

## O. Comparative Determinations of Orientation in Injection-Molded Thermotropic Liquid-Crystalline Copolyester (TLCP) Plaques

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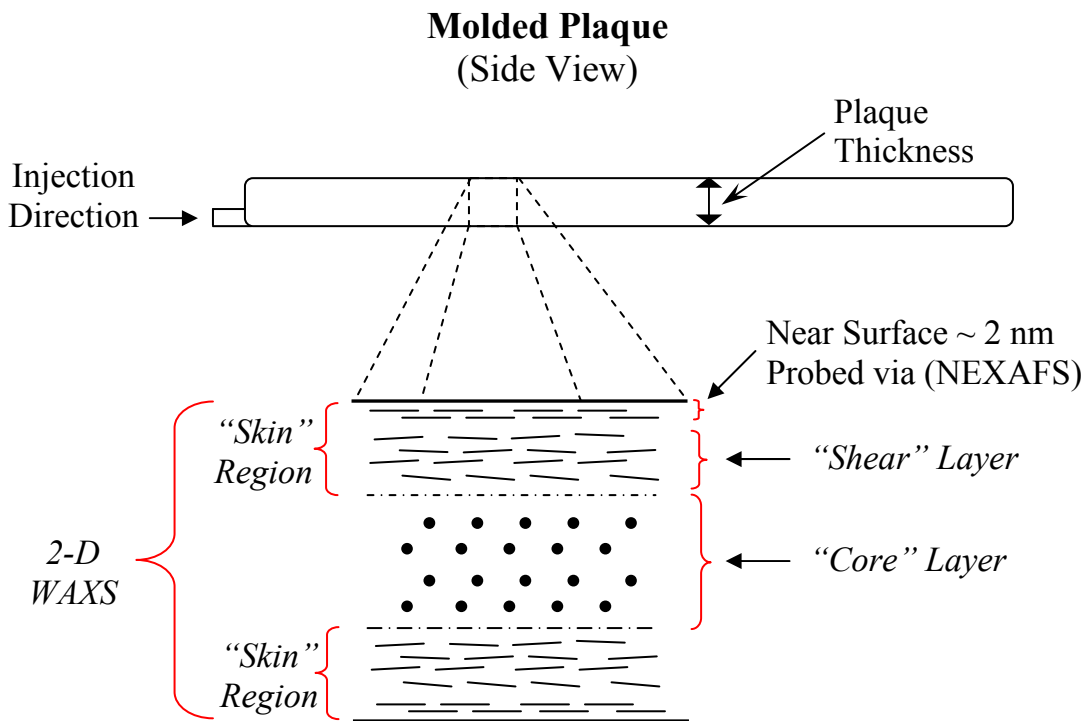
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### **Introduction**

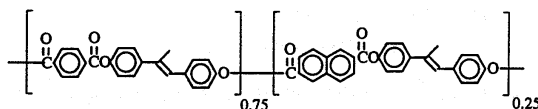
Thermotropic liquid-crystalline polymers (TLCPs) combine the virtues of superior tensile properties with the ability to injection mold with very easy flow through the spontaneous ordering of molecules. These attributes are keys to the use of these materials in high-performance electrical connectors for which the attainment of high physical properties in one dimension is a key requirement. A critical processing issue is the development of high anisotropy during TLCP processing. Although the concurrence of high tensile properties and high directional orientation is of great benefit in fiber spinning, severe anisotropy can be a plague in obtaining balanced properties in net-shape injection-molded parts. The rigid nature of the mesogenic segments in TLCP molecules usually leads directly to a high orientational bias favoring the direction of flow with injection molding and other directional processing of thermotropes [1,2]. Upon recrystallization, the high molecular orientation often leads to very favorable properties in the direction of orientation and lower physical properties in the transverse direction.

Characterizations were previously performed for the direction of greatest strength in relatively narrow injection-molded tensile bars fabricated from Celanese VECTRA® 6-hydroxy-2-naphthoic acid/6-hydroxybenzoic acid (HBA/HNA) type-

copolyesters by Dreher, et al. [3] These researchers showed that tensile modulus increases linearly with the Hermans orientation function. Molding a plaque or other part with a broad aspect ratio, however, will incur much greater flow complexity and, therefore, more complex states of orientation. Shear flow dominates near the surface while transverse stretching dominates near the mid-plane, [4] resulting in bimodal cross-ply orientation, as schematically shown in Figure 1. Depending upon thickness, a “skin/core” structure also results with a high molecular alignment in the “skin” that may be maximized in a direction different from that in the “core.” Shear asserts increasing dominance with decreasing sample thickness. Accordingly, the emphasis in this study concerns the molding of plaques under a systematic set of conditions and thicknesses, and then characterizing the resulting bimodal orientations. Near-edge x-ray absorption fine structure (NEXAFS) was used to determine the molecular orientation in the near surface (2 nm deep). Two-dimensional wide-angle x-ray scattering (2-D WAXS) in transmission was used to determine average orientations of the “skin” and “core” layers and their directions of greatest magnitude by performing, when necessary, deconvolution of the scattering associated with the bimodal contributions from the “skin” and “core” layers. The results from NEXAFS and 2-D WAXS were then compared to define the state of orientation in the plaques.



**Figure 1.** Idealized representation of an injection-molded plaque cross-section illustrating the various levels of morphology present along the plaque thickness direction. 2-D WAXS in transmission averages structural information through the sample thickness while NEXAFS probes molecular orientation over depths of 2 to 3 nm in the near surface layer.



**Figure 2.** Copolyester of 4, 4'-dihydroxy- $\alpha$ -methylstilbene (DH $\alpha$ MS).

**Experimental**

**Materials and Fabrication:** The TLCP utilized in this study is a copolyester containing 4,4'-dihydroxy- $\alpha$ -methylstilbene (DH $\alpha$ MS) as the mesogen and a terephthalate/isophthalate/2,6-naphthalenedicarboxylate molar ratio of 65/10/25.[5] The chemical structure for the TLCP based upon DH $\alpha$ MS is shown in Figure 2. Sample plaques were fabricated using a Boy 30T2 injection-molding machine with which both melt and mold temperatures were readily controlled. The plaques fabricated for the results presented in this paper

measure 76 mm x 76 mm and were molded with a coat-hanger gate. An insert mold with polished faces was utilized permitting the fabrication of plaques of various thicknesses from 0.8 mm to 3.2 mm. Polymers with molecular weights of about 35,000 g/mol were evaluated. Usually “fast” fill times of 1 s were utilized, but some additional molding performed at a “slow” 5 s. It was ascertained that the samples required surface cleaning to remove contaminants before the NEXAFS examination. The cleaning was performed using a 1% solution in de-ionized water of Alconox Liqui-Nox® cleaning agent with a Bransonic 220

ultrasonic cleaner for a duration of 10 min. Both the initial presence of contaminants and their effective removal were verified for selected samples by atomic-force microscopy (AFM) using a Topometrix 2000 AFM.

### Near-Edge X-ray Absorption Fine Structure

**Determinations of Surface Orientation:** As is apparent from the previous discussion, the contribution to the orientation of the skin layer is difficult to deconvolute from that of the core of a molding. Plummer et al. [6] and Dreher and coworkers [3] attempted to qualitatively determine the skin orientation in TLCP moldings using WAXS of microtomed layers. Layer orientation in injection-molded plaques of 6-hydroxy-2-naphthoic acid/6-hydroxybenzoic acid (HNA/HBA) (58 mol % HBA and 42 mol % HNA) random type copolyesters was determined by Pirnia and Sung [7] using Fourier transform infrared (FT-IR) attenuated total reflection (ATR) dichroism. This technique enabled these researchers to determine relative orientation encompassing a depth of material 5  $\mu\text{m}$  below the sample surface. Using measured dichotic ratios to calculate the orientation parameter, the skin, intermediate layers and core were characterized for a series of samples cut from positions along injection-molded plaques by progressively removing material by milling. An alternate, less laborious, and less intrusive means, however, of determining surface orientation with a much smaller "footprint" ( $\sim 1 \text{ mm}^2$ ) presents itself in the form of NEXAFS.

NEXAFS is a synchrotron source soft x-ray spectroscopy technique that is sensitive to the orientation of phenyl groups in the direction of melt flow via the intensity,  $I$ , of the partial electron yield (PEY) of Auger electrons of  $1s \rightarrow \pi^*$  transition of the C=C bonds in the C K edge. The technique using PEY is sensitive to the top 2 nm of a surface. The orientation is determined through a series of measurements of the C K edge spectrum over a range of incident angles,  $\theta$ , ( $20^\circ$ ,  $30^\circ$ ,  $40^\circ$ ,  $55^\circ$ ,  $60^\circ$ ,  $70^\circ$ ,  $80^\circ$ , and  $90^\circ$ ) of a monochromated linearly-polarized ultraviolet (UV) beam relative to the sample surface. This technique has been successfully used to determine the orientation of LC alignment on rubbed polyimide substrates by Stöhr and Samant [8] and by Pattison et al. [9] The NEXAFS was performed on the NIST/Dow Soft X-ray Materials Characterization Facility, U7A, at

the National Synchrotron Light Source, Brookhaven National Labs. Using the technique of Stöhr and Samant, the PEY intensity  $I(\theta)$  is predicted to take the form:

$$I(\theta) = A + B \sin^2 \theta \quad (1)$$

regardless of the degree of orientation. Based on the method by Kramer recently published by Pattison et al., [9] the molecular orientation parameter,  $S_{\text{Surface}}$ , was calculated using:

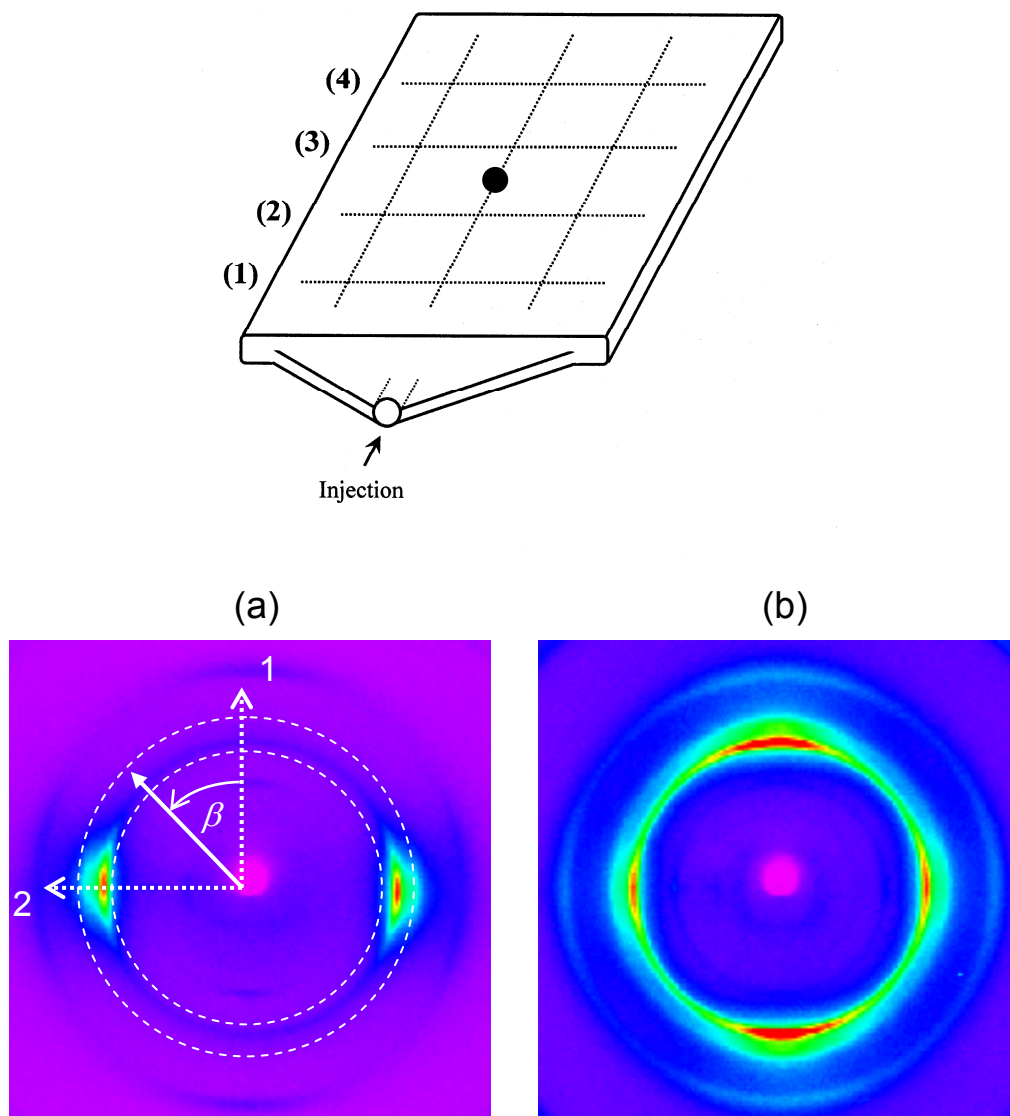
$$S_{\text{Surface}} = \left( 1 - \frac{2(A+B)}{A + \frac{B}{6P}(3P-1)} \right) \quad (2)$$

where,  $P$  is the beam polarization (0.85 in this case).

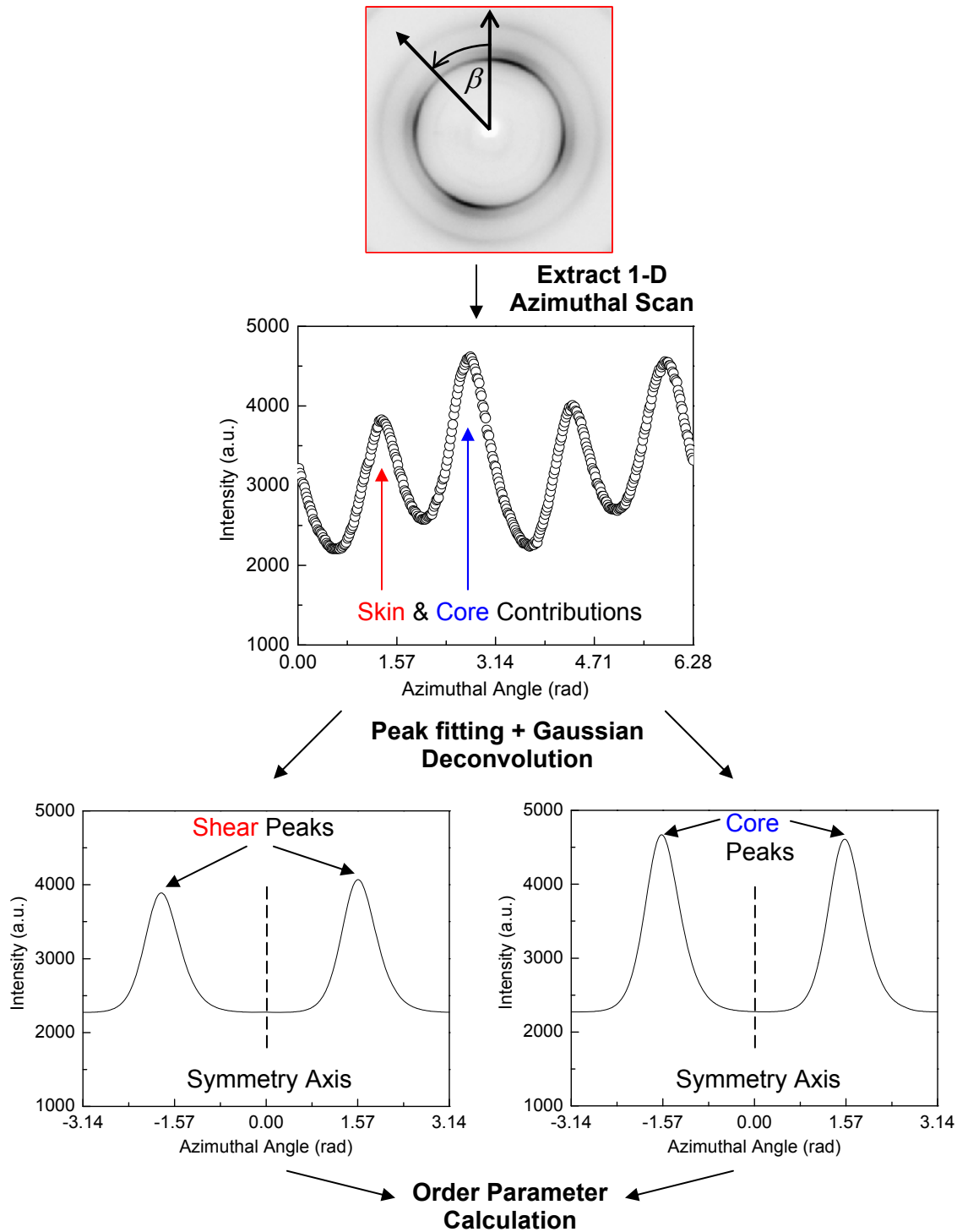
### 2-D WAXS Data and Analysis Procedure of Injection-Molded Plaques:

An orientation map for each plaque type was determined by 2-D WAXS performed at 20 keV ( $0.62 \text{ \AA}$ ) for multiple positions on the samples using the 5BM beam line of the DuPont/Northwestern University/Dow Collaborative Access Team at the Advanced Photon Source of Argonne National Lab. An incident x-ray beam with a 1-mm-diameter size was used. A Mar CCD detector was used to collect  $512 \times 512$  pixel raw x-ray scattering patterns with 15-second exposures. The WAXS patterns were obtained in positions corresponding to the grid shown in Figure 3. Although this information is very useful, there are significant bimodal contributions from both the core and the skin in the WAXS patterns obtained for the thicker plaques, examples of which are shown in Figures 3 and 4.

Details of the data analysis techniques employed are given by Rendon, et al. [10] The following section contains a simplified summary. The 2-D WAXS patterns usually indicate the presence of two discrete populations of orientation: one parallel to the flow direction and the other transverse to the flow direction. As evidenced in all of the patterns, nematic crystalline peaks always diffract perpendicular to the orientation direction. Scans made along this horizontal region of the plaque suggest the dominance of transverse-orientation modes relative to shear-flow modes manifested by



**Figure 3.** Physical orientation of an injection-molded plaque along with two representative 2-D WAXS patterns taken for a centerline position of a: (a) 0.8-mm-thick molded plaque showing uniaxial contribution to the orientation due to shear flow and a (b) 3.2-mm-thick plaque showing bimodal orientation populations due to shear and extension. The arrow indicates the principal direction of flow. The plaque examples were processed at constant fast fill time of 1 s with melt and mold temperatures of 270°C and 45°C, respectively. The overlays in (a) define the coordinates and range of the scattering wave vector,  $q$ , used for the extraction of azimuthal scans;  $\beta$  is the azimuthal angle measured away from the vertical filling direction. Dotted lines indicate the path locations where 2-D WAXS measurements were performed 15 mm apart.



**Figure 4.** Data analysis procedure used to extract azimuthal intensity scans describing the scattering contributions due to shear ('skin') and extension ('core'). Two  $I(\beta)$  scans are extracted from a single 1-D 'bulk' sample azimuthal scan via a Gaussian deconvolution of azimuthal intensity peaks. Resulting scans are subsequently processed to compute  $S_{Shear}$  and  $S_{Core}$ .

strong crystalline peaks, which are indicative of higher degrees of molecular orientation. Away from the centerline position, the bimodal character switches direction indicating that the transverse mode has rotated relative to molecular orientation at the centerline.

An assumption of uniaxial orientation is not appropriate when studying complex flow kinematics where both shear and extensional flows occur across the entire thickness of the sample. In order to obtain a quantitative measure of orientation, azimuthal intensity scans were extracted from 2-D scattering patterns at the scattering vector  $q$  location of the nematic crystalline peaks. Because of the crystalline nature of the peaks, selecting a relatively narrow  $q$  range of intensity was sufficient in maximizing the intensity available for computing azimuthal scans. Background subtraction was performed on the WAXS patterns for each plaque. The baseline correction values correspond to the lowest value of intensity observed for the experiment with the highest degree of molecular orientation. Each measurement is an average of all structure levels that the beam encounters when passing through the thickness of the plaque or slit-flow channel in the case of steady isothermal flows.

Quantitative determination of skin, core, and bulk degrees of molecular orientation in molded plaques involved computing order parameters from azimuthal intensity scans extracted from 2D WAXS patterns collected in transmission. Because 1D azimuthal scans contain information averaged through the entire plaque sample thickness, 'skin' and 'core' contributions to the orientation must be computed separately, as shown in Figure 5. Herman's order parameters that reflect the localized *skin* contribution to the bulk molecular orientation are computed from 1D azimuthal intensity scans that only contain peak information due to *shear flow*. Similarly, localized *core* contributions to the bulk molecular orientation are computed from azimuthal scans which only contain peak information due to transverse extension. These azimuthal scans are generated by applying a Gaussian deconvolution method (using a software platform known as Peakfit®) to the original 'bulk' azimuthal intensity scan that effectively generates two different sets of intensity peaks (i.e., two new azimuthal scans) each containing information from either shear or

transverse modes of orientation. Having done this, it is assumed that the uniaxial orientation to compute the corresponding order parameters can be based upon the Herman's convention, viz.,

$$S = \frac{1}{2}(3 \cos^2 \beta - 1) \quad (3)$$

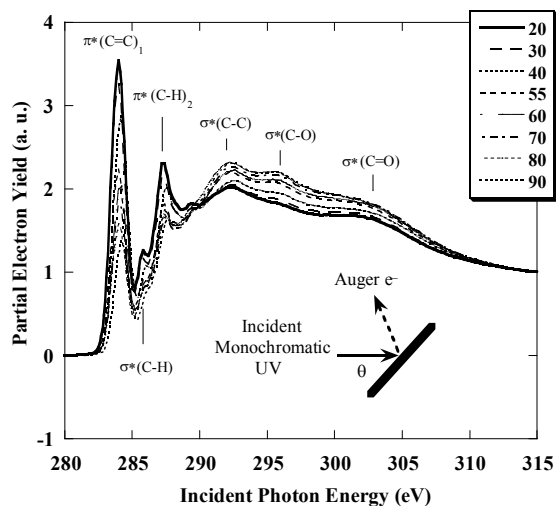
where the limit of perfect orientation this quantity yields a value of 1 and 0 indicates a randomized orientation state. The procedures are described further by Bubeck and co-workers [11].

#### **Atomic force microscopy of plaque surfaces:**

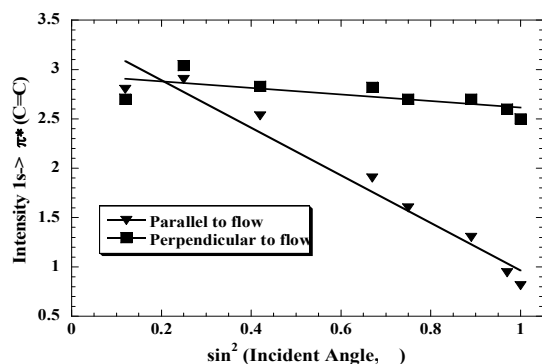
AFM examinations were performed using a Topometrix 2000 in oscillating mode on the surfaces of a selected number of DH $\alpha$ MS copolyester plaques. Confirmation via AFM of the benefit of ultrasonic surface cleaning of surfaces intended for NEXAFS has already been mentioned in this section. Given that NEXAFS is a surface-spectroscopy technique, knowledge of the surface topology of the plaques does prove useful. The AFM revealed two principal topological features on the plaque surfaces: a fine texture on the order of 1 nm in height, and a much broader feature in the form of corrugations with low gradient slopes on the order of 8 nm in height and 200 nm in width at the base. The broad corrugations are aligned in the principal direction of flow. Neither feature was deemed likely to significantly interfere with the NEXAFS measurements.

### **Results and Discussion**

An example of a set of NEXAFS C K edge spectra for the surface skin of an injection molded plaque is shown in Figure 5. The spectra were measured as a function of incident angle of the UV beam relative to the sample surface. The sample was cut from the middle of the vent-end edge of a plaque molded with a melt temperature of 245°C and a mold temperature of 45°C. The  $\pi$  (C=C) peaks from the in-plane C=C bonds are minimized when the polarized UV beam is perpendicular to the surface and the complementary  $\sigma$  orbital peaks are correspondingly maximized. This result is consistent with molecular alignment in the plane of the plaque skin. The intensity of the  $\pi$  (C=C)<sub>1</sub> peak varies linearly with  $\sin^2$  of the incident angle,  $\theta$ , an example of which is shown in Figure 6. Using the resulting intercept  $A$



**Figure 5.** Representative NEXAFS C K edge spectra for a DH $\alpha$ MS copolyester plaque surface. Spectra collected at varying angle of incident beam relative to the surface. Beam polarization is aligned with the direction of maximum orientation. Process parameters: melt temperature = 290°C, mold temperature = 45°C.



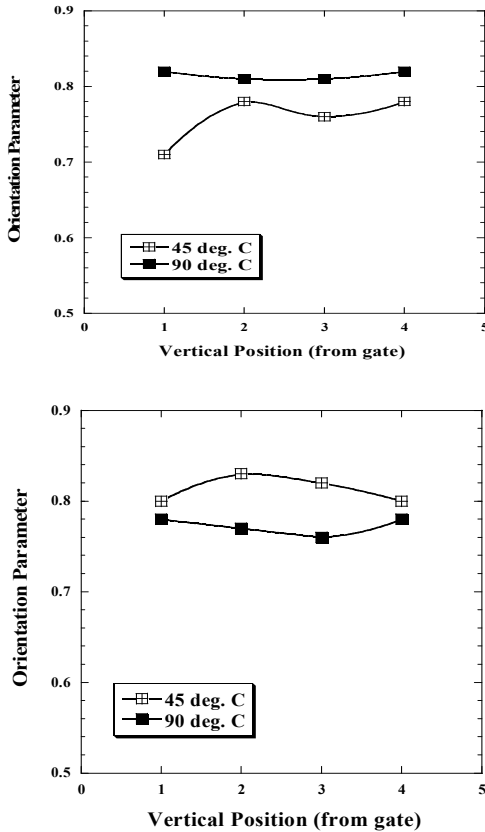
**Figure 6.** Analysis of C=C  $\pi^*$  absorption intensity dependence on incident angle, from which molecular order parameter in surface region may be extracted. Angular dependence of resonance is shown parallel and perpendicular to the principal direction of shear flow at the surface. Beam polarization was aligned parallel and, then, perpendicular to the principal flow direction to obtain the two sets of data.

and slope  $B$  of  $I(\theta)$  versus  $\sin^2\theta$  using equations 1 and 2 permits the determination of molecular order parameter,  $S_{\text{Surface}}$ . The nearly flat slope for the case of orientation perpendicular to the flow direction indicates that the surface orientation of the molecules in the plane is predominantly nematic uniaxial. Order parameters derived from the

NEXAFS analyses were found to be greatest along the centerline of the plaques and typically range from about 0.70 to 0.85 depending on position and processing conditions. The most consistent results are obtained for very smooth surfaces that retain the polish finish of the mold faces and when the 20° incident angle spectrum is omitted from the calculation of  $S_{\text{Surface}}$ .

The following discussion of results proceeds from relatively simple cases of flow-induced surface orientation along sample center lines in plaques that are coat-hanger gated to the more complex cases involving orientation states away from the centerline and with a narrow gate. The plaques are 72 mm x 72 mm and were injection-molded with a tool fitted with a “coat-hanger” gate, which permits a relatively even flow of polymer into the mold. This configuration was chosen in order to study less complex filling conditions and to be a source of plaques from which tensile samples with relatively simple orientation states could be machined and mechanically characterized. The mechanical data for these plaques has been reported elsewhere. [12] Tensile modulus and fracture stress were found to obey a ‘universal’ correlation called an anisotropy factor ( $AF$ ) derived from 2-D WAXS measurements of molecular orientation projected onto the axis of the tensile specimens.

NEXAFS examination made along the center line of four plaques is reported in terms of molecular orientation of the near-surfaces. The effect of mold temperature on surface orientation is shown in Figures 7a and 7b for two melt temperatures. At a melt temperature of 290°C, orientation parameter  $S_{\text{Surface}}$  ranges from about 10 to 20 percent more for a 45°C mold temperature than for a 90°C mold temperature – a result which is consistent with what one might expect as a result with more rapid cooling and crystallization derived from the colder mold. If a more unusual melt temperature of 245°C is chosen at the low end of the melting transition, then the relative orientations obtained for the same two mold temperatures reverse their ranking for retained surface orientation. The higher mold temperature is required to obtain relatively uniform orientation for the four plaque positions, particularly on the gated end (Position 1).



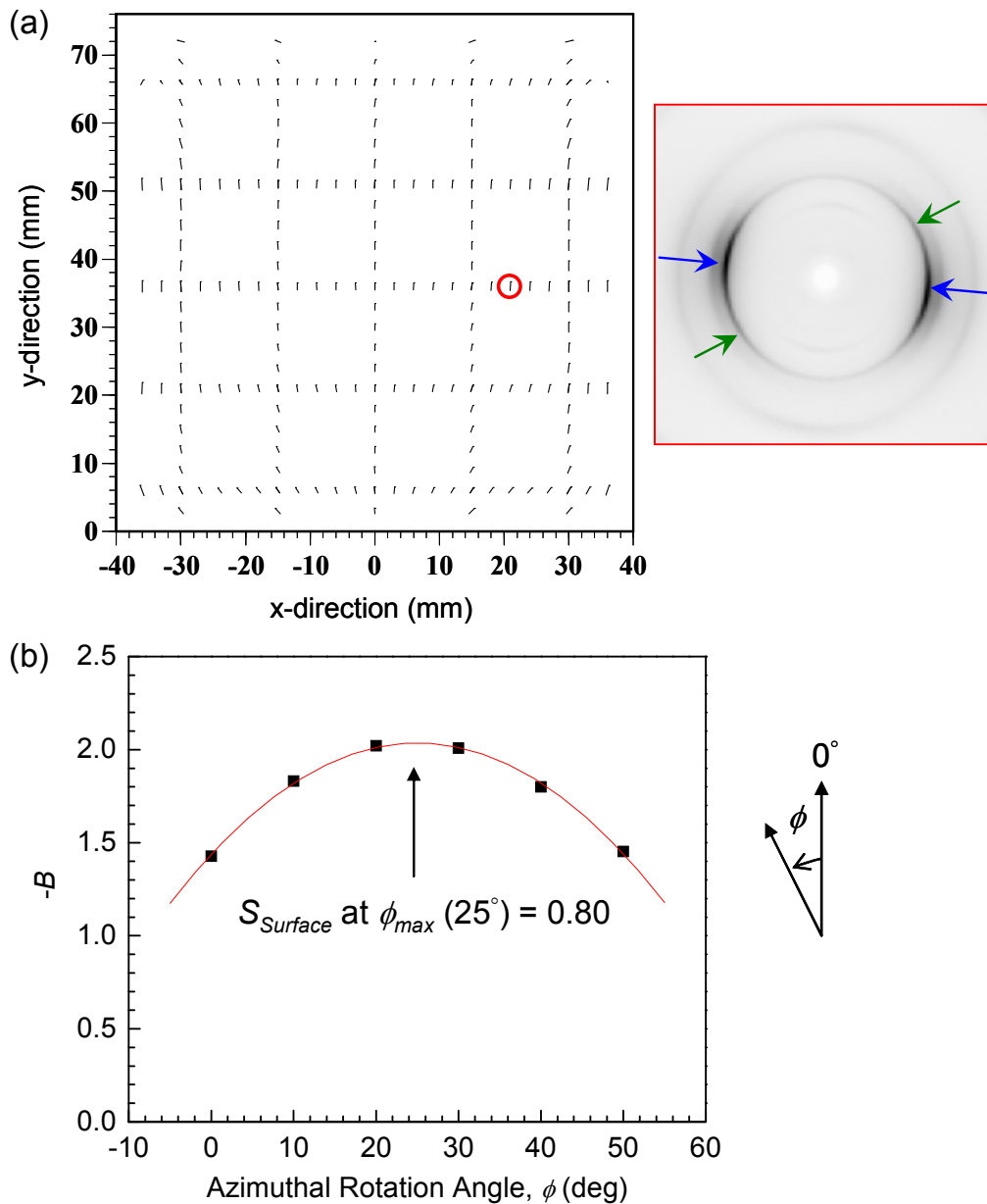
**Figure 7.** A comparison of orientation parameters  $S$  for two mold and two melt temperatures derived from the NEXAFS method as a function of vertical position from the gate in the centerline of two 1.6 mm thick injection molded 76 mm x 76 mm DH $\alpha$ MS plaques. (a) Conditions: 290°C melt temperature; 45°C and 90°C mold temperatures. (b) Conditions: 245°C melt temperature; 45°C and 90°C mold temperatures. The numbered positions correspond to those indicated in Figure 3.

Results obtained off from the centerline for a series of six plaques are covered in the following discussion. Figure 8 consists of an example 2-D WAXS pattern for one of the plaques (plaque no. 1), a surface orientation map derived from the 2-D WAXS, and a plot of slope  $B$  versus azimuthal angle derived from multiple NEXAFS measurements taken at the position indicated aside from the center line. The molecular orientation parameter  $S_{Surface}$  is indicated for the maximum slope. The position is nearly equidistant between the gate and vent edges and the centerline and the side edge. Arrows in the 2-D WAXS pattern indicate scattering contributions

due to “skin” shearing kinetics and mid-plane extension in the “core” associated with melt flow. The surface orientations obtained by 2-D WAXS are shown in a surface orientation map of the plaque and the angle of maximum surface orientation is indicated. The processing conditions and thicknesses, and values of corresponding values of  $S$ , as determined by 2-D WAXS and NEXAFS, are summarized in Table 1. Also included are: the azimuthal rotation angle  $\phi_{max}$  associated with the maximum surface molecular orientation from NEXAFS; and the azimuthal angle  $\phi_{max}$  indicative of the average orientation direction in the “skin” region, as determined by WAXS.

The results for plaques nos. 1 and 2 are tabulated for nearly identical processing conditions (45°C mold temperature, 1.6 mm plaque thickness, and 1 s fill time), the only difference being the melt temperature (290°C versus 270°C). The nominal peak melting point for the TCLP was 290°C in a broad melting range of 240°C to 300°C. The principal loss of orientation associated with the 20°C decrease in melt temperature was realized in the core where extensional flow dominates. Corresponding decreases in mechanical properties in the direction of maximum orientation have also been observed with the decrease in melt temperature. The molecular orientation on the near-surface  $S_{Surface}$  about 2 to 3 nm deep decreased slightly (0.80 vs. 0.76) with the melt temperature decrease while  $S_{Shear}$  was more greatly affected (0.55 vs. 0.48), reflecting the fact that the WAXS results from orientation averaged over a much greater thickness into the sample than does NEXAFS.

Halving the thickness for plaque no. 3 to 0.8 mm and maintaining a melt temperature of 270°C resulted in an overall increase in  $S_{Shear}$  from 0.48 to 0.66, but no change in molecular orientation  $S_{Surface}$  at the near-surface. The orientation in the core  $S_{Core}$  became essentially equivalent with  $S_{Shear}$  because the filling flow in general at the thickness is dominated by shear. The molecular orientation at the near surface (2 nm to 3 nm deep) was observed to decrease slightly from 0.76 to 0.74. Doubling the thickness for plaque no. 4 from 1.6 mm to 3.2 mm resulted in a sharp decrease in the molecular orientation of the “skin,” but with much less influence on the near surface orientation. Shear flow



**Figure 8.** WAXS and NEXAFS characterization of an example 1.6 mm thick DH $\alpha$ MS plaque. (a) Vector plot representation of molecular orientation using the second-moment tensor description of anisotropy and the average orientation direction (See Refs. 10 and 12). The x-ray pattern was collected at the specified sample position (on vector plot) where WAXS and NEXAFS measurements were performed. *Blue* arrows in the x-ray pattern indicate scattering contribution due to “skin” shearing kinematics and *green* arrows indicate scattering contribution due to mid-plane extension in the “core.” (b) Plot of the slope from  $I(\theta)$  given in Equation 2 versus azimuthal rotation angle,  $\phi$ . Maximum surface orientation ( $S_{surface} = 0.80$ ) was found for the example at  $\phi_{max} = 25^\circ$ . The sample was extracted from a plaque processed at 1 s fill time with melt and mold temperatures of 290°C and 45°C, respectively.

**Table 1.** Summary of molding conditions and resulting orientation parameters for 76 mm x 76 mm injection-molded plaques. <sup>a</sup>Near-surface molecular order parameter obtained by NEXAFS computed using Equations 1 and 2. <sup>b</sup>Order parameter obtained by WAXS describing the shear (or skin) contribution to the orientation. <sup>c</sup>Order parameter obtained by WAXS describing the core contribution to the orientation. <sup>d</sup>Azimuthal rotation angle associated with the maximum surface molecular orientation from NEXAFS. <sup>e</sup>Azimuthal angle indicative of the average orientation direction in the skin region as determined by WAXS.

Plaque No.	Thickness (mm)	T <sub>melt</sub> (°C)	T <sub>mold</sub> (°C)	Fill rate (s)	<sup>a</sup> S <sub>Surface</sub>	<sup>b</sup> S <sub>Shear</sub>	<sup>c</sup> S <sub>Core</sub>	<sup>d</sup> φ <sub>max</sub> (deg)	<sup>e</sup> β <sub>max</sub> (deg)
1	1.6	290	45	1	0.80	0.55	0.24	25.0	20.0
2	1.6	270	45	1	0.76	0.48	0.17	15.0	10.0
3	0.8	270	45	1	0.76	0.66	N/A	19.3	15.0
4	3.2	270	45	1	0.74	0.22	0.28	12.9	8.0
5	3.2	290	90	5	0.71	0.50	0.24	7.3	2.0
6	3.2	245	90	5	0.71	0.29	0.27	19.5	14.0

has much less influence for the thicker mold and time for cooling to the point of crystallization is longer, which both mitigate against maximizing orientation.

The data for plaques nos. 5 and 6 set up a comparison of the effects of two melt temperatures (290°C and 245°C, respectively) at slower fill times of 5 s. The mold thickness was 3.2 mm and melt temperature was 90°C in both cases. While the near-surface molecular orientation  $S_{Surface}$  remained constant, the molecular orientation in the core  $S_{Core}$  and shear  $S_{Shear}$  (which reflect the result

of flow and the average orientation deeper into the plaque) decreased by about 40% for the lower melt temperature. This comparison is an illustration of where obtaining enhanced flow at the optimum melting point trumps the relative time to crystallize the TLCP in the interior. Although the *magnitude* near-surface molecular orientation  $S_{Surface}$  remained constant, its *direction* of greatest magnitude shifted by about 12 deg.

For every case, the molecular orientation of the near-surface  $S_{Surface}$  varied far less than the changes in orientation associated with  $S_{Shear}$ . This result is most likely associated with the fact that the material at the mold surface is the first to crystallize. The directions of maximum orientation for  $S_{Surface}$  and  $S_{Shear}$ , as indicated by the azimuthal angles φ<sub>max</sub> and β<sub>max</sub>, always coincided well.

The range of values for molecular orientation  $S_{Surface}$  reported here are similar in kind and magnitude to

those reported by Pirnia and Sung using the surface-specific technique of FT-IR ATR dichroism. [7] The sampling depth for the IR technique is about 5 μm, whereas with NEXAFS the depth is under 3 nm. We have obtained similar data by a very similar FT-IR method on samples for which 2-D WAXS and NEXAFS data have also been obtained. As one might expect, the values of  $S$  obtained by IR are close, but typically about 5% less than by NEXAFS.

Future work will entail characterizations of the state of orientation using a 6-axis sample manipulator for positions distanced from the centerline. The ability to rotate the sample azimuthally will enable the accurate determination of surface orientation in the regions of high bimodal complexity with more efficiency than by the individual rotation of small samples cut from plaques. The orientation results shall be utilized in processing models (e.g., Moldflow®, Folgar-Tucker) to predict the optimum processing conditions for the fabrication of net-shape parts. Process optimization of TLCPs can lead to a means of fabricating structural components with less weight. Through the National Science Foundation, the United States Council for Automotive Research and DOE are helping to fund this research with the reduction of vehicle weight as an ultimate goal.

### Summary

The influences of molding parameters and mold thickness on the anisotropy, skin-core morphology, and mechanical properties of injection-molded DHαMS copolyester TLCP were studied. The

contributions of shear and extensional flows on the bimodal orientational character of the moldings were characterized by a combination of 2-D WAXS and NEXAFS.

1. The maxima for molecular orientation  $S_{Surface}$  obtained by NEXAFS for the near-surface were found to be in the 0.7 to 0.8 range for all cases.
2. Mold thickness was found to influence  $S_{Skin}$  and  $S_{Core}$  obtained from 2-D WAXS much more strongly than melt temperature within the nominal processing range of 270°C to 300°C.
3. Correlation of the directions for the maxima of  $S_{Surface}$  (2 mm depth) and  $S_{Skin}$  (~0.4 mm depth) was found to be very good.
4. The equivalency of NEXAFS with the FT-IR ATR techniques as measures of surface orientation was found to be good.  $S_{Surface}$  is about 5% greater by NEXAFS.
5. NEXAFS has proved to be effective at determining the orientation of the very surface of the skin layer.

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