Orientation Distribution in the Noncrystalline Regions of Biaxially Drawn Poly(ethylene terephthalate) Film: A Chain-Intrinsic Fluorescence Study

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SYNOPSIS

We have studied development of the in-plane distribution of "amorphous orientation" during sequential and simultaneous biaxial drawing of poly(ethylene terephthalate) film, using polarized intrinsic fluorescence. The machine direction (MD) draw ratio was always fixed at 3.5, and the transverse direction (TD) draw ratio was varied. The rate of increase in the proportion of TD-oriented chains with increasing TD draw ratio is almost identical in the sequential and simultaneous processes up to a draw ratio of 2.7. At this point, sequential drawing starts to involve transverse realignment of MD-oriented chains, which accelerates redistribution of orientation from the MD to the TD. Consequently, in sequential drawing, a "balanced" biaxial orientation distribution is achieved at a TD draw ratio significantly below the MD draw ratio, whereas at the same TD draw ratio in the simultaneous process, MD orientation remains dominant. At equal MD and TD draw ratios, the noncrystalline chains in sequentially drawn film are predominantly oriented along the TD, but their orientation distribution is isotropic in simultaneously drawn film. High-temperature annealing at fixed dimensions diminishes the proportion of TD-oriented chains in films with transverse draw ratios < 2.5. We attribute this to a more highly developed crystallite network in the MD, which constrains orientational relaxation along the MD. A balanced distribution of amorphous orientation is directly responsible for achieving balanced tensile strength and balanced extensibility. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Commercial production of poly(ethylene terephthalate) (PET) film involves drawing unoriented, amorphous film in two orthogonal directions, either sequentially or simultaneously. In both the sequential and simultaneous processes, draw temperatures are usually in the range 10–30°C above the glass transition temperature, and a final heat-setting step at about 200°C imparts dimensional stability to the film.

Recent research on the sequential process has focused on the development of the microstructure during the first draw and its dependence on strain

rate, draw temperature, and molecular weight.[1-8] This information should ultimately permit improved understanding of how the microstructural state obtained during the first draw influences structure development during the transverse draw—an area of research begun by Heffelfinger and Schmidt in the mid 1960s.[9] Research on the simultaneous processes (tenter frame and blow-molding techniques) has involved characterization by transmission electron microscopy,[10] measurement of optical anisotropy, both in-plane and out of plane,[11] and orientation analysis of various crystal planes by wide-angle X-ray scattering.[10-15] Apart from seeking to maximize tensile strength, modulus, and dimensional stability of biaxially drawn PET film, an important goal of current research is to improve control over the in-plane direction dependence of these mechanical properties.[15-18] In particular, it is often desirable to

obtain balanced mechanical properties along the two draw axes.

Since the direction dependence of the mechanical properties is influenced by the distribution of molecular orientation in the plane of the film, suitable methods for characterizing orientation distributions in both the crystalline and noncrystalline regions are required. Whereas orientation distributions in the crystalline regions of PET film have been characterized by WAXS pole figure analysis, there was no means available for *directly* obtaining orientation distributions in the noncrystalline regions until the recent development of the chain-intrinsic fluorescence technique.[7,19] An indirect method, involving incorporation of fluorescent probes, has been used to characterize amorphous orientation distributions in biaxially drawn polypropylene and poly(vinyl alcohol) films,[20,21] but it is uncertain whether the angle of alignment of the probe with the polymer chain remains constant during drawing and after heat treatment.

In the present study, we examine (1) the suitability of the chain-intrinsic fluorescence technique for characterizing the in-plane distribution of noncrystalline orientation in biaxially drawn PET film; (2) the development of noncrystalline orientation distribution in sequential and simultaneous processes, under identical conditions of draw temperature and strain rate; and (3) the relative influence of the orientation distributions in the noncrystalline

and the crystalline regions on achieving balanced mechanical properties.

EXPERIMENTAL

Materials

Amorphous, unoriented PET film was prepared at DuPont, Circleville, OH. It is additive free, 0.2 mm thick, and has a number-average molecular weight of 20,000.
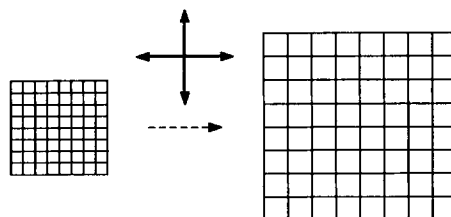
Drawing Procedures

The amorphous, unoriented film was drawn on a T.M. Long Biaxial Stretcher, employing blown-air heating. In the sequential process, the unoriented film was drawn at constant width in one direction, defined as the machine direction (MD), to a draw ratio of 3.5. It was then drawn, at constant width, in the transverse direction (TD) to the desired draw ratio [Fig. 1(a)]. In both drawing operations, the draw temperature was 95°C and the nominal strain rate was 1.5 s^{-1}.

In the simultaneous process, MD and TD drawing were performed at the same time [Fig. 1(b)]. The MD draw ratio was always 3.5, and the TD draw ratio was varied. The strain rate in both directions and the draw temperature were identical to those

(a)   Biaxial Sequential
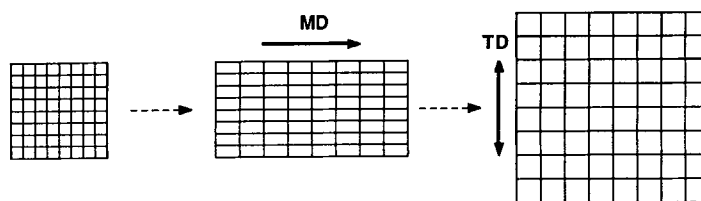
(b)   Biaxial Simultaneous

Figure 1   Schematic representation of the sequential and simultaneous biaxial drawing processes.

used in the sequential process. After drawing, some of the films were heat-set at 200°C for 5 min, under fixed dimensions.

Intrinsic Fluorescence Measurements

Extensive discussion of the intrinsic fluorescence technique, together with details of our experimental setup, have been published elsewhere.[7] The PET dimers were excited at a wavelength of 340 nm and, with polarizer and analyzer parallel, the film specimen was rotated. The intensity of fluorescence emission (at λ_{em} = 390 nm) was measured every 10° of rotation, and polar plots of the in-plane angular distribution of polarized fluorescence intensity were thus obtained. These polar plots reflect the distribution of amorphous orientation in the plane of the film.

It should be noted, however, that birefringence can significantly influence emission intensity.[22-24] Birefringence has the largest influence when the polarizers are at 45° to the draw direction and has no influence when they are at 0° and 90° to the draw direction. Since no correction for birefringence was made in this study, intensity values measured outside the machine and transverse draw directions may be subject to some error. We are investigating the birefringence effect in greater detail, but we currently believe that the polar plots shown here provide a reliable qualitative representation of the in-plane distribution of amorphous orientation.

To avoid the birefringence problem and to obtain an accurate, quantitative assessment of the proportion of noncrystalline chain segments oriented along the MD and the TD, we have calculated an "orientation ratio," R, as follows:

$$R_{MD} = \frac{I_{MD}}{I_{MD} + I_{TD}}, \quad R_{TD} = \frac{I_{TD}}{I_{MD} + I_{TD}}, \quad (1)$$

where I_{MD} and I_{TD} are the emission intensities obtained with, respectively, the machine and transverse draw directions of the film parallel to the polarization direction. Clearly, no correction for birefringence is required in this case.

Birefringence, X-Ray Diffraction, and Density

To determine birefringence, the refractive index was measured parallel to the MD and the TD (n_{MD} and n_{TD}), using a Reichert-Jung Abbé Mark 2 refractometer. Wide-angle X-ray diffraction pole figure analysis was carried out with a Picker four-circle

single-crystal diffractometer, using crystal monochromatized CuKα radiation. Further details are given elsewhere.[25] Film density was measured by the density gradient column method, with carbon tetrachloride and n-heptane as column liquids. Volume fraction crystallinity was calculated from density,[26] using an amorphous density value of 1336 kg/m^3, and crystalline density values of 1457 kg/m^3 for as-drawn film and 1510 kg/m^3 for annealed film.[8]

RESULTS AND DISCUSSION

Sequential Drawing

The in-plane angular distribution of polarized fluorescence intensity for film drawn one-way to a draw ratio of 3.5 is shown in Figure 2. As expected, the intensity distribution shows that in-plane orientation of noncrystalline chains is essentially along the draw direction (MD), with a randomly oriented component giving rise to some intensity along the TD. Computation of the second moment of the orientation function, $\langle P_2(\cos \Theta) \rangle_a$, gives a value of 0.37. Annealing this film at 200°C with fixed dimensions reduces $\langle P_2(\cos \Theta) \rangle_a$ to 0.32, presumably as a result of molecular relaxation. The volume fraction crystallinity of the drawn film is 0.16, calculated from the density value of 1355.8 kg/m^3, and becomes 0.33 (1339.3 kg/m^3) after annealing.

Unannealed film with an MD draw ratio of 3.5 was subsequently drawn to various draw ratios in
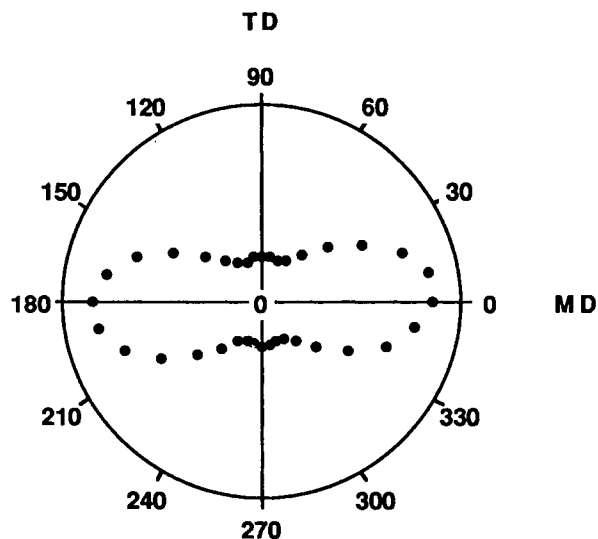
Figure 2 In-plane angular distribution of polarized fluorescence intensity for film drawn one-way (along the MD) to a draw ratio of 3.5.

(a)   **As Drawn**   (b)   **Annealed**
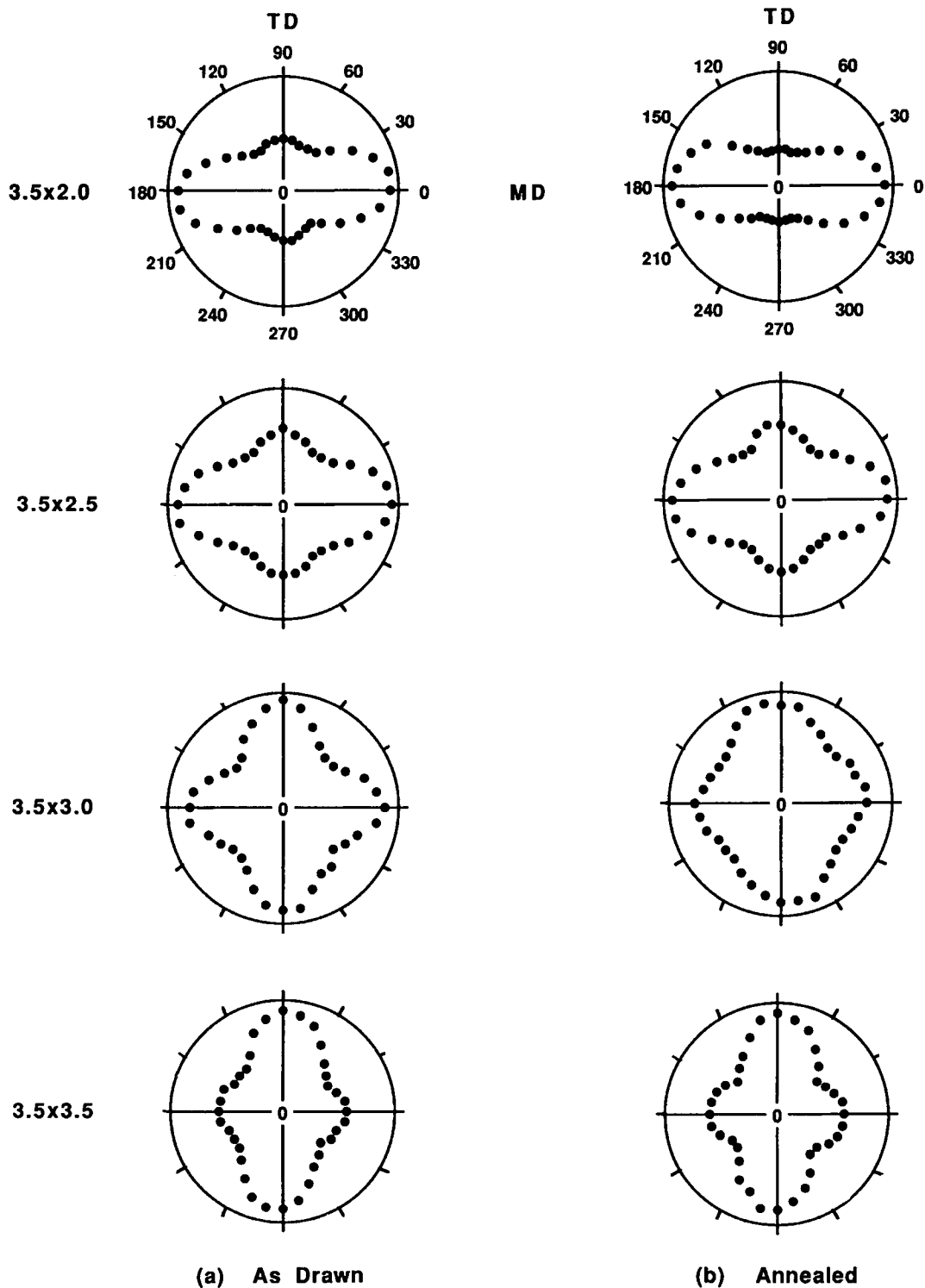
Figure 3   In-plane angular distribution of polarized fluorescence intensity for film drawn biaxially by the sequential process: (a) as drawn; (b) heat-set at 200°C. The MD draw ratio is always 3.5 and the TD draw ratio varies.

the TD. The polar plots in Figure 3(a) clearly show an increasing proportion of noncrystalline chains oriented along the TD with increasing TD draw ratio. At a TD draw ratio of 3.0, there is an almost equal proportion of noncrystalline chains oriented along the TD and MD axes, and at a TD draw ratio of 3.5, the chains become predominantly oriented along TD. After fixed-dimension heat treatment at 200°C [Fig. 3(b)], there is some redistribution of amorphous orientation in the 3.5 × 2.0 film, such that the proportion of TD-oriented chains diminishes. This was found to occur in all the films having a transverse draw ratio less than 2.5. At higher draw ratios, only the 3.5 × 3.0 film is visibly influenced by the thermal treatment, which appears to have caused an increase in the randomly oriented component.

These effects are shown more quantitatively in Figure 4, where the TD and MD orientation ratios [see eq. (1)] are plotted as a function of TD draw ratio. A "balanced" orientation distribution—having an equal proportion of TD- and MD-oriented chain segments—is achieved at a TD draw ratio of almost 3.0 in the unannealed films and 2.9 in the annealed films. The fact that a balanced orientation distribution of noncrystalline chain segments does not occur at equal MD and TD draw ratios can be explained as follows: During transverse drawing, orientation of chains along the TD involves realignment of MD-oriented chains in the TD direction. The reduction in the number of chains oriented along the MD as the TD orientation increases causes the balance point to occur at a TD draw ratio significantly less than the MD draw ratio of 3.5.

The decrease in the proportion of chain segments oriented along TD after fixed-dimension annealing is quantitatively apparent from Figure 4(b): At transverse draw ratios less than 2.5, the TD orientation ratio is significantly lower than in the unannealed films. This preferential relaxation of orientation in the transverse direction probably arises from a more highly developed MD-oriented crystallite network that constrains relaxation of noncrystalline chains aligned in the machine direction. When the transverse draw ratio exceeds about 2.5, however, a more effective TD-oriented crystallite network has been formed, and the orientational relaxation (if any) occurs to a roughly equal extent in both draw directions.
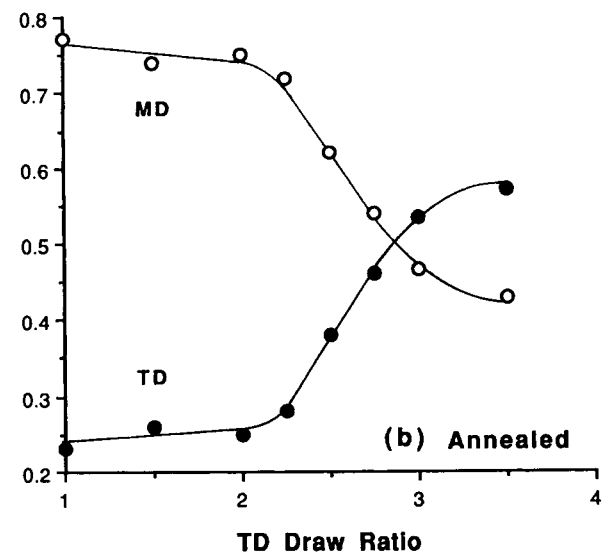
Simultaneous Drawing

A series of films were produced by simultaneous, biaxial drawing, such that the MD draw ratio was


Orientation Ratio

(a) As Drawn

TD Draw Ratio

Orientation Ratio

(b) Annealed
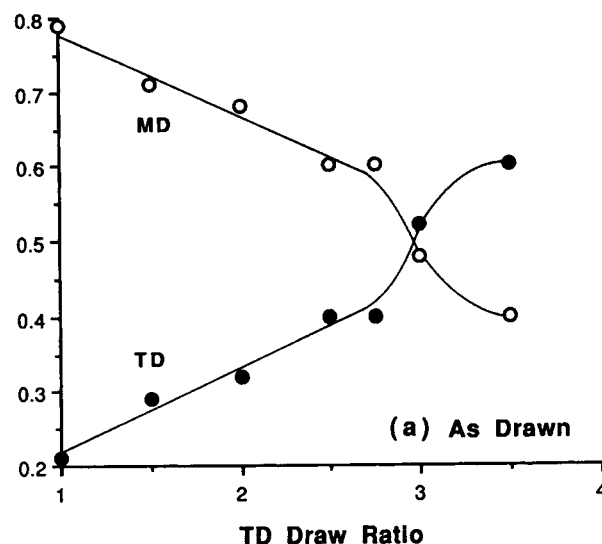
TD Draw Ratio

Figure 4 Orientation ratio vs. TD draw ratio for film drawn biaxially by the sequential process: (a) as drawn; (b) heat-set at 200°C. The MD draw ratio is always 3.5.

always 3.5 and the TD draw ratio was varied. The draw temperature and the extension rate were identical to those used for the sequentially drawn films. It is noteworthy that in the simultaneous drawing process of this study the extension rate was the same in the MD and the TD. Consequently, for TD draw ratios less than 3.5, true simultaneous drawing occurs up to the final TD draw ratio and is followed by further MD drawing.
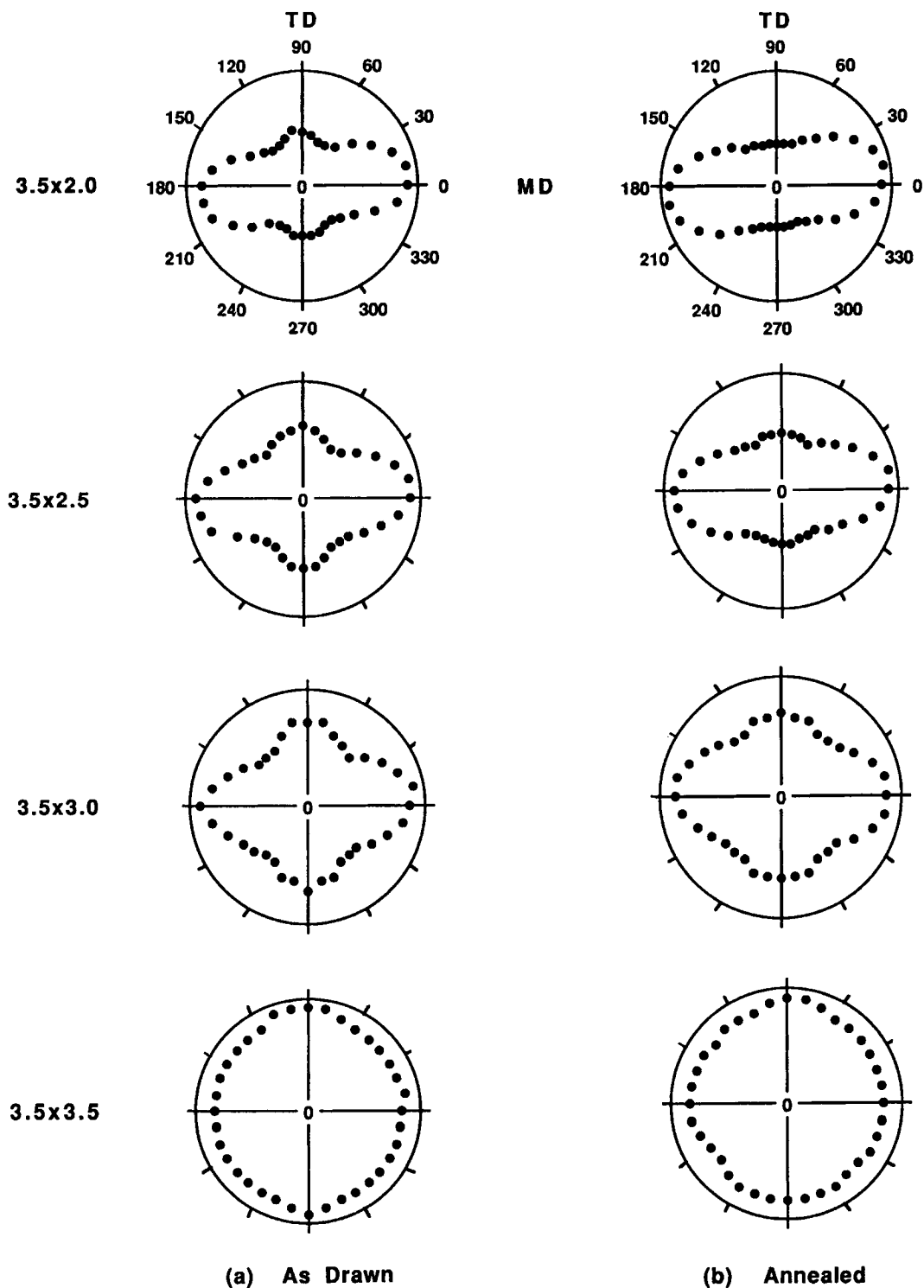
Figure 5   In-plane angular distribution of polarized fluorescence intensity for film drawn biaxially by the simultaneous process: (a) as drawn; (b) heat-set at 200°C. The MD draw ratio is always 3.5 and the TD draw ratio varies.

Comparing Figures 3(a) and 5(a) reveals that development of the in-plane distribution of amorphous orientation for sequential and simultaneous drawing is remarkably similar up to a TD draw ratio of 2.5. However, whereas equal biaxial orientation of the amorphous phase is achieved at a TD draw

ratio of about 3 in the sequentially drawn films, MD orientation remains dominant at that draw ratio in the simultaneously drawn films. The film drawn simultaneously to an equal MD and TD draw ratio of 3.5 clearly displays an isotropic orientation distribution, which cannot be achieved by the sequential process. Annealing the simultaneously drawn films at fixed dimensions causes a reduction in the proportion of TD-oriented chains when the transverse draw ratio is 2.5 or less [Fig. 5(b)]. This effect is of similar magnitude to that found in the sequentially drawn films. In the 3.5 × 3.0 film, the heat treatment seems to have caused an increase in the proportion of randomly oriented chains, as was found with sequential drawing.

In Figure 6, the orientation ratios are plotted for the entire series of simultaneously drawn films, before and after annealing. Prior to annealing, the transition from a predominantly MD-oriented distribution of noncrystalline chains to an isotropic distribution occurs linearly with increasing TD draw ratio. For process control of the structure, this is advantageous.

It is informative to superimpose the orientation ratio plots for the sequentially and simultaneously drawn films that were not annealed (Fig. 7). The curves clearly coincide up to a draw ratio of 2.7, beyond which the increase in the proportion of TD-oriented chain segments accelerates in sequential drawing while continuing to increase at a constant rate in simultaneous drawing. This indicates that in sequential drawing transverse realignment of MD-oriented chains begins at a TD draw ratio of 2.7, causing rapid redistribution of orientation from the MD to the TD, and it follows that, below a draw ratio of 2.7, transverse orientation occurs entirely at the expense of the randomly oriented component.

Structure–Property Relationships

For both series of annealed films, tensile modulus, tensile strength, and elongation at break were measured along the MD and the TD (Figs. 8 and 9). As would be expected, modulus and strength increase in the TD with increasing TD draw ratio, while decreasing in the MD. The observed decrease in TD extensibility with increasing transverse draw ratio is also expected. Of particular interest for the present study is the "crossover" point, at which a given mechanical property becomes equal in the MD and the TD.

In the sequentially drawn films, the crossover point for modulus occurs at a TD draw ratio of about 2.7, and for both tensile strength and elongation at break, it occurs at 2.9 (Fig. 8). Recalling that the
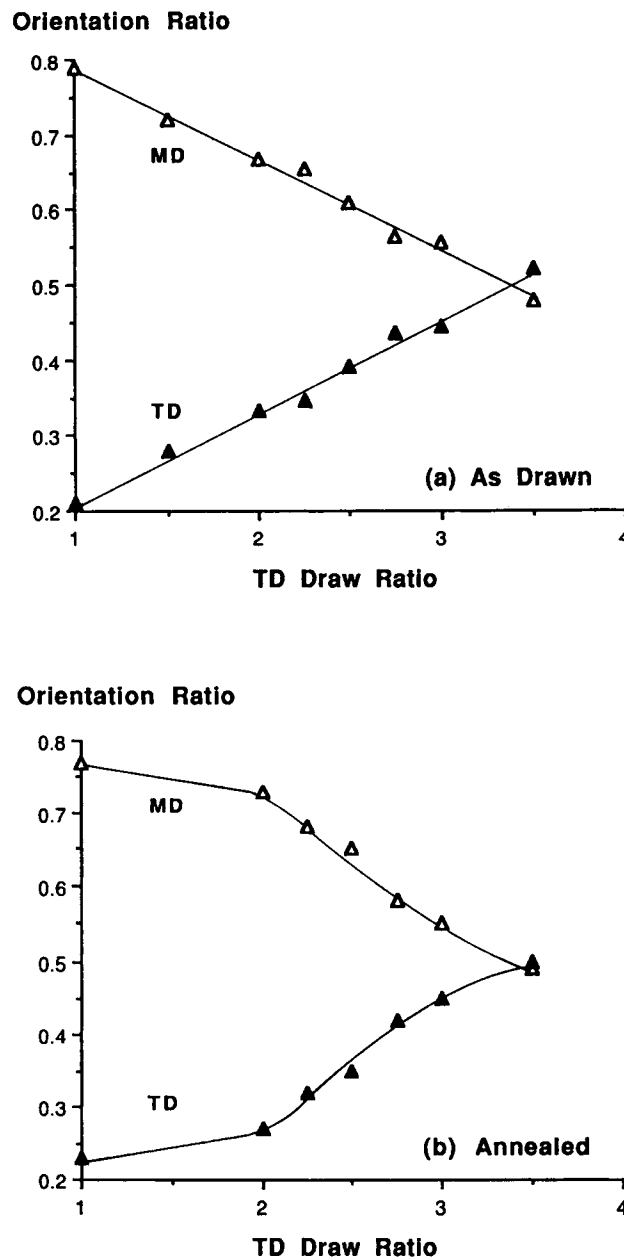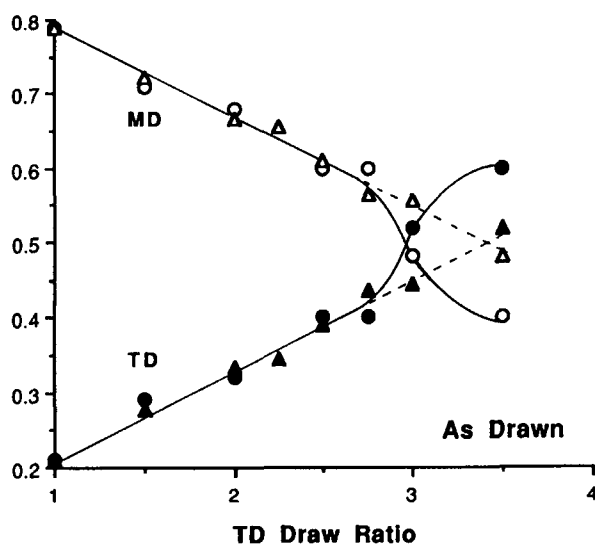

Figure 6   Orientation ratio vs. TD draw ratio for film drawn biaxially by the simultaneous process: (a) as drawn; (b) heat-set at 200°C. The MD draw ratio is always 3.5.

orientation ratio curves for these films also cross over at a transverse draw ratio of 2.9, it is clear that for tensile strength and extensibility balanced mechanical properties coincide with the achievement of a balanced distribution of amorphous orientation. On the other hand, the crossover points for modulus and orientation ratio differ by a small but significant amount.

An important motivation for the present study was that, in the sequentially drawn films, the cross-
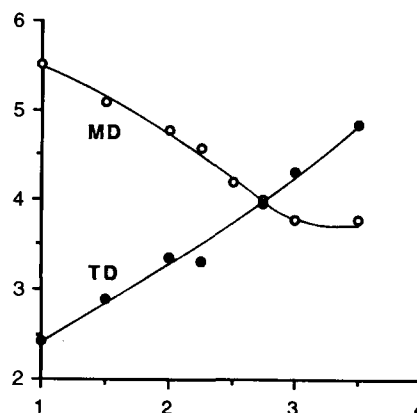
Orientation Ratio

Figure 7 Orientation ratio vs. TD draw ratio for film drawn biaxially by the (O, ●) sequential and (△, ▲) simultaneous processes. [Superimposition of Figs. 4(a) and 6(a).]

over point for tensile strength and elongation at break could not be adequately predicted by birefringence and X-ray measurements. Zero birefringence ($n_{MD} - n_{TD} = 0$) was found to occur at a TD draw ratio of 2.7, significantly below the balance point draw ratio for these mechanical properties. This indicates that equal biaxial distribution of amorphous orientation is predominantly responsible for achieving balanced tensile strength and extensibility and that equal biaxial distribution of overall orientation (crystalline and noncrystalline) is a better predictor of balanced modulus properties. Although the overall level of crystallinity is about the same in all the annealed films (Fig. 10), the distribution of crystallite orientation in the plane of the film changes with increasing TD draw ratio. Our wide-angle X-ray scattering studies reveal that in the sequentially drawn films crystallite orientation becomes equal along the MD and the TD at a transverse draw ratio around 2.2–2.3 [25]. Therefore, the balance point for crystallite orientation bears no direct relationship to the balance point for any of the mechanical properties studied.
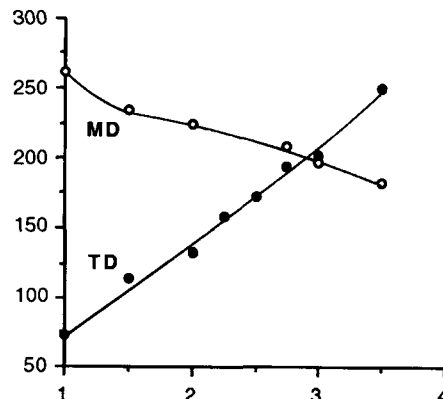
For simultaneously drawn films, the balance point for all three mechanical properties occurs at a TD draw ratio of 3.5 (Fig. 9), which is exactly the draw ratio at which an isotropic distribution of amorphous orientation is achieved. Of course, the relative importance of amorphous, crystalline, and overall orientation in the achievement of balanced mechanical

properties can only be deduced from the study of sequentially drawn films. In the case of simultaneous drawing, balanced mechanical properties occur when
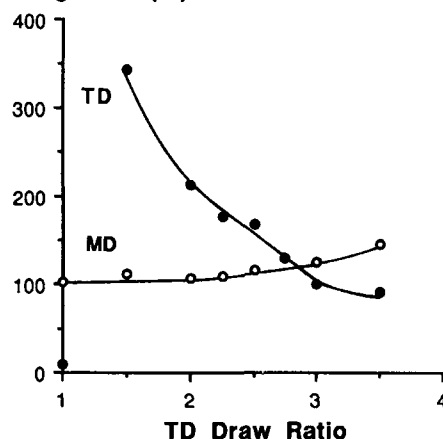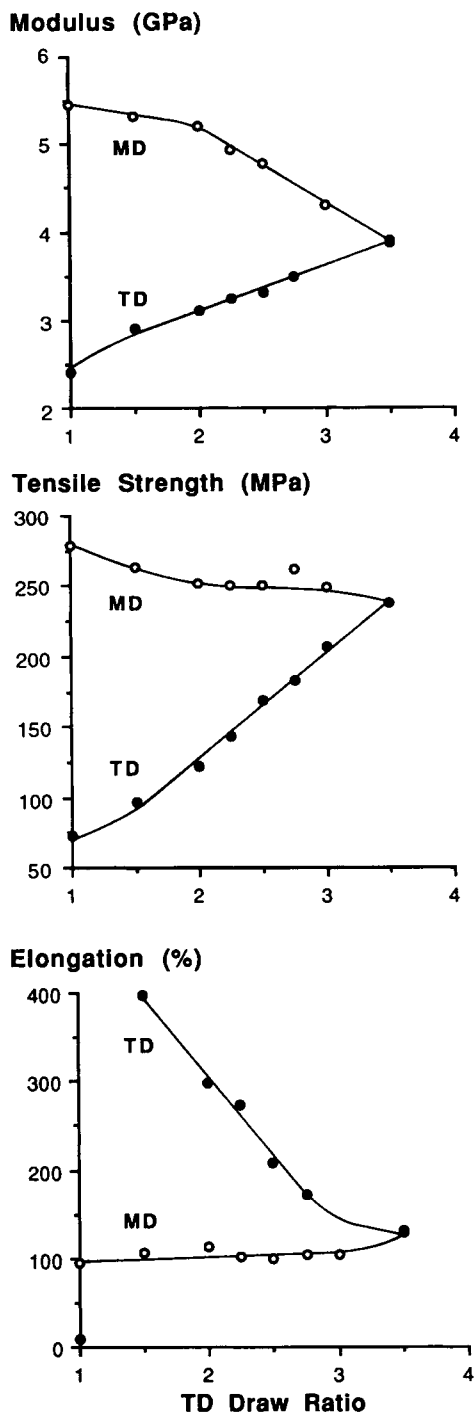

Figure 8 Modulus, tensile strength, and elongation at break as functions of the TD draw ratio for films drawn biaxially by the sequential process. The MD draw ratio is always 3.5. All the films were heat set at 200°C after drawing.

Modulus (GPa)

Tensile Strength (MPa)

**Elongation (%)**

TD Draw Ratio

Figure 9 Modulus, tensile strength, and elongation at break as functions of the TD draw ratio for films drawn biaxially by the simultaneous process. The MD draw ratio is always 3.5. All the films were heat-set at 200°C after drawing.

the distribution of amorphous, crystalline, and overall orientation are all isotropic, and no conclusions can be drawn about their relative influence.

Finally, we wish to draw further attention to the observation that in sequential drawing balanced crystallite orientation occurs significantly before balanced amorphous orientation, indicating that, under the temperature and strain-rate conditions used, crystallites realign in the transverse direction more readily than do uncrystallized chains. This observation has significant implications for understanding deformation mechanisms in sequential biaxial drawing, and we are currently investigating it in greater detail.

CONCLUSIONS

The chain-intrinsic fluorescence technique is suitable for studying the in-plane orientation distribution of noncrystalline chains in PET film. Computation of an "orientation ratio" permits quantitative assessment of changes in the proportion of amorphous chain segments oriented along the MD and the TD and does not require corrections for birefringence effects.

Density (kg/m³)
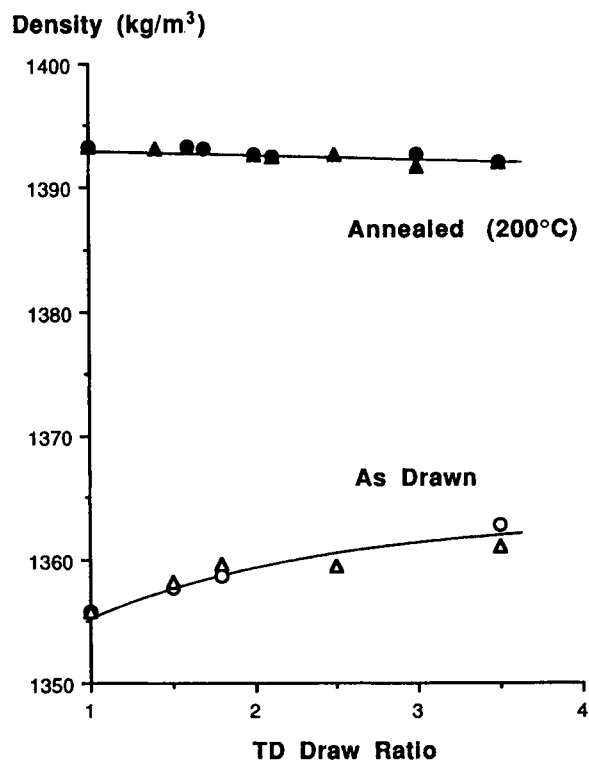
TD Draw Ratio

Figure 10 Film density vs. TD draw ratio for films drawn biaxially by the sequential ($\bigcirc$, $\bullet$) and simultaneous ($\triangle$, $\blacktriangle$) processes. The MD draw ratio is always 3.5. The density values correspond to crystallinities in the range 0.16–0.22 for as-drawn films and about 0.33 for annealed films (see Experimental section).

Above a certain TD draw ratio, the increase in the proportion of transversely oriented chain segments with increasing transverse draw ratio is faster in the sequential process than in the simultaneous process. There is strong evidence that in this regime sequential drawing involves realigning in the TD chains that were MD-oriented after the first draw. Consequently, a balanced biaxial orientation distribution occurs *before* the TD draw ratio becomes equal to the MD draw ratio. When the TD draw ratio is equal to the MD draw ratio, the noncrystalline chains in the sequentially drawn films are predominantly oriented along the TD. In simultaneously drawn films, however, the orientation distribution is isotropic at equal MD and TD draw ratios.

Annealing at 200°C with fixed dimensions seems to cause a larger proportion of chains to relax along the TD than along the MD at low TD draw ratios, indicating higher molecular constraints in the MD direction. At higher draw ratios, the orientation ratio is unaffected by heat treatment, but there is evidence that the proportion of randomly oriented chains increases in some of the films.

Obtaining equal tensile strength and equal elongation at break in the machine and transverse directions appears to be entirely dependent on achieving a balanced distribution of amorphous orientation—the orientation of crystallites plays no detectable role.

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