

## NOTES

## Time Effects in Polymer Melt Viscometers

Time changes in the flow rate of polymer melts in capillary viscometers under constant applied load have been noted by several workers,<sup>1-6</sup> and a number of explanations have been put forward. Several effects appear to be involved. The most important of these with regard to routine testing is a continued increase of flow rate with time (called effect *A* hereafter). This has been explained by both Skinner and Charley in terms of the decreasing pressure drop across the barrel as the melt height decreases. The effective pressure at the capillary inlet and the resulting flow rate will thus increase continuously with time. A time effect of much shorter duration has been described by Schreiber and Rudin and the existence of short duration effects was mentioned by Skinner.

During viscosity measurements on polythene melts in this laboratory, these time effects were examined. The capillary instruments used were the Melt Flow Indexer<sup>7</sup> (M.F.I.) and a gas operated High Shear Viscometer<sup>8</sup> (H.S.V.)

Two short term effects were noted (called effects *B* and *C* from now on). In the determination of Melt Flow Index, these effects are eliminated by delaying the measurement for some time after the load is applied. However, when viscosity is being measured over a range of applied load, such a procedure would considerably extend the time involved, and many flow curve measurements do not allow for these effects.

Effect *B*: When a load is applied, the output rate falls with time and reaches a minimum value; the increase in output rate of effect *A* then becomes noticeable. The change in the output rate is 10-30% and is complete in 5-10 min.

It is thought that this effect is due to the elastic deformation of the melt in the barrel. When the load is first applied the amount of material pushed through the die is the sum of the elastic and viscous components. As the melt in the barrel approaches and eventually reaches the equilibrium deformed state, the elastic component decreases to zero. The measured flow rate is then due to viscous flow alone. If a large load is first applied and is then replaced by a smaller load, the elastically deformed melt can recover partially. Part of the applied load is balanced by this recovery process so that the flow rate is low when the load is changed but increases up to the level of viscous flow.

A similar type of elastic deformation is observed in a cone and plate viscometer when the load is first applied. The angular velocity of the cone is initially large but decreases rapidly to the level corresponding to a viscous flow. The time involved in this case is very short, less than a minute.

The amount of polymer elastically extruded through the capillary may be estimated as the difference between the total flow over the duration of the time effect and the viscous flow component extrapolated back over this period. This was done for a sample of low density polythene of M.F.I. 0.2 over a range of applied pressure on the H.S.V. The amount extruded was proportional to the pressure and decreased as the resistance to flow of the capillary increased as shown in Figure 1. Both smooth and distorted extrudates were obtained in the range of pressures considered, i.e., elastic deformation of the melt in the barrel depends only on the applied pressure and is not influenced by the change in flow behavior through the die.

The approach of the melt to its equilibrium distorted state, i.e., the change in the flow rate, could be represented by a single exponential term over most of the range. An appreciable tail lying above the exponential plot was observed on most samples, and deviations from the exponential also occurred initially. These latter deviations may be associated with the second time dependent effect (even when this could not be detected otherwise).

Effect *C*: The second time effect was of short duration, less than two minutes; the flow rate was initially very low but climbed rapidly to merge in with the effects described above. This effect was not always present—in particular, it was only rarely observed on the H.S.V.—and the magnitudes were not at all reproducible.

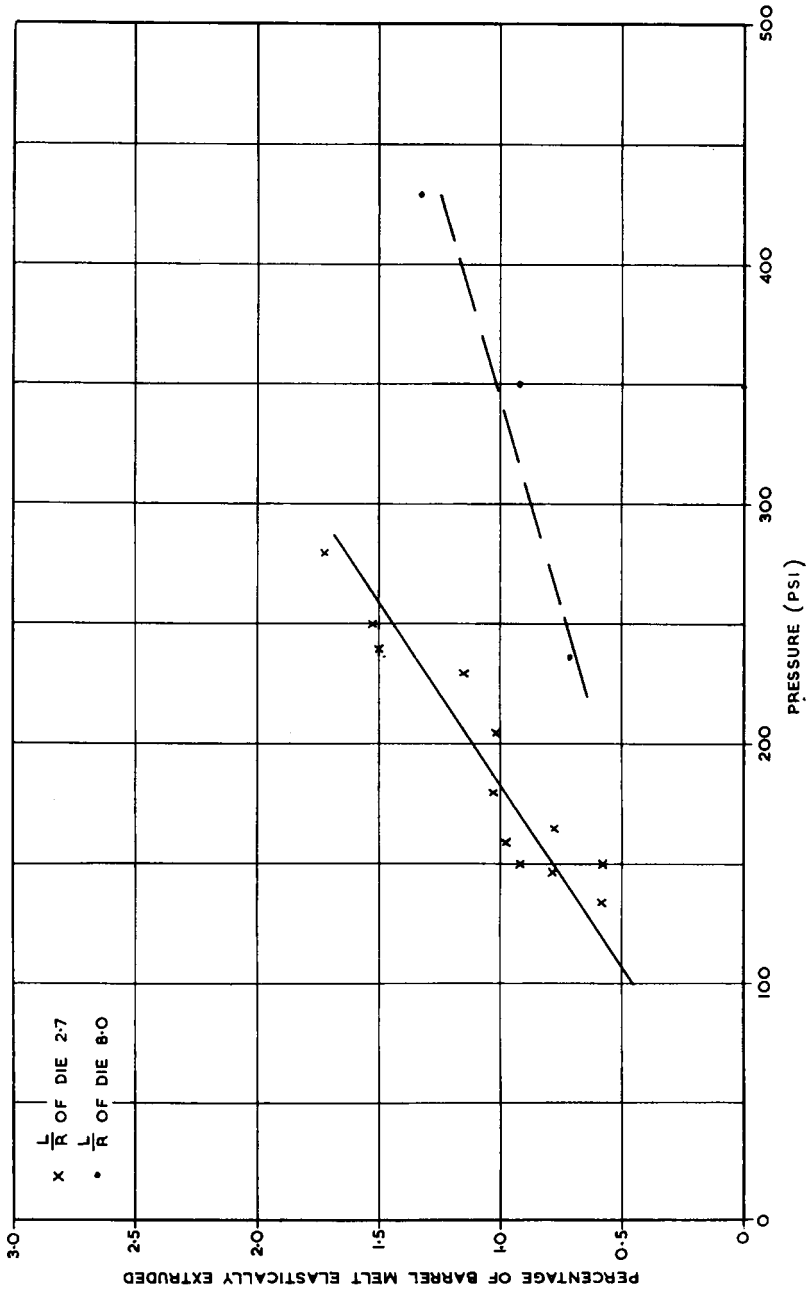


Fig. 1. Elastic extrusion of barrel melt.

This is due to compression of gas bubbles in the melt. When the load is first applied, compression or compaction of the melt is occurring and the piston is moving rapidly but the amount of material forced out of the barrel is small. Since the reproducibility is poor, it seems unlikely that bubbles of volatile material in the polymer, i.e., monomer, are a major contributor to the effect; if this were so, consistent results would be expected. However, the trapping of air in the melt during loading would lead to the poorly reproducible behaviour observed. Since the effect occurs much more frequently in the piston instrument than in the gas operated instrument, the trapping of an air cushion between the piston and the melt seems to be the major factor. Although rapid movement of the piston observed when a load is first applied is mainly due to effect *C*, effect *B* also causes an increase in the rate of piston movement, which lasts over a longer period.

The swelling of the extrudate also varies with time. Over the long term change, (effect *A*) swelling and flow rate increase together, following the law:

$$\frac{\text{extrudate diameter}}{\text{capillary diameter}} = \text{constant } X \log (\text{flow rate})$$

In the initial period of extrusion, however, the swelling behaviour differs from that of the flow rate. It is initially low by some 3%, and increases slowly. The time period is of the same order as that of effect *B*. A few samples did not follow this pattern and the swelling decreased with time, paralleling the flow rate change.

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### *The Glass Temperature of Asphalt*

Very little is known about the glassy state properties of asphalt particularly about the glass temperature  $T_g$ , and the factors which affect it. Considering the important applications of asphalt which involve low temperature exposure it would seem very valuable to have an estimate of the  $T_g$  of this material. In addition, it has been reported that this property varies with asphalt composition,<sup>1</sup> and a measurement of  $T_g$  could conceivably provide an important and simple method for differentiating between various asphalt samples. Wada and Hirose have conducted specific volume-temperature measurements on a series of asphalt samples with varying asphaltene contents and have observed a direct relationship between asphaltene content and  $T_g$ .<sup>1</sup> It was observed that  $T_g$  decreased from 2° to -37.5°C. when the asphaltene content decreased from 61.9 to 0 weight percent. An asphaltene content of 28.6%, a value which falls somewhat above the range normally encountered (10-20%), had a  $T_g$  of -22.5°. In the present study broad-line nuclear magnetic resonance spectroscopy was applied to the