QUANTITATIVE POLE FIGURE ANALYSIS OF ORIENTED POLYETHYLENE FILMS

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ABSTRACT

Depending on their molecular compositions and thermomechanical histories, extruded polyethylene (PE) films can exhibit large variations in their (usually row-nucleated) semicrystalline morphologies. In order to measure their textures quantitatively, we have optimized a procedure for the acquisition and analysis of x-ray pole figure data. Film orientation studies are often concerned with the alignment of PE molecules relative to the process machine direction (MD), thus it is of great interest to obtain a quantitative distribution of the (002) pole figure, which is parallel to the crystalline chain axes but cannot be directly measured. Using the popLA software suite this is achieved through successive mathematical operations. The first manipulation entails tilting the (110), (200) and (020) pole figures in order to project their distributions onto a plane perpendicular to MD. Next a quantitative orientation distribution function (ODF) is calculated to produce a set of fourth order generalized spherical harmonics. From these coefficients the original pole figures are recalculated and the (002) pole figure is generated. We then plot the distribution of crystalline chain axes relative to MD. We conclude that the c-axis distributions are generally not radially symmetric about MD, an assumption that is inherent in second order analyses, such as Hermans' function or directional cosine approaches. Orientation variations have been observed in films made by different processes, as well as in films made by a given process but under different conditions. Distinctly different orientation distributions are also seen in films made under identical conditions, but with different molecular compositions.

INTRODUCTION

Polyethylene films produced by cast and blown tubular extrusion processes represent one of the largest classes of widely used polymeric materials; accordingly, PE films have been studied extensively. Much has been done in the literature to categorize the various semicrystalline morphologies present in pristine films and to understand the development of texture during the extrusion process. In these studies the term "orientation" has been applied in a number of ways.

Some authors relate the three principal crystalline axes of the microcrystallites to the three principal processing directions: the direction along the length of the process line or machine direction (MD), the direction across the width of the process line or transverse direction (TD) and the film normal direction (ND). Others refer to the relationship of a given polymer chain relative to the rest. For our purpose we adopt a simple yet practical definition for orientation in an extruded film as "the relative number of molecular chains parallel to MD." It is rooted in the concept of chain elongation relative to the principal processing direction, and is not confined to chains within crystallites.

Characteristic of PE film extrusion is the evolution of a very complex structure caused by parallel crystallization and orientation mechanisms. Widely used variables associated with extrusion processing are the temperature, $T_m$, draw ratio (Dr), blowup ratio (Bur), film thickness, freeze line height and axial take-up velocity. Microstructures can also vary with molecular parameters such as MW, MWD, branching, melt viscosity, axial and transverse stress components and melt relaxation time.
As a semicrystalline polymer, PE exists as two phases: a crystalline phase wherein the chain segments pack together in a regular way, and an "amorphous" phase in which the chains assume a disordered (albeit often oriented) arrangement. The chains are parallel to the c-axis in the orthorhombic PE unit cell. The packing of the chains is different in the a-direction than along the b-direction. As a consequence the crystals grow at different rates and deform differently along these two directions.

The fundamental crystalline habit produced by the packing of PE unit cells is a lamellar platelet in which the c-axes of the chains are perpendicular, or nearly so, to its broad basal surface. The b-axis is the direction of fast growth of these crystallites, so that a general lamella is shaped more like a ribbon than a platelet. Twisting lamellar ribbons grow radially outward from their nucleation sites and the final geometry of the resulting superstructure is strongly influenced by the type of nucleation center, the stress under which crystallization occurs, and the density, e.g. structure, of the molecules.

The bulk properties of films are determined by their degree of crystallinity and type of lamellar bundling, intercrystalline connectivity and preferred orientation of chains in both the "amorphous" as well as crystalline fractions. Many studies have attempted to make correlations between the microcrystalline texture and physical performance parameters (esp. tear strength). There also have been numerous studies on the variation of texture within deformed films in order to understand their failure mechanisms. Wide angle x-ray diffraction pole figure analysis provides a quantified assessment of the microcrystalline texture in oriented materials.

In an oriented material, the relative intensity of the Bragg peaks varies as the sample is rotated with respect to the incident beam, and it is the graphical display of this intensity variation plotted as a function of sample tilt which generates a "pole figure". A separate pole figure can be obtained for each different Bragg diffraction condition that is satisfied by the sample, and is of sufficient intensity (i.e. a "pole") to be monitored as the sample is tilted about the Euler angles. Each pole figure is a stereographic projection that transforms the 3-dimensional data set into a planar representation and plots the number of diffraction plane normal vectors as a function of their direction within the sample.

We have optimized the pole figure generation capabilities of our diffractometer for application to PE films. In PE, three sets of crystal planes have Bragg reflection intensities that are strong enough to be monitored for the production of a pole figure. Their Miller indices are: (110) the strongest, (200) of lesser intensity and parallel to the crystal a-axis, and (020) also of lesser intensity but parallel to the b-axis. After the raw data has been collected, each pole figure must be corrected for background contributions and absorption effects. Additional processing by our "in-house" software formats pole figure data for input to "popLA" (Pole figure Orientation Programs - Los Alamos), a public domain pole figure processing and display program suite. This allows pole figure data to be manipulated (e.g. rotated) and displayed in popLA's conventional fashion, but also enables data to be imported to other mathematical processing and display software packages. In addition to qualitative comparisons, the "popLA" suite provides for an unprecedented level of quantification through its ability to generate orientation distribution functions (ODFs) in the form of generalized spherical harmonics. This provides the ability to quantify orientation in terms of a three dimensional distribution, and affords a tremendous advantage over traditional second order quantitative analyses, which just provide a single number average. Using three complete pole figures, Roe-Krigbaum coefficients can be generated up to fourth order for PE films. Using these coefficients as input, "popLA" can generate the (002) c-axis pole figure, which cannot be directly measured. The thirteen ODF coefficients can also be imported into other programs, for example, in order to investigate mathematical correlations between them and any number of processing and performance variables.

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DATA ACQUISITION

Crystalline texture analysis by means of wide angle x-ray diffraction pole figures measures the orientation of crystallites in polycrystalline materials with respect to processing directions. This is functionally achieved with an experimental configuration that monitors the intensity of a given Bragg reflection as the sample is incrementally tilted about the full range of Euler angles.

Prerequisite to the generation of quantitative orientation distribution functions (ODF), however, is the need for quantitatively accurate x-ray diffraction measurements. For polyolefin samples this entails in-depth determination of optimal slit widths, background subtractions, absorption coefficients, and the mathematical addition of reflection and transmission data used to obtain complete pole figures. Our data acquisition methods address hardware issues that optimize the experimental configuration to ease operation as well as maximize signal/noise ratios. Much of this work has consisted of empirical measurements for optimizing the experimental geometry and ascertaining the linear response of our detector assembly.

Although the manufacturer’s manuals recommend operating conditions which can produce distinctly recognizable wide angle diffraction profiles for polymers, we have determined that the optimal data acquisition conditions for polyolefins are functions of sample thickness, angular divergence of the source and angular convergence at the counter. In our experimental geometry, a complete pole figure is formed from two sets of measurements: one in which the beam is transmitted through the sample and the other in which the beam is reflected relative to the sample surface. With this system we have been able to produce high quality data which reveal a wide range of orientation for several sample sets.

But the most significant procedural improvements have been software developments in the areas of background subtraction and absorption correction as well as in data smoothing and display. An important software feature allows the corrected data to be formatted as input to the popLA suite for advanced computational analysis of pole figures.

Subtraction of an accurately determined background is an important step in the quantification of pole figures. The intensity of the background underneath any given diffraction peak must be subtracted from the total peak intensity in order to obtain diffraction intensities which represent information from only the crystalline fraction. The importance of high precision background measurements is emphasized when arbitrary background values are used to process a raw data set. Huge changes are observed in the corrected pole figure for just small variations in background values. Thus painstaking accuracy must be employed to ensure the validity of quantitative pole figure analysis. After much empirical work with pressed pads and other methods of trying to eliminate crystal orientation we determined that a background signal from the low angle scattering edge of the broad peak, upon which the sharper crystalline peaks sit, furnishes a straightforward and internally normalized intensity for the scattering contribution from the noncrystalline fraction. For us this entails the acquisition of another complete set of pole figure data, collected at a θ which is not a Bragg angle, but rather monitors the intensity of the amorphous halo.

A direct measurement of the sample’s linear absorption coefficient is also necessary. As the sample is tilted away from the incident beam normal condition, the effective thickness that the x-rays must traverse increases. Because density and thickness of the sample have an effect on x-ray intensities either transmitted through or reflected off the sample, x-ray data must be corrected for absorption in order to be quantitative. After correcting for the background and doing absorption calculations with arbitrarily selected values, it becomes clear that data correction is, in fact, extremely sensitive to the linear

absorption coefficient, \( \mu \), used in the calculation. Due to complicated changes in \( \mu \) resulting from changes in crystallinity, we find tabulated values to be inapplicable for our types of semicrystalline hydrocarbon materials. This plus the fact that sample thickness measurements are relatively awkward and inaccurate suggests that, if we are to be quantitative in our analyses, \( \mu T \) (\( T \) = thickness) for each specific sample must be independently measured. Thus we now employ a Beer's law method for directly measuring \( \mu T \).

After dealing with the assorted complications, we have established a reproducible and relatively fast method for obtaining high quality, quantifiable WAXPF data from oriented polyolefin (esp. PE) films. A complete quantitative data "set" includes a measurement of the linear absorption (e.g. "\( \mu T \"), three WAXRD patterns: one in reflection mode and two in transmission mode with MD horizontal and vertical, raw pole figures about three distinct crystallographic axes, and background pole figures for each of the corresponding poles. All this data is obtained from a single sample, mounted but once in a single sample manipulator (e.g. the pole figure attachment).

To illustrate the efficacy of our improved methods we employ a sample set of LLDPE films, comprised of two different resins fabricated under four different process conditions: cast at high and low draw ratios, and blown at high and low blow-up ratios (cf. Figure 1). These films exhibit substantial differences in their toughness properties, and provide important insight about stress-induced crystal growth. The textures of all these films indicate some degree of "row-nucleated" structure, wherein the \( b \)-axes (the direction of fast crystal growth) are roughly perpendicular to the machine direction (MD). For cast films, the \( b \)-axes point mostly along the transverse direction (TD). For films blown under high transverse stress (e.g. blow-up ratios), a substantial normal direction (ND) component of \( b \)-axis orientation becomes superimposed on the TD growth patterns. This suggests that the preferred direction of crystal growth for extruded films lies in the plane of the film, along TD. However, for films blown with higher transverse stresses, a growth component emerges along ND (the quenching thermal gradient).

![Figure 1. Row Nucleation in LLDPE Films.](image-url)
DATA ANALYSIS

To understand why an extruded film sample displays a given mechanical response when stressed, it is necessary to understand the physical processes involved during deformation. Knowledge of the microstructure can be gained from various characterization methods including optical birefringence, polarized IR absorption, thermal analyses, high resolution microscopy, and small angle neutron and x-ray scattering. None of these methods provides a complete and quantitative characterization, rather they form a complementary data set from which information about total chain orientation and crystallite dimensions, as well as lamellar sizes and organization can be inferred. It is also difficult, and in many cases impossible, to adequately quantify lamellar orientation distributions from such a collection of data.

If the distribution of crystallographic axes can be assumed to have cylindrical symmetry about the principal processing directions, then an orientation distribution function for any given axis inclined at an angle $\theta$ relative to any given direction can be expressed as a Legendre polynomial of order $n$.

$$
\langle P_n \rangle = \frac{\int_0^{\pi/2} I(\theta) \sin(\theta) P_n(\cos \theta) d\theta}{\int_0^{\pi/2} I(\theta) \sin \theta d\theta}
$$  \hspace{0.5cm} (1)

For $n = 2$ the three most popular methods for determining molecular orientation have been optical birefringence, infrared dichroism and x-ray diffraction, and the second order Legendre polynomial reduces to the well known "Hermans" orientation function, also simply referred to as "P2":

$$
\langle P_2 \rangle = P_2(\cos \theta) = \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right).
$$  \hspace{0.5cm} (2)

Some Raman, fluorescence and NMR methods can also provide "P4" data. This is adequate for cases involving fiber symmetry, but has proven to be inadequate for systems with orthorhombic symmetries (such as PE films). Only WAXRD can provide information which can express $\langle P_n \rangle$ to higher orders in non-cylindrical systems.

Some authors have attempted to expand the applicability of second order ODFs to film geometries by forming linear combinations of P2 functions that represent different axes arranged about different directions. The case of a 2-dimensional Hermans' distribution function is shown graphically in Figure 2a.

Figure 2. Graphical representations of second order ODFs.
For parallel orientation along MD (complete chain alignment), $P_2 = +1$. For perpendicular orientation along MD (complete chain anti-alignment), $P_2 = -1/2$. And for isotropic orientation relative to MD (complete randomness), $P_2 = 0$. An alternative but equivalent second order expression of the average crystalline axes alignment relative to the film processing directions can be represented graphically in terms of their directional cosines (Figure 2b).

For polymers $<P_2>$ represents the statistical average of the chain axes with respect to some preferred processing direction (e.g. MD); it depends on the relative intensity, angular position and shape of the orientation distribution. Consequently, a given $<P_2>$ value can correspond to any number of different distributions. A second problem associated with using $<P_2>$ as the only quantification parameter is that a null value can be obtained for either an isotropic sample, as would be expected, or for a highly oriented sample with a narrow conical distribution of chains inclined at $\theta = 54.7^\circ$ (the so-called "magic" angle). A final difficulty that arises from using Legendre polynomials to express orientation is the assumption of cylindrical symmetry. Films have orthorhombic symmetry and, consequently, the expansion of ODFs in a Legendre series is unwarranted. In addition to these three difficulties, it is also true that numerous attempts have failed to correlate $<P_2>$ numbers with a myriad of performance properties (tear strength, stress coefficients, degree of row-nucleation, et. al.) Thus it is clear that $<P_2>$ taken alone is not suitable for quantifying the distribution of molecular chains in extruded PE films.

As an alternative here we pursue a more comprehensive approach that employs generalized spherical harmonics (of which Legendre polynomials are a subset) as the expansion series for expressing unique order distribution functions. This approach is significantly more complicated than the cylindrical harmonics method and has only recently (thanks to the emergence of the new generation of computers) been feasible for application by non-specialists. This methodology provides the ability to calculate and plot "missing" pole figures, e.g. the (002) distribution of crystalline chains, and from this we are better able to make sense out of $<P_2>$ or direction cosine expressions. C-axis pole figures can also provide a guide to sampling the most representative lamellar populations by high resolution microscopy.

Higher order ODFs are expressed in terms of generalized spherical harmonics, an $n$th order three dimensional series expansion. The highest order of the expansion, $n$, is determined by the symmetry of the unit cell (orthorhombic for PE), the symmetry of the sample (orthorhombic for a film), and the amount of data (e.g. number of pole figures = 3 for PE).

$$w(\theta, \phi, \eta) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=-m}^{m} W_{lmn} Z_{lmn}(\cos \theta) e^{-im\phi} e^{-in\eta}$$  \hspace{1cm} (3)

The resulting $W_{lmn}$ or "Roe-Krigbaum" coefficients are the $lmn$th moments of the ODF, which result directly in the $f_{lmn}$ orientation factors.

$$f_{lmn} = 4\pi^2 \left[ \frac{2l + 1(l + m)(l + n)!}{2(1 - m)!(1 - n)!} \right]^{1/2} W_{lmn}$$  \hspace{1cm} (4)

It should be noted that the Legendre polynomials are inherent in the spherical harmonic expansion as the $f_{l00}$ ($l$ = even terms, i.e. $f_{200} = <P_2>$, and $f_{400} = <P_4>$). Hence our second order distribution functions can be derived directly from the Roe-Krigbaum coefficients for comparison with second order values measured by other methods.

Up to this point, all of our pole figure displays have mapped MD to the top and TD to the sides to provide a view of the pole distributions sighting down ND. This choice of projections is a direct result of the nature of data collection wherein the x-ray beam is in large transmitted through the sample. However, the choice of projection is arbitrary and can be changed easily using popLA to rotate the pole figures by $90^\circ$ about some selected axis. As illustrated here in Figure 3, we have rotated the (110), (200)
and (020) distributions by 90° about TD in order to project them along MD (this is the first step towards quantifying the "orientation" according to our practical definition, because it rotates all data for viewing down MD).

Figure 3. Rotation of Pole Figures Using “popLA”.

It is interesting that the (110) pole figure exhibits a toroidal distribution about MD, the (200) exhibits a conical distribution about MD, and the (020) is roughly equatorial about MD. It is also noteworthy that these distributions are not generally cylindrical about MD, which illustrates the error in assumption of cylindrical symmetry associated with using solely a Legendre expansion.
The ability to regenerate original pole figure distributions using our calculated $W_{lnn}$ coefficients as input to "popLA" is illustrated in Figure 4 for one of the films in our LLDPE study. Assuming two planes of mirror symmetry about the ND and TD axes, "popLA" only calculates the first quadrant of each pole figure.

For the purpose of direct comparison we have taken the original set of pole figures and rotated them for viewing the distributions of the crystallographic axes about MD (as in Figure 4). The fourth quadrants of these original data are displayed as the bottom of each (half) pole figure. The rotated pole figures are then used for calculating the $W_{lnn}$'s, which are then used to recalculate the original data. The recalculated pole figures are displayed as the top of each (half) pole figure. Although not exact, the recalculated (110) and (200) pole figures match up fairly well with the original data. The recalculated (020) does not match up quite as well, but does maintain symmetry and relative trends in intensity variations. From these we conclude that the recalculated pole figures are a reasonably fair representation of the original data.

Figure 5 illustrates the calculation of pole figures from the $W_{lnn}$'s determined from the original data for the same sample used in Figure 4. Note the recalculated (110), (200) and (020) pole figures match those shown in Figure 4. But here we also extract the distribution of the (002) pole figure which is also plotted. Finally we have obtained the direct graphical analog of our practical definition of orientation: "the relative number of molecular chains parallel to MD." This pole figure suggests that a population of crystalline c-axes points along all three processing directions, with a slightly higher population towards ND. There appears to be a strong depletion of c-axes centered at about 40° from ND towards MD.

![Figure 5. Calculation of c-axis (002) Pole Figures Using "popLA".](image)

Figure 6 shows the calculated (002) pole figure for each of the six films in our LLDPE sample set. Clearly there exists a wide variation in the relative alignments of their crystalline chain axes along MD.
The heavy concentration of c-axes centered at about 40° from ND towards TD in the cast films appears "inverted" compared to the depletion of c-axes in the same region for blown films fabricated from resin "A". The concentric distribution of chains in resin "B" (high Bur) is consistent with a low overall degree of orientation as we speculated earlier for a nearly isotropic material, and correlates with the highest MD tear.

Thus we conclude for our selected sample set:

a) In all films the b-axes are more or less perpendicular to MD. This suggests some degree of row-nucleation in all and that the direction of lamellar growth is confined to the TD/ND plane.

b) Preferential TD orientation of b-axes in cast films vs. preferential ND orientation in blown films suggests that there is some reorientation of lamellae during biaxial deformation.

c) Chain axes (c-axes) in cast films point strongly along the MD/ND equator but fall off sharply as ND is approached; whereas the c-axes are more isotropically distributed in blown films and more depleted along the MD/ND equator, and we have a strong ND component.

d) At high blow-up ratios, resin "B" leads to a relatively isotropic distribution of crystallites, while resin "A" leads to "uniaxial" type orientation about MD.

DISCUSSION

We have optimized the pole figure generation capabilities of our wide angle x-ray diffractometer for application to PE film samples. This has entailed much empirical work and custom computer programming focussed along the lines of determining the best options for removal of the amorphous background signal and learning how to compensate for x-ray absorption, as well as in data smoothing and display. An important software feature allows the corrected data to be formatted as input to the popLA suite for advanced computational analysis of pole figures. With this system we have been able to produce high quality data which reveal a wide range of orientation for several sample sets.

Because film orientation studies are concerned with the alignment of PE molecules relative to the process machine direction (MD), it is of great interest to obtain a quantitative distribution of the (002)
pole figure, which is parallel to the crystalline chain axes but cannot be directly measured. Using the popLA software this is achieved through successive mathematical operations. The first manipulation entails tilting the (110), (200) and (020) pole figures 90° about the transverse axis to project their distributions onto a plane perpendicular to MD. Next a quantitative orientation distribution function (ODF) is calculated to produce a set of fourth order generalized spherical harmonics. From these coefficients the original pole figures can be recalculated and the (002) pole figure is generated.

CONCLUSIONS
From the (002) pole figure we can determine the most representative sampling of lamellar populations for microscopy analyses. It is important to recognize that the c-axis distributions are generally not radially symmetric about MD, an assumption that is inherent in second order analyses, such as Hermans' function or directional cosine approaches. Orientation variations have been observed in films made by different processes, as well as in films made by a given process but under different conditions. Distinctly different orientation distributions are also seen in films made under identical conditions, but with different molecular compositions.

An important insight about stress-induced crystal growth has emerged upon examination of several blown and cast films comprised of various LLDPEs or HDPEs. The textures of all these films indicate a "row-nucleated" structure, wherein all the b-axes (the direction of fast crystal growth) are roughly perpendicular to the machine direction (MD). For cast LLDPE as well as HDPE films blown under low transverse stress, the b-axes point mostly along the transverse direction (TD). For films blown under high transverse stress (e.g. blow-up ratios), a substantial normal direction (ND) component of b-axis orientation becomes superimposed on the TD growth patterns. This suggests that the preferred direction of crystal growth for extruded films lies in the plane of the film, along TD. However, for films blown with higher transverse stresses, a growth component emerges along ND (the quenching thermal gradient).

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