Orientation Development in Tubular Film Extrusion of Polystyrene

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Synopsis

The tubular film extrusion of atactic polystyrene is described. The in-plane and out-of-plane birefringence of the polystyrene film was determined and compared with both the kinematics (drawdown, blow-up ratio) and applied tensions and bubble pressures. The data can be correlated by comparing the birefringences with the stresses acting in the film at the position of vitrification. The data compare quantitatively with Oda, White, and Clark's correlation developed for the birefringence of samples vitrified during shear and uniaxial extensional flow. The experimental results are interpreted in terms of White and Spruiell's biaxial orientation factors.

INTRODUCTION

Tubular film extrusion (Fig. 1) is a major industrial process for the manufacture of film. Despite its importance, relatively little has been published on structure development in tubular film extrusion. No studies have appeared on orientation developed in amorphous polymers. There have been published investigations of the morphology and crystalline orientation in polyethylene[1–5] and polybutene-1[6,7] films prepared by the tubular process. These studies have usually only given limited attention to the kinematics of the film formation process and none to the stress fields. Rohn[6] appears to have realized the problems involved but his handling of both the dynamics of the process and the structural analysis of the films is not satisfactory. The studies of Maddams and Preedy[5] of tubular film extrusion would seem the most comprehensive and best to date, but their kinematic considerations are too qualitative and they do not measure the stresses developed in the film formation process.

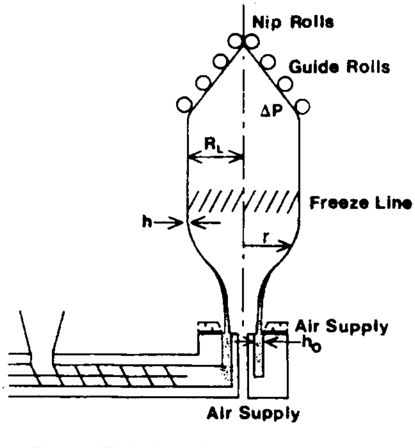

Fig. 1. Tubular film extrusion process.

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This is the first of a series of articles which will characterize orientation and crystalline morphology development in tubular film extrusion. We will contrast film structure to kinematics and applied stresses. These articles represent an extension of earlier investigations in our laboratories on structure development in polymer processing[8–14] especially as related to melt spinning[8–11] and injection molding.[12–14] In the present article we consider orientation development in tubular film extrusion of polystyrene. It is important to note that in tubular film extrusion the elongational flow kinematics and stress fields lead to biaxial orientation, and it is important to critically discuss representations of this orientation before we proceed.

BACKGROUND

Representation of Orientation and Orientation Factors

The subject of orientation distributions in polymer systems and its representation has received considerable attention in the literature.[9–29] In crystalline polymers, wide angle x-ray diffraction (WAXS) and construction of pole figures[2,3,5,20–24] allows a complete representation of the distribution of reflecting plane normals in space. In many instances, the distribution of polymer chain axes and crystallographic axes can also be determined. However, this is not possible in amorphous polymers where the common experimental techniques which may be applied, such as birefringence,[11–17,24–29] and dichroism,[17,19,25,26] yield only the second moments of the distribution.

It is possible to develop useful representations of orientation in terms of the second moments of the distribution which are determined by birefringence and dichroism. This was first done by Hermans and his co-workers[15,16] using the anisotropic characteristics of the polarizability tensor for the case of uniaxial fiber orientation. A similar development is possible with the conductivity or attenuation tensors. The representation of biaxial orientation in terms of orientation factors was initiated by Stein[19] and has since been considered by Kawai et al.[25–28] in a series of articles, as well as by Desper and Stein[24] and by White and Spruiell.[29] The work of Stein and Kawai et al. defines orientation factors in terms of Euler's angles defined with respect to a characteristic (e.g., machine) direction. This is an awkward method of formulation and results in asymmetry of representation with respect to the machine and transverse direction. Wilchinsky[20] and Desper and Stein[24] suggested using values of averaged mean-square cosines of angles between crystallographic axes and machine and transverse directions. White and Spruiell[29] propose biaxial orientation factors based upon the anisotropy of the polarizability (or attenuation) tensors and the angles used by Wilchinsky, Desper, and Stein. For the case of an amorphous polymer, these orientation factors take the form[29]:

$$f_1^B = 2\,\overline{\cos^2\phi_{c1}} + \overline{\cos^2\phi_{c2}} - 1 \tag{1a}$$

$$f_2^B = 2\,\overline{\cos^2\phi_{c2}} + \overline{\cos^2\phi_{c1}} - 1 \tag{1b}$$

where c refers to the chain direction, while 1 and 2 refer to the reference directions (e.g., machine and transverse directions, respectively).

These orientation factors have the range of values from (−1) to (+1) as shown in Table I. We indicate the special cases of isotropy (orientation factors zero), and three different types of uniaxial orientation and planar orientation. Note that, in the uniaxial case, the orientation factors reduce to the well-known Hermans' orientation factor. For planar orientations, $f_1^B$and f_2^B may vary from 0 to 1. As macromolecules tend toward orientation parallel to the film normal, f_1^B and f_2^B become negative.

The orientation factors defined by eq. (1) may be determined from the birefringences Δn_{13} and Δn_{23} through[29]

$$f_1^B = \frac{\Delta n_{13}}{\Delta^\circ} \tag{2a}$$

$$f_2^B = \frac{\Delta n_{23}}{\Delta^\circ} \tag{2b}$$

where Δ° is the intrinsic birefringence.

To evaluate f_1^B and f_2^B, we must know the intrinsic birefringence Δ°. For the data of this article, we need the value of Δ° for polystyrene. The value of Δ° for this polymer has been considered by Gurnee[30] and Stein[31] among others. A reasonable value would appear to be about (−0.15).

Kinematics and Dynamics of Tubular Film Extrusion

The kinematics and dynamics of tubular film extrusion first received attention by Pearson[32] and later in more detail in a series of articles by Pearson and Petrie.[33–35] If we take 1 as the machine direction, and 3 as the thickness direction, we may express the velocity gradients in a tubular film process according to Pearson and Petrie[34] as:

$$\frac{\partial v_1}{\partial \xi_1} = \frac{Q \cos\theta}{2\pi R h}\left[-\frac{1}{h}\frac{dh}{dz} - \frac{1}{R}\frac{dR}{dz}\right] \tag{3a}$$

$$\frac{\partial v_2}{\partial \xi_2} = \frac{Q \cos\theta}{2\pi R h}\left(\frac{1}{R}\frac{dR}{dz}\right) \tag{3b}$$

$$\frac{\partial v_3}{\partial \xi_3} = \frac{Q \cos\theta}{2\pi R h}\left(\frac{1}{h}\frac{dh}{dz}\right) \tag{3c}$$

TABLE I

Range of Values for Orientation Factors

Orientation	Reference Direction[a] 1	Reference Direction[a] 2
Isotropic	0	0
Uniaxial machine direction	$(3\,\overline{\cos^2\phi_{c1}} - 1)/2$	0
Chains parallel to MD	+1	0
Uniaxial transverse direction	0	$(3\,\overline{\cos^2\phi_{c2}} - 1)/2$
Chains parallel to TD	0	+1
Equal biaxial (planar or non-planar) (Same as uniaxial normal direction)	$(1 - 3\,\overline{\cos^2\phi_{c3}})/2$	$(1 - 3\,\overline{\cos^2\phi_{c3}})/2$
Chains parallel to ND	−1	−1
Planar	$\overline{\cos^2\phi_{c1}}$	$\overline{\cos^2\phi_{c2}}$
Planar equal biaxial	+½	+½
Planar equidirection (random about ND)	+½	+½

[a] $\overline{\cos^2\phi_{c1}} + \overline{\cos^2\phi_{c2}} + \overline{\cos^2\phi_3} = 1.0$.

Here Q is extrusion rate, R is bubble radius, and h is film thickness. For uniaxial extension

$$\frac{\partial v_2}{\partial \xi_2} = \frac{\partial v_3}{\partial \xi_3} \tag{4a}$$

$$\frac{1}{R}\frac{dR}{dz} = \frac{1}{h}\frac{dh}{dz} \tag{4b}$$

If we are able to impose this throughout the process, it follows that R/h is constant and the drawdown ratio (V_L/V_0) is related to bubble shape and film thickness by

$$\frac{V_L}{V_0} = \frac{h_0^2}{h_L^2} = \frac{R_0^2}{R_L^2} = \frac{1}{B^2} \tag{5}$$

For V_L/V_0 greater than unity, the blow-up ratio $B = R_L/R_0$ is less than unity. For equal biaxial extension in film extrusion,

$$\frac{\partial v_1}{\partial \xi_1} = \frac{\partial v_2}{\partial \xi_2} \tag{6a}$$

$$-\frac{1}{h}\frac{dh}{dz} - \frac{1}{R}\frac{dR}{dz} = \frac{1}{R}\frac{dR}{dz} \tag{6b}$$

If we are able to impose these kinematics, it leads to R^2h being constant and the drawdown ratio V_L/V_0 being related to blow-up ratio by

$$\frac{V_L}{V_0} = \left(\frac{h_0}{h_L}\right)^{1/2} = \frac{R_L}{R_0} = B \tag{7}$$

The drawdown ratio is equal to the blow-up ratio. Large V_L/V_0 requires large blow-up ratios. Experimental studies of the kinematics of tubular film extrusion are reported by Farber and Dealy[36] and by Han, Park, and Sheety.[37–39]

The force balance on tubular film is most readily developed from membrane theory as has been discussed by Alfrey.[40] The first explicit derivation and discussion was in a series of articles by Pearson and Petrie,[32–35] who show that it simplifies to the expressions

$$F_L = 2\pi Rh\ \sigma_{11} \cos\theta + \pi\Delta p\ (R_L^2 - R^2) \tag{8}$$

$$\Delta p = \frac{h\sigma_{11}}{R_1} + \frac{h\sigma_{22}}{R_2} \tag{9}$$

where σ_{11} is the stress in the machine direction, σ_{22} in the circumferential (transverse) direction, F_L is the drawdown force, Δp the bubble pressure, and R_1 and R_2 the principal radii of curvature of the film. At the freeze-line

$$R_1 = \infty$$

$$R_2 = R_L$$

$$\cos\theta = 1 \tag{10}$$

$$\sigma_{11} = \frac{F_L}{2\pi R_L h_L} \tag{11a}$$

$$\sigma_{22} = \frac{R_L \Delta p}{h} \tag{11b}$$

Experimental studies of tubular film extrusion dynamics are reported by Han and Park[37] and Wagner.[41]

There have been other studies of interest in tubular film extrusion. Temperature profiles and heat transfer have been investigated by Menges and Predohl,[42] Ast,[43] and Petrie.[44] Bubble dynamic instabilities are described by Han and Park[38] and Han and Shetty.[39]

Rheo-Optical Behavior and Frozen-in Orientation

It is well established that the birefringence developed in flowing polymer melts with flexible chains is governed by the Rheo-Optical law[45–49] which may be stated

$$\boldsymbol{n} = \tfrac{1}{3}(\mathrm{tr}\,\boldsymbol{n})\boldsymbol{I} + C\boldsymbol{\rho} \tag{12}$$

where $\boldsymbol{n}$ is the refractive index tensor; $\boldsymbol{I}$, the unit tensor; $\boldsymbol{\rho}$, the deviatoric stress tensor; and C, the stress–optical constant. Matsumoto and Bogue[50] have verified eq. (12) to be valid for polystyrene under nonisothermal conditions.

Various investigators studying polyethylene terephthalate,[51–53] polystyrene[11,12,54–56] and high-impact polystyrene[57] have shown that the orientation developed during flow in these melts as measured by birefringence is frozen-in at vitrification. Equation (12) was verified for vitrified polystyrene by Oda, White, and Clark[11] in uniaxial extension, simple shear flow, and melt spinning. They proposed eq. (12) has a general method for prediction of orientation distributions in fabricated polystyrene parts. This was subsequently verified for injection molding by Dietz, White, and Clark[12,13] and independent researches by Janeschitz-Kriegl.[56]

White and Dietz[14] have specifically proposed applying this approach to tubular film extrusion. They conclude that birefringences in such film will be related to process conditions through

$$\Delta n_{12} = n_1 - n_2 = C\left[\frac{F_L}{2\pi R_L h_L} - \frac{R_L \Delta p}{h_L}\right] \tag{13a}$$

TABLE II
Polystyrene Films Prepared by Tubular Film Process

Sample	V_L/V_0	(h, μm)	B	F_L (N)	Δp, Pa	σ_{11}, MPa
U1	46	76.4	0.6	3.04	0	1.32
U2	61	40.6	0.76	3.07	0	1.98
U3	74	38.1	0.8	3.82	0	2.50
U4	79	28.0	0.84	4.00	0	3.39
U5	103	20.1	0.88	4.18	0	4.71
U6	117	16.0	0.92	4.67	0	6.32
U7	130	11.4	0.92	4.88	0	9.25
1	33	17.3	2.5	2.70	2.7×10^2	1.21
2	39	14.0	2.6	2.67	2.7×10^2	1.43
3	46	11.4	2.6	2.62	2.7×10^2	1.76
4	52	10.2	2.5	2.58	2.7×10^2	2.01
5	59	5.3	2.2	2.61	2.7×10^2	4.45
B$_i$	6.2	13.0	6.0	1.29	0.72×10^2	0.33

$$\Delta n_{13} = n_1 - n_3 = C\frac{F_L}{2\pi R_L h_L} \tag{13b}$$

It should be noted that these are actually relationships between orientation and process conditions. Equation (13) may be rewritten in terms of the White–Spruiell orientation factors using eq. (2) as:

$$f_1^B = \frac{C}{\Delta^\circ}\frac{F_L}{2\pi R_L h_L} \tag{14a}$$

$$f_2^B = \frac{C}{\Delta^\circ}\frac{R_L \Delta p}{h_L} \tag{14b}$$

EXPERIMENTAL

Materials

The polymer used in these experiments was a commercial polystyrene, Dow Styron 678U (MI = 12.0), similar to the polymer rheologically characterized in a series of studies from our laboratories.[58,59] It was extruded at 180°C.

Film Extrusion Apparatus and Operating Procedure

The polystyrene films were produced using a 3/4-in. Rainville screw extruder with an annular blown film die (i.d. = 1.496 cm, o.d. = 1.605 cm).

The axial tension, F_L, of the film during processing was measured with a Tensitron web tension sensor. The pressure within the bubble was measured with a manometer through a tube connected to the die. The extrusion rate was measured by weighing the product for a predetermined time interval during steady-state operation.

Two series of films were produced. The first series of seven films, labeled U1–U7, were produced with no internal pressure and were approximately uniaxial. The films in this series had drawdown ratios (V_L/V_0) of 46–130. A second series of five films were made with an approximately constant blow-up ratio (B) of 2.5. These films had drawdown ratios in the range 33–60 and are labeled 1–5. One film was produced with a blow-up ratio 6.0 with equal biaxial extension according to eq. (7). A detailed summary of the films prepared is presented in Table II.

Birefringence of Films

Birefringence measurements were made with respect to both the machine and transverse directions, Δn_{12}, and with respect to the machine and thickness directions, Δn_{13}. This was accomplished using an instrument equivalent to that of Stein,[60] which allows a sample to be rotated and tilted in the incident polarized light beam.

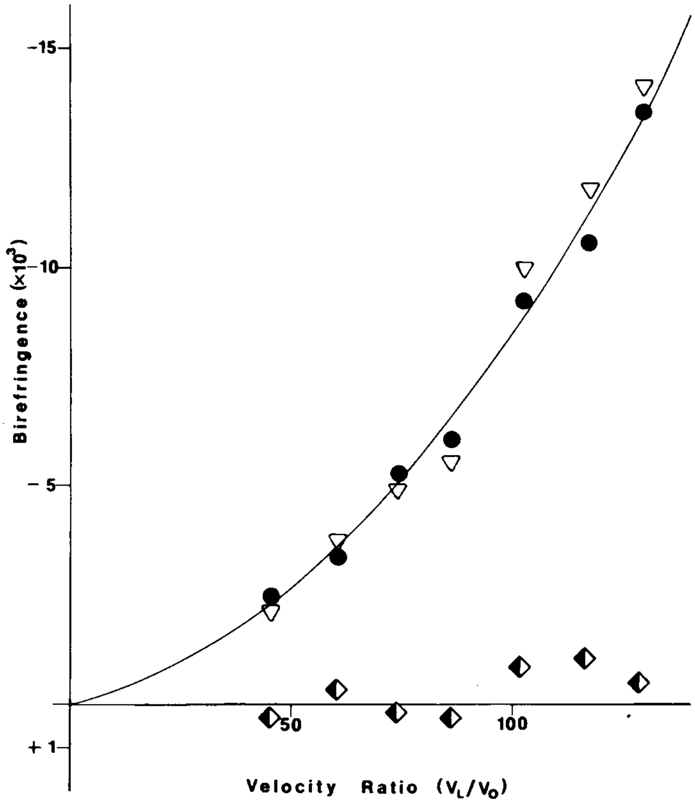

Fig. 2. Birefringence of polystyrene tubular film as a function of drawdown conditions, uniaxial. ▽, Δn_{12}; ●, Δn_{13}; ◆, Δn_{23}.

RESULTS

In interpretating our results, we take 1 as the machine direction, 2 as the transverse or circumferential direction, and 3 as the normal or thickness direction. We have determined the birefringences Δn_{12} and Δn_{13} as a function of the drawdown ratio V_L/V_0 for all samples. We plot these values in Figures 2 and 3.

For the approximately uniaxial case, we have

$$\Delta n_{13} \sim \Delta n_{12} < 0$$

with

$$\Delta n_{23} \sim 0 \tag{15a}$$

with the magnitude of Δn_{13} increasing with drawdown.

For the constant blow-up ratio series ($B \sim 2.5$) we have labeled the films as indicated 1–5, Figure 2. Here

$$\Delta n_{12} < 0$$

$$\Delta n_{13} < 0$$

$$\Delta n_{23} < 0$$

$$|\Delta n_{13}| > |\Delta n_{23}| \quad \text{or} \quad |\Delta n_{12}| \tag{15b}$$

Birefringences $|\Delta n_{12}|$ and $|\Delta n_{13}|$ increase with the drawdown ratio.

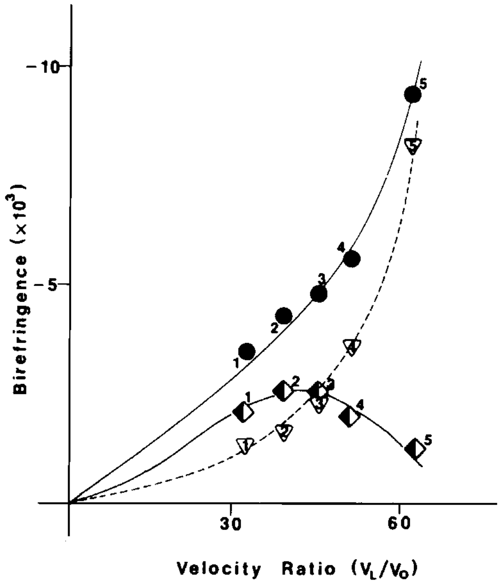

Fig. 3. Birefringences of polystyrene tubular film as a function of drawdown for $B \sim 2.5$. ▽, Δn_{12}; ●, Δn_{13}; ◆, Δn_{23}.

For the biaxial film

$$|\Delta n_{12}| \sim 0.25 \times 10^{-3}$$

$$|\Delta n_{13}| \sim |\Delta n_{23}| \qquad (15c)$$

In Figure 4, we have followed the procedure of Oda, White, and Clark[11] and plotted Δn_{ij} as a function of $\sigma_i - \sigma_j$, the difference in principal stresses at the line of vitrification. The principal stresses σ_1, σ_2, and σ_3 at this line in tubular film extrusion are σ_{11} and σ_{22} given by eq. (11) and σ_{33} taken as zero.

The Δn_{ij} and $(\sigma_i - \sigma_j)$ data correlate in a reasonably linear manner and the data agree rather well with the results of Oda et al. which are also shown in Figure 4. This is equivalent to agreement with eq. (13).

DISCUSSION

The birefringence Δn_{12} and Δn_{13} data of Figures 2 and 3 can be expressed as f_1^B and f_2^B. For the approximately uniaxial case of Figure 2, we have

$$f_1^B > 0$$

$$f_2^B \sim 0 \qquad (16a)$$

with f_1^B increasing with drawdown ratio, V_L/V_0. From Figure 3, the data at constant blow-up ratio gives

$$f_1^B > 0$$

$$f_2^B > 0 \qquad (16b)$$

f_1^B increases with drawdown, but f_2^B decreases slightly. For the equal biaxial film

$$f_1^B = f_2^B \sim 0.01 \qquad (16c)$$

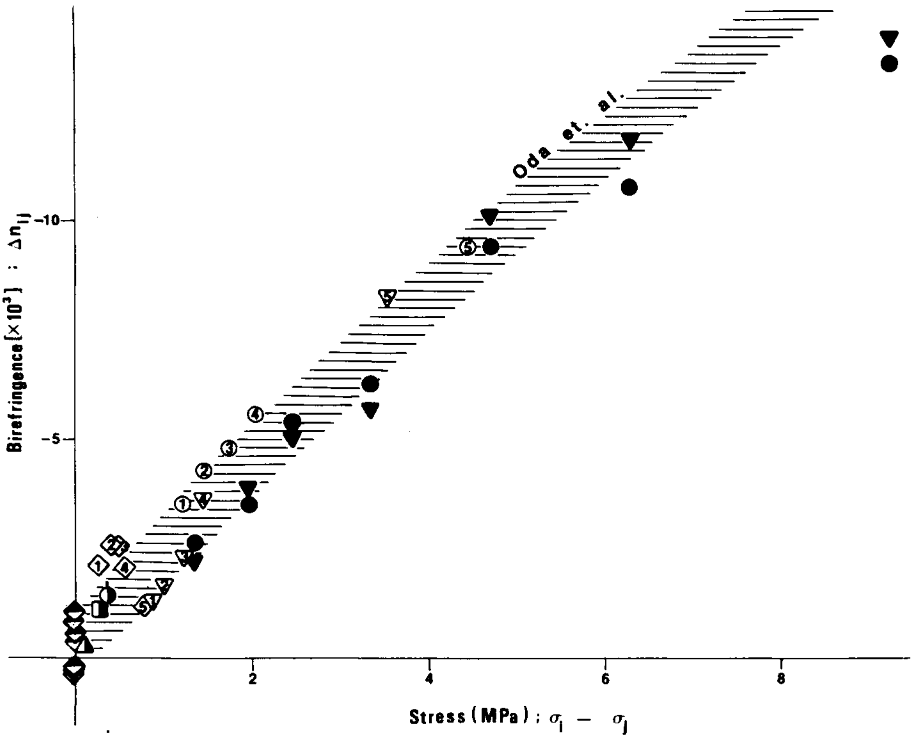

Fig. 4. Birefringence of polystyrene films as a function of applied stresses at vitrification for tubular film extension. Comparison with Oda, White, and Clark correlation. ▼, Δn_{12}; ●, Δn_{13}; ◆, Δn_{23}; where $B < 1$. ▽, Δn_{12}; ○, Δn_{13}; ◇, Δn_{23}; where $B = 2.2 \sim 2.6$. ▲, Δn_{12}; ◑, Δn_{13}; ◨, Δn_{23}; where $B = 6$.

These results for the orientation factors are plotted in Figure 5 as f_1^B vs. f_2^B. For such a plot, all states of orientation lie within an isosceles triangle as discussed by White and Spruiell.[29] Because of the relatively modest orientations generated in the polystyrene blown films, only the region near the origin of f_1^B vs. f_2^B space is shown. Uniaxial states lie along the coordinate axes, while states of equal biaxial orientation lie along the line at 45° to either coordinate axis. As expected, the data for the uniaxial films lie along the f_1^B axis. All of the data lie in the upper quadrant indicating that the chain orientation in the samples is intermediate between random (isotropic) and planar (chains parallel to film). For a blow-up ratio of ~2.5, the data proceeds with increasing drawdown from a position near the equal biaxial orientation line to a position representing nearly uniaxial orientation.

It is striking that the equal biaxial film has rather low orientation levels. This is despite the high blow-up ratio. In order to achieve biaxial orientation, the blow-up ratio must equal the drawdown ratio. This severely limits the drawdown and the level of stresses which can be developed.

The agreement between our data, White and Dietz prediction,[14] eq. (13), and Oda, White, and Clark's[11] correlation is of great importance. It allows a priori predictions of birefringence from process conditions for tubular film extrusion of polystyrene. Presumably, the approach could be readily extended to blown films of other amorphous polymers; it would be necessary only to know the stress

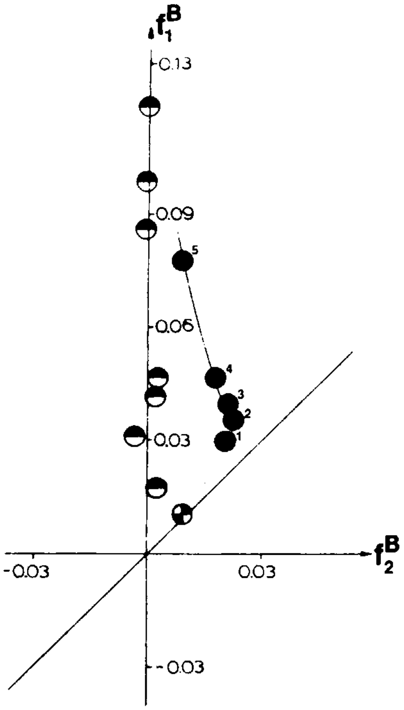

Fig. 5. Representation of biaxial orientation factors of extruded polystyrene tubular film on a triangular diagram. ⊖, Uniaxial polystyrene; ⊕, biaxial polystyrene.

optical coefficient and the intrinsic birefringence of the polymer. The work of Hamana, Matsui, and Kato,[51] Benaim,[52] and Yasuda, Sugiyana, and Yanagawa[53] suggests applicability to polyethylene terephthalate films (which do not crystallize). Perhaps more significantly, it shows the validity of this approach in multiaxial extensions and encourages its use to interpret other multiaxial processing operations such as blow molding or thermoforming.

Finally, it must be stated that the approach used here cannot be applied directly to semicrystalline polymers such as polyethylene and polypropylene since no account is taken in the present analysis of orientation produced by oriented nucleation and growth process occurring during crystallization under stress. This problem will be considered in more detail in future research.

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