

X-Ray Diffraction Orientation Studies on Blown Polyethylene Films. I. Preliminary Measurements

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Synopsis

X-Ray diffraction pole figure measurements have been made on six films blown from high-density polyethylene. Five were prepared on an experimental unit; the sixth, blown on commercial equipment, had a higher degree of overall orientation thus enabling more extensive results for the a -, b -, and c -axis distributions to be obtained. The results provide information on the orientation present, how it may be related to the stress crystallization process of Keller and Machin, and the dependence of the tear strengths in the machine and transverse directions on the orientation. The typical behavior, with the a and c axes at 90° and both at an angle to the plane of the film, is 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 predicted relative tear strengths, obtained from the concentration of c axes inclined towards the machine direction, are in line with the experimental values. There is some evidence that transcrystallization in the surface layers of the films may lead to a better balance of the tear strengths in the machine and transverse directions.

INTRODUCTION

Although the blown film process is now widely used for the production of thin thermoplastic films from materials such as polyethylene, poly(vinyl chloride), and poly(vinylidene chloride), the fundamental aspects of the process have not been studied in detail. Pearson¹ and Pearson and Petrie^{2,3} attempted to determine the factors relevant to the blowing process, from a theoretical viewpoint, and very recently Han and Park⁴ have considered the effect of elongational viscosity, deformation, heat transfer, and bubble instability. Rather more attention has been paid to some specific properties of blown films, particularly from polyethylene; and several workers have considered the orientation processes that occur during film blowing.

An outline of the film blowing process will prove useful for summarizing this previous work. The molten polymer is extruded through an annular die and the molten tube or parison leaving the die is drawn upwards by a take-off device. Air is introduced at the bottom of the die, thus inflating the tube and forming a bubble. An air ring is used to cool the hot bubble and solidify it at a point above the die exit. The inflated solidified bubble is flattened as it passes through nip rollers, which also serve to provide the axial tension to draw the film upwards and to form an air-tight seal, so that a constant slightly positive pressure is maintained in the bubble.

There are several variables in the blowing process, they include: (1) the temperature of the melt leaving the extruder; (2) the draw ratio, the amount by which the parison is stretched in the extrusion direction, and defined as the ratio

of the film velocity at the freeze line to the mean velocity in the die, calculable from the geometry of the die and the geometry and density of the film; (3) the blowup ratio, defined as the ratio of the film-tube diameter at the freeze line to the die diameter; and (4) the freeze-line height, often used as a measure of the cooling conditions, which is the distance between the extruder exit and the freeze line, the point at which the molten film crystallizes. Although it is usual to hold the melt temperature within a limited range more latitude is permissible in the case of the other three factors which, as should be noted, are to some extent interdependent in practice.

Three methods are in common use for the detection and characterization of orientation in polymers. They are polarized infrared absorption, birefringence, and X-ray diffraction; of these the third is the most useful in the case of reasonably crystalline materials such as polyethylene. The examination of hot extruded low-density polyethylene films by Holmes et al.,⁵ using a flat plate X-Ray camera, stimulated the more detailed studies of subsequent workers. Holmes et al. concluded that the a axis of the unit cell lies along the extrusion (machine) direction and their findings were supported by the work of Aggarwal, Tilley, and Sweeting,⁶ also using the flat plate technique. It was also concluded that the c axis, the polymer chain direction, tends to orient perpendicular to the extrusion direction.

However, Keller⁷ proposed an alternative type of orientation, termed row orientation, in which the b axis takes up a preferred orientation perpendicular to the machine direction, and the a and c axes are randomly distributed with cylindrical symmetry about the b axis. He pointed out that very careful analysis would be required to distinguish between the two types of behaviour, and that a reasonable degree of orientation would be a prerequisite. This led Holmes and Palmer⁸ to reexamine and extend the work of Holmes et al.⁵ Working with films from low-density polyethylene they concluded that the precise type of orientation obtained is a function of the blowing conditions, although they did not attempt a detailed correlation. In general, it is intermediate in character between a axis and row orientation. They also noted the presence of some unoriented material.

The subsequent work of Lindenmeyer and Lustig⁹ represented a substantial advance in two respects. They pointed out the fundamental limitation of the flat plate camera technique, in that large areas of the sphere of orientation are not sampled. This is particularly so for the most significant directions, the three principal sample axes and the orthogonal planes formed by these axes. They used the method of pole figures to measure the complete distribution of the a and b axes and, in the case of high-density polyethylene, the c -axis distribution. They also showed that the orientation of the c axis cannot, in general, be deduced from measurements of the a and b -axis distributions. The previously held belief that the polymer axis tends to orient perpendicular to the extrusion direction is therefore an inaccurate conclusion drawn from incomplete data. They were able to correlate their results with measured mechanical properties for a series of films prepared over a limited range of blowing conditions.

An alternative approach, the use of mathematical orientation functions to express the results of pole figure measurements, has been developed by Desper¹⁰ who, working with films from high- and low-density polyethylenes, found a range of textures. The orientation functions, which give second-order averages of the c -axis distributions, may be used to test the predictions of particular orientation

models. They also have the advantage that they may be correlated directly with results from birefringence and infrared dichroism measurements.

The purpose of the present work has been twofold. Recent advances in the computer interpretation of pole figure measurements have led to improved results and in the case of highly drawn polyethylene Lewis et al.¹¹ have obtained a resolution of one to two degrees in latitude and longitude. The application of the technique to blown films should therefore give improved specificity. Secondly, previous workers have only covered a limited range of film blowing conditions, and more detailed studies are desirable to assess their influence on the type of orientation obtained, and on possible correlations with mechanical properties such as tear strengths. In this paper we report the results of a series of preliminary measurements on five films from a laboratory blowing unit and one with a higher degree of orientation from a commercial film blowing unit. Subsequent parts relate to measurements on a range of films of the latter type.

EXPERIMENTAL

Five of the films examined were blown on a modified film blowing unit of the type produced as an accessory to Brabender plastographs and Plasti-Corders and their extruders, from an experimental Rigidex-type high-density polyethylene with a melt index of 12–13. The various combinations of blowing conditions were chosen to give films of approximately equal thickness, nominally 25 μm , to facilitate the comparisons of their tear strengths. Values for the tear strengths in directions parallel to the machine and transverse directions were measured by BS 2782 method 308B using an Elmendorf tear tester. This method uses an un-notched specimen and the value obtained, expressed in millinewtons, is a measure of the resistance to tear initiation and propagation. The blowing conditions and the results of tear strength measurements for five films, selected from the larger number examined as being representative of the whole range of observed orientation behavior, are given in Table I. The sixth film was blown from Shell LPPE 040 high-density polyethylene, with a melt index of 7.9, on a full scale Demag HDPE films unit based on a 60 mm extruder. The melt indices of this polymer and the experimental Rigidex material were measured by ISO method R1113, procedure 7.

It should be noted that the values for the draw ratios, freeze line heights, and tear strengths are subject to significant errors. The draw ratio relies on the output rate from the extruder remaining constant, on the linear speed of the haul

TABLE I
Preparational Details and Tear Strengths for the Six Films Examined

Film No.	Blowup ratio	Draw ratio	Freeze line height (cm)	$\frac{\text{Freeze line height}}{\text{Draw ratio}}$	Tear strength mN		
					MD	TD	
Brabender	1	3.9	4.1	15	3.7	270	77
	2	3.9	4.1	2	0.5	193	274
	3	5.2	3.1	15	4.8	248	78
	4	5.2	3.1	16	5.2	322	93
	5	4.7	3.4	9	2.6	295	157
Demag	5	~5	—	—	—	—	

off rolls being exactly as set and on there being no slip between the blown film and the rolls. The uncertainty in the draw ratio will probably amount to $\pm 10\%$. There is some difficulty in holding the freeze line height constant during a particular run and the quoted values are subject to uncertainties of ± 20 mm in the case of films 1, 3, and 4, with smaller errors for films 2 and 5. The nonreproducibility of the tear strength measurements is largely the result of the fact that there is no control over the direction in which the tear runs once it has been started. The values quoted in Table I are the averages of measurements on several specimens and should be precise to $\pm 10\%$. In view of the essentially semiquantitative nature of the x-ray orientation measurements the uncertainties in the tabulated draw ratios, freeze line heights, and tear strengths do not prove a practical limitation.

Films of $25 \mu\text{m}$ thickness do not give measurable diffraction intensities and it is necessary to stack approximately 20 of them to give a total thickness of some $500 \mu\text{m}$. This is conveniently done by drawing a grid on the film and then cutting out disks 2.5 cm in diameter. These disks are aligned by means of the grid lines and are bonded together with a small amount of a water-based glue. The composite so obtained shows only polyethylene diffraction peaks together with a small amount of additional scattering from the adhesive.

The samples were mounted on the standard specimen table of a Schulz texture goniometer. $\text{CuK}\alpha$ radiation was used and measurements were made at 5° pitch spiral for every 360° of rotation. The (110) and (200) poles of the five Brabender films were measured, together with the (020) poles of films 2 and 4, for which sufficient intensity was available. The greater orientation of the Shell LPPE 040 film enabled results to be obtained for the (200), (110), (020), and (011) poles. The pole figures were calculated from the experimental data by the method described previously.^{11,12} A computer program was written to calculate orientation functions^{13,14} from the texture goniometer data.

RESULTS

Calculation of the Degree of *c*-Axis Orientation

The computer program for interpreting the results of pole figure measurements in terms of orientation functions provides information on the parameter $\langle \cos^2\phi hkl, z \rangle$ where hkl is the particular reflecting plane being measured and z is a specific reference direction in the sample being examined.^{13,14} Given that suitable reflecting planes are available, it will be possible to calculate $\langle \cos^2\phi a, z \rangle$ and $\langle \cos^2\phi b, z \rangle$; and then for an orthorhombic system such as polyethylene, $\langle \cos^2\phi c, z \rangle$ may be found from $\langle \cos^2\phi a, z \rangle + \langle \cos^2\phi b, z \rangle + \langle \cos^2\phi c, z \rangle = 1$. Consequently, with accurate diffraction data for only two diffraction planes, e.g., (110) and (200), $\langle \cos^2\phi \rangle$ -type orientation functions for any crystallographic direction, such as the c axis, may be computed. As Desper¹⁰ has pointed out this does not imply that the c -axis distribution is known. What are obtained are certain second-order averages of the c -axis distribution. However, in that it is reasonable to expect that the tear strength of a film will be proportional to the number of chain axes lying in a plane perpendicular to the tearing direction,⁹ it is pertinent to calculate orientation functions of the type $\langle \cos^2\phi c, x \rangle$,

$\langle \cos^2\phi_{c,y} \rangle$, and $\langle \cos^2\phi_{c,z} \rangle$, and attempt to relate them to the measured tear strengths in two convenient directions in the plane of the film.

The machine or extrusion direction (MD) is an obvious reference direction, not least because it is readily established by visual inspection of the film. The directions in the plane at 90° to this, the transverse direction (TD); and the sheet normal (SN) then provides the second and third reference directions. Values for $\langle \cos^2\phi_{c,MD} \rangle$, $\langle \cos^2\phi_{c,TD} \rangle$, and $\langle \cos^2\phi_{c,SN} \rangle$ have been calculated from the experimental results for the five Brabender films and are given in Table II. A comparison of the values in the three columns with the measured tear strengths in the machine and transverse directions (Table I) reveals no correlation. This deduction is not surprising in view of the conclusions of earlier workers that, in general, more than one type of orientation is present. In these circumstances functions of the type $\langle \cos^2\phi_{khl,z} \rangle$ yield far too general an average of the overall orientation to be of value for correlation with measured tear strengths. If sufficient orientation were present to permit a measurement on the (002) reflection, thus giving direct information on the c -axis distribution, the use of orientation functions would probably be fruitful. The one result with the more oriented Demag film suggests that there is a correlation between the $\langle \cos^2\phi \rangle$ orientation functions and the tear strengths but results for a larger number of films of this type are required to substantiate this surmise.

Visual Interpretation of Pole Figures

In view of the failure of the orientation function approach to yield useful information, other than with the one Demag film, a detailed visual interpretation of the pole figures was attempted. The (110) and (200) pole figures for samples 1 and 3 are shown in Figure 1; the (110), (200), and (020) pole figures for sample 2 and those for the (110) and (200) planes of sample 5 in Figure 2; and for all three planes of sample 4 in Figure 3. With these pole figures the MD is the line running vertically north to south, in a geographical sense, and the TD is the east to west equatorial line. The SN direction is the line perpendicular to the plane of the pole figure passing through the center of the pole. In all cases the maxima of the (200) pole figures are situated in the SN-MD plane and are elongated to a certain extent in the transverse direction. The positions of the maxima along the SN-MD plane, measured with a Wulff net, are given in Table III and some degree of dependence on the cooling conditions after blowing is evident. The greater the rate of cooling the closer the maxima are to the sheet normal direction. For example, films 1 and 2, which have the same draw and blowup ratios, but differ in freeze line height, have their maxima at 59° and 46° , respectively, from SN. It is also evident that for similar cooling conditions the higher the draw ratio the closer the maximum becomes to the sheet normal direction.

TABLE II
 c -Axis Orientation Functions for the Five Brabender Films

Film No.	Orientation functions		
	$\cos^2\phi_C$, MD	$\cos^2\phi_C$, TD	$\cos^2\phi_C$, SN
1	0.383	0.366	0.251
2	0.308	0.429	0.262
3	0.292	0.408	0.299
4	0.306	0.395	0.298
5	0.339	0.398	0.262

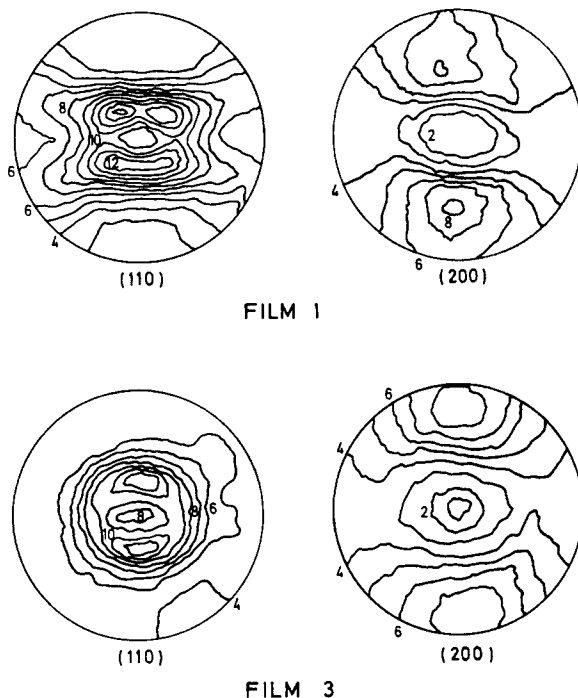


Fig. 1. (110) and (200) pole figures for films 1 and 3. The contours are numbered in order of increasing pole density.

The interpretation of the (110) pole figures is equally interesting. Films 1 and 2, with a high draw ratio, give maxima 20° to 30° along the MD direction and considerably elongated in the TD direction. This effect is enhanced by rapid cooling and is particularly noticeable in the case of film 2. The films of lower draw ratio have a more symmetrical distribution of contours about the MD and TD directions. They are more concentrated with respect to SN as they do not extend to the edge of the pole figures but cover a range of 20° to 30° , in contrast to those of films 1 and 2. More generally, films obtained under more rapid cooling conditions, e.g., film 2, show a higher degree of orientation and this is readily discernible both from the (110) and (200) pole figures.

The (020) pole figure for film 2 shows a well defined maximum in the SN-TD direction plane with the main maxima disposed about TD. Two maxima are observed in the case of film 4. The more pronounced of these is along SN and the weaker one along TD.

(200), (110), (020), and (011) pole figures, superimposed upon Wulff nets for ease of interpretation, for the Shell LPPE040 film, are shown in Figures 4-7. It is obvious that a greater degree of orientation is present than in any of the five Brabender films and this permits a more detailed interpretation in terms of the disposition of the *a*, *b*, and *c* axes with respect to the machine direction, transverse direction, and sheet normal.

Consider first the (020) pole figure, which gives information directly about the unit cell *b* axis, which lies in the growth direction of the folded polymer chain. The maxima are along TD, with a spread of some 40° to 50° towards SN and about 10° towards MD. This result fixes the position of the *b* axis. Figure 8, which is the stereographic projection of the unit cell of polyethylene, shows that

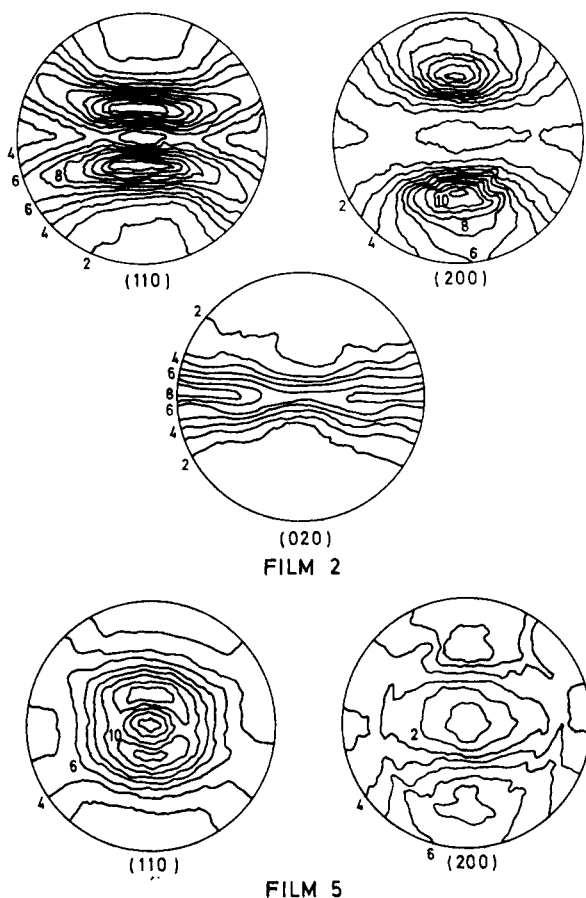
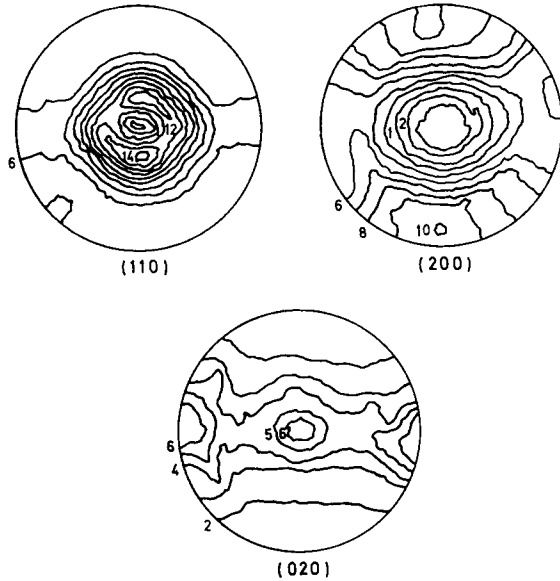


Fig. 2. (110), (200), and (020) pole figures for film 2 and (110) and (200) pole figures for film 5.

the (110) poles lie on a great circle between the (200) a axis and the (020) b axis and make an angle of 33° with the latter. The (110) pole figure (Fig. 5) has maxima on the great circle passing through the transverse direction and making an angle of about 40° with the sheet normal; the maxima lie at about 32° from TD along this great circle. If the (110) pole figure is superimposed upon a Wulff net rotated through 90° the degree of elongation in the SN/TD plane can be established. The combined interpretations of the (020) and (110) pole figures show that the a axis is between SN and MD, making an angle of about 40° with the former. This deduction is confirmed by the (200) pole figure, specific for a -axis orientation, which has maxima at about 38° from SN. The position of the a axis is therefore established unambiguously.

Finally, consider the (011) poles, which lie between the (020) and (002) poles at an angle of 25° with the c axis (Fig. 8). The (011) pole figure (Fig. 7) has maxima lying on the great circle passing through TD at an angle of 50° to SN and about 25° from the SN/MD plane. These maxima elongate in the SN/TD plane. When the results from the (020) and (011) pole figures are combined it establishes that the c -axis maxima lie between MD and SN at about 50° to the latter. Hence, because the a axis has maxima at 50° to SN and the c axis at 50° to SN they are at right angles, as shown in Figure 9. The results of Lindenmeyer and Lustig,⁹ which indicate that the a and c axes are apparently aligned in the



FILM 4

Fig. 3. (110), (200), and (020) pole figures for film 4.

same direction, are presumably a special case arising from the fact that their films were highly unbalanced, with very good tear strengths along TD, very poor ones along MD and TD/MD ratios of 25 to 1 and greater. They should not be regarded as typical of blown polyethylene films.

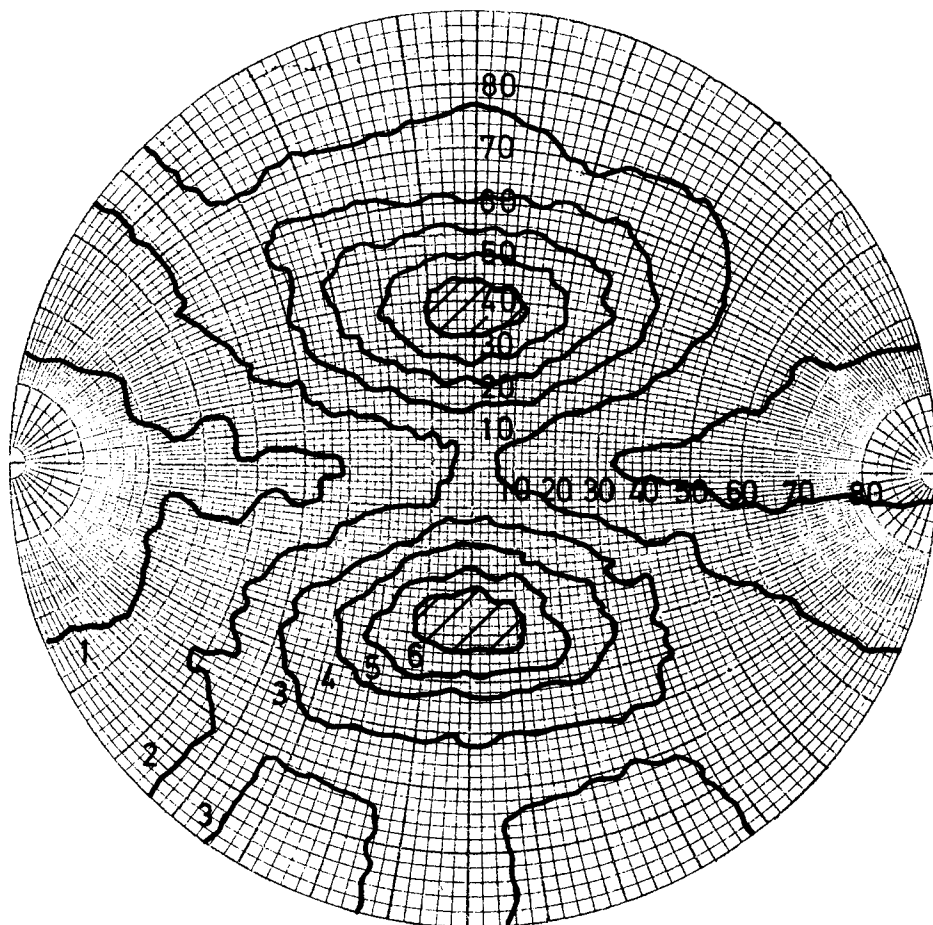
The (020) pole figure shows that there is a spread of $\pm 10^\circ$ in the position of the *b* axis. If a similar spread is assumed in the case of maxima in the other three pole figures it is possible to deduce the *c*-axis distribution. The result, which should be regarded as no more than semiquantitative, is shown as Figure 10.

DISCUSSION

The observed orientation in a particular film represents the net effect of the orientation resulting from stresses at various stages of the blowing process and any reorientation, from relaxation effects, which may occur. During the passage of the melt through the die it will be subject to a shearing stress and there will probably be some orientation along the extrusion direction leading to partial *c*-axis alignment along MD. When the melt leaves the die this shear stress will vanish and the *c* axis may reorientate partially towards SN, with the *a* axis

TABLE III
Positions of the (200) Pole Maxima from the Sheet Normal for the Five Brabender Films

Film No.	Position (deg)
1	59
2	46
3	78
4	80
5	62



(200)

Fig. 4. (200) pole figure, superimposed upon a Wulff net, for a film from Shell LPPE 040 blown on a Demag unit.

moving proportionately towards MD. Further orientation will occur as the result of the stretching in the axial and transverse directions during blowing and the axial tension from the nip rollers will also favor *c*-axis orientation along MD. If there is an additional reorientation it will probably occur during the crystallization stage from the melt. The overall effect, therefore, may be rather complex but, on the basis of this simple model, it does seem likely that slower cooling conditions will favor relaxation and reorientation.

In order to make a more detailed interpretation of the pole figures it is necessary to work in terms of specific models for the crystallization process under stress and for the reorientation processes. This topic has been the subject of considerable study and the widely accepted model is that of Keller and his colleagues, the row orientation process.^{7,15,16} This is based on the results obtained with slightly crosslinked polyethylene, which can be drawn in the molten state. Polyethylene samples usually contain molecules covering a range of molecular weights and the high molecular weight fraction, which has an extended chain form with the *c* axis parallel to the machine direction, still exists in the melt.

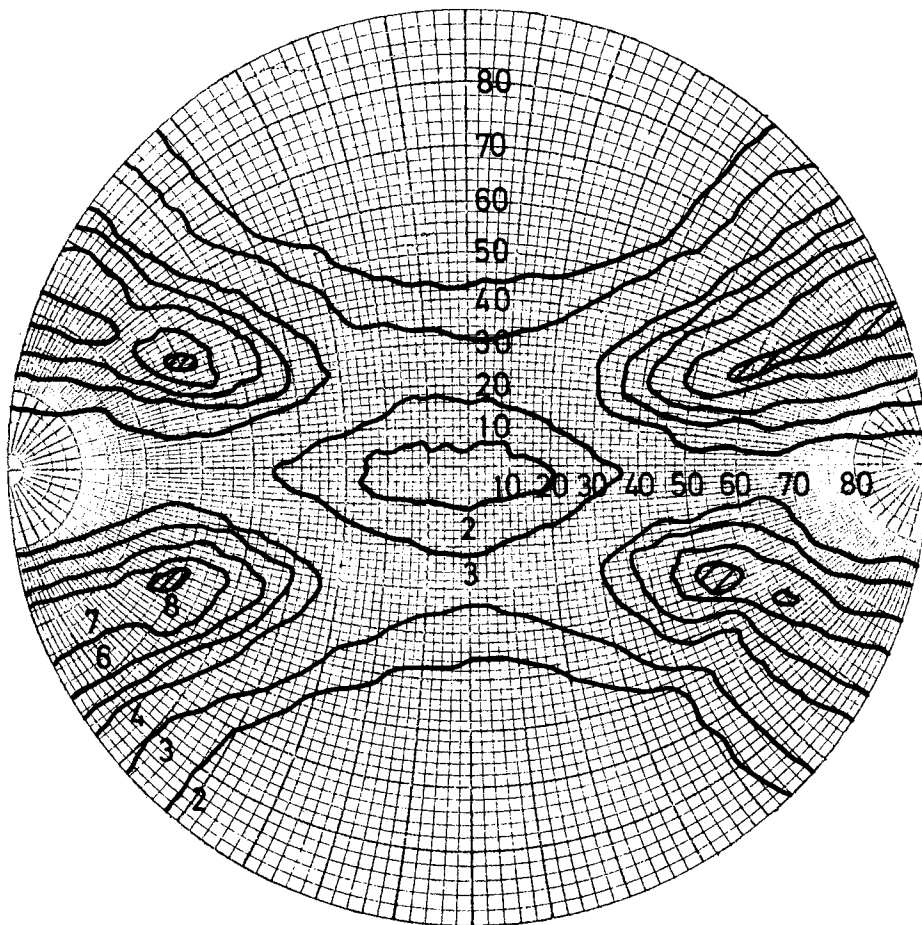


Fig. 5. (110) pole figure, superimposed upon a Wulff net, for film from Shell LPPE 040 blown on a Demag unit.

When cooling occurs these extended chains act as nucleating points for bulk crystallization. As this takes place along the length of the extended chain the new crystallization can only occur radially. This results in the preferential orientation of b , the growth direction, perpendicular to the machine direction. In the case of a thin film this will be along the transverse direction.

This secondary crystallization occurs as the conventional chain folded lamellar growth. Under conditions of low stress the lamellae twist completely, as in normal polyethylene spherulites. The texture is then that of parallel spherulitic discs, with the disc normals aligned parallel to the stress direction. When the stress is high the molecules are aligned along the stress direction; the lamellae are flat and oriented with their normals parallel to the stress direction.

It then follows that under low-stress conditions the a and c axes should be randomly oriented in the MD-SN plane, whereas at high stress, the a axis should lie along SN. However, it is also possible for the a axis to be oriented at an angle to MD, for two reasons. Keller⁷ has observed that non-uniform lamellar twisting can occur with intermediate stress conditions. The turnover is rather abrupt

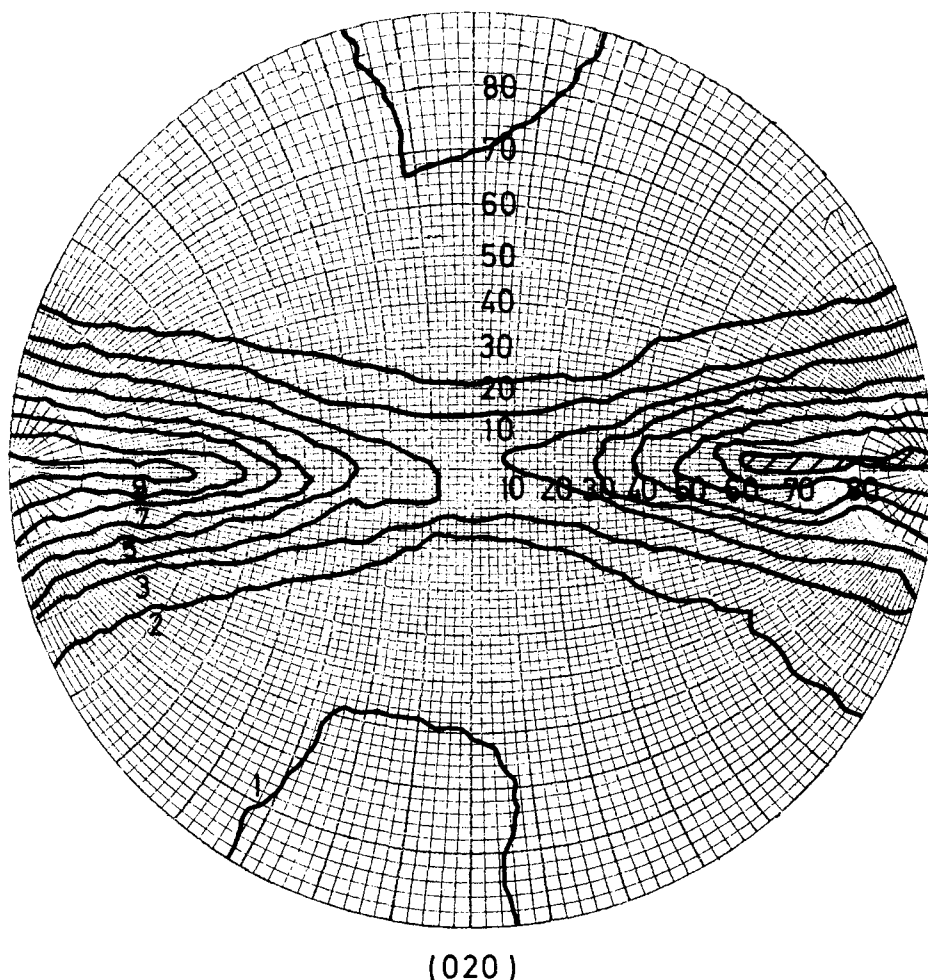
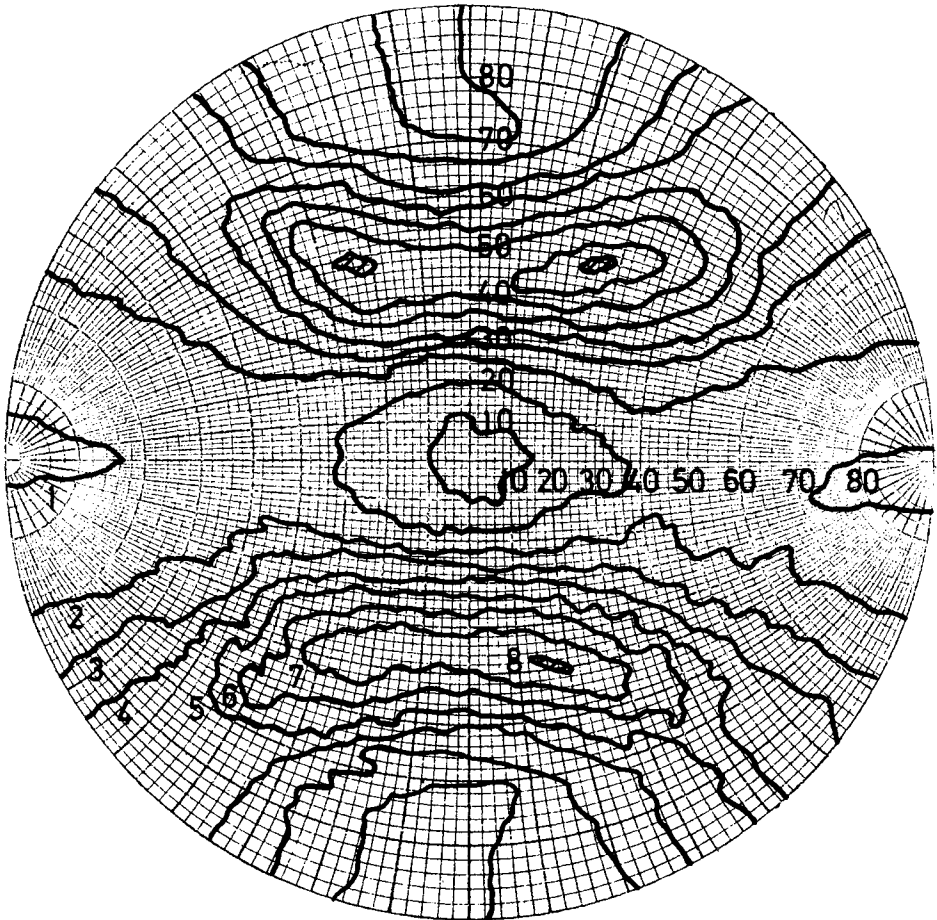


Fig. 6. (020) pole figure, superimposed upon a Wulff net, for a film from Shell LPPE 040 blown on a Demag unit.

and there is a comparatively long distance between twists. There will then be discrete concentrations of a and c axes rather than random distribution. Secondly, these twisted lamellae may undergo interlamellar slip at elevated temperatures, in a manner analogous to that occurring with rolled and annealed polyethylene sheets.

Drawing or rolling polyethylene into sheets leads to a (110) [001] texture.¹¹ Small angle x-ray diffraction studies show that although the c axis is parallel to MD the lamellar surfaces are not perpendicular to this direction but are inclined at approximately 45° .^{17,18} When the sheet is annealed, just below the melting point of the polymer, shrinkage occurs. This causes a rotation of the a and c axes about the transverse b direction, because the compressive forces stored in the extended amorphous chains are released on account of the increased molecular mobility. Because of the relatively large amount of shrinkage these forces act mainly along MD. In practice, the degree of rotation of the a and c axes is dependent on the level of the heat treatment.

It is obviously necessary to exercise caution in applying this relaxation process,



(011)

Fig. 7. (011) pole figure, superimposed upon a Wulff net, for a film from Shell LPPE 040 blown on a Demag unit.

observed by Keller and colleagues, to blown polyethylene films because there are differences in two respects. Although the changes observed by Keller are comparatively rapid,¹⁷ the time scale is still probably slow by comparison with the cooling of blown films just below the solidification temperature. Secondly, the blowing stresses are still present. However, the fact that the process of solidification with blown films is a gradual one probably favors relaxation and reorientation and should compensate for the shorter time scale. The crystallization process will begin with the very high molecular weight material and will proceed over a temperature interval, which may amount to some degrees, until the material of lowest molecular weight has solidified. In these circumstances it is not difficult to visualize the occurrence of some reorientation. As is the case with the relaxation of the shear stress after the melt leaves the die the reorientation will involve the movement of the *c* axis away from MD.

Both reorientation processes will depend upon the cooling conditions as will the overall level of orientation because, for a given polymer, the elongational viscosity at a particular point somewhere between the die exit and the freeze line

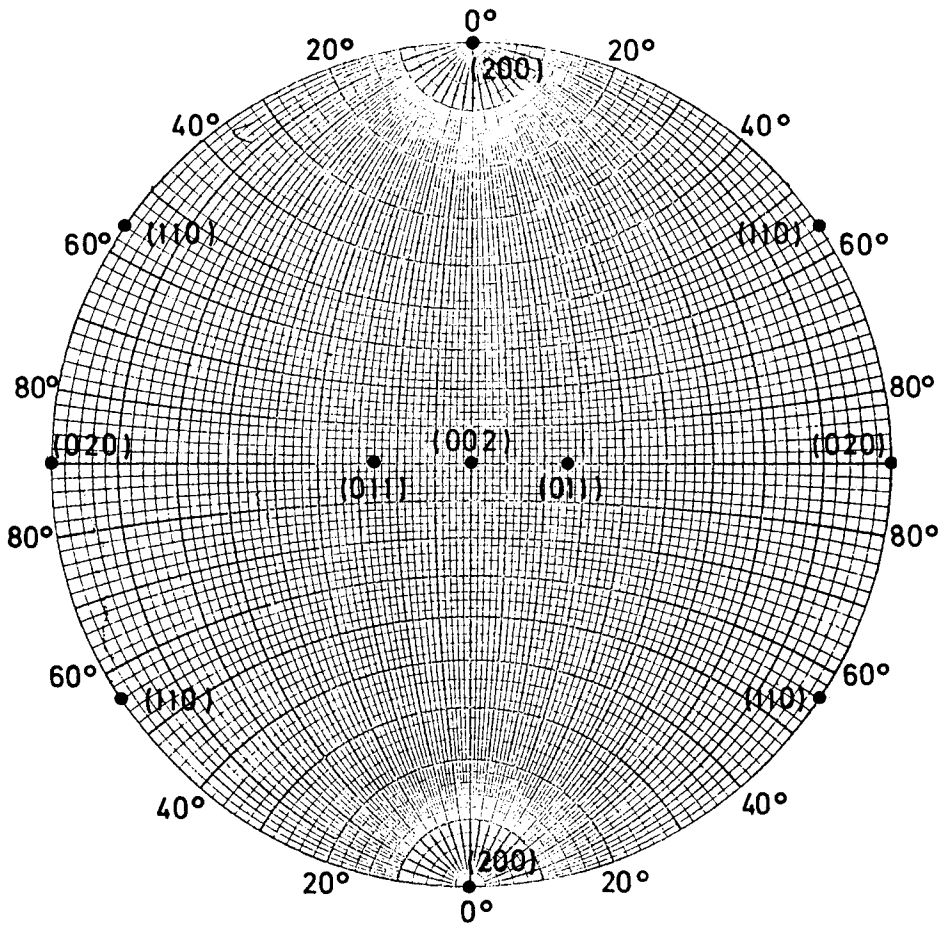


Fig. 8. Stereographic projection of the unit cell of polyethylene.

will depend on the temperature and hence the cooling rate, and as the elongational viscosity increases so will the stress. Keller and co-workers did not define their terms low, intermediate and high stress but it is clear that the conditions of lowest stress will occur during the blowing of films from low-density polyethylene and will favor either pure a -axis orientation or one with the a axis at an angle between SN and MD. This then accounts for the results of Holmes et al. The blowing of high-density polyethylene will lead to higher stress conditions with an increasing tendency towards c -axis orientation.

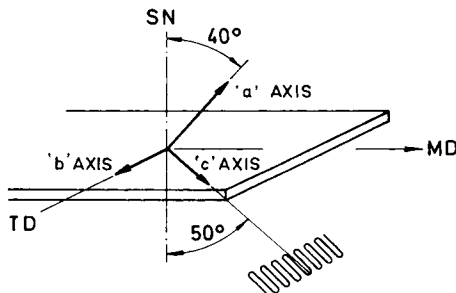


Fig. 9. Placement of the a , b , and c axes of the polyethylene unit cell in a film blown from Shell LPPE 040.

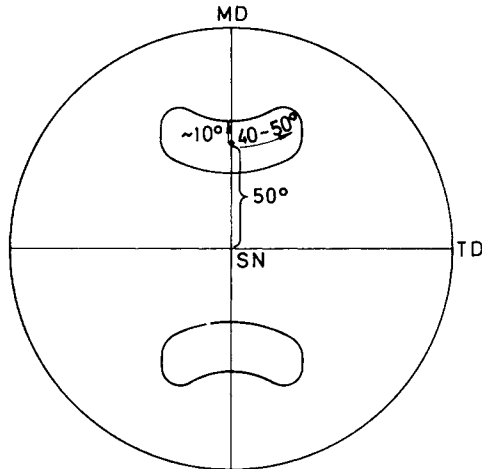


Fig. 10. *c* axis distribution for a film blown from Shell LPPE 040.

It may also be necessary to take into consideration a third factor, the transcrystallization process. This occurs as the result of nucleation at the surface. The resulting crystallites are forced to grow in a direction normal to the film surface and as this growth is in the crystallographic *b* direction there is orientation of the *b* axis towards the film normal. The *a* and *c* axes are randomly disposed in the plane of the film and so the tear strength for the transcrystalline material will be isotropic in this plane. Hence, if a significant proportion of such material is present it will lead to a better balance between the tear strengths along MD and TD.

The work of Eby¹⁹ and of Fitchmun and Newman²⁰ has shown that preferential surface nucleation is favored by a relatively high-temperature gradient between the surface and the center of the film and this, in turn, is best achieved by rapid cooling. For example, Eby examined films which were cooled at various rates and found a threefold variation in the thickness of the transcrystalline layer. Although these studies were made on hot pressed films thicker by an order of magnitude than the blown films now under consideration, it is reasonable to suppose that the formation of transcrystalline material will be governed by the same factors although because of the relative thinness of the blown films a transcrystalline surface layer of a particular thickness will constitute a greater proportion of the total than in the case of the much thicker hot pressed films. Fitchmun and Newman also stressed that to avoid the formation of the conventional spherulitic structure there should be complete melting of the crystal embryos, by taking the temperature well above the melting point. This destruction of conventional nucleating centres may be a function of time as well as of temperature and it is possible to visualise circumstances in which a sample held in the molten state for a relatively long period of time is more likely to give transcrystalline material than one subjected to a short time above the melting range.

By combining the various factors which influence orientation it is possible to formulate a descriptive scheme for the changes that occur during film blowing, although these should not be regarded as discrete independent steps. The first stage is the occurrence of some *c*-axis orientation, as the result of the shear stress to which the melt is subjected in the die, although there may be a partial loss of

this orientation after the melt leaves the die. There will be additional *c*-axis orientation because of the axial component of the blowing stress and also the draw-off tension. Then, in the molten state after drawing and blowing but with the stress still present, the high molecular weight fraction crystallizes in the extended chain form with the *c* axis along MD. Hence, the proportion of high molecular weight material may have a significant effect on the morphology and, probably, the mechanical properties of the film. The final degree of *c*-axis orientation will depend upon the overall level at the time that bulk crystallization commences and the reorientation that occurs during the interval from the crystallization of the highest to the lowest molecular weight components. The higher the axial stress, and this will be partly determined by the overall stress during blowing as this is resolvable into axial and radial components, the greater should be the degree of *c*-axis orientation along MD. In the case of slow cooling there may also be a limited degree of reorientation below the crystallization temperature range by the Keller mechanism. The rate of cooling may also influence the formation of transcrystalline material.

It is possible to interpret the pole figures for the five Brabender films in reasonable detail in terms of these various factors occurring during the blowing process. In so doing it is also convenient to consider more carefully means for assessing the cooling rate because, as noted above, this is one of the relevant factors in determining the amount of stress present and the degree of reorientation as the result of relaxation. Although the freeze-line height has been widely used for this purpose, presumably because it is convenient to measure, it is of limited value. Ideally, the factor used should be the time taken for the material to crystallize. The nearest measure of this that can be obtained from the information available in this work is a "cooling rate" based on the time taken for material to cool from the die to the freeze line. This is only reasonable when the temperature at exit from the die and the throughput are the same. In this paper the quotient of the freeze line height and the draw ratio, which is inversely proportional to this cooling rate, is used. Values for these quotients are given in the fifth column of Table I and it is apparent that the spread of the values is smaller than that of the freeze line heights. Nevertheless, the two criteria give the same results, in that films 1, 3, and 4 have slow cooling rates, film 2 a fast rate with film 5 intermediate and faster than its companion films 3 and 4 blown at the same lower draw ratio.

Consider first films 1 and 2, prepared with the same draw ratio but with slow and fast cooling, respectively. In the former case there should be a greater degree of reorientation and the *a* axis should lie nearer to MD than with fast cooling. This is in line with the results; in fact, the positions reverse in the two cases so that with film 1 the *a* axis lies closer to MD, whereas the reverse is true with film 2. This should lead to a better tear strength along TD in the case of film 2 and this proves to be so. In both cases there is a spread of the *a*- and *c*-axis distribution along TD, indicative of the effect of transverse stress, and this should give a reasonable MD tear strength. This expectation is realized. Film 2 has a better balance of tear strengths than film 1 and this might be taken as an indication for the presence of transcrystalline material. The fact that it also had the faster cooling rate is also in line with this surmise. However, in the absence of direct crystallographic evidence the conclusion can only be very tentative.

With films 3, 4, and 5 there is less overall orientation and a greater spread in the transverse direction, showing that the transverse stress is playing a more

important role. This is as expected in view of the larger blowup ratios used. Film 5 was prepared using comparatively fast cooling conditions and has about the same disposition of the a and c axes as film 2. This again indicates a relatively good TD tear strength. Furthermore, the larger spread of c axes along TD suggests a high MD tear strength and these predictions are confirmed by the experimental results. Films 3 and 4 were prepared using appreciably slower cooling conditions and show the interchange of the a and c axes with respect to SN and MD already noted with film 1, and for the same reason. As with film 1 a low TD tear strength is predicted but the MD tear strength should be high because of the c -axis spread along to TD.

It is difficult to draw any conclusions about the possible presence of transcrystalline material in the case of films 3, 4, and 5 based on a consideration of the tear strengths. The balance is best for film 5 and this is the material prepared with the highest cooling rate. However, film 4 was the only one of the five for which there was sufficient intensity to measure the (020) pole figure and in this case (Fig. 3) a clear maximum centered around SN is in evidence. This suggests the presence of transcrystalline material, although the film was cooled slowly and has a poor balance of tear strengths. There is clearly insufficient evidence from the present limited study to decide if transcrystallinity occurs appreciably, under what conditions it is formed and the extent to which it affects the tear strengths.

The (020) pole figure for the Shell LPPE 040 film (Fig. 6) shows no sign of a maximum about SN and transcrystalline material must be substantially absent. More generally, the detailed interpretation which is possible with this film, because of its greater degree of overall orientation, is wholly in line with the essentially qualitative results from the five Brabender films. Although this one Demag film is not necessarily representative it fits into the general pattern by having the a and c axes inclined at an angle to SN and MD. It has therefore proved possible to account qualitatively for the orientational behavior and the tear strengths of the films studied in terms of a combination of generally accepted crystallization processes. Nevertheless, it is clearly desirable to confirm these deductions by measurements on a wider range of films blown from a number of high-density polyethylenes using a variety of blowing conditions. Furthermore, in view of the higher degree of orientation found in the one film from a commercial blowing unit, leading to pole figures capable of a more quantitative interpretation, it is desirable to concentrate on this type of sample.

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