

X-Ray Diffraction Orientation Studies on Blown Polyethylene Films. III. High-Stress Crystallization Orientation

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Synopsis

X-Ray diffraction orientation measurements have been made on a wide range of films blown from three high-density polyethylenes, to determine more precisely the conditions which lead to the high-stress crystallization type of orientation. The most extensive measurements relate to films from Hostalen GM 9955F; the results show that there is a very wide range of orientational behavior. Under very low-stress conditions there is almost pure *a*-axis orientation; with very high stress there is substantial *c*-axis orientation, both with reference to the machine direction. Commercial blowing conditions give rather high stress and the *a* axis is inclined at 60° to 70° to the machine direction in the sheet-normal-machine-direction plane. Calcium stearate, used to improve the surface finish, increases the stress for a given set of machine conditions and, of these, a high draw ratio and a low extrusion temperature are most effective in promoting high-stress crystallization. The less extensive results for an experimental Rigidex grade and Shell LPPE 040 fit into this overall pattern; for a given set of blowing conditions they have lower stress than the Hostalen polymer. Commercial blowing conditions give an *a*-axis inclination of about 45°.

INTRODUCTION

X-Ray diffraction pole figure measurements on films blown from three types of high-density polyethylene have shown^{1,2} that two types of orientation occur, often simultaneously. The first, and more normal, is the result of conventional crystallization processes. The *a* and *c* axes are at 90° with both at an angle to the plane of the film and this type of behavior is readily accounted for in terms of the stress crystallization mechanism of Keller and Machin.³ The second type of orientation is analogous to that found in cold drawn polyethylene^{4,5} under conditions where necking occurs. The term high-stress crystallization is used² to describe the second type of orientation, because much higher stresses occur during the necking process; it is then convenient to designate the first type as low-stress crystallization.

The type of orientation obtained is dependent on both the blowing conditions and the type of polyethylene used. With an experimental Rigidex grade and with Shell LPPE 040 large amounts of low-stress orientation are always obtained. However, the results suggest that certain combinations of machine conditions give significant amounts of the high-stress type of orientation. In the case of Hostalen GM 9955F the high-stress material appears to form readily over a rather wide range of machine conditions. In particular, measurements on films for which the blowup and draw ratios were substantially constant, but the quotients of the freeze-line height and draw ratio covered a range of values, showed that high-stress orientation is favored particularly by slower cooling conditions.

Nevertheless, the range of films examined was insufficient to elucidate the relative importance of the four machine parameters melt temperature, blowup ratio, draw ratio, and cooling rate.

The purpose of the present work has been twofold. In the case of the Rigidex and Shell polymers, films covering a somewhat wider range of blowing conditions have been examined, in an attempt to establish more clearly if a significant proportion of high-stress crystallized material can be obtained. With the Hostalen polymer, films from a series of blowings in which the four machine conditions were varied in a systematic and largely independent manner have been measured, in the hope of obtaining a better understanding of the high-stress crystallization process.

EXPERIMENTAL

All the films examined were blown on a full-scale Demag HDPE Film unit based on a 60 mm extruder, from three types of high-density polyethylene; an experimental Rigidex grade with a melt index of 12–13, Shell LPPE 040 having a melt index of 7.9, and Hostalen GM 9955F whose melt index is 7.5. These three values were determined by ISO method R1113 procedure 7. Calcium stearate was not used in the preparation of the films from the Hostalen polymer, in distinction to those considered in Paper II.² The relevant machine conditions for the Rigidex and Shell films are given in Table I and for the Hostalen films in Table II. No cooling rate data are available for the films blown from the Shell and experimental Rigidex polymers, documented in Table I. The Hostalen films listed in Table II fall into three groups; with films 10–17, no screw speed information is available but the cooling rates are probably meaningful on a comparative basis. The screw speeds for films 18–24 were the same as were 25–30, but the values differ in two cases. Hence, the cooling rates for films within a particular group may be compared. The blowing conditions for the Rigidex and Shell polymers lay within the reasonable range for commercial production except in the case of film 5, where the melt temperature was significantly lower. In this latter case the film showed appreciable variations in thickness.

The Hostalen films fall into two groups. In preparing the first eight, the melt temperature was held constant but the blowup ratio and the draw ratio were varied. With the remaining thirteen films an attempt was made to separate the

TABLE I
Preparational Details for Nine Films Blown from Shell LPPE 040 and from an Experimental Rigidex Grade

Film No.	Polymer	Melt temperature (°C)	Blowup ratio	Draw ratio
1	Shell LPPE 040	215	5	~5
2	Shell LPPE 040	235	3	~8
3	Shell LPPE 040	235	7	~3.5
4	Shell LPPE 040	250	5	~5
5	Shell LPPE 040	182	4.88	not known
6	Experimental Rigidex grade	215	5	~5
7	Experimental Rigidex grade	235	3	~8
8	Experimental Rigidex grade	235	7	~3.5
9	Experimental Rigidex grade	250	5	~5

TABLE II
Preparational Details for 21 Films Blown from Hostalen GM 9955F

Film No.	Melt temperature (°C)	Blowup ratio	Draw ratio	Freeze-line height (cm)	Freeze-line height / Draw ratio
10	203	3.3	3.4	17.5	5.2
11	203	2.9	9.2	17.4	1.9
12	203	4.8	5.1	17.5	3.5
13	203	6.0	3.5	17.5	5.0
14	203	4.1	13.1	17.5	1.3
15	203	6.4	7.4	17.5	2.4
16	203	5.6	15.4	17.5	1.1
17	203	6.5	13.8	17.5	1.3
18	184	1.0	3.5	16	4.6
19	185	1.0	2.9	55	1.9
20	185	4.2	2.7	45	1.7
21	185	3.9	2.7	15	5.6
22	194	1.0	~30	80	~2.67
23	194	1.0	~30	low	small
24	194	0.5	~60	low	small
25	234	1.0	2.9	18	6.2
26	234	1.0	2.9	55	19.0
27	234	4.9	2.7	55	20.4
28	235	4.8	2.7	18	6.7
29	235	1.0	~30	80	~2.7
30	235	1.0	~30	20	~0.67

effects of draw ratio, blowup ratio, melt temperature, and film cooling rate (freeze-line height). It was not possible to prepare satisfactory films using all possible theoretical permutations; nevertheless, a wide range of melt temperatures and blowup ratios was achieved, together with a significant variation in the draw ratios and the freeze-line heights.

The methods used for measuring the pole figures and for expressing the results in terms of the intensity profile along the machine-direction-sheet-normal (MD-SN) plane of the (200) pole figure have been described in Paper II.²

RESULTS

The intensity profiles for films 1 and 2 (Shell LPPE 040) are shown in Figure 1; those for films 3 and 4 are essentially similar to film 2, except that the amount of unoriented material may be a little greater. The profile for film 2 is typical of those previously encountered with films from the Shell polymer² and it indicates the presence of low-stress orientation only. This type of orientation is also present in film 1 but the significantly higher intensity at the maximum shows that the overall degree of orientation is greater than in most films of this type.

Film 5 (Shell LPPE 040) varied appreciably in thickness and two portions were cut from it for examination. The thinner one was of 25 μm average thickness and the thicker one had the average value 35 μm ; the intensity profiles are also shown in Figure 1. The maximum in the case of the thicker film is at about 45°, showing that low-stress orientation is the major type present. Nevertheless, the high-intensity values in the vicinity of the sheet normal direction indicate that significant amounts of high-stress orientation are also present. The trend

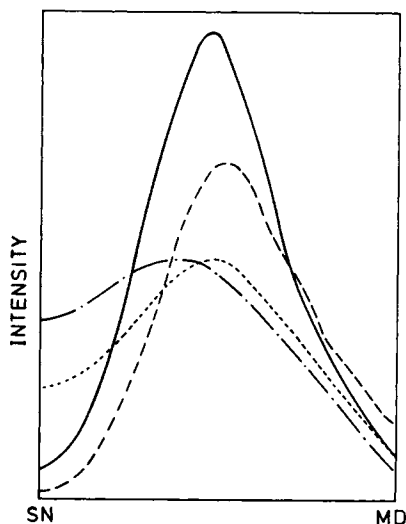


Fig. 1. Intensity profiles across the (200) pole figures in the MD-SN plane for films 1 (—); 2 (---); 5, 25 μm thickness (- · - ·); and 5, 35 μm thickness (···) blown from Shell LPPE 040.

towards high-stress orientation is still more pronounced in the case of the thinner film and although a quantitative interpretation of the profile is not possible it is clear that this type of orientation is present to an appreciable extent. Presumably, at the relative low-melt temperature used the stress is greater and is also more marked in the thinner regions of the film, as might be expected.

The intensity profiles for films 6 and 7 (experimental Rigidex grade) are shown in Figure 2 those for films 8 and 9 are essentially similar to film 6. These three are typical of the low-stress type of orientation. The profile for film 7 indicates that it has low-stress orientation but the height at the maximum shows that the overall orientation is lower than that of the three other films from the Rigidex polymer. The higher intensities in the vicinity of the sheet normal direction show the presence of a significant amount of high-stress orientation. This result indicates the rather complex interdependence of orientation with the blowing parameters and in the case of film 7 the high-draw ratio, which predisposes towards axial (*c*-axis) orientation, probably becomes significant. Nevertheless, the difference in behaviour from the corresponding material (film 2) blown from Shell LPPE 040 is somewhat surprising, unless the cooling rates, which are not known, are very different.

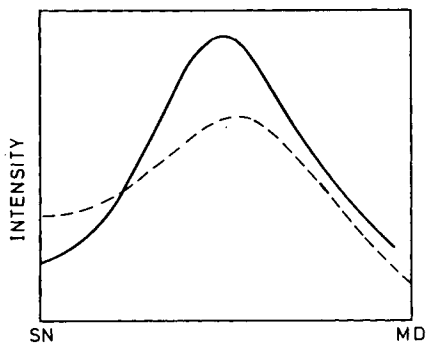


Fig. 2. Intensity profiles across the (200) pole figures in the MD-SN plane for films 6 (—) and 7 (---) blown from an experimental Rigidex grade.

The intensity profiles for films 10, 12, 14, and 16, blown from the Hostalen polymer are shown in Figure 3. Those for films 11, 13, 15, and 17 are similar, in each case, to those for the next lower number in the series. The profile for film 10 is of the low-stress type of orientation and this is also the major feature in the case of film 12, although there is some unoriented material present and some high-stress orientation. This latter type has increased in film 14 and very much in the case of film 16, for which the profile is not greatly different from that of the thin portion of the Shell LPPE 040 film blown at 182°C. However, the melt temperature was held constant in the case of films 10–17 from the Hostalen polymer and the increased incidence of the high-stress type of orientation is the result of the increasing blowup and draw ratios, particularly the latter.

In considering how to group the remaining Hostalen films, 18–30, for interpretational purposes, this deduction and the earlier one² that the higher the melt temperature the lower the proportion of high-stress orientation, suggest that they should be considered in order of anticipated increasing stress. The results to date then suggest that films 25 and 26, made with small blowup and draw ratios and a high-extrusion temperature, will have the lowest stress. They will probably be followed by films 27 and 28, made at the same temperature but with a higher blowup ratio and 18 and 19 and 20 and 21, pairs of films prepared at a much lower temperature with low blowup and draw ratios and high blowup and draw ratios. Finally, if the effect of draw ratio is more marked than that of melt temperature, the sequence should be films 29, 30, 22, 23, and 24, the last of these with the highest stress conditions of the sequence. This ranking may only prove approximate but it should be useful for enlarging on what has already been deduced.

The results for films 25, 26, 27, and 28 are shown in Figure 4 and they indicate a type of behavior not previously encountered with the Hostalen polymer. Film 25 has its maximum at about 80° from the sheet normal direction, i.e., there is almost complete *a*-axis orientation, and it is at about 70° with film 26. The slight shift away from near *a*-axis orientation in the latter case represents the influence of the slower cooling and the consequent relaxation.¹ The behavior is also apparent with films 27 and 28 but with these the maxima have moved towards SN, although they are still on the MD side of the 45° position, hitherto regarded as typical of films having low-stress orientation.

Films 18, 19, 20, and 21 give the familiar profile with the 45° maximum but

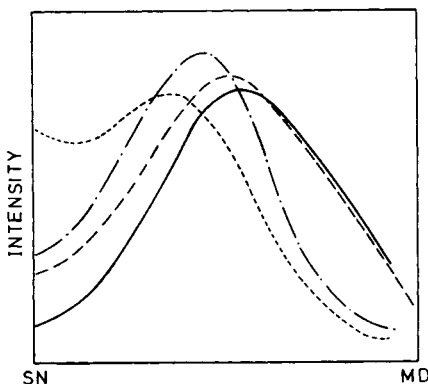


Fig. 3. Intensity profiles across the (200) pole figures in the MD-SN plane for films 10 (—), 12 (---), 14 (- · - ·), and 16 (···) blown from Hostalen GM 9955F.

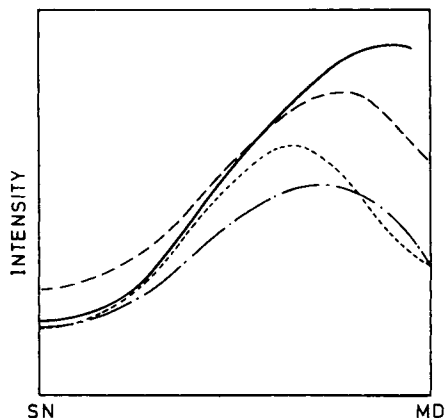


Fig. 4. Intensity profiles across the (200) pole figures in the MD-SN plane for films 25 (—), 26 (---), 27 (- · - ·), and 28 (···) blown from Hostalen GM 9955F.

the latter pair have appreciably greater intensities in the vicinity of SN than the former, showing that the high-stress type of orientation is beginning to occur. The differences between the two films in each pair are minimal and it is clear that once higher stress conditions are approached changes in the cooling rate become a secondary factor. The concentration of the high-stress oriented polymer is considerably greater in the case of films 29 and 30 as the profile of the former, shown in Figure 5, demonstrates. The profiles for the remaining films, 22, 23, and 24, are also shown in Figure 5. These films were prepared under very atypical conditions, with a relatively low-melt temperature and a high degree of uniaxial draw. It is, therefore, not surprising that increasing amounts of high-stress (*c*-axis) orientation occur, particularly in the case of film 24 where the crystallographic behavior approaches that of cold-drawn polyethylene.

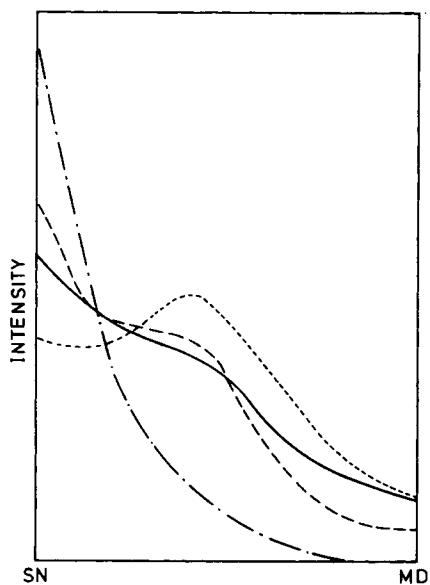


Fig. 5. Intensity profiles across the (200) pole figures in the MD-SN plane for films 22 (—), 23 (---), 24 (- · - ·), and 29 (···) blown from Hostalen GM 9955F.

Hence, the progression from *a*- to *c*-axis orientation follows the trend outlined above on the basis of a provisional estimation of the relative degrees of stress during blowing. The abnormal blowing conditions used for the production of most of the films in the group 18–30 led to considerable variations in their thickness. However, where these deviated from the normal value of about 25 μm they were in the direction of increasing thickness, by as much as an order of magnitude. Hence, no effect upon the orientation is anticipated because additional high-stress orientation and transcrystallinity will only occur with films that are thinner than average.

DISCUSSION

The results for the Hostalen polymer are of considerable interest for two reasons, one of a rather specialist character and the other general. In the case of the various films for which the results have been reported in Paper II,² 1% of calcium stearate was added, to improve the surface finish for commercial purposes. The films examined in the present instance were prepared solely to obtain as wide a range of blowing conditions as possible and no calcium stearate was added. When the intensity profiles for films prepared under similar blowing conditions, with and without calcium stearate, are compared it is clear that this additive exerts an appreciable influence in determining the type of crystallization and hence the type of orientation that is obtained. When it is absent there is a greater tendency towards the more normal type of low-stress crystallization.

The influence of the calcium stearate may be for two reasons, in connection with the stress during the blowing process and in the nucleation process at the onset of crystallization. Although no experimental evidence is available it is probable that the presence of this additive will affect the elongational flow properties in the direction of increasing stress. Its effect upon the nucleation process and the subsequent crystallization is a matter for speculation. A much wider and more detailed study would be required to elucidate the mechanism; for present purposes it is significant in the context that an additive incorporated into the polymer for commercial quality purposes has an influence on the type of orientation obtained.

The second and more general deduction is that the types of orientational behavior obtained from films blown with a very wide range of conditions are much greater than those suggested by the previous work,² although they are wholly in accord with the two types of orientation known to exist, from this work and from studies on heavily cold-drawn polyethylene.^{4,5} The limited work on films from low-density polyethylene had indicated that substantially complete *a*-axis orientation could occur,^{6,7} although, in general, there is some rotation of the *a* axis so that it is inclined at an angle to the TD/MD (film) plane. At the other extreme, with conditions giving very high stress, the *a* axis lies along SN and the *c* axis along MD. This is analogous to the orientation found in heavily cold-drawn polyethylene, although this similarity in the crystallographic sense does not have a parallel morphologically, because the blown films have the normal lamellar structure,⁸ whereas cold drawn polyethylene at high draw ratios has a fibrillar structure.^{9,10}

The range of behavior of the *a*-axis inclination is shown in Figure 6 and it should be stressed that although the mean direction, for a particular inclination to SN or MD, lies in the SN/MD plane, there is a symmetrical spread in the

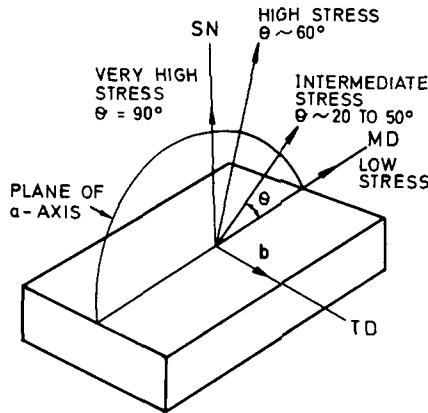


Fig. 6. Representation of the a -axis orientation in the MD-SN plane as a function of stress during the film blowing process.

SN/TD plane about the SN/MD plane. Similarly, the b direction shown is the mean of a symmetrical distribution. As has already been noted² the spread of the a - and b -axis distribution in the SN/TD plane is larger for high-stress orientation than for the low-stress type. Apart from the extreme cases of a - and c -axis orientation along MD the stress level usually encountered in the production of blown films leads to an a -axis inclination of angles between about 20° and 50° to MD. When there is a higher level of stress, such as to give a proportion of the high-stress crystallized material, the a axis is inclined at an angle of at least 60° to MD.

The relatively limited number of results for the Rigidex and Shell polymers fit into this general pattern. Over the range of conditions useful for commercial film production the stress level comes into the intermediate category and low-stress orientation always predominates. The one film made with a low-melt temperature fits into the high-stress category and it would no doubt be possible to achieve similar results at marginally higher melt temperatures by using considerably larger draw ratios. The results for the Hostalen films also suggest that at melt temperatures of about 250°C and very low draw ratios significant a -axis orientation will be obtained.

To summarize, the two types of orientational behavior found in blown polyethylene films, resulting from high- and low-stress crystallization, occur in varying proportions with the balance determined by the particular polymer used and by the four blowing parameters, melt temperature, blowup ratio, draw ratio, and freeze line height. Of these four the draw ratio probably exerts the greatest influence. The factors responsible for the behavior of a particular polymer do not emerge clearly from the present work and it would be necessary to examine a wider range of high-density polyethylenes to establish if the Hostalen material is atypical in giving a significant proportion of high stress orientation. The role of the additive calcium stearate in influencing the balance between the two types of orientation is also not well understood at present.

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