ments to the polymer, since extraction with acetone or methanol completely removes the occluded solvent.

Figure 1 shows that the unsaturation (measured by reaction with perbenzoic acid) of cyclized rubber must be lower than 65% of that of the original rubber for solvent retention to occur, and thereafter the amount of solvent retained increases as the unsaturation falls.

The nature of the association between the solvent and cyclized rubber cannot from information at present available be specified, but the formation of a clathrate type of compound is unlikely, since markedly different sizes of solvent molecules are retained to similar extents.

A similar degree of solvent retention is exhibited by cyclized gutta-percha.

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Distortion of Polyethylene Extrudates

When molten polymers are extruded through dies, distortions in the extrudate appear at high shear rates. Visual observation of the flow through capillary dies with square-edged inlets[1–4] indicated (*1*) that the melt formed a natural approach cone with an included angle of 30–40°; (*2*) that the melt trapped in the "stagnant" zone directly above the shoulder of the die and outside the approach cone circulated within this zone; (*3*) that extrudate irregularities originated at the die inlet. Some disagreement exists on this point, based in part on the short length of the dies used.[5,6]

The melt flow experiments reported in this note were carried out with a commercial polyethylene designated DFD-0114 (Union Carbide Plastics Co.) having a density of 0.922 g./cm.^{3} at 25°C. A screw extruder fed melt into a channel of 1-in. diameter[3] leading to a capillary die 11.44 cm. in length, with a 0.175-cm. radius and an included inlet angle of 60°. A removable cylindrical insert terminating in a 60° conical tip fitted snugly into the conical inlet. It had a capillary of 0.177-cm. radius and 2.42-cm. length, which was a direct extension of the first capillary. The upper surface of the insert was flat, i.e., it changed the entry to the capillary from an included angle of 60° to one of 180°.

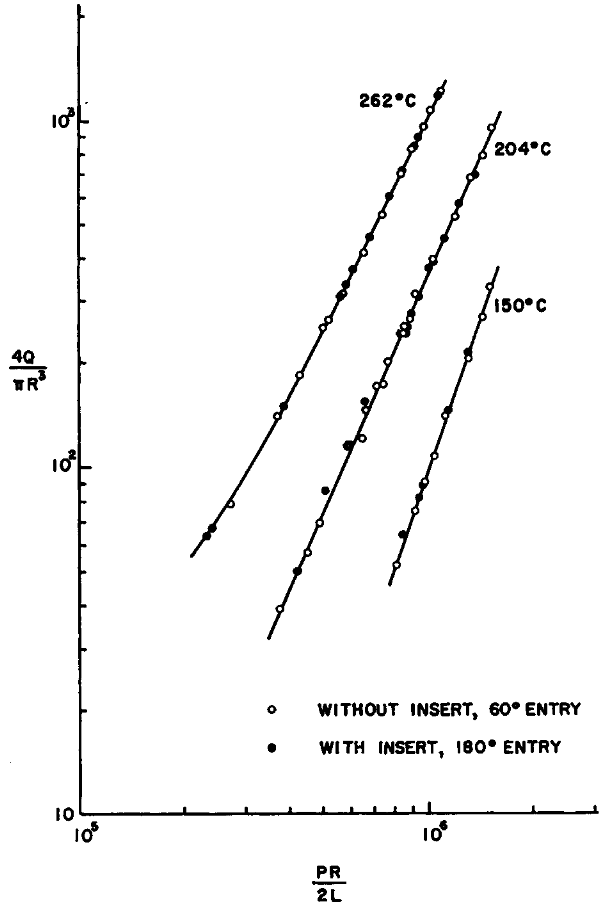

Fig. 1. Flow curves obtained with and without square-edged insert coincide despite extrudate irregularities introduced by insert.

With the square-edged insert, the extruded rod became wavy above a critical shear rate D_c.[3] Between 50 and 600 sec.$^{-1}$, D_c is related to temperature by

$$D_c = 1.79 \times 10^8 \exp\{-12{,}783/1.987T\}$$

Without the insert, no extrudate irregularity was observed at any of the three temperatures throughout the range of shear rates tested. The highest shear rates attained without the insert were from four to six times larger than the critical shear rates with the insert. Streamlining the inlet retards the appearance of extrudate distortions by at least that factor. This agrees with previous results[2–4] but disagrees with Metzner's data.[7]

The origin of the irregularities in the extrudate is at the capillary inlet, since the only change introduced in the die geometry by the insert, which brought on these irregularities, was an increase in entry angle. Upstream propagation of the irregularities from the die exit[6] is unlikely, considering that the length-radius ratio is 79.

The isothermal flow curves determined with and without the insert coincide, despite the fact that distorted extrudates were obtained with the insert over most of the flow curve at

150°C. and over half of the flow curve at 204°C. (see Fig. 1). There is no change in slope in the logarithmic flow curves at the critical shear rates which were observed with the insert, namely, 52 sec.$^{-1}$ at 150°C. and 244 sec.$^{-1}$ at 204°C.[7]

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