Orientation in Cold-Rolled Polypropylene

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Changes in crystal orientation produced during deformation of crystalline polymers are influenced by the manner in which the polymer molecules are arranged into crystals and the crystals held together. Conversely, through the study of orientation one may infer certain structural features of the polymer pertaining to the mechanical behavior of the polymer. In the work reported in this paper, sheets of isotactic polypropylene having initially random orientation were rolled at temperatures below the crystalline melting point, and the nature of the orientation thereby produced was investigated by x-ray diffraction methods previously used in a study of orientation in films.[1]

SAMPLE PREPARATION

Polypropylene of 250°C. melt index and density of 0.901 g./cc. was molded at about 450°F. into pads 6 x 6 x $^1/_8$ in. While still in the mold, the pads were quickly reheated to 550°F., held at that temperature for 5 min., and then cooled to room temperature in about half an hour. Finally, they were annealed in a vacuum oven for 4 hrs. at 275°F.

The rolling was carried out on a calender with 6 in. diameter rolls, both rotating at the same speed.

TABLE I
Dimensional Changes Due to Cold Rolling

Rolling temp., °F.	Sheet in stack	Ratio final/initial dimension		
		Thickness	Rolling direction	Transverse direction
75	1 (top)	0.50	1.80	1.07
	2	0.54	1.90	1.10
	3	0.44	2.05	1.10
	4 (bottom)	0.48	1.95	1.08
275	1 (top)	0.44	2.2	1.1
	2	0.41	2.2	1.1
	3	0.44	2.2	1.1
	4 (bottom)	0.46	2.2	1.1
75	—	0.162	4	1.5

As it was impractical to obtain laminae from the interior of a rolled sheet, such specimens were simulated by plying up four sheets and rolling the stack as a unit. After being rolled, the sheets were separated and examined individually. Stacks of sheets were rolled in one direction to one half the initial thickness with roll temperatures of 75° and 275°F. The thickness reduction was carried out gradually in about thirty passes. A sample was also rolled at 75°F. to about one sixth its initial thickness. In this case, it was difficult to roll a stack; therefore, a single sheet was used. Deformation ratios as a result of rolling are listed in Table I. It can be noted that the deformation in the transverse direction was relatively small.

The positive rolling direction was designated as the direction the rolls would move if the sample were stationary.

X-RAY DIFFRACTION PROCEDURES

For the purpose of this study, it was adequate to specify the orientation of a crystal plane by the direction of its normal. This was conveniently expressed in spherical coordinates ϕ,ψ, where ϕ is the colatitude and ψ is the longitude. The direction of a plane normal can also be represented by the point of intersection of the normal with a unit sphere about the origin. This sphere will be referred to as the coordinate sphere.

For a specific set of crystal plane indices, the concentration of $\{hkl\}$ plane normals oriented in the direction ϕ,ψ is designated by a distribution function $I(\phi,\psi)$. This function was evaluated from quantitative measurements of x-rays diffracted from these oriented planes. Specifically, $I(\phi,\psi)$ was taken proportional to the integrated intensity.

Experimentally, $I(\phi,\psi)$ was determined with a diffractometer equipped with pole figure devices. The reference direction $\phi = 0$ was selected normal to the plane of the sample, and the rolling direction was chosen as $\phi = 90°$, $\psi = 0$. The procedures used for measuring the peak diffracted intensities from the $\{hkl\}$ planes as a function of ϕ and ψ are described in an earlier publication.[1] The peak intensities were multiplied by the integral line widths to give integrated intensities. A correction was made for absorption when a transmission type of pole figure device[2] was used, and an instrumental correction was made when a reflection type was used. The latter correction was needed to compensate for the observed deviations from a constant value of the integrated intensity measured as a function of ϕ for an ideal random sample. A flat sample of tightly packed, fine polypropylene powder was assumed to fulfill the random sample requirements sufficiently closely and hence was used as a standard in determining the instrumental correction empirically.

Distributions $I(\phi,\psi)$ were determined for the $\{040\}$ and $\{110\}$ planes of monoclinic polypropylene.[3] For several samples these distributions were evaluated over the entire surface of the coordinate sphere. From these were made qualitative interpretations about the nature of the orientation. Also, a quantitative measure of orientation in the direction $\phi = 0$ was cal-

culated directly for the plane normals. A convenient quantity for this purpose is the mean square cos ϕ, which can be evaluated from the distribution by the following equation:

$$\langle \cos^2\phi \rangle_{av}$$
$$= [\int_0^{1/2\pi} \int_0^{2\pi} I(\phi,\psi) \cos^2\phi \sin\phi \, d\psi \, d\phi] / [\int_0^{1/2\pi} \int_0^{2\pi} I(\phi,\psi) \sin\phi \, d\psi \, d\phi] \quad (1)$$

A comparable quantity for the c axis orientation in the $\phi = 0$ direction can then be calculated in terms of $\langle \cos^2\phi \rangle_{av}$ for the $\{040\}$ and $\{110\}$ planes by the equation:

$$\langle \cos^2\sigma \rangle_{av} = 1 - 0.901 \langle \cos^2\phi_{040} \rangle_{av} - 1.099 \langle \cos^2\phi_{110} \rangle_{av} \quad (2)$$

where σ is the angle between the c axis of a crystal and the $\phi = 0$ direction. This equation is a special case of the more general relationships derived elsewhere.[1,4] In a crystal the molecule backbone is parallel to the c axis, hence the orientation function $\langle \cos^2\sigma \rangle_{av}$ is a measure of molecular orientation in the crystallized fraction of the polymer.

Orientation functions in some other reference direction, q, can also be calculated from the distribution function $I(\phi,\psi)$. This involves choosing a new set of spherical coordinates ϕ_q,ψ_q such that $\phi_q = 0$ in the q direction, and transforming any direction from the old to the new coordinates. Thus, the original distribution of concentration of plane normals can be presented in the new coordinates. Then eqs. (1) and (2) expressed in the new coordinates give the orientation functions in the q direction.

For some special cases, it is possible to simplify calculations by making use of the orthogonality relationships:

$$\langle \cos^2\phi_x \rangle_{av} + \langle \cos^2\phi_y \rangle_{av} + \langle \cos^2\phi_z \rangle_{av} = 1 \quad (3a)$$

$$\langle \cos^2\sigma_x \rangle_{av} + \langle \cos^2\sigma_y \rangle_{av} + \langle \cos^2\sigma_z \rangle_{av} = 1 \quad (3b)$$

where x, y, and z are any three mutually orthogonal directions. It is evident from these equations that for complete randomness all the orientation functions have a value of $1/3$ in any direction.

EXPERIMENTAL RESULTS

The pads, prepared in the manner described in a preceding section, were checked for randomness before being used in the rolling experiments. A rough check was first made by comparing the diffractometer traces (at $\phi = 0$) with the trace for the powder sample. The relative intensities were very similar, thus satisfying a necessary condition for randomness on the basis that the powder was random.

For one of the pads selected at random, $I(\phi,\psi)$ was measured for the $\{040\}$ and $\{110\}$ planes. The coordinate ϕ was changed in 10° increments and, at each value of ϕ, $I(\phi,\psi)$ was measured continuously as a function of ψ. For both planes, there was essentially no variation in $I(\phi,\psi)$ as ψ was varied. However, some variation with respect to ϕ was observed, leading to an

estimated standard deviation in $I(\phi,\psi)$ over the coordinate sphere of 1.7% for the $\{110\}$ planes and 7% for the $\{040\}$ planes.

From these distributions, the orientation functions were computed in the direction normal to the plane of the sample by eqs. (1) and (2). Because of the nonvariance of $I(\phi,\psi)$ with respect to ψ, an orientation function will have the same value along any direction in the plane of the sheet. Therefore, the functions in the plane of the sheet can be easily evaluated from the values in the direction normal to the sample by using eqs. (3a) and (3b) in which two of the orthogonal directions are in the plane of the sheet.

Values of the orientation functions thus obtained are listed in Table II. The orientation functions for the plane normals and c axis were all sufficiently close to $1/3$ so that orientation in the pad could be considered random within the accuracy of the measurements. This pad was assumed to be representative of the set of pads prepared.

TABLE II
Oriented Function for Randomized Pad

Orientation function	Normal to plane of sample	In plane of sample
$\langle \cos^2 \phi_{040} \rangle_{av}$	0.339	0.331
$\langle \cos^2 \phi_{110} \rangle_{av}$	0.329	0.335
$\langle \cos^2 \sigma \rangle_{av}$	0.334	0.333

Values of $I(\phi,\psi)$ were similarly measured for a pad rolled at room temperature to one half its initial thickness. This pad was second from the top in the stack (see Table I). Data by the reflection technique ($0 \leqslant \phi \leqslant 50°$) were obtained from the lower surface of this pad, i.e., the surface at the center of the stack. These data are replotted in the form of pole figures in Figure 1.

Information on the c axis orientation can be deduced from qualitative consideration of the pole figures and by calculating $\langle \cos^2\sigma \rangle_{av}$. Both these approaches will be discussed.

From a qualitative interpretation of the pole figures, it was concluded that the c axis has two preferred directions inclined approximately 30° to the rolling direction, i.e., has the coordinates $\phi = 60°$, $\psi = 0$ and $\phi = 120°$, $\psi = 0$. The reasoning leading to this conclusion is indirect and proceeds as follows. If the c axis were preferentially oriented in the rolling direction, then the direction of the normals to the $\{hk0\}$ planes would be concentrated on the coordinate sphere within a circular band passing through the points $(\phi = 90°, \psi = -90°)$, $(\phi = 0)$, and $(\phi = 90°, \psi = 90°)$. This is not the case here, for these are maxima to either side of this hypothetical band. However, if the preferred c axis direction is still confined to the longitude $\psi = 0$, but makes an angle ϵ with the rolling direction, then the band will be tilted through an angle also ϵ. Hence, if the c axis has the two aforementioned directions of preferred orientation, there will be two bands, one passing through the points $(\phi = 90°, \psi = -90°)$, $(\phi = 30°, \psi = 0)$, $(\phi = 90°$
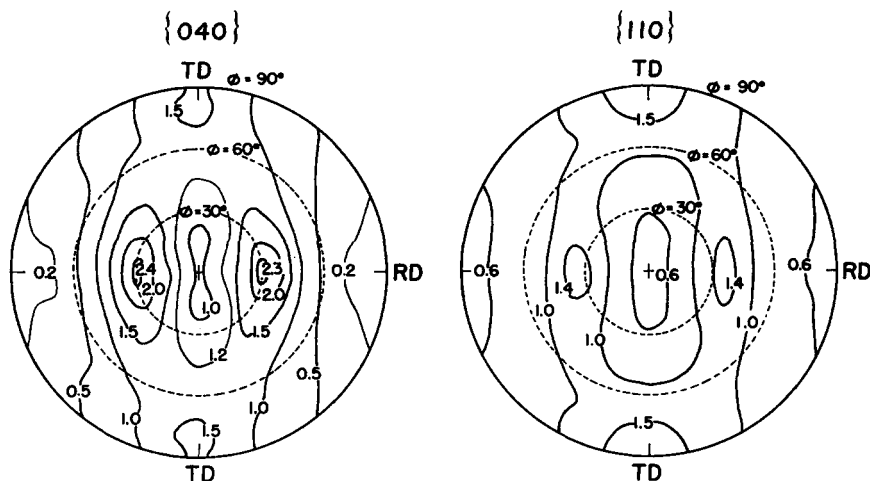
Fig. 1. Pole figures for sheet rolled at 75°F. to 0.54 of its initial thickness. Contours of constant $I(\phi,\psi)$ are projected onto equatorial plane of coordinate sphere. Rolling direction (RD) and transverse direction (TD) are indicated.

$\psi = 90°$), and the other passing through ($\phi = 90°$, $\psi = -90°$), ($\phi = 30°$, $\psi = 180°$), ($\phi = 90°$, $\psi = 90°$). The observed regions of high $I(\phi,\psi)$ concentration do indeed fall within such bands, confirming the inclined c axis hypothesis.

Orientation functions were calculated by eqs. (1) and (2) in the normal direction and the rolling direction. Those in the transverse direction were obtained by using eqs. (3a) and (3b). The values of these functions are listed in Table III. An expected increase of $\langle \cos^2\sigma \rangle_{av}$ in the rolling direction was realized along with decreases in the normal and transverse directions.

TABLE III
Orientation Functions for Pad Rolled at Room Temperature to 0.54 of its Initial
Thickness

Orientation function	Rolling direction	Transverse[a] direction	Normal to plane of sample
$\langle \cos^2 \phi_{040} \rangle_{av}$	0.219	0.347	0.434
$\langle \cos^2 \phi_{110} \rangle_{av}$	0.291	0.395	0.314
$\langle \cos^2 \sigma \rangle_{av}$	0.483	0.253	0.264

[a] By difference, using orthogonality relationship.

The direction in which $\langle \cos^2\sigma \rangle_{av}$ is a maximum can, in some simple cases, be determined without recourse to extensive calculations. Consider the three mutually perpendicular planes in the coordinate sphere formed by (a) the normal to the sheet and the rolling direction, (b) the normal and transverse directions, and (c) the rolling and transverse directions. If $I(\phi,\psi)$ is symmetrical across these three planes, and if $\langle \cos^2\phi \rangle_{av}$ in the rolling direc-

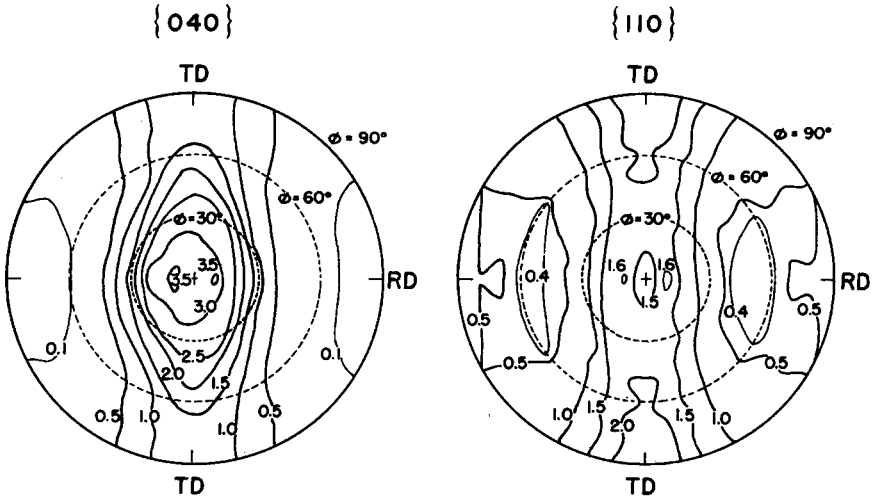$\{040\}$ $\{110\}$

Fig. 2. Pole figures for sheet rolled at 75°F. to 0.162 of its initial thickness.

tion is less than that in the transverse and normal directions, then $\langle\cos^2\phi\rangle_{av}$ is smaller in the rolling direction than in *any* other direction (see the Appendix for proof). If this condition holds for both the $\{040\}$ and $\{110\}$ planes, then it follows from eq. (2) that $\langle\cos^2\sigma\rangle_{av}$ is maximum in the rolling direction.

Applying these considerations to the pole figures in Figure 1 and neglecting the rather small deviation from symmetry, one may conclude that the direction of maximum $\langle\cos^2\sigma\rangle_{av}$ is in the rolling direction.

Pole figures in Figure 2, for the sample cold-rolled to one sixth its initial thickness, are similar in general features to those in Figure 1. However, they indicate the two preferred c axis directions inclined about 10° to the rolling direction, and a stronger average orientation in the rolling direction. The latter point is confirmed by a higher value of $\langle\cos^2\sigma\rangle_{av}$ in the rolling direction (0.694 vs. 0.483). The complete set of orientation parameters in the three principal directions calculated by eqs. (1) and (2) are listed in Table IV. It can be noted that the orthogonality conditions of eqs. (3a) and (3b) are very nearly fulfilled. This is a check on the accuracy of the

TABLE IV

Orientation Functions for Pad Rolled at Room Temperature to 0.162 of its Initial Thickness

	Reference direction		
Orientation function	Rolling direction	Transverse direction	Normal to plane of sample
$\langle\cos^2\phi_{040}\rangle_{av}$	0.109	0.326	0.559
$\langle\cos^2\phi_{110}\rangle_{av}$	0.189	0.417	0.387
$\langle\cos^2\sigma\rangle_{av}$	0.694	0.248	0.072

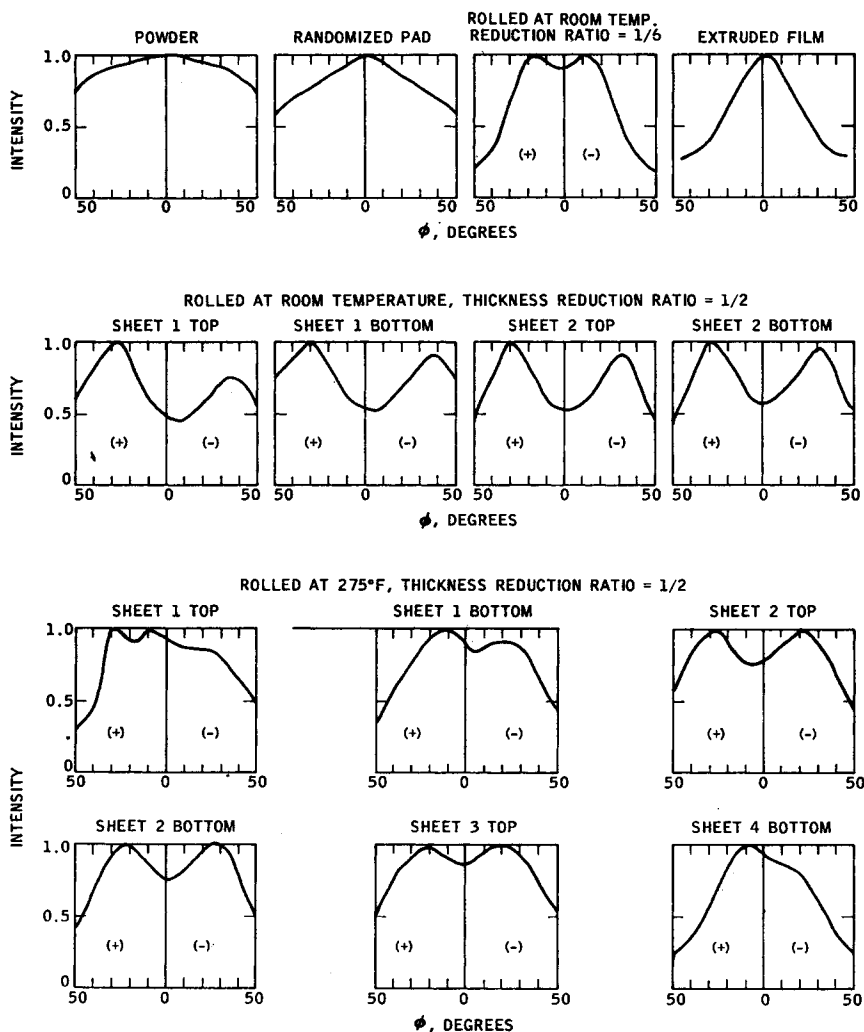Fig. 3. Relative {040} intensity scans for plane normals along longitudes $\psi = 0$ and $\psi = 180°$ (to right and left of origin, respectively). Intensities are not corrected for various factors. For rolled samples, inclination of c axes in plane of scan are given by ϕ coordinate of normals, regions corresponding to positive or negative inclination being indicated.

calculations since the same experimental data were manipulated in the three sets of calculations.

A cursory comparison of orientation among samples, such as among the sheets of a stack, was made from {040} intensity profiles taken along the longitudes $\psi = 0$ and $\psi = 180°$. This simple procedure was feasible since some of the main features of the orientation deduced from the pole figures are revealed in the $I(\phi,\psi)$ profiles, and the major contours of the $I(\phi,\psi)$ profiles also show up in the intensity profiles. The successful application of

this procedure presupposes some knowledge of the general nature of the orientation in the samples compared.

Intensity profiles in the range $0 \leqslant \phi \leqslant 50°$ for a number of samples are shown in Figure 3. Profiles for the powder and randomized pad are included to show the extent of the variations of intensity with ϕ for these samples due to causes other than orientation. For the rolled specimens, the c axis inclination is designated $(+)$ if its direction points away from the center of the stack, this direction being taken from the vertex of the acute angle formed by the c axis with the rolling direction.

It can be noted that profiles for the surfaces that were in contact with the rolls (top of sheet 1 and bottom of sheet 4) show a pronounced asymmetry favored by a higher concentration of c axes with positive inclinations. This may be associated with the observed tendency of material to pile up before the rolls, especially at the higher temperature. Within a stack, however, the surfaces show rather symmetrical profiles quite similar to each other. Thus, the orientation appears to be about the same at all levels throughout a stack, with the exception of a relatively thin layer near the surfaces that are in contact with the rolls.

The effects of roll temperature at about the same thickness reduction ratio also can be noted in Figure 3. At 275° the preferred direction of c axis orientation has a smaller inclination than at room temperature (ca. 25 vs. 30°) and the orientation is less pronounced in the preferred directions at the higher temperature.

For the pad rolled at room temperature to one sixth its initial thickness, the intensity profile shows two high and closely spaced peaks. This implies a smaller c axis inclination and greater $\langle \cos^2 \sigma \rangle_{\mathrm{av}}$ than in the case of rolling at room temperature to one half the initial thickness.

An intensity profile for an extruded film also is included in Figure 3. In contrast to the profiles for the rolled pads, the profile for the film shows a single peak located at $\phi = 0$, implying a preferred orientation in the extrusion direction. The value of the orientation function $\langle \cos^2 \sigma \rangle_{\mathrm{av}}$ is 0.53 for the film,[1] a value between those for the pads rolled at room temperature to a thickness reduction ratio of one half (0.48) and one sixth (0.69).

DISCUSSION

One of the distinctive features of the c axis orientation in cold-rolled polypropylene is the presence of a pair of preferred directions making equal angles with the rolling directions. The following explanation is offered to account for this phenomenon.

As a pad is rolled, the tensile component of force along the rolling direction produces a local partial necking down within the sample. This is indicated in Figure 4 as occurring in some elemental lamina. Because the extent of the deformation is limited by the separation of the rolls, the entire cross section cannot be necked down. Furthermore, the necking down cannot continue uniformly in one lamina because this deformation would
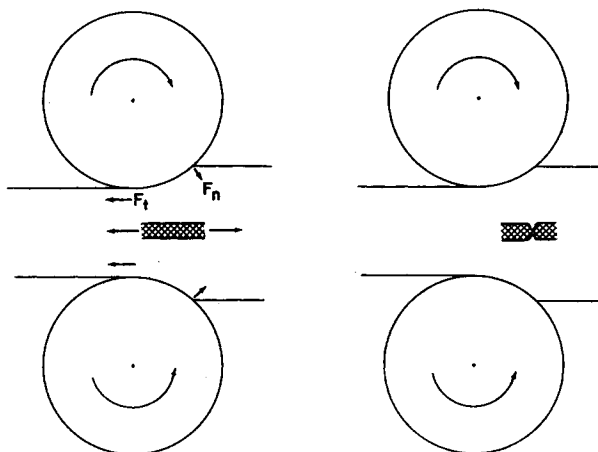
Fig. 4. Deformation during rolling. Tangential force F_t and component of normal force F_n exert tensile stress on elemental lamina, causing it to neck down.
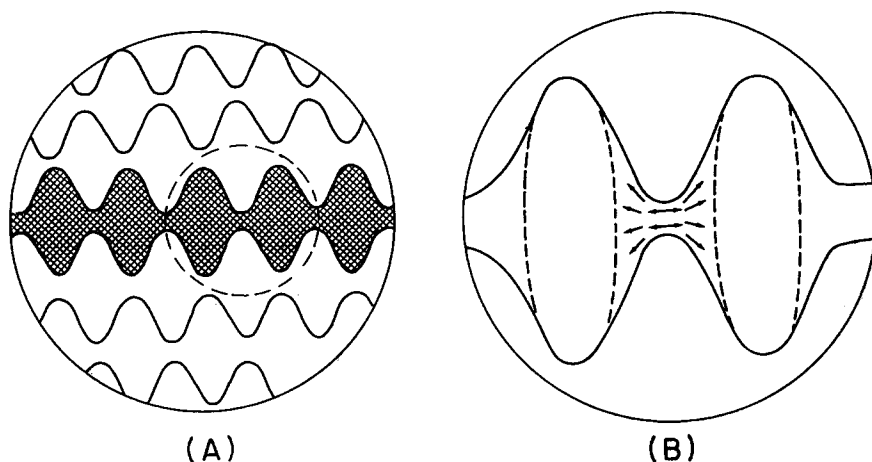

(A)   (B)

Fig. 5. Deformation after rolling: (A) sectional representation similar to that in Figure 4, showing intermittent necking down of the elemental lamina (crosshatched), adjoining laminae similarly necked down; (B) enlargement of section, indicated by broken circle in (A), showing direction of preferred orientation of c axis following lines of strain.

exert large stresses on adjacent laminal and cause them to neck down locally. A continuation of this process is visualized as causing a deformation indicated schematically in Figure 5A. Assuming that the crystal c axis orients in the direction of the "flow lines," one obtains substantial regions in which the c axis has a positive inclination to the rolling direction, along with equivalent regions of negative inclination (Fig. 5B). With more severe rolling, the orientation in the rolling direction will be stronger, and the angle of inclination of the preferred orientation will be smaller.

APPENDIX

It is shown below that the orientation function $\langle \cos^2\phi \rangle_{av}$ has a minimum in one of the principal directions if certain symmetry conditions are fulfilled.

Consider a unit sphere in Cartesian coordinates. Crystallographic directions will be indicated by unit vectors from the center of this sphere and the distribution function by $I(x,y,z)$. Let the distribution be symmetrical across the xy, xz, and yz planes; then the value of $I(x,y,z)$ is unchanged by changing the signs of x, y, or z. A further restriction imposed on the distribution is that $\langle \cos^2\phi_y \rangle_{av}$ is less than $\langle \cos^2\phi_x \rangle_{av}$ and $\langle \cos^2\phi_z \rangle_{av}$. We wish to show that $\langle \cos^2\phi \rangle_{av}$ is smaller in the y direction than in *any* other direction.

Let any arbitrary direction be represented by a unit vector $\mathbf{q} = \mathbf{i}x_0 + \mathbf{j}y_0 + \mathbf{k}z_0$ for which x_0 and z_0 are not zero simultaneously. The orientation function in the $\mathbf{q}$ direction, $\langle \cos^2\phi_q \rangle_{av}$ can be rather simply expressed if each point on the unit sphere is considered along with its seven other equivalent points. Thus, the sum of the square of the cosines of the angles between $\mathbf{q}$ and each of the vectors $\pm \mathbf{i}x \pm \mathbf{j}y \pm \mathbf{k}z$ is $8(x_0^2x^2 + y_0^2y^2 + z_0^2z^2)$. It can be noted that there are no cross product terms present. By weighting each $\cos^2\phi$ term by its corresponding value of $I(x,y,z)$ and averaging over the surface of the sphere one obtains

$\langle \cos^2\phi_q \rangle_{av}$

$$= [\int (x_0^2x^2 + y_0^2y^2 + z_0^2z^2) I(x,y,z) \, dA] / [\int I(x,y,z) \, dA] \quad (4)$$

where dA is an element of area, and the integration is over a hemisphere. Since

$$\langle \cos^2\phi_y \rangle_{av} = \frac{\int y^2 I(x,y,z) \, dA}{\int I(x,y,z) \, dA}$$

and since analogous expressions hold for $\langle \cos^2\phi_x \rangle_{av}$ and $\langle \cos^2\phi_z \rangle_{av}$, eq. (4) may be rewritten:

$$\langle \cos^2\phi_q \rangle_{av} = x_0^2 \langle \cos^2\phi_x \rangle_{av} + y_0^2 \langle \cos^2\phi_y \rangle_{av} + z_0^2 \langle \cos^2\phi_z \rangle_{av} \quad (5)$$

Replacing y_0^2 by its equivalent, $1 - x_0^2 - z_0^2$, leads to:

$$\langle \cos^2\phi_q \rangle_{av} = \langle \cos^2\phi_y \rangle_{av} + x_0^2 \left\{ \langle \cos^2\phi_x \rangle_{av} - \langle \cos^2\phi_q \rangle_{av} \right\}$$
$$+ z_0^2 \left\{ \langle \cos^2\phi_z \rangle_{av} - \langle \cos^2\phi_q \rangle_{av} \right\} \quad (6)$$

Each of the differences in the braces is positive, by one of the initial assumptions. It therefore follows that $\langle \cos^2\phi_y \rangle_{av}$ is less than $\langle \cos^2\phi_q \rangle_{av}$, which is what we set out to prove.

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Synopsis

Sheets of isotactic polypropylene were prepared to have initially random orientation and were subsequently rolled at temperatures below the crystalline melting point. Their crystal orientation was investigated. The orientation of the *c* axis (fiber axis) was determined from pole figure data obtained by x-ray diffraction. It was found that rolling produced orientation of the *c* axis in two preferred directions in the plane defined by the rolling direction and the normal to the sheet. These two directions made equal angles of inclination with the rolling direction. With increased severity of rolling the component of the orientation vector in the rolling direction increased and the angles between the preferred *c* axis orientation and the rolling direction decreased. Increasing the temperature reduced the angle of inclination of the preferred *c* axis orientation. This double *c* axis orientation was not observed in extruded film. An explanation of the *c* axis orientation in cold-rolled polypropylene is offered on the basis of local necking down within the sample during the deformation.

Résumé

On a étudié l'orientation cristalline dans des feuilles de polypropylène isolactique qui avaient été préparés initialement avec une orientation purement statistique et qui furent ensuite laminées à des températures inférieures au point de fusion cristalline. On a déterminé l'orientation de l'axe *c* (axe de la fibre) à partir de données fournies par la diffraction des rayons-X. On a trouvé que le laminage causait une orientation de l'axe dans deux directions préférentielles dans le plan défini par la direction du laminage et la normale à la feuille. Ces deux directions réalisent des angles d'inclinaison égaux avec la direction de laminage. Lorsqu'on augmente l'intensité du laminage, la composante du vecteur orientation dans la direction du laminage augmente et les angles entre l'orientation préférentielle de l'axe *c* et la direction du laminage diminuent. L'accroissement de la température réduit également l'angle d'inclinaison de l'orientation préférentielle de l'axe *c*. Cette double orientation de l'axe *c* n'a pas été observée dans un film extrudé. On tente d'expliquer l'orientation de l'axe *c* dans le polypropylène laminé à froid sur la base d'un rétrécissement local dans l'échantillon durant la déformation.

Zusammenfassung

Die Kristallorientierung in Blättern aus isotaktischem Polypropylen wurde untersucht, die mit einer regellosen Anfangsorientierung hergestellt und dann bei Temperaturen unterhalb des Kristallitschmelzpunktes gewalzt worden waren. Die Orientierung der *c*-Achse (Faserachse) wurde aus Pol-Röntgenbeugungsdaten bestimmt. Es wurde gefunden, dass das Walzen eine Orientierung der *c*-Achse in zwei bevorzugten Richtungen in der durch Walzrichtung und der Normalen zum Blatt gegebenen Ebene erzeugt. Diese beiden Richtungen schlossen gleiche Neigungswinkel mit der Walzrichtung ein. Mit zunehmender Walzintensität stieg die Komponente des Orientierungsvektors in der Walzrichtung an und die Winkel zwischen der bevorzugten Orientierung der *c*-Achse und der Walzrichtung nahm ab. Auch steigende Temperatur verminderte den Neigungswinkel der bevorzugten Orientierung der *c*-Achse. Die doppelte Orientierung der *c*-Achse konnte bei extrudierten Filmen nicht beobachtet werden. Eine Erklärung für die Orientierung der *c*-Achse in kalt gewalztem Polypropylen wird durch die Annahme einer lokalen Einschnürung innerhalb der Probe während der Deformation gegeben.