and to keep x_6 from changing, it is necessary to choose

$$u_2 = -(ax_5 + bx_6)/c \qquad (4)$$

These are the two equations proposed by Schlossmacher (1973) to keep x_1 and x_6 at 0.000.

Here, it is proposed to use Equation (3) if x_1 is at its upper bound and if the control law calculated from the unconstrained optimal control policy would tend to cause the upper bound on x_1 to be surpassed. Similarly, it is proposed to use Equation (4) if x_6 is at its upper bound and if the control calculated from the unconstrained optimal control policy would tend to cause the upper bound on x_6 to be violated.

In order to obtain a feedback control law for the time-optimal control problem, the procedure presented by Bennett and Luus (1971) may be used. Here, however, a different optimization procedure is used to obtain the best value of the weighting matrix in the quadratic form. The optimization procedure of Luus and Jaakola (1973) is used instead of the procedure developed by Rosenbrock (1960) since it gives considerably better results.

The time-optimal control problem was solved with $K_1 = 0.125$ and various values for K_2. As is shown in Figure 1, it takes longer to reach the origin when K_2 is reduced, that is, when the upper constraint on x_6 is stiffened.

In Figure 2 is shown the control policy when K_6 is taken to be 0.10 and Figure 3 shows the trajectories of x_1, x_3, and x_6 corresponding to this control action. It can be readily seen that the origin is reached rapidly and x_6 is kept below its allowed constraint at all times. Therefore, if control action has a direct effect on the time derivative of a state variable, that state variable may be constrained and the time-optimal problem can be readily handled by the proposed procedure.

It should also be noted that in the absence of constraints the present procedure allows the origin to be reached in 4.8 min. (with a sampling time of 0.5 min.). This is considerably better than 6.0 min. reported by Bashein (1971) for the same problem. Therefore, the procedure which is expected to give only suboptimal results has yielded better results than are possible with a modified linear programming procedure.

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Measurement of Yield Stresses in Thermoplastic Polymer Melts by the Capillary Rise Method

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Wolpert and Wojtkowiak (1972) have recently reported that the leveling of a polymer powder paint is possibly inhibited by a very low level yield stress property of the melt. The data reported in the Wolpert paper can be explained by a yield stress of about 30 dynes/cm^2 if the melt surface tension is near 30 dynes/cm. Since these very low stress levels for melts are beyond the strain rate capabilities of ordinary viscometric and rheogoniometric devices, we decided to try a more sensitive tool—the capillary rise experiment. We report analyses of the equilibrium rise of a yield-stress fluid and the rise rate of a Bingham fluid as well as the results of one experiment.

THEORY

The equilibrium rise of a Newtonian fluid is characterized by the balance of surface tension forces against gravitational forces. This balance reads, for the configuration in Figure 1:

$$2\sigma\pi R \cos\beta = \rho g \pi R^2 l_2 \sin\theta \qquad (1)$$

where σ is the fluid surface tension, β is the contact angle between the capillary surface and the fluid, ρ is the fluid density, and g is the acceleration of gravity. Equation (1) may be solved for the capillary rise l_2

$$l_2 = \frac{2\sigma \cos\beta}{\rho g R \sin\theta} \qquad (2)$$

Thus, for a given fluid l_2 may be made as large as desired by decreasing the capillary diameter and decreasing the angle θ.

If the fluid possesses a yield stress, the equilibrium capillary rise will be limited by an additional force. Surface tension forces will be balanced against the sum of gravitational and yield forces, and in place of Equation

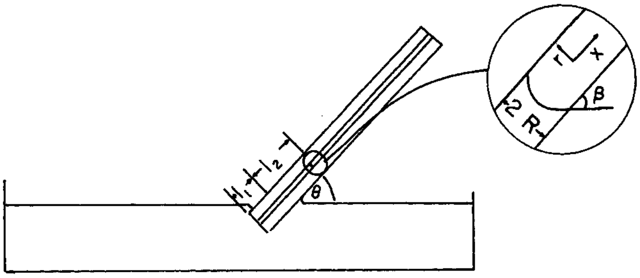

Fig. 1. Schematic of capillary rise

(1), one has

$$2\sigma\pi R\cos\beta = \rho g\pi R^2 l_2 \sin\theta + 2\tau_y \pi R(l_1 + l_2) \qquad (3)$$

where τ_y is the yield stress. Again, solving for the capillary rise,

$$l_2 = \frac{2\sigma\cos\beta - 2\tau_y l_1}{\rho g R\sin\theta + 2\tau_y} \qquad (4)$$

It is clear from Equation (4) that the capillary rise is limited to small values unless τ_y is identically zero. Equation (4) also allows for a capillary depression even when the contact angle is positive. Clearly, to experimentally measure τ_y one wishes to make l_1 as large as practically possible. Equation (4) may be used for determination of the yield stress:

$$\tau_y = \frac{2\sigma\cos\beta - \rho g R l_2 \sin\theta}{2(l_1 + l_2)} \qquad (4a)$$

DYNAMICS

To do a capillary rise experiment with a polymer melt requires a lengthy rise time. To get some idea of the dynamics of the experiment, one must examine the behavior of a particular yield-stress fluid. The simplest such fluid is the Bingham plastic (see Fredrickson, 1964) whose stress above the yield stress is related linearly to shear rate, for example, in simple Couette shearing:

$$\tau = \tau_y + \mu_p \frac{du}{dy} \quad \text{if} \quad \tau > \tau_y$$

$$\frac{du}{dy} = 0 \quad \text{if} \quad \tau \leqq \tau_y$$

It is clear that with the very high viscosity of melts, the dynamics may be described by a pseudo steady state. Washburn (1921) and recently Szekely et al. (1971) have thus described capillary rise of ordinary viscous liquids. Assume that the pressure gradient driving the fluid up the capillary is given by the time dependent departure from the equilibrium of Equation (3) and that the surface tension parameter $\sigma\cos\beta$ is constant. We have then, in the cylindrical polar coordinates defined in Figure 1:

$$0 = \frac{1}{r}\,\frac{\partial(\tau_{rx} r)}{\partial r} - \frac{\partial p}{\partial x} - \rho g \sin\theta \qquad (5a)$$

$$\tau_{rx} = -\tau_y + \mu_p \frac{\partial u_x}{\partial r} \ (\text{for } r > R_y \text{ where } \tau_{rx}(R_y) = -\tau_y) \qquad (5b)$$

$$-\frac{\partial p}{\partial x} = \frac{\dfrac{2\sigma\cos\beta}{R} + l_1 \rho g \sin\theta}{l_1 + l_2} \qquad (5c)$$

The momentum equation (5a) is readily solved

$$\tau_{rx} = -\left(-\frac{\partial p}{\partial x} - \rho g \sin\theta\right)\frac{r}{2} \equiv -\tau_w \frac{r}{R} \qquad (6)$$

so that

$$R_y = \frac{2\tau_y}{-\dfrac{\partial p}{\partial x} - \rho g \sin\theta} \qquad (7)$$

and equilibrium is reached when $R_y = R$ or $\tau_w = \tau_y$. The average velocity may now be calculated, and the result is a standard one (Buckingham, 1921). The average velocity is identified with the rise rate,

$$\frac{dl_2}{dt} = \frac{d(l_1 + l_2)}{dt} \equiv \frac{dl}{dt}:$$

$$\overline{u} = \frac{dl}{dt} = \frac{R\tau_w}{4\mu_p}\left\{1 + \frac{1}{3}\left(\frac{\tau_y}{\tau_w}\right)^4 - \frac{4}{3}\,\frac{\tau_y}{\tau_w}\right\} \qquad (8)$$

where

$$\tau_w = \frac{2\sigma\cos\beta - R l_2 \rho g \sin\theta}{2l} \qquad (9)$$

Equation (8) may be further simplified:

$$\frac{d\lambda^2}{d\xi} = 1 - \left(1 + \frac{4}{3}\Gamma\right)\lambda + \frac{1}{3}\Gamma^4 \frac{\lambda^4}{(1-\lambda)^3} \qquad (10)$$

where we have defined

$$\Gamma \equiv \frac{2\tau_y}{R\rho g \sin\theta}, \quad \text{a dimensionless yield stress} \qquad (11a)$$

$$\lambda \equiv l\,\frac{R\rho g \sin\theta}{2\sigma\cos\beta + R l_1 \rho g \sin\theta}, \quad \text{the dimensionless rise} \qquad (11b)$$

$$\xi \equiv t\,\frac{R(R\rho g \sin\theta)^2}{4\mu_p(2\sigma\cos\beta + R l_1 \rho g \sin\theta)}, \quad \text{dimensionless time} \qquad (11c)$$

The results may be expressed then as a one-parameter family of curves of λ versus ξ with Γ as the parameter. Figure 2 shows this plot for four representative values of the yield stress parameter. Note that the approach to equilibrium is faster for a fluid with finite yield stress than it is for a Newtonian fluid. The appropriate initial condition for (10) is $\lambda = 0$ at $\xi = 0$, and the steady state value of λ (as $\xi \to \infty$) is $\lambda = 1/1 + \Gamma$.

It is clear from the formulation, Equations (8) to (11), that the dynamics enable one to determine the viscosity μ_p if $\sigma\cos\beta$ is known. That is, the initial rate, dl^2/dt is inversely proportional to the viscosity:

$$\mu_p = \frac{R(2\sigma\cos\beta + R l_1 \rho g \sin\theta)}{4\dfrac{dl^2}{dt}} \qquad (12)$$

If the fluid can indeed be characterized as a Bingham plastic, the quantity μ_p should be simply the ordinary zero shear or plateau viscosity.

EXPERIMENT

A very simple but long-duration experiment was carried out to determine the yield stress of Fisher Scientific poly(methylmethacrylate). The powdered polymer was placed in a watch glass and was melted in a nitrogen atmosphere at 220°C. A carefully cleaned glass capillary tube of 0.15-cm. inside diameter was then inserted at an angle of 20° into the melt. This assembly was then held in a nitrogen-purged oven at 220°C for approximately 26 days. We made the experiment of very long duration because we were uncertain as to the viscosity of the melt and wanted to ensure a close approach to equilibrium. Essentially all of the rise occurred over the first seven to ten days and no further rise could be detected after this period.

RESULTS

As we note in the discussion, the interpretation of the experiment is open to some question, however, our best estimates from the experiment are

$$l_2 = 0.40 \pm 0.1 \text{ cm}$$

$$l_1 + l_2 = 1.70 \pm 0.05 \text{ cm}$$

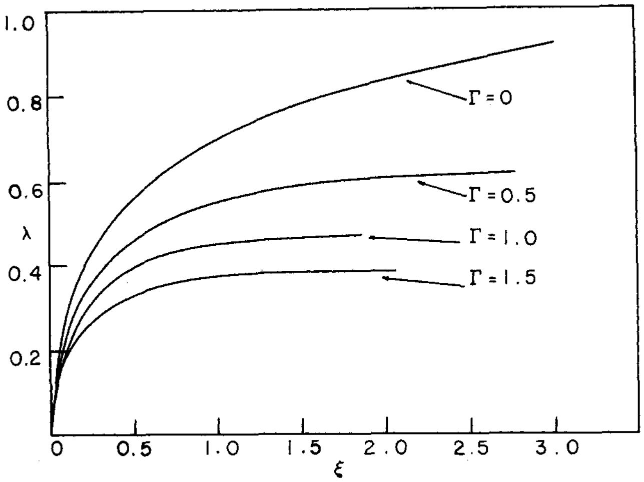

Fig. 2. Solution to the dynamic equations (10).

$$\beta = 30°$$

To complete Equation (4a) requires some other values:

$\theta = 20°$
$R = 0.075$ cm
$\rho = 1.18$ g/cm^3 (from Brandrup and Immergut, 1966)
$\sigma = 30$ dynes/cm (the same estimated value used by Wolpert and Wojtkowiak, 1972)

Equation (4a) then gives $\tau_y = 12$ dynes/cm^2 for this melt.

DISCUSSION

The nonzero yield stress obtained in this experiment is, of course, surprising in the light of accepted notions of the rheological properties of straight-chain thermoplastic polymer melts. The emphasis in the present paper is on the capillary rise experiment as a means of measuring yield stresses, and we report our experiment as a preliminary, nondefinitive result. The exact nature of the polymer which we used is uncertain so that there may be some degree of branching which results in a low yield structure not ordinarily present in thermoplastics. Additionally, it is possible that some cross-linking or other polymerization occurred over the long duration of this experiment. This awaits further investigation.

While we have confidence in the order of magnitude of the measured yield stress, because of experimental uncertainties there is some question as to the precise value of this yield stress.

Bubbles

During the period of melting, small bubbles of monomer and probably of nitrogen appeared in the otherwise homogeneous melt. These bubbles adhered to the watch glass, dimpled the surface, and even found their way into the capillary tube. The qualitative effect of these bubbles should be to reduce the effective density ρ in Equation (4a) and thus to increase the yield stress. The presence of the bubbles also led to some uncertainty in the position of the free surface of the melt. The bubbles could probably be eliminated by melting the polymer slowly under vacuum.

Contact Angle on the Inclined Tube

The experiment was designed and carried out before the analysis was done properly. We had believed that the tube needed to be inclined to measure very low yield stresses. The inclination of the tube made for a further difficulty in interpretation. The surface was depressed on one side of the tube and elevated on the other side so that the exact position of free surface relative to the capillary height was uncertain. This problem can be corrected by simply orienting the capillary vertically.

Surface Tension

The value of surface tension used here is not a measured one, but it is an estimate based on typical values for organic liquids. If the yield stress is nonzero, any equilibrium measurement of surface tension will be affected; however, the capillary rise experiment can be used to determine both τ_y and σ. For two experimental runs with the same diameter capillary, but at two different depths of immersion. l_1 and l_1', Equation (4) gives

$$\sigma\cos\beta = \frac{\rho g R \sin\theta}{2} \, \frac{l_2' l_1 - l_2 l_1'}{l_1 + l_2 - l_1' - l_2'} \tag{13}$$

$$\tau_y = \frac{\rho g R \sin\theta}{2} \, \frac{l_2 - l_2'}{l_1 + l_2 - l_1' - l_2'} \tag{14}$$

Since these very low stresses are difficult to measure, the existence of a yield stress may possibly be a rather general occurrence amongst polymer melts. The usual rheogoniometric data measures shear stresses in melts only down to about 300 dynes/cm^2, or one order of magnitude above that surmised by Wolpert and Wojtkowiak. The yield stress could then easily be missed. We feel that more precise measurements are called for, and this technique seems to hold promise.

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NOTATION

l_1, l_2 defined in Figure 1
$l = l_1 + l_2$
R = capillary diameter
u = velocity of fluid in the capillary
β = contact angle, Figure 1
Γ = dimensionless yield stress, Equation (11a)
θ = angle of inclination of the capillary tube, Figure 1
λ = dimensionless rise, Equation (11b)
ξ = dimensionless time, Equation (11c)
μ_p = plastic viscosity of the melt
ρ = melt density
σ = equilibrium surface tension of the polymer melt
τ_y = yield stress of the melt

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