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Total Applied Shear in Capillary Extrusion

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Synopsis

Viscoelastic properties of polymer fluids are single-valued functions of shear stress or shear rate only at high total applied shear. These parameters may vary with applied shear under milder shear histories. The mean total shear in capillary extrusion is shown to be a function of orifice geometry. Apparent flow curves can be measured at various total shear values by changing the length/radius ratio of the capillary. The true shear stress and true shear rate at the orifice wall correspond to infinite total shear conditions. The true flow curve and elastic parameters like die swell are not measured at equivalent total shear unless the capillary is extremely long.

VISCOELASTIC PROPERTIES AND SHEAR HISTORY

It is well known that the apparent viscosity of thixotropic materials tends to decrease with increased total applied shear at a given shearing rate.[1] The same phenomenon may be observed at relatively low total shear with polymer melts and solutions. References 2 to 10 comprise a partial list of reports showing variations of apparent viscosity and (in some cases) shear recovery, extrudate die swell, shear modulus, and normal stress differences with total shear strain applied to polymeric liquids. Although such effects may not be significant when the total shear has exceeded a certain value, it seems intuitively likely that this limiting shear history will vary with polymer molecular weight and concentration.

Studies in which viscoelastic properties of polymer fluids have been related quantitatively to total shear have used coaxial cylinder viscometers (in rotational or translational motion) or cone-and-plate devices, since the total shear can be readily measured in such instruments. In a rotational coaxial cylinder device, for example, the rate of shear, $\dot{\gamma}$, at the wall of the bob is given by[11,12]

$$\dot{\gamma} = \frac{2\Omega r_c^2}{r_c^2 - r_b^2} \tag{1}$$

where r_c and r_b are the respective radii of the cup and bob and Ω is the angular velocity of the rotating member. Since

$$\Omega = \frac{d\theta}{dt}, \tag{2}$$

with θ the angle of rotation from rest, the total shear γ can be expressed as

$$\gamma = \int \dot{\gamma} dt = \frac{2r_c^2}{r_c^2 - r_b^2} \int_0^t \left(\frac{d\theta}{dt}\right) dt = \frac{2r_c^2}{r_c^2 - r_b^2}\theta. \tag{3}$$

Similarly, in a cone-and-plate viscometer, the total shear is

$$\gamma = \int_0^t \dot{\gamma} dt = \int_0^t \frac{\Omega}{\psi} dt = \frac{1}{\psi} \int \left(\frac{d\theta}{dt}\right) dt = \frac{\theta}{\psi} \tag{4}$$

where θ is again the total angle of rotation and ψ is the cone angle.

The total shear γ_t at the wall of a rod falling into a fluid contained in a coaxial outer cylinder is given by[4]

$$\gamma_t = \frac{(r_a^2 - r_t^2)^2 L}{r_t[(r_a^2 + r_t^2)\ln(r_a/r_t) - (r_a^2 - r_t^2)]r_a^2} \tag{5}$$

where r_t and r_a are the radii, respectively, of the rod and cylinder, and L is the immersion depth of the rod (initially zero). With this instrument, recent results in our laboratory indicate that the apparent viscosity of polymer melts varies inversely with total shear and with rate of dissipation of shear work. Estimates of other fluid properties such as recoverable shear, normal stress differences, and shear modulus seem, however, to depend only on total applied shear.

Capillary extrusion rheometers are more commonly used than the other instruments cited because of their ease of operation and similarity to industrial processing equipment for thermoplastics. Estimates of total shear in normal capillary extrusion would thus be of considerable value. This communication presents such a calculation.

CAPILLARY EXTRUSION

The apparent shear rate $\dot{\gamma}_a$ in capillary extrusion is

$$\dot{\gamma}_a = \frac{4Q}{\pi r^3} \tag{6}$$

where Q is the volumetric flow rate of the fluid and r is the orifice radius. The apparent shear stress τ_a is defined by

$$\tau_a = \frac{Pr}{2l} \tag{7}$$

where l is the orifice length and P is the observed extrusion pressure. The total shear applied in the capillary, γ_a, is

$$\gamma_a = \int_0^{t_a} \dot{\gamma}_a dt = \dot{\gamma}_a t_a \tag{8}$$

at fixed $\dot{\gamma}_a$. Here, t_a is the time under shear in the capillary. The time

t_a in eq. (8) can be evaluated by equating it to the mean residence time in the capillary on a volume transit basis[6,13,14]:

$$t_a = \frac{\pi r^2 l}{Q}. \tag{9}$$

An equivalent form for t can be written as the quotient of the capillary length l and the velocity of the fluid $v(R)$ at radial position $R(0 < R < r)$. Since the mean velocity is $Q/\pi r^2$, this reasoning leads again to eq. (9) as the mean residence time. It also indicates that the residence time is infinite at the orifice wall, since the fluid velocity is zero there if the capillary is wetted. This conclusion coincides with that reached from other considerations below.

Combination of eqs. (6), (8), and (9) gives

$$\gamma_a = \frac{4l}{r}. \tag{10}$$

The mean total shear γ_a applied in the capillary is thus seen to be a function only of orifice dimensions. When the primary data from this technique are used to estimate the apparent viscosity η_a from

$$\eta_a = \frac{\tau_a}{\dot{\gamma}_a}, \tag{11}$$

the corresponding total shear is given by eq. (10).

The effects of capillary dimensions on $\dot{\gamma}_a$ are removed by converting experimental data to true shear stress τ_w and true shear rate $\dot{\gamma}_w$ at the orifice wall. It remains now to calculate the corresponding total shear γ_w.

The wall shear rate is given by the Mooney-Rabinowitsch relation[15,16]:

$$\dot{\gamma}_w = \frac{4Q}{\pi r^3}\left(\frac{3n+1}{4n}\right) = \dot{\gamma}_a\left(\frac{3n+1}{4n}\right) \tag{12}$$

where

$$n = \frac{d \log \tau_w}{d \log \dot{\gamma}_a}. \tag{13}$$

The wall shear stress τ_w can be estimated by several methods. One technique equates τ_w to the τ_a measured in a very long capillary. In that case, γ_w is very large or infinite in the limit, eq. (10).

A more convenient approach to τ_w uses the Bagley end-correction method[17] in which the extrusion pressure required for a given $\dot{\gamma}_a$ is plotted linearly against the l/r ratios of a series of orifices. The resulting negative intercept on the l/r axis is the end correction e in the relation

$$\tau_w = P/2\left(\frac{l}{r} + e\right). \tag{14}$$

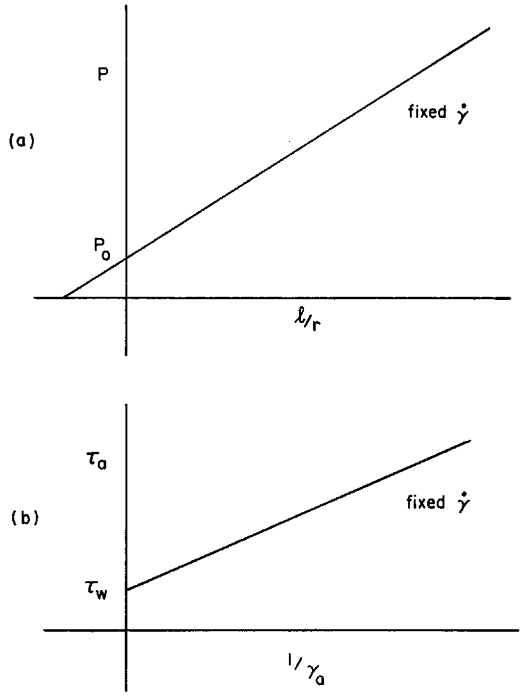

Fig. 1. End-correction plot: (a) extrusion pressure vs. orifice dimensions; (b) shear stress vs. reciprocal total shear.

Another method uses two capillaries with different lengths and identical radii.[18] Comparison of extrusion pressures at given $\dot{\gamma}_a$ yields

$$\frac{P_1 - P_2}{l_1 - l_2} = \frac{2\tau_w}{r} \tag{15}$$

where the subscripts refer to corresponding lengths and pressures.

Both the latter techniques are consistent with the plot in Figure 1a. This relation can be represented as

$$P = P_0 + 2\tau_w(l/r) \tag{16}$$

where P_0 is the (extrapolated) extrusion pressure with a zero-length orifice.

Equations (7) and (16) give

$$\tau_a = \frac{P_0 r}{2l} + \tau_w \tag{17}$$

From eq. (10),

$$\tau_a = \tau_w + \frac{2P_0}{\gamma_a}. \tag{18}$$

Equation (18) (depicted in Fig. 1b) shows that τ_w is τ_a at infinite total shear. Thus, the last two methods cited for estimating τ_w and the use of a very long capillary are all equivalent to adjusting the experimental data to conditions of infinite applied shear in the capillary. This conclusion can, of course, be reached directly from the considerations mentioned above of residence time as a function of radial position of the fluid in the capillary.

Apparent viscosity can be investigated as a function of total shear by using capillaries of various l/r ratios with eq. (10). The limiting value, at infinite total shear, is obtained as shown from τ_w and $\dot{\gamma}_w$.

It should be noted that t_a and γ_a, eqs. (9) and (10), refer to the mean residence time and applied shear in the capillary. The corresponding values at the capillary wall are t_w and γ_w. Both the latter quantities are infinitely large, if the polymer fluid does not slip on the orifice wall. Apparent viscosity can be measured at finite γ_a and at infinite total shear γ_w, as shown above. Elastic parameters of the fluid can, however, only be measured at γ_a. It seems likely that the elastic nature of polymer fluids is insignificant under applied shear corresponding to γ_w.

DISCUSSION

Equation (10) is consistent with several well-known observations in capillary extrusion. For example, the apparent viscosity η_a decreases with increased l/r ratio at fixed $\dot{\gamma}_a$ up to a limit beyond which further increases in (l/r) have no significant effect.[19,20] Such phenomena are also observed in other viscometers in which total shear or time of shearing are directly measurable.

Die swell is known to decrease with increasing l/r ratio at fixed shear rate, and this change can be related to transit time in the capillary.[14,21] From eq. (10), however, an alternate relation is available in terms of total shear. The latter relation is perhaps more easily interpreted in terms of behavior of an elastic, entangled network. Die swell, which is measureable only in capillary viscometers, can be compared at equivalent total shear with elastic parameters available from other instruments.

An alternative derivation to that presented would consider t to be total time under shear, rather than time in the capillary. In that case, the effective length/radius ratio of the orifice is $(l/r) + e$, where e is the Bagley end correction, and eq. (10) would be amended to

$$\gamma'_a = 4\left(\frac{l}{r} + e\right). \tag{10a}$$

The calculated total shear could differ, then, from those estimated from eq. (10), but the conclusion that τ_w and $\dot{\gamma}_w$ correspond to infinite total shear would still apply.

Some qualification of the term "infinite total shear" is appropriate. Experimental observations in capillary and other viscometers indicate that increased severity of shear history, as reflected in γ, may eventually produce a rheological state which does not change significantly with further increase in γ_a. This state is thus equivalent to that at infinite γ_a. These conditions may be experimentally accessible at finite γ_a for polymer systems which do not have extensive entanglement networks, because of low polymer molecular weight, low concentration, high branch frequency, and so on. For other polymer systems, however, the infinite total shear rheological state will be attainable only by extrapolation.

The total shear estimated in this article is that applied in the capillary, or in the capillary and entrance region if eq. (10a) is used instead of eq. (10). Screw extruders produce considerable shear in the reservoir as well, and the behavior of fluids sensitive to shear history differs between screw-fed and gas- or piston-driven extruders.[22]

The considerations described above show that the analysis presented leads to reasonable results. A cause-and-effect relation between total applied shear and viscoelastic properties of polymer fluids in capillary extrusion has, nevertheless, not been established, since other explanations can be offered for all the observed effects. The analysis is, however, open to experimental testing. The same fluid should behave comparably in capillary and other viscometers at equivalent total shear if the reasoning outlined here is correct and if total shear is the dominant factor in shear history. Preliminary results from this laboratory indicate that apparent viscosity is influenced by shear work dissipated as well as by total shear, but other parameters such as normal stress differences respond directly to total applied shear.

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