

A Comparison of Measurements of the Viscoelastic Properties of Polymer Melts by Means of the Han Slit/Capillary Rheometer and the Weissenberg Rheogoniometer

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Synopsis

Measurements were taken of the viscoelastic properties of six polymer melts by means of the Weissenberg rheogoniometer and the Han slit/capillary rheometer. Polymers investigated were three high-density polyethylenes of different polydispersity, a low-density polyethylene, a polypropylene, and a polystyrene. The range of shear rates tested was from about 5.0×10^{-3} to 10 sec^{-1} with the Weissenberg rheogoniometer, from about 10 to 10^2 sec^{-1} with the slit rheometer, and from about 10^2 and 10^3 with the capillary rheometer: the temperature of measurement was 200°C . The three different apparatuses give consistent results over almost six decades of shear rates, yielding satisfactory correlations of shear viscosity to shear rate and of normal stress difference to shear rate.

INTRODUCTION

Many polymeric materials of industrial importance, for instance, polymeric melts, can be classified as viscoelastic liquids in the sense that they flow under the action of applied pressure and yet have some of the properties usually associated with rubber-like solids. Therefore, a better understanding of the viscoelastic properties of polymer melts 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, because the viscoelastic properties are intimately related to processing conditions, for example, to molding temperature or extrusion temperature. It also helps one to choose the right kind of processing equipment.

There has been a continuing interest and effort spent by rheologists on developing experimental techniques for measurement of the rheological properties of viscoelastic fluids. Much has been concerned with dilute polymeric solutions, but comparatively little 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 viscoelastic fluids. 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. Until very recently, the first three types of instrument listed above, characterized as rotational-type rheometers, had been used mainly for polymeric solutions. In recent years, some efforts have been spent on modifying the rotational-type instrument for its use in polymeric melts. Consequently, several researchers¹⁻⁴ have recently reported measurements of the viscoelastic properties of polymeric melts, namely, flow curves and normal stresses, using the rotational-type instrument (e.g., Weissenberg rheogoniometer). However, use of the rotational-type instrument for polymeric melts is limited to low shear rates. In the case of the Weissenberg rheogoniometer, for example, the range is below 10 sec.⁻¹ The exact upper limit of operable shear rates may vary slightly from material to material, because at a certain value of shear rate the polymeric melt in a rotational instrument starts to exhibit flow instability, commonly referred to as "secondary flow," or "radial flow."

In view of the practical limitation of the rotational-type instrument, a capillary-type instrument appears to be most attractive to polymeric melts because it is not limited to low shear rates. For this reason, the industry has long used a capillary-type instrument in conjunction with an Instron, the so-called Instron capillary rheometer. However, there has been some theoretical argument against the method of Philippoff and Gaskins⁵ of determining the elastic properties.

Nevertheless, Han and his co-workers⁶⁻⁹ have recently suggested a new means of determining the viscous and elastic properties of polymeric melts still using a capillary-type instrument. More recently, Han¹⁰ has also constructed a slit-type instrument and demonstrated that the slit and capillary rheometers produce essentially the same information. Han¹⁰ 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 crosslinkages 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.

The essence of Han's idea lies in the measurement of wall normal stresses along the axis of longitudinal direction (i.e. flow direction) when using either a capillary or slit geometry. Such measurements then permit one to obtain the viscous property from the slope of the axial normal stress distribution (i.e., the pressure gradient) and the elastic property from the exit pressure, which is the extrapolated value of wall normal stress to the exit of the die from pressure readings within the die. The concept of exit pressure is of particular significance because, according to Han,^{6,7} the exit pressure P_{exit}

is equal to the normal stress difference $\tau_{11} - \tau_{22}$ in polymer melt flow, that is,

$$\tau_{11} - \tau_{22} = P_{\text{exit}}. \quad (1)$$

It should be remembered that the normal stress difference $\tau_{11} - \tau_{22}$ is the quantity one gets from the rotational-type instrument as a measure of the elastic property of the material under investigation. Hereafter, the slit and capillary instruments devised by Han will be referred to as the "Han slit/capillary rheometer." We call it "rheometer" instead of "viscometer" because the experimental data obtained from this instrument supply information of both the viscous and elastic properties, on the basis of a rigorous theoretical development.^{6,11}

At this point, some of the earlier developments in the use of the capillary instrument are worth mentioning, particularly in connection with exit pressure measurements. Sakiadis¹² was the first to measure exit pressures of a 10% aqueous solution of poly(vinyl alcohol) flowing through a capillary and attempted to relate the measurements to the elastic properties of the fluid. Later, White¹³ raised a number of questions in regard to the accuracy and interpretations of the experimental data by Sakiadis. The first reported measurements of the exit pressure of polymer melts were those of Arai¹⁴ and Mori and Funatsu.¹⁵ As pointed out by Han et al.,⁶ Mori and Funatsu¹⁵ made an inconsistent assumption in their attempt to relate exit pressure to normal stress difference, resulting with an erroneous expression.

However, Han et al.^{6,11} were the first to suggest the use of eq. (1) for polymer melts in capillary flow. Moreover, Han¹⁰ demonstrated that eq. (1) is still valid even when a slit geometry is used instead of a capillary. Therefore, what makes the use of either a capillary or slit geometry notable for the determination of the rheological properties of polymer melts is the possibility of using eq. (1).

The primary objective of the present paper is to make a comparison of rheological measurements obtained by means of the Han slit/capillary rheometer and the Weissenberg rheogoniometer. The Weissenberg rheogoniometer was chosen because so far this is one of the few instruments which is believed to give reliable rheological data. In order to accomplish these objectives, two laboratories collaborated: One laboratory carried out measurements of wall normal stresses using the Han slit/capillary rheometer, and the other laboratory undertook measurements using the Weissenberg rheogoniometer.

EXPERIMENT

Apparatus and Experimental Procedure

For the measurement of wall normal stresses along the die axis, both slit and capillary (circular) rheometers were used. In order to avoid any noticeable influence of entrance effects, a capillary die having an L/D ratio of 20 was chosen, and the reservoir-to-capillary diameter ratio, D_R/D ,

used was 16, the capillary diameter being 0.125 in. According to a recent study by Han and Kim,⁸ a choice of $D_R/D = 16$ appears to be large enough not to have a reservoir effect. Details of the die design and experimental procedure are given in an earlier paper by Han et al.⁷

The slit die used has an aspect ratio of 10, which was referred to as die no. 1 in a previous paper by Han.¹⁰ The reservoir diameter D_R used in the present study was 2.0 in., as opposed to 1.5 in. in the previous work.¹⁰ Details of the die design and experimental procedure are also given there.¹⁰

The range of shear rates tested was: from about 10 to about 10^2 sec^{-1} in the slit die, and from about 10^2 to about 10^3 in the capillary die. The temperature of measurement was 200°C in both slit and capillary die experiments. The expressions used to calculate the shear rate $\dot{\gamma}$, shear stress τ_{12} , and normal stress difference $\tau_{11} - \tau_{22}$ are as follows:

For the capillary rheometer:

$$\dot{\gamma} = \left(\frac{3n + 1}{4n} \right) \dot{\gamma}_w \quad (2)$$

where $\dot{\gamma}_w$ and n are defined by

$$\dot{\gamma}_w = \frac{32Q}{\pi D^3} \quad (3)$$

$$n = \frac{d \ln \tau_{12}}{d \ln \dot{\gamma}_w} \quad (4)$$

$$\tau_{12} = \left(-\frac{\partial p}{\partial x} \right) \frac{D}{4} \quad (5)$$

$$\tau_{11} - \tau_{22} = P_{\text{exit}}. \quad (1)$$

For the slit rheometer:

$$\dot{\gamma} = \left(\frac{2n + 1}{3n} \right) \dot{\gamma}_w \quad (6)$$

where n is as defined in eq. (4) and $\dot{\gamma}_w$ is given by

$$\dot{\gamma}_w = \frac{6Q}{wh^2} \quad (7)$$

$$\tau_{12} = \left(-\frac{\partial p}{\partial x} \right) \frac{h}{2} \quad (8)$$

$$\tau_{11} - \tau_{22} = P_{\text{exit}}. \quad (1)$$

In eqs. (2) through (8), Q denotes the volumetric flow rate; $-\partial p/\partial x$ denotes the pressure gradient; D is the capillary diameter; w is the slit width, and h is the thickness of the slit.

A commercial cone-and-plate apparatus, the Weissenberg rheogoniometer (Model R18), was used to measure the torque T and total thrust F as a

function of angular velocity Ω . A cone with an angle θ of 4.0042° and a plate with a diameter D of 2.5 cm were used. From the measurement one obtains the shear rate $\dot{\gamma}$, shear stress τ_{12} , and normal stress difference $\tau_{11} - \tau_{22}$ from the well-known expressions

$$\dot{\gamma} = \Omega/\theta \quad (9)$$

$$\tau_{12} = \frac{2AT}{2\pi D^3} \quad (10)$$

$$\tau_{11} - \tau_{22} = \frac{8F}{\pi D^2} \quad (11)$$

The range of shear rates tested was from about 5.0×10^{-3} to about 10 sec^{-1} , and the temperature of measurement was 200°C .

The operating procedure of this instrument is given in the *Operating Manual* prepared by Sangamo Controls, Inc.¹⁶

Material

Materials investigated were three high-density polyethylenes having widely different molecular weight distributions, a low-density polyethylene containing much long-chain branching, a polystyrene, and a polypropylene. Table I gives the molecular characteristics of the polymers investigated.

In the past, these materials were used by Han and his co-workers⁶⁻¹⁰ on several occasions. However, this is the first time that all these materials were tested under the identical die arrangements (e.g., $L/D = 20$, $D_R/D = 16$) and that the same materials were investigated using the Weissenberg rheogoniometer for comparison purposes.

RESULTS AND DISCUSSION

Figure 1 shows plots of viscosity versus shear rate, and Figure 2 shows plots of normal stress difference versus shear rate for the six 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. In preparing these plots from the Han slit/capillary rheometer data, the true shear rate was used, which is given by eq. (2) for the capillary rheometer, and by eq. (6) for the slit rheometer. It should be noted that, in Figure 2, according to eq. (1), exit pressures are directly plotted against shear rate from the Han slit/capillary rheometer data. Readers who are not familiar with the ways of preparing the plots given in Figures 1 and 2 using the Han slit/capillary rheometer data should consult several previous papers by Han.^{6,7,10,11}

It is seen from Figures 1 and 2 that the three different apparatuses employed in this study give consistent results, yielding remarkably good correlations.

TABLE I
Molecular Characteristics of the Polymers Investigated

Sample code	Polymer	Manufacturer	Melt index	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
DMDJ 4309	high-density polyethylene	Union Carbide Corp.	0.2	2.0×10^3	1.68×10^6	84
DGNB 3825	high-density polyethylene	Union Carbide Corp.	0.2	1.4×10^4	2.20×10^6	16
DMDJ 5140	high-density polyethylene	Union Carbide Corp.	0.8	2.0×10^4	1.66×10^6	8
PEP 211	low-density polyethylene	Union Carbide Corp.	3.5	2.0×10^4	4.00×10^6	20
Styron 686	polystyrene	Dow Chemical Co.	2.5	1.02×10^6	2.89×10^6	2.83
E-115	polypropylene	Enjay Chemical Co.	5.0	4.28×10^4	4.44×10^6	10.38

As mentioned above, the Weissenberg rheogoniometer is limited to low shear rates, say, below 10 sec^{-1} . However, the Han slit/capillary rheometer has no such limitation. It should be noted that the range of shear rates in the use of the Han slit/capillary rheometer can be made much lower

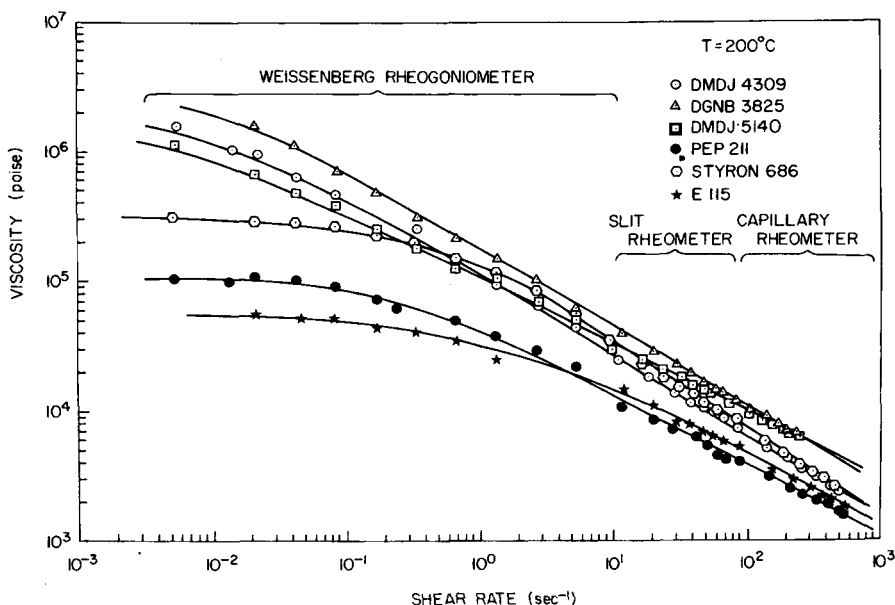


Fig. 1. Plots of shear viscosity versus shear rate for six polymers investigated ($T = 200^\circ\text{C}$).

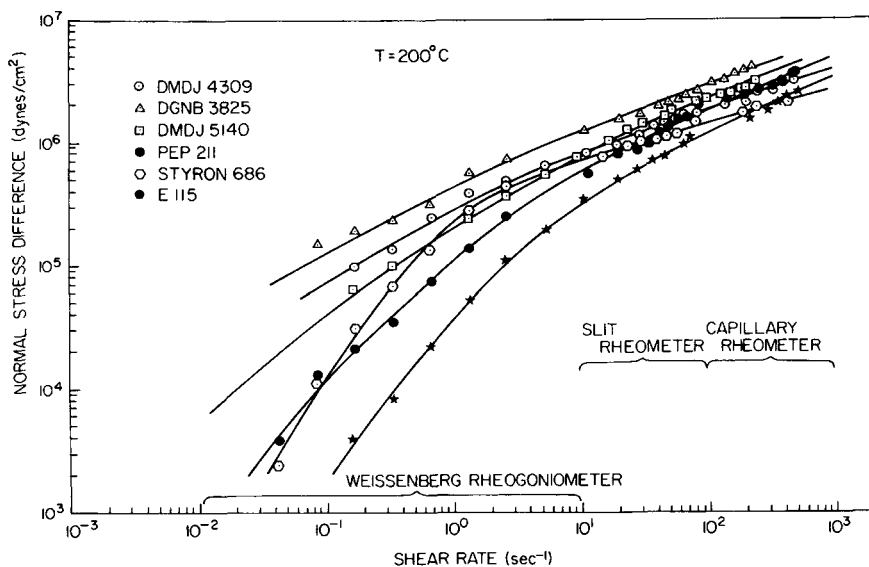


Fig. 2. Plots of normal stress difference versus shear rates for six polymers investigated ($T = 200^\circ\text{C}$).

than that investigated in this study, by either using a melt pump of small capacity or making the slit opening and capillary diameter large enough, whichever is more convenient.

It should be noted that, in using eq. (1), an assumption was made implicitly that, as the 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. In the past, there was some theoretical argument against this assumption. A test of this assumption by means of some direct experimental technique is very crucial to accepting Han's concept of "exit pressure," although the results given in Figure 2 indirectly support the assumption.

Very recently, Han and Drexler¹⁷ have had an opportunity to directly test this assumption. These authors used both flow birefringence technique and streak photography to study a possible "exit effect" in the flow of polymer melts through a transparent slit die. The flow birefringence technique was used to measure stress-birefringent patterns of flowing polymer melts at the exit region, and the technique of streak photography was used to measure the movement of tracer particles suspended in the flowing polymer melts at the exit region. Han and Drexler¹⁷ have *not* observed any noticeable exit effect in their experiment. Therefore, it can be concluded that the extrapolation of pressure readings to the exit of the die is valid, and that values of exit pressure thus obtained should represent the elastic behavior of polymer melts in fully developed Poiseuille flow.

Lastly, it seems worth mentioning that there has been some effort spent on determining normal stress difference from die swell measurements.¹⁸⁻²⁰ Whereas the measurement of die swell provides useful information, it is not always easy to obtain accurate die swell data. Moreover, die swell measurements do not provide the viscous properties of a melt, whereas the measurement of wall normal stresses along the die axis either in a slit or capillary geometry provides both the viscous and elastic properties with considerable accuracy, as has been demonstrated in Figures 1 and 2 of this paper.

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