

Determination of True Flow Curves from Capillary Rheometer Data

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Synopsis

The evaluation of polymer melt viscosity versus shear rate has been customarily done by a time-consuming graphical method, which corrects for non-Newtonian behavior and pressure losses at flow transitions. It is shown by mathematical analysis that the flow data in terms of applied pressure and apparent shear rate can be treated by a semigraphical method, in which calculation of the true flow curve can be done with a computer. Moreover, it is possible in some cases to program the data treatment entirely for computer calculation. Results obtained by the proposed method are in excellent agreement with those obtained by the older graphical method.

INTRODUCTION

The behavior of polymer melts when extruded through capillaries has been the subject of numerous investigations, because rheological studies of this kind can be used for establishing useful correlations with polymer flow in such processing equipment as extruders and injection-molding machines. At the same time rheology reflects the molecular structure of polymers, especially the molecular weight. Complications arise however, in evaluations of the melt flow properties through a capillary, because polymers have both an elastic and a shear-sensitive nature. An entrance correction, or Bagley correction¹ must be used for pressure losses at flow transitions, and a non-Newtonian correction, or Rabinowitsch correction² must be used for converting the apparent shear rate to a true shear rate. Until now only graphical methods have been used for accurate evaluations of the true viscosity of polymer melts, except in cases in which a so-called power-law³ flow relation appears to exist. Grant and Diekmann⁴ recently proposed an empirical formula for carrying out the calculation numerically with six independent parameters, but the method is not suitable for undefined polymers.

The purpose of the present paper is to propose a simplified but equally accurate method of treating the experimental data derived from capillary measurements in polymer melts. One advantage of the proposed method is that after two curves of flow versus pressure are drawn from a relatively small amount of experimental data, the rest of the former tedious graphical derivation of true viscosity versus true shear rate curves can be programmed

for computer calculation. Because of the numerous types of polymers studied much computer time can be saved by the operator's decision concerning flow type. However, since the method is purely mathematical, in some cases it could be entirely programmed on a computer, so that true viscosity can be obtained as a function of true shear rate directly from experimentally measured data.

THEORY

I. General Theory

The general theory for obtaining flow properties of polymer melts from the capillary rheometer data has been reviewed.⁵⁻⁷ When a melt flows through a capillary of diameter D and length L under an applied pressure difference P across the ends of the capillary, the true shear rate at the wall, $\dot{\gamma}_{TW}$, and the true shear stress at the wall, τ_{TW} , are calculated according to the following equations:

$$\dot{\gamma}_{TW} = 1/4\dot{\gamma}_a[3 + (d \log \dot{\gamma}_a)/(d \log \tau_{TW})] \quad (1)$$

$$\tau_{TW} = P/4[(L/D) + (L/D)_{ent}] \quad (2)$$

$$\dot{\gamma}_a = 4Q/\pi R^3 \quad (3)$$

where $\dot{\gamma}_a$ = apparent shear rate, Q = volume flow through the capillary per unit time, R = radius of capillary, $(L/D)_{ent}$ = the Bagley correction, and $(d \log \dot{\gamma}_a)/(d \log \tau_{TW})$ = the Rabinowitsch correction. The viscosity is calculated from the following definition:

$$\eta = \tau_{TW}/\dot{\gamma}_{TW} \quad (4)$$

For a Newtonian melt, the Rabinowitsch correction equals unity and the Bagley correction is given as a constant of Couette, which is the distance required to produce a well-developed parabolic velocity profile and which is constant for any system (the constant of Couette⁵ (i.e., L/R) is given as 0.824 by Reileigh, 0.805 by Scheader, and 0.566 by Bondi). To evaluate the flow properties of a non-Newtonian melt, whose viscosity is different for each shear rate, both the Bagley and the Rabinowitsch corrections must be determined. The Bagley correction is a function of shear rate; since the response of the polymer melt is influenced by the molecular structure, it varies from one material to another.

II. Graphical Method

According to the graphical method of evaluating these two corrections, the shear rate obtained at various pressures is first plotted for each of several capillaries as shown in Figure 1. Two or more capillaries must be used in order that the Bagley correction may be evaluated. At an arbitrarily chosen shear rate the pressure for each capillary (P_1 , P_2 , and P_3 in Fig. 1) is plotted against the capillary geometry L/D ratio. The pressure

varies linearly with the L/D ratio, and the intercept on the L/D axis yields the Bagley correction for the chosen shear rate. Then τ_{TW} can be calculated with eq. (2). The τ_{TW} 's are then plotted against apparent shear rate on a log-log scale. The Rabinowitsch corrections at each shear rate

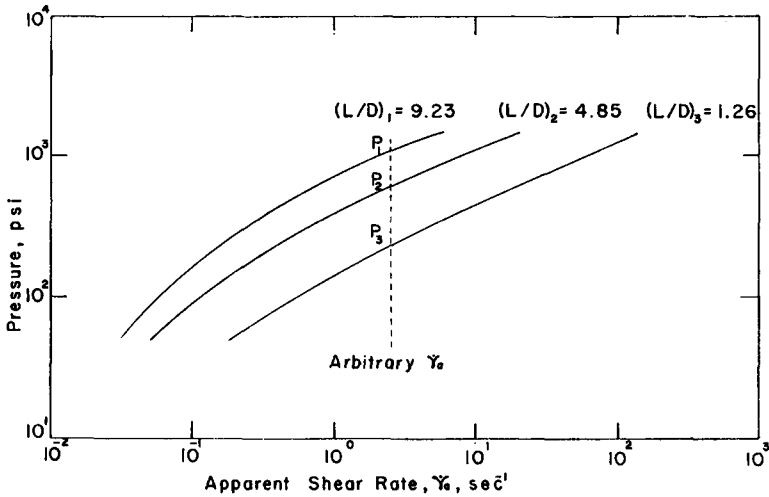


Fig. 1. Flow data for Plexiglas V-100, Type 415, at 400°F.

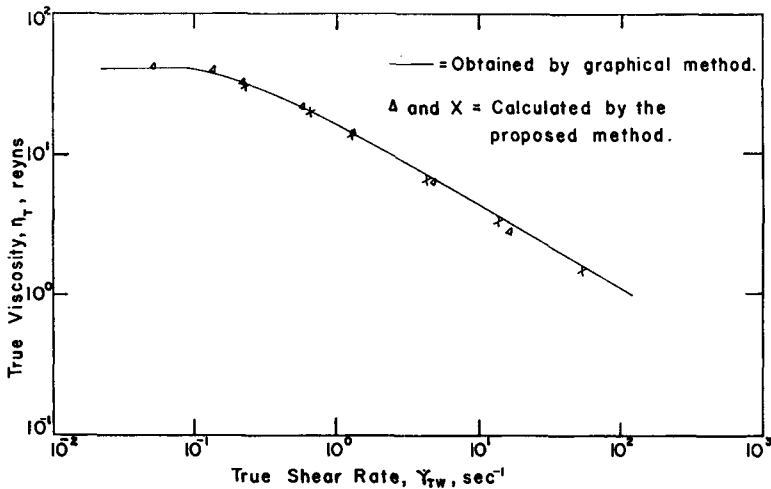


Fig. 2. Flow curve of Plexiglas V-100, Type 415, at 400°F.

are obtained by graphical differentiation of $\log \tau_{TW}$ versus $\log \dot{\gamma}_a$ at arbitrary shear rates. Thus, three sequential graphical analyses and numerous calculations of eqs. (1)–(4) for small intervals of shear rate are required with the graphical method. This is a time-consuming task.

III. Proposed Method

To avoid the laborious graphical procedures of evaluating Bagley and Rabinowitsch corrections at numerous shear rates, eqs. (1), (2), and (3) were analyzed mathematically, and τ_{TW} and $\dot{\gamma}_{TW}$ were represented by experimental quantities. If data from two capillaries, say $(L/D)_1$ and $(L/D)_2$ are available, the results are:

$$\dot{\gamma}_{TW} = 1/4\dot{\gamma}_a[3 + (P_1 - P_2)/(n_1P_1 - n_2P_2)] \quad (5)$$

$$\tau_{TW} = (P_1 - P_2)/4[(L/D)_1 - (L/D)_2] \quad (6)$$

where n_1 and n_2 are $(d \log P)/(d \log \dot{\gamma}_a)$, the subscripts 1 and 2 indicate the capillary, and P_1 and P_2 are pressures at an arbitrary $\dot{\gamma}_a$ for capillaries 1 and 2, respectively.

By using these relations and eq. (4) the quantities τ_{TW} and $\dot{\gamma}_{TW}$ are calculated after the parameters P_1 , P_2 , n_1 , and n_2 at an arbitrary $\dot{\gamma}_a$ are obtained from Figure 1. Since η and γ_{TW} must be obtained at small intervals of $\dot{\gamma}_a$, eqs. (4), (5), and (6) were programmed on a computer. If pressure data from more than two capillaries are available for the calculation, eqs. (5) and (6) can be written for different pairs of (L/D) 's. The average of the calculated $\dot{\gamma}_{TW}$'s and τ_{TW} 's will give a more accurate result.

The parameter n_i is easily obtained by measuring the slope of $\log P_i/(\log \dot{\gamma}_a)$ graphically. However, n_i may be obtained directly from the experimental data by utilizing Stirling or Bessel formulas⁸ for a rheometer capable of measuring the shear stress at constant intervals of apparent shear rate; or, if $\log P$ is expressed as a function of $\log \dot{\gamma}_a$, then n_i can be obtained by differentiation.

Although the Bagley and the Rabinowitsch corrections are not needed separately, they can be calculated:

Bagley Correction

$$\begin{aligned} Pe &= [(L/D)_1P_2 - (L/D)_2P_1]/[(L/D)_1 - (L/D)_2] \\ &= [(L/D)_1P_3 - (L/D)_3P_1]/[(L/D)_1 - (L/D)_3] = \dots \quad (7) \end{aligned}$$

where Pe is the Bagley correction in terms of the pressure drop; that is, when P is plotted against L/D in the graphical method, Pe is extrapolated as the intercept on the P axis, while $(L/D)_{ent}$ is extrapolated as the intercept on the L/D axis.

Rabinowitsch Correction

$$\begin{aligned} (d \log \dot{\gamma}_a)/(d \log \tau_{TW}) &= (P_1 - P_2)/(n_1P_1 - n_2P_2) = \\ &= (P_1 - P_3)/(n_1P_1 - n_3P_3) = \dots \quad (8) \end{aligned}$$

In the special case in which the pressure varies linearly with the change in $\dot{\gamma}_a$, and the shear dependence of pressure is the same for different orifices, then $n_1 = n_2 = n = \text{constant}$, and eq. (5) is simplified to

$$\dot{\gamma}_{TW} = 1/4\dot{\gamma}_a[3 + 1/n] \quad (9)$$

Equation (9) is commonly known as a power law.

The derivations of the equations in this section are given in the Appendix.

IV. Application to a Slit Die

The proposed method is also applicable to a capillary having a slit geometry, which is, in practice, used for sheet extrusion. For the slit die of breadth b and width d , where $b \geq 10d$, it can easily be shown that

$$\tau_{TW} = (P_1 - P_2)/2[(L/d)_1 - (L/d)_2] \quad (10)$$

The true rate of shear at the wall for a slit rheometer is then given as

$$\dot{\gamma}_{TW} = {}^{1/3}\dot{\gamma}_a[2 + (d \log \dot{\gamma}_a)/(d \log \tau_{TW})] \quad (11)$$

where

$$\dot{\gamma}_a = 6Q/bd^2 \quad (12)$$

Thus, the Rabinowitsch correction can be given in the same form as eq. (8).

RESULTS

To compare the two methods for obtaining flow curves, an acrylic molding powder, Plexiglas V-100, Type 415 (trademark of Rohm and Haas Company), was studied at 400°F. with a De Bell-Richardson capillary extrusion rheometer. The data expressed as applied pressure versus apparent shear rate are given in Figure 1 for three capillaries. Since the capillaries have rather low L/D ratios, the Bagley correction becomes quite significant. The flow curve for Plexiglas V-100, Type 415, was calculated by the graphical method and is shown as the solid curve in Figure 2. Various points were calculated by the proposed method and are indicated by triangles and crosses in Figure 2; they correspond to the data from capillaries 1 and 2 and capillaries 2 and 3, respectively. The agreement between the two methods is excellent.

Appendix: Derivation of Equations

The Bagley correction $(L/D)_{\text{ent}}$, can be expressed in terms of a pressure loss Pe . Thus, eq. (2) can be rewritten as

$$\tau_{TW} = (P - Pe)/4(L/D) \quad (\text{A-1})$$

Since τ_{TW} at an arbitrary $\dot{\gamma}_a$ is assumed to be constant [i.e., eq. (4) is assumed to be valid] regardless of the L/D ratio of the capillary, and the material is at constant temperature, one can equate τ_{TW} at a given $\dot{\gamma}_a$ for various L/D ratios. Then,

$$\tau_{TW} = P_1 - Pe/4(L/D)_1 = P_2 - Pe/4(L/D)_2 = \dots P_i - Pe/4(L/D)_i \quad (\text{A-2})$$

Therefore,

$$Pe = [(L/D)_1 P_2 - (L/D)_2 P_1]/[(L/D)_1 - (L/D)_2] = [(L/D)_1 P_3 - (L/D)_3 P_1]/[(L/D)_1 - (L/D)_3]$$

If data from i number of L/D ratios were available, then $i!/2(i-2)!$ simultaneous equations can be written for Pe . All equations should yield the same Pe value. When only two L/D ratios are used, the substitution of Pe into eq. (A-1) gives

$$\tau_{TW} = (P_1 - P_2)/4[(L/D)_1 - (L/D)_2] \quad (A-3)$$

The Rabinowitsch correction can be arranged into the following form:

$$(d \log \dot{\gamma}_a)/(d \log \tau_{TW}) = (\tau_{TW}/\dot{\gamma}_a)[1/(d \tau_{TW}/d \dot{\gamma}_a)] \quad (A-4)$$

Differentiating eq. (A-3) with respect to $\dot{\gamma}_a$ yields:

$$\begin{aligned} (d \tau_{TW})/(d \dot{\gamma}_a) &= \{^{1/4}[(L/D)_1 - (L/D)_2]\} [(dP_1)/(d \dot{\gamma}_a) - (dP_2)/(d \dot{\gamma}_a)] \\ &= \{^{1/4}[(L/D)_1 - (L/D)_2]\} [(P_1/\dot{\gamma}_a)(d \log P_1)/(d \log \dot{\gamma}_a) \\ &\quad - (P_2/\dot{\gamma}_a)(d \log P_2)/(d \log \dot{\gamma}_a)] \\ &= (P_1 n_1 - P_2 n_2)/4 \dot{\gamma}_a [(L/D)_1 - (L/D)_2] \end{aligned} \quad (A-5)$$

Substituting the result back into eq. (A-4), we obtain

$$\begin{aligned} (d \log \dot{\gamma}_a)/(d \log \tau_{TW}) &= 4 \tau_{TW} [(L/D)_1 - (L/D)_2] / (P_1 n_1 - P_2 n_2) \\ &= (P_1 - P_2) / (P_1 n_1 - P_2 n_2) \end{aligned}$$

Substitution of this equation into eq. (1) gives eq. (5).

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Résumé

L'évaluation de la viscosité d'un polymère fondu en fonction de la vitesse de cisaillement a été généralement effectuée par une méthode graphique demandant beaucoup de temps et qui tient compte du comportement non-Newtonien et des pertes de pression au cours des transitions d'écoulement. On montre par analyse mathématique que les données d'écoulement relatives à la pression appliquée et à la tension de cisaillement

apparente peuvent être traitée par une méthode semi-graphique par laquelle le calcul de la courbe d'écoulement vrai peut être effectué grâce à une machine à calculer. De plus, il est possible, dans certains cas, de programmer le traitement des résultats pour un calcul entièrement par "computer." Les résultats utilisant la méthode proposée sont en accord excellent avec ceux obtenus par l'ancienne méthode graphique.

Zusammenfassung

Die Ermittlung der Viskosität von Polymerschmelzen als Funktion der Schergeschwindigkeit erfolgte gewöhnlich mittels einer zeitraubenden graphischen Methode, bei der Fehler durch nicht Newtonsches Verhalten und durch Druckverluste bei Fließübergängen eliminiert werden. Durch mathematische Analyse wird gezeigt, dass die Fließdaten in Form des angewandten Drucks und der scheinbaren Schergeschwindigkeit mittels einer halbgraphischen Methode behandelt werden können, mit deren Hilfe die wahre Fließkurve in einem Computer erstellt werden kann. Ausserdem ist es in manchen Fällen möglich, die Datenbehandlung gänzlich für eine Computerberechnung zu programmieren. Die bei der vorgeschlagenen Methode erhaltenen Ergebnisse stimmen mit denen aus der älteren graphischen Methode ausgezeichnet überein.

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