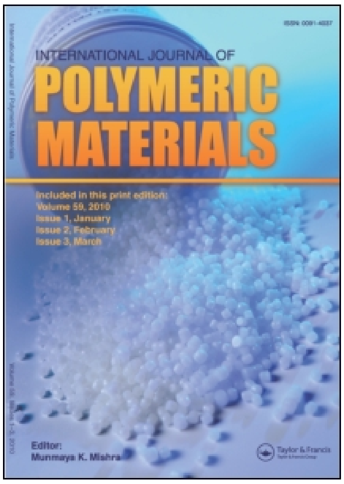

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Further Studies on Solid-State Extrusion of Linear Polyethylene and Binary Systems of Linear Polyethylene and N-Paraffin

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Further Studies on Solid-State Extrusion of Linear Polyethylene and Binary Systems of Linear Polyethylene and *n*-Paraffin

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The extrusion characteristics of the binary system of high density polyethylene and *n*-paraffin in the temperature region from the room temperature up to 80°C was investigated in connection with the previously proposed equation of extrusion pressure. The agreement between the extrusion characteristics observed and estimated was quite good, and the applicability of the equation was confirmed in wider range of extrusion conditions. The extrusion pressure decreases with increasing quantity of blended *n*-paraffin. This fact was explained as due to the lubricating effect of *n*-paraffin as well as the decrease of yield stress. The super structure of the material was examined and the existence of voids between the fibrillar structure of the extrudate was estimated. The existence of the voids were most remarkable in the extrudates obtained at lower extrusion temperatures. The extrudates of blended materials showed opaque appearance.

INTRODUCTION

It has been reported in the previous paper[1] that highly oriented and transparent extrudates of linear polyethylene were obtained by extruding a solid sample under high pressure through a tapered die at temperatures higher than 80°C and below the melting point. The transparent appearance of the extrudate suggests the absence of voids. The structure of the extrudate was investigated by small-angle and wide-angle X-ray measurements and by observations with

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an electron microscope. In those experiments, the extrudate was found to display a very high degree of c-axis orientation up to the value of orientation function of $f_\epsilon = 0.994$. The extrudate was composed of closed packed thin fibrils of the diametrical dimension about 300 Å and showed the long periods of 200 to 300 Å along the extrusion direction. The extruding process was analyzed on the basis of the tensile properties of the polymer with an approximate method which assumes polyethylene as a plastic material.[2]

The purpose of the present study is to investigate the extrusion characteristics of the binary system of high density polyethylene and *n*-paraffin in the temperature region from the room temperature up to 80°C to confirm the applicability of the previously reported equation of extrusion[2] to the binary system which shows different stress–strain characteristics from polyethylene itself.

EXPERIMENTAL

1 Materials

Starting materials for extrusion experiments are high density polyethylenes, Hizex 1200J (Mitsui Petrochemical Ind., Co., Ltd.), Novatec JV040 (Mitsubishi Chemical Ind., Co., Ltd.) and Sholex 4002B (Nihon Olefin Ind., Co., Ltd.). Their melt indices are 9.2, 4.0 and 0.2 respectively. Sholex 4002B is a copolymer of ethylene with butene-1. The others are homopolymers. Billets of these materials were cut out from blocks prepared by the usual compression molding. Billets and *n*-paraffin blends of polyethylene were prepared by mixing both components on hot rollers at 145°C and then by molding and by cutting into a billet in the same way as the straight polymer samples. Three kinds of commercial grades *n*-paraffin A, B and C, whose melting points were 50°, 70° and 108°C, respectively, were used. Table I summarizes characteristics of the materials.

2 Extruding device and extruding procedure

Figure 1 illustrates a cylinder-piston type device for the extrusion experiments. The cylinder of the diameter 10 mm was charged with a billet, and warmed by the heater wound around the cylinder and by the hot plates of the oil press. The device was placed between the hot plates of an oil press, and the piston was pressed down into the cylinder with the oil press under constant pressure. The length of the extrudate from the outlet of the die to the head of the extrudate was measured. The dies mainly used in this experiment were those of the half vertical angle $\alpha = 20°$, inlet diameter $2R = 10$ mm and of outlet diameter $2r = 2.0$ to 5.0 mm. We will use a degree of processing $(R/r)^2$

TABLE I

Characterization of polyethylene samples

	Density[a] g/cm^4	M.I.[b]	M_η[c]	Branched $-CH_3$ group[d] %
Hizex 1200J	0.969	9.2	4.7×10^4	0.5
Novatec JV040	0.967	4.4	5.4×10^4	0.3
Sholex 4002B[e]	0.945	0.16	9.4×10^4	0.5

[a] Measured by flotation methods in water and methanol mixture at 20°C.

[b] ASTM D-1238-57T.

[c] Calculated from intrinsic viscosity in tetraline at 130°C, according to Thung's equation.[15]

[d] Number of $-CH_3$ branches per 1000 carbon atoms. Determined from infrared absorption spectra.

[e] For this sample, 3.4 $-C_2H_5$ branches/100 CH_2 were estimated from infrared absorption spectra.

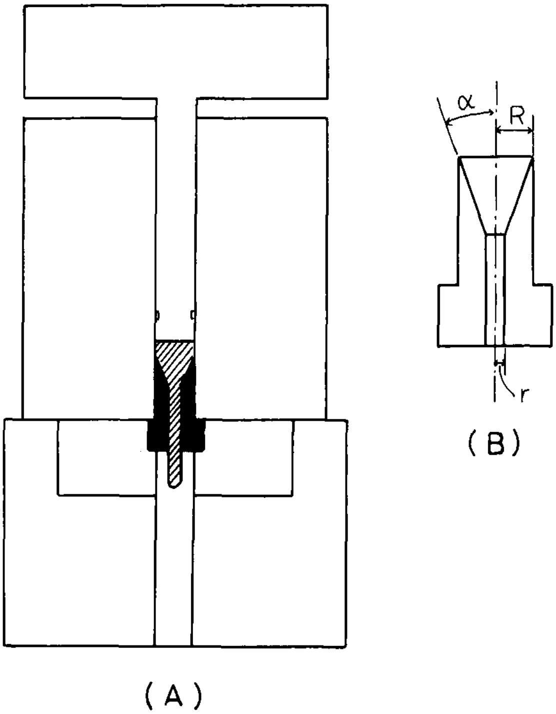


FIGURE 1 Device used for extrusion experiments, (a) piston, cylinder and die assembly, (b) vertical section of the die.

as a measure of the degree of deformation, which corresponds to the draw ratio of stretched samples.

3 Other measurements

The uniaxial tensile testing was conducted by using a Tensilon UTM-III-T, with an air oven (Toyo Measuring Instruments Co.). The experiments were carried out at various temperatures and at the cross-head velocity of 5mm/min. A scanning electron microscope JSM-U3 (Nihon Denshi Co.) was used to observe the structure of extrudates. In addition, morphological and structural investigations were made by small-angle and wide-angle X-ray measurements. The measurements were made at room temperature by means of a small-angle camera and also by a flat-plate camera with a point-collimation system. Nickel-filtered CuKα radiation was used. The long periods were calculated according to Bragg's equation.

ANALYSIS OF EXTRUSION CHARACTERISTICS

1 Formulation of extrusion Pressure

Sachs[3] suggested the theoretical equation to estimate the pressure necessary to extrude plastic materials through a conical die in a steady state. Recently, Imada *et al.*[2] extended it by taking account of the work-hardening effect in polymeric materials and obtained Eq. (1).

$$\sigma_0 = -(1 + B)\int_0^{\epsilon_f} Y(\epsilon)\exp(B\epsilon)d\epsilon + \left(\frac{R}{r}\right)^{2B}\sigma(\epsilon_f) \tag{1}$$

where $\epsilon_f = 2ln(R/r)$, $2R$ and $2r$ are the inlet and outlet diameter of the die, σ_0 is the pressure at the die inlet. (ϵ_f) the pressure at the die outlet and $Y(\epsilon)$ is the yield stress of the polymer for deformation up to the true strain ϵ. The value of B is equal to μoct α, where μ is the coefficient of friction between the billet and the inner surface of the die, and α is the half angle of the die. Koerber and Eichinger[4] suggested a correction of Sachs' equation concerning the shear stress necessary for changing the moving direction of the material at the die inlet and outlet. According to them, a compensating term should be added to Sachs' pressure. This term is $(2/3\sqrt{3})\,Y(\epsilon_i)\tan\alpha + (2/3\sqrt{3})\,Y(\epsilon_f)\tan\alpha$, where ϵ_i and ϵ_f are the true strains at the die inlet and outlet, respectively. If $Y(\epsilon_i) = 0$, the latter term alone remains as the Koerber–Eichinger effect, which will be discussed in a later section.

2 Stress–strain Properties

The true stress determined by the uniaxial tensile testing was used for the value of $Y(\epsilon)$. The methods for the measurements of true stress and true strain were described in the previous paper.[5] The smoothing of the obtained tensile data was performed according to Eq. (2) after an appropriate selection of values of σ^*, ϵ^* and c.

$$\log(\sigma/\sigma^*) \cdot \log(\epsilon/\epsilon^*) = -c \tag{2}$$

where the value of c is characteristic of polymer species and $c = 0.384$ in the case of polyethylene.[5] The value of σ should be restricted to $\sigma > \sigma^*$, and that of ϵ, $\epsilon < \epsilon^*$. In Figure 2 the true stress vs. true strain curves for linear polyethylene at 30°, 90° and 110°C (a), and for the blend system with *n*-paraffin (b) are shown.

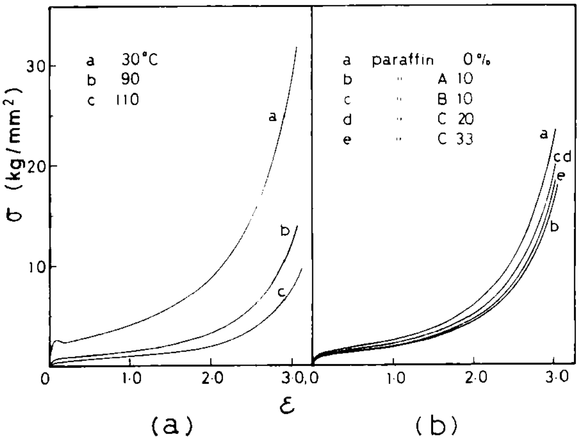


FIGURE 2 True stress–true strain curves of (a) Hizex 1200J 30°, 90° and 110°C, and (b) Novatec JV040 and its blends with *n*-paraffin at 50°C. These data are nicely fitted by Eq. (2), with the values of $c = 0.384$ for all of the measurements, $\epsilon^* = 5.75$ for all 3 cases of Hizex 1200J (a), and $\epsilon^* = 5.55$ for Novatec JV040 (b), and $\sigma^* = 1.28, 0.46, 0.27$ for a, b and c of (a), respectively, and $\sigma^* = 0.80, 0.58, 0.68, 0.69$ and 0.62 for a, b, · · · ·, e of (b), respectively.

RESULTS

1 Extrusion characteristics

As reported in the previous paper,[2] the steady state rate of extrusion remains practically zero when the extruding pressure is in a range below a certain critical value (extrusion pressure). As soon as the pressure increases beyond the critical pressure, the extrusion takes place smoothly. However, when the extrusion experiments are carried out at high degree of processing, i.e. large value of $(R/r)^2$, the increase of extrusion rate was not so rapid as in the case of low degree of processing. In the cases of high degree of processing, if the pressure is further increased, the cracks and defects are generated and finally the extrudate is fractured. The critical value of pressure, extrusion pressure, is almost independent of the extrusion temperature. It is important from the technological point of view to know the limiting value for smooth extrusion. In the case of Hizex 1200J and Novatec JV040, such a successful extrusion can be done with the degree of extrusion below $(R/r)^2 = 11.1$, while in the case of Sholex 4002B, nylon 6[2] and polypropylene[6] below $(R/r)^2 = 8.2$, 4.0 and 6.3, respectively. Figure 3 shows the plots of these values of limiting degrees

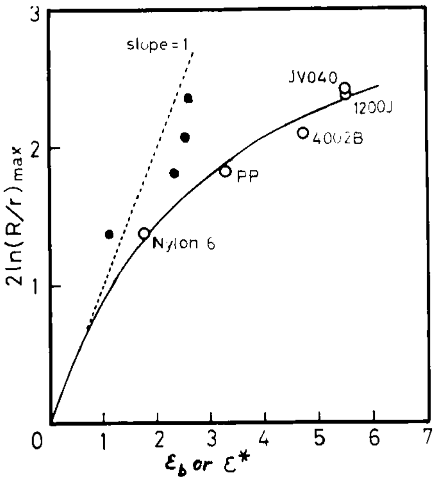


FIGURE 3 Maximum degree of processing for smooth extrusions of each material vs. true strain ϵ^* and true strain at break ϵ_b from tensile data at velocity 5 mm/min. ϵ^* (○), ϵ_b (●).

of processing against the tensile breaking strain ϵ_b in the true strain units and ϵ^* of Eq. (2). The fracture in extrusion process takes place when the strain of the extrudate attains the value of breaking strain. As it is not easy to estimate the breaking strain, the use of the parameter of ϵ^* seems to have some advantage, though the correlation between $ln(R/r)_{max} - \epsilon^*$ is not linear. In Figures 4 and 5, the plot of the extrusion pressure against the logarithmic degree of processing $2ln(R/r)$ and the calculated curves from Eq. (1) are compared for two kinds of polyethylene and the blends with *n*-paraffin. To estimate the extrusion pressure according to Eq. (1), the tensile true stress at the speed of the cross-head separation of 5 mm/min was used as $Y(\epsilon)$. Since the extrusion pressure calculated from the true stresses at the cross-head velocities of 5, 20

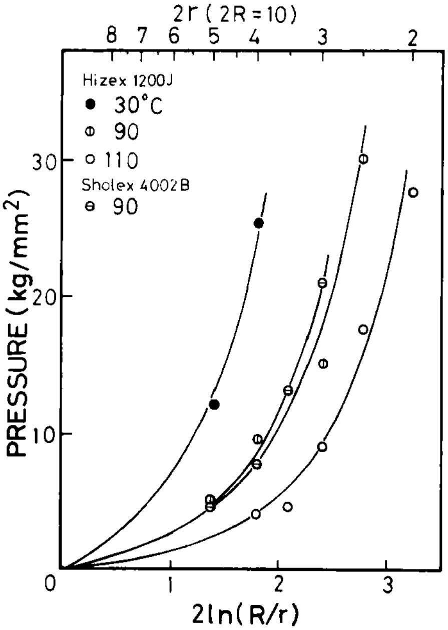


FIGURE 4 Extrusion pressure vs. degree of processing of polyethylene; Hizex 1200J (●, ◐, ○) and Sholex 4002B (⊖). Solid lines are curves calculated from tensile data on the assumption of procedure (II).

and 50 mm/min were almost identical within some percentages, the effects of the extension rate on the calculated extrusion pressure may be neglected. The detailed discussions on the methods of calculation of extrusion pressure from the tensile data by using Eq. (1) will be given in the later section. In this way, some technical data for the solid-state extrusion of the polymeric materials can be predicted from the tensile data.

2 Super-structure of extrudate

Extruded samples of high degree of processing prepared at relatively low temperatures such as 50°C are less transparent than those obtained at the temperatures higher than 80°C. The extrudates of the blend with *n*-paraffin were not so transparent.

Table II gives the list of the samples used for the morphological and structural examinations. Figures 6 and 8(a) show the wide-angle and small-angle X-ray scattering patterns of the extrudates at the room temperature or 50°C. These wide-angle scattering photographs indicate the lower degree of orientation of polyethylene crystals in comparison with the extrudates obtained at higher temperatures. Two diffractions, $2\theta = 19.5°$ strong, $2\theta = 25.3°$

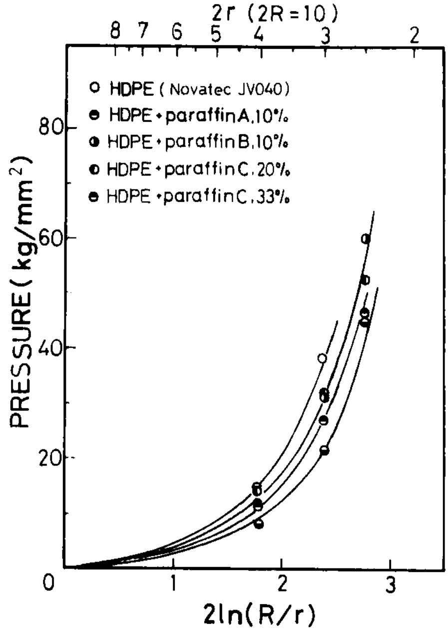


FIGURE 5 Extrusion pressure vs. degree of processing of Novatec JVO40 and its blends with *n*-paraffin. Solid lines are curves calculated from tensile data on the assumption of procedure (II).

weak, could be found besides the diffractions due to the usual orthorhombic crystals. These two diffractions can be assigned to the monoclinic crystals of polyethylene.[7] Those diffractions could not be observed in the case of the extrudate extruded at the temperatures higher than 80°C.

The extrudates of blended materials were examined by extracting *n*-paraffin, by incorporating with biphenyl as swelling agent,[8] and by subsequent removal of the agent. The density of biphenyl is 1.150 g/cm^3 at 25°C. The difference between the densities of biphenyl and polyethylene crystal is about 0.15 g/cm^3. This value is comparable with that of the difference between the densities of the crystal and amorphous regions in reversed sign. Figure 7 represents diagrammatically the relations between those treatments and the compositions of the samples. Table II also lists these blended, extracted, and swelled samples.

Figure 8(a), (b) and (c) show the wide-angle and small-angle X-ray scattering patterns of the samples B, C and D of Table II, respectively. The diffractions due to the crystals of biphenyl were observed as well as those of polyethylene crystals in the case of sample D as shown in Figure 8(c). The small-angle scattering photographs of sample B, Figure 8(a), exhibits weak scattering

TABLE II

Notes on samples

Sample	Content of sample
A	Translucent sample obtained by extruding Hizex 1200J at 25°C up to the degree of processing $(R/r)^2 = 4.0$.
B	Translucent sample obtained by extruding the blend material of Hizex 1200J and *n*-paraffin B (10%) at 50°C up to the degree of processing $(R/r)^2 = 11.1$.
C	Opaque sample obtained by extracting *n*-paraffin from sample B by toluene at 75°C for 10 hrs.
D	Opaque sample obtained by swelling sample C in the bath of biphenyl at 75°C for 10 hrs.
E	Opaque sample obtained by removing biphenyl with CCl_4 from sample D.
F	Opaque sample obtained by extruding the blend material of Hizex 1200J and *n*-paraffin B (33%) at 50°C up to the degree of processing $(R/r)^2 = 11.1$.
G	Opaque sample obtained by extracting *n*-paraffin from sample F by toluene at 75°C.

intensity peak both on the meridian and on the equator. Both maxima spread widely in parallel with the direction of equator. The long period estimated from the meridional maximum was $L = 158$ Å. The long period along the direction of extrusion was also estimated on the sample which was obtained by extracting *n*-paraffin from the sample B, i.e. sample C, to be $L = 180$ Å. The scattering intensities of the sample C on the equator was very strong in comparison with those of the sample B. The long period of the sample D, which was obtained from the sample C by incorporating with biphenyl, was estimated from the photograph of Figure 8(c) to be $L = 192$ Å. The intensity of the meridional scattering was increased by incorporation of biphenyl and the equatorial diffraction almost disappeared. The small-angle scattering pattern of the sample D was similar to that of the extrudates obtained at higher extruding temperatures in those features mentioned above. Finally, when biphenyl was removed by extracting with CCl_4 the small-angle scattering pattern resumed the features of that of the sample C.

Figure 9 shows the scanning electron microphotograph of the fractured surface of the sample C. The bundles of fibrils of lateral diameters of thousands

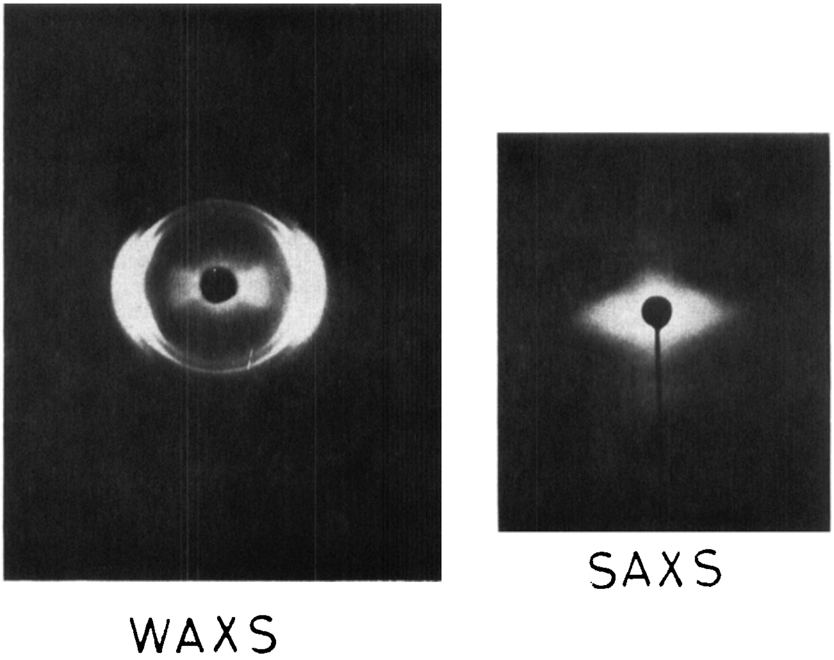


FIGURE 6 Wide-angle and small-angle X-ray scattering of sample A. Long period is $L = 138$ Å.

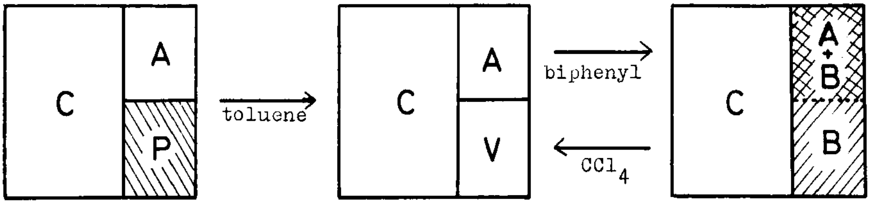


FIGURE 7 Diagrammatical representation of the reactions between the treatment by solvents and the compositions of extrudates.

SAMPLE B → SAMPLE C → SAMPLE D
(P: 10%)
SAMPLE E ←
SAMPLE F → SAMPLE G
(P: 33%)

C: Polyethylene Crystalline Region
A: Polyethylene Amorphous Region
P: Phase of *n*-Paraffin
B: Phase of Biphenyl
V: Voids

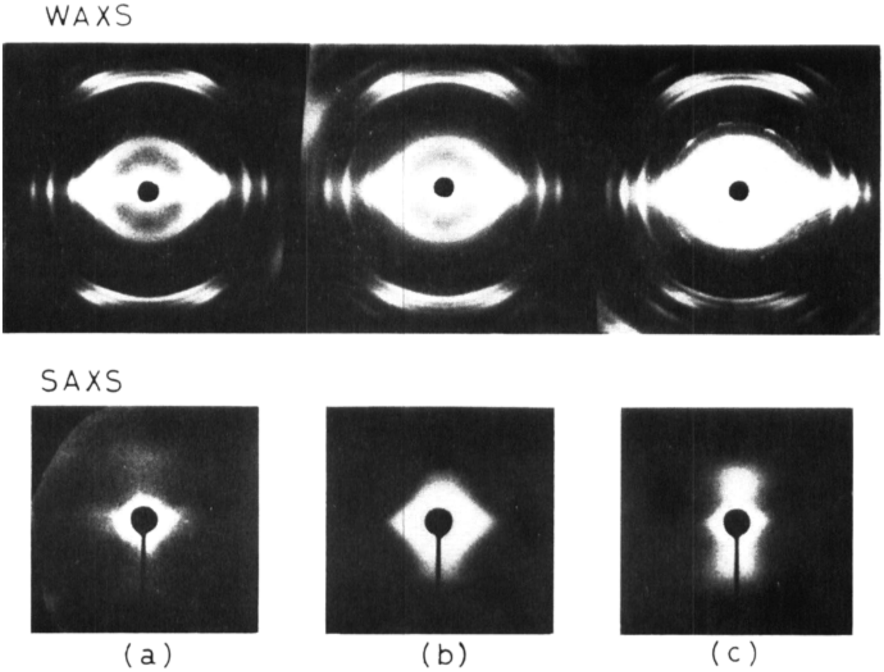


FIGURE 8 Wide-angle and small-angle X-ray scattering of (a) sample B, (b) sample C and E and (c) sample D.

of angstroms are aligned along the extrusion direction. The bundles were observed being entangled with each other.

Another series of samples which starts from the sample containing 33% of *n*-paraffin are also listed in Table II as the samples F and G. Figure 10(a) shows the wide-angle X-ray scattering photograph of the sample G, and (b) and (c) show the small-angle X-ray scattering of the sample F and G, respectively. The wide-angle X-ray scattering pattern of the sample F is not shown because it was almost similar to that of the sample G, Figure 10(a). As revealed by comparing Figure 10(a) with Figure 8(a) the orientation of polyethylene crystals in the blended samples was greatly diminished by increasing the quantity of blended *n*-paraffin from 10% up to 33%. Meridional diffractions were not found in the small-angle scattering of the sample F, as shown in Figure 10(b). These features of the wide-angle and small-angle scattering patterns are similar to those of the early stages of the deformation of the spherulites in the stretched polyethylene samples.[9] As shown in Figure 10(c), the meridional scattering appeared again in the small-angle scattering pattern of the sample G, which was obtained by extracting *n*-paraffin from the sample F, with remarkable intensity and the envelope of the shape of the long ellipse laying its longer axis in parallel with the equator.

Figure 11 shows the scanning electron microphotograph of the sample G. In the bottom right-hand corner of the figure an enlarged printing of a spot in the original photograph is shown. As shown in Figure 11 the bundles of thin lamellae whose lateral dimensions were 700–800 Å were observed being aligned along the direction of extrusion. This kind of bundle structure of lamellae seemed to be restricted in the regions corresponding to the sectors of

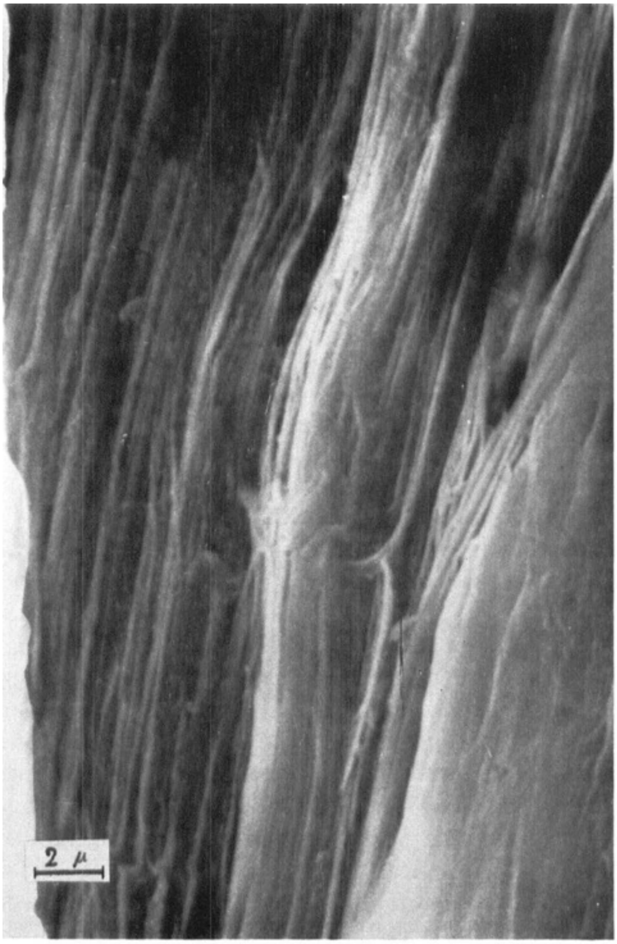
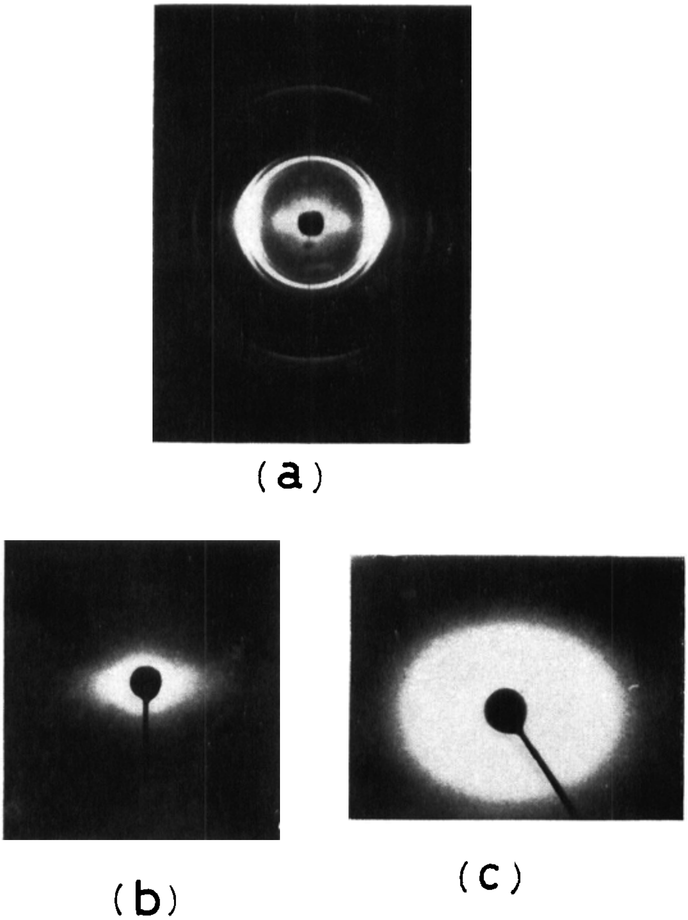


FIGURE 9 Scanning electron microphotograph of sample C.



(a)

(b)

(c)

FIGURE 10 (a) Wide-angle X-ray scattering of sample G, and small-angle X-ray scattering of (b) sample F and (c) sample G.

the original spherulites directed to the extrusion direction (polar sectors). Residual parts of the original spherulites (equatorial sectors), are supposed to remain unchanged. Such an explanation of the scanning electron microphotographs is consistent with the observations of the small-angle X-ray scattering and with the mechanism of the deformation of spherulites proposed by Keller *et al.*[10] Figure 11 shows cobweblike fine fibrils spanned between the bundles of the fibrils. It is interesting to notice that they shoot out perpendicular to the main bundles of straight fibrils to go across the voids.

The long periods along the extrusion direction of the blend samples of various blend ratios extruded at 50°C are constantly $L = 150$ Å, and increase with increasing extrusion temperatures. Figure 12 shows the dependencies of the long periods of the samples of pure polymers with different degrees of processing on the extrusion temperatures.

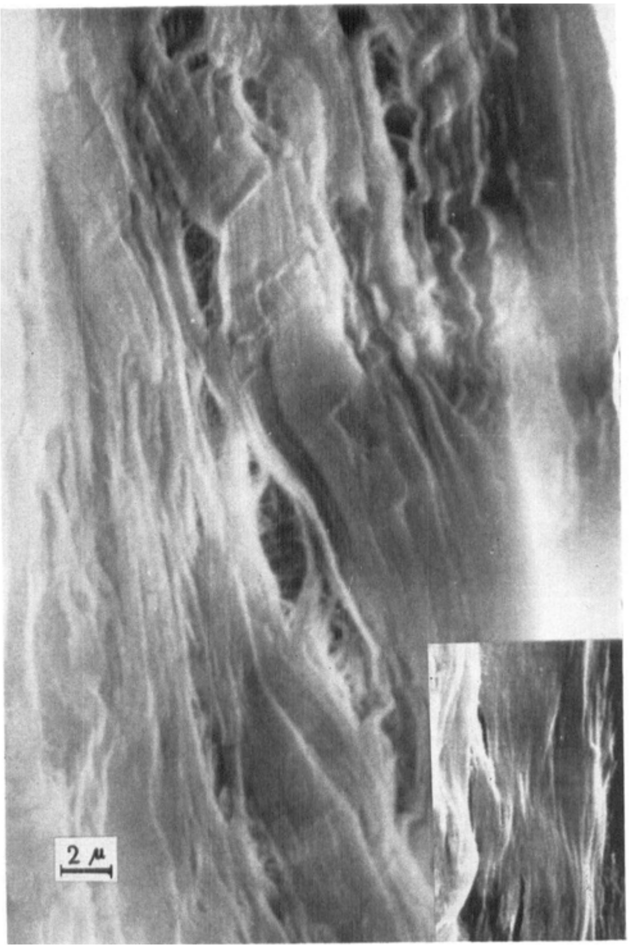


FIGURE 11 Scanning electron microphotograph of sample G.

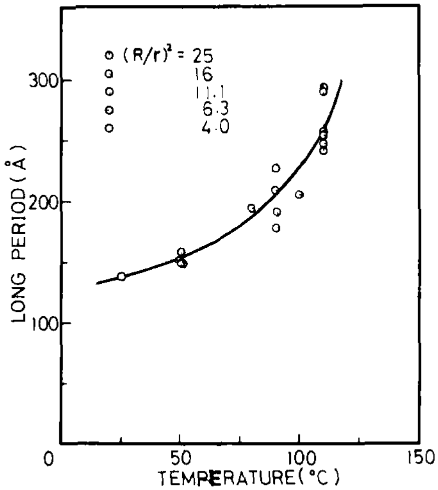


FIGURE 12 Long period of extrudates vs. extrusion temperature.

DISCUSSIONS

1 Extrusion characteristics

If we calculate extrusion pressures by substituting μ of Eq. (1) with trial values of frictional coefficients, we can find the value of μ with which the best fit of the observed and calculated extrusion pressures were obtained. In this procedure, it is necessary to estimate the additional term of Eq. (1), $(R/r)^{2B} \cdot \sigma(\epsilon_f)$. Koerber and Eichinger's proposal is to substitute the whole term with the values of $2\,Y(\epsilon_f)(\tan\alpha)/3\sqrt{3}$. However, according to the process of the integration of the original differential equation, the correct form of the term seems to be $(R/r)^{2B} \cdot \sigma(\epsilon_f) = 2(R/r)^{2B}\,Y(\epsilon_f)(\tan\alpha)/3\sqrt{3}$. In both cases no account was taken of anisotropy of the yield stress of highly deformed polymers when $Y(\epsilon_f)$ is used. The correction term of the first case, i.e. Koerver–Eichinger correction as it was, gives negligibly small values in comparison with the values of the first term of Eq. (1), and both methods could not be considered to be more reasonable than to neglect the term by setting $\sigma(\epsilon_f)$ to zero. Thus, following two methods, I and II, will be examined in the following paragraphs of this section to evaluate Eq. (1) by setting $\sigma(\epsilon_f)$ as follows.

(I) $$\sigma(\epsilon_f) = 0$$

(II) $$\sigma(\epsilon_f) = \frac{2}{3\sqrt{3}}\,Y(\epsilon_f)(\tan\alpha) \qquad (3)$$

We found the different sets of frictional coefficients which gave the best agreement between the calculated and observed values for each procedure I or II. The values of such frictional coefficients are given in Table III, which are almost independent of the grades of polyethylene and *n*-paraffin, in both procedures. Their dependence on the blend ratio of *n*-paraffin and that on the extrusion temperature are shown in Figures 13 and 14, respectively. The decrease in the value of frictional coefficient with the increase of the blend ratio as shown in Figure 13 is reasonable, because *n*-paraffin is frequently used as a sliding agent for polyethylene or polyvinylchloride. On the other hand, Figure 14 represents that the value of μ decreases with increasing extrusion temperature. The frictional coefficient of polymeric materials increases with increasing temperature during which the temperature remains below the glass transition of the sample, while it decreases with increasing temperature if the temperature rises above the glass transition temperature.[11] Thus, it is difficult to estimate the value of the frictional coefficient under the conditions of solid state extrusion, unless the viscoelastic properties of the polymer have been fully known. The values of μ coefficient estimated from our extrusion experiments at 25°C were 0.23 according to method (I), and 0.20 according to method (II). These values are close to the values estimated by other authors with different methods of experiments,[12,13] although those estimations were done under conditions which are different from those of our extrusion experiments in the temperatures or in the loads on the frictional surfaces.

As shown in Figures 4 and 5, the extrusion pressures calculated from Eq. (1) according to methods (I) or (II) agreed with the observed values.

TABLE III

Frictional coefficients of various polyethylene systems calculated from tensile data according to Eq. (1) on the assumptions of the procedures (I) and (II)

Samples	Extrusion temperature (°C)	Frictional coefficient (I)	(II)
Hizex 1200J	30	0.230	0.200
	90	0.182	0.167
	110	0.167	0.146
Sholex 4002B	90	0.189	0.167
Novatec JVO40	50	0.220	0.197
Novatec JVO40 + paraffin A (10%)	50	0.204	0.189
Novatec JVO40 + paraffin B (10%)	50	0.211	0.189
Novatec JVO40 + paraffin C (20%)	50	0.197	0.182
Novatec JVO40 + paraffin C (33%)	50	0.175	0.153

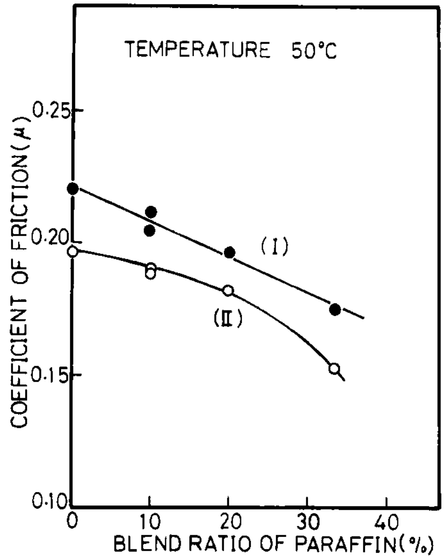


FIGURE 13 Coefficients of friction as functions of blend ratio of paraffins in Novatec JV040.

The temperature of extrusion was 50°C, and the values of the coefficients were estimated according to the equations I, (●) or II, (○) of Eq. (3). The data are the same as those given in Table III of corresponding lines.

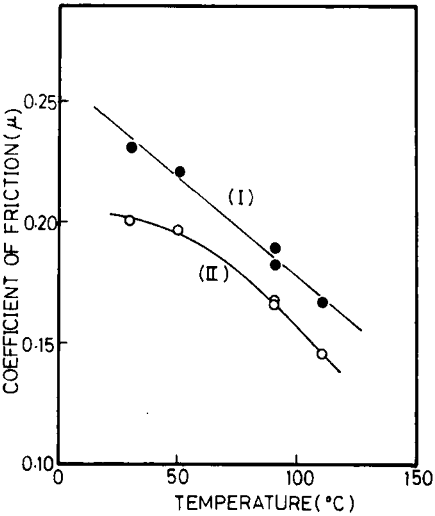


FIGURE 14 Coefficients of friction as functions of extrusion temperatures.

The data are the same as given in Table III for Hizex 1200J, Sholex 4002B and Novatec JV040 straight polymers without taking care of the differences between those grades. As the methods of estimation, see the caption of Figure 13.

2 Super-structure

Orientation of polyethylene crystallites diminishes with increasing fraction of n-paraffin. The value of $Y(\epsilon)$ also decreases with the increase of n-paraffin.[5] Thus, it seems that the space between the lamellar crystals of polyethylene might be filled with n-paraffin in the blend samples. The lamellae would easily slip away from each other when the billets underwent deformation process in the die hole. In this situation the stress is not enough to deform the crystalline lamellae and, in some cases, it might not be enough to deform a spherulite as a whole. It is also concluded that n-paraffin did not mix with polyethylene in molecular order, at least in the crystalline phase. This fact is also confirmed by careful inspection of X-ray diffraction patterns of blended samples as well as the fact that the mechanical properties of the blended samples suggest mechanically parallel combination of two independent phases.[5]

When the swelling agent, biphenyl was added to the extrudate, the long period increases. After subsequent extraction of biphenyl, the long period returned to the value of the sample C, as the whole view of the small-angle X-ray scattering resumed the features of the sample C, i.e. original sample of the swelling experiment. On this viewpoint, swelling with biphenyl and deswelling of it is a reversible phenomenon. The fact that the long period along the extrusion direction increased after the addition of the agent suggests that biphenyl was incorporated into the fibrils as well as in the regions surrounding the fibrils.

Eq. (4) gives the intensity of n-th diffraction in the small-angle region of X-ray scattering with a regular stacking of lamellae.[14]

$$I_n \propto (\rho_c - \rho_a)^2 \sin^2(\pi n t/P) = (\Delta\rho)^2 \sin^2(\pi n t/P) \tag{4}$$

where ρ_c and ρ_a are the densities of the lamellar crystals and amorphous regions, respectively, and P is the periodicity of lamellar stacking, and t is the thickness of the interlamellar amorphous zone. If $(\Delta\rho)^2$ is considered to be constant, the intensity of $n = 1$ takes the maximum value at $t/P = 1/2$. As described in the previous section, the long period of the sample swelled with biphenyl was longer than that of the original unswelled extrudate, while the orientation of the crystalline regions was unchanged and the intensity of the meridional scattering increased. It seems that the amorphous regions in microfibrils are expanded without changing the orientation of lamellar stacking. As the values of the density differences, $(\Delta\rho)^2$, in the sample before and after the treatment are not considered to be so much different from each other, the increase of the scattering intensity after the treatment seems to be due to the effect of the increase in thickness of the amorphous regions, t.

Extrudates obtained at higher temperatures above 80°C had a transparent appearance and showed no equatorial distribution of scattering intensity. It seems that there are no voids in between the dense aggregates of microfibrils. A weak but distinct scattering was found along the equator in the cases of the samples obtained by extruding at the temperatures lower than 50°C. This scattering disappeared when the samples were treated with biphenyl, showing that the fluctuation of electron density distribution was due to the voids being in between the bundles of microfibrils.

CONCLUSION

(1) Extrudates obtained by extruding linear polyethylene and its blends with *n*-paraffin at temperatures of 30° and 50°C with the degree of processing as high as 11.1 showed somewhat transparent appearance. With increasing amounts of *n*-paraffin, the transparency of extrudates tends to decrease.

(2) These extrudates showed lower orientation of polyethylene crystallites than the extrudates of pure polyethylene extruded at temperatures higher than 80°C. The wide-angle diffraction revealed the coexistence of the monoclinic system for the lower temperature extrudate of polyethylene.

(3) The low temperature extrudates showed the small-angle X-ray scattering patterns which indicated the existence of voids, whereas the high temperature extrudate did not. Scanning electron microphotographs showed that the parts of the original spherulitic texture were retained in the extrudates which contained 33% *n*-paraffin.

(4) It was confirmed that the equation of extrusion which was reported previously by us was applicable to the extrusion of two component materials, such as polyethylene and *n*-paraffin, in the cases of which the inhomogeneous deformation occurred remarkably.

(5) Koerber–Eichinger effect and the effect of additional shear stress at the inlet and exit of the die cone were examined. The estimation of these effects is concerned with the evaluation of the frictional coefficient. In all of the cases assumed, including the case where the effect was neglected, frictional coefficients in the range of the values 0.20–0.23 have given good estimation of extrusion pressures. Thus, the adequacy of one of these effects cannot be estimated in this point of view.

(6) The values of the frictional coefficient decrease with increase of the quantity of blended paraffin and also with increasing temperature of extrusion.

References

1. K. Imada, T. Yamamoto, K. Shigematsu, and M. Takayanagi, *J. Mater. Sci.* **6**, 537 (1971).
2. K. Imada, T. Yamamoto, K. Kanekiyo, and M. Takayanagi, *J. Soc. Mater. Sci. Japan (Zairyo)* **20**, 606 (1971).

3. G. Sachs, *Z. angew. Math. u. Mech.* **7,** 235 (1927).
4. F. Koerber and A. Eichinger, *Mitt. K. W. Inst. Eisenforschung,* **22,** 57 (1940).
5. S. Maruyama, K. Imada, and M. Takayanagi, *Intern. J. Polymeric Mater.* **1,** 211 (1972).
6. K. Nakamura, K. Imada, and M. Takayanagi, unpublished data.
7. H. Kiho, A. Peterlin, and P. H. Geil, *J. Appl. Phys.* **35,** 1599 (1964).
8. J. Descamps-Carlier, G. A. Homes, and J. J. Point, *Macromol. Chem.* **109,** 1 (1967).
9. G. Meinel, N. Morosoff, and A. Peterlin, *J. Poly. Sci.* A-2, **8,** 1723 (1970).
10. L. Hay and A. Keller, *Kolloid-Z.* **204,** 43 (1965).
11. L. Nielsen, "Mechanical Properties of Polymers", Ch. 9, Reinhold Pub., New York (1962).
12. M. A. Marcucci, *Soc. Plastics Eng. J.* **14,** 30 (1958).
13. *Soc. Polymer Sci. Japan,* "Rheology Handbook", Maruzen, Tokyo (1965), p. 276.
14. R. Hosemann and S. N. Bagchi, "Direct Analysis of Diffraction by Matter", North Holland Pub. Co., Amsterdam (1961).
15. L. H. Tung, *J. Poly. Sci.* **36,** 289 (1959).