The Influence of Initial Morphology on the Physical and Mechanical Properties of Extruded High Density Polyethylene Fibers

W. T. Mead[a]; Roger S. Porter[a]

[a] Materials Research Laboratory, Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts

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W. T. MEAD and ROGER S. PORTER

*Materials Research Laboratory, Polymer Science and Engineering Department
University of Massachusetts, Amherst, Massachusetts 01003*

Ultra-oriented high density polyethylene fibers have been produced by solid state extrusion of various polyethylene morphologies prepared in the reservoir of an Instron Rheometer. A constant extrusion temperature and pressure were used in the following studies: (a) high density polyethylene melted at 170°C and then cooled at ~ 1°C min^{-1} to the desired extrusion temperature below the ambient melting point; (b) a molten sample removed from the rheometer and quenched into an ice-water bath and subsequently extruded; (c) a chain-extended polyethylene prepared by crystallization at 0.49 GPa and 200°C; (d) various chain-folded morphologies prepared by isothermal crystallization between 134°C and 200°C and pressures from 0.12 to 0.49 GPa.

The properties of the fibers have been assessed by birefringence, thermal expansivity, differential scanning calorimetry, small angle X-ray scattering, modulus, and tensile strength. Fibers produced from the various isothermally-crystallized morphologies attained, at deformation ratios 20–30, a birefringence (in the draw direction) greater than a perfect polyethylene single crystal value (c-axis) of 0.059 and a maximum modulus of 70 GPa. Maximum birefringence was obtained with increasing crystallization temperature and molecular weight of the chain-folded morphology. Extrusion of chain-extended HDPE of molecular weights 5×10^4–147×10^3 produced brittle fracture of the extrudate. This was explained by the high fraction of segregated low melting polymer between the chain-extended lamellae.

INTRODUCTION

The morphological changes of high density polyethylene (HDPE), occurring during solid state extrusion after isothermal crystallization have been reported

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by Mead and Porter.[1] The extrusion pressure was commonly ~0.23 GPa and secondary crystallization and row nucleation with thin lamellae was observed in the conical die region as well as deformation of spherulitic morphologies.[2] Mead, Desper, and Porter[3] reported results of extrusion over the temperature range 60–140°C and pressures up to 0.49 GPa. A small tensile modulus increase was induced at higher extrusion pressure to 0.49 GPa which may result from the formation of a chain-extended morphology and/or the suppression of secondary crystallization. Such a morphology may affect the resulting fiber properties and this is thus the subject of the study presented herein.

The influence of initial morphology on the achievement of high modulus polyethylene by drawing has been reported by Capaccio et al.[4-6] and Barham and Keller.[7] Cappacio and Ward[4,5] found thermal pretreatment can have a dramatic influence on the rate of draw, but did not appear to affect the ultimate draw ratio. Barham and Keller[7] report that the maximum draw ratio and, hence, modulus achievable from a particular sheet by drawing was dependent on its morphology and molecular weight distribution. In our studies, fibers extruded over the range 60–140°C and up to 0.49 GPa all contained chain folds as indicated by the appearance of a two point small angle X-ray (SAXS) intensity pattern along the fiber axis. Frank[8] has pointed out that the chain folding allows a high degree of chain alignment along the fiber axis without extensive chain continuity along the fiber. Crystallization of HDPE at low pressure gives a chain-folded morphology whereas a microstructure crystallized from the melt at 0.5 GPa contains lamellae up to a few microns in thickness.[9-11] This chain-extended morphology has been shown to be a consequence of crystallization of the hexagonal phase, as reported by the recent review of Bassett.[9] Extrusion of this morphology might produce a high modulus fiber since, as pointed out by Bassett and Carder,[10] oriented chain-extended HDPE possesses high local chain orientation and molecular extension. Attenburrow and Bassett[11] report that Hifax® PE with molecular weight $> 2 \times 10^6$ was ductile up to draw ratios of 5 at 80°C. Lupton and Register[12] extruded a high molecular weight HDPE and produced high strength extrudates. Small angle studies of the extrudates showed that the fold period decreased with draw ratio, possibly a result of the longer fold periods being preferentially drawn to produce a more perfect morphology. At higher crystallization temperature and pressures, the long period of the initial morphology is known to increase. If these morphologies are then extruded there might be a difference between the concentration and period of folds. Lower draw ratio should, in principle, thus be required to extend fully the molecules.

The present study reports a systematic study of the influence of initial morphology on the properties of extrudates: (a) HDPE melted at 170°C and then cooled at ~1°C min^{-1} to the desired extrusion temperature below the

ambient melting point; (b) a molten HDPE removed from the rheometer and quenched into an ice-water bath and subsequently extruded; (c) a chain-extended HDPE prepared by crystallization at 0.49 GPa and 230°C; and (d) various chain-folded morphologies prepared by isothermal crystallization between 134°C and 200°C and at a pressure of ~0.3 GPa.

The properties of the fibers have been assessed by birefringence, thermal expansivity, differential scanning calorimetry, small angle X-ray scattering, and by tensile modulus and strength.

EXPERIMENTAL

Polymers

The Alathon high density polyethylenes series was used (Du Pont). Details of their weight and number average molecular weights is given by Perkins, Capiati, and Porter.[13] A special sample of Alathon 7040 was kindly supplied by Dorothy J. Pollock of Arco Polymers (Monroeville, Penn.) for GPC analysis. GPC analysis of the original pellets indicated that the number of branch points was less than 1 per 10^4 main chain carbon and that M_n was 17,000, $M_w = 7,800$ and $M_z = 228,000$.

Morphology preparation and extrusion

Stainless steel conical dies were used to extrude the HDPE. The die geometry, its draw ratio variation, and the extrusion procedure have been described elsewhere.[1,14] The dies were cleaned with acetone and no lubricant was used. No external load was applied to the extrudate. A paper-clip placed on the extrudate served as a fiducial mark for the cathetometer measurement of extrusion rates.

Several different initial morphologies were prepared for extrusion, namely:

Crystallization at ambient pressure
   a) Annealed HDPE: The HDPE (Alathon 7050) was heated to 170°C in the rheometer reservoir and then allowed to cool ~1°C min^{-1} to the extrusion temperature which was always below the ambient melting point.

   b) Quenched samples: HDPE was heated to 170°C in the rheometer reservoir. The sample contained in the conical die was then quenched in an ice-water bath. The preformed billet was then placed in the rheometer for ~30 minutes at the required extrusion temperature, below the ambient melting point. Pressure was then applied to initiate extrusion.

High pressure crystallization

a) Chain-folded morphologies: These were prepared by crystallization at temperatures between 134°C and 200°C to produce an undercooling according to the equation (in °C)

$$\Delta T = T_m{}^\circ + 200\,P - T_c$$

where $T_m{}^\circ$ is the equilibrium melting point of a perfect polyethylene single crystal (142 ± 1°C),[15] T_c is the crystallization temperature and the melting point increases by 200°C/GPa.[15] The pressure was applied for 30 minutes to achieve an equilibrium state of crystallization. Different undercooling and therefore polyethylene morphologies were obtained by using several applied pressures (0.12, 0.24, 0.39 GPa), and by varying the crystallization temperature. Above 0.24 GPa chain-extended HDPE may be produced.[14–19] The pressure was applied to the melt at an approximate rate of 0.16 GPa min⁻¹. The temperature rise due to the quenching was ~2°C as indicated by the Instron recorder, monitoring the temperature of the barrel, near the specimen. It is possible that such a slow quench may give rise to chain-extended polyethylene.[16] After crystallization was apparently complete as judged by zero piston velocity, the heaters were switched off and the polyethylene was allowed to cool to the extrusion temperature. Volume changes during the cooling were measured by recording the piston height change above the sample.

b) Chain-extended morphology: With increasing crystallization pressure (> 0.24 GPa) chain-extended morphologies may be produced. At the highest crystallization temperature and pressure used (250°C, 0.49 GPa) teflon plugs were used, with diameters equal to that of the barrel, to prevent leakage. A small hole was drilled centrally in the half-inch long plug, which was placed between polymer and piston and thus prevented air from being trapped between plug and plunger or sample and teflon plug. Crystallization rates were measured by observing the time dependence of the downward plunger movements. Six to eight hours were used for crystallization times for formation of the chain-extended HDPE.

Characterization techniques   Melting endotherms for the initial and extruded morphologies were determined by a Perkin-Elmer differential scanning calorimeter (DSC) Model 1B. Heats of fusion and crystalline weight fraction were determined in the usual way. Further details of DSC operation and the TMS thermal expansion attachment are described by Mead and Porter.[16]

The modulus and tensile strength measurements were made on extruded fibers using an Instron TTM and an Instron strain gauge extensometer with a magnification of 10³ for modulus. A fiber of ~40 cm length was clamped at each end and subjected to an increasing load. Moduli were measured at 0.1 % strain. The strain gauge extensometer, having a measurement specification of

2.5 cm between its ends, was placed at varying points to evaluate differences along the fiber. The extension rate for modulus tests was 0.05 cm min^{-1} and 0.5 cm min^{-1} for tensile strength measurements. No corrections are applied for compliance of the machine when reporting strain to fracture results as well as the modulus dependence on aspect ratio. All tests were performed at room temperature.

Any variation in molecular weight and distribution because of possible degradation due to the high pressure treatment was checked with a Waters Associates Model 200 Gel Permeation Chromatograph at Arco Polymers by Dorothy Pollock. The solvent, σ-dichlorobenzene was pumped at a rate of 2 ml min^{-1} through six styagel columns with maximum pore sizes of $10^{6.7}$ linear 10^6, $10^{4.6}$, 10^3 and $10^{2.7}$ Å.

Electron micrographs were obtained on surfaces fractured in liquid nitrogen. A Japan Electron Optics Scanning microscope, Model JSM-1 was used.

Small angle X-ray analysis of the fibers was undertaken using a Warhus camera with nickel filtered CuK$_\alpha$ radiation and 0.1 mm pinhole collimation. The fibers were placed in an evacuated chamber and exposed to a 20 mA beam current operating at 35 kV. Intensity SAXS studies were conducted using a Kratky camera with Ni filtered CuK$_\alpha$ radiation. The intensities were collected through a 60 μm receiving slit by a NaI scintillation detector and electronic pulse height analyzer. No slit desmearing techniques were used since highly oriented fibers were being characterized.

RESULTS AND DISCUSSION

Extrusion characteristics of initial morphologies

Figure 1 is a plot of the apparent elongational viscosity versus extrudate length of chain-folded and chain-extended morphologies with crystallization temperatures as shown: η_E is defined as $\sigma_z/\dot{\gamma}$ where σ_z is the axially applied pressure and $\dot{\gamma}$ is the elongational rate $\dot{\gamma} = (1/L)(dL/dt)$ where dL/dt is the velocity of the fiber of length L at the die slit. A detailed description of extrusion rates for a chain-folded HDPE morphology extended from 60–140°C has been discussed by Mead and Porter.[1] For HDPE crystallized at 134°C and 0.49 GPa and extruded at 80°C and 0.49 GPa the apparent elongational viscosity increases rapidly with length and the logarithm of η_E increases approximately linearly with draw ratio for extrusion at 80°C. On extrusion at temperatures greater than 120°C the form of the viscosity curves is similar to those obtained at 0.49 GPa except that initial rates are too high for easy measurement. Extrusion of chain-extended polyethylene at 134°C and 0.49 GPa also produced fibers at a rate too high to measure. The apparent elongational viscosity curves for HDPE crystallized between 220–250°C at 0.49 GPa approach a limit of
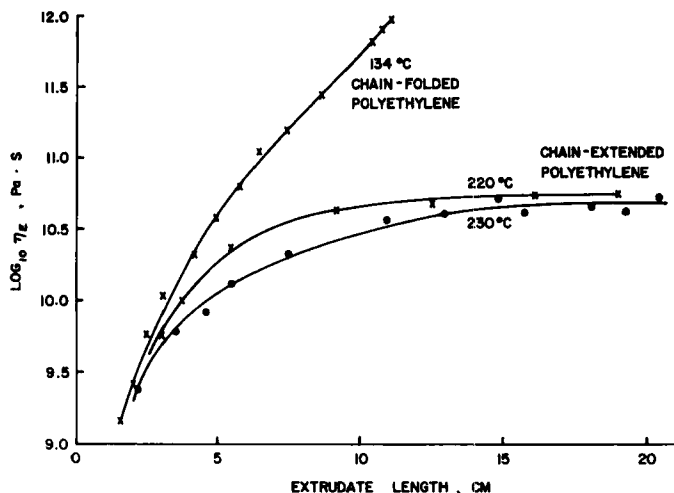
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FIGURE 1   Variation of apparent elongational viscosity with extrudate length for extrusion of chain-folded and chain-extended morphologies (Alathon 7050, $M_w = 52,000$) with crystallization temperatures as shown.

$\sim 10^{10.5}$–10^{11} Pa·s. The drawing mechanism in which the non-crystalline orientation increases cannot occur for extruded chain-extended polyethylene having a crystalline weight fraction of unity. The interlamellar or non-crystalline component of the polymer appears to determine the strain hardening, and flow rate and drawing mechanism of the crystallized polyethylene undergoing solid state extrusion. As discussed below the Young's modulus of the extruded chain-extended HDPE also approaches a limiting value between 30–50 GPa.

The chain-extended polyethylene was extruded at 60°C at relatively high rates ~ 0.3 cm min^{-1}. These fibers did not have any higher modulus at 60°C than fibers extruded at 120°C. Mead, Desper, and Porter[3] have shown that at lower extrusion temperature only the non-crystalline orientation of the fiber increases while the crystalline orientation function decreases. Drawing experiments have been reported by Attenburrow and Bassett[11] for chain-extended HDPE of viscosity average molecular weight greater than 2×10^6. The drawing temperature was 80°C which is possibly near the α relaxation region for polyethylene[17] although the dispersion temperature will possibly vary with molecular weight and crystalline weight fraction. The stress–strain curve showed local yielding and strain-hardening with a stress at fracture of 16 MPa.

The extrusion rates for an initial, chain-extended PE morphology did not significantly vary with weight average molecular weight from 52,000 and 147,000. Apparent elongational viscosities obtained by extruding chain-folded morphologies of high molecular weight 2–6×10^6 rapidly increased with

draw ratio, the maximum obtainable draw ratio decreasing with the molecular weight. The apparent elongational viscosities for chain-extended polyethylene of molecular weight $\sim 10^6$ rapidly increase with draw ratio and approach values typical of chain-folded morphology.

The formation of chain-extended polyethylene must deplete the fraction of intercrystalline amorphous material and with increasing crystalline formation c-axis slip is more probable.

DSC measurements: initial morphology

Figure 2 shows the atmospheric (0.1 MPa) melting endotherms of Alathon 7050 HDPE prepared by crystallization at 0.49 GPa at the several crystallization temperatures shown. The morphologies were cooled ($\sim 1^\circ$C min^{-1}) from the crystallization temperature to the extrusion temperature (120°C). As the crystallization temperature was increased from 134°C to 230°C, the peak endotherm melting point increases from 133°C to 142°C at 10°C min^{-1} heating rate. In the crystallization range 134–200°C only one peak melting point is observed. Annealing above 210°C at 0.49 GPa produces multiple (4) peaks. In this temperature and pressure range where chain-extended PE is produced the density increases and heat of fusion rapidly increases from 55 to 67 cal gm^{-1}.

Bassett et al.[18-23] have shown that the multiple peaks are associated with melting of segregated PE of lower molecular weight. The area of the minor peaks of the endotherm curves occurring in the temperature range 124–125°C and 131–133°C increase with crystallization temperature. Bassett et al.[20,21] observed in the melts of HDPE samples crystallized at 0.3 GPa minor, peaks which fall into two sets ≤ 137.4 and ≥ 138.1, associated with chain-folded and

CRYSTALLIZATION TEMPERATURES

200 °C   210 °C   220 °C   230 °C
55.1 cal gm^{-1} 55.7 cal gm^{-1} 61.0 cal gm^{-1} 67.9 cal gm^{-1}
                                        141 °C

133 °C   142 °C
                137 °C

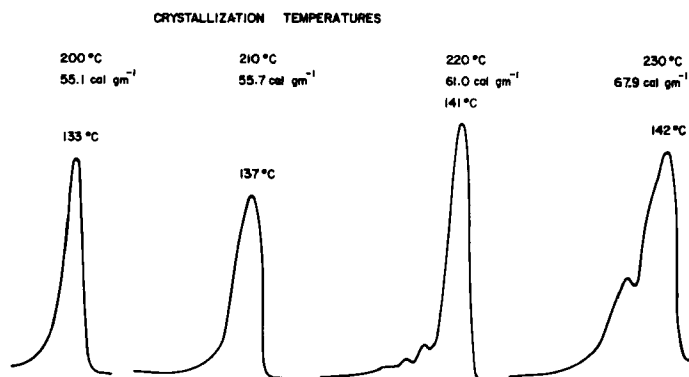FIGURE 2   Melting endotherms observed at 0.1 MPa and 10°C min^{-1} differential scanning calorimetry heating rate after crystallizing high density polyethylene (Alathon 7050, M_w = 52,000) at 0.49 GPa and crystallization temperatures as shown.

chain-extended crystallization. To provide an estimate for formation of these new peaks, a quantity termed "the peak area fraction", P_F, was introduced. Bassett *et al.*[20-23] defined P_F as the area of the highest temperature peak on the highest temperature side of the first minimum on the DSC trace below the peak divided by the total area of the endotherm. A similar quantity was used in determining the ratio of chain-extended to chain-folded PE in annealed HDPE fibers. Both the density and heat of fusion increased approximately linearly with P_F. As the crystallization temperature is increased from 210–220°C, P_F increases by $\sim 10\%$. Variations of P_F may, therefore, be correlated with the mechanical properties.

DSC measurements: extruded fibers

Figures 3 and 4 show the peak melting point of the DSC endotherm curves and the crystalline weight fraction versus draw ratio respectively for extruded fibers of Alathon 7050 HDPE crystallized at the indicated temperatures. The crystalline weight fraction increases with crystallization temperature at 0.49 GPa. However, the peak melting point of the DSC endotherm of the extruded chain HDPE fibers show a slight decrease with increasing crystallization temperature. It is likely that the lamellae have become disrupted during the 0.49 GPa extrusion since extrusion of chain-extended HDPE produced fragments of the fiber unable to support their own weight. Attenburrow and Bassett[11] have argued that the crystal thickness and melting point of chain-
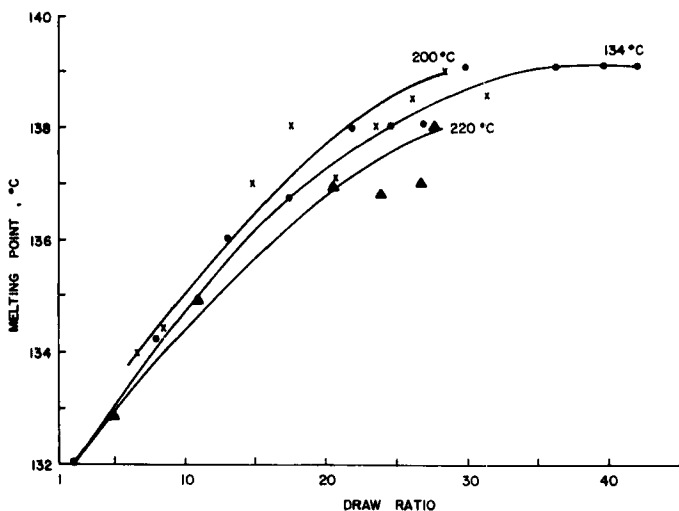

FIGURE 3   Dependence of melting point on draw ratio for HDPE crystallized at 0.49 GPa and crystallization temperatures as shown and subsequent extrusion at 0.49 GPa and 120°C.
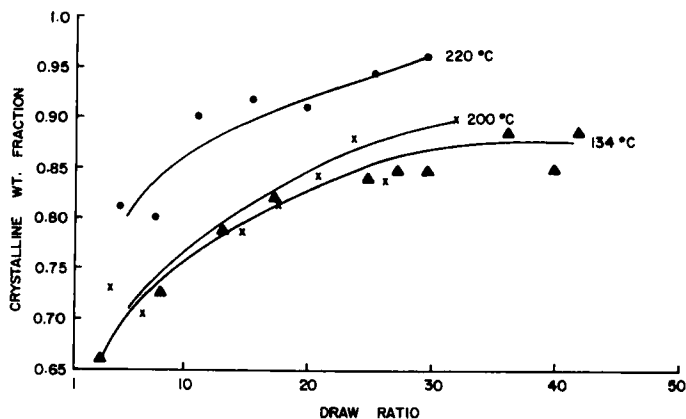
FIGURE 4   Variation of crystallinity of extruded fibers with draw ratio of HDPE (Alathon 7050, M_w = 52,000) crystallized at 0.49 GPa and temperatures as shown and extruded at 0.49 GPa and 120°C.

extended PE provides unequivocal measures of melting during deformation. During deformation of the chain-extended PE, lamellar rotation, voiding, crazing and kink band formation by interlamellar shear may occur. It is likely that the lamellae of the chain-extended PE are partially destroyed or rearranged during the high pressure extrusion to give a less perfect structure.

The melting points for the extruded fibers are approximately a linear function of the initial crystallization temperature, apparently obeying the Hoffman-Weeks equation,[24] until a component of chain-extended PE is formed (by extrusion). The melting endotherms of the extruded chain-extended PE show only one peak melting point compared with the several melting peaks of the original morphology. During extrusion through the conical die these lower melting peaks, possibly due to segregation of the lower molecular weights, are observed.

Thermal expansivity data

Chain extended morphology   Figure 5 shows the linear expansion coefficients of extruded HDPE plotted against draw ratio. The crystallization pressure was 0.49 GPa and the crystallization temperatures are indicated in Figure 5. As the crystallization temperature and draw ratio is increased, the expansion coefficient approaches a negative constant value just less than that of the polyethylene single crystal -1.2×10^{-5} °C^{-1}. The sign and magnitude of the limiting expansion coefficient, -0.6×10^{-5} °C^{-1}, suggests the existence of a chain-extended structure. The fraction of chain-extended PE produced by extrusion of chain-folded PE has been estimated to be $\leq 18\%$.[13] However, the
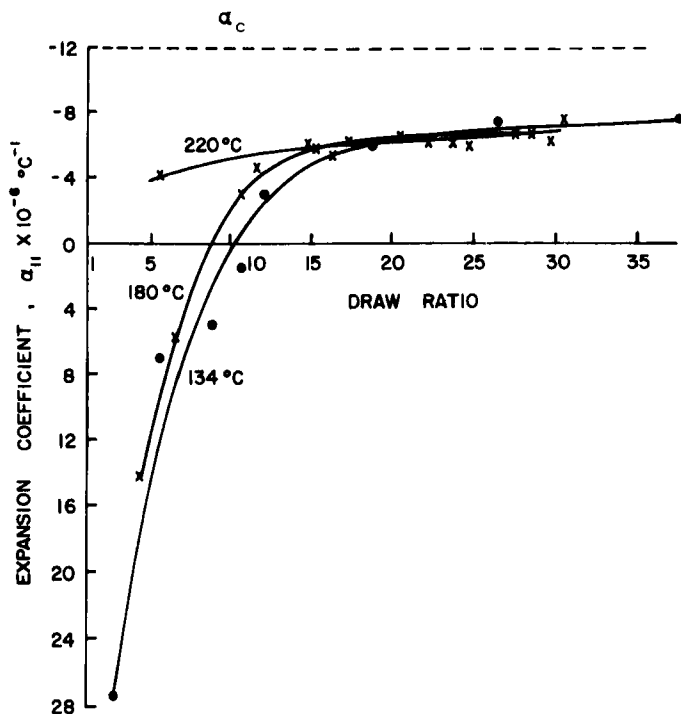
FIGURE 5   Variation of linear expansion coefficient (-120 to $80°C$) with draw ratio of high density polyethylene (Alathon 7050, $M_w = 52{,}000$) crystallized at 0.49 GPa and temperatures as shown and subsequent extrusion at 0.49 GPa and 120°C.

expansion coefficients of the fibers produced by extrusion of chain-folded or chain-extended PE morphology both approach limiting values of -0.6×10^{-6} $°C^{-1}$. This possibility indicates a larger component of chain-extended PE obtained by extrusion of the chain-folded PE.

Modulus measurements

Chain-folded and chain-extended morphologies   Figures 6 and 7 plot the tensile modulus versus draw ratio of HDPE prepared at 0.49 GPa and 0.39 GPa and crystallization temperatures as shown. The extrusion temperature used for these tests was 120°C, a temperature where annealing and structural change (for the crystalline component) are thought to be minimal. The extrusion pressures were 0.49 GPa and 0.39 GPa respectively. The aspect ratio of these fibers was approximately 300, a factor of ten greater than the minimum aspect required for "end effect" corrections. Arridge and Folkes[19] have noted that tensile specimens need to be at least $2b(E/G)^{1/2}$ in length before uniformity of
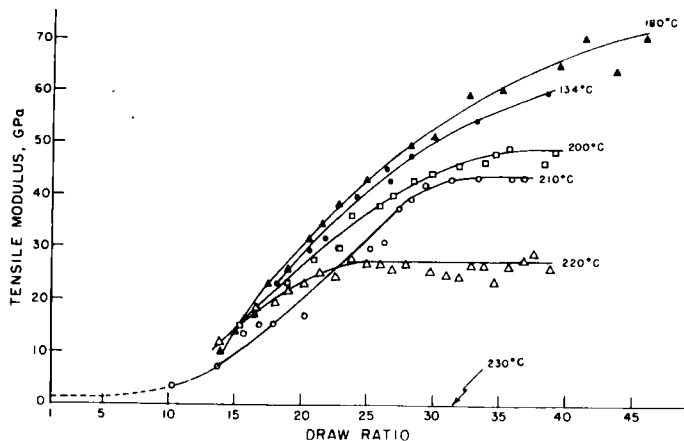
FIGURE 6   Dependence of tensile modulus on fiber draw ratio at various crystallization temperatures. The fibers were crystallized at 0.49 GPa and extruded at 120°C and 0.49 GPa.
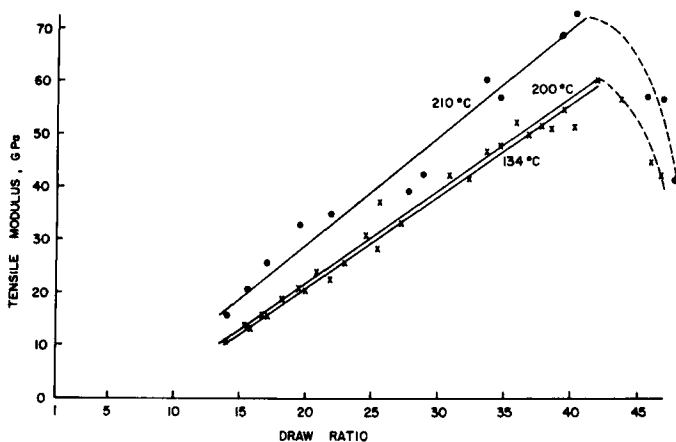
FIGURE 7   Tensile modulus versus draw ratio of extruded high density polyethylene (Alathon 7050, $M_w = 52,000$) crystallized at 0.39 GPa and temperatures as shown. Extrusion temperature and pressure 120°C and 0.39 GPa.

stress over the sample cross section can be assumed: b is the maximum lateral dimension of the sample, E is Young's modulus along the fiber axis, G is the longitudinal shear modulus. If G is assumed to be ~ 5 GPa[25], then if the modulus varies from 5 to 70 GPa, the aspect ratios should be at least 2 and 7.5, before the end effects can be neglected.

In the crystallization temperature region of 200–230°C where the component of chain-extended crystals increases, as assessed by the parameter P_F, the modulus decreases. There thus appears to be an optimum chain-folded/chain-

extended content above which extrusion leads to a drop off in modulus. Above 220°C the fraction of chain-extended HDPE is ~90% yet the tensile modulus of the extrudate is comparable and certainly not greater than extrusion of a chain-folded morphology. This is consistent with experiments of Bassett and Carder[20] who studied the mechanical and physical properties of chain-extended HDPE annealed at 0.53 GPa. (No drawing studies were made on these samples.) Annealing below 236°C led on extrusion to a tensile modulus of ~40 GPa whereas annealing above 240°C resulted in a markedly lower modulus. The change from ductile to brittle behavior in tension along the c-axis for samples annealed above 240°C (in our case 230°C) was explained by Bassett and Carder as due to the segregation of low melting polymer between chain-extended lamellae. These are associated with the endotherm peaks of Figure 2. According to Bassett and Turner[21] the endothermic peaks mark a transition to a new intermediate phase of PE. They showed that the shorter molecules were less susceptible in forming the new phase, and therefore the low molecular weight component will tend to be excluded from the intermediate phase. Brittle fracture occurs because of this segregation of shorter molecules between the chain-extended lamellae. Modulus reduction of the extruded fibers is produced at crystallization temperatures only where CE HDPE is formed. Bassett and Carder[20] concluded that the rise in modulus produced by high pressure annealing is inherently restricted to values appropriate to the proportion of well-defined interlamellar or amorphous regions. Although orientation of the lamellae is expected during extrusion, the brittleness of the fiber is possibly also due to segregation of low molecular weight components producing well-defined interfaces.

According to Lupton and Register[12] extrusion of CE HDPE of high molecular weight ($\sim 10^6$) can produce high strength fibers. Recent work in this laboratory which extends work reported here has shown that chain-extended HDPE consisting of high molecular weight may indeed be extruded to produce high strength fibers.[26] Plastic deformation during drawing of CE HDPE has been reported by Attenburrow and Bassett.[11] They offer explanations for the ductility obtained on deformation of high molecular weight HDPE. With increasing molecular weight the number of interlamellar connections increase which might reduce stresses produced by lamellar slip parallel to the c-axis. The ductility might also be due to an increase in number of tie molecules as well as loops (i.e. trapped entanglements and chain folds). This feature can also be responsible for part of the mechanism for effective drawing. Without trapped entanglements in folds the CE HDPE would be expected to be brittle because of the crystalline interfaces. Extrusion of high molecular weight ($> 10^6$) HDPE produces very low extrusion rates as shown by Mead and Porter.[1] Hydrostatic extrusion and formation of CE HDPE are two possible methods to produce higher extrusion rates.

According to Barham and Keller,[7] the maximum draw ratio and, hence, modulus achievable from a particular sheet depends on morphology, molecular weight distribution, and the presence of a segregated low molecular weight phase. Smith *et al.*[27] have observed a narrow line in the NMR spectra of such sheets which they attributed to the segregation of low molecular weight material during crystallization. The requirement of Barham and Keller of the presence of segregated low molecular weight material for ductile deformation at high draw ratios appears to be inconsistent with the experiments described above in which the presence of the low molecular weights produced brittle fracture.

Quenched, annealed and isothermally crystallized morphologies   Figure 8 shows a plot of modulus versus draw ratio for fibers extruded at 0.23 GPa and 120°C and having different initial morphologies. A quenched HDPE Alathon 7050 as described in the experimental section, a HDPE Alathon 7050 slowly cooled from 160 to 120°C, and Alathon 7050 isothermally crystallized at 134°C and 0.23 GPa were included in these measurements. It appears that Young's modulus of ultra-oriented HDPE is insensitive to the thermal history of the morphology prepared prior to extrusion, providing crystallization pressures are less than 0.3 GPa. Within experimental error, all modulus versus draw ratios results can be represented by one curve. Effective extrusion of these
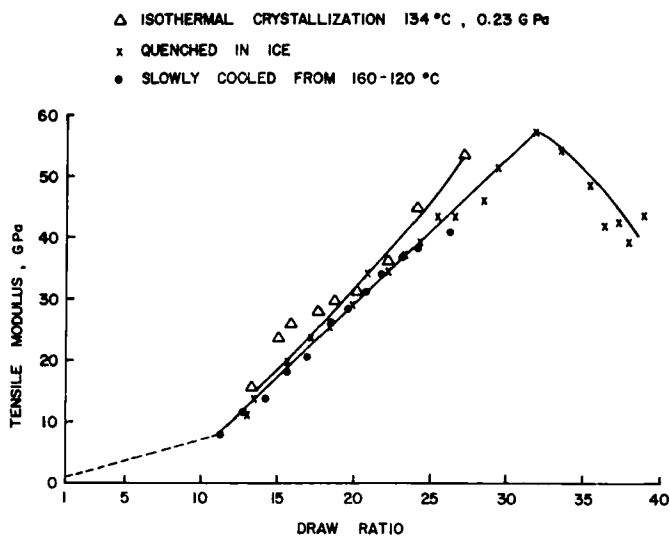

FIGURE 8   Tensile modulus versus draw ratio of extruded HDPE (Alathon 7050, M_w = 52,000) having initial morphologies as shown. Extrusion temperature and pressure was 120°C and 0.23 GPa.

morphologies has been achieved. Moreover, the draw ratio where fracture occurs does not depend markedly on the initial morphology but rather on the extrusion temperature.

Capaccio and Ward[4,5] have also studied the drawing behavior of polyethylene having various thermally-treated morphologies. They concluded that the thermal pretreatment, the crystallization procedure, can have a dramatic effect on the rate of draw, but, consistent with our results, does not appear to markedly influence the ultimate draw ratio and, hence, modulus which can be obtained.

Birefringence measurements

Chain-folded and chain-extended morphologies   Figure 9 shows the birefringence versus draw ratio data of Alathon 7050 HDPE crystallized at 0.49 GPa and at temperatures shown and then cooled at $\sim 1°C$ min^{-1} to 120°C for extrusion at 0.49 GPa applied pressure. The undeformed, initial morphologies exhibited no birefringence, indicating no preferred orientation. With increasing draw ratio the birefringence rapidly increased approaching a limit. The form of these curves has already been discussed.[1,3] It appears that no models or equations are available which predict the variation of birefringence due to morphology changes. The form birefringence was not estimated for these fibers, as had been done previously for isothermally crystallized PE extruded at 0.23 GPa.
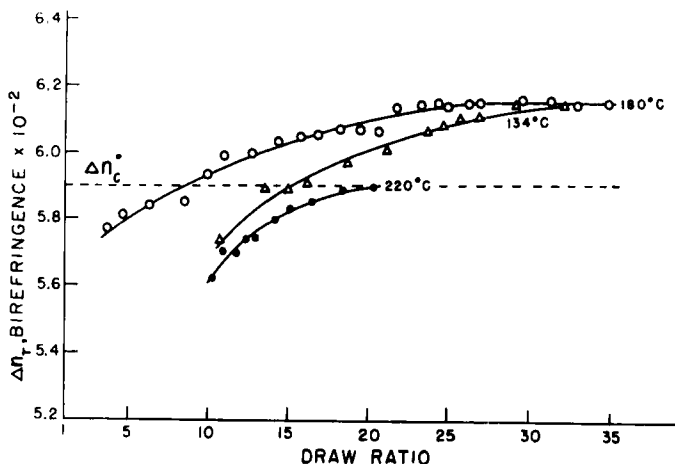
FIGURE 9   Birefringence as a function of fiber draw ratio at various crystallization temperatures. The morphologies were crystallized at 0.49 GPa and extruded at 120°C and 0.49 GPa (Alathon 7050, $M_w = 52,000$).

At lower crystallization temperatures ($< 180°C$), the fiber birefringence rapidly increases, as shown in Figure 9 approaching a limit near 0.061. This value is greater than the intrinsic birefringence of the crystalline phase. The crystalline orientation functions by X-ray for a fiber extruded at 134°C and 0.23 GPa is 0.9960 ± 0.002. A birefringence of 0.061 can only be explained by a contribution of the strained non-crystalline phase, if the distortion and form birefringence contributions are negligible. The intrinsic birefringence of the amorphous or non-crystalline phase is higher than the crystalline phase, because of internal field effects as discussed elsewhere.[3]

The increase in birefringence for extrudate from increasing initial crystallization temperature may be explained by the corresponding increase in percent of crystallinity and/or by the increase of the birefringence contribution of the strained amorphous, i.e. non-crystalline phase. At 200°C crystallization temperature and above, birefringence decreases. At 220°C it approaches a limiting value of 0.059. This is probably a result of the high contribution of the crystalline fraction which has an estimated intrinsic birefringence of 0.059. The fraction of interlamellar material will be negligible and its birefringence contribution will thus be small.

As full molecular extension is approached at the highest crystallization temperatures and pressures, there is a change from ductile to brittle behavior on drawing, apparently because of the reduction in concentration of chain entanglements and number of tie molecules and folds for preventing crack propagation. Moreover, as the interlamellar content decreases the chain-extended morphology cannot be further drawn. Hence the birefringence of fibers made after crystallization at 230°C and above must approach a limit of 0.059, determined by the high orientation and volume fraction of the crystals. The birefringence of the fibers decreases from 0.061 to 0.059 as the crystallization temperature is increased above 180°C because the birefringence contribution of the non-crystalline phase decreases, as well as the crystalline orientation as shown by the wide angle X-ray diffraction photographs discussed below.

Mead, Desper, and Porter[3] studied the effect of increasing molecular weight on the properties of fibers obtained by extruding at 134°C and 0.23 GPa for morphologies isothermally crystallized at 134°C. Keeping the crystallization conditions constant, a higher total molecular orientation was obtained on increasing molecular weight. Moreover, Figures 7 and 9 show that for a given molecular weight, increasing the crystallization temperature also increases the measured birefringence of the fiber (up to a higher limit). Hence, using the same crystallization procedure, the birefringence is expected to be greater at any crystallization temperature if the molecular weight of the HDPE is increased. The birefringence of ultra-oriented fibers with draw ratio obtained by

extruding precrystallized morphologies of Alathon 7026, with $M_w = 147,000$ is shown in Figure 10.

Tensile strength measurements

Figure 11 shows tensile strength measurements versus crystallization temperature of Alathon 7050 annealed at 0.49 GPa and extruded at 120°C. The tensile strength of the fibers increases with crystallization temperature. The strength measurements were made on fibers having a draw ratio variation of 5–20 along their length. Brittle fracture occurs at temperatures greater than 220°C. The maximum value of the tensile strength obtained is 0.4 GPa, considerably less than the tensile strength of a PE single crystal which is 13 GPa. Chain ends and other crystal imperfections are limiting.

Zwijnenburg and Pennings[28] have also shown that increasing the crystallization temperature increases the tensile strength of drawn PE. The most important effect of the crystallization temperature on the mechanical properties was considered to be the increase in chain-extended material and the larger lateral dimensions of the backbones, since the melting point of the fiber increased with crystallization temperature. In Pennings' experiments a change of crystallization temperature from 105 to 120°C produced an increase in modulus of 5 and an increase in tensile strength to 3 GPa. In our experiments an increase in crystallization temperature from 134–180°C produces an increase in modulus by a factor of 1.2 and a similar enhancement of tensile
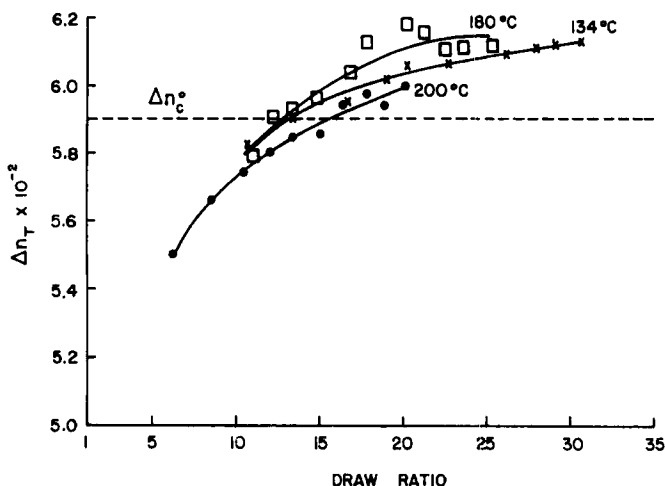

FIGURE 10   Birefringence of ultra-oriented fibers with draw ratio of high density polyethylene (Alathon 7026, $M_w = 147 \times 10^3$) crystallized at 0.49 GPa and temperatures as shown and subsequent extrusion at 120°C and 0.49 GPa.
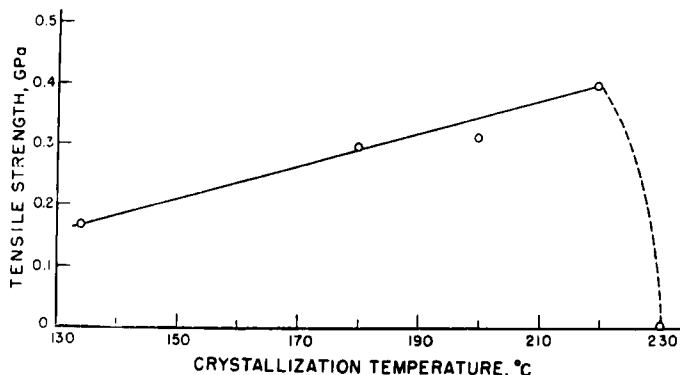
FIGURE 11   Tensile strength of ultra-oriented high polyethylene fibers (Alathon 7050, $M_w = 52,000$) as a function of crystallization temperature.

strength. According to Perkins *et al.*,[13] the tensile strength of the extruded fibers increases with molecular weight of the HDPE; the ultimate tensile strength increases by 3.0×10^3 psi as the average molecular weight increases by 87,000. In Pennings' report M_w was 1.5×10^6. Hence his high value for tensile strength, 3 GPa, and modulus (102.5 GPa) is possibly a result of the high molecular weight used. Lupton and Register[12] have also reported on the crystallization and extrusion properties of ultra high molecular weight polyethylene.

GPC of extruded chain-extended HDPE

Table I shows the average molecular weights of the Alathon 7040 original pellets. Duplicate runs were made to assess reproducibility. Also shown is the average molecular weight of segments of a fiber having draw ratio of 5 and 45. The fiber was prepared by isothermal crystallization at 220°C and 0.49 GPa

TABLE I

Molecular weights by gel permeation

Sample	M_n	M_w	M_z
Alathon 7040: original pellets	18,000	76,000	206,000
Alathon 7040: fiber draw ratio = 5 $\int^a$	13,000	67,000	214,000
	16,000	67,000	210,000
Alathon 7040: fiber draw ratio = 45 $\int^b$	14,000	65,000	191,000
	12,000	64,000	191,000

[a]Initial morphology prepared at 220°C, 0.49 GPa. Fiber prepared by solid state extrusion at 120°C, 0.49 GPa.
[b]Duplicate tests.

and subsequent extrusion at 120°C and 0.49 GPa. The normalized weight distributions of the GPC chromatograms are shown in Figure 12. The drop in molecular weight between the original polyethylene and the undrawn pre-crystallized morphology suggests that a measurable degradation occurred during morphology preparation.

GPC indicates possible degradation, but to a much lesser extent, between the highly drawn structure and the undrawn chain-extended HDPE. This difference could be accounted for by possible thermal degradation at 120°C. At present the degradation produced during drawing remains to be clarified. Attenburrow and Bassett[11] found that many lamellae of high molecular weight chain-extended HDPE were highly sheared by chain slip. Their normalized distributions showed a decrease from 6,400 Å to 5,480 Å as a result of drawing.
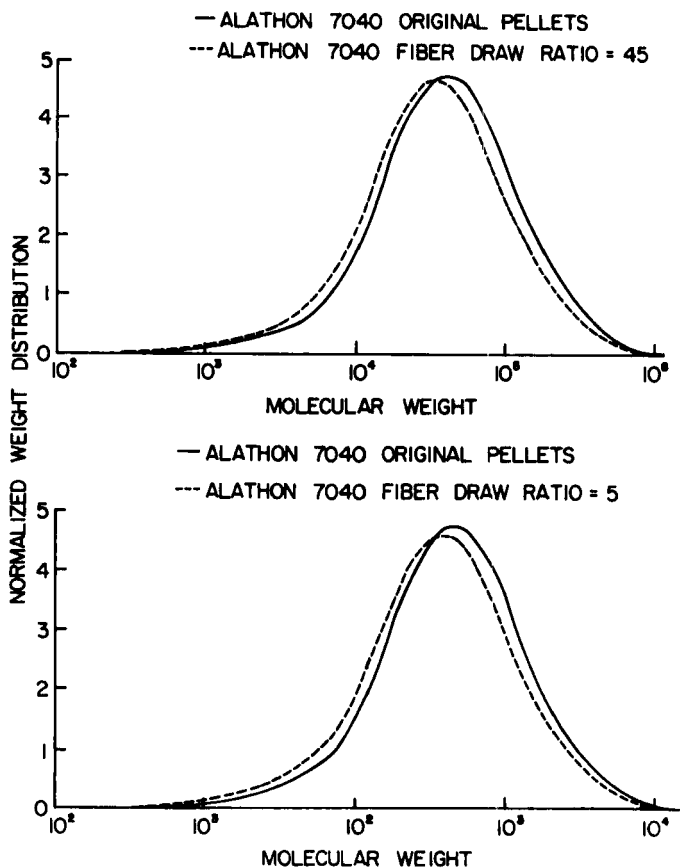

FIGURE 12   Normalized weight distributions of the GPC chromatograms.

X-ray measurements

Small angle X-ray scattering Small angle X-ray scattering has been used to calculate an apparent fold period—or correlations of disordered regions—for the solid state extruded fibers. Quite conventional fold periods of 240–300 Å have already been measured on the special morphologies. The axial long period, indicative of a periodic structure in the solid state extruded specimens, was calculated from meridional maxima of small angle X-ray scattering. For fibers extruded at 134°C and 0.23 GPa the long period has been shown to decrease by ~40 Å with increasing draw ratio. Nakayama and Kanetsuna[29] have also observed similar effects. Importantly, at extrusion temperatures less than 50°C the long period increases with draw ratio. At temperatures above 70°C, Nakayama and Kanetsuma[29] found that the long period decreases with draw ratio, consistent with our observations.

The long period measurements of the solid state extrudate crystallized at 134°C and 0.23 GPa show similarities to the stretching of polyethylene with respect to small angle X-ray scattering. Increasing the extrusion temperature over the range 80–134°C increases the long period by ~50 Å[3]. Corneliussen and Peterlin[30] investigated the effect of drawing temperature on the deformation of PE. They observed that the long period increased rather rapidly with temperature and rapidly increased near the melting point. The final meridional long periods were independent of draw ratio.

Extrudates of slowly cooled and quenched morphologies

Long period measurements of the slowly cooled and quenched samples have been made. Inspection shows, qualitatively, that for the slowly cooled and quenched HDPE extruded fibers the long periods slightly decrease with draw ratio by ~50 Å. At high draw ratios the final meridional long periods are practically independent of the draw ratio and thermal history of the fibers. These results appear to be similar to those obtained by Meinel and Peterlin.[31,32] Their SAXS and WAXS data indicated that at low draw ratios, the microspherulitic structure of the original sample is being destroyed with an eventual transformation to a fiber structure whose long period is independent of draw ratio.

Chain extended HDPE

Fibers obtained by extruding chain-extended HDPE at 0.49 GPa and 120°C after slow crystallization at 230°C and 0.49 GPa still had long periods along the longitudinal axis ~300 Å as shown in Figure 13.

Disruption and diminution of the thick lamellae may occur when extruded to draw ratios of 30. Attenburrow and Bassett[11] found that the majority of

lamellae of chain-extended HDPE survived the drawing process for draw ratios up to the maximum they obtained of 6.5. A small proportion did suffer disruption to produce a low melting tail on the DSC thermogram, although the melting point of the main component was not reduced. Solid state extrusion of chain-extended PE to draw ratios of 30 did produce a slight lowering of melting point. Two peaks were always observed in the conical die and only one high melting peak was obtained from the fibers.

Glenz, Peterlin, and Wilke[32] have studied the size and distortion of crystallites produced by plastic deformation of HDPE. They showed that the size of the crystalline mosaic blocks of the chain-folded morphology changed significantly with drawing. Further studies were undertaken by Suehiro et al.[33] They found that the mosaic block sizes rapidly decreased with drawing and became almost constant in the highly drawn state. Such behavior may possibly
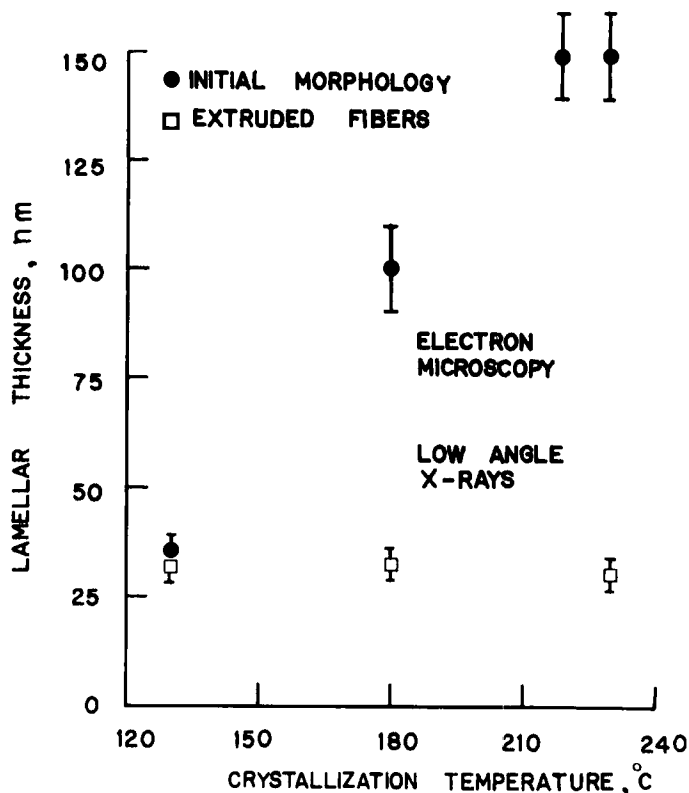

FIGURE 13   Fold period variation (lamellar thickness) of HDPE morphologies (Alathon 7050, $M_w = 52,000$) prepared at 0.49 GPa and crystallization temperatures as shown and corresponding fibers extruded at 0.49 GPa and 120°C.

occur for the extrusion of chain-extended PE to draw ratios of at least 30. Suehiro et al.[33] explained their results by considering the mechanical work exerted on the lamellar crystals rather than the remelting or recrystallization hypothesis as discussed by Glenz et al.[32]

Figure 14 shows a plot of the intensity variation versus Bragg angle for extrusion chain-folded (draw ratio of 35) and chain-extended morphology. The fibers were stacked in a hexagonal array and placed perpendicular to the collimation slit of the Kratky camera. It appears that only with the extruded chain-extended fiber is the intensity maximum almost absent near a Bragg angle of 0.35 degrees corresponding to a long period of ~300 Å. A maximum in the intensity variation of the diffractometer scan is always observed for fibers extruded from the conventional chain-folded morphologies. Figure 15 shows the SAXS pattern obtained from CE HDPE and chain-folded HDPE using pinhole collimation and the Warhus camera. The SAXS pattern for the chain-extended fiber also shows intensity variation along the meridian which is believed to be due to void formation. Indeed the extruded CD HDPE was translucent. The X-ray exposure time for the chain-extended HDPE was five times that for the HDPE extruded at 200°C. However, the intensity of the SAXS pattern of the chain-extended fiber was weaker than for the extruded chain-folded morphology.

The intensity maxima of the SAXS pattern has been discussed by Clark and Scott[34] and Mead, Desper, and Porter.[3] Taylor and Clark[35] have also attached
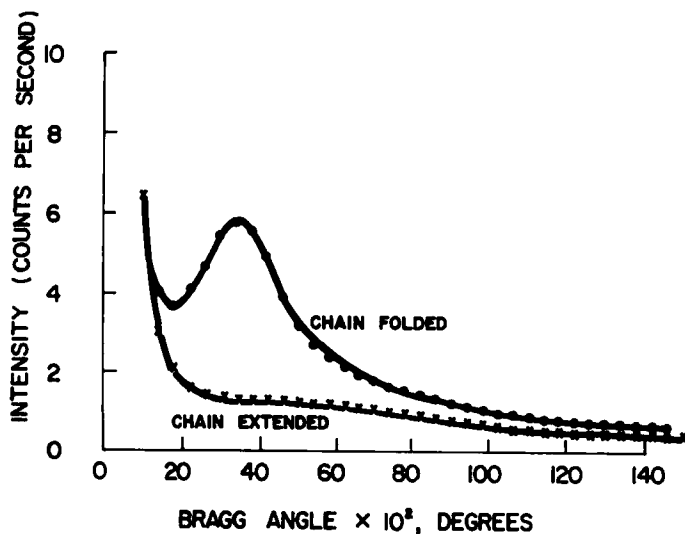

FIGURE 14   Intensity variation versus Bragg angle for extruded chain-folded and chain-extended morphologies. Fiber axis is perpendicular to the slit.
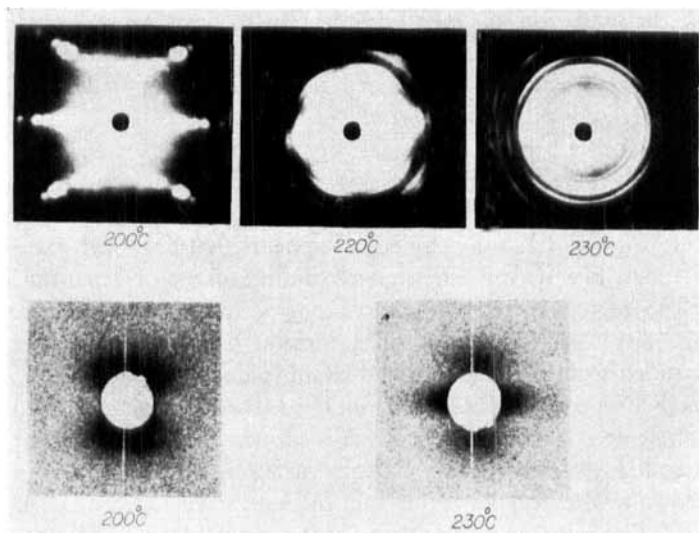
D

FIGURE 15   Wide angle and small angle X-ray diffraction patterns of HDPE (Alathon 7050, $M_w = 52{,}000$) extruded at 120°C and 0.49 GPa. The crystallization pressure was 0.49 GPa and crystallization temperatures are given above. The fiber draw ratio is 10 and the fiber axis is vertical.

prime significance to their SAXS intensity data of ultradrawn polyacetal and polypropylene fibers. The diffractometer scan showed the absence of a peak at high draw ratios and Clark and Scott[34] used this observation in support of a continuous crystal morphology. Chain folds in the ultra-oriented fiber exist only as isolated defects. In our studies the fibers produced from chain-folded morphologies always showed a two point SAXS pattern with a long period along the longitudinal direction. The intensity was reduced with drawing but never eliminated.

Figure 16 shows the intensity variation of the diffractometer scan versus Bragg angle for the extruded CE HDPE and chain-folded morphology (draw ratio of 35) with the fiber axis parallel to the collimation slit. The fiber was produced from the chain-folded morphology by solid state extrusion at 134°C and 0.23 GPa. The intensity maximum near 300 Å is believed to be due to the lateral spacing of adjacent microfibrils, spaced ~300 Å apart, as observed by Southern and Porter.[36]

Wide angle X-ray

Chain-folded and chain-extended HDPE   Figure 15 shows the wide angle diffraction photographs of the high density polyethylene crystallized at the temperatures shown and subsequently extruded at 120°C and 0.49 GPa. The
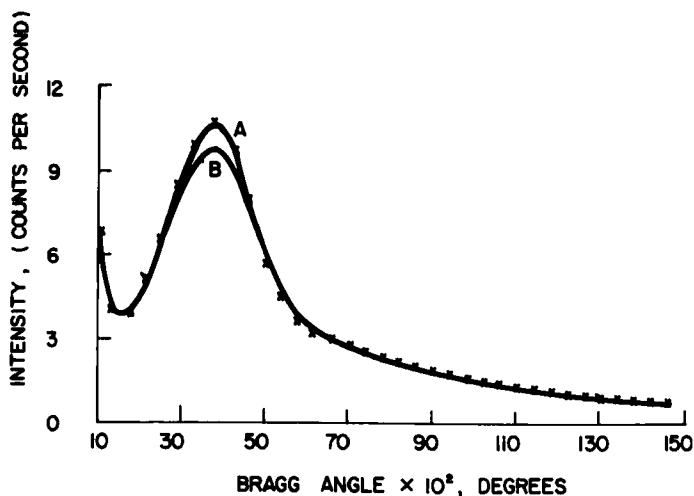
FIGURE 16 Intensity variation (counts per second) versus Bragg angle for the extruded chain-extended (A) and chain-folded (B) morphologies (Alathon 7050, $M_w = 52,000$). Fiber axis is parallel to the collimation slit.

diffraction pattern obtained at 134° is similar to that discussed by Desper *et al.*[37] and Southern and Porter.[36] As the crystallization temperature was increased to 200°C, the wide angle pattern of the extruded fiber became similar to the HDPE crystallized at 134°C and extruded at 120°C. At present the ratio of the intensities of the orthorhombic to monoclinic phase has not been studied for these samples; nor have the crystalline orientation functions been measured. The crystalline orientation function for extruded HDPE crystallized at 210°C and above, must decrease in order to produce the wide angle diffraction pattern shown in Figure 15 which shows the presence of unoriented background rings of the crystalline X-ray reflections. These diffraction rings were also observed by Bassett and Carder[20] and they concluded that these rings were consistent with the separation of low-melting peaks in the DSC traces, since once excluded the low molecular weight polymer may subsequently recrystallize independently of the majority of the polymer. The WAX-ray photograph should show the existence of the normal orthorhombic subcell structure. However, at high temperatures and pressures, Bassett *et al.*[38] showed, using optical and X-ray studies, that the intermediate phase had a hexagonal structure.

Electron microscopy

Fracture of highly drawn chain-folded HDPE near the tip of the conical die showed similar features as described by Southern and Porter[36] and Southern and Wilkes.[39] SEM revealed a series of ribbons aligned parallel to the flow
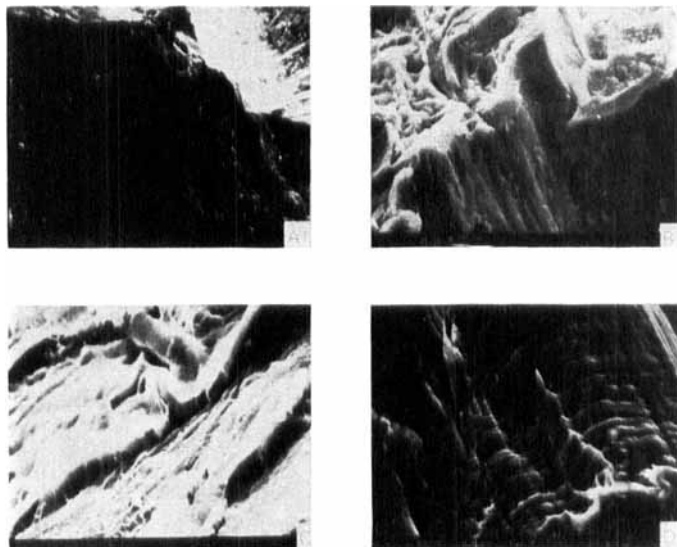
FIGURE 17   Electron micrographs of chain-extended HDPE (Alathon 7050, $M_w =$ 52,000) fractured in liquid nitrogen after solid state deformation through a conical die. (A) Fracture plane in deformed cone; (B) fracture plane perpendicular to flow direction; (C) fracture at low draw region of deformed cone; (D) fracture parallel to extrusion axis of drawn fiber.

direction. Microfibrils were observed ~ 300 Å diameter. Figure 17 shows electron micrographs of chain-extended HDPE fractured in liquid nitrogen after solid state extrusion through a conical die at 120°C and 0.49 GPa. In Figure 17A the fracture surface of the deformed cone region is shown. The fracture plane of the chain-extended plug in the conical die was also conical shaped. The included angle of the conical fracture surface decreased with increasing draw ratio and decreasing die diameter perpendicular to the extrusion axis. The alignment of the chain-extended lamellae increases with draw ratio in the die profile. At the highest draw ratio at the tip of the die gross rotation and interlamellar shear may occur during the extrusion. The lamellae orient with cylindrical symmetry in the die and have a conical angle of approximately 20° at the die exit. However, extrusion through the die appears to disrupt the lamellae of the CE HDPE and produce brittle fracture of the resulting fiber. Since Bassett has shown[20-23] that the structure of CE HDPE is a large-scale copy of chain-folded HDPE, then it is expected that extrusion of chain-folded HDPE results in the microfibrils being oriented with cylindrical symmetry along the extrusion axis. The microfibrils are possibly packed within a conical angle of $\sim 3°$, as indicated by the crystalline orientation function.[37] Figure 17D shows the fracture surface of the fiber after the solid state extrusion.

DISCUSSION

The volume fraction and orientation of the interlamellar phase appears to be of paramount importance in determining the drawing behavior of the fiber. It is possible that the number of "tie chains" decreases and the crystalline volume fraction increases with crystallization temperature and pressure of HDPE. The non-crystalline phase is unable to sustain the stress imposed by the well-defined interfaces of the crystalline phase. Extrusion of "chain-extended" polyethylene of molecular weight in the range 5×10^4 to 147×10^3 produces brittle fracture of the extrudate, the fraction of segregated low melting polymer between the chain-extended lamellae being sufficiently high to produce a brittle fracture. As the non-crystalline volume fraction approaches zero, the bire-fringence of the fibers attains the value of 0.059 for a perfectly oriented crystalline phase. The maximum birefringence of the extruded fibers is obtained with increasing crystallization and molecular weight of the initial chain-folded morphology. Quenched and annealed HDPE produced similar modulus variation with draw ratio and both attained a similar high draw ratio. This maximum draw ratio was slightly lower than those obtained by isothermal crystallization at high temperatures and pressures greater than 0.24 GPa. Such suggests, but does not prove, that segregation of short molecules of slowly cooled PE is necessary for the achievement of high draw ratios.

The attainment of a fiber with a maximum fraction of chain-extended crystallites uniaxially aligned along the fiber axis is only one of the require-ments for obtaining the highest possible strength. Interlamellar material also contributes to high strength.

The preparation and extrusion conditions for maximum modulus can now be considered in view of the study by Mead and Porter[1] of a given morphology extruded over a wide temperature range and the present study of the influence of the initial morphology on fiber properties. Extrusion of chain-extended lamellae has produced fibers with maximum moduli of 50 GPa, similar to the mechanical behavior of oriented chain-extended HDPE.[20,21] Fibers produced from low molecular weight HDPE ($\sim 10^4$) and at high crystallization tempera-ture and pressures, 230°C and 0.49 GPa, have moduli which are 1/60–1/70 the theoretical crystal modulus, because of the well-defined crystal interfaces. Solid state extrusion of well-oriented chain-folded lamellae has produced a maximum modulus of 70 GPa. Extrusion of well-oriented chain-folded lamellae even at pressures of 0.49 GPa produces fibers with lamellae having long periods between 250–300 Å along the fiber axis.

The intensity of the small angle X-ray scattering pattern decreases with increasing crystallization temperature for HDPE, and so for HDPE with molecular weight $\sim 10^4$ the highest crystallization and pressures should be used without fractionation effects[40,41] and sufficient chain-extended PE to

produce segregation of the low molecular weight material and brittle fracture during extrusion. The extrusion temperature that produces the highest draw ratio prior to fracture is near the HDPE ambient melting point where the crystalline orientation function is >0.9960 and crystallinity is 85 percent. Lowering the extrusion temperature reduces conformational relaxation of the non-crystalline phase but fracture readily occurs at low draw ratio. The extrusion temperature range where the average orientation function is a maximum and where crystallinity is not sufficiently reduced or disrupted by the compressive forces is 120–130°C.

In Table II a comparison is made between the properties (maximum values) of the extruded HDPE and those of the single crystal. Only the total birefringence of the fiber is greater than the intrinsic birefringence of the crystalline

TABLE II

Comparison of physical properties of U.Mass ultradrawn HDPE fibers (in the chain direction) with single crystal characteristics

Physical property	Polyethylene single crystal	Properties of U.Mass ultradrawn high density polyethylene fibers
Modulus, GPa	240, 290[8,42,43]	70
Tensile strength, GPa	13[44]	0.4
Strain to fracture, %	6[44]	$\sim 10 M_w = 60,000$
Minimum and maximum obtainable draw ratio prior to fracture	Calculated minimum draw ratio required to fully extend chain (7) = 8.6 for $M_w = 10^4$ 8.6 for $M_w = 10^6$	Extrusion at 60°C, $M_w = 60 \times 10^3$ maximum obtainable draw ratio of 13.8 Extrusion at 134°C, $M_w = 147 \times 10^3$ maximum obtainable draw ratio = 40
Linear expansion coefficient, 10^{-5} °C^{-1}	a-axis + 22[45] b-axis + 3.8 c-axis − 1.2	-0.9 ± 0.1, fiber axis
Melting point, °C	145.5°C[46]	139°C (at 10°C min^{-1} DSC scan rate)
Crystalline fraction	Crystallinity density,[47] 1.008 g cm^{-3} Amorphous density, 0.855 g cm^{-3}	0.85 Extrusion of chain-folded PE 0.95 Extrusion of chain-extended PE
Crystal orientation function	1.000	0.996 ± 0.002
Total birefringence	$\eta_a = 1.514$[48] $\eta_b = 1.519$ $\eta_c = 1.575$ $\Delta\eta_c = 0.059$	0.0618 ± 0.002[a]

[a] A value of 0.0637 ± 0.0015 was obtained by Dr. H. De Vries using the same fiber.

phase, accepting its value as 0.059. The birefringence of 0.062 ± 0.002 (and measured by Dr. H. DeVries as 0.0637 ± 0.0015) is one of the highest values reported for HDPE. Recently Czornji and Wunderlich[49] measured a value of

0.063 $\pm$ 0.002 from chain-extended morphologies. It appears that solid state extrusion of chain-folded morphologies produces fibers having birefringence comparable with chain-extended morphologies. However, the maximum modulus of the fiber is only one-fourth of the theoretical value. The linear expansion coefficient of the fibers at high draw ratios is -0.9 ± 10^{-5} °C^{-1}, comparable with the c-axis expansion coefficient of the polyethylene ortho-rhombic unit cell. Only the extruded chain-extended morphologies showed an absence of the small angle long period (see Figure 14). The fragments of the extruded CE HDPE may have an ultra high tensile modulus. However, continuous fiber lengths have not yet been obtained.

A further study of the extruded extended chain morphology should consider the properties of fibers obtained using higher molecular weights than used in this study, so that sufficient tie molecules and possible entanglements exist to draw the chain-extended lamellae. Ferguson, Hoehn, and Hebert[50] and Cappacio et al.[5,6] have shown that high molecular weight polyethylene leads to reduced crystallinity and crystalline order and a large fraction of tie molecules producing a highly continuous composite superstructure. Further studies should also consider the effect of annealing and persistence of orientation of the chain-extended morphology above the melting point[49] to overcome the brittle fracture of the extrudate which has been observed in the present study.

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