interpretation for this can be given as follows. For viscoelastic liquids, the tube entry pressure losses can be attributed to two factors: Couette losses, as in the Newtonian liquids, and elastic energy stored in the flowing viscoelastic liquid as it is sheared. The stored elastic energy is believed to be partially dissipated after the fluid enters the tube, reaching a steady value which is converted to completely recoverable elastic energy.

4. Exit Region

In the exit region two anomalous phenomena, die swell and exit pressure, are observed in polymer melt flow. The swell phenomenon has been known for many years and much literature has been published on the subject (10, 11, 12). However, the existence of exit pressure in polymer melt flow has only recently been recognized (13, 14, 15, 16, 17). The reason for it seems to be very simple. Die swell can be easily observed from extrudate, while exit pressure can be determined only when one starts to measure pressure distribution with elaborate instrumentation.

Swelling of the extrudate on emerging from a capillary is typical of non-Newtonian viscoelastic liquids and is believed to be related to their elastic properties. From the structural point of view, die swell is accompanied by a disorientation of macromolecules which have been "parallelized" within the capillary due to the high shear field. From the rheological point of view, on the other hand, it is believed that die swell occurs as a result of recovery of the elastic

deformation imposed in the capillary. It is clear that a deformed element of fluid exhibiting retarded elasticity will not recover its elastic deformation instantaneously as it emerges from the capillary. Instead, while recovery is proceeding, it will travel some distance from the exit of the capillary. This distance will depend on the velocity of the fluid element leaving the tube exit and the characteristic time of the material concerned.

Har et al. (15) have recently obtained a definite correlation between die swell and exit pressure. Hence, the physical interpretation for the exit pressure is essentially the same as that for die swell. In this section we will first derive some fundamental equations which will be used to correlate the measured values of die swell and exit pressure with normal stress difference. We will then present methods for measuring exit pressure and die swell in a capillary type instrument. Finally we will discuss how one can analyze experimentally determined exit pressure and die swell data in order to obtain rheological information on melt elasticity and flow properties of polymer melts.

4.1 Theoretical Development

Writing the force balance equation around the portion of the liquid jet between Sections 1 and 2 of Figure 7,

$$2\pi \int_0^R \rho V^2(r) r dr - \pi R_j^2 \rho V_j^2 = 2\pi \int_0^R S_{zz}(r, L) r dr \quad (26)$$

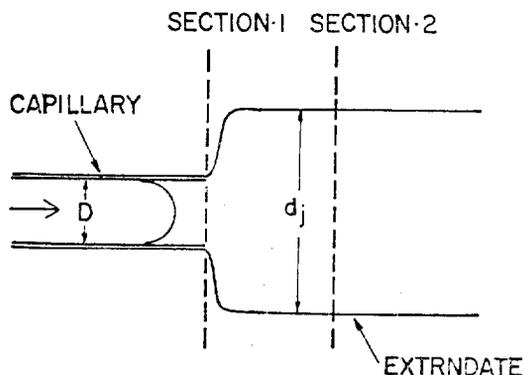


Fig. 7 Sketch of the exit region with die swell

in which

- $V(r)$ = Velocity of the liquid in the tube
- R_j = Radius of the extrudate at its maximum die swell
- V_j = Free jet velocity at maximum die swell
- ρ = Density of the liquid
- $S_{zz}(r)$ = Normal stress in flow direction.

In Eq. (26) the left hand side represents the difference in momentum flux of the fluid between Sections 1 and 2, and the right hand side represents the external force which is the total stress in the flow direction integrated over the entire cross section of the tube.

Replacing r with τ_{zr} by use of Eq. (10) and by the continuity equation

$$\pi R_j^2 \rho V_j = \pi R^2 \rho \bar{V} \quad (27)$$

Eq. (26) may be rewritten as

$$\rho \int_0^T V^2(r) \tau_{zr} d\tau_{zr} - \frac{\rho \bar{V}^2}{2} \left(\frac{D}{d_j}\right)^2 \tau_w^2 = \int_0^T S_{zz}(r, L) \tau_{zr} d\tau_{zr} \quad (28)$$

where d_j is the maximum extrudate diameter and \bar{V} is the average velocity of the liquid in the tube as defined by Eq. (7). Differentiating both sides of the above equation with respect to τ_w and using Leibnitz's rule, one has, after some rearrangement,

$$S_{zz}(R, L) = \frac{\rho \bar{V}^2}{n} \left\{ (n+1) \int_0^1 2 \left(\frac{V(r)}{\bar{V}}\right)^2 \frac{r}{R} d\left(\frac{r}{R}\right) - \left(\frac{D}{d_j}\right)^2 \left[n+1 + \frac{d\left[1n \frac{D}{d_j}\right]}{c\left[1n \frac{8\bar{V}}{D}\right]} \right] \right\} \quad (29)$$

If one assumes that the fluid is represented by a power law as expressed in Eq. (16), Eq. (29) becomes, after the integration of the first term by use of Eq. (23),

$$S_{zz}(R, L) = \frac{\rho D^2}{64n} \left(\frac{8\bar{V}}{D}\right)^2 \left\{ \frac{(n+1)(3n+1)}{(2n+1)} - \left(\frac{D}{d_j}\right)^2 \left[n+1 + \frac{d\left[1n \frac{D}{d_j}\right]}{d\left[1n \frac{8\bar{V}}{D}\right]} \right] \right\} \quad (30)$$

Now, from the definition of the deviatoric stress, $S_{zz}(R)$ is given by

$$S_{zz}(R, L) = -p_{R,L} + \tau_{zz}(R) \quad (31)$$

in which $p_{R,L}$ is the wall isotropic pressure at the tube exit. On the other hand, integrating the radial component of the equation of motion, Eq. (2), gives

$$p_{R,L} = p_{O,L} + \tau_{rr}(R) + \int_0^R (S_{rr} - S_{\theta\theta}) d 1n r \quad (32)$$

where $p_{O,L}$ is the isotropic pressure at the center of the tube exit. Eliminating $p_{R,L}$ from Eqs. (31) and (32) gives

$$S_{zz}(R, L) = (\tau_{zz} - \tau_{rr})_R - \left[p_{O,L} + \int_0^R (S_{rr} - S_{\theta\theta}) d 1n r \right] \quad (33)$$

Again, from the definition of the deviatoric stress, one has

$$S_{rr}(R, L) = -p_{R,L} + \tau_{rr}(R) \quad (34)$$

Use of Eq. (34) in Eq. (32) gives

$$S_{rr}(R, L) = - \left[p_{O,L} + \int_0^R (S_{rr} - S_{\theta\theta}) d 1n r \right] \quad (35)$$

Therefore, combining Eqs. (33) and (35) gives

$$(\tau_{zz} - \tau_{rr})_R = -S_{rr}(R, L) + S_{zz}(R, L) \quad (36)$$

where $S_{zz}(R, L)$ is given by Eq. (30). Eq. (36) now represents the primary normal stress difference as the sum of the two quantities on the right hand side: $-S_{rr}(R, L)$ and $S_{zz}(R, L)$. Hence, measurement of these two quantities determines the primary normal stress difference, i. e., melt elasticity.

Note, however, that $S_{rr}(R, L)$ is the wall radial normal stress at the exit of a tube, which is measurable without disturbing the flow in the tube. Since the pressure measurement is opposite in direction to that of the radial normal stress component, we can say that (13,14)

$$p_{\text{Exit}} = -S_{rr}(R, L) \quad (37)$$

and then Eq. (36) may be rewritten as

$$(\tau_{zz} - \tau_{rr})_R = p_{\text{Exit}} + S_{zz}(R, L) \quad (38)$$

Hence, Eq. (38) indicates that measurement of exit pressure and die swell determines uniquely the primary normal stress difference, i. e., melt elasticity,

which is of utmost importance in practical operation with polymeric materials.

Note that the assumptions made in the derivation of the expressions above are that the fluid is described by a power law and that the fully developed velocity profile prevails at the tube exit. However, it can be shown later that the assumption of a power law is not necessary for polymer melts in practice (13,14).

4.2 Experimental Determination of Die Swell

The method commonly used to obtain the die swell ratio of polymer solutions involves photographing the polymer stream as it exits from a horizontal capillary. The relaxation time of solutions is generally so short that complete swelling occurs close enough to the capillary exit for the effect of gravity to be negligible. The case of polymer melts is not, however, so simple.

In the past the following techniques have been used to obtain melt die swell data:

- The same method as is used for solutions (18).
- Vertical extrusion of a short length of polymer which is frozen (no attempt being made to control the manner) with a micrometer (11).
- A refinement of method (b) in which the extruded melt is held at the extrusion temperature for a period of time in order to permit complete relaxation (19).

In methods (b) and (c) a density correction of the form

$$\frac{d}{d_0} = \left(\frac{\rho_0}{\rho} \right)^{\frac{1}{3}} \quad (39)$$

is usually made, where

d = swelled diameter of melt at extrusion temperature

d_0 = swelled diameter of frozen polymer

ρ = density of melt

ρ_0 = density of frozen polymer.

Method (a), although the most direct and least complicated, is not suitable for polymer melts. The reason for this, as will be demonstrated subsequently, is that the melt relaxation time is so long that complete expansion cannot occur in a region close to

the capillary exit.

Method (b) represents a distinct improvement but is subject to the following objections:

(1) It has not been indicated whether or not the polymer used to obtain the die swell passed through the entrance during the extrusion time.

(2) The use of the density correction is questionable. This is particularly true in the case of polymers which crystallize since the solid density is known to depend on crystallization kinetics.

In order to eliminate these sources of possible error, Han and Charles (20) have recently devised a method which is, in essence, a modification of method (c). The experimental procedure for the measurement of die swell developed by these authors is as follows:

(1) Polymer flows through a capillary device and into a chamber which is maintained at the same temperature as the capillary. The chamber is equipped with a small removable pyrex window.

(2) When a steady state has been achieved, the window is removed and the polymer stream (still flowing) is cut at the exit.

(3) Flow continues until a stream of about 3 inches in length has emerged. At this point flow is stopped and the small window replaced. (Thermocouples within the chamber indicate that the removal of the window causes a temporary decrease of no more than 5°C.)

(4) Pictures are taken of the suspended stream at various time intervals until the melt has fully relaxed.

(5) The melt diameter is then determined by comparison of the melt images to that of a standard.

In Figure 8, die swell of a high density polyethylene has been plotted for several rates of shear as a function of time after exiting the capillary. The die used had a diameter of 0.125 inch and a length of 0.507 inch ($L/D=4$). It can be seen that complete relaxation requires approximately two or three minutes. This result agrees reasonably well with what one would expect from Bagley's observation of the "snap-back" effect in the entrance region. In addition to this, die swell measurements were obtained at several rates of shear. In all cases measurements were taken approximately three minutes after the polymer left the capillary. The results are shown in

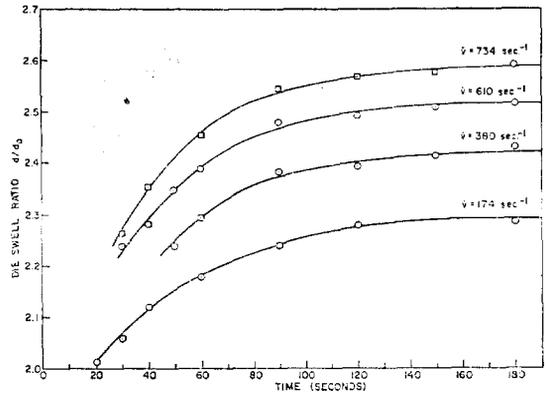


Fig. 8 Die swell versus time for high density polyethylene at 180°C

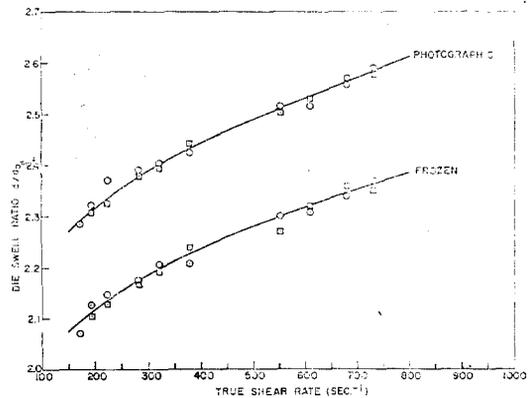


Fig. 9 Die swell versus shear rate for high density polyethylene at 180°C

Figure 9. On the same figure are the results obtained by using method (c) above. A density correction factor (ρ_0/ρ) of 0.67 was used for the freezing method. This value was supplied by the polymer manufacturer. It can be seen that measurements obtained from the frozen polymer were consistently lower than those obtained by the photographic technique. It is felt that this is due primarily to the crystallization consideration previously mentioned. There may be other factors operating during solidification, such as thermal stress generation, but there is not enough information available to make speculation worthwhile.

4.3 Experimental Determination of Exit Pressure

Representative axial pressure distributions for high density polyethylene at various shear rates are shown in Figure 10 for $L/D=4$. Details of the experimental technique of the pressure measurements have been given in a number of papers by Han et al. (13, 14, 15). It can be seen from this figure that insofar as the pressure gradient is concerned, the flow has become fully developed within one diameter of the entrance. This constant pressure gradient can be used directly to determine the shear stress at the wall without the need of employing the Bagley correction (1). The shear stress is given by Eq. (6).

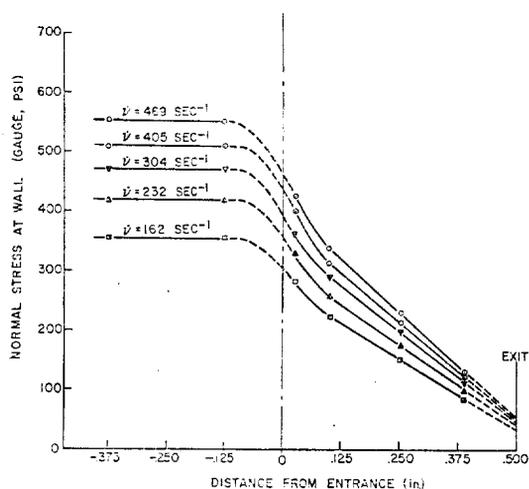


Fig. 10 Pressure profiles for high density polyethylene at 200°C ($L/D=4$)

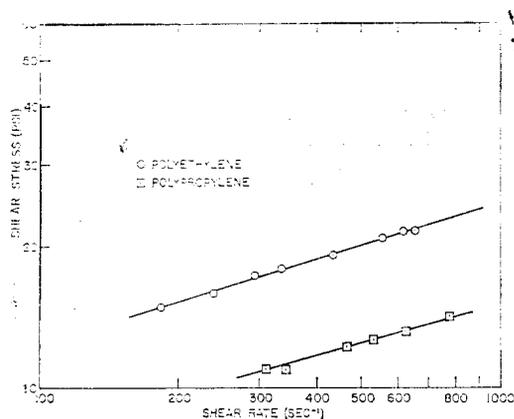


Fig. 11 Wall shear stress versus shear rate

Representative flow curves, plots of shear stress versus shear rate, are given in Figure 11. It is seen that, to a very good approximation, the flow curves can be represented by the power law expression, Eq. (19).

It is worth noting, also, in Figure 10 that an extrapolation of the straight line portion of pressure profiles to the exit of the die yields **non-zero** gauge pressure, called exit pressure^(13,14,15), which increases with shear rate.

As a viscoelastic fluid flows it deforms and in so doing it both dissipates energy by a viscous mechanism and stores energy by an elastic mechanism. Once a steady flow has been achieved, the fluid continues to dissipate energy by the viscous component but retains a fixed amount of elastic energy. The primary normal stress difference, which is a manifestation of this stored elastic energy, then remains constant and non-zero during the steady flow. If, as is assumed, the flow remains fully developed right up to the exit, then the primary normal stress difference at the exit will be non-zero. Since, as was shown in the introductory remarks, the exit pressure is directly related to the steady flow normal stress difference, it too will be non-zero. Furthermore, it is known that the primary normal stress difference in steady shear flow is an increasing function of shear rate. This implies that the exit pressure will also increase with shear

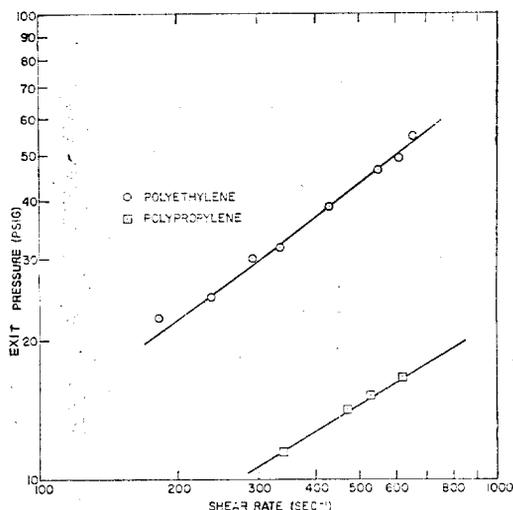


Fig. 12 Exit pressure versus shear rate ($L/D=4$)

rate. This has all been confirmed experimentally as shown in figure 12.

Use of Eq. (38) was made by Metzner and his coworker¹³⁾ with the die swell data on polymeric solutions, in which these authors assumed **zero** exit pressure without having made any actual measurements of the exit pressure. However, Sakiadis²¹⁾ measured the exit pressure with polymeric solutions and showed in fact **non-zero** exit pressure. In the light of Sakiadis' result for the measurement of exit pressure of polymeric solutions, the calculation of the primary normal stress difference from Eq. 38) with die swell measurement alone (i. e., setting $P_{Exit} = 0$) does not seem to be reasonable. Moreover, there is no justification for assuming zero exit pressure a priori without taking actual measurements. If the magnitude of the measured exit pressure term is very small, as compared to the die swell term, one can then neglect the exit pressure term with full justification.

On the other hand, in the flow of polymer melts, a calculation has been shown¹⁶⁾ that the die swell term is orders of magnitude smaller than the exit pressure term, so that Eq. 38) can be reduced to

$$(\tau_{zz} - \tau_{rr})_R \cong P_{Exit} \quad (40)$$

for practical purposes. This suggests that in polymer melt flow, the measurement of the pressure profile alone can give the flow curve as well as the normal stress difference which is indeed a remarkable result. Therefore the result of Figure 12 is essentially information on the behavior of the primary normal stress difference with change in shear rate. It is clearly shown that the primary normal stress difference is an increasing function of shear rate, as predicted from most constitutive equations.

One should note at this point that the theoretical expressions, either Eqs. 38) or 40), are based on the assumption that flow is fully developed at the exit of the tube. In other words, the existence of fully developed flow must be confirmed before any attempt is made to use the data obtained from the exit pressure and die swell to predict the normal stress effects.

The effect of entrance length on fully developed flow has been a controversial subject because different

authors have reported different values of entrance length in their studies. The criterion of "constant pressure gradient" has long been accepted as a necessary and sufficient condition for fully developed flow in Newtonian fluids. However, there is ample evidence in the literature that "constant pressure gradient"

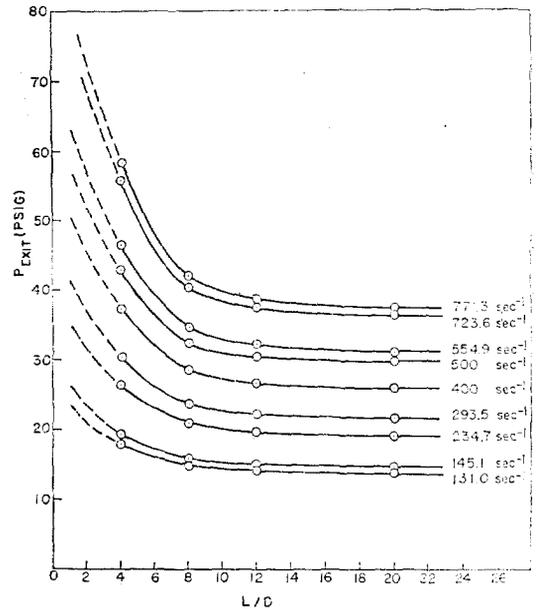


Fig. 13 Exit pressure versus L/D ratio for high density polyethylene at 180°C

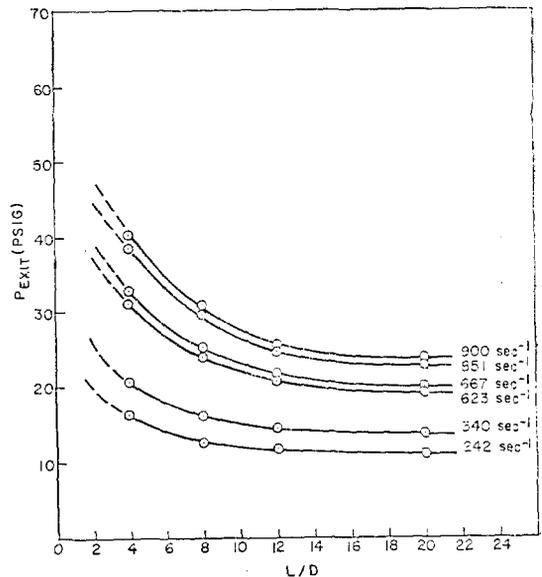


Fig. 14 Exit pressure versus L/D ratio for polypropylene at 180°C

is not a sufficient condition, through a necessary one, fully developed flow in viscoelastic fluids¹⁵). In the past, measurement of extrudate die swell has been used as a criterion for fully developed flow of viscoelastic fluids, suggesting the capillary length at which extrudate die swell no longer changes. Han and Charles⁹) have recently proposed a criterion for fully developed flow based on their measurements on the exit pressure as a function of the L/D ratio, together with the measurement of die swell versus L/D .

In Figures 13 and 14 are plotted exit pressure vs. L/D for high density polyethylene and polypropylene, respectively, with shear rate as a parameter¹⁵). The shear rate reported in the figure is true shear rate calculated by the Rabinowitch-Mooney equation. It can be seen also that exit pressure decreases rapidly with L/D at low values of L/D and then levels off at L/D about 16. This result is rather interesting.

It would be very interesting to measure die swell as a function of L/D , and then compare the dependency of exit pressure on L/D with that of die swell on L/D . Figure 15 shows the correlation of die swell with L/D , indicating that die swell levels off at L/D about 20¹⁵).

There are three things which deserve special attention in the results shown above. First, pressure gradient appears to become constant at L/D about 2, while both exit pressure and die swell are decreasing considerably at that value of L/D . Therefore it seems clear that constant pressure gradient is not a sufficient

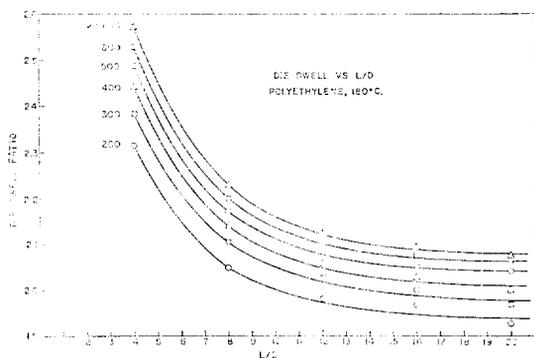


Fig. 15 Die swell ratio versus L/D ratio for high density polyethylene at 180°C

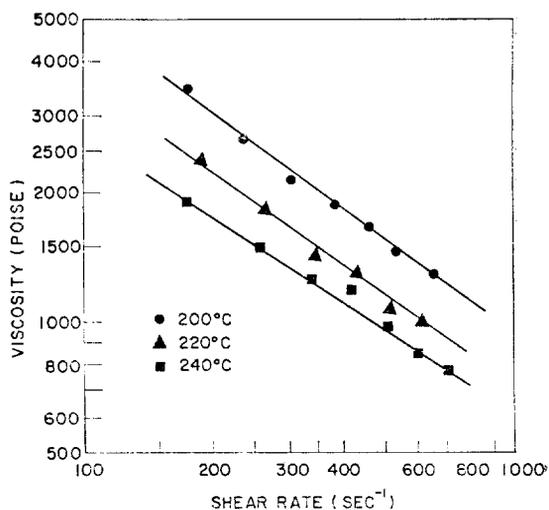


Fig. 16 Viscosity versus shear rate for polystyrene melts at three different temperatures

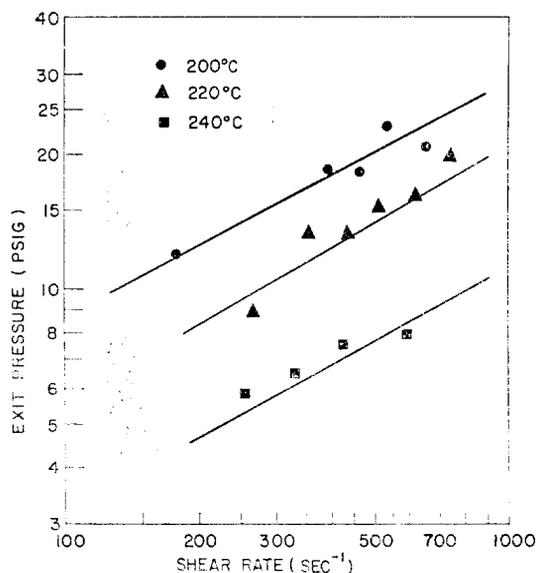


Fig. 17 Exit pressure versus shear rate for polystyrene melts at three different temperatures

criterion for fully developed flow. Secondly, the exit pressure vs. L/D curves seem to level off starting at slightly lower values of L/D than the die swell vs. L/D curves. Since both the exit pressure and die swell are believed to be manifestations of elastic behavior, it may be expected that in principle, both exit pressure and die swell should level off at the same value of L/D . However, one should also com-

pare the sensitivity of these separate measurements of exit pressure and die swell. In general, the die swell measurement is more sensitive than the exit pressure measurement. Considering experiments of this type, the results of Figures 13 and 14 can be considered remarkably good. Further more one kind of measurement checks the other kind of experiment in a consistent manner.

To demonstrate the accuracy in pressure measurement, the dependency of viscosity and exit pressure on temperatures is shown in Figures 16 and 17, respectively. It can be seen from these results that both melt viscosity and exit pressure (i.e. melt elasticity) are clearly related to the temperature, as might be expected.

At this point it would also be interesting to see if Newtonian fluids exhibit exit pressure. If exit pressure is indeed a manifestation of the elastic behavior of viscoelastic fluids, then Newtonian fluids should not exhibit it. To demonstrate it one should choose a Newtonian fluid which has a viscosity comparable in magnitude to that of polyethylene, for instance, under the same flow conditions. Han et al.¹⁵⁾ chose such a fluid, called Indopol H1900, which is a low molecular weight polybutene. Figure 18 shows the pressure profile for Indopol H1900. The result indicates no exit pressure for such a fluid.

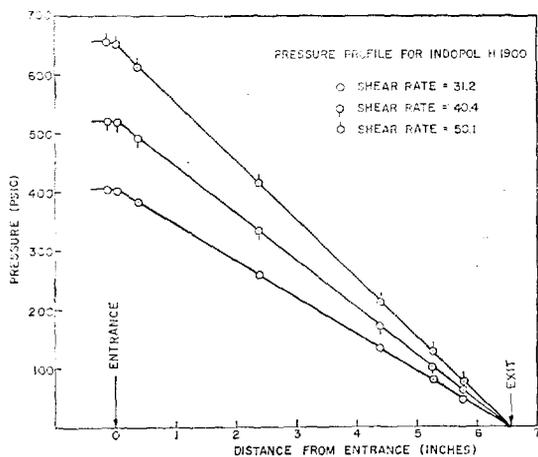


Fig. 18 Axial pressure profiles of a Newtonian fluid (Indopol H1900)

One can now conclude from these results that the existence of exit pressure is a clear manifestation of the normal stress effect of viscoelastic fluids, i.e., elastic effect.

5. Concluding Remarks

At present a practical method of measuring the elastic properties of polymer melts is needed, a method which could be readily adapted to various types of commercial equipment for polymer processing. In particular a method is needed that is not limited by shear rate. In past decades much effort has been devoted to developing experimental techniques of measuring the viscoelastic properties of polymeric materials. Basically there are two types of rheometer; a) the rotational type (cone-and-plate, parallel-plate and coaxial cylinder), and b) the capillary type. Until recently, these rheometers have been widely used for polymer solutions; they have often been used to test various constitutive models, but relatively little work with polymer melts has been reported in the literature. This is mainly because, in general, the experimental measurement of the elastic properties of polymer melts is rather difficult compared to that of solutions.

For polymer melts, use of the rotational rheometer is limited by low shear rates due to flow instability; for instance, with the Weissenberg rheogoniometer, it is a well-recognized fact that polymer melts start to extrude from the gap between the cone and the plate at shear rates, say even below 10 sec^{-1} .

Use of the capillary rheometer for polymer melts has been extensive because it is not limited by low shear rates. However, the validity of the method of analyzing the experimental data by means of the so-called "entrance effect correction" is subject to serious question, because some of the assumptions made for the method do not have a proved justification²⁾. Furthermore, the method of the "entrance effect correction" involves quite a bit of labor because one needs to make experimental runs with different capillary length-to radius ratios. Therefore, for practical purposes, this method is not too attractive.

The method of using exit pressure for determining the normal stress difference (i. e., melt elasticity) was discussed above, which is due to Han and his coworkers^(13,14,15). This method is believed to be one of the most practical and attractive tools. The basic idea lies in the recognition of the existence of exit pressure. Moreover, it has been clearly demonstrated that the measurement of wall normal stress profiles alone, as a function of flow rate, can give rise to complete information on both the viscous property (i. e. flow curves) and the elastic property (i. e. normal stress difference) of the polymer melts flowing through a circular tube.

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