ORIENTATION TEXTURE FROM POLYMERIC MATERIALS USING SCATTERING METHODS

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Abstract

Orientation is an important determinant of the end-use properties of many products made from polymers. Scattering methods using x-rays and neutrons provide direct means of assessing such orientation texture. Oriented microstructural features possessing distance scales on the order of 10 nm to 1000 nm manifest themselves through anisotropic small-angle scattering (SAS). Oriented semicrystalline polymers exhibit anisotropic scattering in the wide-angle diffraction (WAD) range. This presentation provides an overview of the theoretical and experimental basis for measuring and interpreting these effects. Data on oriented lamellar microstructures are used to demonstrate the challenges that arise in this area.

Introduction

Many polymer products are highly engineered materials derived from sophisticated processes that seek to control crystallinity and morphology. A great deal of effort is expended in attempts to elucidate the relationships between structure and properties in such materials[1,2]. Scattering methods are one useful way to characterize the structures resulting from such processing, which makes scattering methods important tools in process research. Unfortunately, most of the approaches to interpreting scattering data are largely qualitative because sorting out the quantitative complexities of the relevant methods has proved to be daunting.

This work seeks to provide guidance that might be used to bring modern computing power and modern computerized instrumentation to bear on the problem of characterizing anisotropic microstructure in industrially important polymeric materials. The approach is heavily mathematical in the hope that more plastics engineers will come to appreciate the potential for more quantitative descriptions of polymer morphology.

Scattering from Oriented Microstructures

The formal basis for using scattering methods to characterize orientation texture can be summarized by:

$$I(\underline{\mathbf{Q}}) \propto \int p(\underline{\underline{\mathbf{R}}};\underline{\mathbf{A}}) \left| F(\underline{\underline{\mathbf{R}}}\underline{\mathbf{Q}};\underline{\mathbf{A}}) \right|^2 d^3\underline{\underline{\mathbf{R}}}\, d^m\underline{\mathbf{A}}. \quad (1)$$

Eqn. 1 differs from the formulas given in standard textbooks[3-6] in the way it highlights the role of orientation. In eqn. 1 Q is the momentum transfer vector for the scattering process. It is described by

$$\mathbf{Q} = \{\cos\phi\,\sin\chi,\ \sin\phi\,\sin\chi,\ \cos\chi\}, \quad (2).$$

where the angles χ and ϕ are defined with respect to the sample coordinate system. $\underline{\mathbf{Q}}$ is explicitly identified as a vector in this equation in order to call attention to the three-dimensional character of the scattering function. I($\underline{\mathbf{Q}}$) is the intensity scattered into an element of solid angle at the angles specified for $\underline{\mathbf{Q}}$. The vector $\underline{\mathbf{A}}$ holds the parameters that define the character of the scattering elements, while $\underline{\underline{\mathbf{R}}}$ is a matrix that characterizes the orientation of the selected microstructural element through an appropriately chosen set of rigid body rotation angles. The function $p(\underline{\underline{\mathbf{R}}};\underline{\mathbf{A}})$ is a joint probability density function over the space of rigid body rotation angles and the microstructure parameters. We have chosen to use this representation because the orientation texture and the form of the microstructural elements are often correlated.

In some instances it is possible to calculate physical properties of materials as a suitable integral over the product of $p(\underline{\underline{\mathbf{R}}};\underline{\mathbf{A}})$ and a function describing the relevant property[2,7]. This is only rarely achieved in practice.

The modulus of $\underline{\mathbf{Q}}$ is q = $4\pi\sin\theta/\lambda$ where θ is the angle through which the scattered particle is deflected and λ is the wavelength of the radiation used in the experiment. The angles χ and ϕ specify the orientation of the scattered beam with respect to the body coordinate axes of the specimen.

F($\underline{\mathbf{Q}};\underline{\mathbf{A}}$) is the "form factor" for the microstructural elements producing the scattering; it is defined by

$$F(\underline{\mathbf{Q}};\underline{\mathbf{A}}) = \int_{V(\underline{\mathbf{A}})} \left(\rho(\mathbf{r};\underline{\mathbf{A}}) - \bar{\rho}\right)\exp\left(i\underline{\mathbf{Q}}\bullet\mathbf{r}\right)d^3\mathbf{r}, \quad (3)$$

where $\rho(\underline{\mathbf{r}};\underline{\mathbf{A}})$ is the "scattering length density", $\bar{\rho}$ is the average of $\rho(\underline{\mathbf{r}};\underline{\mathbf{A}})$ over the entire specimen, V is the volume of the domain that defines the microstructural element, and $\underline{\mathbf{r}}$ is defined with respect to the principal axes of the domain. Eqn. 3 is a spatial Fourier transform whose form is sensitive to the shape of the domains and to the density correlations existing within them (as specified by the vector $\underline{\mathbf{A}}$). Eqn. 3 also demonstrates that the strength of the observed signal is

proportional to the contrast between the microdomain structure and the rest of the material being studied.

Eqn. 1 is a weak generalized scattering function because it does not recognize density correlations across domain boundaries. Interfering factors such as voids, inclusions, matrix density fluctuations, and other background contributions are also ignored. Generalizations that incorporate such factors are beyond the scope of the present discussion. Simulations of scattering patterns using eqns. 1 and 3 must necessarily be based on idealized models because the complexity of real microstructures makes the calculations very difficult.

The Importance of Symmetry

In view of the three-dimensional character of I($\underline{\mathbf{Q}}$) it is important to consider how symmetry affects data collection and interpretation. The first case to be considered is the one in which $p(\underline{\mathbf{R}};\underline{\mathbf{A}})$ is a uniform function of $\underline{\mathbf{R}}$, i. e. - all rotations are equally probable. In this case the scattering is isotropic so that all of the information that the sample is capable of providing can be extracted by scanning the intensity along a radial line in $\underline{\mathbf{Q}}$ space. If the density function is spherically symmetric and if there are no correlations between microdomains this information provides a complete description. Glatter[8] and Svergun[9] have developed general methods for extracting useful structural information from isotropic scattering patterns created by randomly oriented particulate scatterers, including anisometric ones. Some laboratories prefer this approach because it minimizes instrumentation costs.

If a spatial direction can be chosen such that the scattered intensity does not vary when this direction is used as a rotation axis then this direction is said to define an axis of fiber symmetry in the specimen. The 2-dimensional scattering function obtained by recording data everywhere in a plane that contains the axis of fiber symmetry provides complete information in this case. Modern area detector technology facilitates this in the small-angle scattering case. The curvature of the Ewald sphere in wide-angle scattering means that step scanning methods work best for collecting diffraction data from fibrous polymers. Processes that can produce materials with fiber textures include spinning, extrusion through a slit die, and deformation in a channel die[10].

The function $p(\underline{\mathbf{R}};\underline{\mathbf{A}})$ in WAXS is known as the "crystallite orientation distribution function" (CODF). The CODF in the case of fiber symmetry is uniform in two of the rigid body rotation angles and peaked in the angle that controls the tilt away from the fiber axis.

It is difficult to use SAS to characterize structures for which there is an axis of fiber symmetry perpendicular to the plane of thin films. In this case the incident beam would have to be parallel to the surface of the film in order to generate a suitable SAS pattern. This leads to contamination of the scattering signal by artifacts arising from total reflection. In such cases scattering measurements at oblique incidence to the plane of the film[11] have been found to produce useful, if incomplete, information.

Even in those cases where isotropy or fiber symmetry is thought to prevail it is wise to collect enough scattering data to confirm these hypotheses. If the sample is neither isotropic nor fiber symmetric then an effort must be made to sample the full three-dimensional scattering pattern.

Pole Figure Analysis - Orientation Texture Determination in the WAD Regime

The methods for sampling and interpreting the 3-dimensional character of scattering in the WAD regime are well established[7] under the label of "pole figure analysis." The microdomains of interest are crystallites. The more or less strict 3-dimensional periodic character of the atomic density over the volume of a crystallite leads to an exceptionally simple representation of the form factor as

$$F(\underline{\mathbf{Q}};\underline{\mathbf{A}}) = \sum_{h,k,l} F_{hkl} g\left(\left(\underline{\mathbf{Q}} - \underline{\mathbf{G}}_{hkl}\right)^2;\underline{\mathbf{A}}\right), \quad (4).$$

where g is a sharply peaked function whose width is controlled by crystallite broadening, lattice disorder, strain effects, etc.; the subscripts h, k, and l are the familiar Miller indices; the $\underline{\mathbf{G}}_{hkl}$ are the reciprocal lattice vectors determined by the crystal structure of the material; and the F_{hkl} are the corresponding structure amplitudes. The dependences embodied in the $\underline{\mathbf{A}}$ vector are generally weak, so that $p(\underline{\mathbf{R}};\underline{\mathbf{A}})$ can be treated as a function of the rotation angles only (the CODF).

Because of the discrete nature of the reciprocal lattice the intensities in WAD experiments are confined to a finite set of spherical shells in $\underline{\mathbf{Q}}$ space. The radius, q, of the shells is defined by Bragg's law, which takes the form $d_{hkl} = 2\pi/q$ in our notation. The distribution of intensity on a given shell as a function of χ and ϕ is the "pole figure" for the corresponding family of reflections. For the purpose of this discussion it is sufficient to say that methods for plugging eqn. 4 into eqn. 1 and forming sets of equations that can be used to "invert" suitable data sets into CODF's exist[7]. The methods have limitations and it is fair to say that WAD experiments on polymers present additional challenges that have led to limited application of CODF methods in these materials.

The existence of stronger radiation sources, more effective computing tools, and improved detection capabilities may create a potential for opening up this area of structure analysis. Novel materials whose performance is

strongly dependent on orientation effects may also create more demand for analytical tools of this kind.

Orientation Texture in SAS

Except for certain block copolymer morphologies and colloidal crystals it is rare to find anything approaching a discrete reciprocal lattice in the SAS regime. Form factors for the microstructural elements giving rise to SAS are typically smoothly varying functions that fall off rapidly with increasing scattering angle. Polydispersity is also common in such microstructures, so that the **A** vectors in eqn. 1 have a distribution that must be averaged over. This tends to smear out any distinctive features in the form factors.

If the scattering elements are sufficiently anisometric, e.g. rodlike or disklike, their form factors will be localized in **Q** space. For rodlike morphologies the most intense parts of the form factor will be found in a plane normal to the rod axis. Similarly, for disklike structures the form factor is concentrated along a line normal to the plane of the disk.

For semicrystalline polymers a correlated stack of thin disks[12] is a useful first approximation to the lamellar microstructures observed by electron microscopy. The parameters that enter into the description of this morphology include the number of disks in the stack, the average spacing between centers (a.k.a. the "long period"), the average thickness of the disks (a.k.a. the "lamellar thickness"), the gradient between crystalline and amorphous regions, and the variances of these quantities.

Figure 1 is a typical SAXS pattern from a lamellar polymer. Lee, Phillips, and Lin[12] have discussed the shape of this curve for various levels of structural order. The rate at which the intensity falls off as one moves away from the axis of the director in **Q** space is determined by the lateral extension of the disks. For the time being we restrict our discussion to the limiting case where the lateral extension is much greater than the total thickness of the stack, so that the intensity decays rapidly as one traverses the radial direction in the **Q** space of a single stack. This means that information regarding the lateral dimensions of the stack is effectively hidden under the beam stop in real experiments.

From the above discussion it is reasonable to characterize the orientation texture of lamellar stack microstructures by the joint probability distribution of two angles: χ, the angle between the director of the stack and a suitably chosen reference direction in the sample, and ϕ, the angle between the projection of the director onto the plane at right angles to the reference direction and a second reference direction orthogonal to the first one (see Figure 2). The reference directions are usually related to the conditions under which the material was processed.

Describing Microstructures

The space spanned by the three rigid-body rotation angles and the components of the **A** vector is known as the "parameter space" for the microstructure. In this sense describing the microstructure of a material can be regarded as the process of specifying values of $p(\underline{\mathbf{R}};\underline{\mathbf{A}})$ throughout parameter space such that the calculated values of I(**Q**) match the observed ones over the whole of accessible **Q** space. The parameter space is multidimensional, with one or more dimensions for each descriptor used to characterize the microstructure.

There are basically three approaches to accomplishing this: graphical interpretation, non-linear least-squares fitting, and linear least-squares fitting following discretization. All three approaches require the user to specify a functional form for the form factor (as defined by eqn. 3) and that the data being fitted be "complete" enough to allow the parameters to be extracted in a meaningful way. For the present purpose it is sufficient to say that it is very difficult to meet these requirements. Efforts are under way in some laboratories to simulate scattering patterns on computers in the hope of validating functions that can be used for fitting.

Cold-Extruded Polyethylene - An Example

Figures 3 and 4 present WAXS and SAXS data that exemplify the complexities of orientation texture analysis for an industrial product while also demonstrating the value of the insights that can be gained. The material is a shotgun shell casing extruded by forcing a billet of crystalline high-density polyethylene through an annular die. Clark and Boone[13] have previously presented the details and interpretation of this structure.

The 110, 020, and 002 pole figures in figure 3 show that the unit cells of the crystal structure are effectively in a single crystal orientation with a modest mosaic spread. The c axes of the unit cell are predominantly parallel to the extrusion direction while the b axes are predominantly normal to the surface of the thin sheet, and the a axes are concentrated along the transverse direction of the sheet.

The three-dimensional SAXS pattern, depicted schematically in figure 4c, is built up from SAXS patterns taken along the N, T, and M directions. The teardrop shaped concentrations of intensity correspond to the locations of scattering maxima from lamellae whose directors are concentrated near the M-N plane, with a relatively narrow distribution of tilt angles with respect to M. This is the kind of structure for which full 3-dimensional SAS data must be collected.

Since the WAXS data shows that the molecular chain axes are strongly aligned, one must infer that the surfaces of the lamella are tilted with respect to the chain axes. The character of the SAXS pattern also shows that distance between lamellar surfaces increases as the lamellar tilt increases. As noted earlier Clark and Boone[13] have discussed this morphology in detail. The dilemma of quantitative application of scattering methods to interpreting microstructure in polymers is well illustrated by the fact that even for data of such good quality there have been no successful simulations. This is because there is no functional form available for the form factor that allows simulations of the SAXS data. Likewise the existence of the amorphous halo and the broad, overlapping peaks in the WAXS data have interfered with attempts to simulate the pole figures.

In spite of these difficulties, the data that has been obtained on this system has demonstrated clearly how the orientation factors affect the performance of this and similar materials in their end use. The high degree of orientation of the chain axes provides a material that is very tough in extension along the M direction. Likewise the coherence of the lamella in their lateral direction (tangential to the cylindrical shell casing) provide toughness in this direction.

Similar findings have been seen in biaxially oriented films, blow-molded beverage containers, and many other uses of plastics that depend on well-engineered properties. Current simulation work in our laboratory and others on both model systems and real materials is opening up promising pathways for taking the technology of texture characterization by scattering methods from the qualititative into the quantitative realm.

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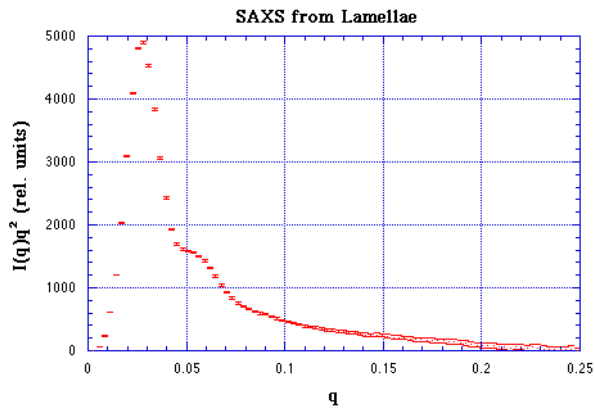
Illustrations

Figure 1 – Example SAXS pattern from semicrystalline HDPE. Material consists of randomly oriented lamellar stacks.
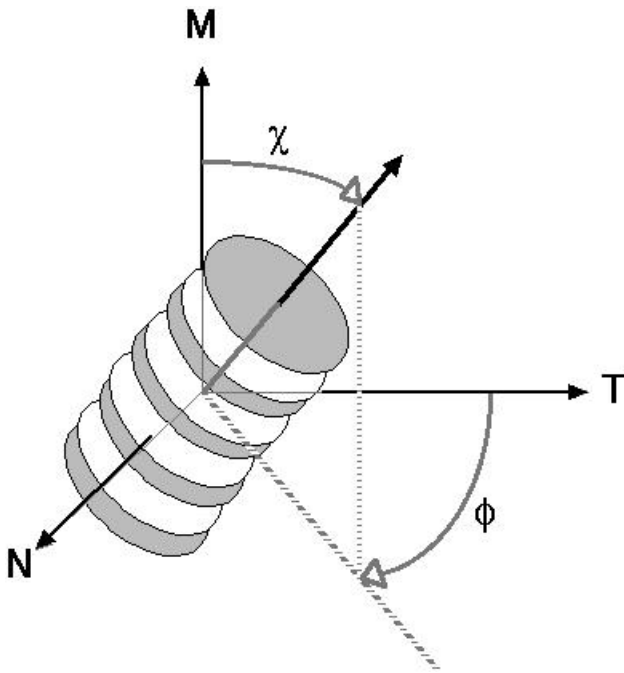

Figure 2 – Schematic illustration of lamellar stack microstructure. The directions M, T, and N are three orthogonal axes commonly taken with reference to processing directions (Machine, Normal, and Transverse). The orientation angles ϕ and χ and their relationship to the specimen directions are shown. Different shadings represent regions of differing scattering power.
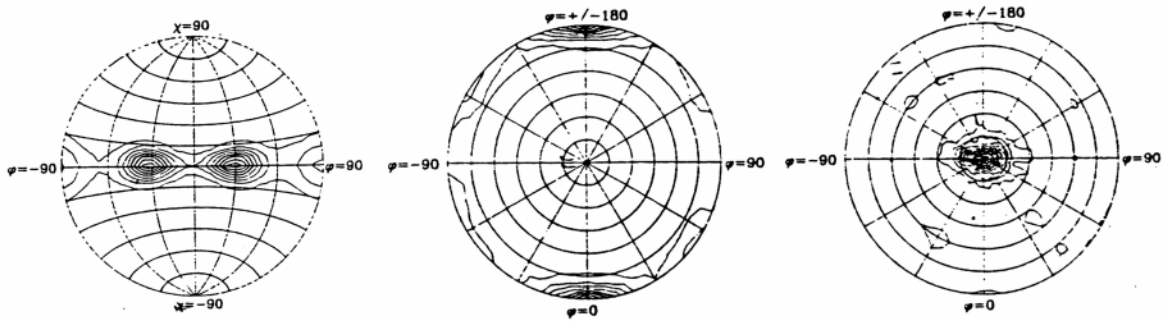
Figure 3 – PoleFigures for shotgun shell casing specimen. Left to right are the 110, 020, and 002 pole figures plotted as isointensity contours on the surface of the unit sphere.. The sharpness of the maxima demostrates that the deformation process has produced an orientation texture that is essentially that of a single crystal with a broad mosaic spread.
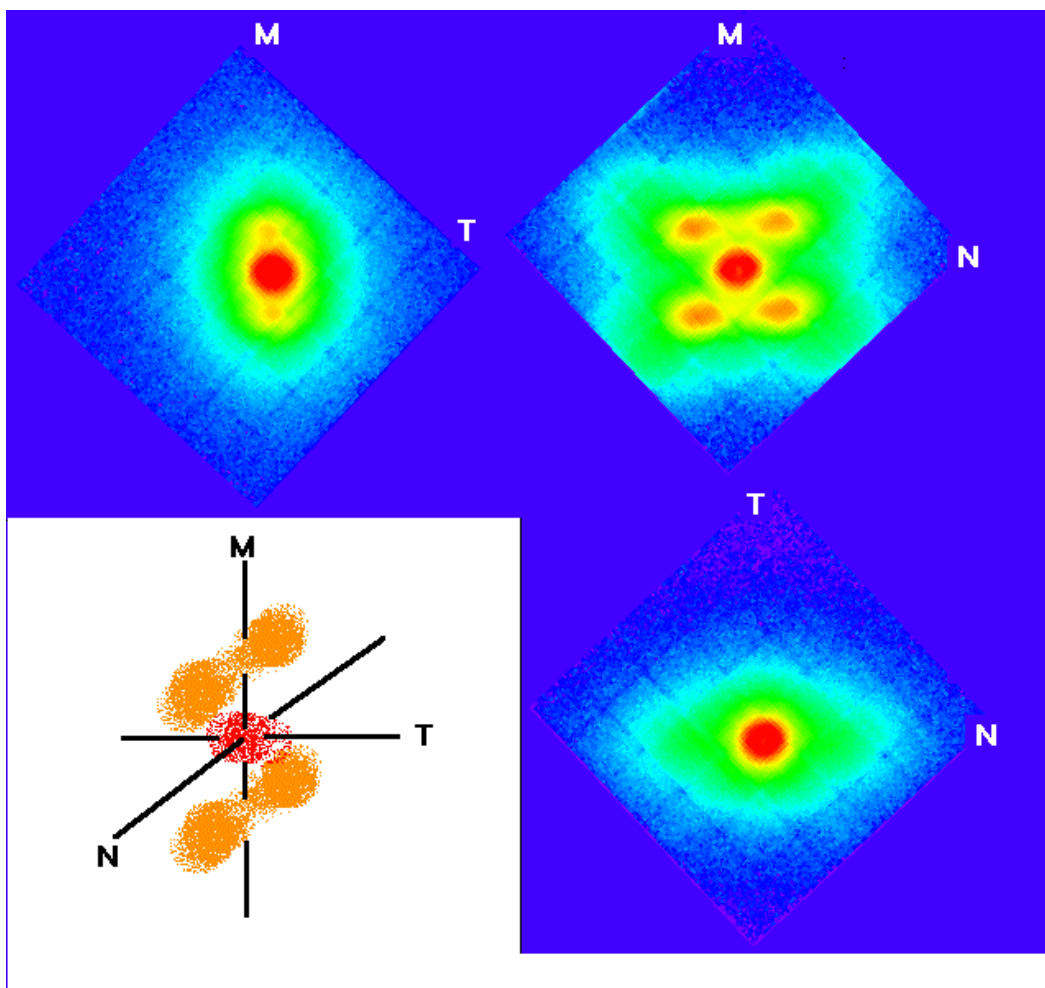

Figure 4 – Principal sections from 3-d SAXS pattern for shotgun shell casing specimen. Top left - the beam is incident along the radius of the cylinder (N direction). Top Right – beam incident tangential to cylinder wall – (T direction). Bottom right – beam incident along extrusion direction (M). Lower left – schematic reconstruction of isointensity surface of 3-d SAXS pattern seen in perspective view.

Keywords: Microstructure; small-angle scattering; diffraction; orientation texture.