Hydrostatic Extrusion under Back Pressure of High-Density Polyethylene

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Synopsis

The possibility of hydrostatic extrusion of solid polymer under back pressure has been studied. Operation of equipment is described that permits hydrostatic extrusion under back pressure at elevated temperatures. To understand how the pressure influences hydrostatic extrusion, extrusions of polyethylene under back pressure up to 392 MPa were conducted at temperatures below the melting point of polyethylene at atmospheric pressure (T_m^1). Furthermore, hydrostatic extrusion in the solid phase could be conducted at temperatures beyond T_m^1, since the melting point of polyethylene increased markedly with increasing back pressure.

INTRODUCTION

Hydrostatic extrusion of metals was first tried by Bridgman.[1] He also conducted tensile test experiments on several metals under hydrostatic pressure and observed that ductility increased as pressure increased. The process of hydrostatic extrusion has been developed in many laboratories.[2] Experiments on hydrostatic extrusion of a range of difficult materials have been described by Pugh and Low.[3] Hydrostatic extrusion of solid polymers has been reported by Buckley and Long,[4] Bunney and Cassin,[5] Alexander and Wormell,[6] Gibson et al.,[7] and others.[8,9]

The effect of hydrostatic pressure on the mechanical properties of polymers has been investigated by Pugh et al.[10] and many other authors. Furthermore, it is well known that extended chain crystals of polyethylene can be obtained by crystallization from the melt under high pressure.[11] As the melting temperature of the polymer increases with increasing pressure, effects of pressure on structural changes of the polymer during extrusion are of particular interest and importance in the study of structure and properties of extrudates.

In previous papers[12,13] we discussed the molecular orientation and the structural changes of high-density polyethylene. In this paper the possibilities of hydrostatic extrusion of high-density polyethylene under back pressure were investigated at elevated temperatures. Particular attention was paid to the influence of pressure and temperature on deformation of the polymer.

Regarding hydrostatic extrusion under back pressure, Pugh and Low[3] have been reported that the technique called fluid-to-fluid extrusion, or differential-pressure extrusion, allows brittle materials to be worked cold. Buckley and Long[4] found that the application of back pressure is of little benefit in the extrusion of brittle polymers, e.g., poly(methyl methacrylate). Avitzer et al.[14] studied the deformability of brittle composite, e.g., fiber-reinforced composites of aluminum. Then, plastic deformation was performed by hydrostatic extrusion into a receiver pressure, called pressure-to-pressure extrusion. Bhateja and Pae[15]
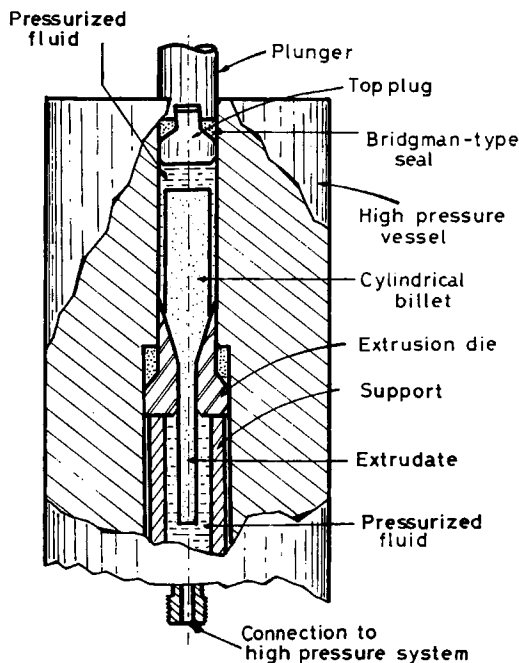
0021-8995/79/0023-2543$01.00

Fig. 1. Schematic of apparatus for hydrostatic extrusion under back pressure.

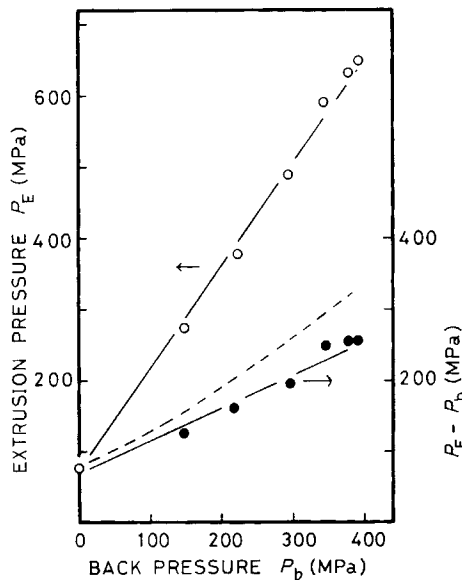Fig. 2. Relationship between back pressure P_b and extrusion pressure P_E. Extrusion temperature $T_E = 90°C$, extrusion ratio $R'_E = 6.4$: (○) extrusion pressure P_E; (●) differential pressure $P_E - P_b$.

investigated fluid-to-fluid extrusion of polyimide at room temperature. However, little has been reported on the hydrostatic extrusion of solid polymers under back pressure at elevated temperatures. To know the possibilities of the extrusion of polymers under back pressure at elevated temperatures is undoubtedly
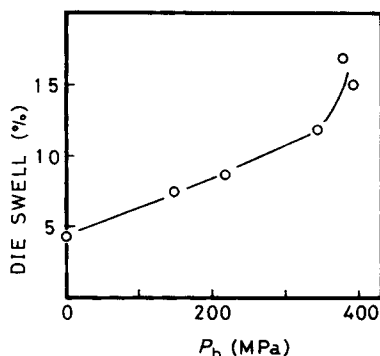
Fig. 3. Amount of die swell of extrudates obtained under back pressure. $T_E = 90°C$, $R'_E = 6.4$.

of interest in connection with the technique of hydrostatic extrusion of a range of difficult polymers or brittle polymers.

EXPERIMENTAL

Hydrostatic Extrusion Under Back Pressure

High-pressure container

A general view of the apparatus for hydrostatic extrusion under back pressure is schematically shown in Figure 1. The high-pressure container (especially manufactured by Kobe Steel Ltd) can be used at pressures up to 700 MPa with a billet 6 mm in diameter. The container consists essentially of an extrusion cylinder (diameter 7 mm), a die, a cylinder for back pressure, and a piston head. Dies have a throat 2.0 and 2.5 mm in diameter and 10 mm long, and a semicone angle α of 10°.

Extrusion

Commercial rods of high-density polyethylene, Hizex 5100B (Mitsui Petrochemical Co., Ltd.), with M.I. of 0.25 and M_v of 85000, were used as the starting materials. A nose was machined on one head of the billet (diameter 5.0_5 or 6.0 mm, length 50 to 60 mm). The extrusion apparatus, the loading, and the temperature control are similar in principle to those described in the previous paper.[12] Loads were applied and controlled by a tensile testing machine (Toyo-Baldwin Co, Ltd. UTM-I-5ton) capable of giving a constant load on the plunger during the extrusion. The back pressure can be generated up to 500 MPa by a pressure unit (manufactured by Kobe Steel Ltd.) that consists of two hand pumps, a pressure intensifier, an electric pressure gauge, and a relief valve. The fluid used as pressure medium was glycerol.

The process of hydrostatic extrusion under back pressure of solid polyethylene was as follows: (1) A billet with a nose was pressed on the die cone at ambient temperature to make an initial fluid seal. (2) The extrusion cylinder was filled by the fluid (glycerol). (3) Load was applied to the plunger and at the same time the back pressure was generated by the pressure unit, differential pressure being maintained nearly constant. (4) After the desired back pressure had been attained, the extrusion container was heated up to the extrusion temperature T_E.
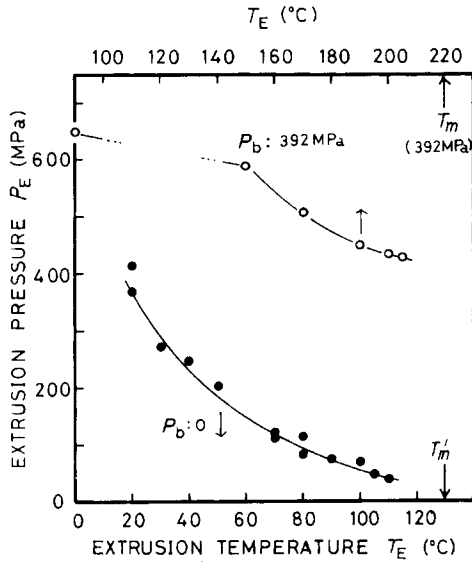
Fig. 4.   Relationship between extrusion pressure and extrusion temperature above T_m^1. $R'_E =$ 6.4:   (O) $P_b = 392$ MPa; (●) zero back pressure.
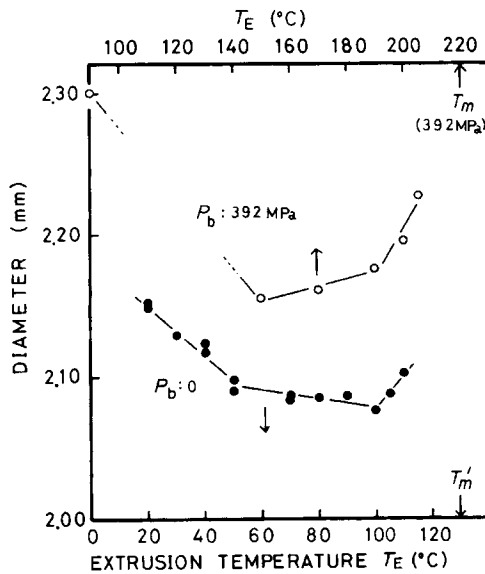

Fig. 5. Diameters of extrudates obtained at elevated temperatures: (O) $P_b = 392$ MPa; (●) zero back pressure.

The extrusion temperature was selected below the melting temperature of polyethylene under back pressure.   (5) After a certain time, the plunger was forced in by an appropriate load and hydrostatic extrusion was conducted.   (6) The back pressure was controlled to be as constant as possible by a relief valve during the extrusion.   (7) After the container had been cooled to below 80°C, the pressure of the container and the back pressure were reduced to atmospheric pressure.   (8) Then, the specimen was taken out of the container.
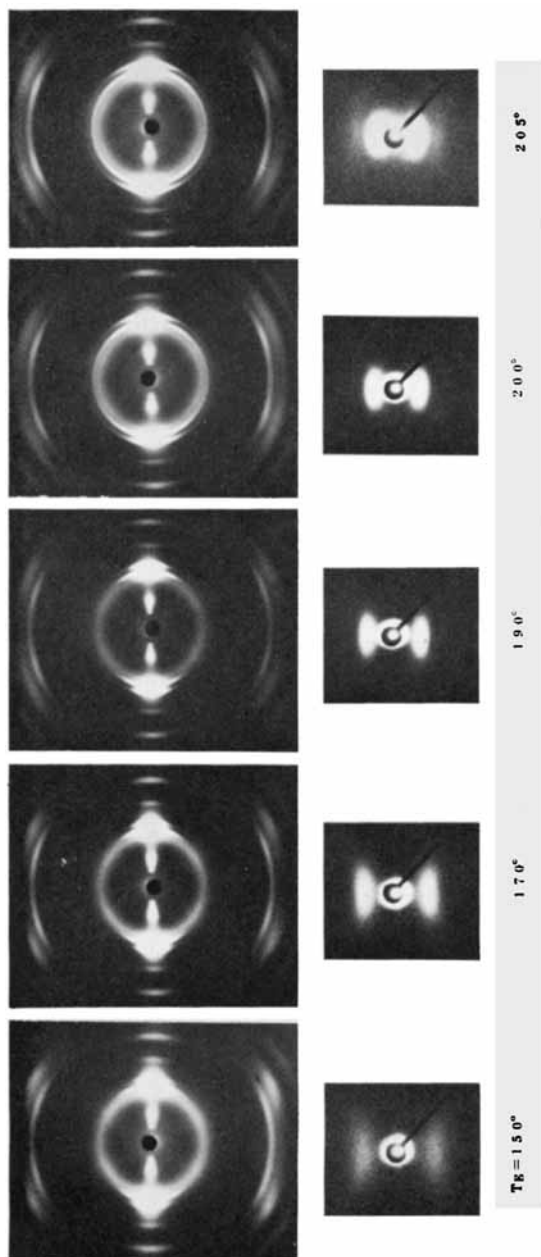
Fig. 6. Wide-angle and small-angle x-ray diffraction patterns of extrudate obtained at temperatures beyond T_m^1. $R_E' = 6.4$, $P_b = 392$ MPa.
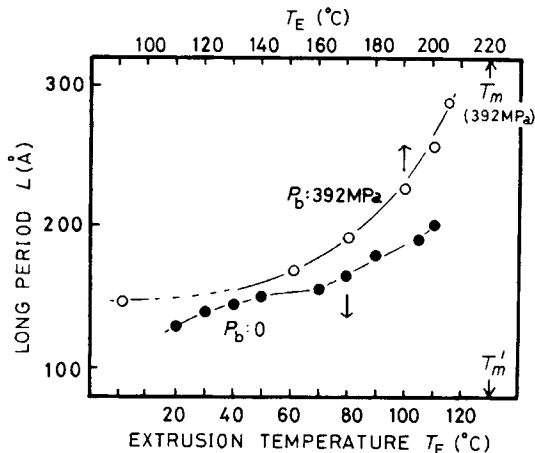
Fig. 7. Axial long period L of extrudates ($R'_E = 6.4$).

Characterization

The extrudates thus obtained were characterized by the following methods. Wide-angle x-ray diffraction patterns were obtained by using Ni-filtered Cu $K\alpha$ radiation (35 kV, 15 mA) with a flat camera. Small-angle x-ray scattering patterns were taken with a vacuum camera (Rigaku-Denki). Ni-filtered Cu $K\alpha$ radiation (50 kV, 90 mA) by means of Rota Unit RU-3SH (Rigaku-Denki) and pinhole collimators 0.3 and 0.2 mm in diameter were used. The melting temperature of the extrudate was measured with a Perkin–Elmer Model DSC-2 differential scanning calorimeter. The density was measured by the density gradient column method in a mixture of ethanol and water at 25°C.

RESULT AND DISCUSSION

Extrusion at Temperatures Below the Melting Point of Polyethylene at Atmospheric Pressure

The normal melting point at atmospheric pressure T_m^1 of the rod of Hizex 5100B polyethylene was about 130°C. To understand how the pressure influences the hydrostatic extrusion, extrusion under back pressure was conducted at temperatures below T_m^1 with an extrusion ratio of $R'_E = 6.4$. At low extrusion temperature, $T_E = 40°C$, extrusion under a back pressure of 196 MPa generated cracks on the surface of the extrudate. However, an extrudate with a smooth surface can be obtained without difficulty at room temperature by means of the usual hydrostatic extrusion without back pressure. As the melting point of polyethylene increases markedly with increasing pressure, the mobility of molecular chains or the deformability of crystallites may decline with increasing back pressure. At $T_E = 70°C$, extrudates with $R'_E = 6.4$ were obtained under back pressure P_b up to 294 MPa. Furthermore, at $T_E = 90°C$, extrudates could be obtained under P_b up to 392 MPa. The surfaces of the extrudates were quite smooth.

Extrusions were conducted at $T_E = 90°C$ under the different back pressures. Constant load was applied to the plunger during the extrusion so as to keep the extrusion rate low (between 4 and 8 mm/min). The extrusion pressure P_E was
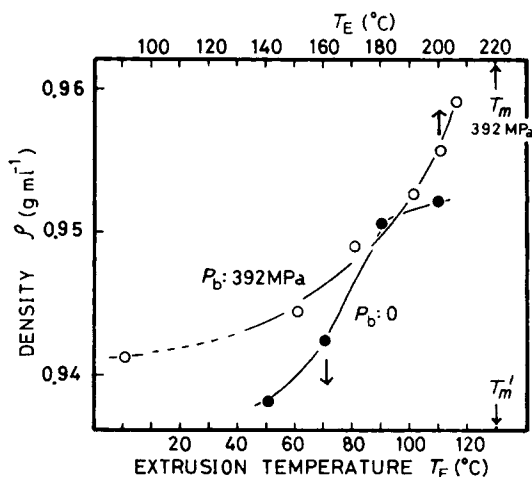
Fig. 8. Density of extrudates ($R'_E = 6.4$): (O) $P_b = 392$ MPa; (●) zero back pressure.

estimated from the test machine load and piston cross-sectional area, where a redundant load due to the friction between the cylinder and the high-pressure seals on the piston head was corrected. Figure 2 shows the relationship between the back pressure P_b and the extrusion pressure P_E. The conclusion to be drawn is that the influences of back pressure is to increase the extrusion pressure. The differential pressure, $P_E - P_b$, also increased with increasing back pressure.

It is well known that the melting temperature of polymers increases with increase in pressure. Wunderlich[16] found that the melting temperature of polyethylene increases approximately 0.02°C/atm. The melting temperature of the rod of Hizex 5100B polyethylene under pressure of 392 MPa, measured by using a high-pressure dilatometer, was about 220°C. The difference between the melting temperature of the extrudate under back pressure and the extrusion temperature increases with a rise in back pressure. Thus, the rise in back pressure apparently corresponds to the drop in extrusion temperature.

TABLE I
Extrusion Conditions and Properties of Extrudate Obtained Under Back Pressure

Extrusion conditions		Properties	
Extrusion ratio R'_E	9.0	Melting point[a]	
		T_{m1}	112°C
		T_{m2}	131.9°C
		T_{m3}	136.8°C
Extrusion temperature T_E	200°C		
Extrusion pressure P_E	473 MPa	Degree of orientation f_c	0.987
Back pressure P_b	392 MPa	Long period L	225 Å
Differential pressure $P_E - P_b$	81 MPa	Mean dimension of crystallite normal to (020) planes, l_{020}	~360 Å
Appearance	transparent smooth surface	Density	0.9612 g/ml

[a] T_{m1} is the temperature of initiation of DSC fusion trace; T_{m2} is the peak temperature of DSC fusion trace; T_{m3} is the temperature of end of fusion.
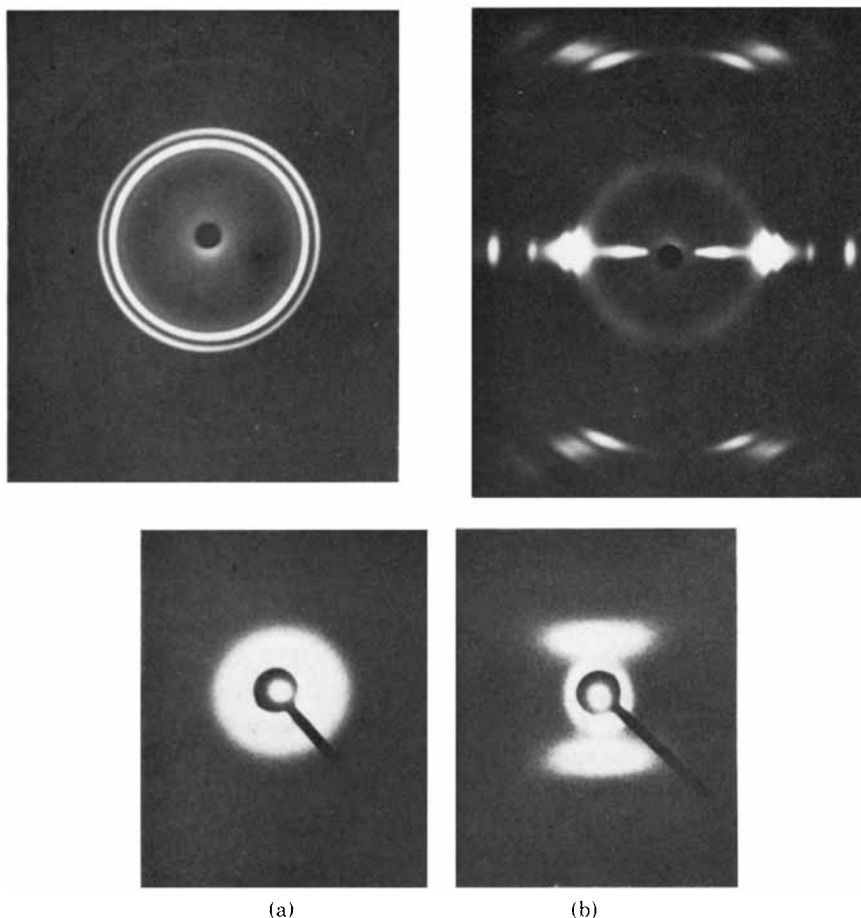
(a)   (b)

Fig. 9. Wide-angle and small-angle x-ray diffraction patterns of (a) nondeformed portion of rod which had been heat treated at 200°C under P_b of 392 MPa, and (b) extrudate for $R'_E = 9.0$ obtained at 200°C under P_b of 392 MPa.

In the previous studies,[17] on the usual hydrostatic extrusion (i.e., zero back pressure), the dependence of the extrusion pressure on the extrusion temperature T_E (°C) was found experimentally to be given by the formula

$$\log P_0 = -aT_E + b \qquad (1)$$

where P_0 (kgf/cm^2) is the minimum pressure required for extrusion, and a and b are constants. For the extrusion of $R'_E = 6.4$, a and b were 0.087 and 3.54, respectively. The extrusion temperature ($T_E = 90°C$) under different back pressure was reduced at atmospheric pressure as a function of the supercooling by using the data[18] of the pressure dependence of the melting temperature of folded chain crystals. The differential pressure required for extrusion was then estimated by substituting the temperature into eq. (1). The result is indicated by the broken line in Figure 2. The differential pressure ($P_E - P_b$) is slightly lower than the pressure expected from eq. (1) and the pressure dependence of the melting temperature. It is shown that the rise in back pressure corresponds to the drop in extrusion temperature.
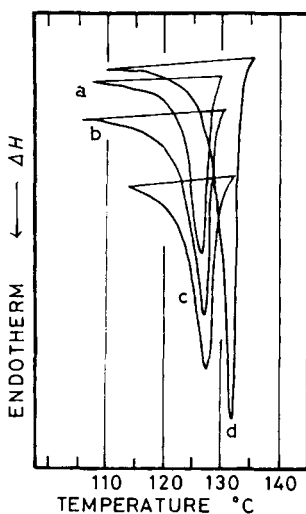
Fig. 10. Melting curves of extrudates determined by DSC-2. (a) $R'_E = 6.4$, $T_E = 90°C$, $P_b = 0$; (b) $R'_E = 6.4$, $T_E = 90°C$, $P_b = 392$ MPa; (c) $R'_E = 6.4$, $T_E = 200°C$, $P_b = 392$ MPa; (d) $R'_E = 9.0$, $T_E = 200°C$, $P_b = 392$ MPa.

The melting points of extrudates obtained at 90°C under back pressure were determined by DSC. In all of the extrudates a single melting peak was found. The samples were heated at a rate of 10°C/min. The peak temperature was almost constant in the range of 127 to 128°C.

Forming processes of thermoplastics often pose problems of dimensional control. The diameter of extrudate is not always equal to the die aperture owing to the elastic recovery, the so-called die swell, and the spring-back. Figure 3 shows the amount of die swell of the extrudates obtained under back pressure. The percentage die swell is expressed as $100(D_e - D_d)/D_d$, where D_e and D_d are the diameter of extrudate and die aperture, respectively. The amount of die swell increased with increasing the back pressure and the necessary extrusion pressure. Here, the die swell is due to a combination of the ordinary elastic recovery of the extrudate emerging from the extrusion die orifice and of the recovery of the volume of the amorphous region as the back pressure is reduced to atmospheric pressure.

Extrusion at Temperatures Above T_m^1

$R'_E = 6.4$

The effect of pressure on the melting temperature of polyethylene makes it possible theoretically to extrude the polyethylene rod in the solid state at temperatures above T_m^1. The melting temperature of the rod of Hizex 5100B polyethylene measured by using a high-pressure dilatometer was about 220°C at 392 MPa. Therefore, the polyethylene rods can be extruded in the solid state at temperature below 220°C under a back pressure P_b of 392 MPa.

Hydrostatic extrusions under a back pressure P_b of 392 MPa at an extrusion ratio R'_E of 6.4 have successfully been carried out. Figure 4 shows the relationship between the extrusion pressure and the extrusion temperature. As seen in the usual hydrostatic extrusion without back pressure, the extrusion pressure re-

quired for extrusion under P_b of 392 MPa was decreased with increase in extrusion temperature T_E. The differential pressure, $P_E - P_b$, also decreased with increasing T_E.

Figure 5 shows diameters of extrudates obtained under P_b of 392 MPa at elevated temperatures. Also diameters of extrudates obtained by means of the usual hydrostatic extrusion (i.e., zero back pressure) are shown in Figure 5. The die swell of extrudates obtained under back pressure is significantly higher compared to the usual hydrostatic extrusion. In the case of $P_b = 0$, there are discontinuities at 50 and 100°C. The curve for the hydrostatic extrusion under back pressure has two discontinuities corresponding to the usual hydrostatic extrusion.

Figure 6 illustrated the wide-angle x-ray diffraction patterns and the small-angle x-ray scattering patterns of the extrudates that were obtained under the conditions shown on Figure 4. In the wide-angle x-ray photographs, the (110), (200), (210), and (020) diffractions have maxima on the equator. The photographs show a "fiber diagram." It seems that the orientation of crystallites does not depend on the extrusion temperature. However, at $T_E = 200$ or 205°C, the x-ray diffraction photograph indicates slightly lower orientation.

Small-angle x-ray scattering photographs showed diagrams with two intensity maxima. As the extrusion temperature increases, the intensity maxima increase in intensity and the maxima are getting near to the center. At $T_E \leq 190$°C, the small-angle x-ray scattering photograph showed a diagram with intensity maxima elongated perpendicular to the meridian (i.e., a line-shaped two-point pattern). On the other hand, at $T_E = 200$ or 205°C, the intensity distribution is composed of small arcs.

In Figure 7 the axial long period L increases monotonically with the extrusion temperature. The axial long period of the extrudate obtained by means of the usual hydrostatic extrusion without back pressure is also shown in Figure 7. The pressure dependence of the lamellar thickness of polyethylene grown from dilute solution has been investigated by Wunderlich.[19] Also, the lamellar thickness of polyethylene crystallized from the melt under high pressure has been measured by Rees and Bassett[20] and many others. Rees et al.,[20] on crystallization of a polyethylene fraction of about 4500 Å at 5.0 kbar pressure, found an increase in lamellar thickness from about 2000 to 3300 Å as a function of crystallization temperature (190 to 230°C). The long period after extrusion under back pressure is not very large in contrast to crystallization from the melt under pressure. The extrudates give a periodicity of 150 to 290 Å. The noticeable difference, compared with L of extrudate obtained without the use of back pressure, is that L increases considerably at T_E near the melting point under back pressure.

Figure 8 shows the density of extrudates obtained at different extrusion temperatures. The density increased as the extrusion temperature increased. In contrast to the change in density of extrudates obtained without back pressure, the increase in density with T_E under back pressure is great.

$$R'_E = 9.0$$

Hydrostatic extrusion under back pressure P_b of 392 MPa at $R'_E = 9.0$ was conducted. The extrusion temperature was 200°C. Table I contains a summary of the extrusion conditions and the characterization of the extrudate. The

density of the extrudate was larger than that at $R'_E = 6.4$ (shown in Fig. 8). In the previous paper[12] it was reported that the extrudates obtained for $R'_E = 9.0$ without the use of back pressure showed highly oriented fiber structure and were highly transparent. The extrudate obtained under the conditions shown in Table I is also slightly transparent and has a smooth surface.

Figure 9(a) illustrated the wide-angle and small-angle x-ray diffraction patterns of the nondeformed portion of a rod which had been heat treated at 200°C under P_b of 392 MPa. Figure 9(b) illustrated the x-ray diffraction patterns of the extrudate. It is apparent that high molecular orientation occurs during the hydrostatic extrusion under back pressure. The degree of c-axis orientation f_c attained a value of 0.987. The small-angle x-ray diffraction photograph showed a two-point diagram elongated perpendicular to the meridian, and the scattering intensity was very large. The axial long period (225 Å) was smaller than that (255 Å) at $R'_E = 6.4$ and $T_E = 200$°C. The axial long period of the extrudate obtained by means of the usual hydrostatic extrusion without a back pressure decreased slightly with increasing deformation ratio. The fiber structure of the extrudate obtained under a back pressure of 392 MPa is thought to consist of stacks of chain-folded lamellae.

Figure 10 shows melting curves determined by differential scanning calorimetry. By way of comparison, curves of extrudates obtained under different conditions are shown [Figs. 10(a) to 10(c)]. The melting points of extrudates (b) and (c) obtained for $R'_E = 6.4$ under P_b of 392 MPa were almost equivalent to that (a) obtained without the use of back pressure. However, the melting curve of extrudate (c) ($R'_E = 6.4$, $T_E = 200$°C, $P_b = 392$ MPa) somewhat tailed toward a higher temperature. In contrast to the extrudates for $R'_E = 6.4$, (a) to (c), the melting point of extrudate (d) obtained for $R'_E = 9.0$ under P_b of 392 MPa was distinctly higher.

SUMMARY AND CONCLUSIONS

Studies have been made on the operation of equipment and the possibilities of hydrostatic extrusions of solid polymer under back pressure at elevated temperatures. It is possible to hydrostatically extrude a solid polyethylene rod under back pressure in a wide range of temperatures. The influences of back pressure on extrusion conditions were investigated. Furthermore, the molecular orientation and the structure of extrudates were characterized. The x-ray diffraction patterns of extrudates obtained under back pressure at temperatures above T_m^1 (the normal melting point of polyethylene at atmospheric pressure) bear a close resemblance to those obtained by the usual hydrostatic extrusion (i.e., zero back pressure). The results and conclusions of this study can be summarized as follows:

1. Extrusions under back pressures up to 392 MPa were conducted at temperatures below the normal melting point at atmospheric pressure T_m^1. At low extrusion temperatures (e.g., $T_E = 40$°C), the extrusion under a back pressure P_b of 196 MPa generated cracks on the surface of the extrudate. The deformability of crystallites may decrease with increasing back pressure.

2. Continuous extrusion could be obtained under P_b of 392 MPa at 90°C. It is shown that the rise in back pressure corresponds to the drop in extrusion temperature.

3. At temperatures above T_m^1, the polyethylene rod can be extruded in the solid state under back pressure.   The extrudates obtained under some conditions were transparent and had a smooth surface.

4. The wide-angle x-ray diffraction photographs of extrudates obtained under back pressure showed c-axis orientation.

5. The axial long period and the density of extrudates obtained under P_b of 392 MPa increased as the extrusion temperature increased up to 205°C.

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