Uniaxial and Biaxial Orientation Development and Mechanical Properties of Polystyrene Films

KIYOICHI MATSUMOTO,* JOHN F. FELLERS, and JAMES L. WHITE,
Polymer Engineering, University of Tennessee, Knoxville, Tennessee 37916

Synopsis

Uniaxially and biaxially oriented polystyrene films were prepared in a biaxial stretching machine. The state of orientation was determined by birefringence measurements and represented in terms of a set of biaxial orientation factors f_j^B. The data are plotted on an isosceles triangular diagram whose coordinates represent the orientation factors f_1^B, f_2^B. Tensile force–elongation curves were obtained on the films in the machine stretching direction (MSD) and at various angles to the MSD in the plane of the film. The isotropic film is brittle, while uniaxial films yield in the machine direction but are brittle in the transverse direction. The biaxially oriented films exhibit ductile yielding in all directions in the plane of the film.

INTRODUCTION

The importance of orientation to the mechanical properties of polymeric glasses such as polystyrene is well known.[1–11] Most early investigators limited their attention to unixial orientation, which gave improved mechanical properties in the stretch direction, but neglected the deterioration of properties in the transverse direction. During the mid-1960s, Cleereman[12–14] reported a substantial biaxial toughening of amorphous glassy polystyrene by rotating the core of an annular injection mold during the injection process. This was attributed by Cleereman to the development of multiaxial orientation in the process. In the present decade, various investigators beginning with Matsumoto, Imamura, and their co-workers[15–18] have reported basic studies of biaxial stretching of amorphous or largely amorphous polymers just above their softening temperature. Thomas and Cleereman[19] have reported basic studies of biaxial stretching of polystyrene and its associated mechanical toughening. Subsequent biaxial stretching studies of polystyrene have been reported by Jones,[8] DeVries, Bonnebat, and Beautemps,[20] and Matsumoto and Iio.[21]

It is the purpose of this article to present a basic study of the development of biaxial orientation in polystyrene films, to characterize this orientation, and determine its influence on mechanical properties. Our studies involve a wider range of processing conditions and film orientations than contained in the earlier pertinent studies of Thomas and Cleereman,[19] Jones,[8] and Matsumoto and Iio.[21] In addition, our interpretations are somewhat different. This article is a continuation of a series on the mechanical properties and development of orientation in polystyrene. Fellers and Chapman[22] have studied the influence of molecular weight and its distribution on mechanical properties. Oda, White, and Clark[23]

* Permanent address: Faculty of Textile Science, Kyoto University of Industrial Arts and Textile Fibers, Matsugasaki, Kyoto, Japan.

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have shown that orientation in vitrified polystyrene is quantitatively related to the stress field at vitrification. This interpretation has been extended to films produced by the tubular process by Choi, White, and Spruiell,[24] which is a companion study to the present article.

REPRESENTATION OF ORIENTATION

It has long been realized that birefringence in deformed polymers measures molecular orientation through and anisotropy of the polarizability.[25–28] Most early investigations of orientation involved uniaxial filaments, and the anisotropy of polarizability of refractive index was used to index the level of orientation through the Hermans orientation factor[25,27]:

$$\frac{\overline{\Delta\alpha}}{\alpha_1 - \alpha_2} = \frac{\Delta n}{\Delta^0} = f = \frac{3\,\overline{\cos^2\theta} - 1}{2} \tag{1}$$

where α is the polarizability; n is the refractive index; $\overline{\Delta\alpha}$ is the averaged anisotropy of polarizability; Δn is the refractive index difference or birefringence, Δ^0 is the maximum or intrinsic birefringence; θ is the angle between a chain segment and the fiber axis; and f is the Hermans orientation factor. Studies of biaxial orientation of more recent date effectively begin with the research of Stein[29–31] in 1957–1966. Stein[30] developed orientation factors based upon Eulers angles to express biaxial orientation. This work was subsequently generalized by Nomura, et al.,[32–34] who represented the orientation distribution in terms of an associated Legendre polynomial expansion and showed that the coefficients correspond to orientation factors including those of Hermans and the Stein biaxial factors.

An alternative approach to biaxial orientation representation is contained in the work of Desper and Stein[31] and has been extended by White and Spruiell.[35] Let 1 and 2 be two orthogonal directions in the plane of the film and 3 the direction perpendicular to the plane film. Using the transformation characteristics of the polarizability tensor, the birefringences Δn_{13} and Δn_{23} may be expressed

$$n_1 - n_3 = \Delta n_{13} = \Delta^0\,(\overline{\cos^2\phi_{1c}} - \overline{\cos^2\phi_{3c}}) \tag{2a}$$

$$n_2 - n_3 = \Delta n_{23} = \Delta^0\,(\overline{\cos^2\phi_{2c}} - \overline{\cos^2\phi_{3c}}) \tag{2b}$$

Again Δ^0 is the intrinsic birefringence and ϕ_{1c}, ϕ_{2c}, and ϕ_{3c} are angles between the chain axis and the directions 1, 2, and 3. White and Spruiell[35] define the biaxial orientation factors:

$$f_1^B = \frac{\Delta n_{13}}{\Delta^0} = \overline{\cos^2\phi_{1c}} - \overline{\cos^2\phi_{3c}} = 2\overline{\cos^2\phi_{1c}} + \overline{\cos^2\phi_{2c}} - 1 \tag{3a, b}$$

$$f_2^B = \frac{\Delta n_{23}}{\Delta^0} = \overline{\cos^2\phi_{2c}} - \overline{\cos^2\phi_{3c}} = 2\overline{\cos^2\phi_{2c}} + \overline{\cos^2\phi_{1c}} - 1 \tag{3c, d}$$

For the case of perfect uniaxial orientation in the 1 (machine) direction,

$$f_1^B = 1 \qquad f_2^B = 0 \tag{4a}$$

For perfect uniaxial orientation in the 2 transverse direction,

$$f_1^B = 0 \qquad f_2^B = 1 \tag{4b}$$

If the orientation is completely perpendicular to the surface of the film,

$$f_1^B = -1 \qquad f_2^B = -1 \tag{4c}$$

We may represent orientation in terms of an isosceles triangle defined in terms of the orientation factors f_1^B and f_2^B (Fig. 1). This may be compared with the suggestion of Desper and Stein[31] to use $\overline{\cos^2 \phi_{ij}}$ and express orientation in terms of an equilateral triangle. This representation was used by Matsumoto and his co-workers.[16,17,21] The corners of the triangle of Figure 1 are located at (1, 0), (0, 1), and (−1, −1). For equal biaxial orientation, f_1^B and f_2^B are equal and the data lie on the principal altitude of the triangle. For equal and perfect biaxial planar orientation, (f_1^B, f_2^B) has the value $(+1/2, +1/2)$. All planar orientations lie on the base of the triangle with the equal biaxial planar position $(+1/2, +1/2)$ and the two states of uniaxial orientation (+1, 0) and (0, +1).

To proceed we need a value of Δ^0 for polystyrene. Theoretical values of Δ^0 have been computed by Gurnee[36] and Stein.[37] Our own calculations, which we present elsewhere, suggest a value of −0.137.

EXPERIMENTAL

Materials

Two commercial atactic polystyrene were used in this study. These were a Dow Styron 685D (melt index 1.6) and a Dow Styron 678U (melt index 12.0).

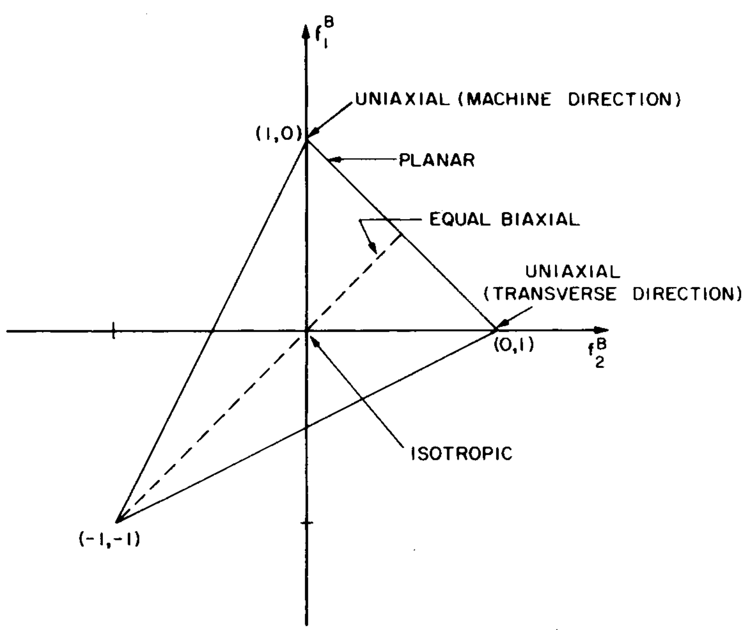

Fig. 1. Orientation triangle.

TABLE I
Birefringence and Orientation Factors for Polystyrene Dow Styron 685D Films

Stretching temperature, °C	Thickness, μm	Birefringence, ($\times 10^{-3}$)			Orientation factor	
		Δn_{12}	Δn_{13}	Δn_{23}	f_1^B	f_2^B
Uniaxially Stretched Films with Free Transverese Direction, 3.0 × 1′, 600%/min						
	130	−12.70	−13.49	−0.80	0.098	0.006
110	141	−13.88	−14.65	−0.77	0.107	0.006
	134	−14.92	−15.65	−0.72	0.114	0.005
	140	−16.91	−17.20	−0.30	0.125	0.002
	131	−16.33	−17.30	−0.98	0.126	0.007
	145	−17.06	−17.49	−0.43	0.127	0.003
	175	−17.97	−18.35	−0.38	0.134	0.003
	145	−17.66	−18.38	−0.72	0.134	0.005
	130	−18.76	−19.16	−0.40	0.140	0.003
115	163	−10.94	−11.77	−0.83	0.086	0.006
	164	−13.27	−13.26	+0.02	0.097	~0.000
	152	−13.42	−13.78	−0.36	0.100	0.003
	151	−13.26	−14.06	−0.80	0.102	0.006
	108	−16.85	−17.90	−1.06	0.130	0.008
	156	−6.11	−6.32	−0.21	0.046	0.002
120	139	−6.54	−6.85	−0.31	0.050	0.002
	149	−6.96	−7.56	−0.61	0.055	0.005
	164	−7.96	−8.52	−0.56	0.062	0.004
	155	−9.90	−9.80	+0.10	0.071	~0.001
130	141	−3.15	−3.20	−0.05	0.023	0.000
	140	−2.98	−3.22	−0.24	0.023	0.002
	138	−3.26	−3.26	+0.00	0.024	0.000
	145	−4.43	−4.73	−0.31	0.033	0.000
	124	−5.31	−5.51	−0.20	0.040	0.002
Unstretched	200 *n* 330	0.00	0.00	0.00	0.000	0.000
Uniaxially Stretched Films with Fixed Transverse Length, 3.0 × 1.0, 600%/min						
	88	−7.55	−9.86	−2.31	0.072	0.017
	102	−8.61	−10.99	−2.38	0.080	0.017
	91	−9.51	−11.90	−2.39	0.087	0.017
110	127	−9.27	−13.04	−3.77	0.095	0.028
	84	−14.85	−17.38	−2.54	0.127	0.019
	91	−7.87	−10.32	−2.54	0.075	0.018
115	84	−9.66	−12.57	−2.91	0.092	0.021
	79	−10.92	−13.33	−2.41	0.097	0.018
	85	−4.26	−5.99	−1.72	0.044	0.013
	74	−4.28	−6.29	−2.01	0.046	0.015
120	75	−5.98	−7.45	−1.47	0.054	0.011
	69	−5.60	−7.43	−1.83	0.054	0.013
	76	−6.91	−8.03	−1.12	0.059	0.008
	99	−5.75	−8.17	−2.42	0.059	0.018
	89	−7.65	−9.59	−1.93	0.070	0.014
	91	−2.61	−3.19	−0.57	0.023	0.004
	86	−2.45	−3.43	−0.98	0.025	0.007
	127	−3.34	−3.71	−0.37	0.027	0.003
	86	−2.46	−3.68	−1.21	0.027	0.009
130	99	−3.15	−3.96	−0.81	0.029	0.006
	78	−3.80	−5.06	−1.26	0.037	0.009

TABLE I (*Continued from previous page.*)

	Two-Way Successive Biaxially Stretched Films, 3.0 × 3.0, 600%/min				
	38	+2.64	−8.84	−11.47	0.064	0.084
115	31	+0.85	−11.78	−12.63	0.086	0.092
	32	+1.41	−5.94	−7.35	0.043	0.054
120	23	+2.08	−6.94	−9.02	0.051	0.066
	28	+1.15	−8.42	−9.57	0.061	0.070
	31	+0.91	−3.64	−4.54	0.026	0.033
130	29	+0.86	−5.29	−6.15	0.039	0.045
	Simultaneous Biaxially Stretched Films, 3.0 × 3.0, 600%/min					
	30	+0.68	−8.04	−8.72	0.059	0.064
	37	+1.11	−9.60	−10.71	0.070	0.078
	33	−0.09	−9.92	−9.82	0.072	0.071
	28	+0.52	−11.07	−11.59	0.081	0.085
115	27	+1.52	−12.53	−14.05	0.091	0.102
	32	−0.26	−6.30	−6.04	0.046	0.044
	28	−0.30	−7.62	−7.32	0.056	0.053
	28	+0.22	−8.83	−9.05	0.064	0.066
120	26	+0.08	−9.01	−9.09	0.066	0.066
	28	−0.22	−2.68	−2.46	0.020	0.018
	32	−0.42	−5.50	−5.08	0.040	0.037
130	36	+0.22	−6.09	−6.31	0.044	0.046

[a] $\Delta n_{12} = n_1 - n_2$, $\Delta n_{13} = n_1 - n_2$, $\Delta n_{23} = \Delta n_{12} - \Delta n_{13} = n_2 - n_3$.

Formation of Oriented Films

The polystyrene pellets were molded into sheets of dimensions 8 × 8 × 0.010 in. in a compression molding press at a temperature of 220–230°C. The sheets were placed in a T. M. Long Biaxial Tester (T. M. Long Co., Inc., Somerville, NJ) and stretched at various rates (usually 600% of initial length per minute). Generally, total extension ratios of 3 were used. The experiments were performed in the temperature range of 110–130°C. It was generally found to be very difficult to stretch the lower-viscosity melt (Styron 678U) because of sheet sagging. The experimental results reported in the next section are for Styron 685D. Sheets were prepared by four different procedures: (1) uniaxially with free transverse direction, (2) uniaxially with fixed transverse length, (3) two-way successive orthogonal biaxial stretching, and (4) simultaneous equalbiaxial stretching.

Measurement of Birefringence

The in-plane and out-of-plane birefringences of the film were measured in an instrument of the type devised by Stein[29] and used by Matsumoto and his coworkers.[15–18,21] This consists of a light source, a polarizer, a spatially positioning sample holder, an analyzer, and a Babinet compensator mounted on an optical bench. The sample holder involves mounting the sample on a goniometer that may be rotated from 0° to 45°. The value of $\Delta n_{12} = n_1 - n_2$ is measured at 0° with light perpendicular to the film. The value of Δn_{13} is obtained from tilting the sample and calculated by means of Stein's formula.[29] From the definitions,

$$\Delta n_{23} = \Delta n_{13} - \Delta n_{12} \tag{5}$$

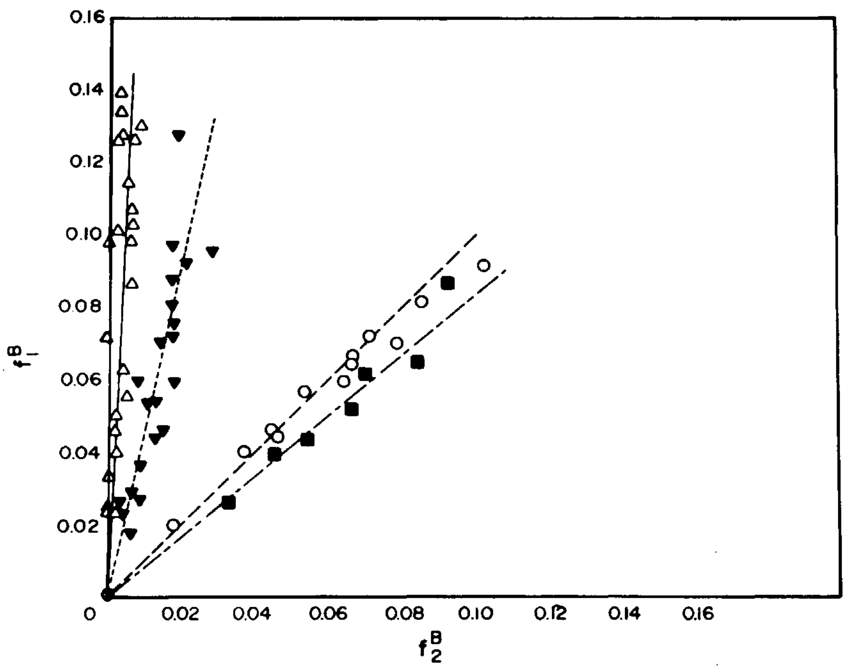

Fig. 2. Plot of birefringence data in the orientation triangle: (⊗) unstretched film; (—△—) uniaxially stretched/free transverse direction; (--▼--) uniaxially stretched/fixed transverse direction; (—■--) two-way successive biaxially stretched; and (--O--) simultaneous biaxially stretched.

Mechanical Properties

The mechanical properties of the films were measured using a table model Instron tensile testing machine. Strips were cut from the film at various angles to the T. M. Long machine stretching directions. Span lengths of 2.0 cm and crosshead velocities of 1.0 cm/min were used.

BIREFRINGENCE

Results

We summarize in Table I in the in-plane Δn_{12} and out-of-plane Δn_{23} and Δn_{13} birefringences of the polystyrene films. The birefringences are zero for the unstretched film. For the uniaxial films with a free transverse direction,

$$\Delta n_{12} \sim \Delta n_{13} < 0 \qquad \Delta n_{23} \sim 0 \tag{6}$$

where Δn_{23} is slightly negative. Similar relations hold for the uniaxial film with a fixed transverse dimension, but Δn_{23} is slightly larger and again negative. Decreasing the stretching temperature increases the magnitude of the birefringences. The maximum Δn_{13} birefringence achieved was −0.0147.

For the successive biaxial and simultaneous biaxial stretched films (i.e., experimental procedures 3 and 4), we have

$$\Delta n_{13} \sim \Delta n_{23} < 0 \qquad \Delta n_{12} \sim 0 \tag{7}$$

Decreasing the stretching temperature again increases the absolute magnitude

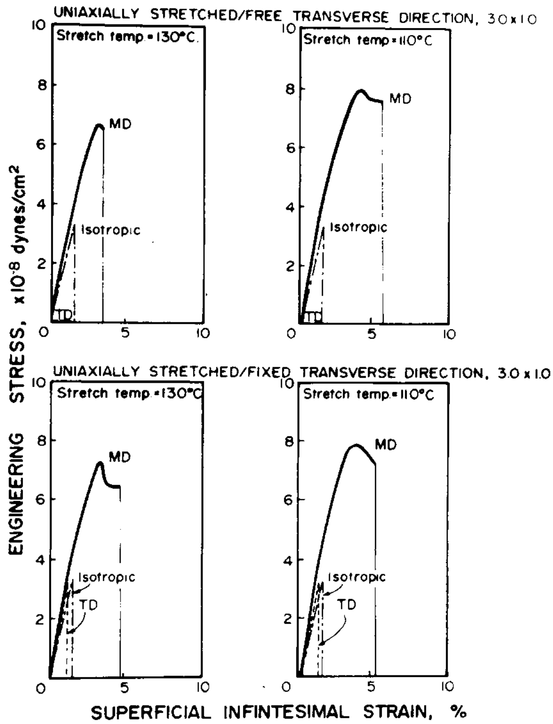

Fig. 3. Engineering stress–strain curves for isotropic and unixially oriented films: (⊗) Unstretched film; (– △ –) uniaxially stretched free transverse directions, (- - ▼ - -) uniaxially stretched/fixed transverse direction, (– ■ - -) two-way successive biaxially stretched; (– – O – –) simultaneous biaxially stretched.

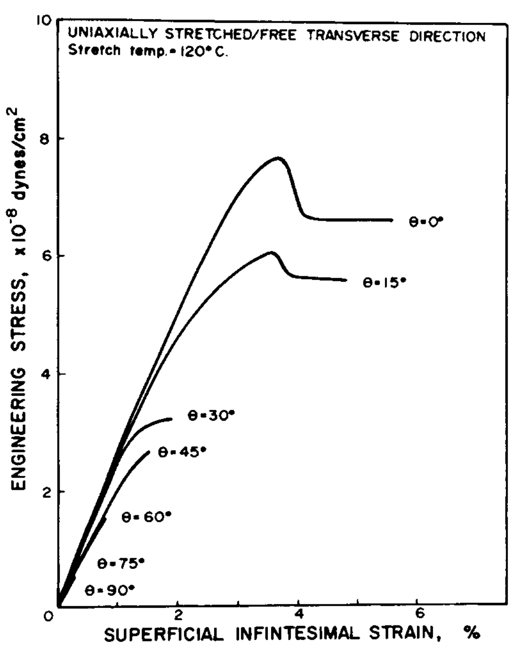

Fig. 4. Engineering stress–strain curves for strips cut at various angles to the machine direction.

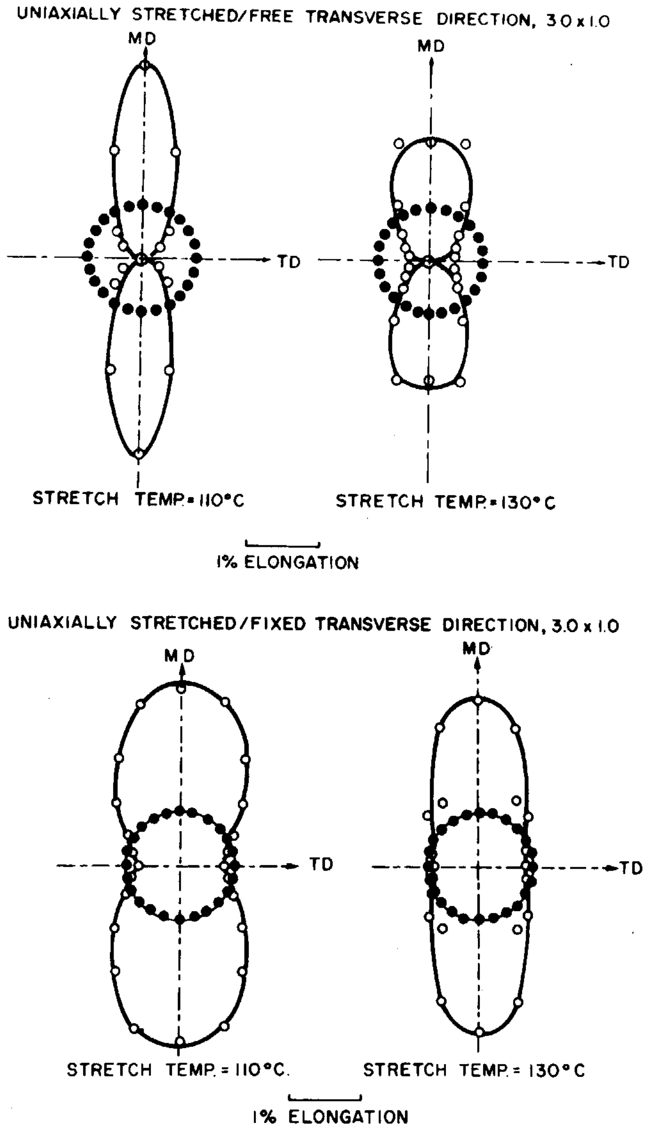

Fig. 5. Elongation to break as function of angle from machine direction for isotropic and uniaxially oriented films.

of the birefringence. The maximum value of Δn_{13} is -0.0126; that of Δn_{23} is -0.0137.

Discussion

We have computed biaxial orientation factors f_1^B and f_2^B for the sample studied using a Δ^0 of -0.14. They are listed in Table I and plotted in Figure 2 in terms of the orientation triangle diagram of Figure 1. The data all fall in the first quadrant, indicating that the macromolecules are on the average more in the

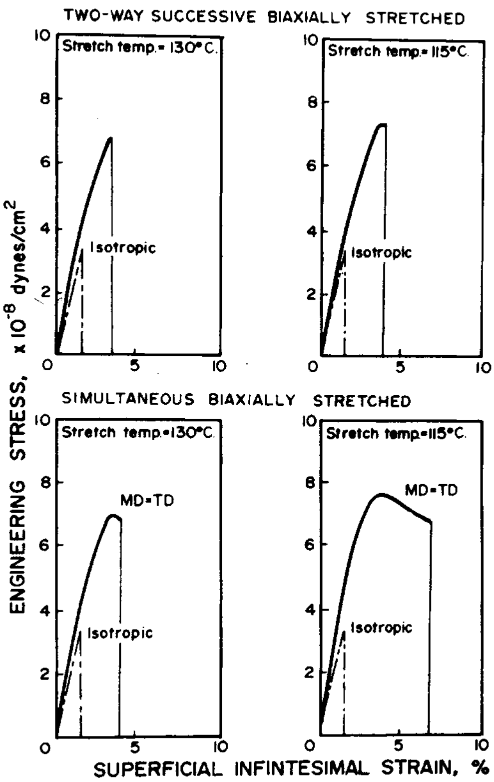

Fig. 6. Engineering stress–strain curves for isotropic and biaxially oriented films.

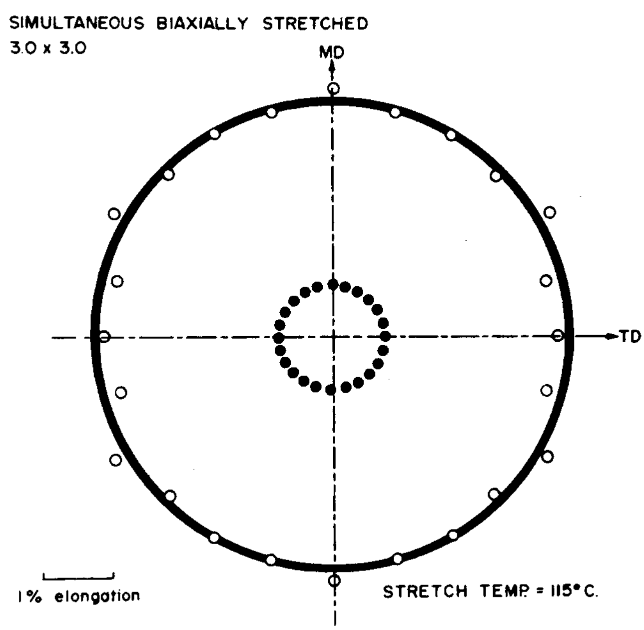

Fig. 7. Elongation to break as function of angle from one of the machine directions of biaxially oriented film.

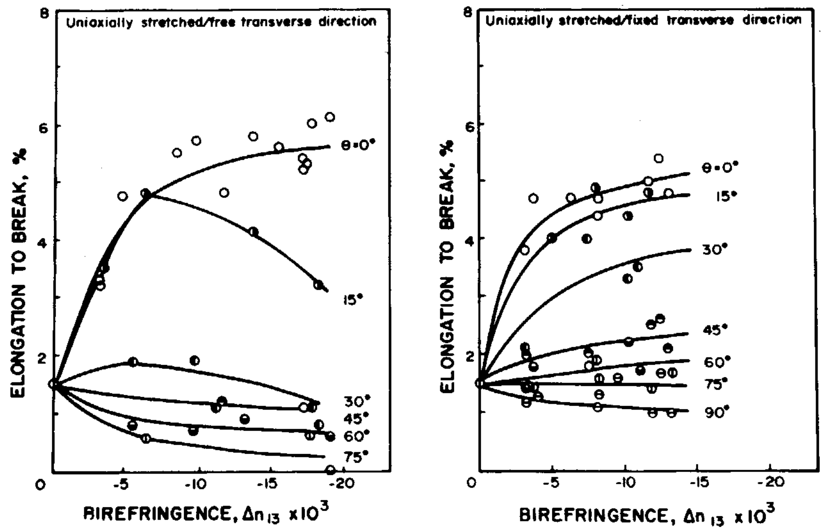

Fig. 8. Elongation to break in different directions as function of birefringence Δn_{13} of uniaxially oriented films.

plane of the film than perpendicular to it. The uniaxial film data lie on the f_1^B axis, and the sequential and simultaneously stretched biaxial films lie on the principal altitude.

The biaxial orientation factor f_1^B of the uniaxial film rises as high as 0.14.

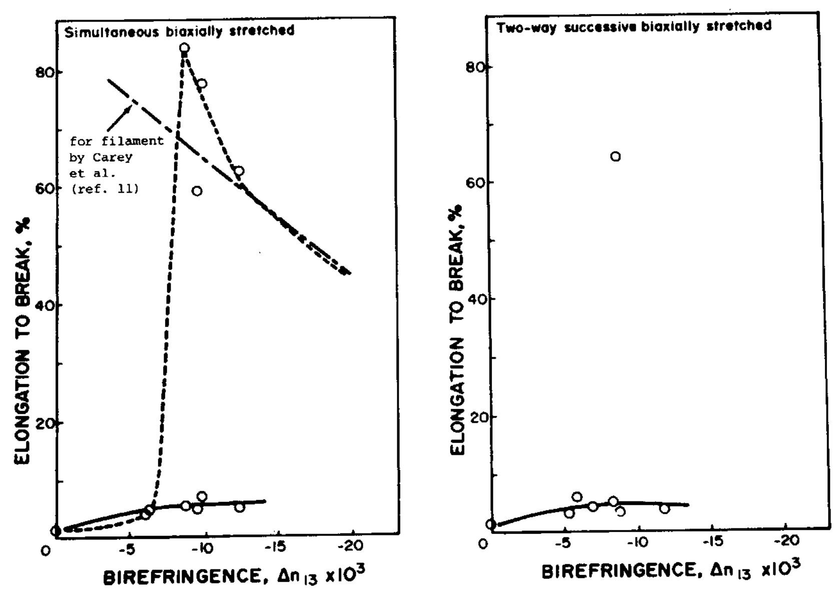

Fig. 9. Elongation to break in different directions as function of birefringence Δn_{13} in a biaxially oriented film. The solid line represents most of the data on the films, the line (– – –) is the data of Carey, Wust, and Bogue[11] on filaments, the (- - -) represent data on a limited number of films with high elongations to break.

Perfect uniaxial orientation results in a value of $f_1^B = 1.0$. The highest value of f_1^B for equal biaxial orientation is 0.10 (with 0.091 for f_2^B) out of a maximum possible value of 0.5 for equal biaxial planar orientations.

MECHANICAL PROPERTIES

Results

Engineering stress (force divided by initial cross section)–superficial infinitesimal strain (elongation divided by initial length) curves are plotted in Figure 3 for the isotropic and uniaxially oriented films for strips of film cut along the machine direction. The isotropic film is brittle and breaks at strains of less than 2%. The oriented films exhibit yield values and much larger elongations to break. In Figure 4 we plot engineering stress–strain curves for strips cut at various angles to the machine direction in uniaxially stretched films. The strip in the machine direction has a yield value and the same behavior as shown in Figure 3. The strip in the transverse direction is brittle and has a small elongation to break. This is emphasized in Figures 5(a) and 5(b) where we plot elongation to break as a function of angle from the machine direction for the isotropic and uniaxially oriented films.

Figure 6 contrasts engineering stress–strain curves for isotropic and biaxially oriented films, while Figure 7 plots elongation to break as a function of angle from one of the machine directions. The biaxially oriented films exhibit yielding and similar mechanical behavior at all directions in the plane. The elongation to break is substantially greater than that for the isotropic films or for the transverse direction of the uniaxially stretched films.

Discussion

Turning first to uniaxial extension, we plot elongation to break in both the 1- and 2-directions as a function of the birefringence Δn_{13}. In Figure 8, elongation to break in the 1-direction follows the trend of the earlier experimental data on filaments of Tanabe and Kanetsuna[10] and Carey, Wust, and Bogue.[11] However, the large elongations to break observed especially at low birefringence are not seen. This may be due to a greater number of defects in the film samples. The modulus E_{1111} (σ_{11}/γ_{11}) and the yield and tensile strength show but modest increases with orientation.

The elongation to break for biaxially oriented films is expressed as a function of birefringence in Figure 9. Elongations to break of 60–80% were obtained on some but not all samples, presumably because of relatively flaw-free specimens. As noted by Thomas and Cleereman,[19] one obtains increased elongation to break with increasing birefringence, with films changing from brittle to ductile and tough. There are only modest changes in modulus or tensile strength.

The results presented in this report are much more substantial than presented by earlier investigators. To move from the isotropic brittle sample to a ductile film with elongation to break of 5% or greater, one need achieve only a birefringence of Δn_{12} or Δn_{13} of -0.005 or an f_1^B or f_2^B of approximately 0.04 or greater.

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References

1. L. E. Nielsen and R. Buchdahl, *J. Appl. Phys.*, **21**, 488 (1950).
2. G. B. Jackson and R. L. Ballman, *SPE J.*, **16**, (1960).
3. G. Raumann, *Br. J. Appl. Phys.*, **14**, 795 (1963).
4. E. F. T. White, B. M. Murphy, and R. M. Haward, *J. Polym. Sci. Polym. Lett. Ed.*, **7**, 157 (1969).
5. L. R. G. Treloar, *Plast. Polym.*, **39**, 29 (1971).
6. H. Wright, C. S. N. Faraday, E. F. T. White, and L. R. G. Treloar, *J. Phys. D., Appl. Phys.*, **4**, 2002 (1971).
7. M. J. Doyle, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 127 (1975).
8. T. T. Jones, *Pure Appl. Chem.*, **45**, 39 (1976).
9. L. Hoare and D. Hull, *Polym. Eng. Sci.*, **17**, 204 (1977).
10. Y. Tanabe and H. Kanetsuna, *J. Appl. Polym. Sci.*, **22**, 1619 (1978); H. Kanetsuna and Y. Tanabe, *J. Appl. Polym. Sci.*, **22**, 2707 (1978).
11. D. A. Carey, C. Wust, and D. C. Bogue, *J. Appl. Polym. Sci.*, **25**, 575 (1980).
12. K. J. Cleereman, U. S. Pat. 3,307,726 (1967).
13. K. J. Cleereman, *SPE J.*, **23**, 43 (1967).
14. K. J. Cleereman, *SPE J.*, **25**, 55 (1969).
15. K. Matsumoto, T. Itagoshi, and R. Imamura, *Sen i Gakkaishi*, **26**, 272 (1970).
16. K. Matsumoto, S. Utsunomiya, and R. Imamura, *Sen i Gakkaishi*, **26**, 303 (1970).
17. K. Matsumoto and R. Imamura, *Res. Rep. Kyoto Univ. Ind. Arts Text. Fib.*, **6**, 159 (1971).
18. K. Matsumoto, M. Maeda, and R. Imamura, *Sen i Gakkaishi*, **29**, T-322 (1973).
19. L. S. Thomas and K. J. Cleereman, *SPE J.*, **28**, 61 (1972).
20. A. J. DeVries, C. Bonnebat, and J. Beautemps, *J. Polym. Sci. Polym. Symp.*, **58**, 109 (1977).
21. K. Matsumoto and H. Iio, *Sen i Gakkaishi*, **35**, T-150 (1979).
22. J. F. Fellers and T. Chapman, *J. Appl. Polym. Sci.*, **22**, 1029 (1978).
23. K. Oda, J. L. White, and E. S. Clark, *Polym. Eng. Sci.*, **18**, 53 (1978).
24. K. Choi, J. L. White, and J. E. Spruiell, *J. Appl. Polym. Sci.*, to appear.
25. P. H. Hermans and P. Platzek, *Kolloid Z.*, **88**, 68 (1939).
26. W. Kuhn and F. Grun, *Kolloid Z.*, **101**, 248 (1942).
27. J. J. Hermans, P. H. Hermans, D. Vermaas, and A. Weidinger, *Rec. Trav. Chim.* **65**, 427 (1946).
28. L. R. G. Treloar, *Trans. Faraday Soc.*, **33**, 277 (1947).
29. R. S. Stein, *J. Polym. Sci.*, **24**, 383 (1957).
30. R. S. Stein, *J. Polym. Sci.*, **31**, 335 (1958).
31. C. R. Desper and R. S. Stein, *J. Appl. Phys.*, **37**, 3990 (1966).
32. S. Nomura, H. Kawai, I. Kimura, and M. Kagiyama, *J. Polym. Sci. Part A-2*, **5**, 479 (1967).
33. H. Kawai, *Proc. 5th Int. Rheol. Cong.*, **1**, 97 (1969).
34. S. Nomura, H. Kawai, I. Kimura, and M. Kagiyama, *J. Polym. Sci. Part A-2*, **8**, 383 (1970).
35. J. L. White and J. E. Spruiell, "Specification of Biaxial Orientation in Amorphous and Crystalline Polymers," University of Tennessee Polymer Science and Engineering Rep. No. 142, Feb. 1979. *Polym. Eng. Sci.*, to appear.
36. E. F. Gurnee, *J. Appl. Phys.*, **25**, 1232 (1954).
37. R. S. Stein, *J. Appl. Phys.*, **32**, 1280 (1961).

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