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Uniplanar-axial orientation in hot-rolled polymers

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The orientations produced by high temperature rolling of polyoxymethylene (126 °C) and polytetrafluoroethylene (150 °C) and nylon 66 are examined by pole figures. No evidence is found to support the theory of Akahane and Mochizuki that it is the plane of the zig-zag chains that orientates into the rolling plane in nylon 66. The classical rolling texture of Bunn and Garner describes the pole figures except for the (100) pole, which is observed at 28° to the transverse direction; in the texture of Bunn and Garner it should occur at 24°. In hot-rolled polyoxymethylene the texture observed corresponds to a unique orientation of the hexagonal unit cell: $(10\bar{1}0)$ planes parallel to the rolling plane and *c*-axis parallel to rolling direction. The polyoxymethylene texture differs significantly from the pseudo-fibre textures observed in the cold-rolled polymer. The rolling texture of hot-rolled polytetrafluoroethylene is similar to that of hot-rolled polyoxymethylene. These results show the plastic slip system in polyoxymethylene and polytetrafluoroethylene to be $(10\bar{1}0)$ [0001].

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1. Introduction

Bunn and Garner [1] observed in the analysis of the crystal structure of nylon 66 that rolling produced orientations of the unit cell with the (010) plane parallel to the roll plane and the [001] direction parallel to the roll direction. We shall refer to this type of orientation as uniplanar-axial [2] (equivalent, though less accurate, terms in use are doubly-oriented or biaxial). Since this early work [1], rolling has not played a prime role in the study of the oriented state, for several reasons. First, drawing is far more important in the manufacture of oriented polymers than rolling. Second, contrary to the observation of Bunn and Garner [1], rolling of polymers does not always apparently produce a simple uniplanar-axial texture. For instance, in cold-rolled polyoxymethylene the texture more nearly resembles that of a fibre (uni-axial), with no clear preference for a crystal plane to lie parallel to the rolling plane [3].

Those crystalline polymers that have been the subject of previous rolling studies include: polyethylene [4-6], polypropylene [7], polytetrafluoroethylene [8], nylon 66 [9], nylon 6 [10], nylon 11 [11, 12], polyvinyl-alcohol [10], polyoxymethylene [3, 13] and polyethylene terephthalate [10, 12]. The best description of crystal lattice orientation is the wide-angle X-ray pole figure, which is a two dimensional analogue of the spatial distribution of plane normals for a given Bragg reflection. In all orientation studies, whether by drawing or rolling, direct mapping of the molecular chain (*c*-axis) distribution is rarely obtained: an exception is in polyethylene [14]. It would appear that a combination of technical difficulties and weakly defined orientations are often the reason for this. The *c*-axis distribution is usually obtained indirectly by comparing two other pole figures. The results of this procedure are often acceptable but can be unreliable for complicated pole figures [15]. This state of affairs is far from ideal since the distribution of molecular axes is usually the piece of information of most value.

To date, pole figures have only been used to examine the rolling textures of three polymers, polypropylene [7], polyethylene [6] and polyoxymethylene [3, 13]. In all these polymers the observed rolling textures are more complicated

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than a simple uniplanar-axial orientation. In cold-rolled polyethylene [4, 5] both (100) and (110) crystal slip planes have been observed to lie preferentially in the rolling plane, depending on the degree of rolling deformation. Heat-treatment of rolled polyethylene removes a twinning texture in favour of a unique orientation of the unit cell, while the *c*-axes are shown (indirectly) to be tilted at a small angle to the rolling direction [6]. In polypropylene [7] the (040) pole figure shows a pronounced tendency for this crystal plane to lie in the rolling plane, with *c*-axes tilted by 10° from the rolling direction. The situation is even more complicated in cold-rolled polyoxymethylene. The molecular axes have a characteristic tilt of about 30° away from the rolling direction for small rolling deformations: this angle reduces to 0° at higher deformations [3]. It is interesting to note that for very *low* degrees of rolling, the first indication of orientation in polyoxymethylene is for the molecular chains to lie at 90° to the rolling direction [13].

The first purpose of the work described in this paper is to determine whether simple Bunn-type [1] uniplanar-axial orientation could be produced in general by hot-rolling. In the rolling of metals it is well known that the simplest rolling textures are produced in hexagonal crystals [16]. Thus we examine the textures of rolled polyoxymethylene (POM) and polytetrafluoroethylene (PTFE), both of which have hexagonal unit cells. In order to roll at elevated temperature, deformation in these polymers is produced by Steckel rolling. The ideal test of uniplanar-axial texture is to examine both $(hki0)$ and $(000l)$ pole figures. This we do for POM, measuring the $(10\bar{1}0)$ and (0009) poles. Despite the weakness of the (0009) reflections, we have a direct measure of the distribution of molecular chains. In PTFE no $(000l)$ is discernible so that molecular distribution is inferred from the measured $(10\bar{1}0)$ pole figure.

A second purpose of the present study is to examine the recent proposal of Akahane and Mochizuki [10]; that in some polymers with planar zig-zag molecular conformation, for example nylon 6, it is the zig-zag plane which lies in the rolling plane. This theory is different from the Bunn theory of crystal plane alignment, only if the zig-zag plane is not coincident with a low index crystal plane. We shall test the theory of Akahane and Mochizuki using rolled nylon 66, because the angle between the molecular zig-zag plane and the (010) crystal plane is very large, so that any departures from Bunn-type orientation should be apparent.

2. Experimental techniques

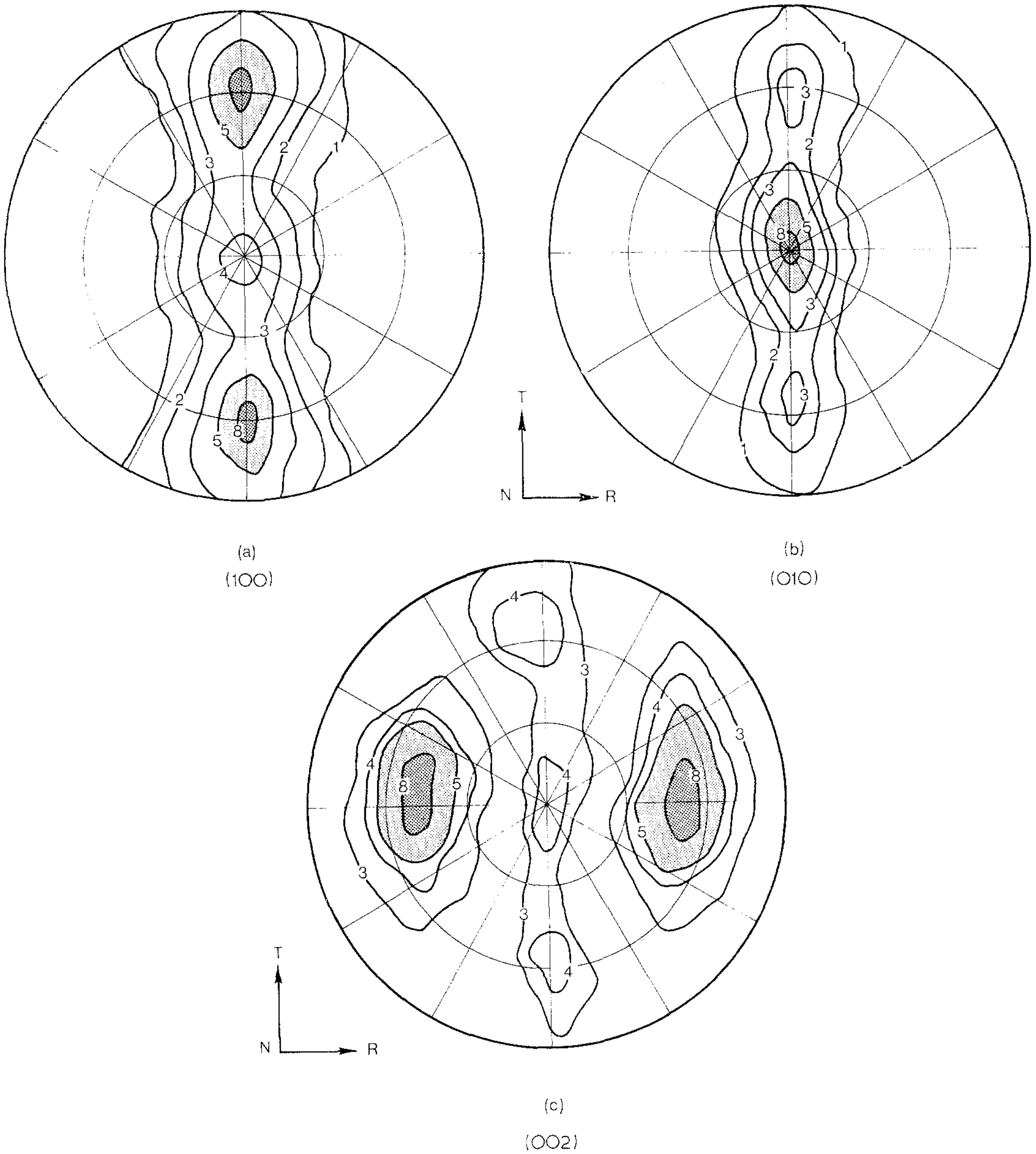
2.1. Preparation of samples

Specimens of oriented nylon were cut from commercial nylon strapping. This product is manufactured by DuPont by high temperature uni-directional rolling [17], and has mechanical properties that are highly anisotropic [18]. The other two polymers used in this study were moulded sheets of POM and PTFE (supplied by G. H. Bloore, Ltd). Specimens 1 × $\frac{1}{4}$ in. in section were machined from these sheets and then oriented by Steckel rolling (pre-roll orientation was checked by X-rays and found to be negligible). In conventional rolling, the work of deformation is communicated to the specimen at the roll surfaces by frictional forces. In Steckel rolling, the main forces are applied by an external tensile load, so that the specimen is pulled through rollers that are not power driven. Steckel rolling is particularly suited for the rolling of polymers at elevated temperature. Details of this rolling process will be published elsewhere [19].

The POM and PTFE sheets were rolled unidirectionally. In both polymers the rate of rolling was 0.5 in. min^{-1}. The temperature of rolling was 126°C for POM and 150°C for PTFE. The amount by which the sample thickness is reduced is a convenient measure of the degree of deformation. (Steckel rolling produces no change in specimen width or density.) Thus the extent of rolling is defined as the (percentage) reduction $100 \times (t_0 - t)/t_0$, where t_0 and t are the initial and final thicknesses. The final reductions in the fully rolled samples were 73% for POM and 62% for PTFE.

2.2. Pole figure technique

Wide-angle X-ray pole figures were obtained from all three polymers using cuboid specimens cut from the rolled samples: the cube edges were about 0.8 mm. A specimen was attached to a fine glass capilliary and mounted on a set of goniometer arcs of a Hilger and Watts 4-Circle diffractometer (CuK_α radiation). In each case automatic scanning was over a full hemisphere and the computer output corrected automatically for background and absorption. A third correction was made for inaccurate specimen alignment (often unavoidable with such small



(a)
(100)

(b)
(010)

(c)
(002)

Figure 1 Pole figures for hot-rolled nylon 66. (a) (100) pole, (b) (010) pole and (c) (002) pole. The plane of projection is the rolling plane.

specimens) on the diffractometer.

In all the pole figures shown below the measured intensities are normalized by dividing by the absolute intensity maximum. Thus each pole figure has a range of intensity contours labelled 1, 2, 3 . . . 9, representing respectively 10, 20, 30 . . . 90% of the absolute intensity maximum.

The orientation of poles is related to the principal axes of the macroscopic rolled sheet, which are labelled R (the rolling direction) T (the transverse direction) and N (the normal to the rolling plane). For rolling textures, it is common to plot hemispheres centred on N. In this study the nylon pole figures will also be plotted centred on N. For rolled POM and PTFE the pole figures are centred on R because this plot displays best the symmetry of the distribution.

3. Experimental results

3.1. Results for nylon 66

The measured pole figures for rolled nylon 66 are shown in Fig. 1. Nylon 66 is triclinic [1] and the three principal poles (100), (010) and (002) are shown respectively in Figs. 1a, b and c. In each case, the poles are mapped over a full hemisphere and projected onto the rolling plane (that is, centred on N). For the sake of clarity, not all contours are shown.

The dominant feature of Fig. 1a is a pair of (100) maxima concentrated in the NT plane at about 28° to the T direction. Also apparent is a weak maximum centred on N; this is a "ghost" caused by the overlap of the (010) reflection. The converse effect is seen in Fig. 1b, in which the dominant feature is the very sharp (010) maximum centred on N, with a pair of much weaker (100) "ghosts" in the NT plane. The reader should note that in Fig. 1b the spread of (010) poles is asymmetric, being greater in the NT plane than in the NR plane. The half-peak widths (contour level 5) are $\pm$ 16° in the NT plane, but only $\pm$ 10° in the NR plane. This is partly due to the above overlap; the point will be pursued further in the discussion.

The distribution of (002) poles is very broad and ill-defined, Fig. 1c. The (002) poles are concentrated near the NR plane at about 50° to N. There are also three extraneous peaks in the NT plane caused by the lack of resolution between the (002) reflections and the very much stronger (100) and (010) reflections. The lower symmetry of the (002) pole figure about the expected mirror planes NR and NT (in contrast to the (100) and (010) pole figures) is attributed to a combination of the intrinsic weakness of the reflection and the relative diffuseness of the distribution.

3.2. Results for polyoxymethylene and polytetrafluoroethylene

POM has a hexagonal unit cell. The strongest reflection is from the $(10\bar{1}0)$ prismatic faces [20]. The next strongest reflections are $(10\bar{1}5)$ and $(11\bar{2}5)$, while the (0009) reflection is extremely weak [20]. The latter arises from the 9/5 helix of the polymer chains. Pole figures for the $(10\bar{1}0)$ and (0009) poles in hot-rolled POM are shown in Fig. 2a and b respectively. PTFE also has a hexagonal unit cell above 19°C, and again $(10\bar{1}0)$ is the strongest reflection. Between 19 and 30°C torsional oscillations along the backbone reduce the *c*-axis order [21]. The ambient temperature during the PTFE diffractometry was (regrettably) about 30°C, so that no $(000l)$ reflection was available for mapping. The $(10\bar{1}0)$ pole figure was the only one measured for hot-rolled PTFE, and this is shown in Fig. 2c.

The POM $(10\bar{1}0)$ poles (Fig. 2a) show low intensity background contours confined close to the NT plane (fibre texture), but with six pronounced maxima at 0, 60, 120, 180, 240 and 300° to the normal direction N. These maxima arise from the six equivalent $(10\bar{1}0)$ reflections from the hexagonal unit cell. The orientation of this six-point pattern with respect to N is such that the unit cell is aligned with one of the $(10\bar{1}0)$ prism faces parallel to the rolling plane. This effect was checked by measuring the $(11\bar{2}5)$ pole figure (not shown) and noting again a six-point pattern of maxima, but this time at 30, 90, 150° etc. to N.

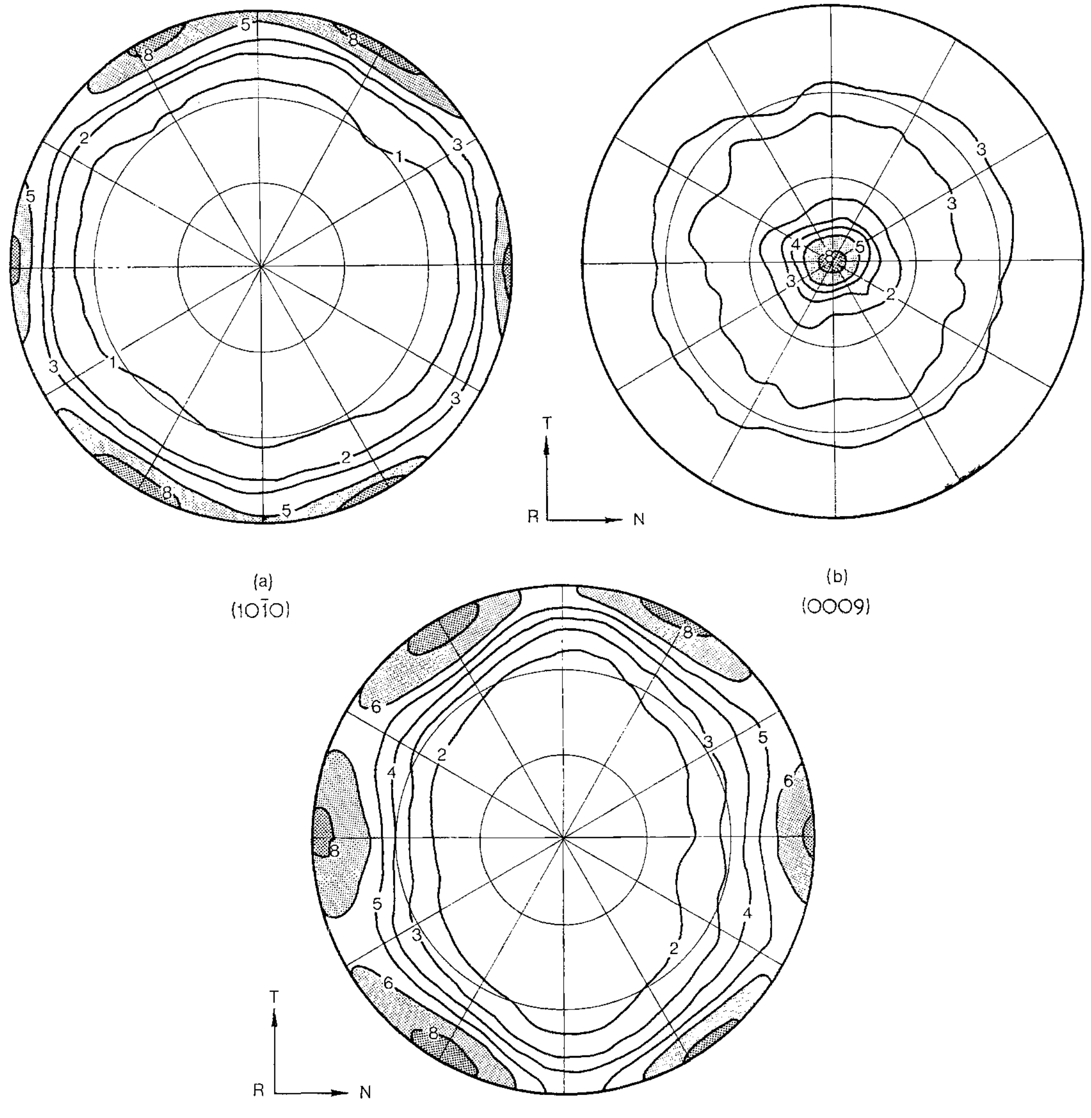
The (0009) pole figure (Fig. 2b) is the first direct measure of molecular chain orientation in POM, and shows a strong *c*-axis alignment parallel to the rolling direction R. There is also a weaker maximum (contour level 3) in this figure, which appears as a ring at about 55° to R. This is a "ghost" from the neighbouring $(11\bar{2}5)$ poles.

The $(10\bar{1}0)$ pole figure for hot-rolled PTFE is strikingly similar to the $(10\bar{1}0)$ pole figure for POM (compare Fig. 2a and c). Again, the characteristic six-point pattern signifies a unique setting of the hexagonal unit cell with the $(10\bar{1}0)$ prismatic faces aligned parallel to the rolling plane. Experimental difficulties with rolling PTFE limited the final rolling reduction to 62%, as compared to 73% for rolled POM. Thus we assume that the molecular chain orientation is not so high as in POM. This is supported indirectly by noting that, in the two $(10\bar{1}0)$ pole figures, the half-width spread out of the NT plane (contour 5) is about 20° for PTFE, but only 10° for POM.

4. Discussion

4.1. Crystal plane orientation in nylon 66

The early work of Bunn and Garner [1] on the crystal structure of nylon 66 established that the (010) crystal plane coincided (or very nearly) with the plane of the hydrogen-bonding between adjacent molecular chains. Bunn and Garner also showed that in a nylon fibre that was subsequently rolled, the (010) crystal planes lay preferentially in the rolling plane, without



(a)
(10$\bar{1}$0)

(b)
(0009)

(c)
(10$\bar{1}$0)

Figure 2 Pole figures for hot-rolled POM and PTFE. (a) (10$\bar{1}$0) pole for POM, (b) (0009) pole for POM and (c) (10$\bar{1}$0) for PTFE. The pole figures are centred on R, the rolling direction.

affecting the *c*-axis alignment of the fibres. A similar result was also obtained by Tanaka *et al* [22]. If in directly rolled nylon 66 the texture is simply the Bunn and Garner type uniplanar-axial orientation, then the measured pole figures should be consistent with the four independent orientations of the triclinic unit cell. These four orientations of the unit cell are shown in Fig. 3 and are labelled I, II, III and IV. Each has a common direction (*c*-axis parallel to R) and a common plane ((010) parallel to the rolling plane). When viewed in *c*-axis projection (along R) there are now only two independent settings of the unit cell. These are shown in Fig. 4a and labelled I(II) and III(IV). In both cells, the plane of the zig-zag methylene sequences is indicated by a heavy line.

The predicted pole figures for this ideal (Bunn and Garner) uniplanar-axial orientation in rolled nylon 66 are shown schematically in Fig. 4b.

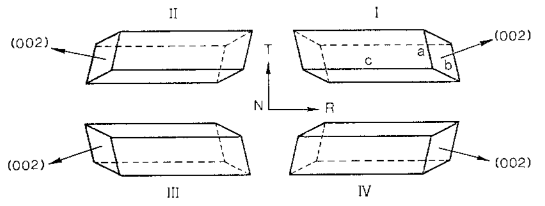


Figure 3 Idealized Bunn and Garner orientation in rolled nylon 66. The four possible orientations of the unit cell (I, II, III, IV) are viewed along N, the normal to the rolling plane.

The position of three principal poles is calculated from the triclinic geometry of the unit cell of α nylon 66. The (010) pole is, by definition, centred at N; the (100) poles appear as a pair of singlets at 24° to T in the NT plane and the (002) poles as pair of doublets at 50° to N and ± 13° away from the NR plane. This predicted pole figure compares fairly well with the measured pole figures. Fig. 1b shows (010) poles centred on N, although they are more spread in the NT plane than in the NR plane. The broad distributions of (002) poles (Fig. 1c) are centred at about 50° to N, and are entirely consistent with a pair of (002) peaks separated by ± 13° from the NR plane. The only significant departure from the predicted pole figure is that the measured (100) poles of Fig. 1a are centred on the NT plane at 28° to T, rather than 24° to T as predicted. We shall return to this discrepancy later, but for the moment assert that the measured pole figures approach those expected from a Bunn and Garner uniplanar-axial orientation. It is convenient at this stage to discuss the recent rolling theory of Akahane and Mochizuki [10] and examine its relevance to rolled nylon 66.

4.2. Molecular plane orientation in nylon 66

Akahane and Mochizuki [10] (A-M) have suggested that, in rolled polymers that contain planar zig-zag chains, uniplanar-axial orientation does *not* involve the alignment of a low index crystal plane into the rolling plane. Rather, it is the plane of the zig-zag chains that is aligned. Their evidence for this comes from three rolled polymers, polyvinyl alcohol, polyethylene terephthalate and nylon 6. In each polymer Akahane and Mochizuki [10] found disagreement between the observed unit cell inter-planar angles and those calculated by assuming that it was a crystal plane that aligned into the rolling plane. For example, in nylon 6, it is commonly believed that the (002) hydrogen-bonded planes align parallel to the rolling plane [23]. Akahane and Mochizuki [10] remove the apparent discrepancies between the inter-planar angles by interpreting the broad (002) diffraction profile as a pair of (002) peaks separated by ± 5°. The (002) planes are then tilted out of the rolling plane by 5°. This tilt is close to the 7° tilt of the zig-zag plane with respect to the (002) plane and it is for this reason that it is proposed that the zig-zag plane is parallel to the rolling plane [10].

The evidence for the A-M theory of molecular plane alignment is not overwhelming, partly because the tilt angles involved are so small (for example, in polyvinyl alcohol, it is only 2°). However, in nylon 66 the tilt angle is about 20°,

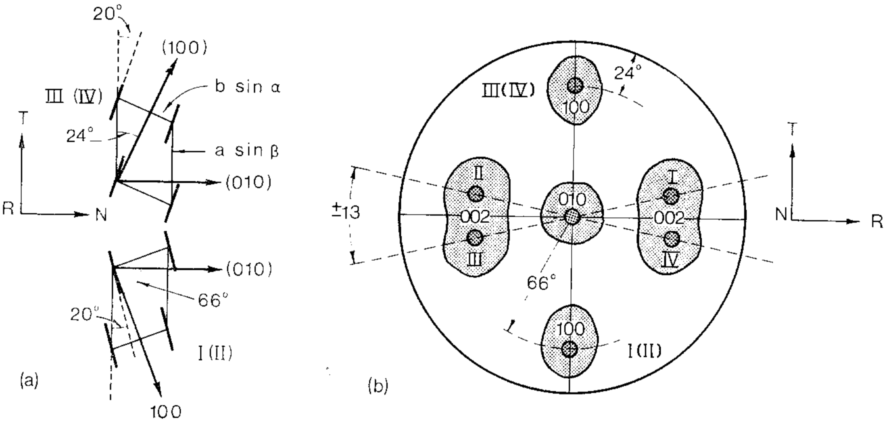


Figure 4 Bunn and Garner orientation in rolled nylon 66. (a) unit cells viewed along the rolling direction (basal plane projection). (b) Predicted pole figures.

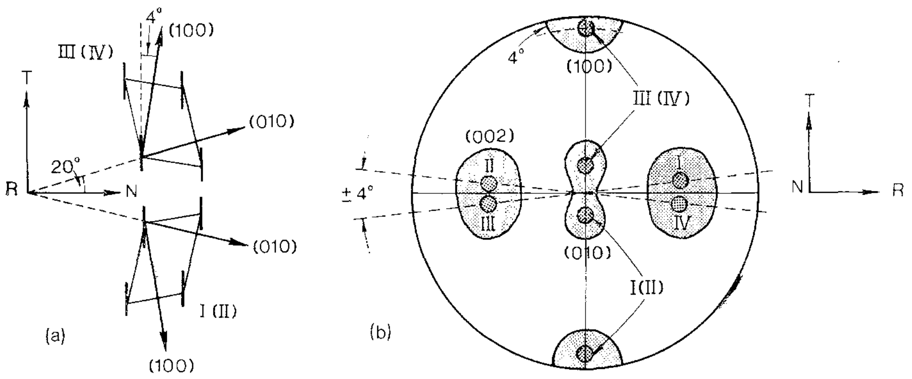


Figure 5 Akahane and Mochizuki orientation in rolled nylon 66. (a) Unit cells viewed along the rolling direction. (b) Predicted pole figures.

so that the effect of molecular plane alignment should be quite apparent. In both nylon 6 and nylon 66 the molecular chains are fully extended planar zig-zags, while in basal plane projection the two crystal structures are closely similar [23]. There is, however, a difference between the two nylon crystals in the setting of the zig-zag plane. In nylon 6 the zig-zag plane is tilted away from the (002) hydrogen-bonded plane by 7° towards the *longer* diagonal of the basal plane projection [23] (that is a projection onto a plane normal to the molecular axis, which in monoclinic nylon 6 is the *b*-axis). In nylon 66, the zig-zag plane is tilted away from the (010) hydrogen-bonded plane by 20° towards the *shorter* diagonal of the basal plane projection (this time the *c*-axis projection) [1]. This tilt angle of 20° is shown in Fig. 4a for the I(II) and III(IV) orientations of the unit cell.

If the A-M theory is correct for nylon 66 then the I(II) oriented unit cell has to be rotated clockwise by 20° about the molecular axis (R) so as to bring the zig-zag plane parallel to the rolling plane. Similarly, the III(IV) oriented unit cell has to be rotated anti-clockwise by 20°. The new orientations of the unit cell (still in *c*-axis projection) are shown in Fig. 5a. A schematic pole figure for the A-M theory is shown in Fig. 5b. The above rotations split the (010) poles into a doublet in the NT plane centred at ± 20° to N. The (100) singlets are shifted to 4° from T and the (002) doublets are now 48° from N and ± 4° from the NR plane.

The A-M theory is unacceptable for rolled nylon 66. The measured (100) pole figure (Fig. 1a) shows no evidence for maxima in the NT plane at only 4° from T. Also, it is difficult to consider the measured (010) profile in the NT plane to be an unresolved doublet separated by 40°, when the total half-width is only 32° (Fig. 1b).

4.3 The location of the (100) pole in nylon 66

To recapitulate, the measured pole figures for rolled nylon 66 are more consistent with a uniplanar-axial orientation of the Bunn and Garner type (crystal plane) than the Akahane and Mochizuki type (molecular plane). There remains, however, the problem that if the (010) planes are exactly coincident with the rolling plane, then (100) poles should appear at 24° to T, and not 28° as observed. We examine in turn three possible explanations of this discrepancy.

4.3.1. Rotations of unit cell

Consider counter rotations of the I(II) and III(IV) species (Fig. 4a) by 4° in the opposite senses to those required for the zig-zag plane alignment (A-M theory). This has the effect of splitting the (010) pole into a doublet at ± 4° to N, with the (100) pole shifted to 28° to T. (Such rotations do not greatly affect the position of the (002) poles.) However, the existence of such a texture imparts a special significance to the plane tilted away from the (010) plane by 4° towards the longer diagonal of the basal plane projection of the unit cell (Fig. 4a). The only possible reason for such an alignment would be if the plane of the hydrogen bonds was not the (010) crystal plane but this new 4° tilt plane.

4.3.2. Distortion of the unit cell

The 24° angle between the (100) poles and T is

TABLE I Comparison of measured lattice spacings with those of the α-structure of nylon 66

Reflection (*hkl*)	Observed Bragg angle $\theta_B(\text{Cu}K_\alpha)$	Observed lattice spacing	Bunn and Garner spacing
(100)	10.21 ± 0.04°	4.35 ± 0.02 Å	4.36 Å
(002)	6.80 ± 0.08°	6.51 ± 0.08 Å	6.40 Å
(010)	11.51 ± 0.04°	3.86 ± 0.02 Å	3.69 Å

derived from the three angles of the triclinic unit cell of the α-structure [1]. The fact that the observed angle is 28° raises the possibility that in hot-rolled nylon 66 the unit cell differs slightly from the one proposed by Bunn and Garner [1]. This is borne out by comparing the measured and calculated lattice spacings (see Table I). The (100) spacing is in exact agreement with the Bunn spacing, but the (002) is about 2% greater than expected. Lattice spacings for (002) greater than the theoretical 6.40Å have recently been observed in mats of solution grown nylon 66 crystals [24]. More significant, however, is the (010) spacing which is almost 5% greater than expected from the Bunn structure.

It is know that cell dimensions in polyethylene are influenced by mechanical deformation and by annealing [25], while in nylon 6 water content is also a factor [26]. But in both cases the changes in lattice spacings are an order of magnitude smaller than the discrepancies found in the present case. Yet we conclude from Table I that in hot-rolled nylon there must be some distortion from the ideal α-structure. This could certainly be a contributing cause of the (100) pole anomaly.

4.3.3. *Overlapping reflections*

Clark [27] has suggested that (100) poles could be shifted by overlap with the much stronger (010) poles. Even more likely is overlap with the strong (110) reflections. These occur at practically the same Bragg angle as for (010) and are very close to (100) poles, being in the NT plane at 40° to T, compared to 28° as observed for (100). Overlap also explains the broader distribution of intensity in the NT plane.

Of these three explanations we find not one which is entirely satisfactory. The resolution of the problem of the (100) pole location awaits further experimental evidence.

4.4. Uniplanar-axial orientation in polyoxymethylene and polytetrafluoroethylene

The rolling texture of hexagonal metals is that of a uniplanar-axial orientation, in which close packed slip planes align parallel to the rolling plane and a slip direction parallel to the rolling direction [16]. In hexagonal polymers, such as POM and PTFE, the $(hki0)$ planes of densest molecular packing are the $(10\bar{1}0)$ planes. The most likely slip system in POM and PTFE we take to be $(10\bar{1}0)$ [0001]. According to the most elementary model for rolling we anticipate a uniplanar-axial rolling texture in which the molecular chain axes are aligned parallel to R and one of the six equivalent $(10\bar{1}0)$ prismatic faces of the hexagonal unit cell are parallel to the rolling plane. This is shown schematically in Fig. 6. The measured pole figures show precisely this texture. Fig. 2a and c confirm the unique orientation of the hexagonal cell faces for both POM and PTFE, and Fig. 2b confirms the chain alignment in POM. These rolling textures are so inherently simple and in accord with elementary principles that it is surprising that they have not been observed before. In our view the difference is primarily due to the high temperature of rolling in our experiments as opposed to the cold-rolling methods used by most authors.

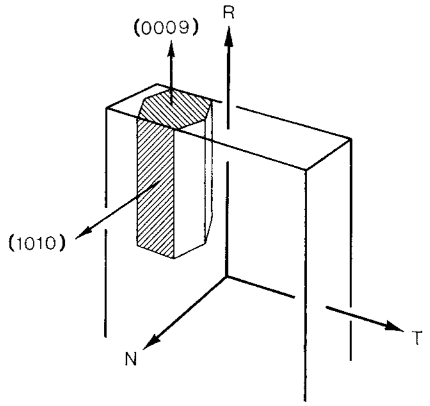


Figure 6 Idealized uniplanar-axial orientation in POM and PTFE, showing the relation between the hexagonal unit cell and the rolled sheet.

4.5. Orientation differences between hot-rolled and cold-rolled POM

Gezovich and Geil [3] have studied the deformation of cold-rolled POM for a variety of different rolling reductions up to 72%. These authors present both wide- and small-angle pole figures, but their analysis of the rolling textures is hampered by not having (0009) pole figures. Instead, molecular chain orientation is inferred by comparing $(10\bar{1}0)$ and $(10\bar{1}5)$ pole figures. For small rolling reductions (less than 50%) chains tilt preferentially at about 30° to R, but as the reduction is increased further the chains become parallel to R [3]. Comparisons between the rolling texture produced by cold-rolling [3] and that for hot-rolling can only be made for the fully rolled specimens. In the cold-rolled polymer, Gezovich and Geil [3] report a final reduction of 72%, which compares with the 73% for the hot-rolled specimen described in this paper.

In the cold-rolled specimen (72% reduction in thickness) Gezovich and Geil find $(10\bar{1}0)$ orientation tending towards that of a fully drawn fibre: the $(10\bar{1}0)$ poles are distributed mainly in the NT plane with a maximum in the T direction, contrary to our observations, Fig. 2a. Gezovich and Geil note also that in the cold-rolled POM there are weak $(10\bar{1}0)$ maxima parallel to the R direction. This implies that some molecular chains are perpendicular to the rolling direction in cold-rolled POM, again contrary to our observations on hot-rolled POM, Fig. 2b.

Gezovich and Geil [3] have explained the quasi-fibre texture of cold-rolled POM, in which $(10\bar{1}0)$ poles tend to lie along the T direction, by assuming that the molecular *c*-axes are preferentially inclined at some angle to the roll direction (R) out of the roll plane (RT). Then by allowing crystals to be randomly oriented about their *c*-axes, the desired $(10\bar{1}0)$ maxima along T may be rationalized. Without (0009) pole figures this interpretation is not conclusive. An alternative explanation of the $(10\bar{1}0)$ maxima along T has recently been reported by Preedy and Wheeler [28]. These authors also find the peculiar Gezovich and Geil texture in POM, this time by rolling at a sub-ambient temperature. Preedy and Wheeler [28] suggest that POM transforms to the orthorhombic phase [29] during low temperature rolling, producing a (100) [001] texture. In this case, the strong maxima along T are due to (020) poles. Upon annealing [28], POM reverts to its normal hexagonal form, resulting in a final rolling texture that tends towards $(11\bar{2}0)$ [0001]. This latter texture was also observed by Gezovich and Geil after annealing [3], although it is clear from their pole figures (Fig. 16, ref. 3) that there is still some *c*-axis tilting.

It remains to be seen whether orthorhombic material is indeed present in cold-rolled POM: pole figures alone are inconclusive evidence for this since the Bragg angles for hexagonal $(10\bar{1}0)$ and both orthorhombic (110) and (200) are so close to each other [29], that rolling orientations are insufficiently high to resolve them. In POM rolled at 126°C there is no chance of any orthorhombic orientation, as the latter phase is unstable above 60°C [30].

Clearly, there is a substantial difference between the hot- and cold-rolled POM textures; but there are also several differences between our experiment and that of Gezovich and Geil [3]. These include the following:

1. type of rolling, in our case Steckel rolling, as opposed to conventional rolling;
2. temperature of rolling, in our case 126°C as opposed to room temperature;
3. rate of rolling, in our case 0.01 in. sec^{-1} as opposed to 1 in. second.

Which of these factors is the more important can only be decided by further experiment. It could be that the tensile stress that follows the roller in Steckel rolling plays an important role (1). Another feature of our rolling experiment may also be important. Prior to high temperature Steckel rolling, a nip is produced in the initially isotropic specimen by application of roller compression at room temperature. This compression imparts a weak $(10\bar{1}0)$ [0001] texture in the region of the nip (there is no sign of any (100) [001] orthorhombic texture, despite roller compression being applied well below the 60° transition). Steckel rolling of POM at 126°C then simply accentuates this $(10\bar{1}0)$ [0001] precursor texture throughout the sheet. In our view, however, the high temperature but very low deformation rate (2, 3), are of greater significance in producing a texture so different from that in cold-rolled POM.

It is important to study the rolling of POM much further in view of the above differences and also because of the relationship between crystal slip systems and rolling textures. It is clear that at low temperatures the slip system operating in POM is complex, and may involve a phase transformation, but at high temperatures our results show that for POM and PTFE the slip system is, as expected, $(10\bar{1}0)$ [0001].

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