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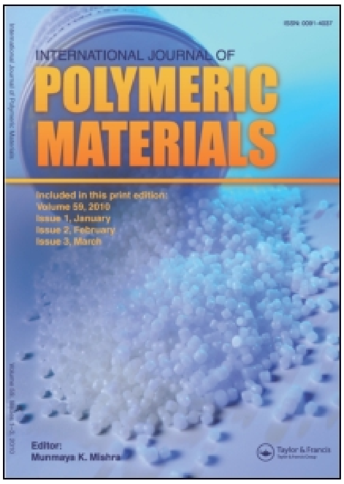

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Polymer Crystallization Induced by Biaxial Stretching During Film Manufacture†

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In the manufacture of semicrystalline polymer films, orientation is commonly introduced. This orientation may be uniaxial, unbalanced biaxial, or balanced biaxial. Machine-direction and transverse stretching may be concurrent or sequential; each orienting process is characterized by a trajectory on the biaxial stress plane and the biaxial extension plane. The presence of uniaxial or biaxial tensile stress strongly affects the process of polymer crystallization, influencing the crystal-amorphous equilibrium, crystallization kinetics, and the resulting polymer morphology. Post-solidification alterations in morphology can be imposed by drawing or heat-setting under biaxial tension, below the crystalline melting point.

The machine-direction and transverse properties of a semicrystalline polymer film depend strongly on the crystalline morphology, and hence on the processing history. The dependence of film properties on processing conditions are well recognized and widely exploited; but the morphology of biaxially oriented films and the structure–property relationships involved are only partly understood.

INTRODUCTION

The course of polymer crystallization is strongly influenced by mechanical stresses. Both "hydrostatic" and "deviatoric" stresses affect the equilibrium melting point, the kinetics of crystallization, and the resulting crystalline morphology—but in different ways.

The problem of crystallization under the influence of deviatoric stresses arises in the manufacture of some semi-crystalline thermoplastic *films*. Thin films can be considered to be two-dimensional analogues of fine fibers, with biaxial stresses and biaxial orientation (balanced or unbalanced) in place of the uniaxial stress and orientation of fibers.[1]

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†Presented at a Symposium on "Flow-Induced Crystallization," at the Midland Macromolecular Institute, August 22–26, 1977, R. L. Miller, Chairman.

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There are several possible ways to employ a trajectory on a two-dimensional map to represent the sequence of biaxial stresses and biaxial extensions encountered in a film process. The stress can be specified by the two principal stresses S_1 and S_2 (S_3 being effectively *zero*), or by the *deviatoric* stresses s_1, s_2, s_3 (which sum to zero). The deformation can be specified by the principal extension ratios λ_1 and λ_2, or by their logarithms ($ln\ \lambda_1$, $ln\ \lambda_2$, $ln\ \lambda_3$), which sum to zero for an incompressible material. S_1 and S_2 are everywhere non-negative in the type of process under consideration.

Figure 1 illustrates various possible ways to present the information regarding stress and deformation sequences. For an *elastic* film, with a one-to-one correspondence between the state of stress and the state of deformation, *either* a stress trajectory *or* a deformation trajectory will provide the necessary information. With *inelastic* films, both a stress trajectory *and* a deformation trajectory are necessary.

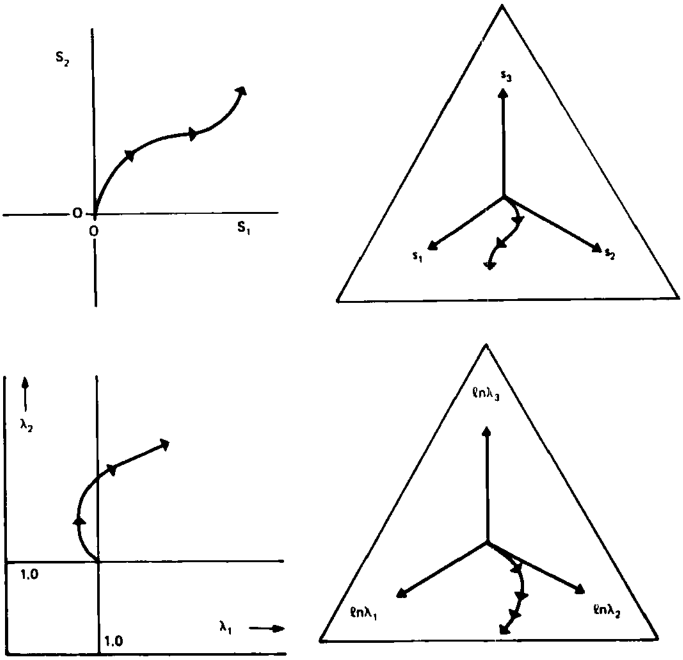

FIGURE 1 Trajectories of biaxial stress and deformation: S = principal stress; s = deviatoric stress; λ = extension-ratio.

Let us examine three particularly simple patterns of stretching:

1) Uniaxial;
2) Uniaxial with *restrained width*;
3) Balanced biaxial.

These are indicated in Figure 2. Each of these three modes of film stretching can be closely approximated in film processing.

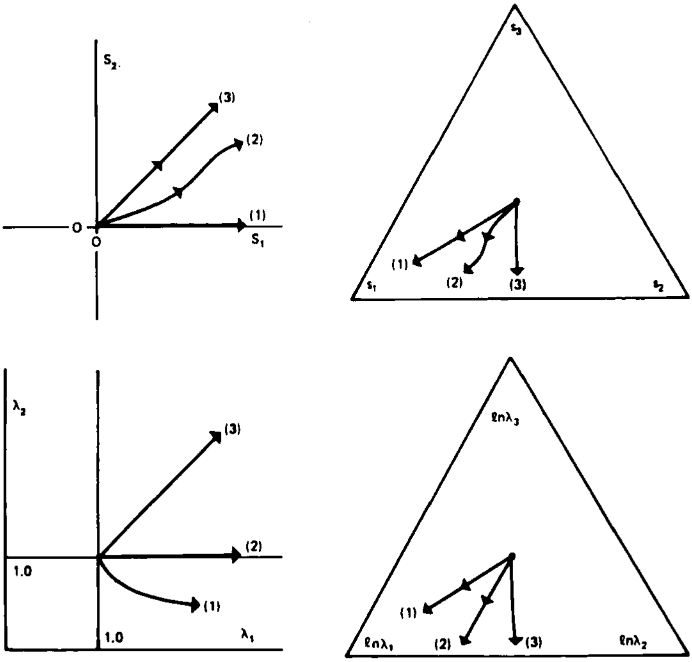

FIGURE 2 Three simple patterns of stretching: (1) uniaxial; (2) restrained width; (3) balanced biaxial.

1) Uniaxial (machine-direction) stretching takes place between two differential-speed rolls which are spaced well apart, or in the region between a slit-die orifice and a rapidly turning chill roll.

2) If two differential-speed rolls are spaced very close together, film is stretched in the machine direction while the width of the film is held nearly constant.[2]

3) Longstreth *et al.*[3] described an eight-sided stretcher which could closely approximate uniform biaxial stretching. Some simultaneous two-way tentering operations also approach this balanced stretching.

The *properties* of films subjected to these three simple stretching patterns would be quite different:

1) Strong in machine-direction, easily split along lines parallel to the machine direction; might be appropriate for film which is to be fibrillated, or cross-laminated (or with some polymers, for general film use).

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2) Strong in machine-direction; moderately strong in width direction; might be appropriate for a tape.

3) Strong in both sheet directions; might be appropriate for use as a film, or sheet to be pressure-formed.

In some film processes, the stretching does not follow any of the above simple patterns. For example, in a bubble process for orienting and crystallizing a metastable supercooled amorphous tube, the biaxial stress and extension-ratio follow *curved* trajectories, as illustrated in Figure 3 (case of low machine tension).[4] The unequal (and shifting) biaxial stretch triggers the crystallization of the supercooled polymer, and guides the development of a crystalline morphology which depends on the biaxial trajectories.

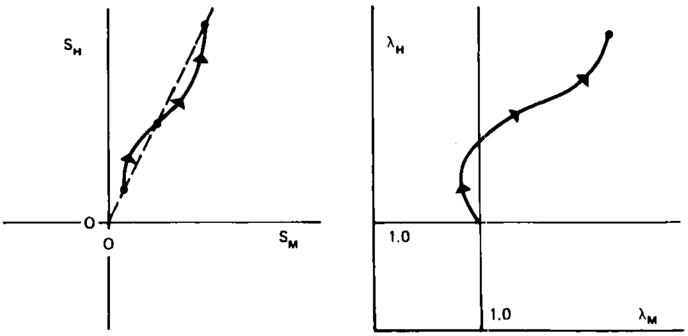

FIGURE 3 Curved trajectories in bubble process (low machine tension): S_M = machine stress; S_H = hoop (transverse) stress.

In other bubble processes, the molten polymer enters the stretching zone at a temperature *above* the crystalline melting point, and is subjected to biaxial stretching to yield an oriented melt, which is then cooled and crystallized.[5]

After crystallization in a biaxially-oriented condition, the film may be subjected to a subsequent biaxial drawing, or to a heat-setting operation (carried out in the presence of a biaxial stress). Such drawing and annealing operations cause further change in the crystalline morphology and in the film properties.

Upon heating, an oriented crystalline film may retract strongly at a temperature well below the crystalline melting point; this property is utilized in *shrink-films*, which find wide application in packaging. Heat-setting can remove the tendency to shrink, and provide a film which is dimensionally stable nearly to the crystalline melting point.

With the above background, we can at least formulate the problems:

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1) How does an imposed biaxial stress or an imposed biaxial strain influence crystallization equilibrium?

2) When a metastable, supercooled, amorphous polymer is subjected to a biaxial stretching operation, during the course of which it crystallizes, how does the trajectory followed on the biaxial stress plane and/or that on the biaxial extension-ratio plane affect the kinetics of crystallization and the resulting morphology?

3) When a molten polymer, above its melting point, is subjected to biaxial stretching and then cooled and crystallized, how do the stretching trajectories affect crystallization kinetics and morphology?

4) When a spherulitic crystalline polymer is subjected to biaxial stretching below its melting point, or when a biaxially oriented crystalline film is further stretched, how does the stretching trajectory affect the resulting morphology?

5) What would constitute an adequate structural characterization of a biaxially oriented, semi-crystalline polymer film?

6) What are the significant structure-property relationships for biaxially oriented, semi-crystalline polymer films?

At the present time, it is possible to answer these questions only in an incomplete manner.

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STUDIES OF CRYSTALLIZATION UNDER BIAXIAL STRESS, AND BIAXIAL STRETCHING OF CRYSTALLINE POLYMER FILMS

Most studies of deviatoric-stress-induced polymer crystallization and post-solidification modification have involved *fibers*, and *uniaxial* stretching. Information obtained on fibers, regarding kinetics of stress-induced crystallization and resulting morphologies, can largely be applied to films subjected to type-1 stress trajectories. However, this is a rather trivial (although important) special case in film manufacture.

Useful reviews of *biaxial* film orientation have been supplied by Park,[5,6] Schuur and Van Der Vegt,[2] and Sweeting;[7] but these deal mainly with descriptions of the processes and properties of the resulting oriented films, rather than with the effects of biaxial stress on crystallization kinetics and morphology.

Oono, Miyasaka, and Ishikawa[8] reported on the crystallization kinetics of biaxially stretched natural rubber. Lightly crosslinked rubber sheets were stretched to (balanced biaxial) extension-ratios of 1.5, 2.0, 2.5, and 3.0, clamped in metal frames, cooled to −27°C, and crystallized at constant extension-ratio. The equilibrium degree of crystallization was reported to decrease with increasing extension-ratio, but the rate of crystallization increased with increasing stretch. The crystallization isotherms were analyzed in terms of the Avrami equation. The Avrami parameter n decreased linearly with extension-ratio, from 3 for unstretched rubber to less than unity for a biaxial extension-ratio of 3.0 (in uniaxial stretching, the value of n has been reported to approach an asymptotic value of unity at high elongations).[9] Upon heating, melting of the (clamped) stretched films occurred over a broad temperature range. The final melting point increased with extension-ratio. The crystallite orientation was studied by X-ray diffraction; the a- and c-axes were reported to lie in the plane of the film, with the b-axis perpendicular to the film.

Lindenmeyer and Lustig[10] reported complete orientation distributions of *a* and *b* crystallographic directions in tubular extruded polyethylene (PE) films (and in the case of high density polyethylene (HDPE) films, c-axis orientation also), as a function of blow ratio. Some investigators had reported that in extruded PE film the a-axis exhibited preferential orientation in the machine direction. Lindenmeyer and Lustig prefer an alternate orientation pattern, originally suggested by Keller,[11] in which the b-axis is oriented perpendicular to the machine direction and the a- and c-axes are randomly oriented with cylindrical symmetry about the b-axis. Biaxial mechanical properties—tensile strength, elongation, modulus, and tear strength—were measured and correlated with the crystalline orientation distributions Morphology was not studied, but the orientation pattern was interpreted as being "support for the row-nucleation model."

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Nagasawa *et al.*[12] studied crystalline orientation in tubular blown films of HDPE and Poly(6-aminocaproic acid) ("Nylon 6").

Garber and Clark[13] studied the structure of blown polyoxymethylene (POM) film. Trajectories of biaxial stress and deformation in the stretching zone were not reported, but presumably machine-direction stretching predominated. Row-nucleated morphology was clearly demonstrated, with machine-direction nucleating fibers as well as transverse lamellar growths being visible in their micrographs. Mechanical properties of the oriented films were markedly different from those of spherulitic POM and strongly anisotropic.

The bubble process for producing Saran† film has received some study.[4,6,14,15] A tube of molten Saran is extruded, quenched to a supercooled (metastable) amorphous state, reheated, and passed over a trapped air bubble. Biaxial stretching in the bubble zone sets off crystallization to yield a biaxially oriented film. Biaxial stress and extension trajectories were

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TABLE I

Types of film orientation

Name	Geometry	Reference	Operator
Random	No orientation	None	None
Planar	Crystal axis parallel to reference plane	Plane	Axis
Uniplanar	Crystal plane parallel to reference plane	Plane	Plane
Axial	Crystal axis parallel to reference axis	Axis	Axis
Plan-axial	Crystal plane parallel to reference axis	Axis	Plane
Uniplanar-axial	Axis parallel to axis and plane parallel to plane	Plane Axis	Plane Axis

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determined, and biaxial mechanical properties measured, for various operating conditions. Crystallization kinetics were not measured (although crystallization was tremendously accelerated by the biaxial stress), and morphology was not determined.

Tanaka and Okajima[16] have reported on the biaxial stretching (both simultaneous and sequential) of polypropylene film having varying amounts of initial crystallinity. Small-angle light scattering (SALS), x-ray diffraction, and birefringence were employed to characterize films which were biaxially stretched to various extension-ratios at elevated temperatures (below T_M after quenching from the melt to temperatures of 0°, 40°, 60° and 100°C to establish an initial level of crystallization.

Heffelfinger and Knox have discussed the manufacture of oriented polyethylene terephthalate (PET) film.[17] Molten PET is extruded and quenched to make an amorphous, ductile sheet (flat or tubular). This supercooled amorphous sheet is reheated and stretched, to yield an oriented semi-crystalline film. Orientation may be uniaxial, balanced biaxial, or unbalanced biaxial. Heffelfinger classifies orientation in films into six types, as listed in Table I.

One-way stretched PET films are reported to approximate closely a "uniplanar-axial" type of orientation. Two-way stretched films are reported to approximate "uniplanar" orientation. To determine the crystalline orientation of a PET film, the authors suggest inspection of at least the (100), (010), and (105) planes, preferably with a pole-diagram for each. Stress–strain curves for specimens cut in the machine and transverse directions are also indicators of structural change (see Figure 4).

Coextruded multilayer films can be produced with individual layers as thin as a few hundred Angstroms.[18,19] If the thickness of a layer of crystallizable polymer is less than the dimensions of some morphological structure of bulk polymer, it is clear that an altered morphology must develop in such a thin layer. Indeed, Mencik, Plummer, and Van Oene[20] have reported such an effect in *blends* of PE and polystyrene (PS). When blends comprising 10% PE and

90% PS were extruded and melt-drawn, the polyethylene formed long, fine ribbons (typically 1,000 Å wide and 500 Å thick). When crystallization took place in these constricted regions, spherulite growth was restricted in two dimensions, and most laminae were oriented with the b-axis directed along the ribbon, and therefore in the machine direction. With very thin continuous layers (as in coextruded multilayer films) one might expect crystallization of a relaxed melt to generate two-dimensional blocked spherulites, with the b-axis oriented in the plane of the film and a- and c-axes randomly oriented.

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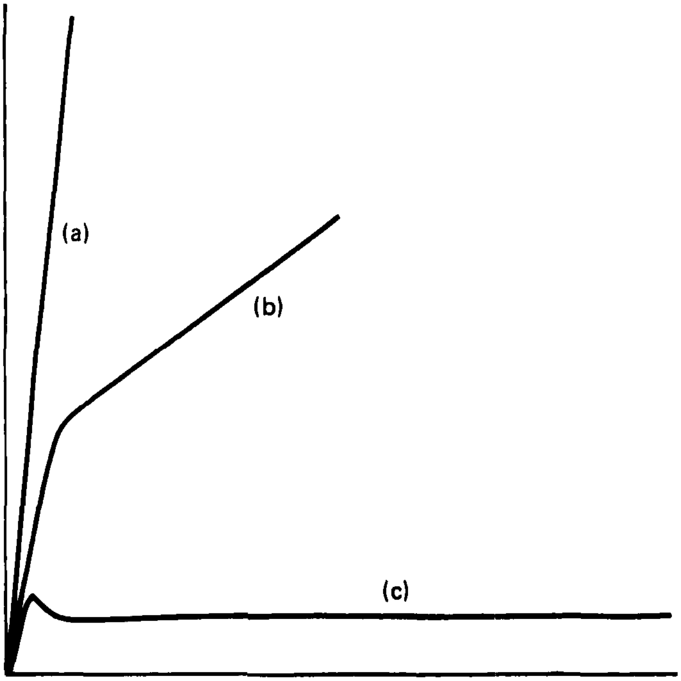

FIGURE 4 Effect of orientation on tensile properties. Engineering stress vs. engineering strain (schematic): (a) uniaxial orientation in direction of test; (b) balanced biaxial orientation; (c) unoriented.

STRUCTURE–PROPERTY RELATIONSHIPS IN BIAXIALLY ORIENTED POLYMER FILMS

The *first-order* effects of orientation—uniaxial, unbalanced biaxial, or balanced biaxial—on properties of crystalline polymer films are pronounced and well recognized; tensile strength, yield stress, and elongation-to-break in the machine and transverse directions can exhibit order-of-magnitude variations. But the utility of an oriented film may depend upon other orientation-dependent properties—e.g. heat shrinkability or dimensional stability—which are related to subtle aspects of structure, established by the detailed processing history. In this deeper sense, it is not clear to this writer what would constitute an adequate structural specification of a biaxially oriented crystalline polymer film.

In the uniaxial case, Samuels[21] has shown that the structure of an oriented semicrystalline fiber can be usefully (although not completely) characterized by three numbers: the crystalline fraction, an orientation factor for the crystalline portion, and an orientation factor for the amorphous portion. Many properties of fibers with different processing histories can be correlated with the values of these three structural parameters, which are subject to experimental determination. It would seem reasonable to hope that a two-dimensional extension of this approach—perhaps utilizing five numerical parameters—could provide a useful, partial specification of the structure of a biaxially oriented semicrystalline film. If the individual parameters were experimentally accessible, and were shown to correlate with the directional properties of films with different processing histories, this would be a modest step towards a fully adequate structure specification.

In view of the multiplicity of biaxial stretching trajectories possible in film processing, the difficulties of complete structural analysis of biaxially oriented films, and the magnitude of the task of determining directionally dependent physical properties, we must conclude that the comprehensive mastery of structure–property relations in these systems will be difficult and slow.

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CONCLUSIONS

Much is known regarding the effects of film manufacturing conditions upon film properties and performance. However, our understanding of the way in which biaxial processing determines supramolecular structure, and how structure determines properties, is fragmentary.

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