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On the Discontinuity in the Flow Curve of Polyethylene

Bagley, Cabott, and West[1] report that in the extrusion of polyethylene there is a critical shear rate above which the extrudate becomes rough, twisted, and distorted, a phenomenon which has been termed melt fracture. Using a linear polyethylene, they found that there is a pressure region in which the output is double-valued and the extrudate filaments can be either smooth or rough, depending on the output value. This is illustrated in Figure 1.

In instruments that operate at constant volume displacement, the extruded filament will be smooth at all pressures below A. It will change to helical (wavy) or rough forms, or both, between A and B. At B, the discontinuity occurs. On further increase of rate of volume displacement, the filament will manifest various, continuous forms of distortion from smooth, to smooth and rough, to very rough. Pressure-sensitive devices will indicate corresponding changes in shear stress between A and B. By operating at different volume displacement rates, curves analogous to Figure 1 can be constructed.

A series of high-density polyethylenes have been characterized with respect to their molecular weight and a molecular weight distribution factor by a rheological method developed by one of us.[2] The data are summarized in Table I. A Baldwin tensile machine, modified to operate as an extrusion rheometer, was used to study the melt fracture properties of these resins. The experiments were carried out at 190°C. with a flat entry die having a radius of 0.035 cm. and a length of 1.05 cm. Results of a typical
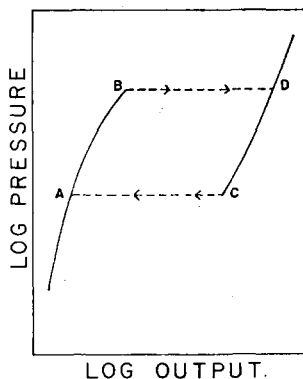

Fig. 1. Flow of a linear polyethylene through a capillary.

TABLE I
Flow Parameters of Resins[a] Studied and Melt Fracture Behavior

Resin	$\eta_0 \times 10^{-5}$, poises[b]	$K\bar{M}_r/\bar{M}_w \times 10^8$ [c]	Type of melt fracture in cycle
A	18.0	13.1	Rough–very rough–rough
B	15.4	9.8	Spiral–rough–spiral
C	17.0	8.2	Smooth–spiral–rough–smooth
D	16.4	7.4	Smooth–spiral–rough–smooth
E	1.08	9.7	No cycle

[a] Ethylene-butene-1 copolymers, 0.950 density.
[b] Zero shear viscosity; see Ref. 2.
[c] Rheological molecular weight distribution factor; see Ref. 2.

TABLE II
Typical Melt Fracture Data (Resin A)

Dial[a]	Pressure, psi $\times 10^{-3}$	Remarks
45	1.55	Smooth extrudate
50	1.64	Helical
60	1.77	Helical
130	2.42	Rough
140	2.47	Rough
150	1.94–2.50	Rough–very rough–rough
160–200	1.96–2.50	Rough–very rough–rough
210	1.96	Very rough
270	2.14	Very rough

[a] Corresponds to volume displacement rates.

run are reported in Table II. A physical description of the filament's appearance, as the pressure fluctuated between A and B, is given in Table I. Other data are graphically reported in Figure 2.

The strong dependence of filament distortion of the molecular weight distribution factor, aside from the expected dependence on molecular weight, is very interesting. High-pressure low-density polyethylenes are known to be of very wide molecular weight distribution. They show rough extrudates to a greater degree than high-density resins.[3] This is in agreement with the data reported here. Similarly, the hysteresis area becomes smaller as the molecular weight distribution is broadened. A conventional low-density polyethylene with a zero shear viscosity of 1.7 $\times$ 10⁶ poises did not yield a hysteresis loop.

The length of the extrudate between cycles was not found to be related to any known parameters. The length of individual sections, i.e., smooth, spiral, or rough, could not be easily defined and also could not be related to any known parameters. However, there were some differences between repeat units when resins A and B were compared with resins B and C.

Lastly, it was determined that the diameter of the extrudate changes little with the change from smooth to spiral flow. A large change occurs between the spiral and rough flows. It appears that the area of the hysteresis loop is a function of the difference in diameter between smooth and rough extrudates. If the difference in diameters is very
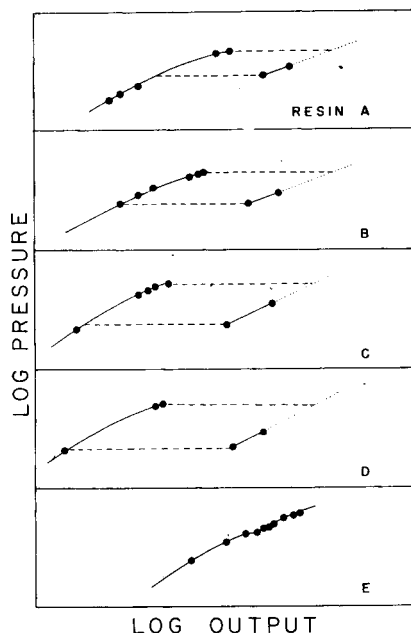
Fig. 2. Composites of melt fracture data.

small, no cycle occurs, as is the case of resin E. A correlation among the diameter of the extrudate, the molecular weight, and the molecular weight distribution is indicated by the data presented here.

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A Simple Method for the Determination of Glass Temperatures of Amorphous Polymers

The glass temperature of an amorphous polymer is of some significance in that it is the temperature at which a marked increase in molecular movement gives rise to an incipient change from glasslike to rubberlike properties. It is commonly obtained from an inflection in the temperature-dependence curve of some physical property such as specific volume[1] or refractive index,[2] measured under standardized conditions of rate of heating.

In the course of a preliminary investigation of the properties of amorphous polymers obtained as fibers (radius < 0.01 cm.) drawn from the "melt," it appeared that a relatively simple method is available for the determination of glass temperatures. A polarizing microscope and the use of a retardation technique reveal the presence of birefringence, the optical axes coinciding with the extinction position of the crossed Nicols. If such a fiber is periodically, immersed in a heated bath containing an inert liquid (e.g., aq. KCl solution, so that temperatures in excess of 100°C. may be realized), above a certain critical temperature, which is reproducible to 0.5°C., the fiber rapidly develops a permanent spiral form. It is believed that the phenomenon is due to a differential stress relaxation effect, possibly related to one described in an investigation into the influence of shearing stress on melt extrudates:[3] as the temperature of the bath reaches the glass temperature, enough mobility of the polymer chains is afforded for the fiber to develop spirality. That relaxation has occurred is confirmed by a decrease in the magnitude of the birefringence (Table I).

TABLE I
Birefringence and Glass Temperatures of Drawn Amorphous Fibers

Polymer	Birefringence		Glass temp., °C.
	Before treatment	After treatment	
Polyvinyl acetate	0.001	<0.001	28
Polystyrene	0.010	0.001	95
Polymethyl methacrylate	0.001	<0.001	75

The values of the glass temperatures of polyvinyl acetate and polystyrene obtained in this way agree quite well with other published data, but assessment in the case of polymethyl methacrylate is more difficult, owing to a diversity in such information.[4] In conclusion, it should be emphasized that the technique, as described, is apparently inapplicable to semicrystalline polymers, probably because of crystallite stabilization, although reference has been made to a method for the measurement of contraction temperatures in synthetic fibers.[5]

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