dence time is increased, there is more time for reaction; hence more sodium hydroxide is used, and the concentration of sodium hydroxide at the outlet of the reactor starts dropping, as can be seen in Figure 3. But as soon as a time equivalent to the new residence time lapses, the concentration effect comes into play and the sodium hydroxide concentration increases. The response curve takes a reverse direction when methyl acetate flow is increased, as can be seen in Figure 4. The tests were conducted at different flow rates; it was found that for even small changes in flow rate the response followed the pattern described below.

In conclusion, there are many factors which affect reactor outlet concentration response, but the important factors that determine the shape of unsteady state response curves are changes in residence time and changes in concentration of the reactants at the inlet of the reactor. The RTD model presented in this paper satisfactorily simulates the dynamics of a tubular reactor for these types of upsets.

NOTATION

C_A = concentration of sodium hydroxide at the outlet of the reactor, mole/liter
C_{A1} = concentration of sodium hydroxide entering reactor before upset, *mole/liter (based on stream A)*
C_{A1} = actual concentration of sodium hydroxide at the inlet of the reactor, after upset (based on mixed *streams of* A and B) $= \dfrac{F_{A1}}{F_{A1}+F_{B1}} C_{AF}$ mole/liter
C_{AF} = concentration of sodium hydroxide entering reactor after upset, mole/liter (based on stream A)
C_{AS0} = steady state concentration of sodium hydroxide at the outlet of the reactor before upset, mole/liter
C_{AS1} = steady state concentration of sodium hydroxide at the outlet of the reactor after upset, mole/liter
C_{A0} = actual concentration of sodium hydroxide at the inlet of the reactor before upset (based on mixed streams of A and B) $= \dfrac{F_{A0}}{F_{A0}+F_{B0}} C_{AI}$ mole/liter
C_{B1} = concentration of methyl acetate entering reactor before upset, mole/liter (based on stream B)
C_{B1} = actual concentration of methyl acetate at the inlet of the reactor, after upset, (based on mixed streams of A and B) $= \dfrac{F_{B1}}{F_{A1}+F_{B1}} C_{BF}$ mole/liter
C_{B0} = actual concentration of methyl acetate at the inlet of the reactor, before upset (based on mixed streams of A and B) $= \dfrac{F_{B0}}{F_{A0}+F_{B0}} C_{BI}$ mole/liter
C_{BF} = concentration of methyl acetate entering reactor after upset, mole/liter (based on stream B)
F_{A1} = flow rate of sodium hydroxide after upset, liter/min.
F_{B1} = flow rate of methyl acetate after upset, liter/min.
F_{A0} = flow rate of sodium hydroxide before upset, liter/min.
F_{B0} = flow rate of methyl acetate before upset, liter/min.
M_0 = $C_{B0} - C_{A0}$
N_0 = C_{B0}/C_{A0}
$-r_A$ = reaction rate, moles/(liter)(min.)
t = time
T_1 = residence time after upset, $V/(F_{A1} + F_{B1})$ min.
T_0 = residence time before upset, $V/(F_{A0} + F_{B0})$ min.
V = volume of reactor, liter
X_A = conversion of A
τ = space time

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Stretching of Viscoelastic Liquids

M. M. DENN and G. MARRUCCI
University of Delaware, Newark, Delaware

Analyses of stretching of a viscoelastic liquid have been interpreted as showing that there is a maximum stretch rate to which the material can be subjected, and several physical phenomena have been explained on this basis. It is shown here theoretically and experimentally that the concept of a limiting stretch rate does not have general validity.

Analyses of the stretching of a viscoelastic liquid have been interpreted to show that extremely large tensile stresses will be experienced in elongational processes which are rapid relative to a characteristic liquid relaxation time (*6, 7*). We show here that the notion of a limiting stretch rate does not have general validity.

THEORY

We assume that the liquid behavior can be represented by a convected Maxwell model

$$\tau^{ij} + \lambda \frac{\mathfrak{d}\tau^{ij}}{\mathfrak{d}t} = 2\,\mu d^{ij} \tag{1}$$

$$T^{ij} = -\,p g^{ij} + \tau^{ij} \tag{2}$$

Here $\mathfrak{d}/\mathfrak{d}t$ is Oldroyd's derivative

$$\frac{\mathfrak{d}\tau^{ij}}{\mathfrak{d}t} = \frac{\partial \tau^{ij}}{\partial t} + v^k \tau^{ij}{}_{,k} - \tau^{kj} v^i{}_{,k} - \tau^{ik} v^j{}_{,k} \tag{3}$$

We visualize the stretching of a column of liquid whose axis is oriented in the x^1 direction, for which the kinematics are represented in Cartesian coordinates by

$$v^1 = \Gamma(t) x^1, \quad v^2 = -\frac{1}{2}\Gamma(t) x^2 \quad v^3 = -\frac{1}{2}\Gamma(t) x^3 \tag{4}$$

$\Gamma(t)$, the stretch rate, is an arbitrary function of time. Equation (1) then reduces to the uncoupled system

$$\tau^{11} + \lambda \left[\frac{\partial \tau^{11}}{\partial t} - 2\Gamma(t)\tau^{11} \right] = 2\,\mu\Gamma(t) \tag{5}$$

G. Marrucci is at the University of Naples, Naples, Italy.

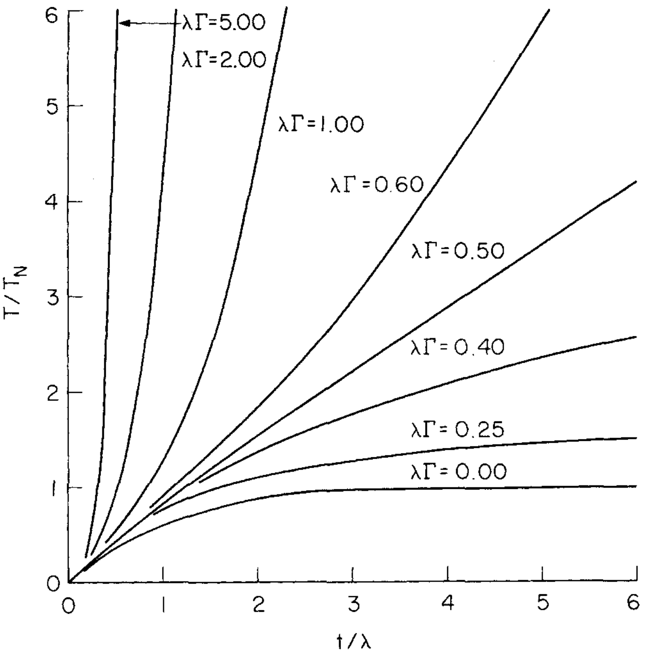

Fig. 1. Tensile stress relative to Newtonian tensile stress versus time relative to relaxation time.

$$\tau^{22} + \lambda\left[\frac{\partial \tau^{22}}{\partial t} + \Gamma(t)\tau^{22}\right] = -\mu\Gamma(t) \qquad (6)$$

The stretching of a liquid element is a transient process for which the virgin state, defined as $t = 0$, is unstressed.

Equations (4) and (5) are readily integrated to yield

$$\tau^{11} = \frac{2\mu}{\lambda}\int_0^t \exp\left[-\int_\xi^t \left(\frac{1}{\lambda} - 2\Gamma(\sigma)\right) d\sigma\right] \Gamma(\xi)d\xi \qquad (7)$$

$$\tau^{22} = -\frac{\mu}{\lambda}\int_0^t \exp\left[-\int_\xi^t \left(\frac{1}{\lambda} + \Gamma(\sigma)\right) d\sigma\right] \Gamma(\xi)d\xi \qquad (8)$$

The condition of a free surface in the direction normal to the axis of stretching requires that T^{22} be zero, in which case we obtain the total axial stress as

$$T^{11} = \tau^{11} - \tau^{22} = \frac{\mu}{\lambda}\int_0^t \exp\left[-(t-\xi)/\lambda\right] \left\{2\exp\left[2\int_\xi^t \Gamma(\sigma)d\sigma\right] + \exp\left[-\int_\xi^t \Gamma(\sigma)d\sigma\right]\right\} \Gamma(\xi)d\xi \qquad (9)$$

For simplicity we denote T^{11} by T, v^1 by v, and x^1 by x. Utilizing the kinematics, one can express Equation (9) as

$$T = \frac{\mu}{\lambda}\int_0^t \exp\left[-(t-\xi)/\lambda\right] \left\{2\left(\frac{x(t)}{x(\xi)}\right)^2 + \frac{x(\xi)}{x(t)}\right\} \Gamma(\xi)d\xi \qquad (10)$$

The tensile stress in a Newtonian liquid, which we denote by T_N, is obtained by taking the limit of Equation (10) as λ goes to zero:

$$T_N = \lim_{\lambda \to 0} T = 3\,\mu\Gamma(t) \qquad (11)$$

Equation (11) is the usual Trouton result, in which the tensile stress is proportional to the instantaneous stretch rate.

CONSTANT STRETCHING

The limiting case of constant stretching is most easily analyzed and has been used frequently to interpret physical phenomena. Here Γ is a constant and the kinematics are

$$x = x_0 e^{\Gamma t} \qquad v = \Gamma\, x_0 e^{\Gamma t} \qquad (12)$$

Equation (10) can then be integrated to give

$$T = \frac{3\,\mu\Gamma}{(1-2\lambda\Gamma)(1+\lambda\Gamma)} - \frac{2\,\mu\Gamma}{1-2\lambda\Gamma}\, e^{-(1-2\lambda\Gamma)t/\lambda} - \frac{\mu\Gamma}{1+\lambda\Gamma}\, e^{-(1+\lambda\Gamma)t/\lambda} \qquad (13)$$

The limiting behavior as $t \to \infty$ for $2\,\lambda\Gamma < 1$ is simply the constant term, which contains the factor $1 - 2\,\lambda\Gamma$ in the denominator. This limiting behavior has been obtained without regard to transients in previous analyses and has been interpreted to suggest that the maximum stretch rate possible in a viscoelastic liquid is always defined by $2\,\lambda\Gamma = 1$ and that extremely large tensile stresses will always be experienced with stretching that approaches the limiting value (*6, 7*). That such reasoning is not entirely correct is demonstrated in Figure 1, where T/T_N is plotted versus t/λ for various values of $\lambda\Gamma$. In particular, at the limiting value the stress satisfies the equation

$$\frac{T}{T_N} = \frac{2}{9}\left(1 + 3\frac{t}{\lambda} - e^{-3t/2\lambda}\right) \quad \text{at} \quad 2\,\lambda\Gamma = 1 \qquad (14)$$

and does not even reach the level of stress in a Newtonian liquid until after a time slightly greater than one relaxation time. An order of magnitude increase above the Newtonian stress requires 15 relaxation times and a relative

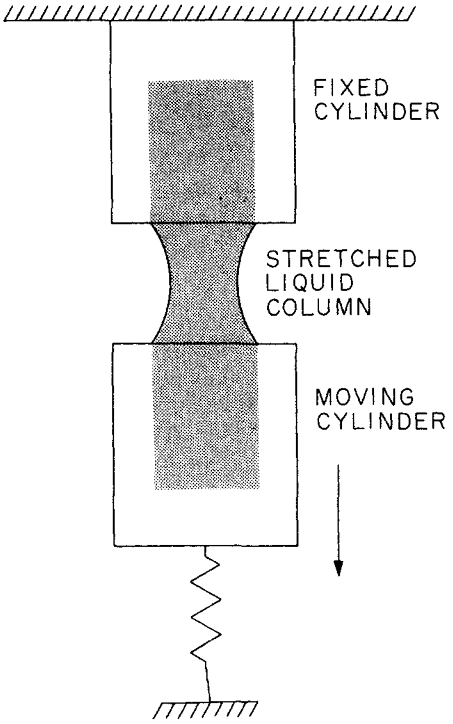

Fig. 2. Schematic diagram of experimental apparatus.

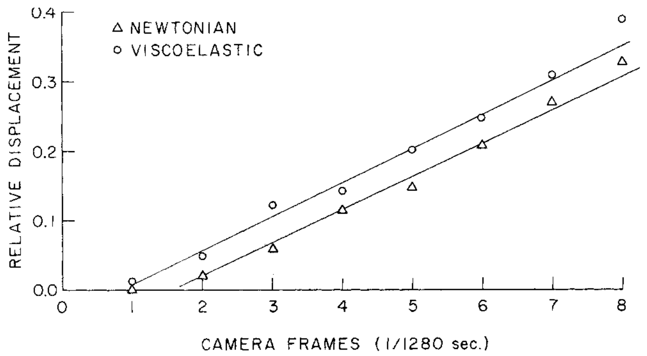

Fig. 3. Displacement of lower cylinder relative to equilibrium position versus time. Origin on the time axis is uncertain.

elongation of more than three orders of magnitude.

The curve for $2\lambda\Gamma = 1$ does represent a critical condition in the sense that for stretch rates lying below that value the rate of increase of relative tensile stress with reduced time is bounded and a finite asymptote is approached, while for higher stretch rates the increase in tensile stress is exponential and there is no finite asymptote. For $2\lambda\Gamma >> 1$ the stress behavior is approximate by

$$\lim_{\lambda\Gamma\to\infty} \frac{T}{T_N} = \frac{1}{3\lambda\Gamma}\, e^{2\Gamma t} = \frac{1}{3\lambda\Gamma}\left(\frac{x}{x_0}\right)^2 \tag{15}$$

EXPERIMENTAL PROCEDURE

We have carried out a simple experimental demonstration of the absence of a limiting stretch rate in a viscoelastic liquid. The apparatus is shown in Figure 2. A liquid column is held by two cylinders, the lower pulled rapidly downward by a strong spring. The cylinders are initially flush, and the motion of the lower cylinder is initiated by shearing a pin which also breaks an electrical circuit and starts a high-speed motion picture camera operating at 1,280 frames/sec. The filled mass of the lower cylinder is $m = 1{,}820$ g. and the spring constant $k = 6.34 \times 10^7$ dynes/cm., which for the Newtonian liquid used here results in a contribution to the motion of the lower cylinder from liquid tensile forces which are estimated to be three orders of magnitude less than the spring force. The position and velocity of the lower cylinders are then approximated by a simple mass spring system, and estimated stretch rates are in excess of 100 sec.$^{-1}$.

Data were obtained on a Newtonian liquid of 86% (volume) glycerine in water, with a viscosity of 0.91 poise, and a viscoelastic liquid of 0.15% (weight) Separan AP30 in 15% (weight) glycerine and water. The latter (known locally as Supergoop) is characterized on a Weissenberg rheogoniometer by

$$\tau^{12} = 17.3\,\gamma^{0.43} \tag{16}$$

$$\tau^{11} - \tau^{22} = 108\,\gamma^{0.59} \tag{17}$$

where the stresses are measured in dynes per square centimeter and the shear rate γ in reciprocal seconds. λ is calculated from the equation

$$\lambda = \frac{\tau^{11} - \tau^{22}}{2\,\gamma\,\tau^{12}} \tag{18}$$

Figure 3 shows the motion of the lower cylinder for Newtonian and viscoelastic liquids. The location of an origin is uncertain to within one camera frame. It is evident that the kinematical behavior of Newtonian and viscoelastic liquids is identical. For the data shown the stretch rates are in excess of 200 sec.$^{-1}$, leading to values of $\lambda\Gamma$ computed from Equations (16) to (18) more than an order of magnitude in excess of the critical value $\lambda\Gamma = 0.5$ over a relative time of order 0.25 t/λ. Were there any validity in the notion of a critical stretch rate, the kinematics would have been substantially altered or there would have been fracture of the liquid column, which was not observed.

DISCUSSION

The notion of a limiting stretch rate has been used to interpret numerous phenomena in viscoelastic fluid mechanics (*6, 7, 10*). The insensitivity of heat transfer probes to the external velocity field, one such phenomenon (*3, 7*) has more recently been shown (*11*) to be a consequence of changes in flow structure resulting from velocities in excess of the velocity for propagation of shear waves in a viscoelastic medium (*2*), resolving the apparent paradox of probe diameter independence implicit in the critical stretch rate analysis. Similarly, the stresses in a converging flow field have been shown to be large but finite (*4, 5*), and not adequate to explain the Uebler effect, in which a bubble is held stationary just prior to the entrance to a small tube from a large reservoir (*6*). This latter effect, too, may depend upon phenomena related to the wave velocity.

We wish to emphasize that during rapid stretching a viscoelastic material is responding like a solid, as suggested in several previous publications (*1, 8*) and illustrated nicely by Middleman (*9*), who implicitly employs some of the observations of this paper. In the case of stretching, however, over a significant time scale solid-like behavior implies small stresses rather than large.

ACKNOWLEDGMENT

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NOTATION

d^{ij} = deformation rate tensor
g^{ij} = metric tensor
p = isotropic pressure
t = time
T = tensile stress
T_N = Newtonian tensile stress
T^{ij} = total stress tensor
x^i = position
v^i = velocity

Greek Letters

γ = shear rate
Γ = stretch rate
λ = relaxation time
μ = viscosity
τ^{ij} = extra stress tensor

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