# LETTERS TO THE EDITORS

## Polymer Flow Irregularities

There have been numerous comments recently concerning the inconstancy of the amount of flow during viscosity experiments using such devices as the melt indexer, the CIL rheometer, and the MCER rheometer developed in our laboratories.[1]   It was shown by Aggarwal and coworkers[2] that one of the reasons for inconstancy of rheological measurements is the friction contributed by material which has flowed into the space between the rheometer barrel wall and the plunger.   Results by Schreiber[3,4] show that another one of the causes for inconstancy of rheological measurements is perhaps a decrease of the melt viscosity of the material as the flow proceeds.   A third explanation for inconstancy of flow experiments has been contributed by Charley;[5,6] he offers the opinion that the inconstancy is due to the changing pressure drop in the rheometer barrel.   This opinion has also been supported by Skinner.[4]

It should be pointed out that because of its method of operation, the MCER offers distinct advantages for studying effects of this sort.   This rheometer offers a continuous record of the flow behavior of the material so that any variation with time can be easily
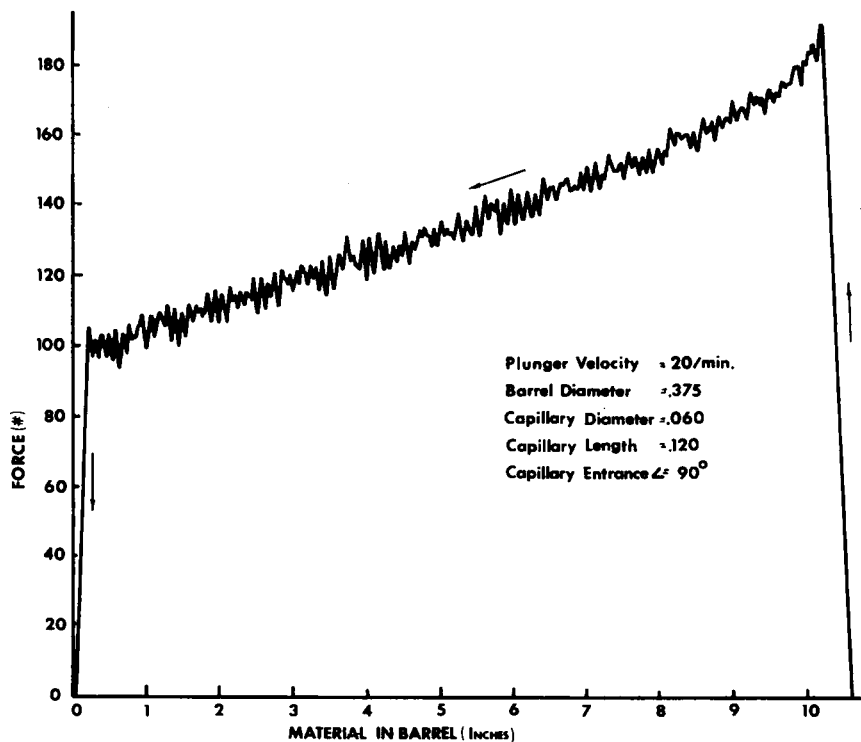


Fig. 1. Polystyrene force trace at 400°F.

studied in some detail.   Figure 1 shows a typical force trace.[3]   In this case the polymer being tested was an anionically polymerized polystyrene with a viscosity average molecular weight of 231,000 and a number average molecular weight of 124,000.

This material was charged to the rheometer barrel and a temperature equilibrium of 400°F. was reached after five minutes.   At that time, the plunger was run into the rheometer barrel at a constant speed of 20″/min. for the entire barrel length.   The initial amount of material filled the barrel to a height of 10.4″.   As shown by Figure 1, the initial force required to push the material through the rheometer under these conditions was 190 lb.   As the plunger proceeded to empty out the rheometer, the force declined to a value of 100 lb.   This run is typical of several obtained from experiments under similar conditions.   The observed decrease in force of 72 lb. (by extrapolating the linear portion of the trace) agrees well with the calculated value of 68 lb. obtained from $\Delta F = 2 \pi L U \eta a/15$ where $L$ is the length of polymer in the rheometer barrel, $U$ is the plunger velocity, and $\eta a$ is the apparent polymer viscosity under the wall shear rate experienced in the rheometer barrel.

The force trace irregularity possibly has two sources.   One source would be the inconstancy in the speed at which the plunger is driven.   The second and probably more serious source of force trace irregularity would be irregularities produced at the capillary entrance by melt fracture.   This was definitely occurring during the run as evidenced by the rough condition of the polymer extrudate.
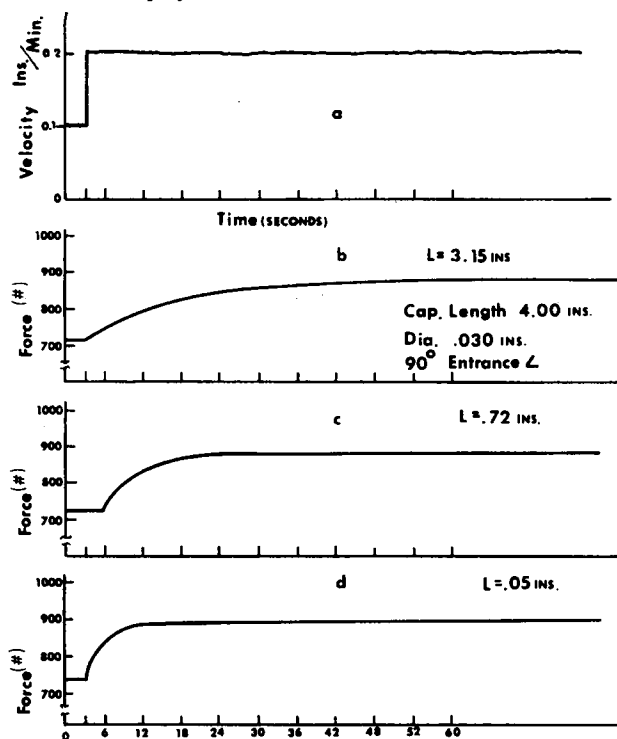


Fig. 2. Polystyrene force trace at 400°F.   Crosshead velocity step 0.1–0.2 in./min.

A second experiment was performed in which the plunger speed was changed from one value to another within a short period of time as measured by a velocity transducer attached to the rheometer plunger.   The effect of changing speed upon the resultant force trace was simultaneously recorded.   The results are shown in Figure 2.   As was to be expected, the change in force lagged somewhat behind the much more rapid change in plunger velocity due to the time-dependent nature of the polymer melt.   Of particular interest is the fact that when this experiment was repeated with different amounts of material present in the rheometer barrel, the viscoelastic effect was severely influenced as shown by the different parts of Figure 2($a,b,c$ and $d$).   It became apparent that a

large amount of material placed in the barrel produced a longer time lag in the force trace change than did a small amount.  These results indicate that the shape of the force-trace-response to a sudden change in crosshead velocity is primarily influenced by bulk viscoelasticity of the polymer melt in the rheometer barrel rather than by shear viscoelasticity in the capillary.  Figure 3 shows that these data can be fitted by single
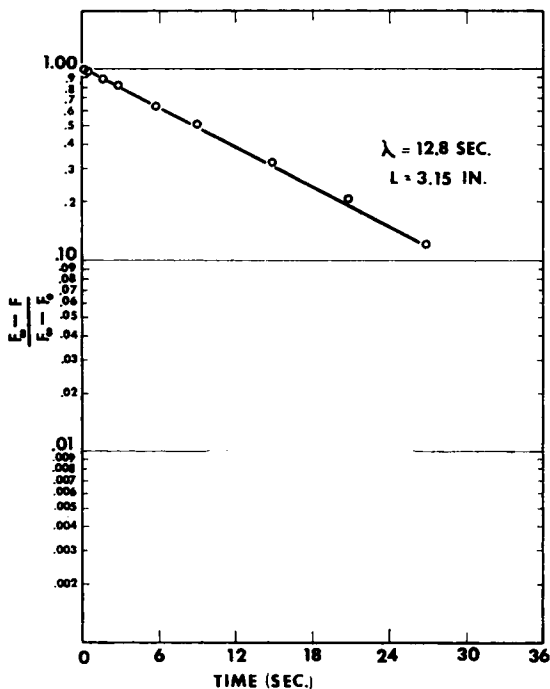


Fig. 3.  Polystyrene force relaxation at 400°F.   Velocity step of 0.1–0.2/min.

relaxation time, since the plot of reduced pressure versus time on semilog scale is nearly linear.

In summary, these experiments show the important influence of the amount of material present in the rheometer barrel preceding the capillary.   There is no question but that a number of phenomena detected in capillary experiments can be traced to the presence of this material.   These effects include:   1. The pressure drop due to the viscosity of the material in the barrel in normal laminar flow.   This effect, of course, becomes most significant when a short and/or large diameter capillary is used which of itself contributes little pressure-drop.   It is apparent that in those experiments which attempt to measure capillary entrance effects by using extremely short capillaries, the pressure drop contributed by material in the barrel will be most significant.  2. Melt fracture turbulence in the rheometer barrel.   This, perhaps, is responsible for short-term force-trace irregularities.  3. Polymer bulk viscoelasticity which would include the time dependent compressibility of the polymer melt in the barrel.

## References

1. Merz, E., and R. Colwell, *ASTM Bull.*, **63** (1958).
2. Marker L., R. Early, and S. L. Aggarwal, *J. Polymer Sci.*, **38,** 381 (1959).
3. Schreiber, H. P., *J. Appl. Polymer Sci.*, **4,** 38 (1960).
4. Schreiber, H. P. and A. Rudin, *J. Appl. Polymer Sci.*, **3,** 122 (1960).

5. Charley, R. V., *J. Appl. Polymer Sci.*, **6**, S19 (1962).
6. Charley, R. V., *Brit. Plastics*, **38**, 476 (1961).
7. Skinner, S. J., *J. Appl. Polymer Sci.*, **5**, S5 (1961).
8. Mendelson, R. A., private communication.

RICHARD L. BALLMAN

Monsanto Chemical Company
Plastics Division
Springfield, Massachusetts

## Single Point Determination of Intrinsic Viscosity

In a recent paper, Solomon and Ciută[1] propose an equation for obtaining the intrinsic viscosity of a polymer by the measurement of the viscosity of the polymer in solution at a single concentration.   The proposed equation is:

$$[\eta] = 1/C \sqrt{2(\eta_{sp} - \ln \eta_{rel})} \tag{1}$$

These authors arrived at this equation experimentally, and justify its validity on the grounds that $1/C \sqrt{2(\eta_{sp} - \ln \eta_{rel})}$ tends to $[\eta]$ as $C$ tends to zero.

In our laboratories we have been using this same equation, which we derived analytically using Huggins' relation:

$$\frac{\eta_{sp}}{C} = [\eta] + K_1[\eta]^2 C \tag{2}$$

The derivation is as follows:

$$\eta_{sp} = [\eta]C + K_1[\eta]^2 C^2 \tag{3a}$$

$$\eta_{rel} = 1 + [\eta]C + K_1[\eta]^2 C^2 \tag{3b}$$

$$\ln \eta_{rel} = \ln \left\{1 + [\eta]C + K_1[\eta]^2 C^2\right\} \tag{3c}$$

Expanding into series, neglecting terms in $C^3$ and higher, and re-arranging, leads to:

$$\ln \eta_{rel} = [\eta]C + [\eta]^2(K_1 - 1/2)C^2 \tag{4}$$

Subtracting (4) from (3a), one obtains:

$$\eta_{sp} - \ln \eta_{rel} = 1/2[\eta]^2 C^2 \tag{5}$$

Transposing, (5) leads directly to (1).

As Solomon and Ciută point out, eq. (1) is a "universal" relation permitting determination of intrinsic viscosities by a single point measurement, without having to use any constants which depend on the interaction of the polymer-solvent system.   It is important to realize, however, that the validity of eq. (1) for any polymer-solvent system depends only on the validity of the Huggins' equation for that system, since eq. (1) is derived therefrom.   On the other hand, use of eq. (1) in conjunction with the classical three point determination and graphical extrapolation is sufficient to establish whether the Huggins equation applies for a given polymer-solvent system.   If the $[\eta]$ obtained by graphical extrapolation agrees with the $[\eta]$ obtained by use of eq. (1) then the Huggins relation applies.   Equation (4) also shows that for values of $K_1 > 1/2$, plots of $1/C \ln \eta_{rel}$ vs. $C$ (used in the determination of inherent viscosities) will have a positive, rather than the usual negative slope.