X-Ray Diffraction Orientation Studies on Blown Polyethylene Films. II. Measurements on Films from a Commercial Blowing Unit

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Synopsis

X-Ray diffraction pole figure measurements have been made on a series of films, blown under various conditions from three high-density polyethylenes. The results are interpreted in terms of two distinct types of orientation. The first, and probably the more normal, is the result of the type of stress crystallization process described by Keller and Machin and has the *a* and *c* axes inclined at an angle to the plane of the film. The second type of orientation is crystallographically analogous to that found in cold drawn polyethylene in having the *c*-axis distribution substantially along the machine direction. This is termed high-stress orientation. The type of orientation obtained is dependent both on the blowing conditions and the particular polyethylene. With an experimental Rigidex grade and with Shell LPPE 040 there are always substantial amounts of the conventional low-stress orientation although certain combinations of machine conditions predispose towards the high-stress form. This latter type forms readily in the case of Hostalen GM 9955F over a rather wide range of machine conditions and appears to be favored by slower cooling conditions.

INTRODUCTION

In the preceding paper[1] the results of x-ray diffraction orientation measurements on six blown polyethylene films were reported. Five of these were prepared on a Brabender experimental film blowing unit and although an essentially qualitative interpretation was placed on the pole figures it proved possible to account for the tear strengths in the machine and transverse directions in terms of a combination of generally accepted crystallization processes. The typical orientational behavior, with the *a* and *c* axes at 90° and at an angle to the plane of the film, was shown to be the result of a composite process involving several types of stress during the blowing operation and a partial relaxation arising at one or possibly two stages of the process. The balance between these opposing influences is clearly determined by the precise blowing conditions. In practice, the various effects determining the final state of orientation should not be regarded as occurring independently, although it may be convenient to visualize them as doing so in order to follow the crystallization and orientation processes.

The greater the concentration of *c* axes inclined towards the machine direction (MD), the greater the tear strength should be along the transverse direction, and the results from the pole figure interpretations correlated with the measured tear strengths. There was some evidence that transcrystallization in the surface layers of the films may lead to a better balance of tear strengths in the machine and transverse directions (TD).

The sixth film considered in the preceding paper was blown on a commercial

Journal of Applied Polymer Science, Vol. 22, 2739–2749 (1978)

0021-8995/78/0022-2739 $01.00

Demag unit and showed a higher degree of overall orientation; hence, a more detailed interpretation of the pole figures, in terms of the overall directions and distributions of the *a*, *b*, and *c* axes, was possible. It is clearly of value to examine a series of Demag films, using a range of high-density polyethylenes and a variety of blowing conditions, because previous workers[2,3] have not done so. The present paper reports the results of such measurements.

EXPERIMENTAL

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: Hostalen GM 9955F with a melt index of 7.5, Shell LPPE 040 having a melt index of 7.9, and an experimental Rigidex grade whose melt index is 12–13. The three melt indices were measured by 1SO method R1113 procedure 7. One series of measurements was made on films blown only from the Hostalen polymer and the relevant preparational details are given in Table I. A more extended study was undertaken on a total of 16 films, blown under a variety of conditions, from the three polymers. The details are collected in Table II. One percent of calcium stearate was added to the Hostalen polymer, in each case, to improve the surface finish of the films. The values for the quotient of freeze-line height and draw ratio may be compared among films in the groups 1–4, 5–8, 9–14 and 15–16 as the same extruder screwspeed was used for the films in a particular group. The values are not absolute and are not comparable between groups; however, they do provide a useful measure of the relative cooling rates for the films in a given group.

The pole figures were measured by the method already described.[1] The (200) pole figure proved most useful for identifying the type of orientation present and in order to simplify its measurement and to locate accurately the maximum in the sheet normal (SN)-MD plane direct measurements were made of the (200) pole density along this plane. These measurements were made by using the Schulz texture goniometer in the transmission mode but with the samples mounted for the reflection mode. The samples were positioned so that diffraction data were obtained for the SN-MD plane. The sample traversed from the diffraction normal to MD to the corresponding direction for SN in 4 min. The diffraction data were corrected for the fall off in intensity at the edge of the pole figure (along MD), the result of the incident beam impinging on the sample at a glancing angle at this stage of the measurement. A correction was also applied for the effect of background scattering and scattering from amorphous regions of the polymer samples.

TABLE I
Preparational Details for Five Films Blown from Hostalen GM 9955F

Film No.	Melt temperature °C	Blowup ratio	Draw ratio	Freeze-line height (cm)	$\frac{\text{Freeze-line height}}{\text{Draw ratio}}$
1	200	6.2	5.8	56.5	9.8
2	200	3.2	12.1	56.5	4.7
3	200	2.8	13.7	14	1.0
4	200	6.3	5.9	34	5.8
5	200	3.1	13.3	34	2.6

TABLE II
Preparational Details for 16 Films Blown from Three Different High-Density Polyethylenes

Film No.	Polymer	Melt temperature (°C)	Blowup ratio	Draw ratio	Freeze-line height (cm)	Freeze-line height / Draw ratio
1	Experimental Rigidex grade	207	2.1	10.9	30.5	2.8
2	Experimental Rigidex grade	206	5.0	6.4	30.5	4.7
3	Experimental Rigidex grade	207	5.2	6.0	68.5	11.5
4	Experimental Rigidex grade	207	1.9	10.7	68.5	6.4
5	Shell LPPE 040	202	2.2	10.5	30.5	2.9
6	Shell LPPE 040	203	4.8	5.5	30.5	5.5
7	Shell LPPE 040	205	4.9	4.4	68.5	15.5
8	Shell LPPE 040	204	2.0	8.9	68.5	7.7
9	Hostalen GM 9955F	238	5.2	5.1	30.5	6.0
10	Hostalen GM 9955F	237	5.0	5.3	38	7.2
11	Hostalen GM 9955F	236	5.2	5.2	46	8.9
12	Hostalen GM 9955F	236	5.4	6.0	53.5	8.9
13	Hostalen GM 9955F	237	5.3	5.1	61	12.0
14	Hostalen GM 9955F	236	5.1	5.3	68.5	13.0
15	Hostalen GM 9955F	235	2.0	11.6	68.5	5.9
16	Hostalen GM 9955F	235	1.9	13.7	30.5	2.2

RESULTS

Pole figures were obtained for the (200), (110), and (011) planes for the five films detailed in Table I. Those for films, 1, 2, and 4 proved to be substantially similar and the results for film 1 are shown as Figure 1. Likewise, those for films 3 and 5 do not differ greatly and the former are shown as Figure 2.

It is clear that two quite different types of orientation are present. The first has the (200) pole maxima inclined at an angle to the machine direction in the SN-MD plane. Films 3 and 5 show this type of behavior. The second type of orientation is characterized by having the (200) pole maximum along the sheet normal, with some elongation in the transverse direction. It is found with films 1, 2, and 4.

The type of orientation encountered in films 3 and 5, essentially similar to that of the five films from the Brabender experimental unit described previously,[1] is that of Keller and Machin,[4] who have accounted for it in terms of a stress crystallization mechanism. The second type of orientation is analogous to that obtained in cold drawn polyethylene[5,6] under conditions where necking occurs. Because much higher stresses occur during the necking process the term high-stress crystallization will be used to describe the process occurring during the preparation of films 1, 2, and 4. It is then convenient to use the term low-stress crystallization to cover the conditions associated with the production of films 3 and 5. The small differences between the pole figures of these two latter films can be accounted for in terms of the presence of some high-stress orientation in a predominantly low-stress material. The two types of pole figures and the disposition of the *a, b,* and *c* axes with respect to the machine and transverse directions for the two types of orientation are shown schematically in Figure 3.

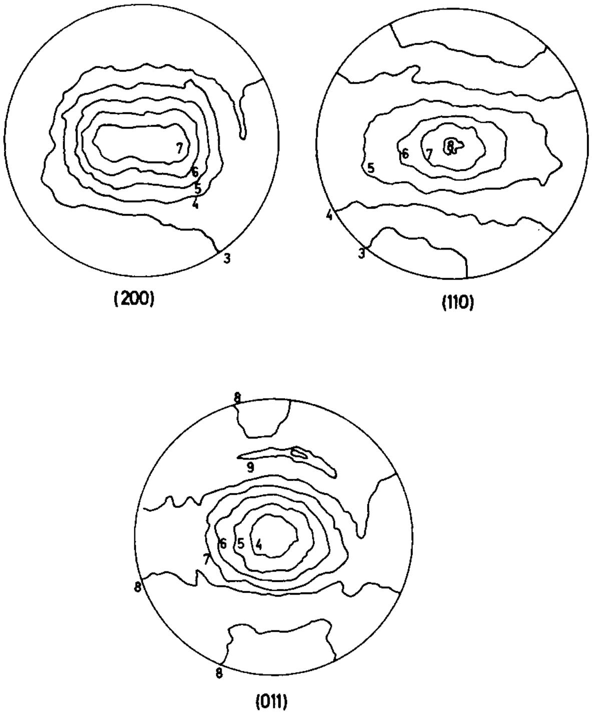
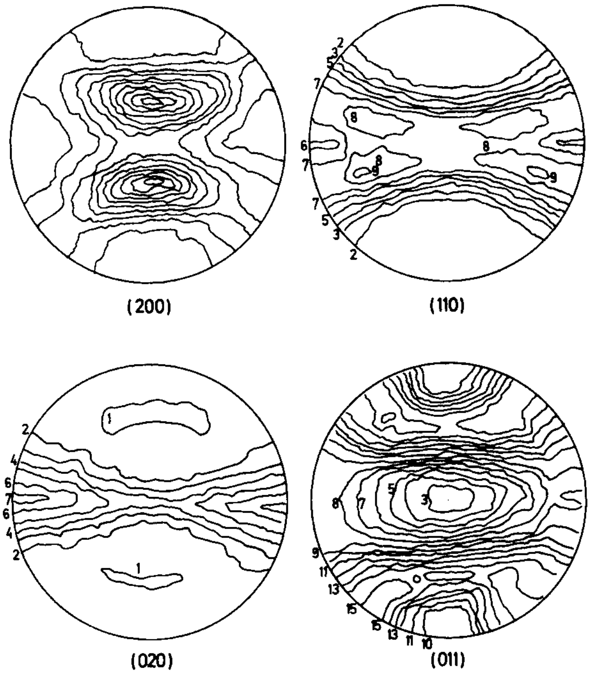


Fig. 1. (200), (110), and (011) pole figures for film 1 blown from Hostalen GM 9955F.

Reference to Table I suggests that the occurrence of high-stress crystallization with films 1, 2, and 4 is to be associated with a particular combination of blowing conditions. These three have the largest values for the quotient of freeze line height and draw ratio, that is, they were prepared under relatively slow cooling conditions. This surmise is further supported by a comparison of the results for films 3, 5, and 2, which have similar blowup and draw ratios but have decreasing cooling rates in that order. Of these only film 2 has the high-stress type of orientation. It is not possible to draw any firm conclusions from these limited results but the occurrence of high stress and hence necking orientation under slow cooling conditions seems reasonable. It might also be expected to occur for larger blowup and draw ratios. These points will be considered in more detail in the subsequent discussion.

Although the two types of orientational behavior have been clearly established the conditions under which they occur cannot be defined with any degree of certainty from the results for the five Hostalen films. The measurements on the 16 additional films were therefore undertaken to obtain further information on this point. It has proved convenient and simple to display the results of the pole figure measurements in terms of an intensity profile along the MD-SN plane of the (200) pole figure. Films having high-stress orientation give maxima about the SN direction but those with low-stress orientation give maxima at about 45° between SN and MD. Films 14 and 5 provide good examples of the two types; their pole figures and intensity profiles are shown in Figures 4 and 5, respectively.

Other types of profiles, basically intermediate between those for low- and high-stress orientation, may be obtained for at least three reasons. The presence



(200) (110)

(020) (011)

Fig. 2. (200), (110), (020), and (011) pole figures for film 3 blown from Hostalen GM 9955F.

of a mixture of the two types of orientation will give a profile of intermediate type, the shape depending on the relative proportions. If there is some low-stress material in a predominantly high-stress sample there will be an inflection or even a subsidiary maximum between SN and MD, whereas a small proportion of high-stress material in the low-stress form will give an asymmetrical profile with the intensity falling away less rapidly on the SN side of the maximum than on the MD side. If there is unoriented material present it will contribute uniformly at all points along the SN/MD direction and the peak will be displaced in a positive direction along the intensity axis. This should be evident near SN and MD, as the tails of the peak will not approach the horizontal axis. Finally, transcrystalline material will give a profile in which the intensity values are low near SN but increase more and more rapidly as MD is approached. Consequently, the presence of some transcrystalline material will lead to an asymmetrical profile, but in the opposite sense to that for a proportion of high-stress material in the low-stress form.

Intensity profiles have been obtained for the 16 films. Those for films 1, 3, 7, 9, 11, 15, and 16, in addition to 5 and 14 already mentioned, have been selected as representative of the range of orientations encountered and are shown in Figures 6 and 7. Although there are substantial differences between the extremes the intermediate differences are less marked and it is necessary to establish what semiquantitative significance may be attached to a particular measurement. Four specimens cut from film 2, which has low-stress orientation and a profile similar to that of film 1, were therefore examined. The intensity values at the maxima show a spread of 13%, there is a spread of 2° in the peak position along the SN/MD direction and the peak halfwidths varied by a maximum of 6%. These differences may arise for several reasons. There will be some nonrepro-

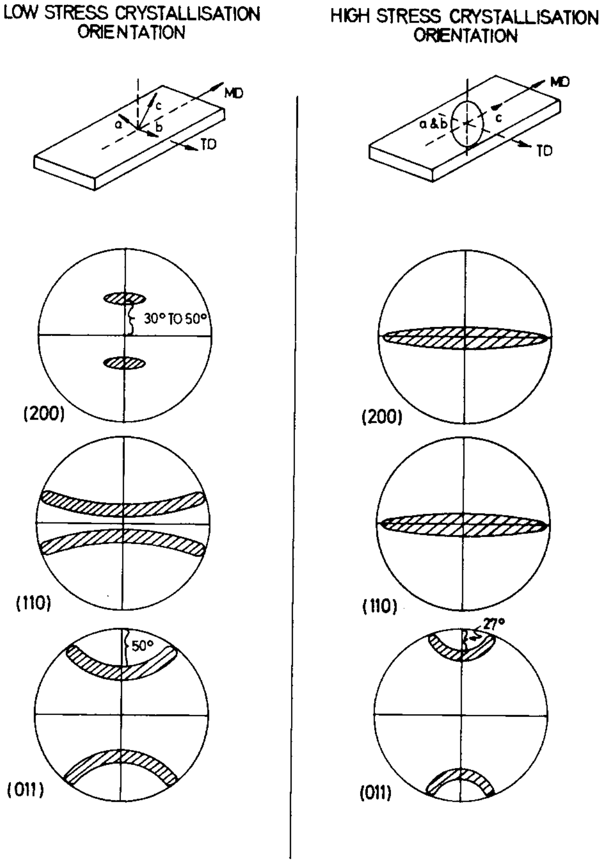


Fig. 3. Arrangement of the crystallographic axes in relation to the machine and transverse directions, and schematic (200), (110), and (011) pole figures for the low- and high-stress crystallization orientations.

ducibility of a purely instrumental nature, occurring in the pole figure measurements. The four samples cut from the film will not be identical because the films were not of completely uniform thickness and may not be absolutely homogeneous with respect to orientational behavior. This would then lead to a slight mixing of different types of profiles, as discussed above. A detailed study would be required to separate the various factors leading to the observed differences in the four films and this has not been attempted and is not warranted. These differences are small by comparison with the range of behavior encountered in the sixteen films and may therefore be ignored.

The films (1–4) from the Rigidex polymer and those from Shell LPPE 040 (films 5–8) all contain large amounts of the low-stress type of orientation. It is also clear from visual inspection that film 3 also contains a significant amount of the high-stress material. Very probably films 1 and 7 contain a lesser proportion. In contrast, films 9–14, from the Hostalen polymer, contain both low- and high-stress types of orientation, the amount of the former decreasing and of the latter increasing throughout the series. As the blowup and draw ratios are substantially constant for these six films it follows that high-stress orientation occurs more readily with the slower cooling conditions. The maintenance of the

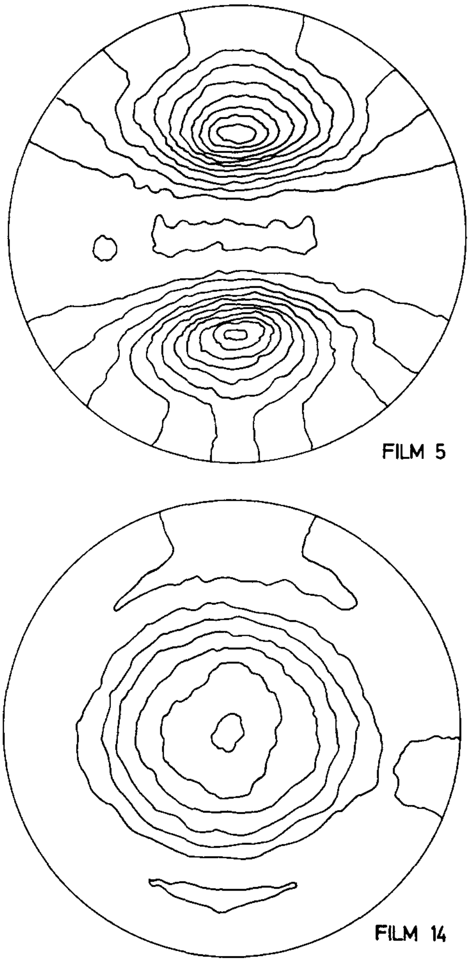


Fig. 4. (200) pole figures for Shell LPPE 040 (film 5) showing a high proportion of low-stress orientation and Hostalen GM 9955F (film 14) with high-stress orientation as the major component.

stress for longer periods of time clearly leads to a greater proportion of high-stress crystallized material. Hence, this type of crystallization process differs from the low-stress behavior where, as previously noted,[1] the slower the cooling rate the greater the reorientation because of relaxation.

The results for film 15 are interesting. Some low-stress crystallized material is present, although the high-stress form still predominates, and the overall shape suggests that there is reasonably good orientation of both types, i.e., the contour lines on the pole figures are relatively close. The blowing conditions of this film differ from those of number 14 in that the blow up ratio is considerably smaller but the draw ratio is greater. Hence, although the two have the same freeze line heights film 15 is subjected to the faster rate of cooling. The formation of some low-stress crystallized material is therefore not surprising. Film 16 was prepared under conditions where, because of the low freeze-line height and the large draw ratio, the rate of cooling is relatively high. The fact that it contains largely low-stress crystallized material is, therefore, in line with the conclusions drawn from the measurements on the other Hostalen films.

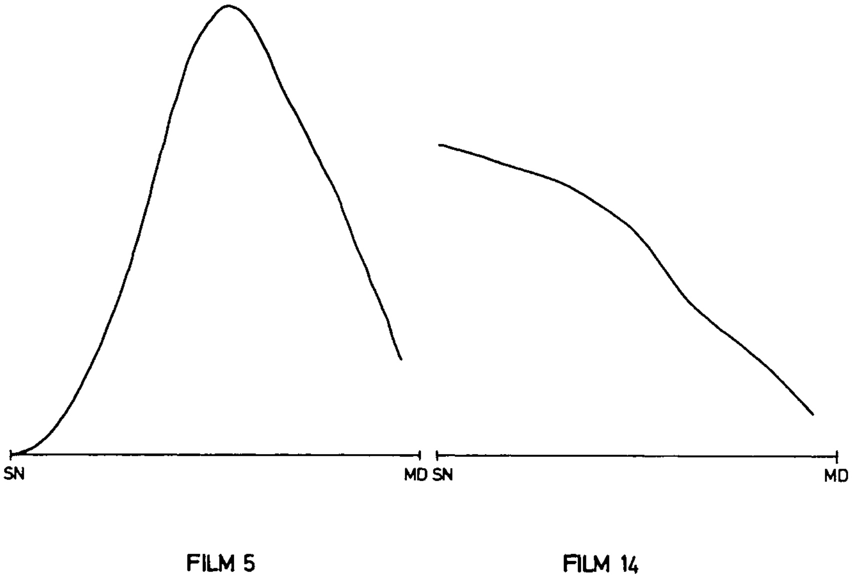


Fig. 5. Intensity profiles across the (200) pole figures in the MD-SN plane for Shell LPPE 040, film 5 and Hostalen GM 9955F, film 14.

DISCUSSION

The presence of two types of orientation in blown polyethylene films has been clearly established. It has also been shown that the proportions in which they are present in a particular film is determined both by the type of high-density polyethylene used and the film blowing conditions employed, notably the cooling rate. It would doubtless be possible to determine the optimum conditions for maximising the concentrations of the two types using empirical studies on a wide range of films but it should be possible to gain a good insight by considering the fundamental processes occurring with the two types of orientation.

The low-stress crystallization process of Keller and Machin[4] will occur when the stress during blowing is relatively low; the rate of cooling is probably not critical. The stress during blowing is the combined result of several factors determined by the blowing conditions and, logically, the rheology of the polymer. The lower the chain mobility the greater should be the stress. For a given polymer this chain mobility, of which the elongation viscosity is a measure, will decease with decreasing melt temperature and this should favor the high-stress type of crystallization. By this line of reasoning, for a given extrusion temperature, the polymer with the lowest degree of chain mobility will show the greatest propensity towards high stress crystallization. The results seem to indicate that Hostalen GM 9955F is this polymer. There should be a temperature range for a particular polymer over which the transition from one type of orientation to the other occurs, given that wholly abnormal blowing conditions are not used.

Within this temperature range the processing conditions also determine the proportions of the two types of orientation. Temperatures in the range 200°–210°C are clearly too high to give much high-stress crystallization with the Rigidex and Shell polymers, even with favorable blowing factors. On the other hand the balance between temperature and blowing conditions around 235°C is ideal for observing the effect of the latter with the Hostalen polymer.

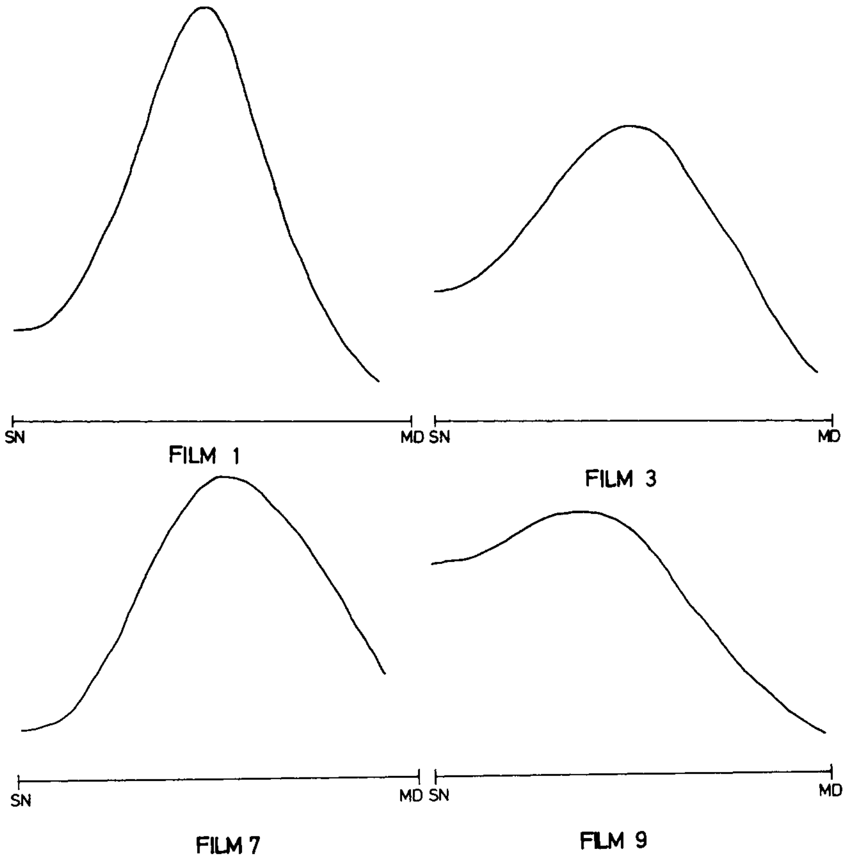
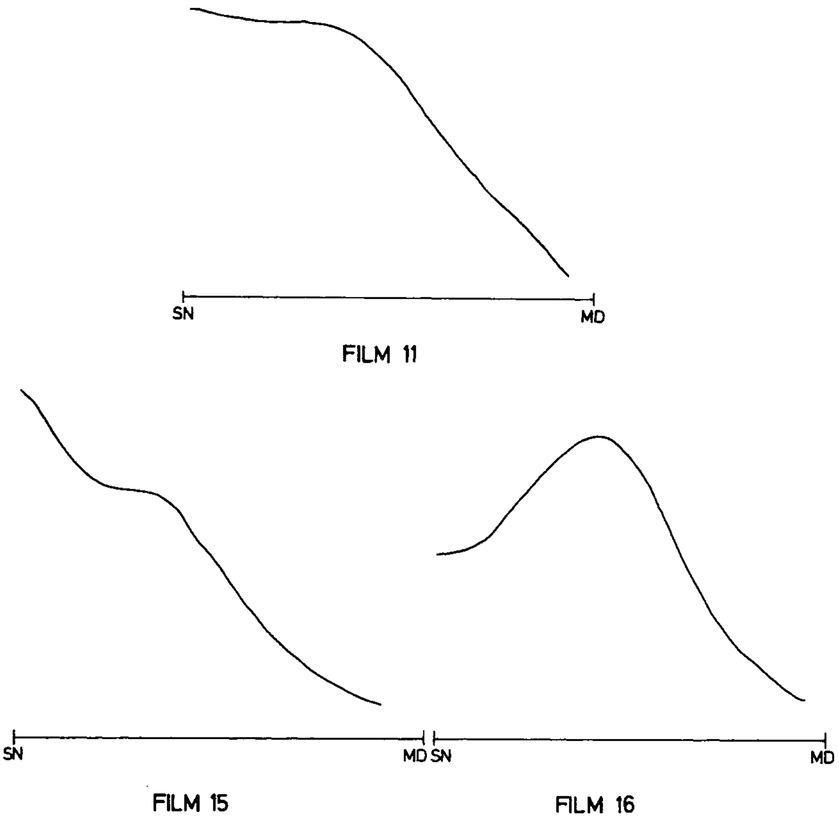


Fig. 6. Intensity profiles across the (200) pole figures in the MD-SN plane for the experimental Rigidex polymer, films 1 and 3, Shell LPPE 040, film 7 and Hostalen GM 9955F, film 9.

An attempt to understand on rheological ground why the high-stress type of orientation occurs relatively readily with the Hostalen polymer has merely served to emphasize the complexity of the problem. Two approaches have been made, in terms of the shear viscosities and elongational viscosities of the Hostalen, Shell, and Rigidex polymers. The shear viscosities are related to the elongation viscosities, although with a pseudoplastic liquid such as a polyethylene melt it may not be quite the simple way suggested by theory. The measured shear viscosities at 190°C for the three polymers show that at rates of shear greater than 10 sec^{-1} the values for the Hostalen polymer are significantly greater than for the other two, and the difference increases with increasing shear rate. At a value of 100 sec^{-1} it is approximately 40%. On the other hand values for the three elongational viscosities, measured by Göttfert Feinwerk Technik Gmbh, show the Hostalen and Rigidex materials to be very similar with the Shell polymer having a value some 30% greater. There is, therefore, no obvious explanation from this evidence for the high-stress crystallization behavior of the Hostalen polymer.

One other possible explanation is in terms of differences in the nucleation and crystallization process. The work of Keller and Machin[4] indicates that the initial step occurs via very high molecular weight material and it is therefore relevant to compare the polymers from this viewpoint. Molecular weight distributions,



FILM 11

FILM 15

FILM 16

Fig. 7. Intensity profiles across the (200) pole figures in the MD-SN plane for hostalen GM 9955F, films 11, 15, and 16.

measured by gel permeation chromatography, showed the Rigidex and Hostalen polymers to be essentially similar in that they have almost symmetrical distributions, but with no significant high molecular weight tail. On the other hand, this feature was very much in evidence with Shell LPPE 040. There is at present, therefore, no explanation for the unusual high-stress crystallization behavior of Hostalen GM 9955F. On the other hand it does seem reasonable to associate the very low-stress orientational behavior of low-density polyethylene during film blowing, manifest in the a-axis type of orientation observed by Holmes et al.,[7,8] with its rheological properties.

The high-stress type of polymer offers scope for a more detailed study of the relative influence of the major processing parameters; the melt temperature, the blowing conditions and the cooling rate, assessed in terms of the quotient of the freeze-line height and the draw ratio. In principle, the examination of a series of films, prepared under conditions in which each parameter is varied systematically with the remaining ones held constant, should provide the results from which the individual effects of all the variables may be deduced.

The authors are indebted to J. L. Shoosmith for considerable assistance with the experimental work, to D. K. Howell, Dr. M. Hulatt, and J. M. Cann of the Technical Service and Applications Division, BP Chemicals Ltd. for supplying the various films examined and for helpful discussions, to Dr. A. J. MacArthur and Dr. G. W. Downs of the Research and Development Department, BP

Chemicals Ltd. for the shear viscosity and molecular weight distribution measurements and to Göttfert Feinwerk Technik Gmbh for supplying the elongational viscosity values. Permission to publish this paper has been given by The British Petroleum Company Ltd.

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Received April 7, 1977
Revised June 2, 1977