

Physical Properties of Extended-Chain High-Density Polyethylene

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Synopsis

Extended-chain high-density polyethylene prepared through crystallization at high pressure is substantially stiffer and somewhat stronger than normal folded-chain HDPE. With weight-average molecular weight in the range normal for molding or extrusion resins, the extended-chain material is inductile and brittle; but with molecular weight near 2,000,000, the resin can be rigid and tough. This rigid, tough material can be converted to articles through some of the solid-state processes developed for metals. The volume-temperature behavior of HDPE at 5000 atmospheres appears to reflect a polymorphic transition between orthorhombic and triclinic phases.

INTRODUCTION

Many reports have described crystalline high-density polyethylene (HDPE) in which molecular segments are arranged in "extended chain" (EC) rather than the normal "folded-chain" (FC) configurations. In most cases, this EC morphology has been obtained through crystallization at relatively high pressures, typically 5000 atmospheres, rather than the pressures to roughly 1500 atmospheres normally used in processing polyethylene. Publications by Wunderlich and his colleagues supply valuable discussions of much of this research.¹⁻⁷

Because of the difficulties inherent in experiments at the relatively high pressures, the EC products have been limited in size, perhaps to no more than a centimeter in the greatest dimension. As a result, published assessments of these materials have been largely restricted to those feasible on small specimens, for example, density by flotation, melting characteristics through differential thermal analysis (DTA), crystallinity and morphology through x-ray diffraction and microscopy.

In the research described below, the objective was to develop a broader understanding of the characteristics of EC HDPE, particularly of its rigidity, strength, and toughness.

EXPERIMENTAL

Apparatus

EC HDPE was prepared through crystallization or recrystallization in a 6000-atmosphere dilatometer or in a 3200-atmosphere mold.

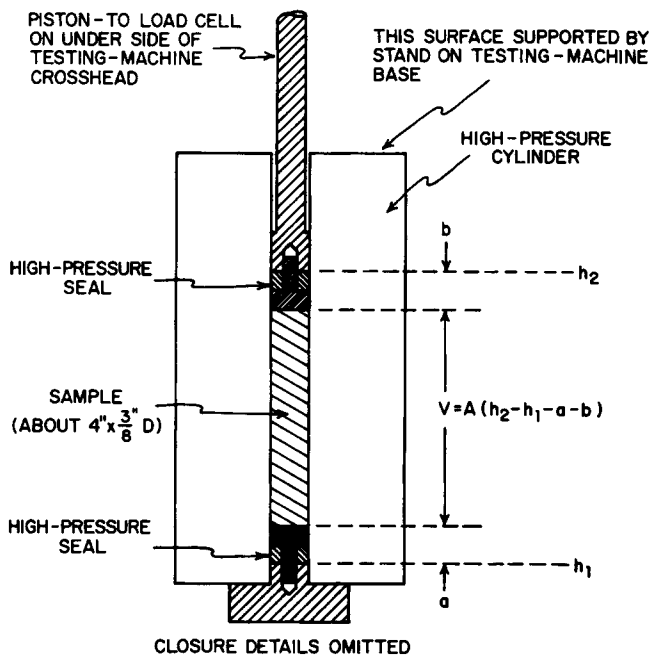


Fig. 1. High-pressure dilatometer (no scale).

The dilatometer, shown schematically in Figure 1, is a modification of a system previously described for flow measurements on polymer melts.⁸ The sample is contained in a steel cylinder $\frac{3}{8}$ in. I.D., 3 in. O.D., and $6\frac{1}{2}$ in. long. Bridgman unsupported-area seals are used to minimize leakage at the tip of the piston and at the bottom of the cylinder. (Sealing rings of Vespel SP-3 polyimide resin, containing 15% molybdenum sulfide, have been effective at pressures of 5000 atmospheres or more at 300°C or more.) The cylinder is mounted above the base of a testing machine (Instron testing machine, 10,000 pounds capacity; see reference 8) and the piston on an electrical force transducer attached to the underside of the testing machine cross head.

The sample is compressed through downward motion of the cross head and the piston, the resulting force appearing on the testing machine recorder. Control circuits within the testing machine move the piston automatically to maintain force at a predetermined value. Through division by the area of the cylinder, measured while free of stress, this force can be construed as pressure. The resulting value is slightly uncertain in that (1) some force is required to overcome friction at the tip of the piston, (2) the effective area of the cylinder changes with pressure, and (3) the force calibration of the testing machine involves an extrapolation. In the measurements below, the precision of pressure control is approximately ± 30 atmospheres, and the total uncertainty appears to be less than a few per cent.

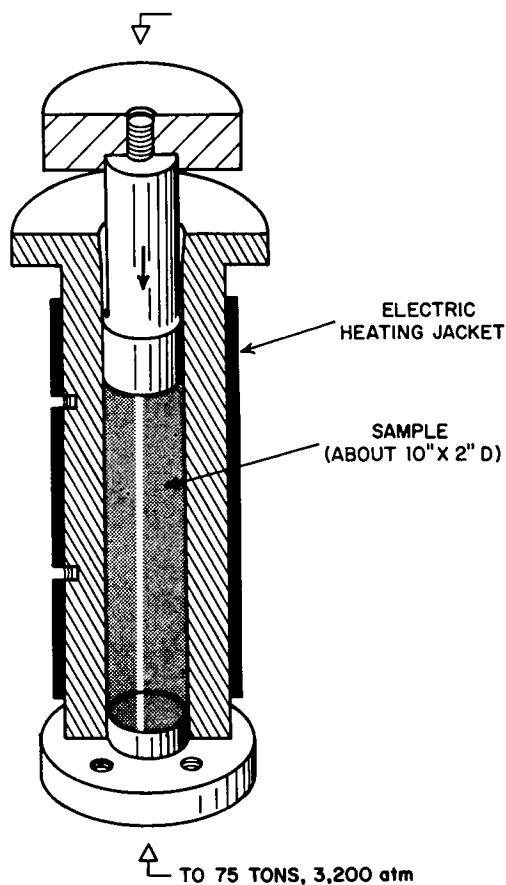


Fig. 2. High-pressure mold (no scale).

Temperature is controlled through electrical heaters to within about $\pm 0.5^{\circ}\text{C}$ at the control point and to within about $\pm 1^{\circ}\text{C}$ throughout the region occupied by the sample. Temperature measurements are made to within about $\pm 0.5^{\circ}\text{C}$ by calibrated thermocouples.

The volume of the sample within the dilatometer can in principle be determined accurately by observing the elevation of the piston as displayed by testing machine indicators. This, however, requires intricate corrections for thermal expansion and mechanical strain throughout the system. In the work below, these corrections have been omitted, so that sample volumes may be uncertain to as much as 5%. However, the volumetric changes indicated by changes in piston elevation are known much more precisely, perhaps to 0.2% or less of the total volume.

The high-pressure mold in Figure 2 consists of a steel cylinder 2.016 in. I.D. by 5.00 in. O.D. by 15 in. long. It is closed at the upper end by a movable steel piston 5.25 in. long and at the lower end by a fixed steel piston or plug 2 in. long. Leakage is avoided at these closures, with high-

viscosity fluids at least, by restricting the diametral clearances between the inner and outer members to the range 0.0005 to 0.001 in. The precision and accuracy of pressure and temperature control within this mold are much poorer than in the dilatometer.

Materials

Experiments were run on four high-density polyethylene resins. These included two commercial resins Alathon [trademark registered by E. I. du Pont de Nemours & Company, Inc.] 7012 and Alathon 7020 high-density polyethylene resins, having molecular weights in the ranges normal for extrusion or injection molding. These normal molecular weights (NMW) are reflected through the values for melt index (ASTM D 1238⁹), 0.52 and 1.5 dg/min, respectively. Although somewhat different in molecular weight, these resins are generally alike in density (near 0.955 g/cc at 23°C), in molecular weight distribution (relatively narrow), and in other physical characteristics. For convenience, these are designated below as NMW HDPE-1 and NMW HDPE-2, respectively, or where differentiation is not needed, as NMW HDPE.

The third material, also available commercially, consisted in Hi-Fax [trademark registered by Hercules, Inc.] 1901 ultrahigh-molecular-weight (UHMW) HDPE. From measurements of the viscosity at 135°C of solutions of this resin in decahydronaphthalene, its weight-average molecular weight appears to be from 2 to 3×10^6 .¹⁰ The ratio of this value to the number-average molecular weight is estimated to be greater than ten.¹⁰ Density at 23°C of normally molded samples is typically near 0.94 g/cc, the high molecular weight evidently restricting the degree to which crystallinity can develop. This resin is designated UHMW HDPE-1.

The fourth resin consisted of an experimental UHMW HDPE having substantially higher molecular weight, judged by its failure to dissolve completely in the viscometric solvent and by the high viscosity of the (partial) solutions. This is termed UHMW HDPE-2.

After crystallization or recrystallization of these materials specimens were machined from them for the tests below. Insofar as feasible, specimen dimensions were those normally used or specified for these tests. However, in a number of cases sample dimensions were not great enough for standard specimens, and specimens of somewhat smaller size were used. As far as could be determined, these small dimensions had no substantial effect on the accuracies of the determinations.

NMW HDPE

A variety of small samples, typically $\frac{3}{8}$ in. in diameter by about 4 in. long, but occasionally as short as $\frac{1}{4}$ in., were prepared from NMW HDPE in the dilatometer at 3000 to 5000 atmospheres. A few were crystallized from the melt by cooling rapidly, in some cases at rates as high as 1°C/min. Most were crystallized isothermally (or nearly so) through compression of

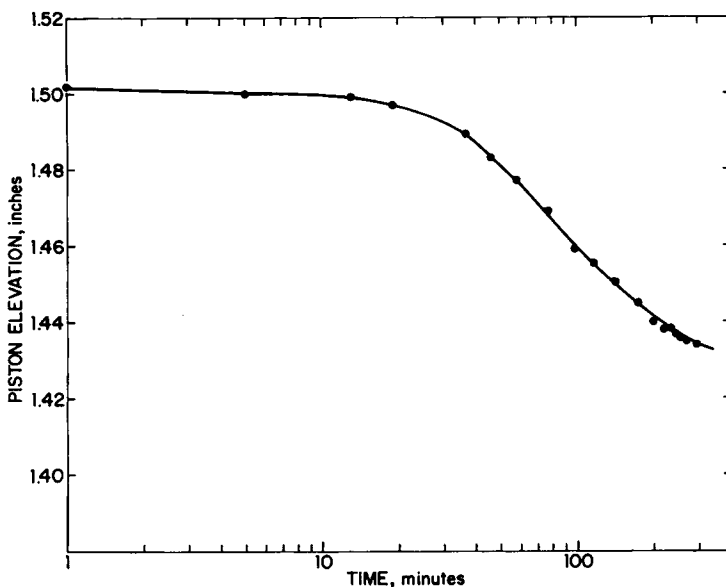


Fig. 3. Crystallization of NMW HDPE-2 at 3000 atm, 203°C. Sample occupies about 3 in. in dilatometer.

the melt. Periods of a few to 8 hr were allowed for crystallization and annealing (Fig. 3). Many were prepared through recrystallization without melting of FC stock obtained through crystallization from melt at relatively low pressure, usually 300 to 500 atmospheres. For convenience, in this discussion the terms "recrystallization" and "recrystallized" will be used only in discussing these latter samples.

In these experiments, serious difficulties were encountered in pushing long specimens from the dilatometer after crystallization or recrystallization. Also, the specimens after removal frequently proved to be cracked so badly that they were valueless for the desired tests. It seemed likely that the sample was being restrained within the dilatometer by high residual radial stresses and that frictional resistance generated at the sample-dilatometer interface by these stresses resulted in irregular sliding and cracking as the sample was forced from the dilatometer. Lubrication at this interface reduced friction and thus made possible the recovery of largely uncracked samples. The lubrication was obtained through (1) use of fluorocarbon film between the sample and the dilatometer wall (preform molded at low pressure, recovered and machined to diameter about 0.01 in. smaller than dilatometer inner diameter, wrapped in Teflon [trademark registered by E. I. du Pont de Nemours & Company, Inc.] FEP-fluorocarbon film, and reinstalled in dilatometer), (2) coating of the dilatometer wall with a TFE-fluorocarbon telomer lubricant (Slip Spray [trademark registered by E. I. du Pont de Nemours & Company, Inc.] Dry Lubricant), or (3) coating with powdered molybdenum sulfide.

TABLE I
FC and EC HDPE—Physical Properties at 23°C, 50% RH

	ASTM ^a	NMW FC HDPE ^b	NMW FC HDPE ^c	NMW EC HDPE ^d	UHMW EC HDPE ^e
Density, g/cc ^f	D 1505	0.95	0.96–0.98	0.97–0.99+	0.96–0.98
Elastic modulus, Kpsi	D 638	170	330–660	500–800	310–440
	^g				
Yield strength, Kpsi	D 1708	3.5	^h	^h	4.2–4.9
Ultimate strength, Kpsi	D 1708	2.8	4.2–5.1	3.8–4.4	4.8–5.7
Ultimate elongation, %	D 1708	600–1000	1–500	1	70–310
Tensile impact energy, ft-lb/in. ²	D 1822	80–100	^h	^h	130–520
Izod impact energy, ft- lb/in.	D 256	0.5–10	^h	^h	14–22 ⁱ
Compressive strength, Kpsi	D 695	3–5		5–9	
Hardness Rockwell	D 785	–20 L		20 L	91 R

^a Although ASTM procedures were followed insofar as feasible, limited sample dimensions compelled frequent use of smaller than standard test specimens.

^b Normally molded or extended.

^c Crystallized rapidly at 3000 atmospheres, 194°C or 195°C.

^d Stock for elastic modulus specimens crystallized slowly at 3000 atm, 203°C; other stock crystallized slowly at 5000 atm, 242°C.

^e UHMW HDPE-1 crystallized through rapid compression to about 3200 atm.

^f At 23° to 25°C.

^g D 638 procedure used on D 1708 specimen.

^h Brittle, no yield.

ⁱ Incomplete break.

Judged through DTA,⁶ the concentration of EC HDPE increases relative to that for FC HDPE as crystallization is slowed or as the period at crystallization temperature and pressure is increased, until EC concentration reaches roughly 50% to 80% following several hours at 3000 atmospheres and approximately 5°C undercooling or essentially 100% following several hours at 5000 atmospheres and similar undercooling.

As shown below, toughness and ductility are quite low. Thus, it is difficult to prepare test specimens and to test these without untoward cracking. Thus, test results on these NMW samples are subject to unusually large uncertainties.

Within these uncertainties, the results on NMW HDPE-1 are not significantly different from those on NMW HDPW-2; that is, the modest molecular weight difference has no perceptible influence on physical properties. Also, no significant differences could be found between crystallized and recrystallized samples.

The physical characteristics of the high-pressure crystallized NMW HDPE samples are described in Table I. These may be summarized briefly as follows:

1. Corresponding to the steady development of EC morphology observed through DTA, density at room temperature increases from 0.955 g/cc to more than 0.99 g/cc, as reported previously.^{1–7}

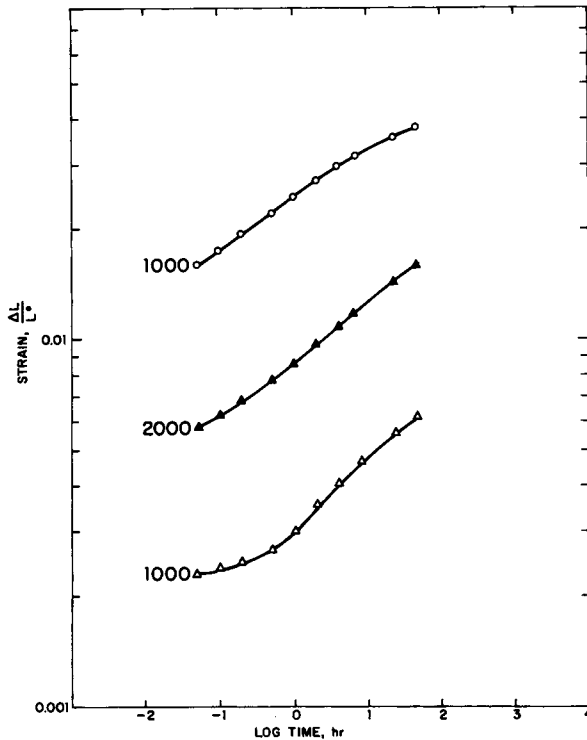


Fig. 4. HDPE, creep in compression, 23°C: (O) 1 Kpsi nominal compressive stress, FC HDPE; (Δ) 1 Kpsi, EC HDPE; (\blacktriangle) 2 Kpsi, EC HDPE.

2. In a parallel fashion, elastic modulus and hardness increase greatly. Similar increases in resistance to deformation can be expected in all aspects of mechanical behavior.

3. Ductility diminishes and virtually disappears so that brittle fracture intervenes before yield can appear.

4. Ultimate strength increases.

5. Paralleling the decrease in ductility, but overriding the increases in modulus and strength, toughness judged through tensile-impact and izod-impact energies drops grossly.

6. In tests of compressive strength the EC materials fail through shear along planes at 45° to the direction of the compressive force, as is normal for brittle materials. In contrast FC stock fails, as is frequently the case for thermoplastics, through "barreling" or diametral growth at substantially lower stresses.

Tests of creep in compression on FC and EC NMW HDPE-1 are summarized in Figure 4. These show much lower strains for EC than for FC HDPE, as is to be expected from the relatively high elastic modulus of EC HDPE. Because of the logarithmic nature of this plot and because of the similarities in the slopes of the three curves, creep rates in terms of the

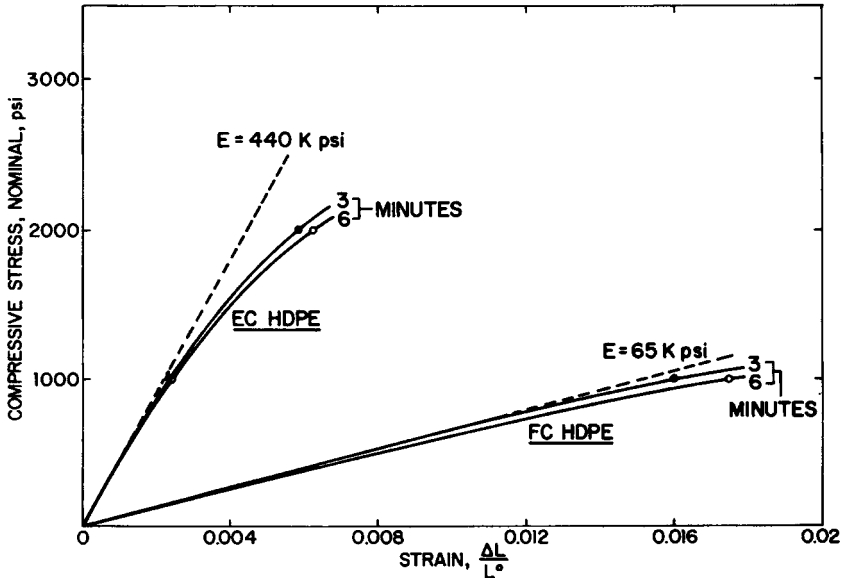


Fig. 5. HDPE isochronal stress-strain behavior, 23°C; E denotes elastic modulus, Kpsi.

derivatives of strain with respect to time at constant stress must be much lower for EC than for FC HDPE.

Similarly, when the creep curves are crossplotted at constant time, as in Figure 5, the isochronal stress-strain curves imply values for the isochronal modulus (limit of the isochronal stress-strain ratio at zero strain) near 440 Kpsi for periods of 3 to 6 min under load, approximately seven times the corresponding values for normal FC HDPE. These isochronal values reflect much greater periods for molecular rearrangements during test than the few seconds afforded in the ASTM procedure for determining elastic modulus. Thus, it is to be expected that the isochronal values are smaller than those in Table I.

Small fragments of EC HDPE crystallized at 5000 atmospheres were processed uniaxially or biaxially between steel rolls to thin "sheet." To minimize fracture of the brittle stock, roll temperatures near 130°C were employed. Material temperatures must have been increased further through the heat generated by the deformations imposed on the specimens (calculated to be roughly 14° to 20°C for unit strain or for length/initial length equal to 2.72). Thus, it is not surprising that DTA indicated some reversion toward FC morphology as a result of this processing.

As many as 12 passes were used with longitudinal deformation ratios to approximately 10 for uniaxially rolled materials and to approximately 3 × 3 for biaxially rolled.

Values for the elastic modulus range from 450 Kpsi to more than 1000 Kpsi for biaxially rolled products, although serious difficulties were encountered in these measurements because of the brittleness of the stock.

Ultimate strengths and elongations are similar to the values in Table I. One sample proved not substantially different in dielectric strength (ASTM D-149)⁹ from normally processed FC HDPE film.

POLYMORPHIC TRANSITION

During melting and crystallization at 5000 atmospheres the V-T behavior in Figure 6 was observed. Since the sample occupied a region about 4 in. long, changes of 0.1 in. in piston location reflect changes of about 0.025 in relative volume. Similar behavior was observed on heating at 0.2 °C/min, but at 1°C/min the inflections near 1.75 in. could not be seen.

In many of the determinations in Figure 6, volume changed quite slowly after temperature change, so that reasonable approximations to steady values would have required impracticably long experiments, perhaps 5 or more hours per determination and several or more days per run at high pressure and high temperature. Further, with the uniaxial compression employed here, the stresses generated in radial directions may be less than that applied by the piston in the axial direction. (In approximate terms through Hooke's law in generalized form the ratio of radial to axial stress will diminish from unity for a Pascalian liquid through very slightly smaller values for slightly elastic polymer melts to values that decrease substan-

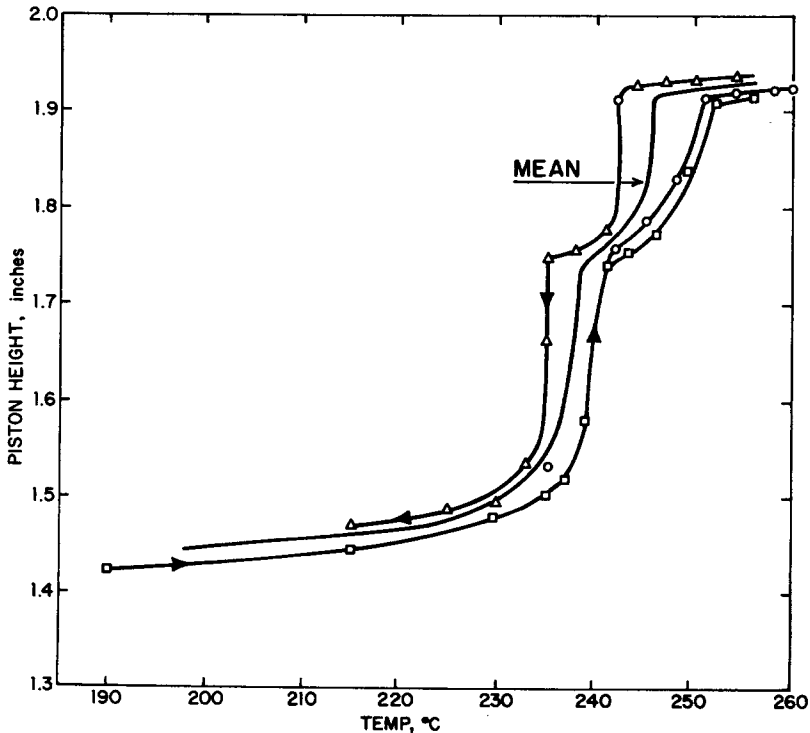


Fig. 6. ΔV -T Diagram. HDPE-1 at 5000 atm: (O) run 1; [□] run 2; (×) run 3.

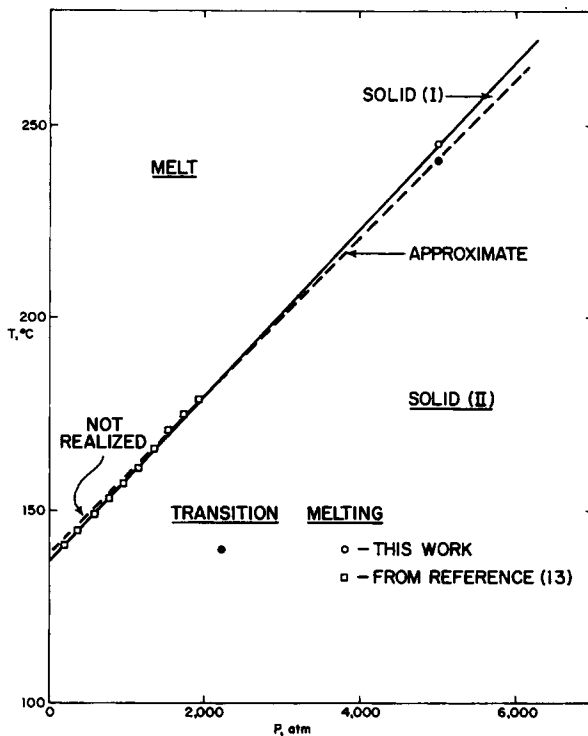


Fig. 7. HDPE tentative T - P diagram: (○) this work; (□) interpolated from reference 13.

tially and progressively as the rigidity modulus of the sample increases. Detailed analyses have apparently not been made for systems like that in Figure 6.)

Thus, the points in Figure 6 are no better than first approximations to the desired values for equilibrium under isotatic conditions. Nevertheless, behavior is generally consistent with the existence of an intermediate curve approximately like the mean in Figure 6 which should be obtainable through sustained observations on a thermally stable polymer.

The mean curve appears consistent with those reported by Bassett and Turner¹¹ and by Hatakeyama and his co-workers¹² and with anomalies at somewhat lower pressures reported by Hellwege, Knappe, and Lehmann¹³ and attributed by these latter to kinetic effects. The combined results appear consistent with the view of Bassett and Turner that behavior at 5000 atmospheres suggests the existence of an unidentified solid phase just below the melting point, at 240° to 245°C judged in terms of Figure 6. For convenience, this may be designated I and the phase stable at lower temperatures, II. One or more equilibria may then exist among melt M, I, and II.

Since no transition behavior has been observed at 5000 atmospheres and temperatures below 240°C, II is likely to be the orthorhombic form well

known at room temperature and 1 atmosphere. The results of Hellwege, Knappe, and Lehmann suggest I becomes unstable in the presence of II at pressures below 1200 to 1500 atmospheres. Extrapolation of Broadhurst's melting and transition temperatures for lower normal hydrocarbons¹⁴ against reciprocal molecular weight suggests that the hypothetical orthorhombic-triclinic transition in polyethylene would appear at about 5°C above the 1-atmosphere orthorhombic melting point if it could be realized.

On these bases, Figure 7 provides a consistent, though tentative, phase diagram for HDPE. Confirmation of this may well require other experimental approaches, for example, x-ray diffraction analyses at high pressure.

In any case, the results suggest it is the incremental expansion of the solid-state lattice, at 240° to 245°C and 5000 atmospheres in Figure 6, that affords the special environment in which FC.HDPE can rearrange to EC. Consistent with this, the temperature-pressure region marked I in Figure 7, however interpreted, is largely identical to that in which the rearrangement is feasible.

RAPID CRYSTALLIZATION AND RECRYSTALLIZATION OF UHMW HDPE

It has been widely recognized that melting temperature at 1 atmosphere increases with the size and perfection of the crystalline regions and that such increases can readily be achieved through crystallization at one atmosphere and relatively high, though submelting temperatures. Figure 8 demonstrates that still higher melting materials can be achieved through

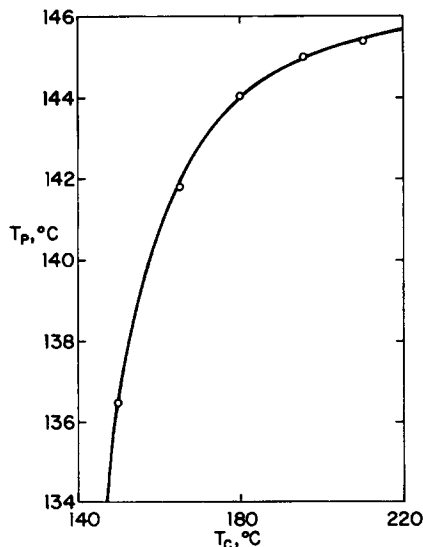


Fig. 8. UHMW HDPE-1, melting temperature vs. uncorrected crystallization temperature (DTA, 10°C/min).

the use of high pressure to increase crystallization temperature above the limit represented by the 1-atmosphere melting temperature. That is, the special high-melting morphologies may be viewed as consequences primarily of the relatively high crystallization temperatures and only secondarily of the high pressure. Similar results were obtained with other NMW and UHMW HDPE resins.

In most of these experiments, small quantities of stock were used, occupying about $\frac{1}{4}$ in. along the dilatometer axis. These were (1) melted and brought to equilibrium at the specified temperature and at low pressure, usually near 400 atmospheres; (2) compressed rapidly, for example, to 5000 atmospheres in about 1 min; (3) cooled under pressure to room temperature; and (4) expanded to 1 atmosphere.

The high melting temperatures were found primarily in material from the central regions of the samples. Presumably, the combined high pressures and high temperatures needed to generate the high-melting morphologies implied by the figure were achieved only in these regions (pressure diminishing downward from the piston, temperature increased as a result of rapid compression, but limited in the outer regions by the cooling effects of the piston and the dilatometer walls).

Similarly, elevated melting temperatures were obtained as a consequence of processing melted UHMW HDPE-1 between steel rolls rotating at room temperature.

High-melting materials were also prepared through recrystallization. Stock was (1) melted at 200°C and low pressure; (2) solidified by compression to ~ 300 atmospheres and cooling to about 120°C; (3) compressed further and heated without melting to 5000 atmospheres and temperatures near 200°C; (4) expanded briefly to the melting region near 2000 atmospheres, insofar as this could be judged under these unsteady conditions; (5) recompressed rapidly to about 5000 atmospheres, the expansion and recompression requiring no more than approximately 5 sec; and (6) cooled and expanded without melting to room temperature and 1 atmosphere.

One-atmosphere melting temperatures were lower for these recrystallized materials than the values suggested by Figure 8. This appears to reflect the cooling introduced through expansion from 5000 atmospheres as opposed to the heating generated through compression in the crystallization. That is, recrystallization takes place at a lower and crystallization at a higher temperature than the chosen initial value.

To obtain these high-melting materials on a larger scale, crystallization and recrystallization were attempted in the high-pressure mold (Fig. 2), accepting the 3200 atmosphere operating limit imposed by its construction.

In crystallization stock was (1) melted and brought to equilibrium at a predetermined pressure and temperature, usually about 300 atmospheres and 150° and 180°C; (2) compressed rapidly (5 to 300 sec) to 3200 atmospheres; (3) cooled at this pressure to room temperature; and (4) expanded to 1 atmosphere. Further cooling in solid carbon dioxide facilitated pushing the sample from the mold.

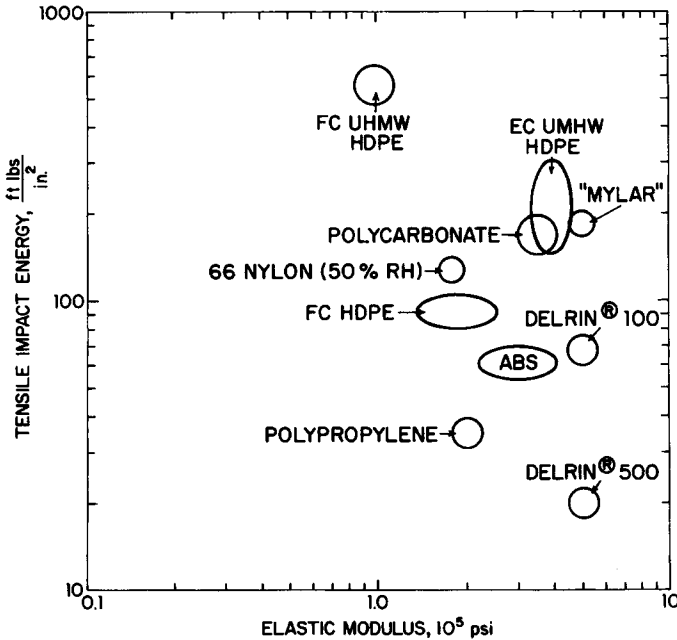


Fig. 9. High-pressure-crystallized UHMW HDPE-1 and 2, tensile-impact energy and elastic modulus (approximate).

The products proved to be extensively, though not completely converted to high-melting material. This could be judged readily through DTA and through the enhanced whiteness and enhanced hardness of the converted regions relative to FC HDPE. The unconverted material amounted to roughly 10% to 25% of the charge located at the walls and toward the bottom of the mold, apparently in regions that were relatively cool during crystallization.

In recrystallization molded FC HDPE stock was expanded briefly from 3200 atmospheres and about 205°C to approximately 100 atmospheres, and then after approximately 1 min recompressed to 3200 atmospheres. Because rapid expansion produced cooling within the mold, the distribution of high-melting product was the inverse of that found in crystallization. That is, the white high-melting product was formed primarily at the mold walls, the material in the central regions retaining FC morphology. The quantities of EC product were much smaller than in direct crystallization.

UHMW HDPE-1 processed in these fashions from starting temperatures of 150° to 180°C has the characteristics summarized in Table I. Briefly, these reflect much of the high rigidity of NMW materials crystallized at high pressures and also much of the toughness of normally processed UHMW HDPE. Figures 9 and 10 show that this high toughness, expressed through tensile-impact energy and izod-impact energy, and high rigidity are combined to degrees which are unusual or novel among thermoplastic resins.

TABLE II
Effects of Temperature on Mechanical Properties

	FC NMW HDPE	FC UHMW HDPE-1 ^a	EC UHMW HDPE-1
Elastic modulus (tension), Kpsi			
-40°C			368
23°C		123	310-440
70°C			104
100°C			42
Yield strength, Kpsi			
-40°C			6.3
23°C		3.2	4.2-4.9
70°C			3.0
100°C			2.0
Ultimate strength, Kpsi			
-40°C	5.0-6.5 (-57°C)		5.4
23°C	1.4-2.8	6.0	4.8-5.7
70°C	1.0-1.3		3.2
100°C			2.5
Ultimate elongation, %			
-40°C	75-100 (-57°C)		47
23°C	600-1000	310	70-310
70°C	600-850		330
100°C			800
Tensile impact strength, ft-lb/in. ²			
-40°C			220
23°C		770	130-520
Izod impact strength, ft-lb/in.			
-40°C	0.8		1-6
23°C	0.5-10	19 ^b	14-22 ^b

^a Normally molded or extruded.

^b Incomplete break.

As shown in Table II, these advantages in mechanical properties are maintained at temperatures as low as -40°C and as high as 100°C.

High-pressure crystallized UHMW HDPE-2 has characteristics intermediate between those of high-pressure crystallized UHMW HDPE-1 and the parent UHMW HDPE resins in normally molded FC form. Presumably, the extremely high molecular weight of UHMW HDPE-2 has restricted crystallization at high pressure relative to that reached with UHMW HDPE-1.

Normally processed UHMW HDPE is well known for high resistance to wear and for low coefficient of friction in dynamic tests against a variety of materials. Table III shows that these attractive characteristics are retained by high-pressure crystallized UHMW HDPE-1.

In tests of fatigue under alternating (30/sec) tensile and compressive stresses at 23°C ambient temperature, high-pressure crystallized UHMW HDPE-1 does not fail through more than 2.2×10^6 cycles at stresses as high as 3000 psi maximum. Life drops to about 9×10^3 cycles at 3250 psi

TABLE III
High-Pressure Crystallized UHMW HDPE-1
Wear and Friction against Carbon Steel^a

Crystallization pressure	Sample	Wear factor ^b	Coefficient of friction
High	1	44	0.14
	2	—	0.14
	3	58	0.17
Low	1	61	0.20

^a Reference 15.

^b In $\text{in.}^3\text{-min} \times 10^{-10}/\text{ft-lb-hr.}$

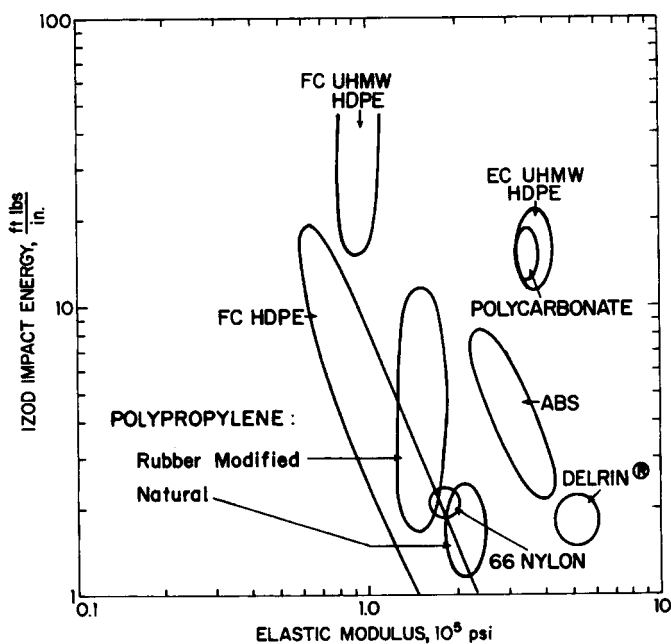


Fig. 10. High-pressure-crystallized UHMW HDPE-1 and 2, Izod-impact energy and elastic modulus (approximate).

and virtually to zero at 3500 psi. The endurance limit may thus be taken to be about 3000 psi, or about 65% of the normal 4500 to 5000 psi yield strength at room temperature.

The dielectric constant (ASTM D 150)⁹ of EC UHMW HDPE-1 appears slightly higher at room temperature and 10^2 to 10^6 hertz than for FC NMW or UHMW HDPE (about 2.4 compared with 2.3 to 2.35). Dissipation factor is higher, especially near 60 hertz. These differences may reflect contaminants in the EC material rather than a significant difference arising out of morphology.

Thin ($1/8$ to $1/4$ in.) transverse sections from the 2-in.-diameter EC UHMW HDPE-1 rods were rolled biaxially to deformation ratios from about 1.8 \times

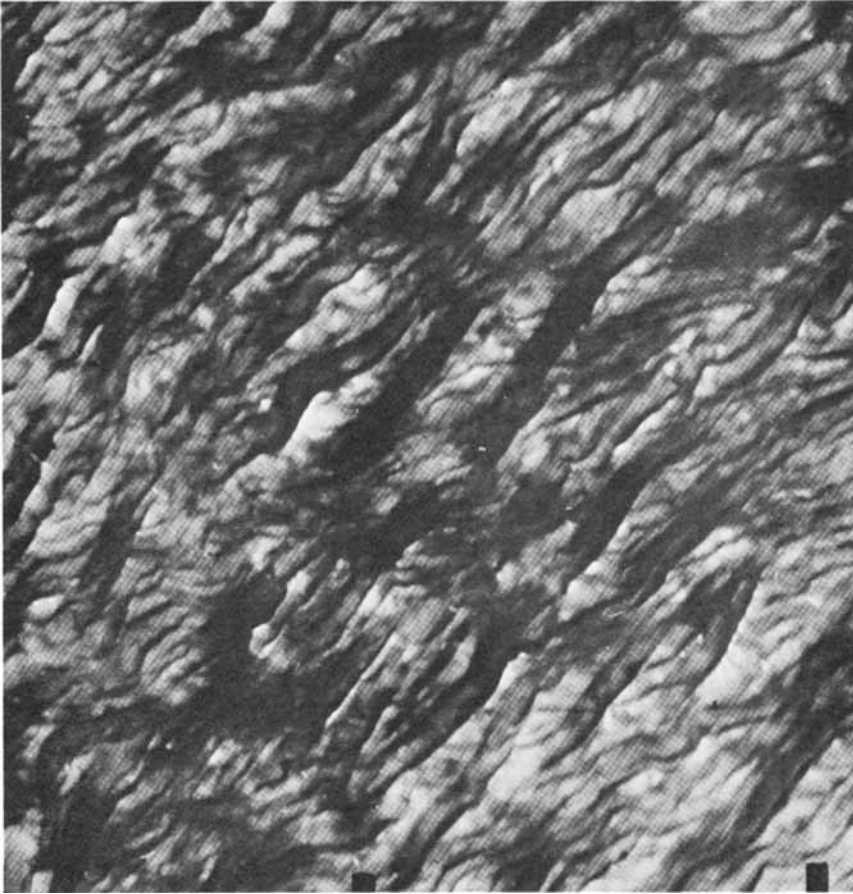


Fig. 11. Transmission electron micrograph of high-pressure-crystallized UHMW HDPE-1.

1.8 to about 2.4×2.4 . The resulting materials are attractively lustrous, presumably because of voids generated during rolling. Elastic modulus ranges from 160 to 360 Kpsi, relatively low in some cases as a result of the rolling. Yield strengths, 5.6 to 6.8 Kpsi, and ultimate strengths, 9 to 12 Kpsi, are higher than for unrolled stock. Ultimate elongation, 120% to 150%, and tensile-impact resistance, 260 to 290 ft-lb/in.², are not significantly different from the values for the parent stock.

The reasons for the special physical characteristics of EC UHMW HDPE must lie in its crystallinity and morphology. These have been investigated only briefly.

Transmission electron microscopy on two-stage replicas of cryogenic fracture surfaces shows the striated bands generally understood to arise from parallel molecules or molecular segments (see ref. 1, for example).

In this case, the bands are typically from 0.1 to 0.5 microns wide. Transmission electron microscopy on microtomed sections shows the structure in Figure 11. Though less well resolved, similar structure can also be observed through microscopy with visible light. Structure like this has not been observed in normally processed NMW or UHMW HDPE, although the possibility that it may appear has not been conclusively eliminated.

X-Ray diffraction studies show little or no scattering at values near 0.3° for the angle 2θ . In normally processed NMW HDPE, scattering in this region typically reflects the presence of fold periods (striae length) from 100 to 500 Å. Thus, in view of the TEM replica photographs, high-pressure crystallization has increased the fold period. At values for 2θ corresponding to very large fold periods, near 0.5 micron, scattering is much greater for the high-pressure crystallized than for the normally processed UHMW HDPE, implying that the x-ray measurements might with greater resolution characterize the increased fold periods more precisely. Relatively high aperiodic scattering in these studies implies relatively high density fluctuations in these high-pressure crystallized samples. Unit cell dimensions are also better defined for high-pressure crystallized HDPE, both NMW and UHMW, than for normally processed HDPE.

Through an analysis based on infrared absorption at 1894 cm^{-1} by valence bonds in "crystalline regions" and at 1303 cm^{-1} by bonds in "amorphous regions," paralleling that developed for tetrafluoroethylene resins,¹⁶ void concentrations appear to be no greater than 1.5% in EC UHMW HDPE-1. At such levels, voids should have no substantial effects on the characteristics above, excepting dielectric strength. There was no evidence in these measurements of infrared frequency shifts as large as 5 cm^{-1} as a result of the high-pressure crystallization.

PROCESSING OF HIGH-PRESSURE CRYSTALLIZED UHMW HDPE

Because the viscosity of melted UHMW HDPE stock is enormous and because crystallization pressures of 3000 atmospheres or more are needed to achieve the special characteristics outlined above, useful articles with these characteristics cannot be prepared through molding or extrusion as these are normally practiced with thermoplastics.

However, forward solid-state extrusion of high-pressure crystallized UHMW HDPE-1 can be used to prepare cups like that in Figure 12. The feed stock consisted in machined cylinders $\frac{1}{2}$ in. in diameter \times $\frac{7}{8}$ in. long. These were forced downward into the mold by a ram load of about 3.5 tons at 70°C through a period of about 4 min. Faster processing should be feasible with stronger tools.

DTA showed that the extruded resin retains the EC morphology of the stock. Slight "springback" (tendency to recover toward the geometry of the stock) was evident, but this was localized in one angular sector, sug-

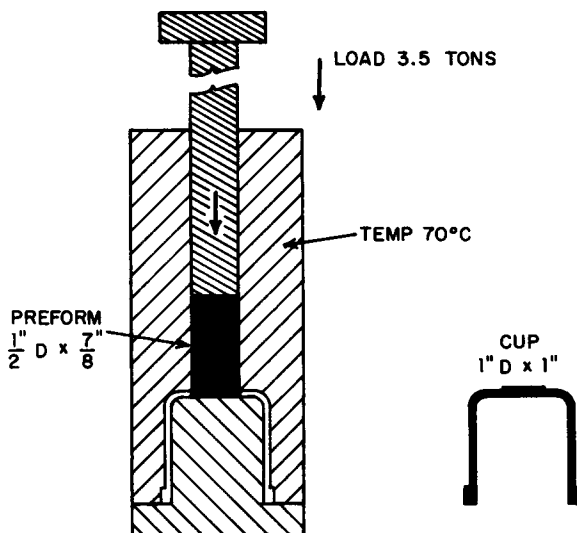


Fig. 12. Solid-state extrusion.

gesting it to be the result of anomalies in the stock or in the mold. The cups are remarkably tough, as shown most clearly in their failure to be shattered by heavy blows from a wood mallet.

Also, thin (0.02 to 0.04 in.) transverse sections from the 2-in.-diameter cylinders of high-pressure crystallized UHMW HDPE-1 were shaped to cups about 1 in. in diameter \times $\frac{1}{2}$ in. deep through the process usually termed "deep drawing" or "cupping."¹⁷ Results were generally good relative to those with other thermoplastics, except that the perimeters of some of the disks and, thus, of the daughter cups disintegrated, since these regions had not been fully converted to EC morphology (see above).

Judged in terms of (1) the ideal cup dimensions that would have been achieved with perfectly plastic stock and (2) changes in cup dimensions with time, particularly when accelerated by heating for 1 hr at 100°C springback is smaller than for most thermoplastics. In particular, annealing of the cups for one hour at 100°C "stabilizes" the cup material against further springback. That is, sections from stabilized cups show much less springback on further heating than do similar sections from unstabilized cups.

Disks from biaxially rolled sections of high-pressure crystallized UHMW HDPE-1 were also drawn to cups. Springback in these was greater than in cups from the parent stock.

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