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# Morphology of Polyethylene Crystallized Under the Simultaneous Influence of Pressure and Orientation in a Capillary Viscometer

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## Synopsis

The morphology of high-density polyethylene crystallized under simultaneous pressure and shear in an Instron capillary viscometer has been examined by scanning electron microscopy, electron microscopy, and selected-area electron diffraction. Two distinct fibrous morphologies were observed in these unusually transparent strands. The outer sheath was composed of fibers, 3000 Å in diameter, aligned parallel to the extrusion direction and apparently interconnected by a lamellar cross texture. A highly crystalline ribbon texture composed of fine fibers, 200–250 Å in diameter, dominated the inner core. Sharp-spot electron diffraction patterns obtained from these central ribbons indicated a high degree of *c*-axis orientation parallel to the fibers and an extended-chain crystal structure. The melting behavior of both irradiated and unirradiated strands examined by differential scanning calorimetry was consistent with the formation of two distinct crystalline morphological units.

## INTRODUCTION

The morphologies of linear polyethylene crystallized from the melt under high pressure and crystallized under shear from both the melt and dilute solution have been reported previously. Wunderlich and others[1–6] have described the extended-chain structure crystallized under static pressures of at least 300 atm. The morphology so produced is characterized by striated, extended-chain crystals in which the molecular axis is oriented parallel to the striations. Pennings and others[7–9] have demonstrated that a fibrous morphology is generated when, for example, a dilute solution of polyethylene (1% in xylene) is stirred during crystallization. Electron microscopy has shown that the individual fibers crystallized under these shearing conditions contain chain-folded lamellae attached to an extended chain central backbone, resulting in a "shishkabob" arrangement. Furthermore, Keller and Hill[10,11] have shown that an analogous, fibrous crystalline structure can be generated when a lightly cross-linked polyethylene is

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cooled from the melt under stress. They reported extensive evidence that that resulting morphology is a consequence of extended-chain backbones acting as sites for nucleation of chain-folded growth in directions perpendicular to the extended-chain crystal structure.

This paper describes the crystalline morphology induced in linear polyethylene when it is crystallized under the simultaneous influence of flow orientation and high pressure realized in the Instron capillary rheometer. The pressure and orientation effects resulted in an unusually transparent high density polyethylene having a significant content of highly oriented crystallites.[12–14] The resulting highly ordered, fibrous texture was observed to have many similarities to morphologies generated in shear-crystallized, high-pressure-crystallized, and cold-drawn polyethylene.

## EXPERIMENTAL

The polymer used in this study was commercially available high-density polyethylene, Dupont Alathon 7050, having number- and weight-average molecular weights of 18,400 and 52,500, respectively. Samples were prepared in the Instron rheometer operated at a constant plunger velocity by using a capillary 0.0508 cm in diameter and 1.55 cm long with a 90° entrance angle. Crystallization was induced under the combined orientation and pressure effects produced at a 0.5 cm/min plunger velocity and a rheometer temperature of 136°C.

After the plunger was activated, a sustained pressure rise was observed (see Fig. 1), together with abnormal extrudate swelling. Both factors were evidence of crystallite formation. Crystallite nucleation and growth were expected, since the equation of state developed by Wunderlich[1] for high-density polyethylene indicated that the melt was definitely in a supercooled state under the existing pressure and temperature. An observed decrease in the linear extrusion velocity, attributed to crystallization, was accompanied by a rapid increase in the pressure to the 1920 atm upper limit available in the Instron rheometer. The pressure trace (Fig. 1) showed a distinct discontinuity at 575 atm which occurred after crystallization had begun. This inflection point implied that crystallization had resulted in a significant contraction of the polyethylene in the reservoir. Plunger motion was halted at 1920 atm, but extrusion was continued at 0.02 cm/min by adjusting pressure.[13] The distinctive sample morphology discussed herein resulted from the intense orientation effects that occurred as the crystallizing polyethylene was forced under 1920 atm from the cylindrical reservoir of 0.9530 cm diameter into the 0.0508 cm capillary. The partially crystalline mass was subjected to high shear as well as pressure, leading to crystal reorganization as well as additional crystallization. The higher crystalline content was confirmed by the increased heat of fusion of the transparent strands obtained from the capillary relative to that of the polyethylene obtained from the reservoir.[12] The specimens were removed from the rheometer after cooling to 114°C under 1920 atm. This cooling cycle