Anisotropy and Dimensional Stability of Biaxially Oriented Poly(ethylene Terephthalate) Films

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Synopsis

Anisotropy in mechanical properties, expansion coefficients, and long-term shrinkage of PET films was determined. The films ranged in thickness from 0.92 to 14 mils. Young's modulus, ultimate strength, ultimate elongation, and coefficient of thermal expansion were strongly anisotropic. This anisotropy was related to orientation in the films. Yield stress and coefficient of hygroscopic expansion were more nearly isotropic. In general, the thin films showed more anistropy than the thick films due to better in-plane orientation in the thin films.

INTRODUCTION

Biaxially oriented poly(ethylene terephthalate) film is a semicrystalline material with very good strength, toughness, and flexibility. It is resistant to many organic and inorganic chemicals and has good electrical insulation properties. In comparison to other commercially available films, PET film has very good dimensional stability, which led to its use in applications such as photographic film, drafting film, magnetic recording media, and flexible electrical circuits. Future development of these and similar products require a good understanding of the properties and dimensional stability of PET film.

Biaxially oriented PET film has been shown to be anisotropic in various mechanical and dimensional properties.[1-4] In addition, the commercial film is metastable in two respects. First, the percent crystallinity of the film is much lower than the equilibrium crystalline content. Second, noncrystalline regions of the film contain frozen-in strains which tend to relax and allow the film to contract. Anisotropy and dimensional instabilities are limiting factors in the PET film applications which require dimensions and properties that are as precise as possible. This study was undertaken to determine the anisotropy of mechanical properties and dimensional changes in PET films of various thicknesses.

PET film is produced commercially by extrusion of a polymer melt which is quenched and then oriented. Orientation involves drawing of the film in the machine direction and in the transverse direction so as to produce balanced mechanical properties. The film is then heat set by restraining it at its stretched dimension and heating briefly to 150 to 230°C. This operation increases the crystallinity of the film and reduces its tendency to shrink. Shrinkage of the film may be further reduced by heating it at a temperature lower than the heat-set temperature and with low stress on the film. Finally, the film is cooled and wound onto rolls.[5]

The drawing operation during film manufacture causes orientation of both crystalline and noncrystalline regions of the film. As crystallites are formed in

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an oriented film, they hold in place many molecular chains that are already oriented. These chains are not free to retract even though the film temperature is above the glass transition temperature of the bulk material.[6] Time- and temperature-dependent relaxation of these ordered noncrystalline regions in PET film has been considered to be the major cause of shrinkage of the film.

Orientation in both crystalline and noncrystalline regions of PET film determines the properties of the film and the anisotropy in the properties.[1,2] Various workers, whose work has been reviewed by Heffelfinger and Knox,[5] have used wide-angle x-ray diffraction to study crystalline orientation in PET films. When the film is drawn uniaxially during its manufacture, the c-axis of the polymer crystal, which is the polymer chain axis, tends to align along the stretching direction.[7] When the film is then drawn in the transverse direction, oriented regions in the film fan out from the machine direction toward the transverse direction, with the degree of transverse orientation increasing with distance from the center of the web, and the c-axes distribute themselves accordingly. The variation in orientation across a film web is the primary cause of anisotropy of film properties.

It is important to note that, because of variations in degree of crystallinity and orientation of crystalline and noncrystalline regions of the film, the properties of PET film vary with location in a roll of film and also from one roll of film to another. Thus, to completely describe the properties of PET films, large numbers of specimens from various rolls of the materials and from various locations within the rolls must be tested. However, relationships among properties of a given film can be determined by measuring all properties of the film from one area of one roll. In this study, one area of each film was used for all measurements.

Since PET films are commercially important materials, the properties of the films have been determined by a number of workers. Mechanical properties such as Young's modulus, yield stress, ultimate strength, and ultimate elongation have been published by film manufacturers,[8-10] but these give properties only in machine or machine and transverse directions. Researchers[2-4] have determined mechanical properties of several PET films and they found that biaxially oriented PET films exhibited significant anisotropy in modulus, ultimate strength, and ultimate elongation. However, they found that yield stress of these films was essentially isotropic. Values for coefficient of linear thermal expansion of several PET films have been published by film manufacturers[8-10] and by Barrall and Logan.[1] A few values for coefficient of hygroscopic expansion have also been published by film manufacturers.[8-10]

TABLE I

Properties of 23-μm (0.92-mil) Biaxially Oriented Poly(ethylene Terephthalate) Film at 25°C, Manufacturer's Data[6]

Ultimate tensile strength, machine direction	172 MPa (25,000 psi)
Stress to produce 5% elongation	103 MPa (15,000 psi)
Ultimate elongation, machine direction	120%
Tensile modulus, machine direction	3.79 GPa (550,000 psi)
Density	1.395 g/cm^3
Coefficient of linear thermal expansion	1.7×10^{-5}/°C
Coefficient of hygroscopic expansion	6×10^{-6}/%R.H.

TABLE II
Extinction Angles of Films

Film thickness, μm	Extinction angle, degrees from machine direction
23 (0.92 mil)	49
76 (3 mils)	45
127 (5 mils)	45
190 (7.5 mils)	55
356 (14 mils)	55

In all of the past studies of anisotropy in biaxially oriented PET films, the question remains as to how anisotropy in mechanical properties, thermal expansion, hygroscopic expansion, and long-term shrinkage can be related to the structure of the films. In this study, properties of PET films of five thicknesses ranging from 1 to 14 mils were determined at various in-plane directions, and these properties were related to orientation in the films.

EXPERIMENTAL

The poly(ethylene terephthalate) films used in this work were commercially available materials with the trade name Mylar (E. I. duPont de Nemours & Co., Inc.). Films 23 μm (0.92 mil), 76 μm (3 mils), 127 μm (5 mils), 190 μm (7.5 mils), and 356 μm (14 mils) thick were included in the study. Published properties of the 1-mil film are shown in Table I.

The principal orientation direction in a film was determined by measuring the extinction angle under crossed polaroids. The extinction angle varies moving across a web of film with values for the extinction angle approaching 90° from the machine direction towards the edges of the web.[2]

Tensile properties of the films were measured using die-cut dogbone-shaped specimens (ASTM D638, type IV). Specimen thickness was measured with a mechanical comparator to ±0.25 μm (±10 μin.). Tests were conducted using an Instron testing machine with a 2.5-cm (1-in.) extensometer for measurement of strain in the specimens. A preload of about 7 MPa (1000 psi) was required to straighten the specimens before the extensometer was applied. The strain rate used was 0.05 min^{-1} for measurement of Young's modulus and 0.5 min^{-1} for measurement of the other properties. At least three specimens were tested at each direction. Tests were conducted at 22°C and 50% relative humidity.

Coefficients of thermal expansion of the films were determined with a DuPont 942 thermomechanical analyzer using the technique of Barrall and Logan.[1] At least three measurements were made at each orientation. The specimens used were 3 mm (0.118 in.) wide with 7 mm (0.275 in.) length between the chucks. Tests were run at a heating rate of 5°C/min.

Coefficients of hygroscopic expansion were measured using 21-cm (8¼-in.) square specimens. Targets were made by lightly scribing crosses on ink spots placed at various points on a circle of approximately 15 cm (6 in.) in diameter. Dimensional changes along the various diameters were measured with a coordinate measuring microscope which read to ±0.25 μm (±10 μin.). Specimens were conditioned in an environmental chamber to 8 ± 1% relative humidity at

TABLE III
Mechanical Properties of Biaxially Oriented Poly(ethylene Terephthalate) Films

Direction[a]	Young's modulus		Yield stress		Ultimate strength		Ultimate elongation, %
	GPa	10^5 psi	MPa	10^3 psi	MPa	10^3 psi	
23-μm (0.92-mil) Film							
MD	4.46	6.47	96	13.9	117	17.0	48
TD	4.61	6.68	100	14.5	140	20.3	50
PO	5.98	8.67	102	14.8	192	27.9	33
TO	3.72	5.40	92	13.4	97	14.1	82
76-μm (3-mil) Film							
MD	5.34	7.74	105	15.2	131	19.0	49
TD	4.92	7.14	103	15.0	121	17.5	61
PO	5.75	8.34	105	15.3	183	26.5	47
TO	3.85	5.58	102	14.8	106	15.4	78
127-μm (5-mil) Film							
MD	5.23	7.58	108	15.6	162	23.5	59
TD	5.09	7.38	107	15.5	145	21.1	66
PO	5.56	8.07	111	16.1	185	26.9	52
TO	4.36	6.32	105	15.6	134	19.4	96
190-μm (7.5-mil) Film							
MD	4.24	6.15	95	13.8	128	18.6	102
TD	4.88	7.08	97	14.1	150	21.8	92
PO	5.46	7.92	102	14.6	190	27.6	70
TO	3.63	5.26	90	13.1	116	16.8	117
356-μm (14-mil) Film							
MD	5.02	7.28	99	14.4	120	17.4	82
TD	5.14	7.46	101	14.7	144	20.9	75
PO	5.41	7.85	101	14.6	162	23.5	70
TO	4.20	6.09	97	14.0	104	15.1	115

[a] MD = Machine direction, TD = transverse direction, PO = principal optical, and TO = transverse optical axes.

TABLE IV
Anisotropy of Mechanical Properties[a]

Film thickness, μm	Young's modulus, %	Yield stress, %	Ultimate strength, %	Ultimate elongation, %
23 (0.92 mil)	23	5	33	43
76 (3 mils)	20	2	26	25
127 (5 mils)	12	2	16	30
190 (7.5 mils)	20	5	24	25
356 (14 mils)	13	2	22	24

[a] Anisotropy is defined here as the average variation of the minimum and maximum values from the mean value for a property.

$22 \pm 1°$C for at least 24 hr for the thinner films and at least 48 hr for the 14-mil film. When the chamber was opened, the specimens were pressed between glass plates and the distances between targets were measured. The specimens were then conditioned to $80 \pm 1\%$ relative humidity at $22 \pm 1°$C for at least 24 hr for the thinner films and 48 hr for the 14-mil film. After pressing between glass plates, the specimen dimensions were remeasured. The specimens were then returned to 8% relative humidity and measured again. Coefficients of hygro-
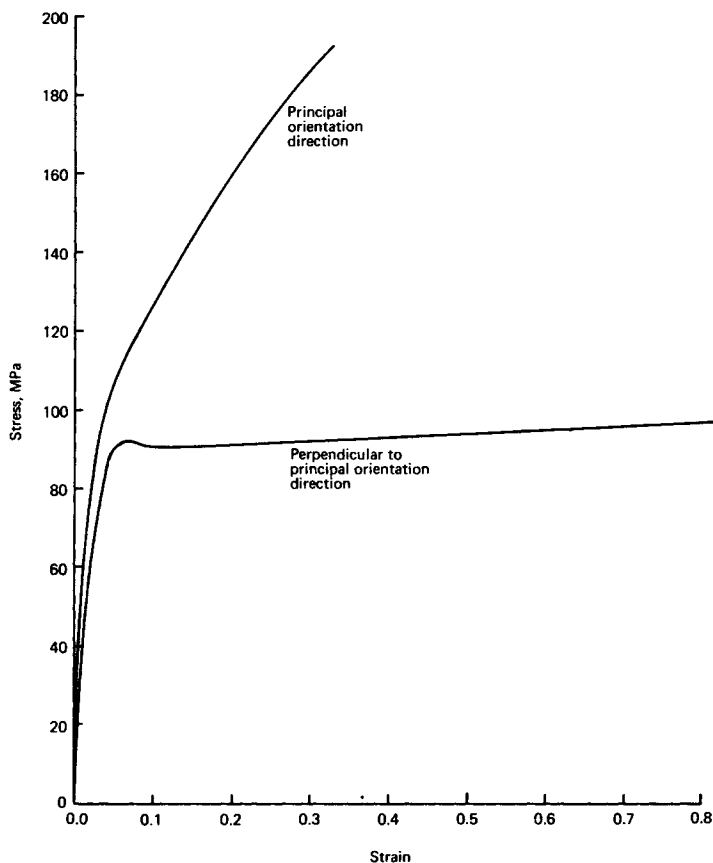
Fig. 1. Stress–strain curves for 23-μm (0.92-mil) PET film parallel and perpendicular to principal orientation direction.

scopic expansion were calculated from the average of the two measurements made by increasing and then by decreasing the relative humidity.

Tests of long-term dimensional stability were conducted using the 21-cm (8¼-in.) square specimens with scribed targets. The specimens were brought to equilibrium dimensions at 22 ± 1°C and 50 ± 1% relative humidity and were then pressed between glass plates during measurement. After the initial measurements, the specimens were placed on aluminum plates separated by spacers and put into a circulating air oven at 60 ± 1°C. After a designated time, the specimens were removed from the oven, returned to the equilibrium conditions of 22°C and 50% relative humidity, and then measured. Samples were tested in triplicate.

RESULTS AND DISCUSSION

Test specimens were cut from 21-cm (8¼-in.) wide strips of the PET films with the length of the strips along the machine direction of the films. The extinction angles, or optical axes, of the films were measured and the values at the center of the strips are given in Table II. At the edges of the strips, the extinction angles varied ±3° from the values at the center of the strips.
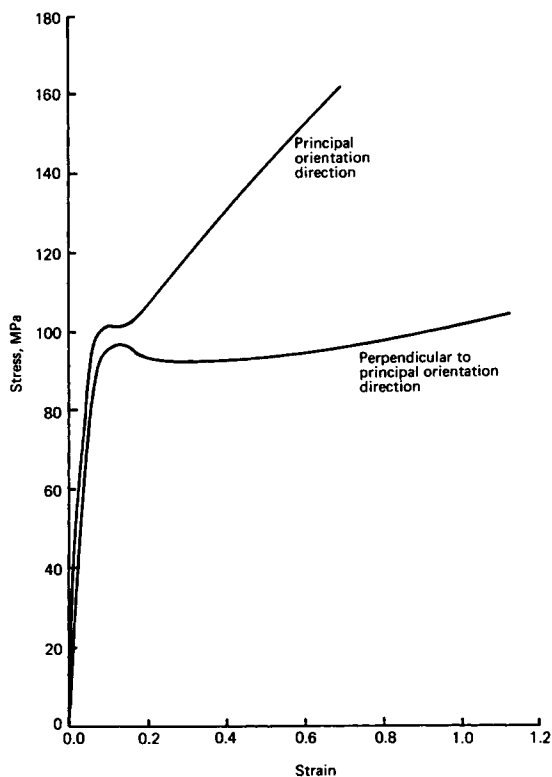
Fig. 2. Stress–strain curves for 356-μm (14-mil) PET film parallel and perpendicular to principal orientation direction.

TABLE V
Coefficients of Linear Thermal Expansion of PET Films, 25 to 50°C

Film thickness, μm	Coefficient, 10^{-6}/°C				Anisotropy, %[a]
	Machine direction	Transverse direction	Principal optical	Transverse optical	
23 (0.92 mil)	14.0	12.6	9.6	20.1	35
76 (3 mils)	26.8	24.5	15.0	30.7	34
127 (5 mils)	20.9	22.6	17.0	26.5	22
190 (7.5 mils)	24.8	24.0	16.2	35.2	37
356 (14 mils)	29.6	28.5	21.7	39.6	29

[a] Average percent variation of minimum and maximum values from mean value.

Mechanical Properties

The in-plane mechanical properties of the five PET films were measured at 15° increments and along the principal and transverse optical axes. Table III shows the mechanical properties of the films along the machine and transverse directions and along the principal and transverse optical axes. It is important to note that, as with most polymeric materials, the properties of PET films are dependent upon temperature and relative humidity. Tests at conditions different from those used here, 22°C and 50% relative humidity, may give significantly different results. Table IV is a tabulation of the anisotropy in mechanical
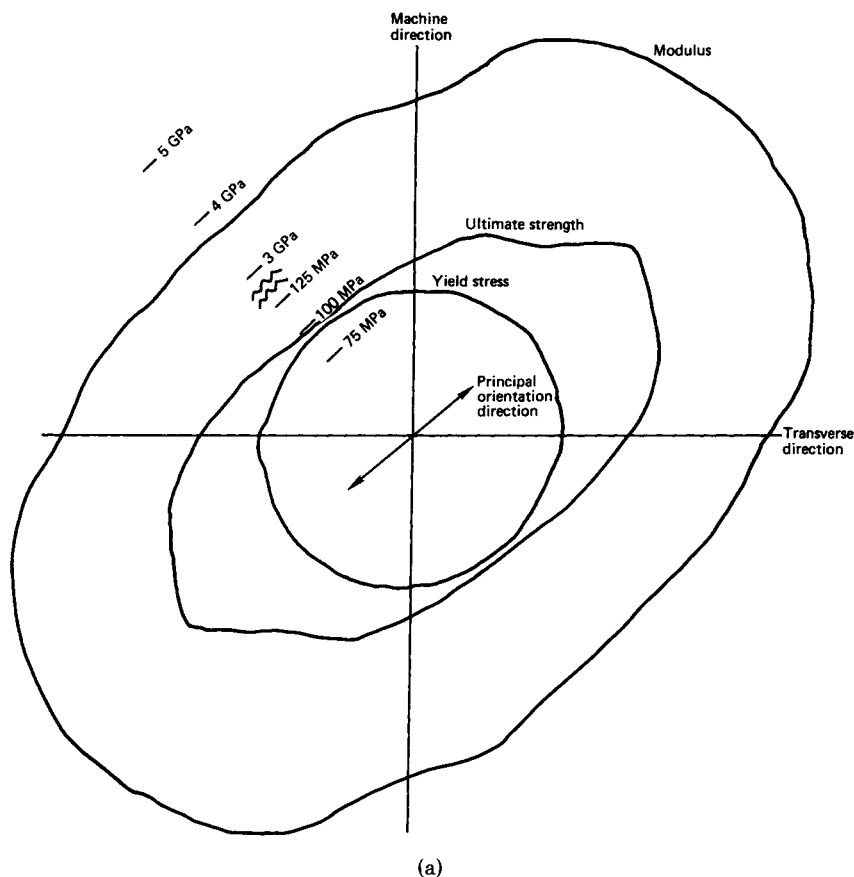
(a)

Fig. 3. (a) Yield stress, ultimate strength, and Young's modulus vs in-plane direction in 23-μm (0.92-mil) PET film. (b) Ultimate elongation vs in-plane direction in 23-μm (0.92-mil) PET film.

TABLE VI
Coefficients of Hygroscopic Expansion of PET Films, 8% to 80% Relative Humidity at 22°C

| Film thickness, μm | Coefficient, 10^{-6}/%R.H. | | | | Anisotropy, %[a] |
	Machine direction	Transverse direction	Principal optical	Transverse optical	
23 (0.92 mil)	6.4	5.6	5.2	6.3	10
76 (3 mil)	8.6	8.5	8.1	8.6	3
127 (5 mil)	7.4	8.5	6.5	8.3	13
190 (7.5 mil)	10.1	9.3	8.9	10.3	7
356 (14 mil)	11.2	10.9	11.0	11.2	1

[a] Average percent variation of minimum and maximum values from mean value.

properties. All five films showed significant anisotropy in Young's modulus, ultimate strength, and ultimate elongation. However, the yield stress was almost isotropic in these films. The 0.92-mil film had the greatest anisotropy, and the 14-mil the least anisotropy. The three films of intermediate thickness were about the same in anisotropy of mechanical properties. In all of the PET films, the
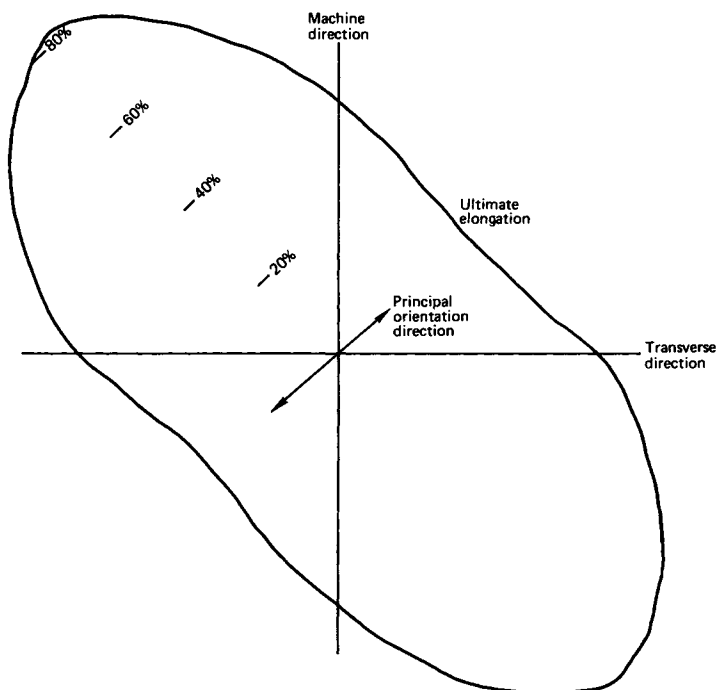
(b)

Fig. 3 (Continued from previous page.)

TABLE VII
Long-Term Dimensional Stability of 76-μm (3-mil) PET Film at 60°C

Time at 60°C, hr	Shrinkage, %	
	Machine direction	Transverse direction
24	0.039	0.037
120	0.068	0.064
288	0.074	0.070
624	0.100	0.090

maximum modulus and ultimate strength and the minimum ultimate elongation were found along the principal optical axis, which is the principal orientation direction in these films. The minimum modulus and ultimate strength and the maximum ultimate elongation were found along the transverse optical axis, which is the direction perpendicular to the principal orientation direction.

Stress–strain curves for the 0.92-mil and the 14-mil films along the principal orientation direction and along the direction transverse to the principal orientation direction are shown in Figures 1 and 2. Stress–strain behavior of the three films of intermediate thickness fall somewhere between the extremes shown here. In the 0.92-mil film significant differences in stress–strain behavior along the two axes are apparent, while in the 14-mil film the two curves show smaller differences, probably due to a lower degree of orientation in the thicker film.

Figures 3 and 4 are plots of the mechanical properties of the 0.92-mil and the 14-mil films using polar coordinates. These figures illustrate the correspondence
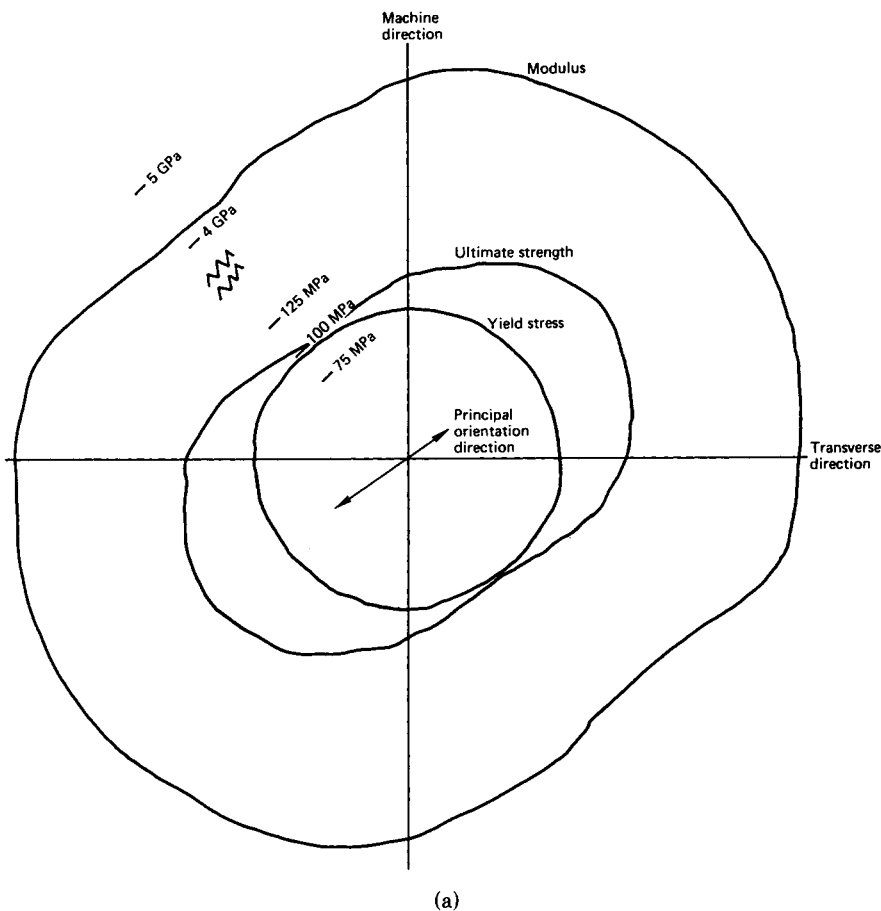
Machine
direction

Modulus

~5 GPa

~4 GPa

Ultimate strength

~125 MPa

~100 MPa

Yield stress

~75 MPa

Principal
orientation
direction

Transverse
direction

(a)

Fig. 4. (a) Yield stress, ultimate strength, and Young's modulus vs in-plane direction in 356-μm (14-mil) PET film. (b) Ultimate elongation vs in-plane direction in 356-μm (14-mil) PET film.

of high modulus, high strength, and low ultimate elongation with the principal orientation direction and of low modulus, low strength, and high ultimate elongation with the direction transverse to the principal orientation direction. Similar plots can be made for the mechanical properties of the 3-mil, 5-mil, and 7.5-mil films.
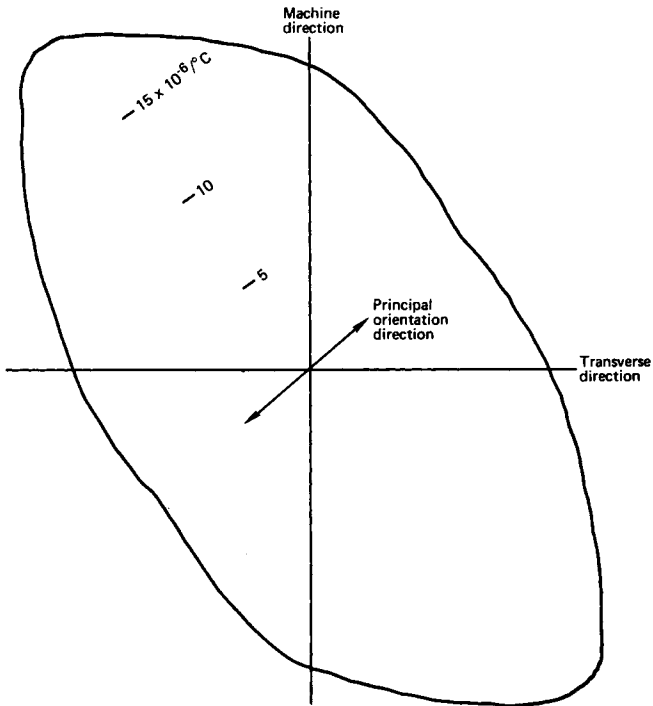
Coefficient of Thermal Expansion

Coefficients of linear thermal expansion of the PET film are given in Table V. The 0.92-mil film had the lowest coefficients of expansion which can be explained by this film having the highest degree of in-plane orientation. The 3-mil and 5-mil films had similar coefficients of thermal expansion, the 7.5-mil film had higher coefficients, and the 14-mil film had the highest coefficients of thermal expansion. All five films showed similar anisotropy in thermal expansion coefficient. In all of the films, the minimum coefficient of thermal expansion was observed along the principal orientation direction, and the maximum coefficient was observed transverse to the principal orientation direction. Figure
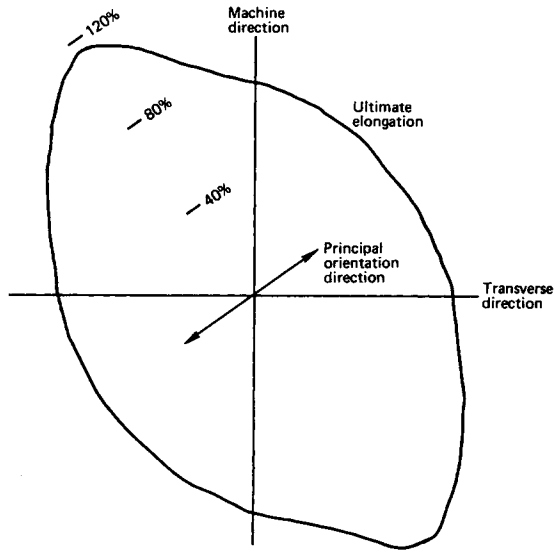
(b)

Fig. 4. (*Continued from previous page.*)

Fig. 5. Coefficient of linear thermal expansion vs in-plane direction in 23-μm (0.92-mil) PET film.

5 is a polar plot of coefficient of thermal expansion versus in-plane direction in the 0.92-mil film and shows the dependence of thermal expansion on direction.

anisotropy in hygroscopic expansion was much less than the anisotropy in mechanical properties or thermal expansion coefficient. Because of this relatively small anisotropy, the relation of orientation to hygroscopic expansion coefficient is not clear from these data. A plot of coefficient of hygroscopic expansion versus in-plane direction of the 0.92-mil PET film is shown in Figure 6.

Long-Term Dimensional Stability

Only a limited amount of work was done on the long-term dimensional stability of PET film. The principal long-term dimensional instability of these materials is shrinkage due to stress relaxation. The amount of shrinkage measured after a particular time interval depends upon the time–temperature–stress history of the film. Previous work on 1.42-mil PET film[11] and on 1.42-mil and 3-mil PET films with a magnetic coating[12] have shown that maximum shrinkage tends to occur along the machine direction of the film and minimum shrinkage tends to occur along the transverse direction. Shrinkage along these two directions in a 3-mil film exposed to 60°C is shown in Table VII. The shrinkage was anisotropic with the larger shrinkage observed along the machine direction of the film and the smaller shrinkage, along the transverse direction.

An annealing treatment allows stress relaxation to occur and thereby reduces shrinkage of the film after annealing. Figure 7 shows shrinkage of a 3-mil film before and after an annealing treatment. Obviously, different annealing treatments will result in varying degrees of stress relaxation.

CONCLUSIONS

Biaxially oriented PET films exhibited significant anisotropy in mechanical properties and coefficient of linear thermal expansion. The films were less anisotropic in hygroscopic expansion. Maximum strength and stiffness, minimum ultimate elongation, and minimum coefficient of thermal expansion were related to the principal orientation direction in a film. Minimum strength and stiffness, maximum ultimate elongation, and maximum coefficient of thermal expansion were found transverse to the principal orientation direction. The coefficient of hygroscopic expansion is less anisotropic than the coefficient of thermal expansion or mechanical properties. The thinnest film had the greatest anisotropy in properties and the thickest film had the least anisotropy. This is attributed to a higher degree of in-plane orientation in the thin film.

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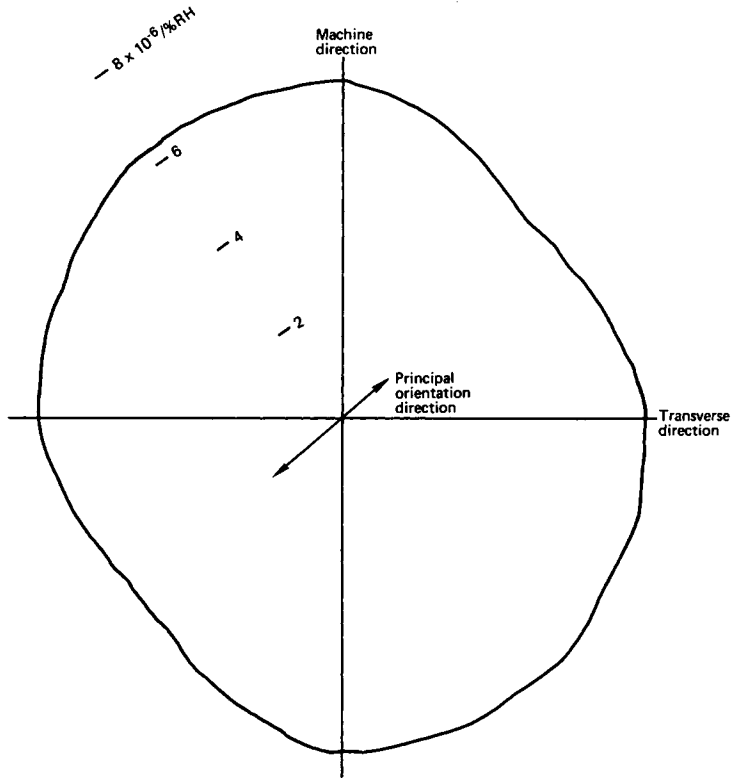7. C. J. Heffelfinger and P. G. Schmidt, *J. Appl. Polym. Sci.*, **9**, 2661 (1965).

Fig. 6. Coefficient of hygroscopic expansion vs in-plane direction in 23-μm (0.92-mil) PET film.
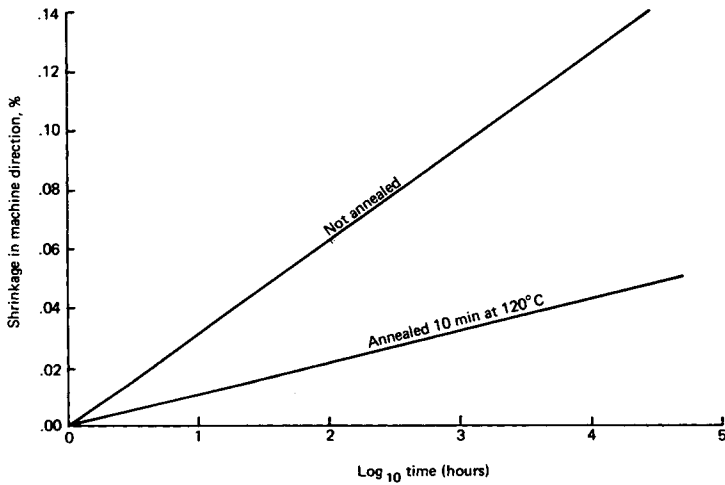

Fig. 7. Shrinkage of 76-μm (3-mil) PET film after exposure to 60°C.

Coefficient of Hygroscopic Expansion

Coefficients of hygroscopic expansion of the five PET films in the range of 8% to 80% relative humidity are given in Table VI. In general, coefficient of hygroscopic expansion tended to increase with increasing film thickness. The

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