

# Quantitative Orientational Characterization of Low-density Polyethylene Blown Films By X-ray and Birefringence

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## ABSTRACT

The effect of two important parameters of film blowing process, i.e., take-up ratio and blow-up ratio, on the overall orientation of low-density blown films have been investigated using birefringence measurements. Furthermore, by combining X-ray diffraction pole figure analysis and birefringence, the White and Spruiell biaxial orientation functions have been determined for afformentioned sample. Within the range of processing condition studied, increasing take-up ratio, increases orientation in both machine and transverse direction. Upon increasing blow-up ratio, orientation in the transverse direction increases and the overall orientation state approaches to equal biaxial one. Characterization of the crystalline regions by pole figure analysis reveals that a and b crystallographic axes preferentially orientate in the film plane and the direction normal to it, respectively. The amorphous regions do not have any preferential orientation.

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### Key Words:

polyethylene;  
blown Films;  
orientation;  
birefringence;  
X-ray diffraction.

## INTRODUCTION

Polyethylene film is probably the largest volume polymeric product, which has a great demand in very large number of sectors such as agriculture, building, and especially packaging. Almost 70% of the commercial LLDPE and LDPE are used in the form of blown films, cast

films, or both [1,2].

The orientational states of crystalline and non-crystalline phases in this product plays an important role in determining its internal structure and thus performance, ranging from mechanical to optical characteristics [3-6]. Therefore, orientation charac-

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terization is of great interest from both technical and theoretical points of view. The greatest challenge is the achievement of biaxial nature in the orientation distribution in blown films. Considerable efforts have been undertaken to define the relationship between the processing condition and structure of PE blown films. It is well recognized that the semi-crystalline morphology of polyethylene blown films is not of the three-dimensional spherulitic type typically attained via crystallization from a quiescent melt. In the blown film process, the crystallization takes place under stress, causing primarily row-nucleated morphologies along extended chains or bundles oriented along the extrusion direction [1]. The models of Keller and Machin [7] have greatly aided in the conceptual understanding of this morphology. Continuous investigation on the orientational behaviour of extruded blown film has been published by many people and the aforementioned model has been usually used to describe the structure of PE blown films in the literature [8-11].

In the present work, the influence of specific process variables on the overall molecular orientation has been investigated by birefringence measurements. Furthermore, by combining pole figure X-ray diffraction and birefringence measurements, a complete quantitative analysis has been undertaken to characterize the crystalline and amorphous orientation in the samples.

## THEORETICAL

White and Spruiell have derived a series of second-moment biaxial orientation functions, which are most commonly employed today to describe the biaxial orientation state of blown films [12]. These functions have the following general forms:

$$f_{zj}^B = 2 \langle \cos^2 \phi_{jz} \rangle + \langle \cos^2 \phi_{jy} \rangle - 1 \quad (1a)$$

$$f_{yj}^B = 2 \langle \cos^2 \phi_{jy} \rangle + \langle \cos^2 \phi_{jz} \rangle - 1 \quad (1b)$$

where, the superscript B refers to biaxial orientation states. z and y are the machine and transverse direction in film plane, respectively (Figure 1). Angle brackets represent average values for all orientations of the axis. For orthorhombic crystals, the subscript j represent directly the a, b, and c crystallographic axis thus producing six biaxial crystalline orientation factors, four of which are independent. The biaxial orientation factors

take values between +1 and -1, with +1 representing perfect orientation, 0 representing random orientation, and -1 representing orthogonal orientation.

Wide-angle X-ray diffraction and birefringence measurements can be used for determining orientation functions. Birefringence,  $\Delta_{ij}$ , measures the overall orientation of the specimen. It is defined as difference in refractive index between the reference directions of Figure 1. As shown by White and Spruiell, the birefringence  $\Delta_{zx}$  and  $\Delta_{yx}$  are related to biaxial orientation factors through the relations [12,13]:

$$\Delta_{zx} = X(f_{zc}^{Bc} \Delta_{cb}^{oc} + f_{za}^{Bc} \Delta_{ab}^{oc}) + (1-X)\Delta_{am}^0 f_z^{Ba} + \Delta n_{form} \quad (2a)$$

$$\Delta_{yx} = X(f_{yc}^{Bc} \Delta_{cb}^{oc} + f_{ya}^{Bc} \Delta_{ab}^{oc}) + (1-X)\Delta_{am}^0 f_y^{Ba} + \Delta n_{form} \quad (2b)$$

where, X is the degree of crystallinity,  $\Delta_{cb}^{oc}$  and  $\Delta_{ab}^{oc}$  are the intrinsic birefringences of the cb and ab planes of orthorhombic crystal lattice,  $f_{zc}^{Bc}$ ,  $f_{yc}^{Bc}$ ,  $f_{za}^{Bc}$ ,  $f_{ya}^{Bc}$  are the biaxial orientation functions of the c and a axes,  $f_z^{Ba}$  and  $f_y^{Ba}$  represent amorphous orientation functions,  $\Delta_{am}^0$  is the amorphous intrinsic birefringence, and  $\Delta n_{form}$  represent the contribution of the form birefringence. The combination of birefringence and X-ray results can lead to determination of the amorphous orientation function  $f_k^{Ba}$ .

Wide-angle X-ray scattering is the best and most exploited technique for measuring crystalline orientation in polymer systems. It is applied to determine the three-dimensional orientation distribution of the crystals in a polycrystalline sample. This is most commonly done through the preparation of pole figures [14]. On a pole figure map, one may observe both the location and intensity of the orientation of a crystalline plane with respect to the x, y, and z reference directions. Moreover, the different orientational states of a system (i.e., uniaxial and biaxial) can be distinguished using pole figure.

With preparing pole figure for several different diffracting planes (hkl) it is possible to determine all of  $\langle \cos^2 \phi_{jz} \rangle$  and  $\langle \cos^2 \phi_{jy} \rangle$  (j = a, b, c). Then, the evaluation of  $\langle \cos^2 \phi_{jz} \rangle$  to the z reference axis can be carried out by refs. [11,12]:

$$\langle \cos^2 \phi_{hkl,z} \rangle = \frac{\int_0^{90} I(\phi) \sin \phi_z \cos^2 \phi_z d\phi_z}{\int_0^{90} I(\phi) \sin \phi_z d\phi_z} \quad (3a)$$

where,

$$I(\phi) = \int_0^{360} I(\phi, \beta_z) d\beta_z \quad (3b)$$

Where,  $I(\phi, \beta)$  represents the intensity distribution measured on the pole figure of the (hkl) plane as a function of the angle  $\alpha$  ( $0 \leq \alpha \leq \pi/2$ ), where  $\alpha = (\pi/2 - \phi)$  and ( $0 \leq \beta \leq 2\pi$ ) (Figure 2).

### EXPERIMENTAL

Low-density polyethylene (LDPE - LLF-0200), with a density of 0.923 g/L and a melt index of 1.86 g/10 min was used in this study.

The tubular film was blown with a 40-mm semi-commercial extruder turning at 15 rpm and equipped with a 130-mm annular die which possesses a 1.10-mm gap. The extrusion temperature was 200 C. The take-up ratio (TUR) was calculated by dividing the take-up speed of the film after the nip rolls and the constant linear velocity of the film tube leaving from the die. The blow-up ratio was calculated by dividing the diameter of the bubble by that of annular die. Two series of films were produced. In series A, the take-up ratio was increased from 8.2 to 24.7 for a constant blow-up ratio of 2.08. In the second series of films (series B), the blow-up ratio was increased for 5 samples from 1.69 to 3.70 for take-up ratio held constant at 8.9.

The three birefringences ( $\Delta_{ij}$ ) were calculated by measuring the refractive indices of the oriented films with an Abbe' refractometer (ERMA, Japan), fitted

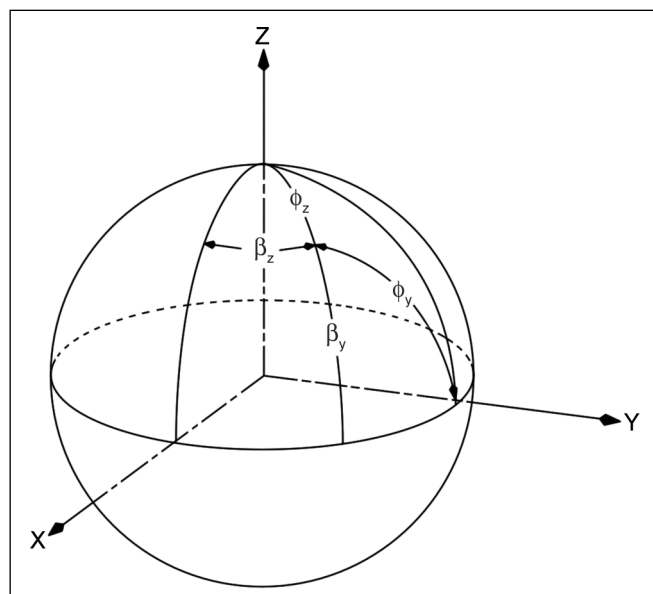


Figure 2. Definition of spherical coordinates [12].

with a Polaroid [15,16]. A mixture of two high refractive index liquids was employed to eliminate the air/solid interface. A sample with dimension of 30 mm x 40 mm was placed on the prism with its MD either parallel or perpendicular to the long axis of the measuring prism. The refractive indices were then respectively read. Three replicate samples were used for each measurement.

Pole figure measurements were made by using nickel-filtered Cu-k $\alpha$  radiation generated by a Jeol (JDX - 8030) X-ray machine operating at 30 kV and 20 mA. The intensities of eqn (3b) are measured by two experimental techniques. The Decker transmission method for  $0 \leq \alpha \leq 75 - \theta$  and the Schultz reflection

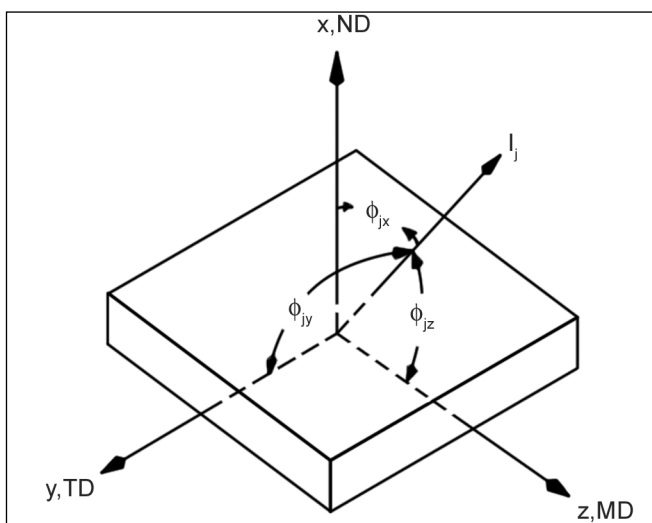


Figure 1. Coordinate system used to specify orientation in polymers [13].

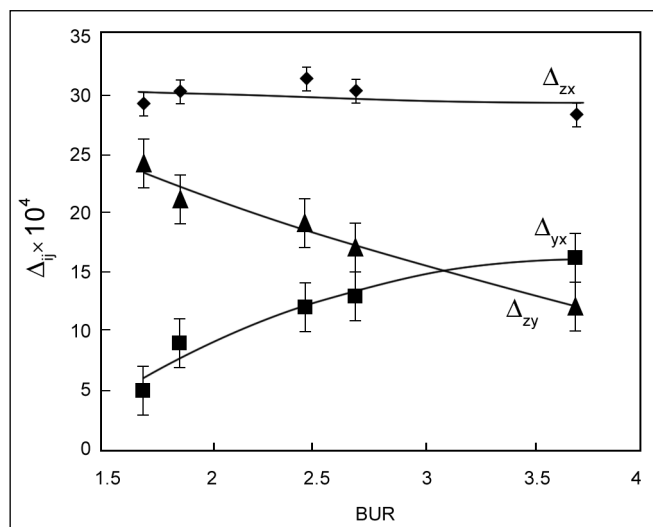


Figure 3. Birefringences as a function of take-up ratio for films with constant blow-up ratio.

**Table 1.** Biaxial orientation factors of the sample (TUR =8.9 and BUR = 1.86).

$f_y^{Ba}$	$f_z^{Ba}$	$f_{yc}^B$	$f_{zc}^B$	$f_{yb}^B$	$f_{zb}^B$	$f_{ya}^B$	$f_{za}^B$
-0.09	-0.03	0.18	0.2	-0.46	-0.62	0.28	0.42

method for remaining  $\alpha$  values up to 90 were used. An angle steps of 5 for  $\alpha$  and  $\beta$  was set during the measurements. Processing software (Jeol) was employed to correct the raw data, connect the two experimental methods and smoothen and finally plot the pole figures.

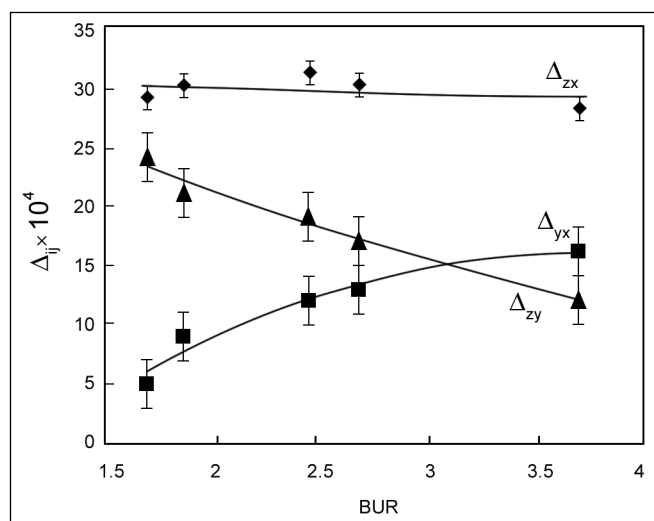
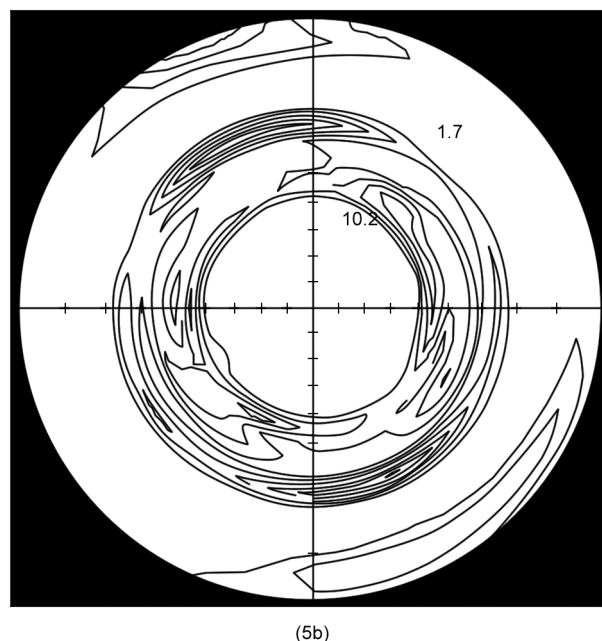
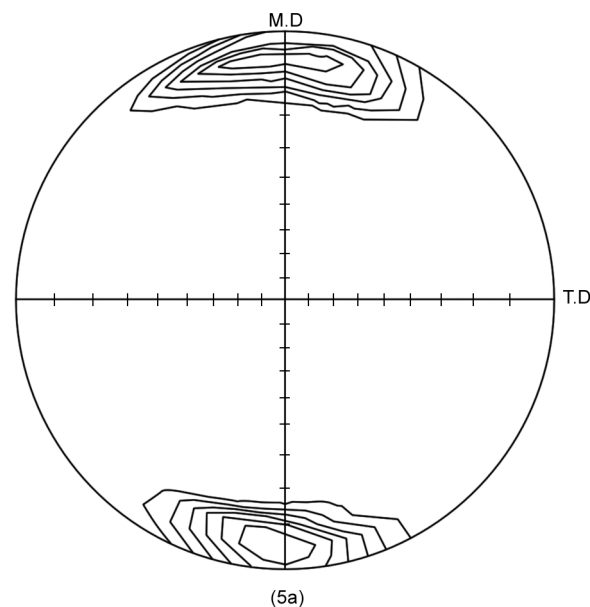
The degree of crystallinity,  $X_c$ , of samples was determined from the heats of fusion obtained by differential scanning calorimetry (DSC).  $\Delta H_f$  values were calculated from sample weights and endothermic peak areas obtained by heating 3 mg film samples at 10 C/min on a V4-Dupont 2000 DSC. Then:

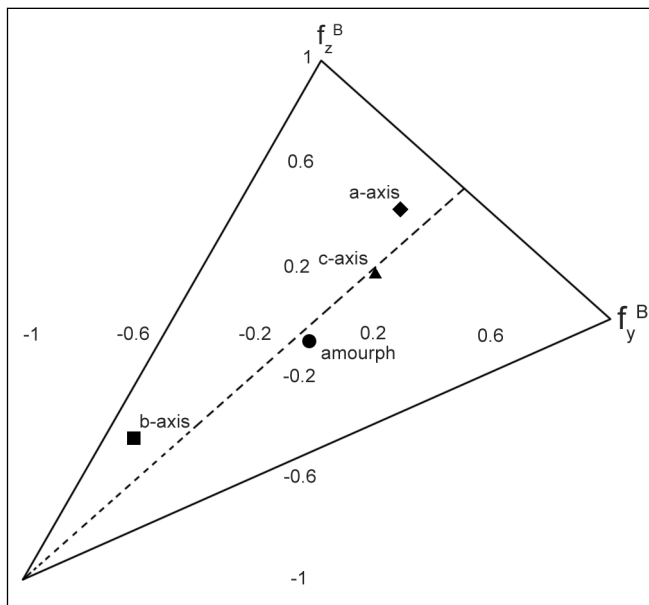
$$\text{crystallinity}(\%) = \Delta H_f / \Delta H_f^0 \quad (4)$$

where,  $\Delta H_f$  is the specific heat of melting of an ideal crystal. For polyethylene, the commonly accepted value of  $\Delta H_f = 293 \text{ Jg}^{-1}$  has been used in this study.

## RESULTS AND DISCUSSION

Figure 3 illustrates the variation of the birefringence as a function of take-up ratio for the blown films of series A. As we observe, by raising the take-up ratio, the bire-

**Figure 4.** Birefringences as a function of blow-up ratio for films with constant take-up ratio.**Figure 5.** Pole figures for (200) and (020) planes of the sample.



**Figure 6.** White-Spruiell orientation triangle containing orientation factors of the sample.

fringes for all films increases,  $\Delta z_x > \Delta z_y > \Delta y_x$ . In other words, the birefringence in the  $zx$  planes increases linearly with take-up ratio. The  $\Delta z_y$  and  $\Delta y_x$  birefringences vary gradually and  $\Delta y_x$  levels off toward a value of 0.0020. For the first sample with smallest TUR, we note that  $\Delta z_x \approx \Delta y_x > \Delta z_y$ , signifying that the film contains a global orientation that is nearly biaxial in the  $zy$  plane. However, as the take-up ratio increases this biaxial orientation is lost.

Figure 4 presents the variation of the birefringence as a function of blow-up ratio for the films of series B. As expected, with enlargement of bubble diameter, the  $\Delta y_x$  birefringence increases and consequently the  $\Delta z_y$  decreases. It is striking to note that the relatively constant birefringence values in the  $zx$  plane with increasing blow-up ratio. For a constant take-up ratio of 8.9, we observe that the overall global orientation remains constant in the  $zx$  plane. For the sample with lowest BUR, we note that  $\Delta z_x \approx \Delta y_x$  and  $\Delta y_x \approx 0$  signifying that the film contains a global orientation that is uniaxial about the MD. However with increasing BUR, global orientation state changes to a nearly biaxial one. These results are comparable to those of Pazur et al. [11] who witnessed the same birefringence trend for increasing BUR at a constant TUR in LDPE.

Figure 5 presents the pole figure results for a LDPE film of the B series having take-up ratio of 8.9 and blow-up ratio of 1.86. In these pole figures the machine direction (MD) is the line running vertically north to

south, in a geographical sense, and the transverse direction (TD) in the east to west equatorial line. The normal direction (ND) is the line perpendicular to the plane of the pole figure passing through the center of the pole.

In Figure 5a, the maxima of the (200) pole figure are situated in the ND-MD plane. This Figure shows a tendency for (200) plane normals i.e., a-axis orientation along the machine direction.

It is seen in Figure 5b that the (020) plane normals (b-crystallography axis) are distributed in all directions, with somewhat higher intensity along the ND.

The biaxial crystalline orientation factors determined from the pole figures (eqns 1 and 3) are plotted in an orientation function triangle diagram [12] in Figure 6 and tabulated in Table 1. Amorphous orientation factors were calculated from birefringence data (eqn 2) with form birefringence neglected (Table 1).

## CONCLUSION

On the basis of observations and calculations, the orientation states in the crystalline and amorphous regions of the sample can be summarized as follows: in the crystalline regions, the a-axis orients nearly planar and b-axis has a strong orientation along the ND. Furthermore, the calculated c-axis orientation function ( $f_{z_c}^B, f_{y_c}^B$ ) seems to suggest an equal biaxial orientation for molecular chain in the sample. In amorphous regions the orientation of molecules are considerably less than crystalline regions. In other words, the crystalline regions are surrounded by isotropic amorphous matrix.

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