

STRUCTURE DEVELOPMENT IN POLYMER PROCESSING

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Abstract - The development of crystallinity and orientation in polymer melt processing operations are critically reviewed. Also discussed are on-line monitoring of structure development in polymer processing operations and relationships between processing conditions and resultant structure.

INTRODUCTION

Polymeric products including fibers, films and molded products play an increasingly important role in commerce. The performance of these products is determined by the character of their structural order. In homogeneous polymers such structural order includes: (i) orientation of polymer chains, (ii) existence of crystalline order and its nature, (iii) superstructure including crystalline morphology, (iv) surface features such as roughness, and (v) internal voids and cracks. In heterogeneous systems such as block copolymers, rubber modified plastics and blends one must also specify phase size, shape and distribution.

The relationship of fabrication or processing conditions to structural order in polymer systems is of great importance. In the present paper, we discuss on-line monitoring of structure development in polymer processing operations and relationships between processing conditions and resultant structure. We begin with a critical discussion of structural characterization of polymer systems. We restrict ourselves to melt processable vitrifying and crystallizing homogeneous homopolymers and emphasize crystallization and orientation.

SPECIFICATION OF STRUCTURAL ORDER

Crystallinity

By crystallinity one generally means three-dimensional molecular level structural order. The concept of such order and its geometric implications was developed in the 19th century, but was not fully exploited until the 20th century with the development of the method of wide angle x-ray diffraction (WAXS) (1). Crystals are described in terms of three-dimensional (Bravais) lattice systems. Beginning with the highest level of crystalline symmetry and decreasing to lower levels of symmetry, one has cubic, hexagonal, rhombic, tetragonal, orthorhombic, monoclinic and triclinic (1). Metals largely crystallize into lattices with high levels of symmetry such as cubic. Polymers usually crystallize into lattice systems with lower symmetries such as orthorhombic, monoclinic and triclinic.

We list the crystalline forms of the more important polymers in Table 1. Atactic polymers such as commercial polystyrenes and polymethyl methacrylates do not crystallize. Polyethylene exhibits an orthorhombic unit cell (2). Polypropylene is polymorphic, possessing more than one crystalline form. The primary crystalline form is monoclinic (3). Nylon-6 is also polymorphic exhibiting both monoclinic (4) and pseudo-hexagonal (5) forms. Nylon-66 is under most conditions in a triclinic form (6). Polyethylene terephthalate crystallizes to a triclinic crystalline form (7).

Crystalline polymers are generally partially crystalline exhibiting significant non-crystalline character. Densities are lower than expected from the unit cell. Polymers are considered to have both crystalline and amorphous phases. Density has long been used as a primary method of estimating the crystalline fraction in polymers. Other methods include: (i) comparisons of WAXS diffraction intensities from crystalline regions and amorphous scattering, (ii) calorimetric measurements of actual compared to theoretical heats of fusions (8, 9).

The structure order of crystalline polymers in ranges of dimension of 50-200 Angstrom units has received considerable attention in the literature. Extensive research largely carried out with small x-ray scattering (SAXS) and transmission electron microscopy (TEM) coupled with observations of polymer single crystals (10) have led to the view that bulk crystallized flexible chain polymers consist of folded chain lamellae with intermediate regions of amorphous material (9, 10).

Orientation

The characterization of polymer chain orientation has a long history. The key early studies in the 1930's and 1940's were by P. H. Hermans and his coworkers (11, 12) on fibers and involve specification of orientation through the anisotropy of polarizability, i.e.

$$f_H = \frac{\alpha_1 - \alpha_2}{\Delta\alpha^\circ} \quad (1)$$

Here α_1 and α_2 are the mean polarizabilities in the axial and radial directions, and $\Delta\alpha^\circ$ the difference in polarizability along and perpendicular to a polymer chain. Hermans et al. show that this is equivalent to

$$f_H = \frac{3\cos^2\phi_{c1} - 1}{2} \quad (2)$$

where $\phi_{c,1}$ is the angle between the fiber axis and the polymer chain axis.

Hermans and Platzek (11) originally discussed the determination of f_H through birefringence Δn_{12} . Here '2' refers to the radial direction. For an amorphous polymer such as polystyrene, f_H is simply $\Delta n_{12}/\Delta^\circ$ where Δ° is the maximum or intrinsic birefringence.

Hermans et al. in the mid-1940's described how f_H could be determined through wide angle x-ray diffraction (WAXS). They later (13) noted that WAXS yields orientation of crystalline and amorphous regions. The two measurements may be used to separate the orientations of the crystalline and amorphous regions (13, 14).

In the 1950's, it was shown that infrared dichroism (14, 15) could also be used to determine polymer chain orientation. During the 1960's, methods such as fluorescence (16, 17) and broad line nuclear magnetic resonance (18) were shown to yield data specifying orientation. In the 1970's, it became clear that orientation could be measured with Raman scattering (19, 20) as well.

As early as 1941, F. H. Muller (21) noted that what is generally of concern is an orientation distribution and not simply the $\cos^2\phi_{c1}$ mean term of Eq. (2). He argued that Eq. (2) corresponds to the second spherical (Legendre) harmonic function $P_2(\cos\theta)$. Muller represents the orientation distribution about a preferred axis in terms of an expansion of even spherical harmonic functions $P_n(\cos\theta)$ contains terms in $\cos^4\phi_{c1}$ as well as $\cos^2\phi_{c1}$ and $P_n(\cos\theta)$ in general will have $\cos^n\phi_{c1}$ as well as lower order terms.

The Hermans orientation factor has been generalized by Stein (22) to represent the orientation of the three crystallographic axis in crystalline polymers. He writes

$$f_a = \frac{3\cos^2\phi_{a1} - 1}{2} \quad f_b = \frac{3\cos^2\phi_{b1} - 1}{2} \quad f_c = \frac{3\cos^2\phi_{c1} - 1}{2} \quad (3a,b,c)$$

Stein describes how to determine f_a , f_b and f_c from WAXS patterns in polyethylene. Hoshino et al. (23) described the evaluation of f_a , f_b and f_c for polypropylene and polybutene-1. Bankar et al. (24) discuss the determination of these Hermans-Stein orientation factors for nylon-6, Danford et al. (25) for nylon-66 and Shimamura et al. (26) for hydroxypropyl cellulose.

Biaxial orientation is of importance in films and bottles. The representation of biaxial orientation through orientation factors was initiated by Stein (27) in 1958. Alternative approaches are discussed in succeeding papers by Wilchinsky (28), Desper and Stein (29), Nomura et al. (30) and White and Spruiell (31). The approach of the latter authors seems to the author the most useful one. Orientation is defined in terms of angles ϕ_{c1} and ϕ_{c2} between the polymer chain axis and the machine '1' and transverse '2' direction. These authors proceeded by generalizing Hermans' arguments on the anisotropy of the polarizability tensor. For amorphous polymers

$$f_{1c}^B = \frac{\alpha_1 - \alpha_3}{\Delta\alpha^\circ} = 2\cos^2\phi_{c1} + \cos^2\phi_{c2} - 1 \quad (4a)$$

TABLE 1. Crystalline forms of most important polymers

Polymer	Crystalline Form	Hermans-Stein Uniaxial Orientation Factors	Biaxial Orientation Factors Eq. (3)
Atactic Polystyrene	Amorphous	Oda et al. (60)	Choi et al. (32)
Polyethylene	Orthorhombic (2)	Stein (22)	Choi et al. (35)
Isotactic Polypropylene	Monoclinic (3) Smectic quenched form (51, 104) Hexagonal (105)	Monoclinic Hoshino et al. (23)	Shimomura et al. (36)
Nylon-6	α -Monoclinic (4) γ -Pseudo-hexagonal (5)	γ -pseudo-hexagonal Bankar et al. (24)	
Nylon-66	Triclinic (6) Pseudo-hexagonal at high temperatures (106) 'Nematic' quenched form (107)	f_c only determined (25)	
Polyethylene Terephthalate	Triclinic (7)	f_c only determined (108)	

TABLE 2. On-line measurements of structure development in melt spinning

Polymer	WAXS	Birefringence	Comments
Polyethylene	Katayama et al. (48) Dees and Spruiell (49) Spruiell and White (50)	Katayama et al. (48)	polymer crystallizes in spinline
Polypropylene	Katayama et al. (48) Nadella et al. (51) Ishizuka and Koyama (52-54)	Katayama et al. (48) Shimizu and Shimazaki (56); Ishizuka and Koyama (57); Nadella et al. (51)	polymer crystallizes
Polybutene-1	Katayama et al. (48)	Katayama et al. (48)	polymer crystallizes
Nylon-6	Bankar et al. (24)	Bankar et al. (24) Hamana et al. (57) Ishibashi et al. (58-60)	crystallizes on bobbin not in spinline unless special heated chambers
Nylon-66	Chappel et al. (47)	Danford et al. (25)	
Polyethylene Terephthalate		Thompson (55) Hamana et al. (58)	birefringence proportional to stress
Polystyrene		Oda et al. (62)	birefringence proportional to stress

TABLE 3. Application of frozen-in flow birefringence hypothesis to predict orientation in fabricated parts

Operation	Polymer	Researcher
Melt Spinning	Polyethylene Terephthalate	Hamana et al. (58) Dumbleton (77)
	Polystyrene	Oda et al. (62)
Tubular Film	Polystyrene	Choi et al. (32)
Injection Molding	Polystyrene	Janeschitz-Kriegl (89) Dietz et al. (87, 88, 90)
Blow Molding	Polystyrene	White and Agarwal (34)

$$f_{2c}^B = \frac{\alpha_2 - \alpha_3}{\Delta\alpha^\circ} = \sqrt{2\cos^2\phi_{c2}} + \sqrt{\cos^2\phi_{c1}} - 1 \quad (4b)$$

These orientation factors reduce to the case of uniaxial orientation when

$$\alpha_2 = \alpha_3 \quad \text{and} \quad \sqrt{\cos^2\phi_{c2}} = \sqrt{\cos^2\phi_{c3}} \quad (5)$$

With the aid of the Pythagorean theorem, introduction of Eq. (5) into Eq. (4) yields

$$f_{1c}^B = \frac{3\cos^2\phi_{c1} - 1}{2} \quad (6a)$$

$$f_{2c}^B = 0 \quad (6b)$$

For the case of isotropy f_{c1}^B and f_{c2}^B are zero. For polymer chains perpendicular to the 12 plane, f_{c1}^B and f_{c2}^B are both (-1). For equal biaxial orientation f_{c1}^B and f_{c2}^B are equal.

It is possible to graphically represent the state of biaxial orientation through a plot of f_{1c}^B versus f_{2c}^B . All data falls within an isosceles triangle with vertex at (-1, -1) and base stretching from (1,0) to (0,1) (Fig. 1).

The biaxial orientation factors of Equation (4) may be generalized to apply to all three crystallographic axes (31). We may write for the j th crystallographic axis

$$f_{1j}^B = \sqrt{2\cos^2\phi_{j1}} + \sqrt{\cos^2\phi_{j2}} - 1$$

$$f_{2j}^B = \sqrt{\cos^2\phi_{j2}} + \sqrt{2\cos^2\phi_{j1}} - 1 \quad (7a,b)$$

The biaxial orientation factors f_{1c}^B and f_{2c}^B for amorphous polymers may be determined from measurements of birefringence through

$$f_{1c}^B = \frac{\Delta n_{13}}{\Delta^\circ} \quad f_{2c}^B = \frac{\Delta n_{23}}{\Delta^\circ} \quad (8a,b)$$

This has been applied to polystyrene in papers by Choi et al. (32), Matsumoto et al. (33) and White and Agarwal (34). Choi, Spruiell and White (35) have evaluated the f_{1j}^B and f_{2j}^B from WAXS measurements on polyethylene. Shimomura et al. (36) more recently have similarly evaluated these biaxial orientation factors for polypropylene from WAXS measurements.

More sophisticated procedures have been developed for characterizing biaxial orientation. Most important among these is the method of pole figures (8, 28, 29, 35, 36) where the distribution of intensities of normals to crystallographic planes of interest is represented in planar stereographic projections.

ON-LINE CHARACTERIZATION

On-line studies of structure development in polymer processing date to the 1960's. Relatively few processing operations have been studied in this manner. Most papers have dealt with melt spinning. A smaller number have considered flow through dies and film extrusion. Most investigations have involved on-line birefringence. A smaller number of researchers have used on-line WAXS.

Flow through dies

The earliest investigation of on-line birefringence in flow through dies is the work of Tordella (37) in 1963. Experiments of Bogue and his coworkers (38) studied birefringence patterns in polymer solutions extensively in the mid-1960's. The birefringence profiles of polymer melts flowing through two-dimensional dies of varying cross-sections has been investigated in more recent years by Wales (39); Han and his coworkers (40-42); Brizitsky,

Vinogradov, Isayev and Podolsky (43); and Arai and his team (44).

The researchers in these studies have not sought to interpret birefringence in terms of molecular orientation but rather as stresses using the Rheo-Optical Law which may be stated (38-46):

$$\tilde{n} = \frac{1}{3} (\text{tr } \tilde{n}) \mathbf{I} + C \tilde{P}$$

$$n_i - n_j = C (\sigma_i - \sigma_j)$$
(9)

where $\tilde{\sigma}$ is the total stress tensor and \tilde{P} the deviatoric stress tensor. Equation (8) is the same as the relation used in classical photoelastic stress analysis by engineers to determine stress fields in solids. Its validity for flowing polymer melts was first proposed by Lodge (45) on the basis of considerations of the characteristics of flexible chain networks of macromolecules. It has since been shown to be valid by many investigators for a range of experiments. Most notable have been the studies of Janeschitz-Kriegl and his coworkers (46).

It is found in these studies of extrusion that high birefringence (and thus chain orientation) occur in converging flow at the entrance of dies. This is most pronounced with low density polyethylene. High birefringence and orientation exist near the die wall as opposed to the centerline - especially at the die exit. The special characteristics of liquid crystalline hydroxypropyl cellulose are discussed by Shimamura et al. (26).

Melt spinning of fibers (see Table 2)

On-line measurements of a fiber spinline with WAXS were initiated in 1964 by Chappel, Culpin, Gosden and Tranter (47). A much more substantial study was published a few years later by Katayama, Amano and Nakamura (48). More recently on-line WAXS investigations have been described by Spruiell and his coworkers (24, 49-51) and by Ishizuka and Koyama (52-54). These studies have involved five different polymers. Polyethylene has been investigated by Katayama et al. (48) and by Dees and Spruiell (49); polypropylene by Katayama et al. (48), Spruiell et al. (50, 51) and Ishizuka and Koyama (52-54); polybutene-1 by Katayama et al. (48); nylon-6 by Bankar et al. (24); and nylon-66 by Chappel et al. (47).

The studies of polyethylene, polypropylene and polybutene-1 all clearly indicate crystallization in the threadline with the occurrence of sharp diffraction peaks. This generally corresponds to a plateau in the temperature profile along the spinline, which is apparently due to the evolution of heat during crystallization. Katayama et al. (48) and later investigators (49) have computed the extent of crystallization as a function of spinline residence time and position. It is concluded that spinline stresses increase crystallization rates. Bankar et al. (24) found that nylon-6 did not crystallize in the spinline. Some crystallization occurs in the spinline for nylon-66.

Polypropylene exhibits bimodal orientation when it crystallizes under uniaxial stress (48, 51). One population has its chain axis parallel to the fiber axis. A second population exhibits an a-axis orientation. It is observed that the c-axis oriented population forms first in the melt spinning process. This suggests an epitaxial growth of the a-axis oriented population.

There have been extensive measurements of optical retardation in a fiber spinline beginning with the studies of Thompson (55). On-line measurements of birefringence for polyethylene, polypropylene and polybutene-1 were reported by Katayama et al. (48). Further studies of polypropylene are contained in the work of Shimizu and Shimazaki (56), Ishizuka and Koyama (57) and Nadella et al. (51). On-line measurements of birefringence in the melt spinning of nylon-6 are reported by Hamana, Matsui and Kato (58), Ishibashi and his coworkers (59-61), Bankar et al. (24) and on nylon-66 by Danford et al. (25). Polyethylene terephthalate (PET) has been investigated by Thompson (55) and by Hamana et al. (57) and polystyrene by Oda, White and Clark (62).

The studies of PET, polystyrene and nylon-6 have generally indicated that the on-line birefringence is proportional to the spinline stress (58, 61, 62) through the Rheo-Optical Law (Equation (4)), i.e.

$$n_1 - n_2 = \Delta n_{12} = C \sigma_{11}$$
(10)

From Equation (2) this means the Hermans orientation factor is proportional to the stress through (62)

$$f_H = \frac{C}{\Delta^0} \sigma_{11}$$
(11)

Studies of on-line birefringence for polypropylene and polybutene-1 which exhibit spinline crystallization generally show a gradually increasing birefringence proportional (57) to the stress followed by an abrupt increase in birefringence where crystallization occurs. This rise may be interpreted using the expression of Hermans et al. (13) (compare Stein and Norris (14)) for the birefringence of a partially crystalline polymer

$$\Delta n_{12} = X f_{c, \text{cryst}} \Delta^{\circ}_{\text{cryst}} + (1 - X) f_{c, \text{amorph}} \Delta^{\circ}_{\text{amorph}} + \Delta n_{\text{form}} \quad (12)$$

where X is the volume fraction of crystalline material, $f_{c, \text{cryst}}$, $\Delta^{\circ}_{\text{cryst}}$ are the Hermans orientation factor and intrinsic birefringence of the crystalline regions and $f_{c, \text{amorph}}$, $\Delta^{\circ}_{\text{amorph}}$ for the amorphous material. Δn_{form} is usually considered negligible. The large rise in Δn_{12} is accounted for by considering $f_{c, \text{cryst}}$ to be much larger for the crystalline material than $f_{c, \text{amorph}}$ for the amorphous material.

The one study for polyethylene by Katayama et al. (48) indicates that the birefringence increases along the spinline, dips and goes through a minimum and then rises rapidly.

Ishibashi and Ishii (60) using on-line birefringence measurements conclude that placing a hot tube around the upper part of a nylon-6 spinline can induce crystallization.

Film extrusion

On-line measurements of structure development in film extrusion are much more limited than investigations for melt spinning. The pioneering research in this area is that by Nagasawa, Matsumura, Hoshino and Kobayoshi (63). They report on-line birefringence measurements for polyethylene, polybutene-1 and nylon-6. The only other on-line studies seem to be those of Stehling, Speed and Westerman (64) who report investigations of small angle light scattering (SALS) for polyethylene.

Nagasawa et al. report birefringence measurements on a tubular film line with blow-up ratio of unity. With each of the three melts, they observe a gradual increase in birefringence to a position where it increases rapidly to an upper plateau. This presumably corresponds to crystallization.

Stehling et al. (64) study SALS patterns on film extruded from a slit die. They note that SALS scattering increases with distance from the die in most cases. In some cases the scattering exhibits a maxima. Generally haze is attributed in these studies to scattering by the surface of the films rather than by their internal structure.

Injection molding

On-line measurements of birefringence development in injection molding have been reported by Han (65) using polystyrene and polyethylene. The measurements on polystyrene were carried out through the cooling and vitrification process. Because of the spatially non-homogeneous character of the polymer as it solidifies, and the thick sections involved, only qualitative investigations are possible. Han interprets his observations using the Rheo-Optical Law for the stress field rather than as molecular orientation.

STRUCTURE OF FABRICATED POLYMER PARTS

Melt spun fibers

There have been many studies of the structure of melt spun fibers as a function of process conditions. Few of these studies have been quantitative in character. The key early studies are those of Kitao, Ohya and their coworkers (66, 67) who related the Hermans orientation factors to process conditions. At about the same time a similar view was adopted by Abbott and White (68) and Dees and Spruiell (49). This has been developed in later years in a series of papers by Spruiell and White and their colleagues (24-26, 50, 51, 62, 68); Ishizuka and Koyama (57); Shimizu, Toriumi and Imai (69) and Yagi and Han (70).

The key to interpretation of experimental data is the observation of Hamana et al. (58), Dumbleton (71), Oda et al. (62) and others that birefringence orientation developed during flow in polystyrene and PET (at low take-up speeds) are vitrified in place (Fig. 2). The birefringence and Hermans orientation factors are proportional to the spinline stress through Equations (9) and (10). This remarkable result as we will see is also found in other processing operations (Table 3).

Dees and Spruiell (49), Spruiell and White (50) and Nadella et al. (5) using Hermans-Stein orientation factors conclude that crystalline morphology in crystallizing polyolefins is similarly determined by the spinline stress (Table 4). Figure 3 contrasts data for five melt spun polypropylenes. This is supported by the earlier correlation of Shimizu and Shimizaki (56) for birefringence and spinline stress of melt spun polypropylene fibers. The variation of the Hermans-Stein orientation factors is however complex. For polyethylene at low stress, the b-axis first becomes perpendicular to the fiber axis as may be seen from the 020

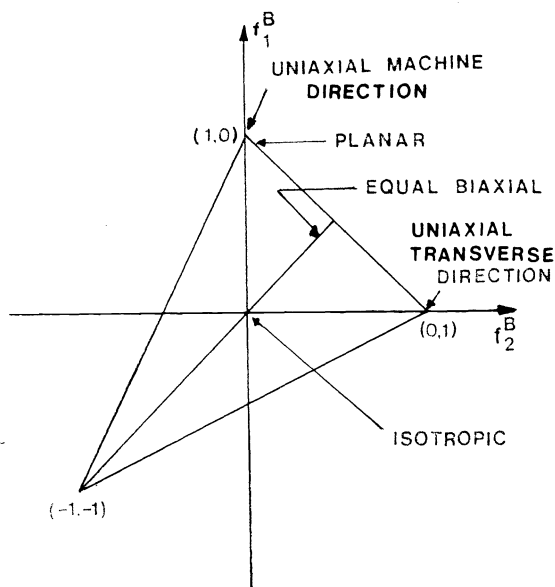


Fig. 1 Orientation triangle

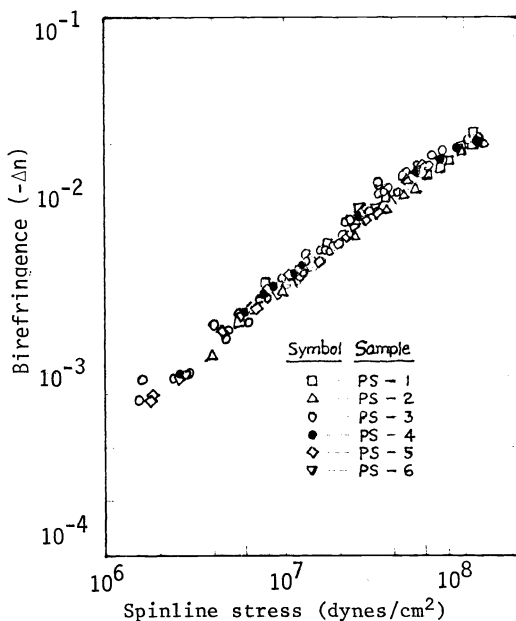


Fig. 2 Birefringence of melt spun polystyrene filaments as a function of spinline stress.

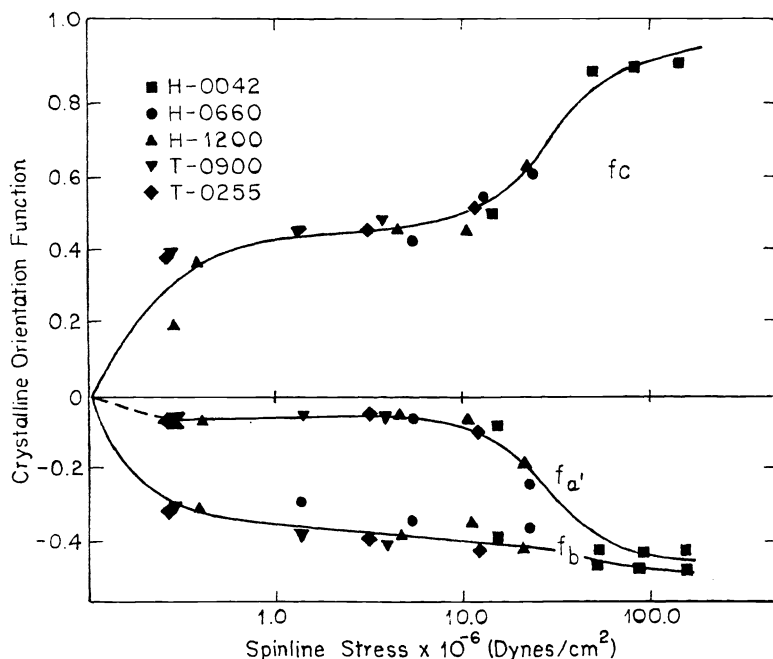


Fig. 3 Hermans-Stein a, b and c axis orientation factors of spun fibers as a function of spinline stress for five polypropylenes.

TABLE 4. Correlation of crystalline orientation with stress fields at position of crystallization

Operation	Polymer	Researcher
Melt Spinning	Polyethylene	Dees and Spruiell (49)
	Polypropylene	Spruiell and White (50)
		Nadella et al. (51)
		Shimizu and Shimizaki (56) (birefringence-stress)
	Nylon-66	Danford et al. (25)
Tubular Film Extrusion	Polyethylene	Choi et al. (85)
	Polypropylene	Shimamura et al. (36) (birefringence-stress)

reflection. The *b*-axis seems to represent a direction of crystal growth. The *a* and *c* axes tend to be randomly distributed. This leads to the appearance of *a*-axis orientation as may be seen in the 200 reflection. At higher stress levels the *c*-axis tends to become parallel to the fiber axis. In terms of the Hermans-Stein orientation factors one has (compare 49, 50, 67, 68):

$$\text{zero stress} \quad f_a = f_b = f_c = 0 \quad (13a)$$

$$\text{low intermediate stress} \quad f_b \rightarrow -0.5 \quad f_a = f_c > 0 \quad (13b)$$

$$f_b = -0.5 \quad f_a = f_c = 0.25 \quad (13c)$$

$$\text{high stress} \quad f_b = -0.5 \quad f_c \rightarrow 1 \quad f_a \rightarrow -0.5 \quad (13d)$$

Generally experimental results on other flexible chain polymers are compatible with this. Such behavior is observed in polypropylene. Polypropylene also exhibits a bimodal crystalline orientation as we have indicated earlier (48, 51).

Studies of polyethylene terephthalate indicate that it crystallizes in the threadline at higher take-up velocities and forms highly oriented filaments (72). The fibers seem also to have a fibrillar void structure in the outer layers apparently due to a drawing process which must happen directly after crystallization. The studies of Shimizu et al. (72) on this topic are of great importance.

Various investigators have noted the development of two point meridional SAXS patterns in fibers with spacings of order 60-200 Å (24, 49, 51, 73). Transmission electron microscopy (TEM) has revealed lamellar structures perpendicular to the fiber axis with similar spacings (73, 74). This has led to the view of row structures and twisting lamellae as described by Keller and Machin (75) and elucidated by Dees and Spruiell (49) for melt spun fibers (Fig. 4).

Film extrusion

There have been few quantitative studies of structure development in film extrusion operations. Choi et al. (32) have determined the birefringence of polystyrene tubular film. Early studies of polyethylene tubular film were described by Holmes and Palmer (76), Lindenmeyer and Lustig (77) and Desper (78). Maddams and Preedy (79, 80) and Choi et al. (35) have compared pole figures (8) for polyethylene tubular film. Shimamura et al. (36) have determined pole figures for polypropylene film.

Choi et al. (32) have related the biaxial orientation factors of Equations (4) and (8) in polystyrene and tubular film to the stress field at solidification. The stresses consist of tensile stresses in the machine direction caused by the take-up rolls and transverse stresses induced by the bubble pressure. The birefringence in the tubular polystyrene film produced was proportional to the difference in principal stresses according to Equation (8), (32), (see Fig. 5), i.e.

$$\Delta n_{12} = C \left(\frac{F_L}{2\pi RH} - \frac{R\Delta p}{H} \right) \quad \begin{array}{l} R = \text{bubble radius} \\ H = \text{film thickness} \end{array}$$

$$\Delta n_{13} = C \frac{F_L}{2\pi RH} \quad \Delta n_{23} = C \frac{R\Delta p}{H} \quad \begin{array}{l} F_L = \text{take-up tension} \\ \Delta p = \text{bubble pressure} \end{array} \quad (14a,b,c)$$

The biaxial orientation factors are proportional to the stress

$$f_{1c}^B = \frac{C}{\Delta^\circ} \frac{F_L}{2\pi RH} \quad f_{2c}^B = \frac{C}{\Delta^\circ} \frac{R\Delta p}{H} \quad (15)$$

This is essentially the same behavior found by Oda et al. (62) for melt spun fibers. As it is easier to develop high tensions rather than inflation pressures, the process favors predominantly uniaxial orientation in the machine direction. Increasing drawdown at fixed blow-up ratio increases uniaxial orientation (Fig. 6).

Choi et al. (35) find the White-Spruiell crystalline biaxial orientation factors, Equation (7), for polyethylene film to be determined by the stress field at solidification (Table 4) (Fig. 7). The functional dependence of $f_{1j}^B - f_{2j}^B$ the difference in principal stresses $\sigma_{11} - \sigma_{22}$ was found to be the same as that determined by Dees and Spruiell (49) for melt spun polyethylene fibers.

Various investigators (75, 81, 82) have found lamellar superstructures in films using SAXS and TEM measurements. Most investigations have been for films produced under uniaxial conditions and reveal row structures of the type observed for fibers. Choi et al. (35) study films produced under equal biaxial conditions. They find the lamellae uniformly distributed in the plane of the film (Fig. 8).

Injection molding

Orientation in injection molded parts of glassy polystyrene has been investigated by Ballman

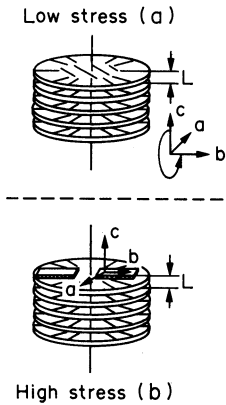


Fig. 4

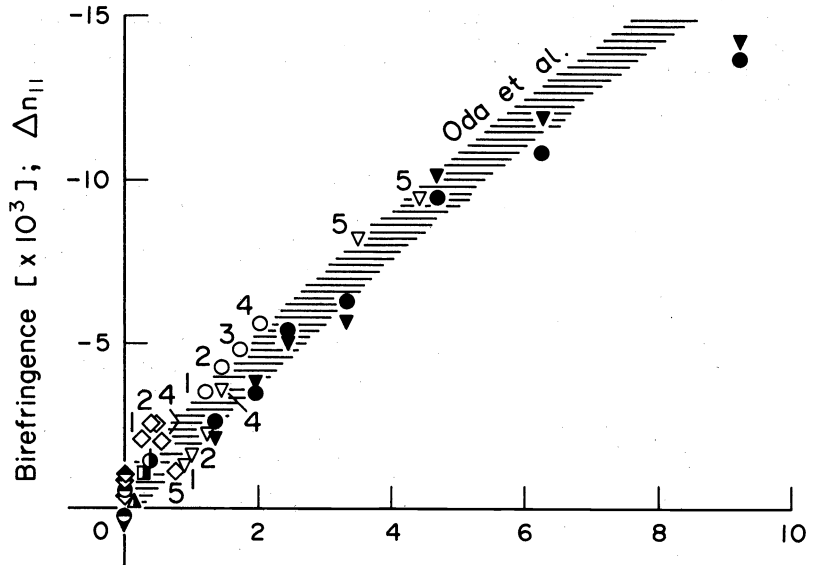


Fig. 5

Fig. 4 Keller-Machin row structure (cylindrite model) for strictly uniaxial samples.

Fig. 5 Birefringence of polystyrene films as a function of applied stresses at vitrification for tubular film extension. Comparison with Oda, White and Clark correlation.

∇ , Δ n_{12} ; \bullet , Δ n_{13} ; \blacklozenge , Δ n_{23} ; where $B < 1$. ∇ , Δ n_{12} ; \circ , Δ n_{13} ; \blacklozenge , Δ n_{23} ; where $B = 2.2 \sim 2.6$. Δ n_{12} ; \bullet , Δ n_{13} ; \blacksquare , Δ n_{23} ; where $B = 6$.

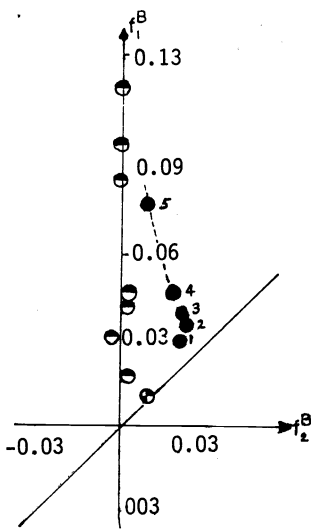


Fig. 6

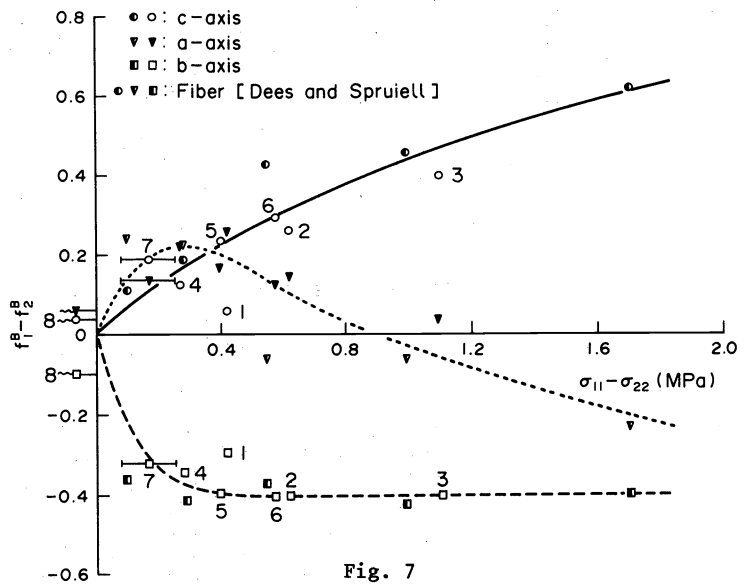


Fig. 7

Fig. 6 Representation of biaxial orientation factors of extruded polystyrene film on a triangular diagram.

\bullet Uniaxial polystyrene. \oplus Biaxial polystyrene.

Fig. 7 Plot of difference in biaxial orientation factors $f_{1j} - f_{2j}$ as a function of $\sigma_1 - \sigma_2 = F_L / 2\pi R h_L - R_L \Delta p / h_L$.

and Toor (83); Wales, Van Leeuwen and van der Vigh (84); Fleissner (85) and various later investigators (86-88). The primary observations have related to birefringence distributions across the thickness of injection molded slabs. If '1' is the direction of flow '2' the direction of shear and '3' the transverse direction, we are concerned with measurements of Δn_{12} and Δn_{13} . These exhibit minima near the center and maxima near but not at the walls.

Ballman and Toor (83) and later more specifically in terms of the frozen-in flow birefringence hypothesis Janeschitz-Kriegl (89) and Dietz, White and Clark (87, 88, 90) interpreted this with a flow mechanism based upon cold walls vitrifying melt near the walls and melt shear proceeding through the center of the cross-section. The analysis is based on the development of stresses through a force balance between the pressure gradient $\partial p / \partial x_1$ and variations of shear stress σ_{12}

$$0 = - \frac{\partial p}{\partial x_1} + \frac{\partial \sigma_{12}}{\partial x_2} \quad (15)$$

with birefringence development being associated with the normal stresses arising in shear flow viscoelastic melts. Following mold filling, birefringence and stresses relax away until vitrification which proceeds inward from the walls. Oda et al. (62) have shown quantitatively using shear creep measurements that frozen-in birefringence is determined by the difference in principal stresses at vitrification. Reasonable agreement is found between theoretical predictions based on calculations for such a model and measured birefringence profiles (87-90).

There have been some optical microscopic studies of cross-sections of injection molded crystalline parts (91-98). High levels of orientation are found near the mold walls and more isotropic character in the center of the cross-section. Heckmann and his coworkers (93, 97) have initiated quantitative orientation measurements presenting both pole figures and $\cos^2 \phi_{c1}$ as a function of position in molded parts. However, there have been no correlations with process conditions.

Clark and Garber (99) and Heckmann and Johnson (97) have shown the existence of row structures presumably folded chain lamellae in injection molded parts using TEM. The core of injection molded parts is founded by optical microscopy to be spherulitic. The outer layers have been found to possess more oriented superstructures.

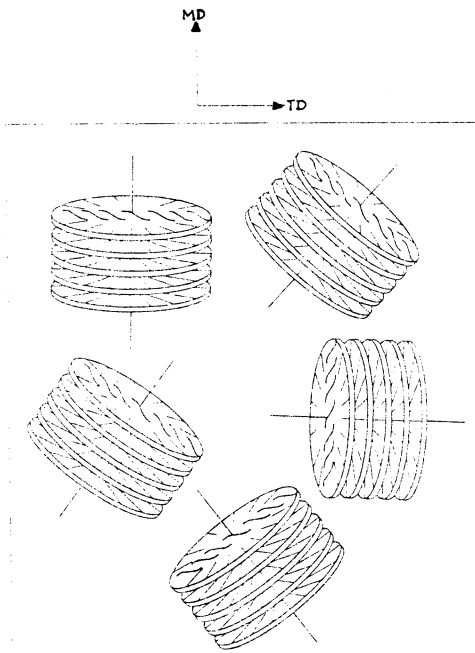


Fig. 8. Morphological model for film with equal biaxial orientation

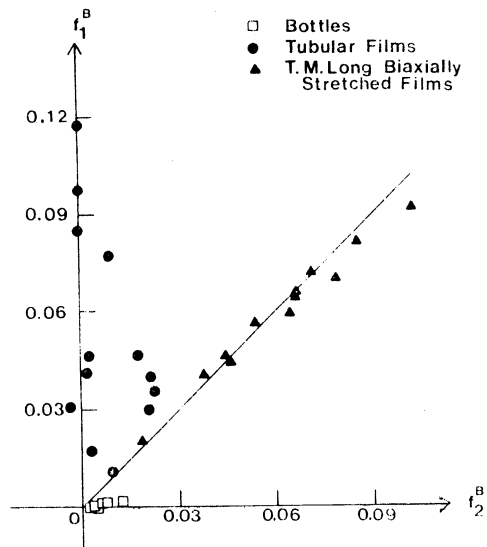


Fig. 9. Orientation triangle showing data of this paper biaxially stretched sheets and tubular film formed from polystyrene.

Blow molding

Orientation distributions in blow molded polystyrene bottles have been investigated by White and Agarwal (34) using birefringence. Biaxial orientation factors were determined as a function of position along the length of the bottle. The orientation was found to be low end primarily in the transverse direction (Fig. 9). More recently Choi, Spruiell and White (100) have undertaken investigations of crystalline orientation and morphology in blow molded bottles. Pole figures and biaxial orientation factors have been evaluated.

White and Agarwal (34) have sought to compare their measured birefringence distributions to predictions of the frozen-in orientation hypothesis for polystyrene bottles. Transverse orientation is determined by inflation pressure. Machine direction orientation is determined by gravity. For an annular cylinder the birefringence would be predicted to be

$$\Delta n_{23} = C \frac{R\Delta p}{h} \quad \begin{array}{l} \text{parison radius} = R \\ \text{parison thickness} = h \\ \text{parison length} = L \end{array}$$

$$\Delta n_{13} = C\rho gL \quad \text{inflation pressure} = \Delta p \quad (17)$$

It is necessary to account for cooling prior to vitrification. Reasonably good agreement is found. As indicated by Equation (16) orientation is primarily in the transverse or hoop direction.

Studies of structure development in stretch blow molding of polyethylene terephthalate bottles have been carried out by Bonnebat, Rouillet and de Vries (101) and Cakmak, Spruiell and White (102). Birefringence and WAXS measurements have been carried out. Pole figures and biaxial orientation factors have been computed by the latter authors. The orientation has been found to be intermediate between equal biaxial and uniaxial in the transverse direction. Kim (103) and Cakmak et al. (102) have studied variations of structure through the cross-section using optical techniques.

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