Abstract

The break-up of capillary jets of very viscous and jellified non-Newtonian liquids has been investigated. Inelastic liquids with strongly shear-dependent viscosities were found to exhibit instabilities very similar to the instability of a Newtonian liquid possessing a viscosity corresponding to the average viscosity inside the capillary. Elastic fluids with strong normal forces having similar shear viscosities, however, were found to be stable. The instabilities observed with the inelastic fluids are related to the time needed to reform the structure of the liquid. For example, it was shown that dilute Carbopol solutions are not time-independent fluids but possess a structural relaxation time which is related to the time required to reform the structure of the fluid. Guidelines are given for the choice of thickening agents when easy atomization of the material is desired.

1. INTRODUCTION

In many practical applications involving atomization, it would be desirable to utilize an additive which thickens the liquid at low shear rates, either to keep solids dispersed or prevent sloshing, while retaining the liquid's ease of atomization under high shear conditions. For Newtonian fluids, the two requirements are not coincident as highly viscous liquids are difficult to atomize\(^1\)\(^-\)\(^3\). Pseudoplastic liquids with shear-thinning properties are therefore mainly used in this context.

It is well known that very viscous shear-thinning liquids vary widely in their atomization behavior. Thus, in a flame-thrower the liquid is a gel with a pronounced yield stress and will not flow at low shear stresses. It will also not atomize when extruded at very high velocities through a nozzle. In spinning applications, it is very important to be able to extrude the thread through a small nozzle at high velocity and with low pressure drop, and to prevent atomization before hardening can occur.

On the other hand, the paint industry uses thickeners to maintain pigments in dispersion and the resultant gel must be easily atomized in a spray-gun. The thickeners used by the paint industry are mostly highly thixotropic in the sense that it takes a considerable and measurable time until they regain their viscosity after being subjected to high shearing stresses.

In a previous paper\(^4\), the stability of laminar jets of non-Newtonian fluids was examined by means of a linearized stability analysis. It was shown that in non-Newtonian fluids with no finite yield stress (viscosity remaining finite as shear stress approaches zero) the growth rate of disturbances is always larger than for Newtonian fluids possessing the same zero shear viscosity. Fluids having a finite yield stress, however, could lead to a completely stable jet.

These theoretical results were surprising as they contradict experimental evidence which has shown that, in very viscous gels, elastic properties (such as high normal stresses) produce stable jets, whereas those gels which are easily atomized (such as paint thickeners) do not possess elastic properties. However, as pointed out in ref. 4, the linearized stability analysis contains one basic shortcoming which, in the present stage of the theory, is very difficult to overcome; this is the assumption that the properties of the fluid leaving the capillary are those of the fluid in a relaxed or equilibrium state. Since the fluid in the capillary is highly stressed, it will take a finite time until all of these stresses are relaxed. In addition, the gel structure of a highly viscous liquid or melt is destroyed under high shear rates and might take a finite time to reform.
In rheology we very often use the term relaxation time quite loosely, i.e. there are several time scales which can be considered to be the relaxation time. One is the time scale related to the dominant frequency of the linear viscoelastic response. Another is related to the normal stresses in a viscometric flow. A third could be the time scale in which a highly sheared liquid regains its viscosity. For a given constitutive equation such as an Oldroyd fluid these relaxation times are uniquely related. One can probably find unique relations for other classes of fluids; however, such relations are not general and only apply within each class of non-Newtonian solutions considered. The widely different behavior exhibited by shear-thinning solutions with respect to their atomization could be related to the difference in the time scale necessary to regain their viscosity after undergoing shearing stresses, or what we propose to call the structural relaxation time.

In our previous paper experiments were conducted using different non-Newtonian solutions of low or medium viscosity. It was found that highly elastic solutions such as concentrated water solutions of polyacrylamide and polyethylene oxide result in stable jets at viscosities far below those required for thickening agents. In dilute solutions of these materials, disturbances are not propagated in the form of exponentially growing waves but rather as a series of droplets connected by threads which thin with axial distance until they rupture. A typical example of the break-up of a dilute viscoelastic jet is shown in Fig. 1. What is especially interesting about the jet break-up of these fluids is that the break-up is dominated by non-linear phenomena very similar to those observed in Newtonian jets excited by low-frequency acoustic disturbances, as shown by Donnelly and Glaberson.

Another phenomenon of interest described in ref. 4 is that dilute but fairly viscous water solutions of Carbopol 934 show a break-up length less than that of water. This is surprising as our theoretical results indicated that the growth rate of disturbances in any non-Newtonian liquid would always be lower than in an inviscid liquid and yet, under the conditions of comparison, water can be assumed to behave like an inviscid liquid. It could be that the relaxation process outside the capillary introduces some initial disturbances of larger amplitude than those appearing in a water jet.

The surprising results with Carbopol solutions as well as the fact that certain thickeners lead to gels which are relatively easy to atomize led us to study in more detail the behavior of very viscous and jellified solutions of shear-thinning materials. Since highly elastic materials cannot be atomized, we thought it would be important to determine if the lack of normal stresses in a non-Newtonian liquid is related to easier atomization. Therefore, we decided to investigate additives whose solutions were rheologically similar to Carbopol, i.e. materials having a shear-thinning viscosity, an absence of elastic phenomena and large thixotropic effects relative to the lifetime of the jet. It was on the basis of these criteria that the test fluids were chosen.

2. THEORETICAL RELATIONS

A capillary jet emerging from a nozzle into the surroundings has small disturbances superimposed on its motion arising from sources such as microscopic burrs on the nozzle wall or from external vibrations. When air resistance can be neglected, Weber has shown that the growth rate of symmetrical disturbances in a Newtonian capillary jet can be obtained from the following secular equation.

\[
F_1 \alpha^2 + \frac{3\eta_0 (Ka)^2 F_2 \alpha}{\rho a^2} = \frac{\sigma (Ka)^2 [1 - (Ka)^2]}{2\rho a^3}
\]

In eqn. (1), the Newtonian fluid of density \( \rho \), viscosity \( \eta_0 \) and surface tension \( \sigma \) flows through a capillary of radius \( a_0 \) producing a jet of radius \( a \). Disturbances

propagate as exponentially growing waves with a growth rate \( \alpha \) corresponding to a wave number \( Ka = 2\pi a/\lambda \), where \( \lambda \) is the disturbance wavelength. The quantities \( F_1 \) and \( F_2 \) involve ratios of Bessel functions of arguments \((Ka)\) and \((la)\) and are given as

\[
F_1 = \frac{Ka}{2} \frac{I_0(Ka)}{I_1(Ka)} \left( \frac{l^2 + K^2}{l^2 - K^2} \right)
\]

and

\[
F_2 = \frac{Ka}{3} \left[ \frac{I_0(Ka)}{I_1(Ka)} + \frac{I_1(Ka)}{I_1(la)} \left( \frac{l^2 + K^2}{l^2 - K^2} \right) \times \left( 1 - \frac{2Kl}{l^2 + K^2} \right) \right]
\]

where

\[
l^2 = K^2 + \alpha / \eta_0
\]

For the experimentally observed case of \( \lambda \gg a \), the Bessel function ratios are approximately equal to unity, so that \( F_1 \approx F_2 \approx 1 \). The jet will be destroyed by the fastest growing disturbance \( \alpha^* \), which is obtained as the solution to \( \partial \alpha / \partial (Ka) = 0 \). Weber assumed the jet break-up time to be inversely proportional to \( \alpha^* \) so that

\[
L = CV/\alpha^*
\]

where \( L \) is the break-up length and \( V \) is the average velocity of the jet, and obtained an expression for the break-up length as

\[
\frac{L}{2a} = C \left( \frac{We^{1/2}}{Re} + \frac{We}{Re} \right)
\]

Here the Weber number is defined as \( We = 2\rho a V^2 / \sigma \) and the Reynolds number is given by \( Re = 2aV / \eta a \). Weber reported a value of 12 for the proportionality constant \( C \), based on the data of Haenlein. Grant and Middleman \(^1\) found, however, that the theory is only in qualitative agreement with experimental data beyond the maximum. They were able to improve the agreement in this region by using empirical correction factors for \( F_3 \) in eqn. (8) and for the constant \( C \) in eqn. (5) which are based on the value of the Ohnesorge number, \( Z_0 = (We_0)^{1/2} / Re_0 \).

3. EXPERIMENTAL RESULTS

3.1 Test fluids

The test fluids consisted of Carbopol-water solutions and dispersions of the following substances:

- MPA 60 in xylene, MPA 60 in odorless mineral spirits and silica EH-5 in water. These fluids all possess a yield stress which will require a finite time to form or break down upon removal of shearing stress. No drag-reducing properties have been observed. MPA 60 is a hydrogenated castor oil derivative which is thixotropic in nature. It has a gellation time of several hours and was chosen in order to see the effects of a fluid whose structural formation time clearly exceeded the jet break-up time. Silica particles are often used in

TABLE 1

Physical properties of the test fluids

<table>
<thead>
<tr>
<th>Test fluid</th>
<th>Concentration</th>
<th>Density (g/cc)</th>
<th>Surface tension</th>
<th>Yield stress (dyn/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbopol 934</td>
<td>0.2% in water*</td>
<td>1</td>
<td>not measurable</td>
<td>8</td>
</tr>
<tr>
<td>(carboxy polymethylene: B. F. Goodrich Co.)</td>
<td>0.6% in water*</td>
<td>1</td>
<td>not measurable</td>
<td>55‡</td>
</tr>
<tr>
<td>MPA 60</td>
<td>24% in xylene</td>
<td>0.872</td>
<td>32.5</td>
<td>800</td>
</tr>
<tr>
<td>(hydrogenated castor oil derivative: Baker Castor Oil Co.)</td>
<td>24% in odorless mineral spirits</td>
<td>0.816</td>
<td>26.0</td>
<td>800</td>
</tr>
<tr>
<td>Silica EH-5</td>
<td>12.4% in water†</td>
<td>1.16</td>
<td>not measurable</td>
<td>2000</td>
</tr>
<tr>
<td>(Cabot Co.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* neutralized with 0.4 g of sodium hydroxide per gramme of Carbopol.
† Triton X-100 (Rohm and Haas Co.) wetting agent added.
‡ Yield stress obtained from Fischer et al.9

formulations to gellify a material when at rest and to impart controlled flow properties under shear flows.

Table 1 lists the test fluids along with some of their pertinent physical properties. Surface tensions for the MPA 60 dispersions were obtained on a Rossano tensiometer by heating the fluids to elevated temperatures, where their gel structure was temporarily destroyed, and extrapolating the data back to room temperature. This technique was ineffective with the Carbopol solutions as well as the silica dispersion because they remained gellified at the elevated temperature and were impervious to the platinum measuring element.

Yield stresses were obtained on the Stormer and Brookfield viscometers, modified so as to produce mathematically treatable data. The procedures used for the measurements and the required end corrections on the rotor are fully described for each instrument by Van Wazer et al.14. Several hours were allowed to elapse in order to detect any movement of the rotor while under an applied torque. This criterion will not detect any fractional revolution of the rotor at rates

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Fig. 2a

Shear stress (dyn/cm²) vs. Shear rate (sec⁻¹)

Fig. 2b

Shear stress (dyn/cm²) vs. Shear rate (sec⁻¹)

Fig. 2. Shear stress/shear rate relations for the test fluids. ▲ 24% MPA 60 in xylene; ● 24% MPA 60 in mineral spirits; ■ 12.4% silica in water; ◼ ● 0.2% Carbopol; □ ● 0.6% Carbopol; --- 0.25% Separan from the data of refs. 17 and 18; unfilled symbols for coaxial cylinder data, filled symbols for capillary viscometer data.

slower than this time period. Values reported for the yield stress of the MPA 60 dispersions are of uncertain accuracy because of the tendency to separate from the rotor while undergoing gellation.

Shear stress/shear rate data at low-medium shear rates were obtained on the modified Stormer and Brookfield viscometers for the Carbopol solutions. Similar measurements could not be acquired with the MPA 60 dispersions because of their thixotropic behavior, while the silica dispersion separated from the rotor, once motion commenced, and did not flow back. At medium-high shear rates, a capillary viscometer was employed. End corrections were eliminated by using two capillaries of the same diameter, but of differing length, at each volumetric flow rate, as discussed by Fredrickson. The relations for calculating shear stresses and shear rates from viscometer data are available in ref. 16. Figure 2 shows the combined results from the coaxial cylinder viscometer and the capillary viscometer for each of the test fluids. Good agreement is seen between the two sets of measurements. For dispersions of MPA 60 and for silica, a comparison of the yield values reported in Table 1 with the flow behavior given in Fig. 2 shows that the yield values are not constant but are functions of the shear history. Also shown in Fig. 2 are data for 0.25% Separan from refs. 17 and 18.

3.2 Procedures
The equipment and techniques used in the jet studies are straightforward and will be described only briefly. Either an Instron mechanical tester or pressurized nitrogen activated the piston of a hydraulic cylinder which contained the test liquid. The fluid flowed from the cylinder, through a section of flexible reinforced hose and past a 50–125 μm filter. These served to minimize the mechanical vibrations that might be present from transmission along the walls of the stainless-steel piping or through the fluid itself and also to trap any contaminant particles. The fluid then entered a cube designed to house a pressure transducer and the capillary. The unit was mounted on a concrete block to dampen vibrations from the surroundings. Nozzles were fashioned from hypodermic needles or tubing by grinding their ends to a flat face. The bores were examined under 100-power magnification for concentricity and surface imperfections. A stage micrometer was used to determine the inside diameter. The length/diameter ratio was usually greater than 100/1 although, in certain experimental runs, shorter nozzles were used to maintain a safe working pressure.

3.3 Qualitative observations
The complete break-up of a laminar capillary jet of 0.2% Carbopol and that of a laminar capillary jet of 24% MPA 60 in xylene are shown in Figs. 3 and 4, respectively. They resemble the behavior of Newtonian capillary jets in that a disturbance is propagated as an exponentially growing wave of approximately constant wavelength. A similar appearance is displayed by capillary jets of 24% MPA 60 in mineral spirits.

Fig. 3. Break-up of a laminar capillary jet of 0.2% Carbopol. Magnification 2.5x; nozzle diameter 0.0414 cm; average jet velocity 438 cm/sec; distance from nozzle tip to midpoint of photograph: (a) 1.2 cm; (b) 7.3 cm; (c) 13.0 cm; (d) 17.3 cm.

Fig. 4. Break-up of a laminar capillary jet of MPA 60 in xylene. Magnification 2.2x; nozzle diameter 0.0414 cm; average jet velocity 258 cm/sec; distance from nozzle tip to midpoint of photograph: (a) 1.8 cm; (b) 3.8 cm; (c) 6.8 cm; (d) 9.4 cm.
BREAK-UP OF A CAPILLARY JET

Fig. 6. Break-up of a capillary jet of 12.4% silica in water. Magnification 1.1x; nozzle diameter 0.180 cm; average jet velocity 1080 cm/sec; distance from nozzle tip to midpoint of photograph: (a) 2.7 cm; (b) 20.3 cm; (c) 35.6 cm; (d) 65.6 cm.

Fig. 5. Break-up of a capillary jet of 0.6% Carbopol. Magnification 2.5x; nozzle diameter 0.0414 cm; average fluid velocity 4710 cm/sec; distance from nozzle tip to midpoint of photograph: (a) 1.4 cm; (b) 26.1 cm; (c) 56.6 cm; (d) 61.6 cm; (e) 67.2 cm.

The uniformly spaced droplets in photograph (d) of Fig. 4 are an additional indication of their formation from a regular wave.

An aqueous solution of 0.6% Carbopol is a semi-rigid gel when at rest, with a moderate yield stress. At very high velocities, the capillary jets formed by this solution are unstable, as is seen from the photographs of Fig. 5. Frictional air drag produces the non-axisymmetric motion that is evident in photographs (c) and (d). The disturbance does not propagate in the form of waves and this is further demonstrated by the random-shaped particles formed at break-up, as in photograph (e).

The sequence of photographs in Figs. 6-8 depicts the changing behavior of a capillary jet of the 12.4% silica dispersion as the average fluid velocity increases. Photograph (a) of Fig. 6 depicts the formation of a non-axisymmetric disturbance on the liquid column as it emerges from the nozzle with an average velocity of 1080 cm/sec. The succeeding photographs, taken at greater axial distances, reveal that the amplitude of the disturbance does not increase and, within the 1.5 m distance available for photography, the jet was stable. Its "screw-like" disturbance pattern is reminiscent of the appearance of molten polymers undergoing melt fracture. When the average capillary velocity has reached 1950 cm/sec, the Fig. 7 photographs show that large amplitude, random disturbances appear on the surface that eventually result in its destruction. Finally, at an average capillary velocity of 2850 cm/sec, the 12.4% silica jet undergoes turbulent break-up and is completely fragmented into irregular particles within a relatively short distance. This behavior is shown in

Fig. 8. In none of this series of photographs was there any evidence of axisymmetric wave propagation of disturbances. This series of photographs has shown that all of the non-Newtonian inelastic test fluids selected were capable of being atomized, which is intuitively surprising since most of them are highly gellified liquids when at rest. Their appearance was seen to be quite different from that of a viscoelastic fluid, as shown in Fig. 1. Since both classes of liquids possess shear-thinning viscosities, the differences in their behavior are probably associated with the presence or lack of elastic properties.

3.4 Quantitative results
Break-up length data were obtained for capillary jets of Newtonian fluids over a wide range of experimental conditions and were found to be in excellent agreement with published results. The apparatus and techniques used in this research can thus be regarded as providing measurements comparable with those of other investigators.

The break-up lengths of capillary jets of 0.2% Carbopol, 24% MPA 60 in xylene and 24% MPA 60 in mineral spirits are shown in Figs. 9, 10 and 11, respectively. A similar set of curves for 0.1% Carbopol taken from ref. 4 is shown in Fig. 12. The break-up length is seen to increase with the fluid velocity and the nozzle diameter, which is also found for Newtonian fluids. Also included in the figures is the predicted break-up length for a power law fluid, representing the solutions of eqns. (8) and (5) using the empirical correction factors for $F_3$ in eqn. (8) and $C$ in eqn. (5) suggested by Grant and Middleman. In using these Newtonian equations to compute the break-up lengths of the inelastic non-Newtonian fluids used in our experiments, the Newtonian viscosity $\eta_0$ and Reynolds number $Re_0$ were replaced by the corresponding average values of the shear-dependent quantities in the capillary defined as

$$\eta(\dot{\gamma}) = \frac{K'}{(4V/\dot{\gamma})^{1-n}}$$

and

$$Re_0(\dot{\gamma}) = \frac{(2ao)^n V^2}{K'g^n - 1}$$

References:
The parameters $K'$ and $n'$ are the constants in the power law relation

$$\tau = K' \left( \frac{4V}{a_0} \right)^{n'}$$  \hspace{1cm} (12)

A surface tension of 60 dyn/cm was also assumed for the 0.2% Carbopol solution in these calculations.

A third curve was included in Fig. 9 which represents eqn. (7), neglecting air resistance, and assuming the Carbopol solution regains its structure instantaneously. In this case the proper viscosity to be used in eqn. (7) would be the zero shear viscosity of the Carbopol solution. However, since the solution possesses a yield stress and does not exhibit a clearly defined zero shear viscosity, $\eta_0$ was approximated by the apparent viscosity at the relatively low shear rate of 0.1 sec$^{-1}$.

It is apparent from Figs. 9-12 that the experimental behavior is in reasonable agreement with the predictions for a Newtonian fluid having a viscosity equal to the average shear-dependent viscosity in the capillary. Where data were taken at a sufficiently high
velocity for a maximum break-up length to be exhibited, it is seen to occur close to the velocity required by the semi-theoretical curves. The $L-V$ curve does not appear to pass through the origin, which is also consistent with the response of a visco-inelastic fluid as the apparent viscosity increases with decreasing flow rate. On the other hand, the break-up length demanded by a capillary jet of 0.2% Carbopol which propagates disturbances at a rate corresponding to its zero shear viscosity (Fig. 9) is seen to be several orders of magnitude above the experimental data. This seems to indicate that for the Carbopol solution the time scale necessary to regain its viscosity or its structural relaxation time is much larger than the time scale of the capillary break-up.

The linear break-up data for capillary jets of 0.2% Carbopol and the two MPA 60 dispersions are plotted in the form of eqn. (7), using eqns. (10) and (11) to represent the viscosity and Reynolds number, and are shown in Fig. 13, where the solid lines indicate the range of published Newtonian results. While considerable scatter is evident, there is a general agreement between the break-up lengths of Newtonian jets and of visco-inelastic jets, when plotted in this manner. This accord represents another strong argument for the belief that the time required to reform the gel structure is large compared with the break-up time of the jet. Had an approximate value of zero shear viscosity been used to correlate the break-up length measurements, the data points would have fallen several orders of magnitude away from the Newtonian results.

![Fig. 13. Correlation of the low-speed jet break-up data for power law fluids with a long structural formation time.](image)

For a Newtonian fluid, Weber showed that when air resistance is negligible, the wavelength of the propagating disturbance is given by

$$\frac{\lambda}{2a} = \frac{\pi}{2} \left( 1 + \frac{3\eta_0}{\sqrt{2}a \rho} \right)^{1/2}$$

(13)

The wavelength of the propagating disturbance wave was measured from photographs taken in the region just prior to break-up. An apparent viscosity was calculated at that point from eqn. (13) using the nozzle diameter instead of the relaxed jet diameter. Table 2 compares the apparent viscosity calculated

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Nozzle diameter</th>
<th>Average capillary velocity</th>
<th>Wave length at break-up</th>
<th>Apparent viscosity from eqn. (13)</th>
<th>Apparent viscosity at average capillary shear rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>24% MPA 60 in xylene</td>
<td>0.0216 cm</td>
<td>330 cm/sec</td>
<td>0.11 cm</td>
<td>0.10 poise</td>
<td>0.45 poise</td>
</tr>
<tr>
<td></td>
<td>0.0263</td>
<td>380</td>
<td>0.25</td>
<td>1.7</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>0.0414</td>
<td>290</td>
<td>0.23</td>
<td>0.21</td>
<td>0.55</td>
</tr>
<tr>
<td>0.2% Carbopol</td>
<td>0.0216</td>
<td>230</td>
<td>0.17</td>
<td>0.79</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>0.0263</td>
<td>650</td>
<td>0.20</td>
<td>0.75</td>
<td>0.087</td>
</tr>
<tr>
<td></td>
<td>0.0414</td>
<td>470</td>
<td>0.30</td>
<td>0.85</td>
<td>0.12</td>
</tr>
</tbody>
</table>

from wavelength measurements on the visco-inelastic jets with the apparent viscosity at the average shear rate within the capillary. If the Newtonian relation, eqn. (13), can be assumed to approximate the disturbance wavelength in non-Newtonian inelastic jets, then differences in the two calculated apparent viscosities should be indicative of structural formation within the liquid during the lifetime of the jet.

The results of Table 2 are consistent with the conclusions drawn from the break-up length data. Capillary jets of 0.2% Carbopol exhibit disturbance wavelengths which denote a limited structural build-up from the apparent viscosity possessed at the capillary exit. The apparent viscosities calculated from wavelength data for 24% MPA 60 in xylene, on the other hand, are generally below those values computed at the average shear rate within the capillary, indicating a higher degree of instability than one would expect for this solution. This increased instability was also found with the 0.1% Carbopol solution which was even more unstable than water, although having a much higher zero shear viscosity.

Although the reasons for the increased instability of the 24% MPA and 0.1% Carbopol solutions cannot be explained at present, it is significant that all the apparent viscosities calculated from wavelength data are of the same order of magnitude as those computed at the average shear rate in the capillary. In contrast, the use of the zero shear viscosity in eqn. (13) demands wavelengths several orders of magnitude larger than the experimental results.

Two of the non-Newtonian inelastic fluids—0.6% Carbopol and the 12.4% silica dispersion—formed capillary jets which did not display any propagation of disturbance waves. The experimental break-up results for 0.6% Carbopol are shown in Fig. 14 together with the predicted curves using the average viscosity in the capillary and an approximation to the zero shear viscosity in eqn. (8). Over the range of velocities measured, the break-up length is seen to decrease with increasing fluid velocity, except for the highest velocity where a slight increase in break-up length occurs. The experimentally measured break-up length is in fair qualitative agreement with the theoretical curve calculated using the average viscosity in the capillary. At lower velocities than those shown in the figure the apparent viscosity in the capillary was too high to obtain break-up length or wavelength measurements on the jet within an experimentally convenient distance. At the high velocities at which break-up could be observed, however, the frictional drag from the surroundings was significant and served to impart a non-axisymmetric motion to the liquid column.

A break-up curve could not be obtained with the silica dispersion because the capillary jets formed by this fluid either were stable or broke up without any definable break-up length. The photographs in Figs. 6–8 demonstrate a decreased stability with increasing velocity and it is assumed that this is a result of aerodynamic forces in the same sense as for the capillary jets of 0.6% Carbopol.

4. DISCUSSION OF RESULTS

Let us restate again the basic facts which we wanted to explain.

(1) Pseudoplastic fluids vary widely in their atomization behavior. While some of them cannot be atomized by standard means, others atomize easily.

(2) Pseudoplastic fluids having large normal stresses (strongly elastic fluids) seem to be more difficult to atomize.

(3) The atomization behavior of these fluids does not seem to correlate well with the existence or absence of yield stresses.

These facts do not agree, even qualitatively, with the predictions of linear viscoelastic theory, which predicts increased instability for viscoelastic liquids.
and a stabilizing influence of a yield stress. We will examine some possible explanations as to why linear theory fails below.

Let us first consider the jellified solutions with high viscosity, which are of real interest in connexion with thickening agents. In order to apply linear viscoelastic theory we have to assume that the liquid jet is fully relaxed and has the properties of the liquid at rest. Now, under these conditions a Newtonian liquid of the same high zero viscosity is for all practical purposes completely stable. While linear theory would predict growth of a wave, the growth rate is too small to allow visual observations to be made in the time scale of a jet. If we assume that for a viscoelastic jet under such conditions, the growth rate is, say, twice as large, it would still be perfectly stable. The fact that very viscous solutions of viscoelastic liquids show no disturbances when atomized does not contradict the predictions based on linear theory. It just makes them irrelevant to the physical problem.

We deal here always with shear-thinning liquids, in order to allow easy extrusion at high zero shear viscosities. For these fluids the stable behavior of the elastic liquid provides no inherent contradiction since we assume that they quickly return to their state of zero shear viscosity upon removal of the shearing stress.

The relatively easy break-up of some very viscous solutions, which, in addition, possess a yield stress, could be explained by assuming that these solutions regain their viscosity only slowly compared with the time scale of the growth of disturbances on the jet. For MPA solutions this can be proved independently. After heavy shearing of these solutions it takes several hours before they regain their original gelatinous consistency.

Thus, such liquids have a long structural relaxation time during which the gel structure is reformed. For Carbopol solutions one does not notice this effect in an ordinary viscometer. However, in atomization experiments we deal with a much shorter time scale than in a viscometer. It is therefore quite reasonable to assume that the easy atomization of Carbopol solutions can be explained by the same arguments which we have made for the MPA solutions.

Very little of previous theoretical work in the rheology of fluids has dealt with thixotropy in this sense. In most of the current molecular models or constitutive equations, thixotropy (or time-dependent behavior of viscosity) is tightly tied in with elastic behavior (e.g., the constitutive equations based on converted derivatives of Maxwell models, or integral models like the BKZ). This seems to overlook a broad class of fluids such as MPA, in which the time-dependent behavior of the viscosity-shear relation is not accompanied by normal stresses. In fact, if we estimate a relaxation time for Carbopol based on normal stresses we would find relaxation times not only much smaller than those of Separan, but also much too short to allow break-up.

We have therefore to make allowance for a slow relaxation process in which viscosity is recovered, which is not associated with normal stresses. This means that the basic molecular processes that lead to a shear-dependent viscosity might be completely different in the two cases, and that the behavior of such liquids is not characterized by their linear viscoelastic relaxation spectrum.

An interesting fact is that all of the liquids that are found to have the properties necessary for thickening agents, namely, very high zero shear viscosity and easy break-up, are non-elastic liquids in the sense that they exhibit only very small normal stresses and show no measurable recoil.

The properties of dilute solutions of non-Newtonian materials are much more difficult to explain. Thus, in dilute solutions both Carbopol and MPA seem to have the ability to promote break-up. Based on break-up length observations, these solutions seem to have a faster growth rate of disturbances than Newtonian solutions with the same apparent viscosity and in some cases even a faster growth rate than an inviscid liquid. This last fact cannot be explained at all. Further work is in progress to elucidate this phenomenon.

As pointed out in ref. 4, dilute solutions of highly elastic liquids, such as Separan, also exhibit phenomena which are difficult to explain. First of all, the break-up is dominated not by wave formation but very often by isolated events, which looks very similar to the non-linear phenomenon occurring in Newtonian fluids when the imposed wavelength is large compared with the diameter. It is difficult to claim that the jet itself is more stable. In Fig. 15 we have replotted some data from our previous work for Separan. No clear cut stability increase can be noticed. A definite stability increase can, however, be noted in the behavior of the thin threads forming connecting individual droplets. These thin threads, while ultimately exhibiting droplet formation, have a life length far in excess of that expected from Newtonian liquids with the same zero shear viscosity. We originally thought that this was due to increased viscosity caused by a stretching motion. However, closer examination

BREAK-UP OF A CAPILLARY JET

(3) elastic solutions seem to regain their viscosity much faster even if their relaxation times are high;
(4) some properties of shear-thinning non-elastic liquids seem to promote wave growth in a yet unexplained fashion; and
(5) atomization experiments provide an interesting area of study to determine relaxation phenomena and test (and sometimes regretfully shatter) our more generalized concepts of non-Newtonian fluids.

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NOMENCLATURE

\( u \) jet radius
\( a_0 \) capillary radius
\( C \) proportionality constant in break-up length relations defined by eqn. (5)
\( F_1, F_2, F_3 \) Bessel function ratios defined by eqns. (2), (3) and (9)
\( K' \) power law parameter in eqn. (12)
\( K_a \) wave number = \( 2\pi a/\lambda \)
\( \lambda \) quantity defined by eqn. (4)
\( L \) jet break-up length
\( n' \) power law parameter in eqn. (12)
\( \Re \) Newtonian Reynolds number based on jet radius = \( 2aV_0/\eta_0 \)
\( \Re_0 \) Newtonian Reynolds number based on capillary radius = \( 2a_0V_0/\rho/\eta_0 \)
\( \Re_0(\gamma) \) generalized Reynolds number defined by eqn. (11)
\( V \) mass average jet velocity
\( V_0 \) mass average capillary velocity
\( W_e \) Weber number based on jet radius = \( 2aV^2\rho/\sigma \)
\( W_{e0} \) Weber number based on capillary radius = \( 2a_0V_0^2\rho/\sigma \)
\( Z_0 \) Ohnesorge number based on capillary radius = \( W_{e0}^{1/2}/\Re_0 \)

Greek symbols
\( \alpha \) growth rate of disturbance wave
\( \eta_0 \) Newtonian viscosity
\( \eta(\gamma) \) apparent viscosity defined by eqn. (10)
\( \lambda \) wavelength of disturbance wave

\( \rho \) fluid density
\( \rho_A \) air density
\( \sigma \) coefficient of surface tension
\( \tau \) shear stress

REFERENCES

