

Squeeze Film Rheology of Polymer Melts: Determination of the Characteristic Flow Curve

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SYNOPSIS

The advantage of the constant-speed squeeze film flow is that the shear rate is not constant but changes with gap height and position. This allows the rheological characterization of a material to be carried out in a shorter amount of experimentation time. A method for determining the characteristic flow curve is proposed. The characteristic flow curves obtained from squeeze film flow is compared with the curves obtained from capillary rheometry are presented. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Squeeze film flow had been analyzed by Stefan¹ in 1874 for Newtonian fluids. Scott² extended this analysis for power law fluids in 1931. Various studies have used squeeze film flow geometry to test constitutive equations.³⁻⁷ Bird and Leider⁸ proposed a method for obtaining the power law constants from a constant load squeeze film flow experiment. This method requires considerable experimentation time. Grimm⁹ later applied Bird and Leider's method and cautioned that the power-law constants can be determined for certain materials and do not work in general cases even at the low squeezing rates.

In this study, constant speed squeeze film flow is analyzed. The advantage of constant speed squeeze film flow is that the shear rate is not constant but changes with gap height and position. This allows the rheological characterization of a material to be carried out in a shorter amount of experimentation time. Furthermore, squeeze film flow closely simulates the flow during various fabrication processes.

In terms of data reduction, with current computational capabilities, it is easy to do a nonlinear regression of the Scott's equation to obtain n and m values. This was also performed and found that it is difficult to determine the shear viscosity when

regressing the whole loading curve data set. This is because only a portion of the loading curve can be described by Scott's equation as the mechanism of flow changes. The loading curve of a constant plate velocity squeeze film flow experiment can be divided into three flow regimes: (1) the initial stage is compression, (2) biaxial extensional flow and shear flow, and (3) shear flow-dominated regime.

In this article, the shear flow regime of the squeeze film flow loading curve is investigated. An alternate method for determining the characteristic flow curve is proposed. Experimental data has been obtained for a natural rubber compound (SMR5), an ethylene propylene rubber (EPDM) and styrene-butadiene-styrene block copolymer (Kraton). These data have then been compared with those obtained from conventional capillary rheometry.

THEORY

A polymer melt sample of cylindrical shape with radius R and thickness $2h_0$ is placed between two horizontal flat plates of the same radius. At times $t \leq 0$, the melt is at rest. At $t = 0$ the plates start to move toward each other at a constant speed \dot{h} . The plate moves a distant Δh (to a specified compression strain, ϵ_c) and then stops. Assuming that a perfect "stick" boundary condition applies between the melt and the plate surfaces and that the quasi-steady-state assumption¹⁰ is valid, the compression force,

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$F(t)$, for a Newtonian fluid is given by the Stefan eq. (1) as

$$F(t) = \frac{3(-\dot{h})\pi\mu R^4}{8h(t)^3} \quad (1)$$

where \dot{h} is the plate velocity, μ the Newtonian viscosity of the melt, and $h(t)$ the half gap height at any time t . For a power law fluid with constants n (power law flow index) and m (power law consistency index), eq. (1) takes the form of eq. (2).

$$F(t) = \frac{(-\dot{h})}{h(t)^{2n+1}} \left(\frac{2n+1}{2n} \right)^n \frac{m\pi R^{n+3}}{(n+3)} \quad (2)$$

The assumptions made for the derivations of these equations are as follows: the fluid is incompressible, the process is isothermal, flow is symmetric, inertial effects are negligible, and the material exuded from between the plates does not contribute to the normal force, $F(t)$. Since the force $F(t)$ is the sum of all local forces at the solid–melt interfaces, then the melt can be assumed to experience an average shear rate with respect to the radial positions. This average shear rate can be found by using the mean value theorem. For a Newtonian fluid the average shear rate at the wall, also called the *apparent shear rate*, $\dot{\gamma}_a$, is given by

$$\dot{\gamma}_a = \frac{\int_0^{2\pi} \int_0^R \dot{\gamma}_{rz|z=h} r dr d\theta}{\int_0^{2\pi} \int_0^R r dr d\theta} = \frac{(-\dot{h})R}{h(t)^2} \quad (3)$$

For a power law fluid this equation becomes the following:

$$\langle \dot{\gamma}_w \rangle = \frac{\int_0^{2\pi} \int_0^R \dot{\gamma}_{rz|z=h} r dr d\theta}{\int_0^{2\pi} \int_0^R r dr d\theta} = \frac{2}{3} \frac{(-\dot{h})R}{h(t)^2} \left(\frac{2n+1}{2n} \right) \quad (4)$$

with

$$\langle \dot{\gamma}_w \rangle = \frac{2}{3} \left(\frac{2n+1}{2n} \right) \dot{\gamma}_a \quad (5)$$

Furthermore, it is assumed that at any time, steady flow prevails and that the force $F(t)$ can thus be described by eq. (2), the Scott equation. This, however, does not restrict the Scott equation to describe

the force–deflection curve of the squeeze film flow experiment. From this, the compression or squeezing (normal) stress, $\sigma(t)$, defined as the force per unit contacting surface area can be expressed as follows:

$$\sigma(t) = \frac{F(t)}{\pi R^2} = \frac{(-\dot{h})}{h(t)^{2n+1}} \left(\frac{2n+1}{2n} \right)^n \frac{mR^{n+1}}{(n+3)} \quad (6)$$

The shear stress at the wall, obtained from the Scott equation is as follows:

$$\tau_w = -(-mR^n) \frac{(-\dot{h})^n}{h^{2n}} \left(\frac{2n+1}{2n} \right)^n \quad (7)$$

As for the shear rate, the melt is assumed to experience an average shear stress at the wall, $\langle \tau_w \rangle$:

$$\begin{aligned} \langle \tau_w \rangle &= \frac{\int_0^{2\pi} \int_0^R \tau_w r dr d\theta}{\int_0^{2\pi} \int_0^R r dr d\theta} \\ &= \frac{(-\dot{h})^n}{h^{2n}} \left(\frac{2n+1}{2n} \right)^n \frac{2m}{n+3} R^n \end{aligned} \quad (8)$$

Comparing eqs. (6) and (8) yields

$$\langle \tau_w \rangle = \frac{(n+3)}{(n+2)} \frac{2h(t)}{R} \sigma(t) \quad (9)$$

for $R \neq 0$, and $n \neq (-2)$.

If a horizontal stress, σ_h , is defined as

$$\sigma_h = \frac{2h(t)}{R} \sigma(t) \quad (10)$$

then,

$$\langle \tau_w \rangle = \frac{(n+3)}{(n+2)} \sigma_h(t) \quad (11)$$

The horizontal stress versus the apparent shear rate in a doubly logarithmic plot will thus yield for a power law fluid a straight line of slope, n , the power law flow index. This procedure is the same as plotting the average shear stress at the wall versus the apparent shear rate using a double logarithmic scale, except that the y -axis is linearly transformed. This is true if the melt behaves like a power law fluid.

Once n has been determined, the actual characteristic flow curve can then be found readily using

eqs. (6) and (11). The apparent viscosity is given by

$$\eta_a = \frac{\langle \tau_w \rangle}{\dot{\gamma}_a} \quad (12)$$

and the average viscosity at the wall is

$$\eta = \frac{\langle \tau_w \rangle}{\langle \dot{\gamma}_w \rangle} = \frac{\eta_a}{\left(\frac{2}{3}\right)\left(\frac{2n+1}{2n}\right)} \quad (13)$$

EXPERIMENTAL

Materials

Three materials were used in this study:

1. Standard Malaysian rubber compounds (SMR5).
 - (a) SMR5-CV60 (constant Mooney viscosity of 60) is denoted as NRA1. (b) SMR5-CV102 (constant Mooney viscosity of 102) is denoted as NRA2, NRB, NRC, NRF, NRG.
2. Ethylene-propylene rubber with some diene monomers added (EPDM 2504) -Vistalon 2504TM (Exxon Chemical Co.). Various amounts of N550 carbon black (Ashland Chemical) and Flexol 815TM (Shell Chemical Co.) processing oil were added to obtain samples with different amounts of carbon black loading.
3. Styrene Butadiene Styrene copolymer-Kraton 3204.TM

Experimental Procedure

The squeeze film flow setup was constructed by retrofitting a servo-hydraulic multi-tester made by CGS Scientific Corporation model 901. A cylindrical sample was placed between the two flat parallel plates. Thin square mylar sheets were used to prevent the polymer melt from contaminating the plates. The sample was heated by two band heaters. Each band heater is controlled by an Omega RTD temperature controller. The time required to reach thermal equilibrium was determined from a calibration plot of sample thickness and the heating time for each material. When the desired temperature equilibrated, the lower plate was activated to approach the upper plate at a set constant speed. After traveling a set distance, the squeezing motion was stopped. The force required to maintain this con-

stant speed was monitored via a 44.5-kN load cell made by Interface Inc., model 1210-AF. The load cell output was then recorded onto a floppy disk via an analog/digital converter board (Metrabyte Dash-16 and wave form scroller board WFS-200) installed in an 80286-based personal computer (Epson Equity III). The stroke output was also recorded to determine the actual distance traveled. The speed was calculated by the time required to move the given distance.

RESULTS AND DISCUSSION

A typical double logarithmic plot of the horizontal stress, σ_h , as a function of apparent shear rate as shown in Figure 1. The polymer does not behave like a power law fluid at short squeezing times. This can be explained by considering the mechanism of the squeeze film flow experiment. The melt is at static equilibrium before it is squeezed. When the plate starts to move, the initial mode of deformation will be compression, similar to the compression of a bonded rubber block. At intermediate times, the melt will then start to undergo shear deformation at the solid-fluid interfaces and biaxial extension at the center. Only at long squeezing times, when the radius to thickness ratio (R/h) is large,¹¹ does the melt undergo predominantly shear flow with negligible biaxial extensional flow. Only at this time does the melt flow like a power law fluid subjected to a

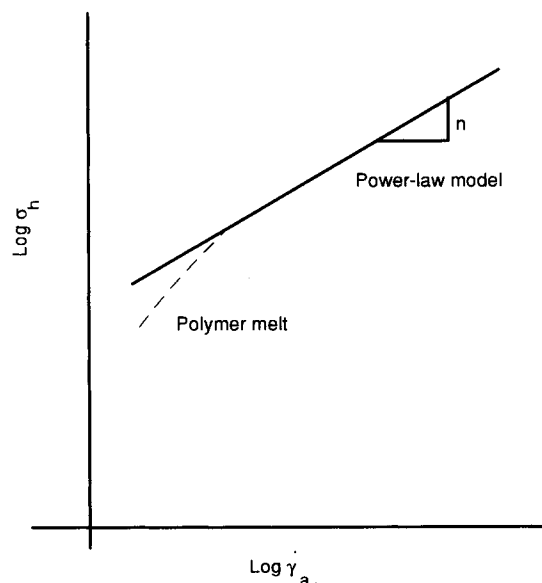


Figure 1 Representation plot of the horizontal stress as a function of apparent shear rate for a power law fluid and a polymer melt.

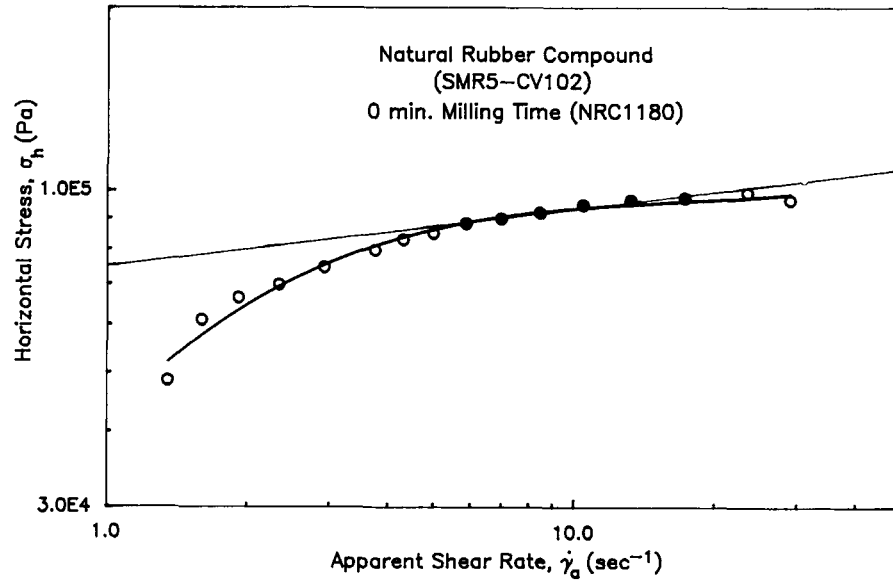


Figure 2 Doubly logarithmic plot of the horizontal stress as a function of apparent shear rate for natural rubber compound.

shear flow field. Therefore, only this region, the linear region, represents the flow of a power law fluid, as illustrated in Figure 2 for natural rubber compound SMR5-CV102.

The power law index, n , can be found from the slope and the characteristic flow curve in the linear region for a given melt behaving like a power law

fluid. Figure 3 shows the measured average shear stress at the wall as a function of the apparent shear rate for natural rubber compound, SMR5-CV102 tested at 125°C, 80% compression strain and a speed of 5 cm/min. Figure 4 shows these data replotted as apparent viscosity as a function of apparent shear rate.

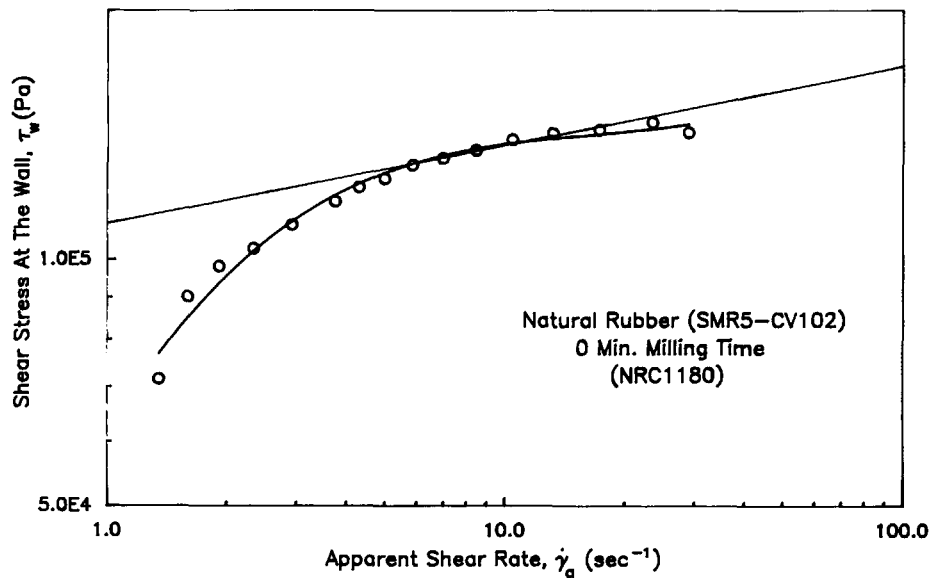


Figure 3 Doubly logarithmic plot of shear stress as a function of apparent shear rate for natural rubber compound. Data obtained from the squeeze film flow experiment.

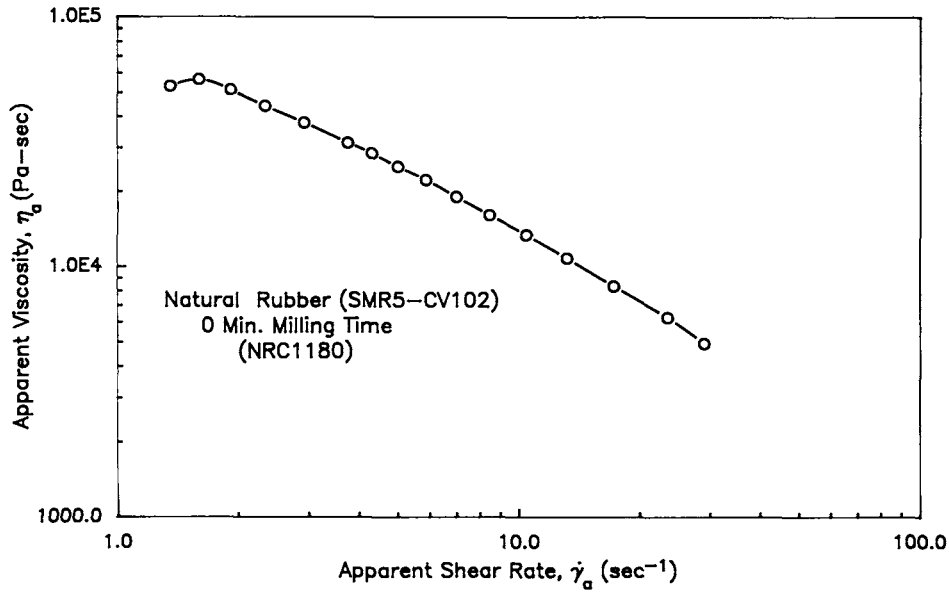


Figure 4 Doubly logarithmic plot of the apparent viscosity as a function of apparent shear rate for natural rubber compound.

However, the linear region as proposed is difficult to determine. In order to determine this region, three samples must be tested at various squeezing speeds. From these three squeezing speed conditions the horizontal stress as a function of apparent shear rate would be expected to fall on a curve or a line (Newtonian and power-law models). This is valid only for continuous media exhibiting continuous prop-

erties. The data points that coincide with this line define the linear region as illustrated in Figure 5 for Kraton 3204. The dashed line is the connecting line about which the linear region falls. Applying this method, the shear viscosity at the wall as a function of the average shear rate at the wall on a doubly logarithmic scale is shown in Figure 6. In this figure, the solid line represent the true viscosity as a func-

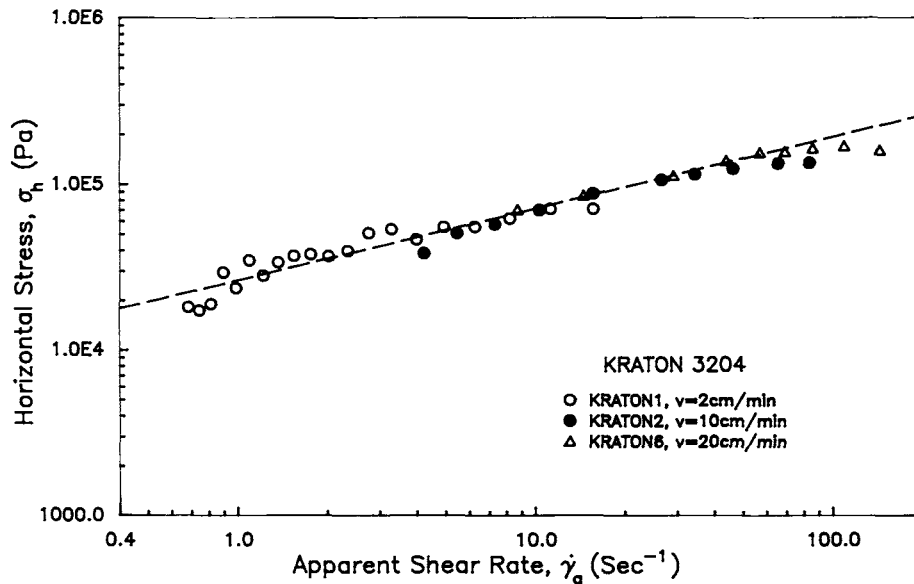


Figure 5 Doubly logarithmic plot of the horizontal stress as a function of apparent shear rate for Kraton 3204 tested at various squeezing speeds.

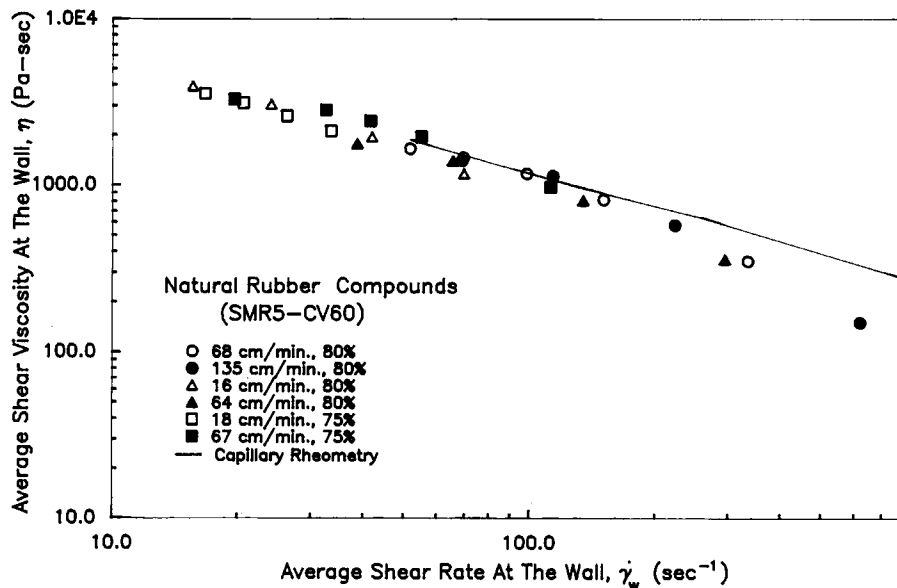


Figure 6 Shear viscosity as a function of shear rate at the wall for natural rubber compound.

tion of shear rate at the wall as obtained from capillary rheometry after the Rabinowitz correction has been applied. Data were obtained from squeeze film

Table I Comparison of the Power Law Constants Obtained from Squeeze Film Flow and Capillary Rheometry Experiments

Material	I.D	Squeeze Film Flow		Capillary Flow	
		n	m (Pa)	n	m (Pa)
SMR5-CV60	NRA1	0.26	33300	0.28	34000
SMR5-CV102	NRA2	0.16	57400	0.16	72600
	NRB	0.12	92000	0.11	97300
	NRCF	0.15	78800	0.17	72500
	NRG	0.14	77800	0.14	87800
	NRC1	0.094	97400	0.094	109400
	NRC2	0.113	72100	0.113	99300
	NRC3	0.15	62700	0.15	82800
EPDM 2504	NRC4	0.15	59400	M.F.	M.F.
	NRC5	0.21	42200	M.F.	M.F.
	NRC6	0.102	79900	0.11	105500
	NRC7	0.123	71050	0.123	97400
	0 phr	0.48	36200	0.51	37600
	0.25 phr	0.49	34100	0.51	37600
	10 phr	0.48	42800	0.5	44700
Kraton 3204	30 phr	0.45	54600	0.45	55300
	Kraton	0.37	35600	0.37	38200

Note: Natural rubber compounds presented are processed differently for each batch.
M.F. = melt fracture.

flow experiments for natural rubber compounds SMR5, EPDM 2504 with various amounts of carbon black N550 loading and those for Kraton 3204 agreed well with the data obtained from capillary rheometry. For SMR5, the agreement for the *n*-values for all samples tested is within ±12% and for the *m*-values within ±27%. For EPDM and Kraton samples, the agreements are within ±10%. These *n* and *m* values are tabulated in Table I.

The proposed procedure, however, requires three test runs which require more experimental time. This time consumption defeats the advantage of the squeeze film flow experiment over other testing methods. It is desirable to obtain the characteristic flow curve from one experimental run. In the present study, an empirical scheme to predict the linear region from the raw loading curve for a single experimental run is proposed based on the linear regions found from the samples tested. Figure 7 is a typical raw loading curve obtained from the squeeze film flow experiment. From point A, the point at which the concavity of the curve changed from downward to upward, a tangent line *L*₁ is drawn. From point B, the point at which the slope of the uprising curve begins to exhibit smaller changes, a tangent line *L*₂ is drawn. At point C, where the slope of the loading curve begins to change abruptly prior to the linear uprise, a tangent line *L*₃ is drawn. From the apex (peak), another tangent line, *L*₄, is drawn. The two tangent lines *L*₁ and *L*₂ intersect at point F that corresponds to time *t*₁. Similarly, the two tangent

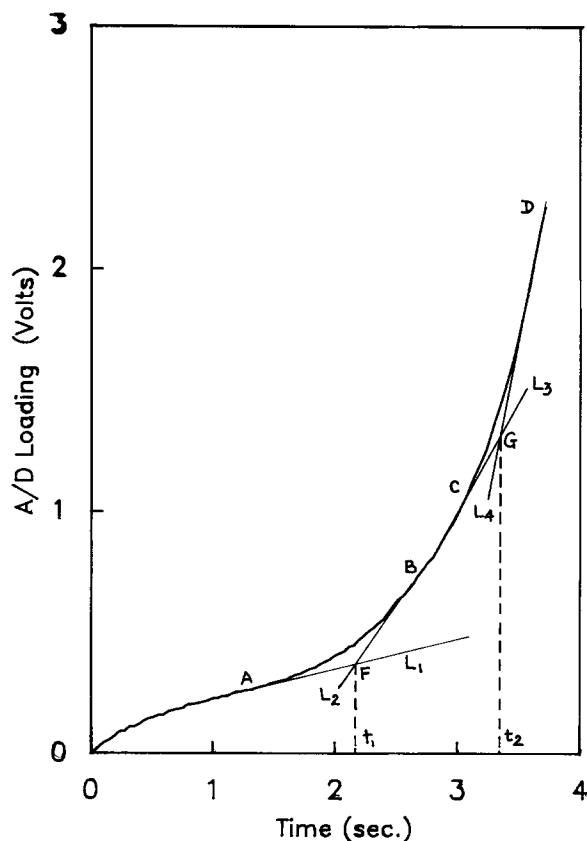


Figure 7 Empirical graphical method of determining the linear region from single squeeze film flow experiment.

lines L_3 and L_4 intersect at point G corresponding to time t_2 . Data points bounded by t_1 and t_2 were found to be in the linear regions for all samples tested. Hence, the linear region can be determined empirically from one squeeze film flow experiment. This gives the advantage of shorter experimental times to obtain the characteristic flow curve relative to other testing methods. At this point, once this linear region is determined, a nonlinear regression based on the Scott's equation can also give the shear viscosity.

A deviation (decrease from capillary rheometer data) in viscosity was observed for all samples tested by squeeze film flow at approximately 75% compression strain. Two possibilities may explain this phenomenon, namely, slippage at high shear rates and viscous heating. If the cause was slippage at high shear rates, then, at higher cross head speeds the onset of a viscosity decrease would not occur at 75% compression strain but should have corresponded to a constant shear rate. This was not observed. Therefore, it is believed that at the end of the test run the material exuding out of the gap contributed

to the effect of viscosity decrease. The flow was disrupted by the high exit pressure. Due to the high exit pressure and the high applied shear rate resulting from the plates moving towards each other, the melt could not flow and hence tended to heat up, causing a drop in viscosity and hence the observed deviations.

CONCLUSIONS

A method to determine the characteristic flow curve from the squeeze film flow experiment is proposed. If the polymer melt behaves like a power law fluid, then a linear region is obtained from a doubly logarithmic plot of the horizontal stress as a function of the apparent shear rate. This linear region can be defined from three different squeezing speeds and the power law constants, n and m , can be determined. In this study, the viscosity data obtained from squeeze film flow have been compared with data obtained from capillary rheometry for natural rubber compounds, SMR5, ethylene propylene rubber with some diene monomers added (EPDM) at various loadings of carbon black N550 and styrene butadiene styrene copolymer (Kraton). Both sets of data agree quite well with maximum deviations of 12% for the n values and 27% for the m values for the natural rubber compounds and maximum deviations of 10% for EPDM and Kraton. An empirical method of determining the linear region from the loading curve of one squeeze film flow experiment is proposed based on the linear regions determined for all the samples tested. This allows the squeeze film flow experiment to be used as a determination method for the characteristic flow curve for a given melt at a shorter experimentation time relative to other testing methods. The squeeze film flow experiment as proposed is a quick and rugged method which lends itself for quality control applications on the shop floor. Its accuracy is not sufficient that it would be able to replace the standard testing methods to determine the viscosity of polymer melts.

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