

Crystallite Orientation in Extruded Polyethylene Film

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Synopsis

The complete orientation distribution of the a and b crystallographic directions have been measured for a series of tubular extruded polyethylene films as a function of blow ratio. The use of pole figures as a means of representing orientation is emphasized and it is shown that the usual technique of using flat plate x-ray diffraction photographs can lead to erroneous conclusions. Increasing the blow ratio has a distinctly different effect upon the orientation of high density polyethylene film in comparison with low density polyethylene film. In contrast with previously published information our results clearly indicate that the c axis does not orient preferentially perpendicular to the extrusion direction. In particular, it is shown that one cannot in general deduce the maximum in the orientation distribution of the c axis from qualitative estimates of the a and b axes distributions. The ultimate tensile strength, elongation, modulus and tear strengths of these films were measured and the results correlated with the orientation of the crystallographic directions.

The orientation of polyethylene films and fibers has been investigated by a number of authors using the methods of x-ray diffraction,¹⁻⁷ polarized infrared dichroism,⁸⁻¹⁰ and birefringence.^{6,10,11} These studies have all attempted to characterize the orientation of the crystallites by some "preferred" or "ideal" arrangement of certain crystallographic axes which is approximated by the actual distribution. For example, there seems to be general agreement^{6,7} that in extruded polyethylene film there is a tendency for the a axis to lie along the machine or extrusion direction. This is sometimes referred to as a relaxed orientation due to its similarity to the orientation assumed by drawn fibers when they are allowed to relax at elevated temperatures.^{2,3} The conclusion has been drawn from these observations that the c axis or polymer axis must tend to orient perpendicular to the machine or extrusion direction. This conclusion is still prevalent in the most recently published work of Aggarwal, et al.,⁷ and elaborate mechanisms have been proposed to account for this peculiar phenomenon.

An alternate orientation called row orientation has been proposed by Keller⁵ in which the b axis takes up a preferred orientation perpendicular to the extrusion direction and the a and c axes are randomly distributed with cylindrical symmetry about the b axis. He shows that such an orientation could be distinguished from a axis orientation only by very careful analysis

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of the x-ray data and only in those few cases where orientation is sufficiently perfect to permit a distinction. Holmes et al.⁶ have re-examined their data and confirmed Keller's interpretation in a few cases but conclude in general that the two cannot be distinguished. Aggarwal et al.⁷ apparently prefer *a* axis orientation over row orientation. All these investigations have assumed cylindrical symmetry about the extrusion directions and both Holmes et al.⁶ and Aggarwal et al.⁷ have attempted to verify that they indeed had such symmetry.

In this paper we report an investigation of the crystallite orientation of extruded polyethylene films in which we have measured the complete distribution of the *a* and *b* axes, and, in the case of high density polyethylene, also the *c* axis distribution. These results are plotted as pole figures for each crystallographic direction. These findings thus provide much more data concerning the actual orientation of crystal axes than has been previously available from flat plate photographs. Furthermore, it can be demonstrated that the orientation of the *c* axis cannot in general be deduced from measurements of the *a* and *b* axes distributions. Thus, the widely held belief that the polymer axis tends to orient perpendicular to the extrusion direction is not indeed an experimental fact but an inaccurate conclusion drawn because of the lack of complete data. Our results are given in terms of an experimentally measured orientation distribution not a "preferred" or "ideal" orientation. It will be shown that such orientation may be readily correlated with measured physical properties of the films.

I. EXPERIMENTAL

A. Materials

The materials used in this study were a high density polyethylene, Marlex 50, made by Phillips Petroleum Co. and a low density polyethylene, DXM-21 made by Union Carbide Plastics Company. These were all tubular extruded films extruded in commercial melt-extrusion equipment with the use of the same die and extruder and with screw speed and machine temperatures constant for each of the two series. The amount of air in the bubble and the take-away speed were adjusted to obtain films that were approximately 1.5 mils in thickness and varied in flat width from 2.5 in. to 13 in. in the case of the high density films and 2.5–15.5 in. for the low density films. The ratio of the flat width to the die diameter, called blow ratio, is generally used in the trade to characterize the amount of transverse stretch and we shall follow this practice. The actual transversed stretch ratio is obtained by multiplying the blow ratio by $2/\pi$.

B. Physical Properties

The physical properties of these films were measured by standard ASTM or TAPPI methods and the results are summarized in Table I. Although the tensile strength and modulus (i.e., stress at 10% elongation) of the high density films is higher than that of the low density films the behavior of

TABLE I

Film	Blow ratio	Tensile strength, psi ^a		Elongation at break, % ^a		Tear strength, g./mil ^b		Stress at 10% elongation, psi ^a	
		MD	TD	MD	TD	MD	TD	MD	TD
DXM-21	1.7:1	4800	1300	150	180	380	90	1630	1010
	3.3:1	3100	2200	240	450	90	80	1130	1030
	6.7:1	2600	2400	300	470	70	160	1050	950
Marlex 50	10.3:1	2300	2700	410	560	150	130	1000	980
	1.7:1	10300	3600	340	20	10	350	4790	3600
	3.3:1	5200	4100	470	20	15	970	3700	4050
	6.7:1	4500	4200	300	30	15	720	3800	4100
	8.7:1	3200	4400	150	40	20	500	2800	4250

^a ASTM Method D 638-58T.^b Elmendorf tear test TAPPI Method #414 without augmented weight.

these properties with increasing blow ratio is qualitatively similar, i.e., the machine direction values decrease and the transverse values increase with increasing blow ratio. On the other hand, the per cent elongation at break and the tear strengths change with blow ratio quite differently for the two different materials.

C. X-Ray Measurements

The x-ray measurements were made using a Norelco x-ray diffractometer, a pole figure goniometer and a flat-plate camera. The usual filtered $\text{CuK}\alpha$ radiation was used. Although the technique for obtaining, correcting and plotting pole figures is described in the literature (ASTM E-81-54T), several points deserve further comment. In order to obtain diffraction from all possible crystal planes it is necessary that the x-ray beam pass through the sample at various angles. This results in a variation in both effective sample volume and the path length. Suitable corrections must be made if the intensities are to be compared. The usual method for correction is to make measurements on a completely unoriented specimen of the material and to convert the observed intensities of the oriented specimen to multiples of the intensity of the random specimen measured at the same angle. In the case of polymer films it is difficult to obtain completely orientation-free samples. We obtained samples with minimum orientation by using a lightly pressed briquette of finely precipitated polymer (a more highly compressed material showed distinct orientation and sometimes even a second crystalline structure).

II. ORIENTATION AND TEXTURE

A. Definitions

Before describing our results it is desirable to discuss the meaning of certain terms that have frequently been used but infrequently defined. In the polymer field, orientation is generally associated with the arrangement of the long axis of the polymer molecule, but it is also misapplied to the process which is most commonly used to produce orientation, namely, the process of stretching. It is understandable to speak of an oriented fiber since one implies by this that the orientation is of the polymer molecule with respect to the fiber axis. However, to speak of an oriented film is almost meaningless, since there is no clear idea of what is being oriented with respect to what.

We shall define orientation as the relationship between some molecular or crystallographic direction (or directions) and the external reference frame of the specimen. Thus, the orientation of the a axis of a particular crystallite in a polymer film could be specified by giving its azimuthal angle (β); with respect to the machine (extrusion) direction and its inclination angle α from the plane of the film. If one wishes to refer to the orientation of all the a axes of all the crystallites in a sample, one has the orientation distribu-

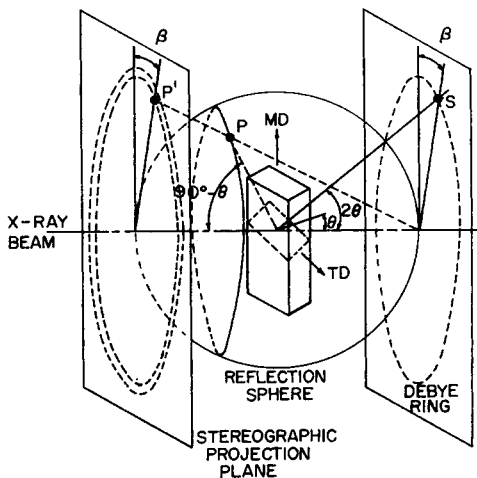


Fig. 1. Illustration of the relationship between the x-ray beam, the Debye ring on a flat-plate photograph, and the pole figure.

tion of the a axes or simply the a axis distribution. The term texture has also been used to refer to the orientation of all of the crystallites in a sample.

B. Representation of Orientation and Texture

A pole figure is the stereographic projection of the normals or "poles" of crystal planes. If only a single crystal is involved several different crystal planes may be shown on a single pole figure. However, to illustrate orientation or texture it is customary to show the poles of only one type of crystal plane on each figure and to indicate pole densities by contour lines. In Figure 1 we illustrate the relationship between the x-ray beam, the Debye ring on a flat-plate photograph, and the pole figure. All crystal planes which can diffract the x-ray beam make an angle θ with the beam and the normals to these planes make an angle of $90^\circ - \theta$ with the beam. Thus, the poles of those crystal planes which diffract as Debye rings in a flat plate photograph are projected into circles on the pole figure. Note that as the Debye ring increases, the corresponding circle (or project of a small circle) representing the locus of the poles decreases (the Debye ring is determined by a cone having a half angle of 2θ whereas the corresponding locus of poles is determined by a cone with the half angle $90^\circ - \theta$).

In considering the pole figures of a film sample it is customary to orient the sample with the machine or extrusion direction in a vertical position and the transverse direction in a horizontal position. It may be necessary to rotate the sample in quite a different way in order actually to record the various diffraction intensities.

C. Advantage of Pole Figures Over Flat-Plate Photographs

In spite of experimental difficulties required to obtain a complete pole figure the advantages become apparent when one compares the amount of

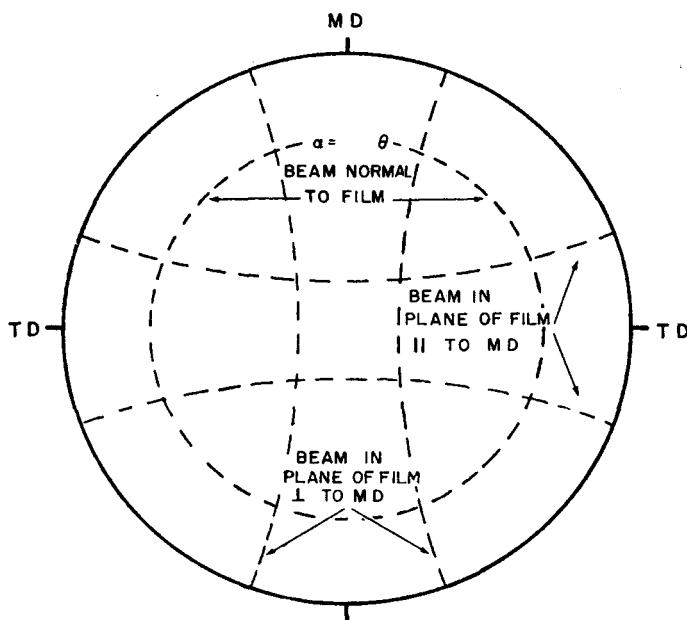


Fig. 2. Illustration of the relationship between the pole figure and the flat-plate photograph. Pole figure of crystal plane with $\theta = 20^\circ$ showing the locus of Debye-Scherrer rings from flat-plate photographs.

information available on such a pole figure with the information which is obtained from the usual flat-plate photograph. In Figure 2 we show an example of the amount of information that is obtained by the usual film technique. Very frequently, the only information taken is a single flat-plate photograph with the x-ray beam normal to the film. For a given crystal plane, this yields information only about those crystal planes whose poles make an angle of θ with respect to the plane of the film. If one does a thorough job he takes two additional photographs with the x-ray beam in the plane of the film, both parallel and perpendicular to the machine direction, and obtains data as indicated by the other two sets of dotted lines in Figure 3. These dotted lines appear to sample reasonably well most of the areas of the pole figure, yet we note that they actually tell us nothing at all about crystal planes whose normals lie in the three principal directions of the film sample (i.e., the machine direction, the transverse direction, and the direction normal to the plane of the film). An example of how completely deceived one could be from these film techniques is shown in Figure 3. This is admittedly a hypothetical pole figure of a crystal plane, but it serves to illustrate a principle. In this example the crystal plane has a preferred orientation in all three of the principal directions of the polymer film. Yet the series of the three flat-plate photographs sample the pole figure in areas where the intensity would differ little from that of a random sample. In other words, if we investigated the orientation of this crystal

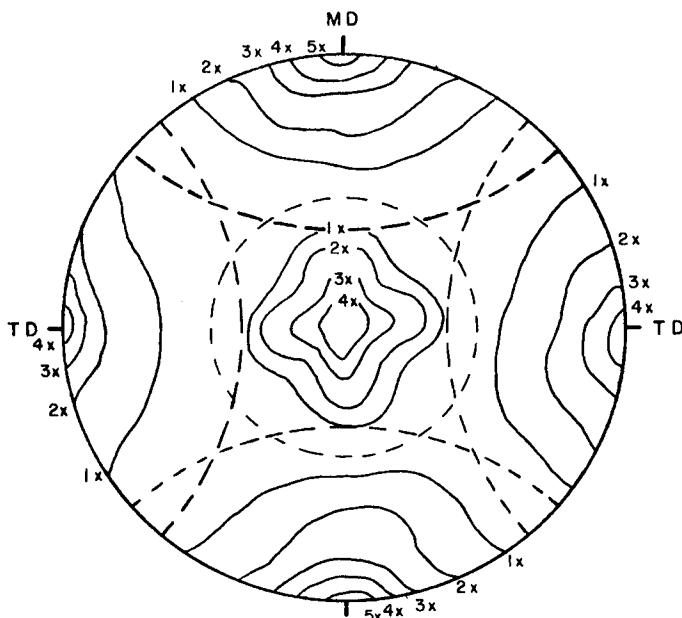


Fig. 3. Hypothetical pole figure with $\theta = 40^\circ$ illustrating how information from the usual flat-plate photographs can fail to show important orientation effects.

plane by the usual film techniques, we would conclude that it was completely random in its orientation.

III. RESULTS AND CONCLUSIONS

Orientation of Extruded Film

The pole figures for the three principal crystallographic directions in tubular extruded Marlex 50 polyethylene film are shown in Figure 4. The blow ratio (1.7:1) is equivalent to essentially zero transverse stretch. In contrast to previously published observations, our results clearly indicate that the orientation of the a axis is in the machine direction but is inclined approximately 45° out of the plane of the film. It is easy to see how earlier observations could have been obtained, since the Debye ring of the (200) plane on a flat-plate photograph would obviously show a maximum in exactly the same place as it would be if the maximum in the a axis distribution were in the machine direction.

The second point which these pole figures make clear is that the b axis orientation is several times stronger than the a axis orientation, a fact which is not at all obvious from flat-plate photographs since the (200) reflection is intrinsically many times more intense than the (020) reflection. Finally the direct measurement of the (002) pole figure shows that the c axis does not orient preferentially perpendicularly to the extrusion direction but has a fairly complicated distribution with maxima at about 45° to

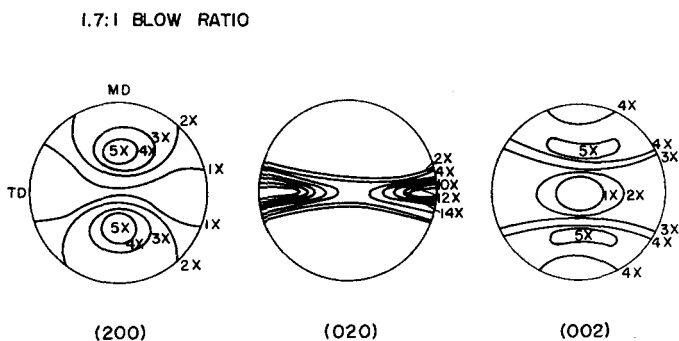


Fig. 4. Pole figures for the three principal crystallographic directions in tubular extruded Marlex 50 polyethylene film. The blow ratio 1.7:1 is equivalent to essentially zero transverse stretching.

the plane of the film in the extrusion direction. The direction normal to the film appears to be the only direction not favored by the c axis.

In Figures 5 and 6 we show the pole figures for the a and b axes of high and low density polyethylene film with various blow ratios. At low blow ratio the orientation of these two materials is essentially the same. However, as the blow ratio is increased, the low density film changes progressively toward a uniaxial texture with the b axis perpendicular to the film and the a axis uniformly dispersed in the plane of the film. Unless there is a strong preferred orientation, the intensity of the (002) reflection, in low density polyethylene film, is too weak to be measured with any accuracy. However, for the high blow ratio film it is safe to assume that the c axis is also uniformly dispersed in the plane of the film. In high density polyethylene film it was not convenient to obtain as high a blow ratio as with the low density film. However, at the highest blow ratio investigated the b axis distribution shows little tendency to change while that of the a axis changes in the same way as in the low density material, but at a much slower rate. In high density film it was possible to measure directly the (002) pole figure, and it can be seen that the c axis changes in much the same way as the a axis.

The tendency of both the a and the b axes to orient in almost exactly the same way is perhaps a little surprising. It may at first seem impossible to have a tendency for both the a and the c axes to orient in the same direction. However, this is exactly what Keller's model of row nucleation would predict. In this model crystallization starts from lines of nuclei in the extrusion direction and growth occurs radially outward in the same manner as in the growth of a spherulite. The direction of radial growth is known to be the b axis, and the a and c axes tend to rotate around this growth direction. If this rotation were completely random there would still exist an overall tendency for a and c axes to have a maximum in the extrusion direction. The fact that the b axis orientation is several times stronger than that of the a and c axes is further support for the row-nucleation model.

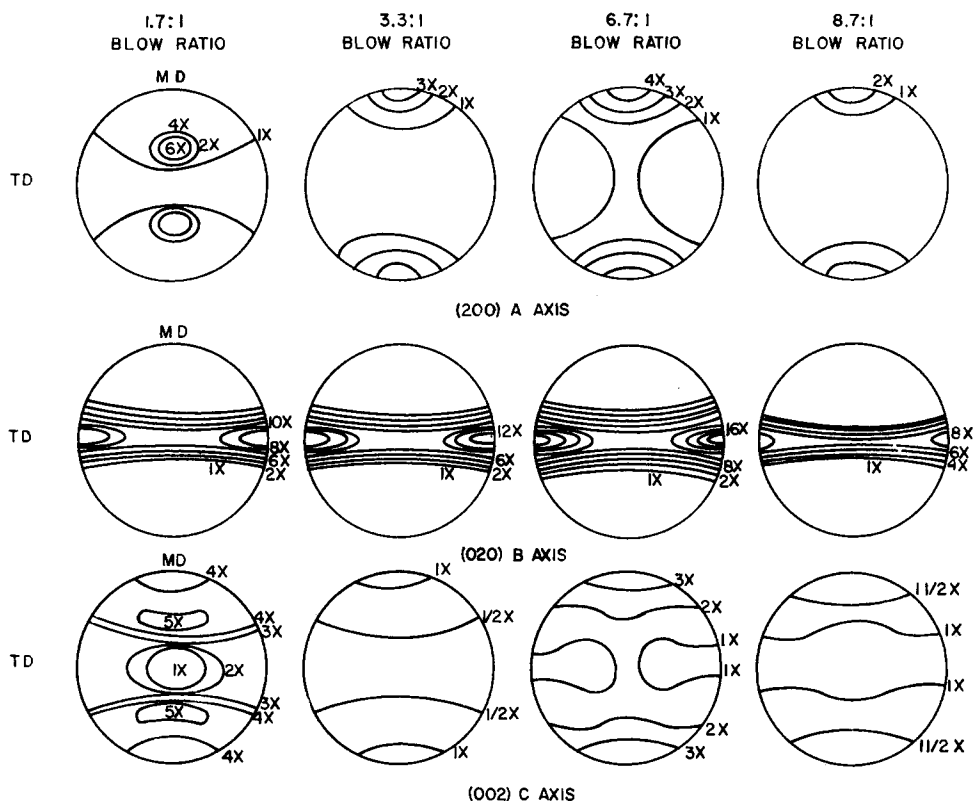


Fig. 5. Pole figure for Marlex 50 polyethylene film as a function of blow ratio.

These observations emphasize the importance of making quantitative measurements over the entire pole figure.

The ultimate tensile strengths, the ultimate elongations, the stress at 10% elongation and the tear strengths are tabulated versus blow ratio in Table I. It is reasonable to expect that tensile strength in a particular direction in a film would, as a first approximation, be roughly proportional to the number of chain axes lying along this direction. This expectation is, in general, confirmed by the data.

It is also reasonable to expect that the tear strength of the film would be proportional to the number of chain axes lying in a plane perpendicular to the tearing direction. Note that the machine direction (MD) tear strengths for Marlex 50 are particularly low and increase only slightly with blow ratio. This agrees with the low number of (002) poles along the equator of the pole figure. Correspondingly, the exceptionally high values of transverse direction (TD) tear strengths are in agreement with the relatively high concentration of (002) poles in the meridional plane perpendicular to the TD direction. Since direct measurement of the (002) pole figure for the low density material was not possible we can only estimate its probable

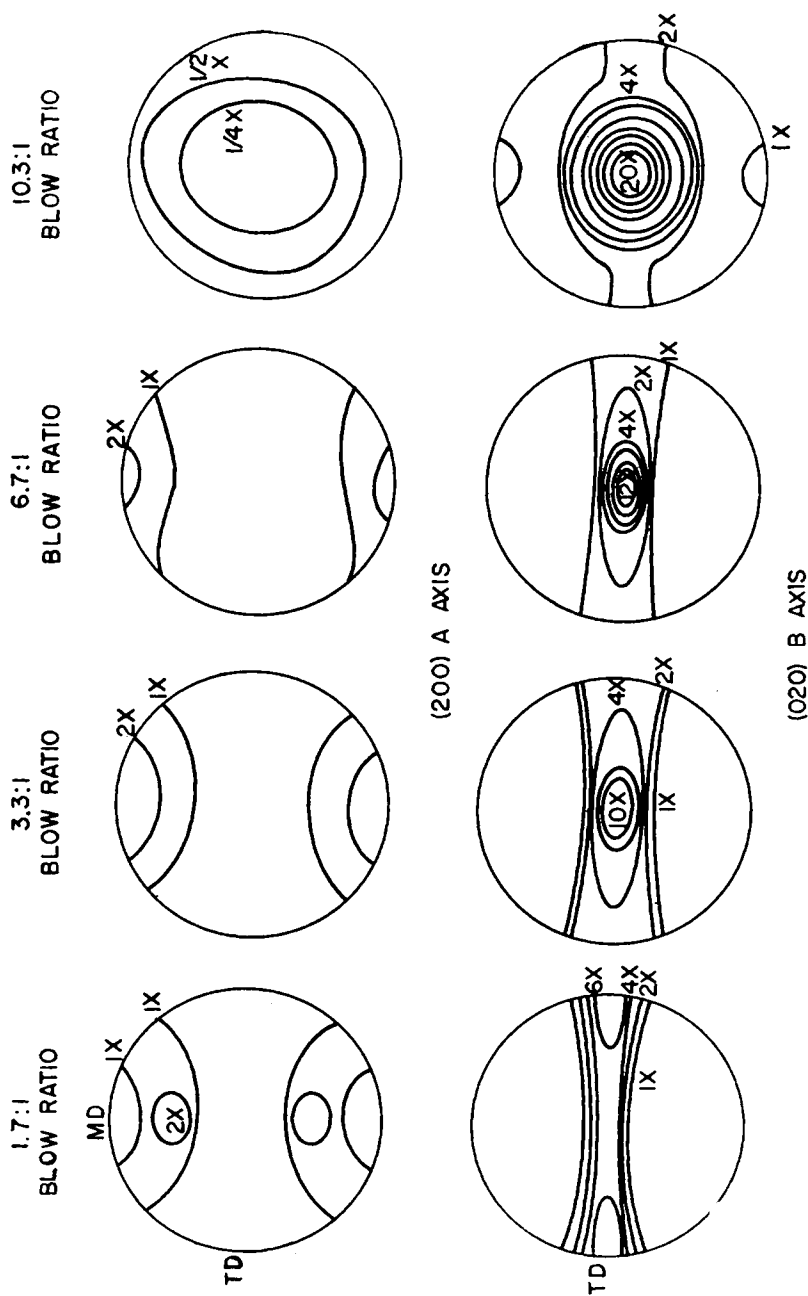


Fig. 6. Pole figure for DXM-21 (low density) polyethylene film as a function of blow ratio.

variation on the basis of other data. These estimates are consistent with the observations made thus far.

Finally, we need to consider an explanation for the elongations. Here the striking feature is the exceptionally low TD elongation for high density film in comparison with the exceptionally high TD elongation in low density film. Furthermore, the low density TD elongation increases substantially with draw ratio whereas the high density increases only very slightly. The key to this problem lies in noting the correspondence between the TD elongation and the MD tear strengths and the MD elongation and the TD tear strengths (Table I). It is quite generally accepted that ultimate properties such as tensile strength and elongations are largely determined by the presence of flaws or defects in the materials. Failure occurs by the propagation of cracks originating from such flaws in a direction perpendicular to the tensile force. Thus, one can rationalize the elongation values (as well as the tensile strength) by simply referring to the explanation for tear strength which determines the propagation of cracks or flaws. Thus, the MD elongation is high because the tear strength in the TD direction is high and transverse cracks propagate with difficulty.

This inverse relationship between tear strength and ultimate properties as a function of draw ratio does not hold for the low density film, and we can attribute this to the fact that in this case increasing blow ratio tends to put more and more chain axes into the plane of the film so that both MD and TD elongations are increased. One would expect that both MD and TD tears should also increase with blow ratio and while this expectation is not evidenced by the data in Table I, neither is it seriously in conflict, save for the first MD point.

In conclusion, although we have not proved exact mechanisms nor explained in detail the physical properties of polyethylene film on the basis of crystallite orientation, we nevertheless believe that an accurate and complete measurement of crystallite orientation using pole figures has gone a long way toward suggesting possible mechanisms. It has cleared up certain distinct anomalies and showed that elaborate mechanisms to explain the orientation of crystallites with their *c* axes perpendicular to the extrusion direction are not necessary.

IV. DISCUSSION

The major results of this investigation are the elucidation of crystallite orientation in polyethylene film, the necessity of measuring the complete orientation distribution, and the danger of drawing conclusions concerning the orientation of the *c* axis from qualitative estimates of the distribution of the *a* and *b* axes. Since our conclusions are different from previously published results it would seem appropriate to discuss what we feel may be the reason for these differences.

Most previous investigators have either assumed or proven to their satisfaction the existence of cylindrical symmetry about the machine direction. With such symmetry it can be shown that one should have equal intensities

along all latitude lines in the pole figure (taking the machine direction as the north pole). It is apparent from our data that such symmetry was not present in the films we examined. Thus, either the films examined by other investigators had quite different orientations or they falsely concluded the presence of cylindrical symmetry about the machine direction, due to the lack of complete data. We are inclined to believe that the lack of complete data is the more likely possibility for the following reasons. The method most commonly used to check for the presence of cylindrical symmetry would be to take a single flat-plate photograph with the x-ray beam parallel to the machine direction. On such a photograph the Debye rings would correspond to latitude lines on the pole figure. Now if such a photograph showed essentially a uniform intensity around each ring one might feel justified in concluding the existence of cylindrical symmetry. However, one must realize that this single photograph examines only a very small portion of the total orientation distribution, namely those latitudes which are θ degrees from the equator. An examination of our data in Figures 4, 5, and 6 shows that at least for the (200), and the (020) planes these latitudes do have very nearly constant intensities until one reaches very high draw ratios which probably were not investigated by others. Pole figures of other crystal planes (110), and (011), (not shown here) indicated similar lack of variation in intensity along latitudes corresponding to their respective values of θ . Aggarwal⁷ used a Weissenberg camera technique but as near as we can tell this was equivalent to scanning along the same latitudes described above. Thus, it is understandable why previous investigations might have concluded the presence of cylindrical symmetry on the basis of limited data.

However, the most important defect in all previous studies has been the failure to realize the limited conclusions that one can draw about the orientation of one crystallographic direction from measurements of others. In a single crystal the knowledge of the orientation of any two axes immediately determines the orientation of all other axes. However, with a distribution of crystal orientations, the knowledge of the orientation of the maxima in the a and b axis distribution does not necessarily fix the location of the maximum in the c axis distribution. This can be readily seen by taking a very hypothetical distribution in which all crystals are completely oriented at random except for ten per cent which have their a axes in a given direction and a different ten per cent which have their b axes at some other direction. This hypothetical distribution places some restrictions on the c axis distribution, but it does not locate the maximum in this distribution or even determine that there is a maximum. Our data clearly show both an a axis and c axis orientation in the machine direction while the b axis is in the transverse direction. Thus, it is not safe to assume that the location of the maxima in the a and b axis distribution determines unequivocally the maximum in the c axis distribution.

As far as we know, this investigation represents the only attempt to measure directly the location of the c axis in polyethylene film by measuring

the intensity of the (002) reflection. This was possible only in the high density material and one must rely on analogy to determine its location in the low density material.

We wish to emphasize that, while it is not possible, in general, simply to determine the c axis distribution from measurements of the a and b axes distributions, in many cases, especially when one has unimodular distributions and high degrees of orientation, one can make deductions with a fair degree of confidence. Furthermore, if one measures the complete a and b axes distributions, we believe that the essential information for the calculation of the c axis distribution is available. Such calculations will be the subject of future publications.

We have said nothing about the existence or orientations of any noncrystalline or amorphous regions. To discuss this question and to relate these x-ray measurements with infrared dichroism and birefringence would require a discussion of the crystallization and orientation mechanisms which goes beyond the scope of this paper.

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Résumé

On a mesuré la distribution de l'orientation complète suivant les directions cristallographiques a et b dans le cas d'une série de films tubulaires de polyéthylène extrudé en fonction du rapport de soufflage. On utilise des figures polaires comme mode de représentation de l'orientation et on montre que l'utilisation de disques photographiques de diffraction aux rayons-X suivant la technique usuelle peut mener à des conclusions erronées. L'augmentation du rapport de soufflage a des effets différents et distincts sur l'orientation d'un film de polyéthylène à haute densité par rapport à un film de polystyrène à basse densité. Par opposition avec les données publiées antérieurement, nos résultats montrent clairement que l'axe c ne s'oriente pas préférentiellement d'une façon perpendiculaire à la direction d'extrusion. En particulier on montre qu'il n'est pas possible de déduire dans la généralité des cas, la distribution d'orientation axiale de l'axe c au départ de l'estimation qualitative des distributions suivant les axes b et a . La force de rupture, l'élongation, les modules et les forces de déchirement de ces films ont été mesurées et les résultats s'accordent avec les orientations des directions cristallographiques.

Zusammenfassung

Die vollständige Orientierungsverteilung der kristallographischen *a*- und *b*-Richtungen wurde für eine Reihe röhrenförmig extrudierter Polyäthylenfilme als Funktion des Blasverhältnisses gemessen. Die Verwendung von Polfiguren zur Wiedergabe der Orientierung wird befürwortet, und es wird gezeigt, dass die gebräuchliche Methode, Röntgenbeugungsaufnahmen auf ebenen Platten zu verwenden, zu irrigen Schlüssen führen kann. Ein Anwachsen des Blasverhältnisses hat im Vergleich zu Polyäthylenfilmen niedriger Dichte einen deutlich verschiedenen Einfluss auf die Orientierung von Polyäthylenfilmen hoher Dichte. Im Gegensatz zu früher veröffentlichten Ergebnissen zeigen unsere Resultate deutlich, dass sich die *c*-Achse nicht vorzugsweise senkrecht zur Extrusionsrichtung orientiert. Es wird im speziellen gezeigt, dass man das Maximum der Orientierungsverteilung der *c*-Achse nicht aus qualitativen Berechnungen der Verteilung der *a*- und *b*-Achsen ableiten kann. Die Zugfestigkeit, die Elongation, der Modul und die Reissfestigkeit dieser Filme wurde gemessen und die Ergebnisse mit der Orientierung der kristallographischen Richtungen in Beziehung gebracht.

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