

LETTER TO THE EDITOR

Polymer Rheology

The recent paper by Schreiber¹ on time dependence of flow of polyethylene in a capillary viscometer described measurements with a very short capillary while a previous communication² discussed work with a melt index apparatus. In rheological studies of high polymers it is very important to ensure that the desired property is being measured. This is often difficult for polymer flow where temperature effects, thermal breakdown, and mechanical problems can all introduce complicating features.

In a capillary rheometer there are two sources of error that may become appreciable with short capillaries of large diameter. In the first place, the measurement usually made is not the resistance to flow of a capillary by itself but of a capillary plus a reservoir, which empties during the course of the experiment. Thus, in an apparatus to which a constant load or pressure is applied, the pressure at the capillary entrance will initially be lower than the applied pressure and will approach the latter as the reservoir empties. Simultaneously the flow will increase.

We can calculate this effect in a melt indexer, assuming a polymer that obeys a power law and ignoring capillary end effects (admittedly a dubious procedure with a length/diameter ratio of 4:1). For the barrel:

$$\frac{(N+3)Q}{\pi r_b^3} = \frac{K(P_b r_b)^n}{(2L_b)}$$

where Q is the flow rate, P_b is the pressure drop through the barrel, L_b is the length of the barrel, r_b is the radius of the barrel, and n is approximately 1.7 for a typical polyethylene.

Writing a similar expression for the capillary, dividing the one by the other, and rearranging, we obtain

$$\frac{P_b}{P_c} = \frac{L_b}{L_c} \left(\frac{r_c}{r_b} \right)^{(n+3)/n}$$

If the melt indexer is filled as completely as possible, L_b is initially 5.8 in. Hence,

$$\begin{aligned} \frac{P_b}{P_c} &= \frac{5.8}{0.315} \left(\frac{0.0413}{0.188} \right)^{4.7/1.7} \\ &= 0.28 \end{aligned}$$

The capillary pressure drop hence will increase from 78 to 100% of the applied pressure. This implies a 50% increase in flow during extrusion if the reservoir is emptied completely. Admittedly, the above calculation is based on

an extreme case but it does serve to show that the effect is appreciable.

It is obvious that this effect is much smaller with capillaries of high length/diameter ratio. In our laboratories we have a Merz-Colwell type of rheometer with a barrel length of 10 in., diam. of $\frac{3}{8}$ in., and capillaries of 60:1 L/D ratio.³ For the above case, if a $\frac{1}{16}$ in. capillary is used, $P_b = 0.02P_c$ under the worst conditions. After an interval of a few seconds the load is virtually constant for most of the materials we have examined. We have noted time-dependent effects but they were of much shorter duration than those described by Schreiber.¹

The second source of error in a rheometer with a plunger or ball is the load required to shear the film of polymer between the plunger and the barrel or reservoir.⁴ With the capillary described above this error may be as much as 2%, so it would certainly be appreciable for a short capillary and would increase with the diameter of the reservoir. The problem then, in designing a rheometer for use with short capillaries is to design a suitable reservoir. If this is too small it can contribute significantly to the overall pressure drop. If it is large, however, plunger or ball fraction may be considerable, and the disturbance to flow at the capillary entrance will also be greater.

The graphs in Figure 1 of Schreiber's paper¹ show that he is using a larger reservoir than that in a standard melt indexer, but no dimensions are given. It is clear from the above arguments that the use of short capillaries with large diameters may present considerable practical difficulties and it would be interesting to know how these may be overcome. In polymer rheology the art of carrying out measurements is very much dependent on detail, and information of this type is therefore of considerable value to other workers in the field.

References

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