MEASUREMENT OF NORMAL STRESSES BY THE CAPILLARY JET METHOD

RYO NAKAMURA* AND NAOYA YOSHIOKA

Department of Chemical Engineering, Kyoto University,
Kyoto, 606

The capillary jet (die swell) method for the measurement of normal stresses has been studied in terms of many variables and rheological descriptions. The present paper deals with diameter effect first reported by Powell and Middleman, and proposes that the most important parameter is the ratio of the inertial force to the elastic stress. When this parameter is greater than 1, the momentum balance equation proposed by Metzner *et al.* gives reasonable values for the first normal stress difference. When this parameter is less than 1, the diameter effect begins to appear and the capillary jet method is not applicable. A more pronounced diameter effect corresponds to smaller values of this parameter.

Introduction

It is well known that the swelling ratio of a jet emerging from a capillary tube is larger for viscoelastic fluids than for purely viscous fluids. Since flow in a tube is not subject to secondary flows, as are other viscometric flows, the capillary jet method is particularly well-suited to measure normal stress differences at high shear rates. However, this method involves other problems as will be discussed below.

The capillary jet method has been mainly applied to dilute polymer solutions. The first theoretical analysis, which has been widely used to predict normal stresses, was that due to Metzner *et al.*⁽⁶⁾. For polymer melts and concentrated solutions, it has been shown by several investigators^(2,4,7,10) that this analysis gives abnormally small values of the first normal stress difference. Moreover, Powell and Middleman⁽⁹⁾ reported that the first normal stress difference of polyisobutylene solutions shows a diameter effect; that is, the smaller the diameter of capillary, the smaller the value of the first normal stress difference. Therefore, it must be concluded that the equation proposed by Metzner *et al.* is applicable only when a certain range.

As to differences between polymer melts or concentrated solutions on the one hand and dilute solutions on the other, the following two factors should be considered: 1) the first normal stress difference is larger for the former than for the latter (at a fixed shear rate); 2) the experimental shear rates are smaller for the former than for the latter, due to an upper

limit having to do with flow instabilities (such as "melt fracture"). Among the variables to be considered in the capillary jet method, an important one is the inertial force of the fluid. This increases with increasing shear rate at a fixed diameter of capillary. Therefore, the available inertia force is smaller for polymer melts (or concentrated solutions) than for dilute solutions.

It is therefore reasonable to assume that the relative level of inertial forces and the elastic forces play an important role, under conditions when the ratio of the inertial force to viscous force is not too small. It will be shown that the analysis of Metzner *et al.* is applicable only when a certain nondimensional parameter, defined as the ratio of the inertial force to the first normal stress difference, is larger than a given value. Since this parameter includes the first normal stress difference (which is the aim of measurement), this conclusion appears to be not useful at first consideration. This criterion is, however, the first condition which must be satisfied and therefore it must be dealt with indirectly.

The purpose of this paper is to show that the diameter effect reported by Powell and Middleman is due to the fact that their measurements were made below the range discussed above; that is, at low values of the inertia/elastic ratio. It will be also shown that their data⁽⁹⁾, calculated in a manner to remove the diameter effect, predict reasonable values for the first normal stress difference.

Basic Equations

The analysis is developed from the following assumptions: 1) the flow is fully-developed at the exit of the capillary; 2) the effects of gravitational force,

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air drag and surface tension on the capillary jet are negligible. The total stress tensor T is expressed as a sum of p , the hydrostatic pressure, and τ , the deviatoric stress tensor.

$$T = -p\delta + \tau \quad (1)$$

In Eq. (1), δ is the unit tensor.

Taking a momentum balance between the tube exit and a position downstream in the capillary jet (at which point the elastic stress and the velocity profile are assumed to be completely relaxed), one obtains

$$\langle T(L) \rangle = \rho \langle u \rangle^2 f_M \left[1 - \frac{1}{f_M} \left(\frac{R}{R_j} \right)^2 \right] \quad (2)$$

Here ρ is density, $\langle u \rangle$ is average velocity, R is the radius of the capillary and R_j is the radius of the jet. f_M is defined by

$$f_M = \int_0^1 2\xi \frac{u^2(\xi)}{\langle u \rangle^2} d\xi, \quad \xi = \frac{r}{R} \quad (3)$$

Therefore, f_M may be calculated once the flow curve of the fluid is known. $\langle T(L) \rangle$ is the average axial normal stress of the jet at the exit of the capillary. When z , r , and θ directions of the cylindrical coordinate system are denoted by 1, 2, and 3, respectively, $\langle T(L) \rangle$ is given by

$$\begin{aligned} \langle T(L) \rangle &= \frac{1}{\pi R^2} \int_0^R 2\pi r T_{11}(r, L) dr \\ &= \frac{1}{\tau_w^2} \int_0^{\tau_w} 2\tau T_{11}(\tau, \tau_w, L) d\tau \end{aligned} \quad (4)$$

where τ_w is the shear stress at the capillary wall.

Eq. (2) is the basic equation for the capillary jet method, and the equation proposed by Metzner *et al.*, is obtained by rewriting Eq. (2) with certain assumptions. Since the value of the term in the bracket [] cannot exceed 1, the average axial normal stress $\langle T(L) \rangle$ is always less than the inertial force $\rho \langle u \rangle^2 f_M$. When the swelling ratio is sufficiently larger than 1, $\langle T(L) \rangle$ is approximately equal to $\rho \langle u \rangle^2 f_M$. This is a hydrodynamic quantity, and therefore, in this range, $\langle T(L) \rangle$ cannot be considered to be directly related to the material quantities (the normal stress differences).

To examine Eq. (2) in detail, both sides of this equation will be divided by the first normal stress difference,

$$(T_{11} - T_{22})_w = \phi(\dot{\gamma}_w) \dot{\gamma}_w^2 \quad (5)$$

where $\dot{\gamma}_w$ is shear rate at the tube wall and $\phi(\dot{\gamma}_w)$ is the coefficient of the first normal stress difference. One thus obtains

$$X_s = \frac{1}{N} \frac{\langle T(L) \rangle}{\phi(\dot{\gamma}_w) \dot{\gamma}_w^2} \quad (6)$$

where

$$N = \rho \left(\frac{D}{8} \right)^2 \frac{f_M}{\phi(\dot{\gamma}_w)} \left(\frac{4n}{3n+1} \right)^2 \quad (7)$$

inertial force per unit cross sectional area/normal stress ratio

$$X_s = 1 - \frac{1}{f_M} \left(\frac{R}{R_j} \right)^2, \text{ die swell number} \quad (8)$$

$\dot{\gamma}_w$ is given by

$$\dot{\gamma}_w = \frac{3n+1}{4n} \dot{\gamma}_{wa}, \quad \dot{\gamma}_{wa} = 8 \frac{\langle u \rangle}{D}, \quad n = \frac{d \ln \tau_w}{d \ln \dot{\gamma}_{wa}} \quad (9)$$

where $D=2R$ is the diameter of the capillary.

The dimensionless parameter N is the ratio of the inertial force per unit cross sectional area to the first normal stress difference. Since $\phi(\dot{\gamma}_w)$ is generally a decreasing function of $\dot{\gamma}_w$, N increases with increasing $\dot{\gamma}_w$ or D . Considering that $X_s < 1$, it is found from Eq. (6) that $\langle T(L) \rangle$ does not correspond to the first normal stress difference when N is smaller than 1. That is, the relative magnitudes of the inertial force and the first normal stress difference are controlling parameters in the capillary jet method.

One now uses the apparent steady state compliance $J(\dot{\gamma}_w)$ defined by

$$J(\dot{\gamma}_w) = \frac{1}{2} \frac{\phi(\dot{\gamma}_w)}{\eta^2(\dot{\gamma}_w)} \quad (10)$$

$\phi(\dot{\gamma}_w)$ is expressed by

$$\phi(\dot{\gamma}_w) = 2\eta_0(\eta_0 J_0) \left[\frac{\eta(\dot{\gamma}_w)}{\eta_0} \right]^2 \left[\frac{J(\dot{\gamma}_w)}{J_0} \right] \quad (11)$$

where η_0 and J_0 are the viscosity and the steady state compliance, respectively, both evaluated at zero shear rate. Both $\eta(\dot{\gamma}_w)$ and $\phi(\dot{\gamma}_w)$ decrease with increasing $\dot{\gamma}_w$. Compared with the dependency of these two quantities on $\dot{\gamma}_w$, $J(\dot{\gamma}_w)$ varies more slowly with $\dot{\gamma}_w^{1,5}$.

Substituting Eq. (11) into Eq. (7), one obtains

$$N = \rho \left(\frac{D}{8} \right)^2 \frac{f_M}{\eta_0 \lambda_N} \left(\frac{4n}{3n+1} \right)^2 \left[\frac{\eta_0}{\eta(\dot{\gamma}_w)} \right]^2 \frac{J_0}{J(\dot{\gamma}_w)} \quad (12)$$

where λ_N is the characteristic relaxation time defined by

$$\lambda_N = \eta_0 J_0 \quad (13)$$

As a special case, when $J(\dot{\gamma}_w)$ can be approximated by J_0 , one has

$$(T_{11} - T_{22})_w = 2 \langle T_{11} - T_{22} \rangle \quad (14)$$

$\langle T_{11} - T_{22} \rangle$ is the average first normal stress difference. Therefore, the following equations are obtained from Eqs. (6) and (17):

$$\begin{aligned} X_s &= \frac{1}{2} \frac{1}{N} \frac{\langle T(L) \rangle}{\langle T_{11} - T_{22} \rangle} \\ N &= \rho \left(\frac{D}{8} \right)^2 \frac{f_M}{\eta_0 \lambda_N} \left(\frac{4n}{3n+1} \right)^2 \left[\frac{\eta_0}{\eta(\dot{\gamma}_w)} \right]^2 \end{aligned} \quad (15)$$

If $\langle T(L) \rangle = \langle T_{11} - T_{22} \rangle$, as proposed by Metzner *et al.*, X_s must be represented as follows:

$$X_s = \frac{1}{2} \frac{1}{N} \quad (16)$$

Table 1 Properties of polymers and solutions

Solution	A	B	C	D
Concentration [g/cm ³]	0.0340	0.0185	0.0106	0.0140
Polymer*	L100	B100	B100	B100
Solvent	tetralin	tetralin	50% tetralin and 50% oil	50% tetralin and 50% oil
η_0 [poise]	1.49	0.678	0.702	1.53
$\lambda_B \times 10^3$ [sec]	1.56	2.19	3.47	6.27

* Both are polyisobutylene

L100: $M_\eta = 0.73 \times 10^6$, B100: $M_\eta = 1.25 \times 10^6$

Since $X_s < 1$, Eq. (16) cannot be hold for $N < 0.5$.

It is reasonable to suppose that X_s changes gradually in the neighbourhood of $N=0.5$. Therefore, to be on the safe side, it may be concluded that the capillary jet method cannot predict the first normal stress difference when $N < 1$ —that is, the measurement must be carried out in the range $N > 1$. Because the controlling parameter N has within it the unknown elastic stress, this conclusion seems to be difficult to apply. This is, however, the first condition to be satisfied and must be dealt with. Whether or not $\langle T(L) \rangle = \langle T_{11} - T_{22} \rangle$ is satisfied in the range $N > 1$ is the next problem to be investigated.

Examination of Powell's Data⁸⁾

The properties of the solutions are summarized in Table 1⁸⁾. λ_B is Bueche's relaxation time calculated from

$$\lambda_B = \frac{12}{\pi} \frac{\eta_0 M_\eta}{cRT} \quad (17)$$

where M_η is the viscosity average molecular weight, c is the concentration (g/100 cc), R is the gas constant, and T is the absolute temperature.

Except for the range $R_j/R \gg 1$, as is the case for polymer melts, the parameter X_s defined by Eq. (8), is a more important variable than R_j/R . Therefore, the original jet expansion data are plotted in the terms of X_s vs. $\dot{\gamma}_w$ in Fig. 1, using a polymer solution ("Solution A") as an example. The inertial force increases with diameter at a fixed shear rate, but X_s decreases. Fig. 2 shows the resultant change in $\langle T(L) \rangle$ at $\dot{\gamma}_w = 2 \times 10^4 \text{ sec}^{-1}$ for various solutions. (This corresponds to Fig. 3 in Powell and Middleman. Their ordinate $(T_{11})_R$ is incorrect as is shown in Appendix). In Fig. 2, the black points at the left hand side are extrapolated ones. Although this extrapolation appears be reasonable at first sight, it should be noted that the values of X_s are overestimated by at least 40%. This means that great care is necessary in extrapolating $\langle T(L) \rangle$.

The various $J(\dot{\gamma}_w)$ for the polymer solutions are approximately independent of $\dot{\gamma}_w$. Therefore, approximating λ_N by λ_B , one can calculate N from Eq. (15).

Fig. 1 Die swell number as a function of $\dot{\gamma}_w$ and D for Solution A

Fig. 2 Diameter dependency of $\langle T(L) \rangle$ at $\dot{\gamma}_w = 2 \times 10^4 \text{ sec}^{-1}$

Symbols are same as in Fig. 2.

Fig. 3 Relation between die swell number and N at $\dot{\gamma}_w = 2 \times 10^4 \text{ sec}^{-1}$

The jet expansion data used in Fig. 2 are plotted in the form X_s vs. N in Fig. 3. As is obvious from Fig. 3, Powell's data are almost in the range $N < 1$. The dotted line in Fig. 3 represents Eq. (16). Notwithstanding some scatter, it may be concluded that X_s is well-correlated with N ; those for $N > 1$ are on the dotted line. As N becomes smaller than 1, the ratio of viscous force to elastic force plays a role and therefore the expansion data must be treated in terms of R_j/R or R/R_j instead of X_s . Comparing Fig. 2 with Fig. 3, it is clear that a more pronounced diameter effect corresponds to the smaller value of N .

Considering that N is calculated without any information about the normal stress difference (except the assumption $J(\dot{\gamma}_w) = J_0$), one may draw the follow-

Symbols are same as in Fig. 1.

Fig. 4 Relation between die swell number and N for Solution A

Symbols are same as in Fig. 1.

Fig. 5 Die swell number reduced to a reference diameter ($D_0=0.271$ cm) for Solution A

ing two conclusions from Fig. 3: 1) in the range $N > 1$, the capillary jet method properly predicts the first normal stress difference; 2) the diameter effect begins to appear as N becomes smaller than 1.

Although it does not always mean that X_s is a function of only N , the parameter X_s in Fig. 1 is replotted against N in Fig. 4. The dotted line represents Eq. (16). It may be concluded that all of the data in the range of $N > 1$ are reasonably well on the dotted line. Therefore, $(T_{11} - T_{22}) = 2\rho\langle u \rangle^2 f_M X_s$ in this range.

In general, the evaluation of N is not easy. λ_N must be estimated in some manner. Moreover, N involves information about the normal stress difference to be measured, in the case when the apparent steady state compliance is a function of shear rate. Accordingly, it is desirable to detect the diameter effect in a simple manner. If the diameter effect is absent, X_s must be inversely proportional to D^2 as is obvious from Eq. (2). Therefore, when experiments are carried out with capillaries of various diameters, plots of $X_s(D/D_0)^2$ vs. $\dot{\gamma}_w$ must lie on the same curve. D_0 is a reference diameter. Fig. 5 shows plots of $X_s(D/D_0)^2$ vs. $\dot{\gamma}_w$ for a solution A. It is reasonable to conclude that the data for $D=0.271$ cm and $D=0.186$ cm lie on the same curve. However, for the

two smaller capillaries, the data are below this curve in the lower range of $\dot{\gamma}_w$. That is, the diameter effect is observed and these data must be rejected in calculating the first normal stress difference.

More simply, when X_s is less than 0.5, the diameter effect will be absent, as is obvious from Eq. (16).

Conclusions

It is concluded that the main cause of the diameter effect is that $\langle T(L) \rangle$ is necessarily less than $\rho\langle u \rangle^2 f_M$. Several of the causes mentioned by Powell and Middleman are minor. The essential conclusions about the capillary jet method may be summarized as follows:

1) $\langle T(L) \rangle$ is not a material function in the range $N < 1$. A diameter effect is observed in this range and a more pronounced diameter effect corresponds to smaller values of N .

2) In the range $N > 1$, $\langle T(L) \rangle$ may be considered as material function and the first normal stress difference can be calculated from $\langle T(L) \rangle$. This proves indirectly that the assumptions made by Metzner *et al.* are satisfied within the accuracy of the experiments.

3) A simple method to detect the diameter effect is as follows; if plots of $X_s(D/D_0)^2$ vs. $\dot{\gamma}_w$ for various diameters are on the same curve, the diameter effect is absent.

4) More simply, in the range $X_s < 0.5$ (corresponding to $N=1$), the diameter effect is absent.

Appendix

If the assumption that the flow is fully developed at the exit plane of the capillary is valid, only $p(0,L)$ (the centerline hydrostatic pressure at the exit) can make up the difference between the large elastic stress, which arises from the material response, and the quantity $\langle T(L) \rangle$. Therefore, $p(0,L)$ cannot be considered to be zero in the range $N < 1$, and the axial normal stress at the capillary wall, $(T_{11})_w$, is given by the following equations:

$$(T_{11})_w = \frac{1}{2} \frac{1}{\tau_w} \frac{d}{d\tau_w} [\tau_w^2 \langle T(L) \rangle] + \frac{1}{2} \frac{dp(0,L)}{d \ln \tau_w} \\ \frac{1}{2} \frac{1}{\tau_w} \frac{d}{d\tau_w} [\tau_w^2 \langle T(L) \rangle] = \rho \langle u \rangle^2 \left[\frac{3n+1}{n} - f_M \right. \\ \left. - \frac{1}{n} \left(\frac{R}{R_j} \right)^2 \left\{ n+1 + \frac{d \ln (R/R_j)}{d \ln \dot{\gamma}_{wa}} \right\} \right]$$

That is, $(T_{11})_w$ cannot be obtained unless $p(0,L)$ is known.

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VELOCITY PROFILE IN VISCOELASTIC FLOW AT THE ENTRY OF A TUBE

RYO NAKAMURA*, NAOYA YOSHIOKA,
MUNEYUKI HIGUCHI¹ AND HITOSHI HIRAI²
*Department of Chemical Engineering, Kyoto University,
Kyoto, 606*

Local velocities were measured for the flow of a viscoelastic fluid from a large pipe into a small one (an abrupt contraction with diameter ratio 3.5). Under certain conditions it was found that the velocity field at the entrance was distinctly different from the expected pattern, which would be one of gradually increasing velocity near the centerline. Rather it was found that the centerline velocity at the entrance was larger than the centerline velocity in the developed downstream flow; or, in other words, a pronounced funneling was observed. This is attributed to the elastic behavior of the material.

Introduction

The flow of a viscoelastic fluid at the entrance of a tube is a typical problem in "nonviscometric" rheology and it is a flow frequently encountered in polymer processing. In prior work this problem has been investigated mainly with respect to the pressure field, and the structure of the velocity field has been deduced from the results. For example, the "Bagley plot" for pressure drop frequently suggests that the velocity profile is fully developed at the entrance. To verify this result, and also to advance the analysis of the entrance flow problem in general, a direct investigation of the velocity field was undertaken.

Qualitative observations have been made for polymer melts by Tordella⁸), Bagley and Birks¹), and Ballenger and White²). They found that the upstream flow pattern is strongly influenced by the elastic properties of the fluids. The main results of these investigations are as follows: 1) the flow is steady up to a certain value of the shear rate, at which point it

becomes unsteady; 2) in the steady flow regime, the fluid enters into the downstream tube through a funnel-shaped region, creating a circulating secondary flow region in the corner; 3) the shape of the funnel depends on the elastic properties of the fluid as well as on the hydrodynamic conditions. Ballenger *et al.*^{2,3}) showed that the incident angle of the funnel (the entrance angle) decreases with increasing elastic properties. It seems that the shape of the funnel changes from a cone to a "wine-glass" shape with increasing elastic properties.

Unfortunately, there are only a few quantitative measurement of entry velocity profiles. Metzner *et al.*⁶) measured point velocities upstream of a contraction and concluded that this convergent flow is approximated by a three-dimensional sink flow. Boger and Rama Murthy⁴) measured developing velocity profiles in the downstream tube as well as in the upstream region. Their results are very interesting, in that they showed that the key factor for the developing flow is the ratio of the friction velocity to the shear wave velocity, rather than the Reynolds number. Whether the velocity profile is fully or partially developed at the entrance depends on the

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¹ Nippon Steel Co., Ltd., Ohita, 870.

² Shinko Pfaudler Co., Ltd., Kobe, 651.