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REVIEW

A Practical Method for Determining the Viscoelastic Properties of Polymer Melts at High Shear Rates

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Abstract

A practical method is presented for determining both the viscous and elastic properties of polymer melts over the range of shear rates which is of practical interest to various polymer operations. The method involves measurement of wall normal stress distribution along a die. The basic concept of die design (capillary/slit/annular die) is discussed, and a summary of the experimental results obtained during the past several years is presented for homopolymers, polymer blends, copolymers, and filled polymers of industrial use in various polymer operations. A new revised theory of Han is used to correctly predict the first and second normal stress difference from exit pressure measurements.

Introduction

There has been a continuing interest in developing experimental techniques for the measurement of the rheological properties of of polymeric materials, and rheologists have spent much effort on it. A better understanding of these rheological properties is very important for many reasons. For instance, it helps one to formulate the mixed polymer systems which would best provide a particular set of physical properties desired of the final product. This is because the rheological properties are intimately related to processing conditions, for example, to molding temperature and extrusion pressure. It also helps one to choose the right kind of processing equipment.

In the past, however, most have been concerned with dilute polymeric solutions, but comparatively few with polymeric melts. On the other hand, polymeric melts are much more important than polymeric solutions, from the point of view of polymer processing.

At present there are several different types of apparatus which may be used for determining the rheological properties of polymeric materials (1, 2, 3, 4). These are 1) the cone-and-plate instrument, the so-called Weissenberg rheogoniometer, 2) the two-concentric-cylinder instrument, 3) the parallel-plate instrument, 4) the capillary instrument, etc. As recently pointed out (5) use of the first three types of instrument for polymer melts is limited to low shear rates, say below 10 $\sec^{-1}$.

On the other hand, although it depends on the type of polymer processing, the range of shear rates which is of practical interest to the polymer processing industry runs much beyond 10 $\sec^{-1}$. It is then clear that only the capillary-type instrument fits the bill. As a matter of fact, this is the reason why the capillary instrument (e. g. the Instron capillary rheometer) has long been used for determining the rheological properties of polymer melts.

While the Instron capillary rheometer has been widely used in the polymer processing industry, there has been some theoretical argument against the method of analyzing its experimental data, in particular the procedure, due to Philippoff and Gaskins (6), for determining the elastic property.

Still, using a capillary-type instrument, several researchers (7, 8, 9, 10, 11) have recently suggested a new means of determining the viscous and elastic properties of polymeric melts. Han (11) has constructructed a slit-type instrument also and has demonstrated that the slit and capillary rheometers produce essentially the same information. Han (11) has noted further that the slit rheometer has certain advantages over the capillary rheometer in that flush-mounting of pressure transducers on the die wall is possible. This is quite important when running tests on the class of thermosetting polymers which form cross-linkages when they remain stagnant in some dead space. The pressure-tap holes which occur in the use of a capillary rheometer unavoidably provide such dead space.

More recently, Han (12) has constructed an annular-type instrument also and demonstrated its usefulness for determing the rheological properties of polymer melts, by applying the same concept as that applied to both the capillary and slit-type rheometers.

The purpose of this paper is first to describe the basic concept of die design for the construction of the Han slit/capillary/annular rheometer and then to present a summary of the experimental results obtained during the past five years, with several homopolymers, polymer blends, copolymers, and filled polymers of industrial use in various polymer operations.

The concept of the Han slit/capillary/annular rheometer

In polymer processing, there are two most important rheological properties. These are the viscosity and elasticity of a polymeric material.

It has long been known to the polymer processing industry that polymer melts exhibit some unusual flow behavior as they enter and exit a die. When polymer melt enters a tube from a large reservoir an excessively large pressure drop occurs at the entry to the die section, which cannot be explained by the viscosity of the melt alone. This excessively large pressure drop has been attributed to the elasticity of the melt (13, 14, 15).

At the exit region of a die, the extrudate swells, giving rise to a ratio of the extrudate diameter to tube diameter (die swell ratio) 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 swelling of extrudate has also been attributed to the elasticity of the melt, and several researchers (16, 17, 18) have attempted to correlate die swell ratio to other elastic properties, i. e. the first normal stress difference. It should be remembered however that the experimental method commonly used to obtain die swell ratio of polymer melts is very difficult, if not impossible, to apply to some polymeric materials, More importantly, the die swell measurement cannot supply information on melt viscosity.

In recent years, Han and his coworkers (9, 10, 19, 20) have made an extensive investigation of the measurement of wall pressure distribution along a circular tube, and demonstrated that such measurement can yield both the viscosity and elasticity of a melt: the viscosity from the slope of the pressure gradient, and the elasticity from an extrapolation of the straight line portion of pressure profiles to the exit of the die, yielding a non-zero gauge pressure, called the "exit pressure".

It should be noted that extrapolation assumes that, as she melt approaches the exit plane of the die, velocity rearrangement is negligible and therefore that extrapolating pressure readings to the exit of the die is valid. A test of this assumption by means of some direct experimental technique is very crucial. Recently, Han and Drexler (21) attempted to test the assumption experimentally by measuring stress-birefringent patterns of flowing melts at the exit region of a slit die, and they indeed found that the disturbance of stresses at the exit plane is negligibly small at least for polymer melts at reasonably high shear rates.

Using capillary dies, Arai (8), Mori (7), Han and his coworkers (9, 10, 19, 20, 22) obtained several important correlations between the exit pressure and other processing variables, such as shear rate, shear stress, and melt temperature. In their analysis, the following equations were used to calculate the shear rate $\dot{\gamma}$, shear stress τ_W

$$\dot{\gamma}=\left(\frac{3n+1}{4n}\right)\dot{\gamma}_W \tag{1}$$

$$\tau_W=\left(\frac{-\partial P}{\partial x}\right)\frac{R}{2} \tag{2}$$

Very recently, Han (22) has developed a revised theory which predicts the normal stress differences from exit pressure measurements:

$$\tau_{11}-\tau_{22}=P_{\text{Exit}}+\tau_W\frac{dP_{\text{Exit}}}{d\tau_W} \tag{3}$$

$$\tau_{22}-\tau_{33}=-\tau_W\frac{dP_{\text{Exit}}}{d\tau_W} \tag{4}$$

in which $\dot{\gamma}_W$ and n are defined by

$$\dot{\gamma}_W=\frac{4Q}{\pi R^3} \tag{5}$$

$$n=\frac{d\ln\tau_W}{d\ln\dot{\gamma}_W} \tag{6}$$

Q denotes the volumetric flow rate, R the capillary radius, $\left(\frac{-\partial P}{\partial x}\right)$ the pressure gradient, and P_{Exit} is the exit pressure.

The most significant result of all in the use of wall pressure measurement is found in eqs. (3) and (4), which state that measurement of exit pressure determines the normal stress differences, i. e. melt elasticity.

Another geometry, which is considered to be equally as simple as the capillary die, is the system of two parallel planes of infinite width. Since, in practice, plates of infinite width are not available, the geometry of a rectangular cross section having a large aspect ratio (the ratio of long side to short side) can be considered as a substitute. The flow can then be treated as one-dimensional instead of two-dimensional and hence, the analysis of flow data obtained from the geometry of a thin slit is very much simplified. It should be noted, however, that as the aspect ratio becomes small, the flow in a rectangular duct must be treated as two-dimensional, which makes the analysis much more complicated. The question then arises as to how large the aspect ratio can be for the flow to be considered one-dimensional. According to Han (11), an aspect ratio of about 10 and greater appears to be satisfactory.

For then thin slit die, the working equations for shear rate $\dot{\gamma}$, shear stress, τ_W, and normal stress difference $\tau_{11}-\tau_{22}$ are given by (11, 22):

$$\dot{\gamma}=\left(\frac{2n+1}{3n}\right)\dot{\gamma}_W \tag{7}$$

$$\tau_W=\left(\frac{-\partial P}{\partial x}\right)\frac{h}{2} \tag{8}$$

$$\tau_{11}-\tau_{22}=P_{\text{Exit}}+\tau_W\frac{dP_{\text{Exit}}}{d\tau_W} \tag{9}$$

where n is as defined in eq. (6) and $\dot{\gamma}_W$ is given by

$$\dot{\gamma}_W=\frac{6Q}{wh^2} \tag{10}$$

and w is the silt width, and h the thickness of the slit.

Still another geometry which is also equally as simple as the slit die for data analysis is the annular die with a very narrow gap between the two coaxial cylinders. This particular flow geometry has been widely used for blown film extrusion in recent years.

For the annular die, the working equations to be used are essentially the same as those for the slit die with the substitution:

$$h=R_2-R_1 \tag{11}$$

$$W=\pi(R_1+R_2) \tag{12}$$

where R_1 and R_2 are the radii of inner and outer cylinders, respectively. Note that in order to have eqs. (7)-(9) applicable to the annular die the ratio of w to h should be sufficiently large. Earlier, Wiley and Pierce (23) reported that $w/h \geq 48.5$ was satisfactory.

Figure 1 gives the schematic layouts of the three different flow geometries: the slit, capillary, and annular dies. Although one can have more than three transducers in one die, only three, the minimum recommended, are shown in the figure. Details of the die design are referred to in previeus papers of the author (9, 10, 11, 12).

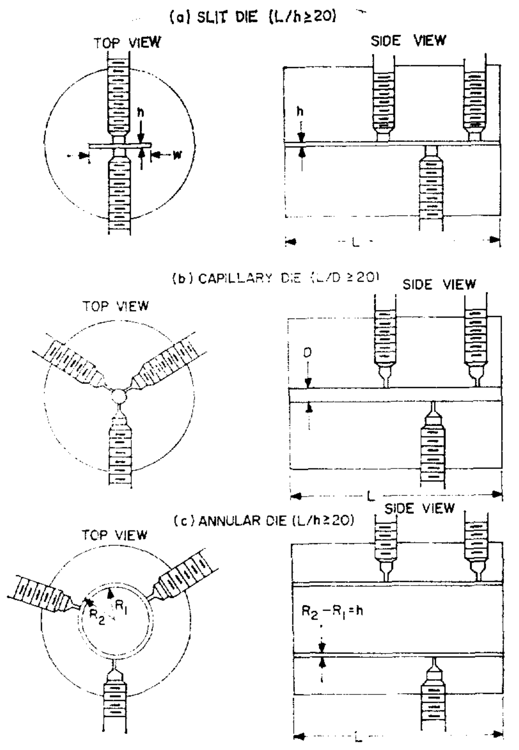

Fig. 1. Schematic of die design: (a) slit die; (b) capillary die; (c) annular die.

There is one important aspect which one has to be aware of in mounting pressure tranducers on the die wall. As schematically shown in *Figure* 1, both the capillary and annular dies cannot avoid having small "pressure-holes", which connect the die wall and the tip of the transducer. This is because, in general, transducers with curved tips are not available. On the other hand, the slit die permits flush-mounting of pressure transducers. Thus, for certain materials (i. e. thermosetting polymers), a slit die has an advantage over either a capillary or annular die, because the flush-mounted melt pressure transducers eliminate any dead space (Stagnant zone) between the tip of the transducer and the flow channel, and thereby prevent thermosetting polymers from residing there and forming crosslinkages.

It is worth mentioning, however, that when polymer melts and concentrated solutions are handled, the presence of pressure-holes has very little effect on the pressure measurement, as had recently been reported by Han (9, 24). The same is not true, in general, when one deals with dilute polymer solution (25).

Some Representative Results

Representative axial pressure distributions for polypropylene melts (180°C) at various shear rates are shown in *Figure* 2 for $L/D=4$. Two observations are worth noting in this figure. One is the curvature of the pressure profiles near the die inlet, indicating that the flow is still developing in this region. The other is the straight line portion of the pressure profiles, indicating that the flow has become fully developed. These observations have been supported by recent experimental studies, which made use of the flow birefringence technique (26, 27, 28).

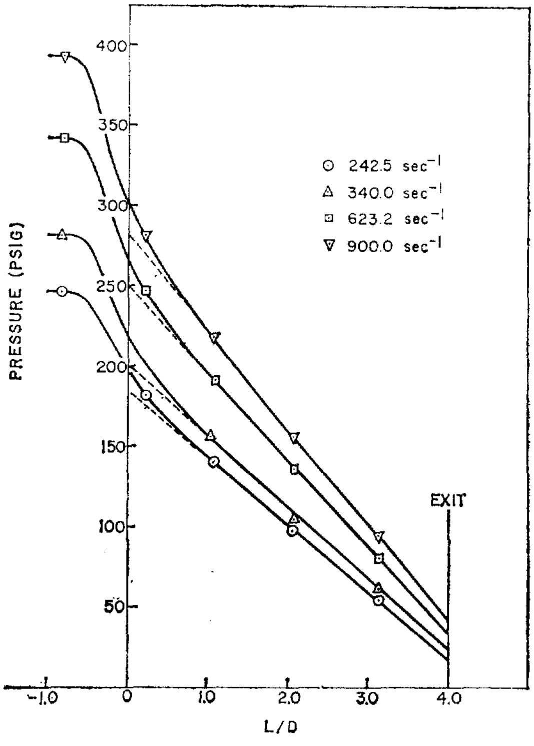

Fig. 2. Representative pressure profiles for high density polyethylene melts at 180°C.

To emphasize it once again, in order to make use of the theoretical concept described above for determining the rheological properties of melts, one has to make sure that wall pressure measurements are taken in the fully developed region, giving a constant pressure gradient.

During the past five years, the author has carried out extensive measurements of wall normal stresses of many polymeric materials, including copolymers and filled polymers. *Table* 1 gives a summary of the materials investigated, the type of die design, and the references where the results of measurement are reported.

In order to demonstrate the reliability of the measurements taken with the Han slit/capillary/annular rheometer described above, some representative results are given in *Figures* 3 and 4. *Figure* 3 shows plots of viscosity versus shear rate, and *Figure* 4 plots of first normal stress difference versus shear rate, for five polymers investigated at 200°C, over six decades of shear rates tested: at low shear rates (0.001~10 $\sec^{-1}$) with the Weissenberg rheogoniometer, at medium shear rates (10~100$\sec^{-1}$) with the Han slit rheometer, and at high shear rates (100~1000$\sec^{-1}$) with the Han capillary rheometer. Note that the capillary die had an L/D ratio of 20, and a reservoir-to-capillary diameter (D_R/D) ratio of 16, and that the slit die had an L/h ratio of 32.8. In preparing these plots from the Han slit/capillary rheometer data, the true shear rate was used, as given by eq.

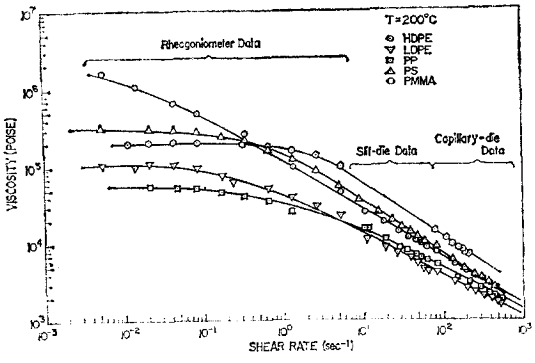

Fig. 3. Plots of shear viscosity versus shear rate for five homopolymers.

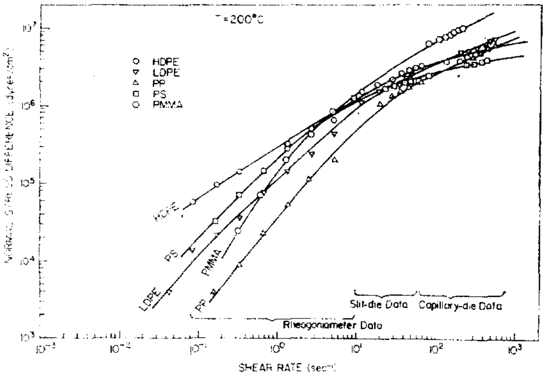

Fig. 4. Plots of the first normal stress difference versus shear rate for five homopolymers.

Table 1. A summary of the rheological measurements taken using the Han slit/capillary/annular rheometer

Materials Investigated	Types of die used	References
Homopolymer		
high density polyethylene	Capillary, Slit, and Annular	5, 9, 10, 11, 12
low density polyethylene	Capillary, Slit, and Annular	5, 10, 11, 12
polypropylene	Capillary, Slit, and Annular	5, 9, 10, 11, 12
polystyrene	Capillary, Slit, and Annular	5, 10, 11, 12, 20
Polymer Blends		
polystyrene/ polyethylene	Capillary, Slit, and Annular	12, 29, 30
polystyrene/ polypropylene	Capillary and Annular	12, 29, 31
polystyrene/ polymethyl methacrylate	Capillary	32
Copolymers		
ABS resin	Slit	33
high impact polystyrene	Slit	33
Filled Polymers		
polypropylene/ $CaCO_3$	Slit	34

More recently, using the slit rheometer, the author (34) carried out a study for determining the rheological properties of filled polymer system, yielding correlations similar to those for homopolymers and blend systems. (See *Table* 1.)

(1) for the capillary rheometer, and by eq. (7) for the the slit rheometer.

It is seen from *Figures* 3 and 4 that the three different apparatuses employed in this study give consistent results, yielding remarkably good correlations.

As mentioned above, the Weissenberg rheogoniometer is limited to low shear rates, say below 10 $\sec^{-1}$. However, the Han slit/capillary/annular rheometer has no such limitation. It should be noted that the range of shear rates in the use of the Han slit/capillary/annular rheometer can be varied, by either using extruders of different capacities or using different sizes of slit opening or capillary diameter, whichever is more convenient.

The Han slit/capillary/annular rheometer has also been used to determine the rheological properties of polymer blends of both compatible and incompatible systems (29, 30, 31, 32), and copolymers such as high-impact polystyrenes and ABS resins(33). (See *Table* 1.)

Versatility of Die Design

The basic concept of the die design, as given schematically in *Figure* 1, can be extended to the design of multiple flow channels. More specifically stated, one can have a number of capillaries (or slits or annular dies) in either serial or parallel arrangement, each having different capillary diameters (or slot openings), as shown schematically in *Figure* 5.

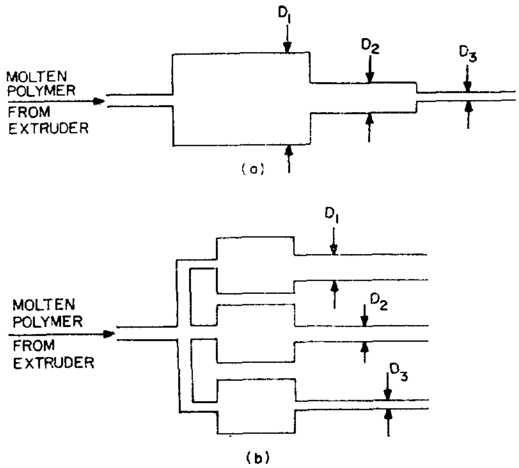

Fig. 5. A schematic of multiple channel dies: (a) serial arrangement; (b) parallel arrangement.

The main advantage of having a multiple channel die lies in that, with a single experiment, one can determine the rheological properties of a given material at as many shear rates as different capillaries (or slits). However, a few things should be kept in mind in the design of a muitiple channel die. When dies are arranged in series (see *Figures* 5*a*) the overall pressure drops will increase, which in turn increases the chances of leakage. On the other hand, when dies are in parallel arrangement (see *Figure* 5*b*), one needs a large extruder in order to reach as high shear rates as those for a single channel die.

From a practical standpoint, when a large extruder is available, the parallel arrangement is more attractive than the serial arrangement. This is because, with the parallel arrangement, one can obtain both the viscous and elastic properties from each flow channel, whereas, with the serial arrangement, one can obtain the elastic property (i. e. exit pressure) from the last flow channel only.

Concluding Remarks

At present a practical method of measuring the viscous and elastic properties of polymer melts is needed, a method which can 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.

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 even below 10$\sec^{-1}$ (35, 36).

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 justification. 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-diameter (L/D) ratios. Therefore, for practical purposes, this method is not too attractive (37).

The method of using exit pressure for determining the normal stress differences (i. e., melt elasticity) was discussed above. 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 fuction 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 differences) of the polymer melts. It should be emphasized, once again, that the method suggested in this paper does not require any end correction.

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