RJ2669(34184)10/22/79
Chemistry

Research Report

ANISOTROPY OF THE COEFFICIENTS OF LINEAR THERMAL EXPANSION AND OTHER
PROPERTIES OF SIX BIAXIALLY ORIENTED FILMS OF POLY(ETHYLENE TEREPHTHALATE)

Andrew Chan
Thor L. Smith

IBM Research Laboratory
San Jose, California 95193

ANISOTROPY OF THE COEFFICIENTS OF LINEAR THERMAL EXPANSION AND OTHER
PROPERTIES OF SIX BIAXIALLY ORIENTED FILMS OF POLY(ETHYLENE TEREPHTHALATE)

Andrew Chan
Thor L. Smith

IBM Research Laboratory
San Jose, California 95193

ABSTRACT: The anisotropy of the coefficient of linear thermal expansion
and of the shrinkage effected by heating specimens to 190°C was determined
on five commercial biaxially oriented films (ca. 3 mils thick) of
poly(ethylene terephthalate) (PET). Expansion coefficients were evaluated
near 25°C and also near 130°C for specimens heated the second time to
190°C. (Specimens contract above 70-80°C during the first heating period.)
The coefficients conform to $\alpha(\theta) = \alpha_\perp + (\alpha_\| - \alpha_\perp)\cos^2\theta$ where $\alpha_\|$ and $\alpha_\perp$ are
the coefficients, at a particular temperature, parallel and perpendicular,
respectively, to the slow optic axis. The minimum expansion coefficients
near 25° and 130°C are $\alpha_\|$ and $\alpha_\perp$, respectively. The data show that JTS-118
(an experimental film from ICI) and Melinex-0 are the most nearly isotropic
near 25° and 130°C, respectively, and that the anisotropy of all films,
except JTS-118, is somewhat less at 130° than at 25°C. At 25°C, $\alpha_\|/\alpha_\perp$ is
related semiquantitatively to the birefringence. The maximum shrinkage
(first heating) tends to be perpendicular to the slow optic axis. The
effect of thermal history and tensile stress on the expansion and shrinkage
of Mylar D were investigated briefly. A special PET film, prepared by
stretching radially a disc of an amorphous PET film, was found to be
isotropic in the plane of the film. DSC measurements were made on the
commercial films.

CONTENTS

I. INTRODUCTION

Biaxially oriented films of poly(ethylene terephthalate) (PET) are manufactured in large quantities by various companies, including Du Pont, ICI, Celanese, and Toray. The tradenames of their respective films are Mylar, Melinex, Celanar, and Lumirror. Heffelfinger[1] has discussed authoritatively the steps in the production of such films. However, his rather informative discussion is qualitative, undoubtedly because many details of the process are proprietary.

The films are produced by a continuous process from a PET resin whose number-average molecular weight is typically between about 15 and 50 × 10^3. In essence, the PET resin is extruded at about 280°C through a flat die onto a cold quenching drum to give an amorphous glassy film. (The glass temperature of amorphous PET is 70°C.) The film is then heated above its glass temperature and passed through two sets of nip rolls. The rolls operate at different speeds such that the film is stretched longitudinally, i.e., in the machine direction, MD. During this operation, the film is oriented uniaxially and some crystallinity (about 20%) develops. Thereafter the film is stretched in the transverse direction (TD) by a so-called tenterframe, and concomitantly the crystallinity increases a few percent. To impart dimensional stability, the film next passes through a chamber at about 200°C, while still restrained. During this "heat-set" operation, the crystallinity increases to about 50%. The resulting film has good mechanical properties, although it still will shrink somewhat, especially when heated above its glass temperature. The film can be

stabilized further by heating it under very low tension at a temperature below the heat-set temperature to relax frozen-in strains. However, commercial films are not stabilized by this process.

The film from most production lines is 120 inches wide; from one line, and possibly more, it is 240 inches wide. From each side of a film 120 inches wide, strips 48 inches wide are cut and wound into rolls. The 24-inch "center cut" is used for special purposes. (While much of the above information is from Ref. 1, some of the specific facts are not given and may be termed "generally known" information.)

Although commercial films are presumably stretched equally in the machine and transverse directions during processing, the physical properties of the final film are not equal in both directions,[2-7] i.e., the film has in-plane anisotropy. Furthermore, the anisotropy varies across a 48-inch wide sheet. For example, the slow optic axis (or extinction angle) for 1.5-mil thick Mylar (142A) changes by about 35° across the sheet;[2,7] similarly, the birefringence varies[2] by 50%. Near the outer edge, the net orientation of crystallites and amorphous material is more nearly parallel to the TD than to the MD; the opposite is true near the edge next to the center cut. Consequently, such physical properties as the modulus, the long-term shrinkage at 35°C, and the coefficient of linear hygroscopic expansion depend on the position in a 48-inch web[7] as well as on the in-plane direction at any point.[2-6] Undoubtedly, other physical properties vary likewise, although illustrative

data have apparently not been reported. Along a line parallel to the machine direction, the properties are essentially constant[7] but not necessarily over long distances.

In a study of 1.5-mil Mylar film, Barrall and Logan[3] investigated, among other things, the expansion and shrinkage of specimens heated at different rates at temperatures up to about 230°C. The specimans were cut such that the angles between the MD and their longitudinal axis were 0°, 45°, and 90°. During heating, a specimen was found to expand up to some temperature, between about 73° and 97°C, that depended on the heating rate and the angle between the longitudinal axis of the specimen and the MD. At higher temperatures, shrinkage occurred. On the other hand, when a specimen had been annealed at some temperature above that at which a non-annealed specimen begins to shrink significantly, the specimen thereafter expanded during heating until the temperature exceeded the annealing temperature. The results from these and other experiments indicate that annealing a film under low tension at an elevated temperature for some appropriate period improves the dimensional stability of the film at low temperatures.

Even below its glass temperature, a film shrinks continuously but at a low rate. Bartkus and Price[4] studied the long-term shrinkage of specimens of 1.5-mil Mylar S and Mylar PB, both parallel and perpendicular to the MD, at four temperatures from 35° to 60°C. Also, they showed that annealing a film for 10 minutes at 120°C reduced its rate of spontaneous shrinkage at 43° and 60°C.

Blumentritt[5] has determined the shrinkage rates, stress-strain characteristics, and the coefficients of linear thermal and hygroscopic expansion[5] of 1.5-mil and 3.0-mil Mylar (type A-PB) films that had been coated on each side with γ-Fe_2O_3 dispersed in a polymeric binder. His data show how these physical properties vary with the angle between the MD and the longitudinal axis of a specimen. For specimens annealed at temperatures somewhat above 100°C, it was found that at lower temperatures the rate of long-term shrinkage was reduced markedly, the modulus was reduced somewhat, the coefficient of linear hyroscopic expansion was increased, and the coefficient of linear thermal expansion was not affected significantly.

Greenberg et al.[8,9] investigated the dimensional changes of spinning disks of flexible magnetic media. Their special apparatus employed a scanning laser beam to monitor the radius of a disk at eighteen equally spaced points. Typically, the spinning speed was 1800 rpm, and the radius of the disk was six inches. Studied in most detail was the IBM Igard media, which is 3-mil Mylar coated on both sides with a magnetic layer 2.5 µm thick. Some tests were also made on the IBM Stallion and Mustang media and the Du Pont Crolyn media.

The following are the principal findings by Greenberg et al.[8,9] on the Igard disks. (1) The hygroscopic expansion is nearly isotropic in the plane; a change in relative humidity from 40% to 30% gave an expansion coefficient of 1.25×10^{-5}/% RH. (2) The maximum and minimum values of the coefficient of thermal expansion were along the principal optic axes;

in the vicinity of 50°C, these expansion coefficients were 3.8×10^{-5} and $2.2 \times 10^{-5}/°C$. (3) The maximum and minimum values of the long-term shrinkage, determined at relative humidities between 15 and 50% and temperatures from 40° to 72°C, were parallel and perpendicular to the MD, respectively. An increase in the relative humidity, and also in the temperature, increased the shrinkage rate significantly. (4) Heat treating a disk reduced the rate of shrinkage significantly; but heating a disk for one hour at 120°C did not alter the hygroscopic expansion coefficient significantly.

Some of these findings differ somewhat from those reported by others. In particular, both Blumentritt[5] and Bartkus[7] have shown that the hygroscopic expansion coefficient is not isotropic in the plane. Also, Blumentritt[5] found that this coefficient is increased by subjecting magnetic media to thermal treatments. It should be mentioned, however, that the properties of flexible magnetic media depend on the position in a 48-inch wide Mylar film (or other types of PET film) from which the media is obtained and quite probably also on the conditions used in coating the film with a magnetic layer.

By using the special apparatus,[8,9] Stephens[10] obtained data on the shrinkage of disks of clear Mylar PB 145 (1.5 mils thick) during rotation at 1800 rpm for long periods at various temperatures and humidities. Other characteristics of the disks were not reported, however.

The above-mentioned studies were made on 1.5-mil Mylar films[2-4,7,10] and on 1.5-mil and 3.0-mil films coated with magnetic layers.[5,8,9] The data in Ref. 6 were obtained on Mylar sheets whose thicknesses were about 5.1, 10.2, and 13.8 mils.

The present study was made to compare certain properties, primarily thermal expansion and shrinkage at elevated temperatures, of 3.0-mil films of biaxially oriented PET produced by three manufactures. Three standard commercial films were studied along with three special films, including one prepared in this laboratory by Lee[11] who stretched radially a disk of amorphous unoriented PET which thereafter was heat-set at an elevated temperature.

II. EXPERIMENTAL SECTION

A. Characteristics of Films Studied

The films studied include Celanar 4500, Melinex-O, and Mylar D produced by Celanese, ICI, and Du Pont, respectively, and supplied to us by R. Nufer (GBG, Poughkeepsie). Also investigated were two experimental films, XM-648 and JTS-118, obtained from Du Pont and ICI, respectively, by E. A. Bartkus (GPD, Tucson). The films received were 11-14 inches wide, presumably cut from rolls 48 inches wide. The width and thickness of the five films are included in Table I. The characteristics of films prepared in a special manner by Lee[11] are given later in this report.

At four points across each strip of film, the slow principal optic axis (the direction of the maximum in-plane refractive index) was determined by examining the specimens under crossed polaroids in a microscope. Values of the angle between the MD and the slow optic axis, measured counterclockwise, are given in Table I. These angles, which are nearly the same for each film at position "W", vary by a relatively small amount from point to point, excluding JTS-118, probably because the sheets were relatively narrow.

The in-plane birefringence of each film at position W (near one edge; see Table I) was determined using a Babinet compensator and monochromatic light of wavelength 5461Å. The results are included in Table II.

The density of each film was determined with a water-zinc chloride density-gradient column. The density was converted into the degree of crystallinity, expressed as weight per cent W, by using the equation

$$W = 100(1/\rho - 1/\rho_a)/(1/\rho_c - 1/\rho_a) \tag{1}$$

where ρ, ρ_a, and ρ_c are the densities of the sample, the amorphous phase, and the crystalline phase, respectively. The values of ρ_a and ρ_c were taken to be 1.331 and 1.470 g/cm^3, respectively.[12] Values of ρ and W are given in Table II.

B. Apparatus for Measuring the Expansion and Shrinkage of Films

The thermal expansion and shrinkage of specimens were determined with a Du Pont thermo-mechanical analyzer (TMA) along with a Du Pont thermal analysis module that serves to control the TMA and to record the data, e.g., to provide a plot of the displacement of the core in the LVDT against temperature. The TMA was modified somewhat, as described by Barrall and Logan,[3] to enable films to be tested.

By using a special template, a specimen whose gage length and width are 0.50 and 0.30 cm, respectively, was mounted in two Invar microchucks which were then attached to quartz stirrups;[3] one stirrup was fixed and the other was coupled to the core of the LVDT. (Specimens were cut with a modified X'ACTO blade.) To eliminate any oscillations of the core-spring assembly, a small weight was placed on the weight-tray of the TMA which applied a tensile stress of about 10 psi to the specimen.

Before testing film specimens, the apparatus was calibrated by measuring the thermal expansion of an annealed quartz bar and also an Invar bar; each was attached directly to the quartz stirrups. Measurements were also made on specimens of pure copper, aluminum, and lead, whose coefficients of linear thermal expansion are known accurately. Each metal specimen was mounted in the microchucks attached to the quartz stirrups. From the obtained data, a procedure was devised for relating the displacement of the recorder pen to the change in length of a film specimen. The calibration measurements showed that the expansion of the Invar microchucks, though quite small, was somewhat greater than that of the quartz stirrups and attached components. Although the latter was almost negligible, the expansion of both the microchucks and the quartz stirrups was accounted for in computing the expansion coefficient of a film specimen.

C. Test Procedure

Specimens were cut at various angles to the slow optic axis near one edge of a sheet (position W; see Table I). A specimen was heated at 5°C per minute to 190°C, then allowed to cool to room temperature, and finally heated again to 190°C.

Typical traces are shown in Fig. 1. During the first heating period, a specimen expands until it reaches a temperature T_i (inversion temperature) near its glass temperature. Thereafter, the specimen contracts; the contraction rate increases rapidly above about 150°C.

During the second heating period, the specimen expands at all temperatures up to 190°C, above which it contracts.

Linear expansion coefficients were obtained from the slopes of straight lines drawn through the curves that represent the expansion near room temperature during the first and second heating periods and through the curve near 130°C that represents expansion during the second heating period. Film shrinkage was obtained from the difference between the initial length of a specimen and its length at room temperature after the first heating period.

Specifically, the expansion coefficient α was obtained from

$$\alpha = \Delta L / L_0 \Delta T \qquad (1)$$

where ΔL is the increase in specimen length produced by a temperature change ΔT and L_0 is either the initial length of a specimen or its length at room temperature before it was heated the second time. That is, the expansion coefficients near room temperature and near 130°C obtained for a specimen heated the second time were based on its length after the first heating period.

III. EXPERIMENTAL RESULTS ON COMMERCIAL FILMS

A. Coefficients of Linear Thermal Expansion

Table III gives the determined values of $\alpha_1(25)$ and $\alpha_2(130)$ along with $\alpha_2(25)/\alpha_1(25)$, where $\alpha_1(25)$ is the expansion coefficient near 25°C obtained from the first heating of a specimen, and $\alpha_2(25)$ and $\alpha_2(130)$ are the coefficients near 25° and 130°C, respectively, obtained from the second heating of a specimen to 190°C. (During the first heating, a specimen contracts at temperatures above T_i, as mentioned before and illustrated in Fig. 1). The quantities in Table III are given at various values of θ, which is the angle measured clockwise between the longitudinal axis of a specimen and its slow optic axis. In turn, the slow optic axis is the direction in which the net orientation of crystals and amorphous material is a maximum. As shown by the ratio $\alpha_2(25)/\alpha_1(25)$, $\alpha_2(25)$ is usually, though not always, somewhat larger than $\alpha_1(25)$. Hence, any analysis of the $\alpha_1(25)$ data should apply reasonably well to $\alpha_2(25)$.

As shown in the Appendix, the angular dependence of α for certain anisotropic materials is given by

$$(\alpha_{\parallel} - \alpha_{\perp}) \cos^2\theta + \alpha_{\perp} = \alpha(\theta) \tag{2}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the expansion coefficients when θ equals 0° and 90°, respectively. This equation represents the present data adequately, as illustrated by Fig. 2 which shows $\alpha_1(25)$ for XM-648 plotted against $\cos^2\theta$. The slope of the line and its intercept on the ordinate show that $\alpha_{\parallel}$ and $\alpha_{\perp}$ are 1.04×10^{-5} and 2.41×10^{-5}/°C, respectively. These values should represent the anisotropy of the expansion coefficient better than those

determined directly, which are somewhat larger. From Eq. (2) and the values of $\alpha_{\parallel}$ and $\alpha_{\perp}$, the curve in Fig. 3 that represents the data on XM-648 was calculated. The curve results from plotting $\alpha_1(25)$ against θ. In a similar manner, the other curves in Fig. 3 and those in Fig. 4 were constructed. Table IV gives the values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ obtained from the plots of $\alpha_1(25)$ and $\alpha_2(130)$ against $\cos^2\theta$.

Figure 3 and the ratio $\alpha_{\perp}/\alpha_{\parallel}$ (Table IV) show that all films, except JTS-118, exhibit considerable anisotropy at 25°C and that the minimum value of $\alpha_1(25)$ for each film is parallel to the slow optic axis. Figure 3 also shows that the shaded circles, which represent the experimental values of $\alpha_1(25)$, are close to the calculated curves and that the open circles, which represent values of $\alpha_2(25)$, tend to lie outside the curves. These experimental data are similar to those reported by Blumentritt[5] who studied 1.5-mil and 3.0-mil Mylar (type A-PB) films coated on each side with particulate γ-Fe_2O_3 dispersed in a polymeric binder.

Figure 4 shows the experimental values of $\alpha_2(130)$ plotted against θ. The curves were calculated from $\alpha_{\parallel}$ and $\alpha_{\perp}$ given in Table IV. Here, the minimum value of $\alpha_2(130)$ for each film is perpendicular to the slow optic axis, determined at room temperature. (Special experiments showed that the optic axis does not change with increasing temperature and that it is unchanged at room temperature after a specimen has been heated to an elevated temperature.) No explanation for this unexpected behavior shall be proposed now.

At 130°C, all films except JTS-118 are somewhat more isotropic in the plane of the film than at 25°C, as shown by the ratio R, defined and given in Table IV. Among the films studied, JTS-118 is the most nearly isotropic near 25°C; but at 130°C, Melinex-0 is the most nearly isotropic, as shown by the ratios of expansion coefficients in Table IV.

Above the glass temperature, which is close to the inversion temperature T_i observed during the first heating of a specimen, the expansion coefficient during the second heating should exceed that below T_i, as was observed (Tables III and IV). Such is expected because the expansion coefficient of an <u>isotropic</u> amorphous polymer above its glass temperature is typically threefold greater, or thereabouts, than below. For the PET films, it is instructive to consider the expansion coefficients, both above and below the glass temperature, in the three mutually perpendicular directions. Toward this end, it is necessary to invoke the well-established fact that the coefficient of volumetric thermal expansion α_v for an isotropic polymer is the same as that for the polymer in an anisotropic state. (If the polymer is semicrystalline, this statement is true only if the degree of crystallinity for the isotropic and anisotropic materials is the same.)

For isotropic PET whose crystallinity is approximately 50%, the reported[13] values of α_v below and above the glass temperature are 19×10^{-5} and 36×10^{-5} $cm^3/cm^3/°C$. For the biaxially oriented PET films, as well as other anisotropic materials,

$$\alpha_v = \alpha_{||} + \alpha_{\perp} + \alpha_t \tag{3}$$

where α_t is the coefficient of linear expansion in the thickness direction. For an isotropic material, each of the three coefficients equals $\alpha_v/3$.

Table V shows that the calculated values of α_t are considerably larger than $\alpha_v/3$, the value for isotropic semicrystalline PET, and also that α_t/α_v is smaller at 130°C than at 25°C. Also, $(\alpha_{||} + \alpha_{\perp})/\alpha_v$ is markedly less than 0.67 (the value for isotropic PET) and is larger at 130°C than at 25°C. Stated otherwise, the PET films are somewhat less anisotropic above the glass temperature than below.

As may be determined from the data in Tables IV and V, the values of $(\alpha_{||} + \alpha_{\perp})$, α_v, and α_t at 130°C divided by the values at 25°C are about 3.2, 1.9, and 1.6, respectively. Thus the fractional increase in the coefficient of areal expansion in going from 25° to 130°C is larger and that for the expansion coefficient in the thickness direction is smaller than that for the coefficient of volume expansion.

Figure 5 shows that $(1 - \alpha_{||}/\alpha_{\perp}) \simeq 6.8 \times 10^{-2} \Delta n$, where Δn is again the birefringence (Table II). This relation and Eq. (2) leads to

$$\alpha(\theta) \simeq \alpha_{\perp}(1 - 6.8 \times 10^{-2} \Delta n \cos^2\theta) . \tag{4}$$

This equation is only an approximation, especially for JTS-118 because its birefreingence (1.83×10^{-2}) is significantly greater than that predicted by the line in Fig. 5.

B. Shrinkage of Films

The shrinkage during the first heating of the specimens to 190°C is
given in Table III and is shown by the plots in Fig. 6. The direction of
maximum shrinkage, though not defined too well, tends to be perpendicular
to the slow optic axis; that is, parallel to the direction in which the
expansion coefficient at 130° is a minimum during the second heating period
(Fig. 4).

Blumentritt[5] has measured the shrinkage under isothermal conditions,
primarily at 60°C but to some extent at temperatures up to 107°C. He
found that the shrinkage is a maximum parallel to the MD. However, he
studied only one type of PET film which, as mentioned before, had a thin
magnetic coating on both sides. Possibly the coating process could
influence the direction of maximum shrinkage, although such has not been
established. In studies of similar magnetic media, Greenberg et al.[8,9]
found that the shrinkage rate at temperatures between 40° and 72°C was
greatest parallel to the MD, as mentioned in the INTRODUCTION.

In the present study, essentially all of the shrinkage occurred above
T_i and under non-isothermal conditions. Also, the direction of maximum
shrinkage, or shrinkage rate, may not be the same above and below the
glass temperature. Thus, the present data are perhaps not related directly
to those representing the slow shrinkage at low temperatures. (Additional
information on shrinkage is given in the following section.)

C. Effect of Thermal History and Tensile Stress on the Properties
    of Mylar D

Specimens of Mylar D were cut from position W such that the
longitudinal axis of each specimen was nearly parallel to the slow optic
axis (Table I). A specimen was heated in the TMA at 5°C per minute to a
temperature t^*, then cooled to room temperature, and thereafter heated to
190°C. The key results are given in Table VI.

After a specimen had been heated to T^*, its inversion temperature T_i
during the second heating period was close to T^*, as has been reported
previously.[3] With a progressive increase in T^*, the shrinkage increases
during the first heating period and decreases during the second heating
period until it becomes only about 0.02% when $T^* = 190$°C.

When T^* equals 90°, 120°, and 160°C, the expansion coefficient near
25°C is the same during the first and second heating periods, within
experimental error. But when T^* equals 190°C, the expansion coefficient
is 7% larger during the second heating, as is shown in the last line of
Table VI.

To investigate the combined effects of tensile stress and thermal
history on the properties of Mylar D, four specimens were cut perpendicular
to the slow optic axis. A specimen was heated in the TMA at 5°C per minute
under a tensile stress σ^* to 190°C, then cooled to room temperature, and
thereafter heated to 190°C under a stress of 10 psi. (This stress is the

minimum at which a specimen can be tested conveniently; see Section II-B.)
The data obtained are in Table VII.

The upper panel in Fig. 7 shows that the inversion temperature during
the first heating increases from 72°C to about 146°C with an increase in
the stress σ^* from 10 to 50 psi and thereafter remains constant at higher
stresses. On the other hand, the inversion temperature during the second
heating ($\sigma^* = 10$ psi) decreases from about 190° to 165°C.

The lower panel in Fig. 7 shows that the expansion coefficient near
25°C during the second heating is sensibly independent of the stress
applied during the first heating but the coefficient near 130°C decreases
progressively with the stress applied during the first heating and
eventually becomes considerably less than that at 25°C. No explanation
can be given of this surprising behavior.

The shrinkage during the first heating decreases with an increase in
the stress but is essentially zero during the second heating of each
specimen (Table VII).

IV. SPECIALLY PREPARED BIAXIALLY ORIENTED PET FILMS

S. P. Lee[11] has recently studied the optical properties, and also determined some mechanical properties, of biaxially oriented PET films that were isotropic in the plane. He prepared the films by stretching radially discs of amorphous PET, 11.3 mils thick, at 85°C to obtain discs approximately 9.0 inches in diameter and 1.4 mils thick. Two of his films were studied with the TMA. The first film had not been heat-set and had a crystallinity of only 22.4%. The second film had been heat-set for 17.5 hours at 180°C to impart dimensional stability; its crystallinity was 50.7%. The draw ratios employed in preparing the first and second films were 2.62 and 2.54, respectively.

Specimens were cut at several orientations from near the center of the film that had not been heat-set. They were tested in the TMA at the usual heating rate up to 190°C. As shown by the data in Table VIII, the expansion coefficients indicate that the film is nearly isotropic and the shrinkage in large, as expected. Also, the inversion temperatures are 10°C lower and the expansion coefficients are larger than those for the commercial PET films and the special heat-set film discussed below. The expansion coefficients are significantly less, however, than that (7.75×10^{-5}/°C) for the amorphous unoriented PET film.

Specimens were cut at different locations and orientations from the heat-set film. The expansion coefficients of these specimens near 25°C (Table IX) are essentially isotropic in the plane.

The behavior of these specimens during the first heating period was most unusual, as shown by the plot of the linear expansion e [$= (L - L_0)/L_0$] against temperature in Fig. 8. With a progressive increase in temperature, a specimen first expanded, then contracted, next expanded again, and finally contracted rapidly. The temperatures for these inversions, designated T_{i1}, T_{i2}, and T_{i3}, are given in Table IX. The temperature T_{i3}, which ranged from 170° to 177°C, is only slightly below the heat-set temperature, 180°C.

The contraction between temperatures T_{i1} and T_{i2} undoubtedly results from the partial release of certain strains frozen in the amorphous phase. These strains must be small and readily relievable, otherwise no inversion would occur at T_{i2} and the linear expansion would become highly negative, as found for the commercial PET films (Fig. 1). Alternatively, the contraction could result from a slight increase in crystallinity or from a reorganization of the crystalline phase. This possibility is deemed unlikely because a DSC curve was featureless over the temperature interval in which contraction occurred.

The total shrinkage that occurred during the heating of a specimen to 190°C was between 1.5 and 2.0%. Because 190°C is 10°C higher than the heat-set temperature, the shrinkage data are not meaningful and thus are not included in Table IX.

During the second heating period, a specimen expanded continuously, as shown by the lower curve in Fig. 8. The expansion coefficient near 25°C

is about $1.9 \times 10^{-5}/°C$, which **exceeds** slightly those observed during the first heating of specimens (cf. Table IX). Near 130°C, the expansion coefficient is $5.7 \times 10^{-5}/°C$, which is typical of those observed on the second heating of the commercial films (cf. Table III).

V. DSC MEASUREMENTS ON COMMERCIAL FILMS

DSC measurements were made on the commercial PET films, each specimen being heated at 5°C per minute. As shown in Table X, a major endotherm (melting) for each film occurred at a temperature T_m^1 between 252° and 256°C. These values agree closely with those (256-258°C) reported by Lawton and Cates[14] who obtained data by DSC on PET samples that had been crystallized for periods between 1 and 96 hours at 200°C and for 1 hour at temperatures from 125° to 235°C.

Three of the five commercial films showed a small secondary endotherm between 221° and 237°C (Table X). While the significance of the secondary endotherm is not known, it has been shown[14] that the temperature T_m^2 of this endotherm depends on the thermal history of the sample. For example, T_m^2 increases with either the time or temperature of crystallization. Also, certain specially treated samples did not show a secondary endotherm.[14]

For unknown reasons, the heats of fusion obtained from DSC traces on the commercial films at T_m^1 varied from about 10 to 20 cal/g. Hence, the data are not reported. Some of the possible reasons why meaningful calorimetric data are difficult to obtain on PET samples are mentioned elsewhere.[14]

VI.   SUMMARY

A comparison was made of the anisotropy of the coefficient of linear thermal expansion and other physical properties, primarily shrinkage, of the following biaxially oriented films (ca. 3 mils thick) of poly(ethylene terephthalate) (PET): Celanar 4500, Melinex-O, Mylar D, and the experimental films XM-648 and JTS-118 obtained from Du Pont and ICI, respectively. Data were also obtained on a biaxially oriented PET film prepared by S. P. Lee who stretched radially a disc of amorphous isotropic PET at 85°C and then heat-set it at 180°C. The properties of this special film are mentioned in this Summary only at the end.

The commercial films obtained for the study were 11 to 14 inches wide. Hence, they had been cut from a roll which, as ordinarily obtained from a manufacturer, is 48 inches wide. In turn, a 48-inch wide roll is obtained from a processed sheet that is either 120 or 240 inches wide.

The angle between the slow optic axis and the machine direction (MD) of a film was measured at four positions across each sheet and was found to be nearly constant, except for JTS-118. Even so, all specimens for the present study were cut from near one edge of each sheet. (The angle of the slow optic axis ordinarily varies considerably across a 48-inch wide sheet.) Measurements were also made of the birefringence and the density; the degree of crystallinity was computed from the latter. The characteristics of the films are given in Tables I and II.

The length of each specimen was measured while it was heated at 5°C per minute to 190°C, after it had been cooled to room temperature, and while it was heated again to 190°C. During the first heating period, but not the second, a specimen contracted (Fig. 1) above the inversion temperature T_i (ca. 70-80°C), which is close to the glass temperature. Evaluated from the data were $\alpha_1(25)$, $\alpha_2(25)$, and $\alpha_2(130)$ which are, respectively, the expansion coefficients near 25°C during the first and second heating periods and near 130°C during the second heating period. Also determined was the total shrinkage during the first heating period.

The expansion coefficients of each film could be represented closely by $\alpha(\theta) = \alpha_\perp + (\alpha_\parallel - \alpha_\perp) \cos^2\theta$ where θ is the angle between the slow optic axis and the longitudinal axis of a specimen, and $\alpha_\parallel$ and $\alpha_\perp$ are the coefficients parallel and perpendicular to the slow optic axis (Figs. 3 and 4). The values of $\alpha_\parallel$ and $\alpha_\perp$ for use in this expression were obtained from plots of $\alpha(\theta)$ against $\cos^2\theta$ (cf. Fig. 2). No special analysis was made of the $\alpha_2(25)$ data because it differed only slightly from $\alpha_1(25)$. (Actually, $\alpha_2(25)$ tended to be slightly larger than $\alpha_1(25)$, as shown in Table III.)

At 25°C, the expansion coefficient was a minimum parallel to the slow optic axis, and thus $\alpha_\perp/\alpha_\parallel$ exceeded unity. Surprisingly, the expansion coefficient near 130°C (second heating) was a minimum perpendicular to the slow optic axis, and hence $\alpha_\perp/\alpha_\parallel$ was less than unity. The values of $\alpha_\perp/\alpha_\parallel$ and $\alpha_\parallel/\alpha_\perp$ in Table IV show that JTS-118 is the most nearly isotropic

at 25°C, that Melinex-O is the most nearly isotropic at 130°C and that
all films, except JTS-118, are somewhat less anisotropic at 130° than at
25°C.

From data at 25°C, it was found (Fig. 5) that $\Delta n \simeq k(1 - \alpha_\parallel/\alpha_\perp)$ where
Δn is the birefringence and k is a constant. Thus, the anisotropy of the
expansion coefficient of a PET film can be related roughly to the
birefringence.

Expansion coefficients in the thickness direction were calculated at
25° and 130°C from $\alpha_\parallel$ and $\alpha_\perp$ and published values of the coefficient of
volumetric thermal expansion below and above the glass temperature
(Table V).

The shrinkage during the first heating of films varied from about
1.0 to 2.8%, depending on the film. The direction of maximum shrinkage,
though not always well defined, tended to occur perpendicular to the slow
optic axis (Fig. 6). Essentially no shrinkage occurred during the second
heating of a specimen.

Data obtained on Mylar D (Table VI) show that if a specimen is first
heated to $T^*(\leq 190°C)$, essentially no shrinkage occurs during the second
heating until the temperature exceeds T^*. Other experiments on Mylar D
(Table VII) show that the inversion temperature T_i is 145°C when the stress
applied during the heating period is 50 psi or more. Also, the shrinkage
that occurs in heating a specimen up to 190°C decreases progressively with

an increase in the applied stress. Again, no shrinkage occurs during the second heating, made with a stress of 10 psi on a specimen, but T_i decreases from 190° to 165°C with an increase in stress during the first heating period (Fig. 7).

Tests made on the special PET film, prepared[11] by stretching radially a disc of amorphous isotropic PET, showed it to be isotropic in the plane of the film (Table IX) and that its coefficient of thermal expansion lies between $\alpha_\parallel$ and $\alpha_\perp$ found for most of the commercial PET films. During the first heating of a specimen to 170°C, the behavior was most unusual. In particular, with a progressive increase in temperature, a specimen first expanded, then contracted, and finally expanded again. At no time during the contraction period did the length of a specimen become less than its initial value at 25°C (Fig. 8). During the second heating, a specimen expanded continuously.

DSC measurements on the commercial films showed a major endotherm, representing melting of the crystallites, at a temperature between 252 and 256°C. For three of the films (Table X), a minor endotherm was observed at a temperature between 221 and 237°C.

ACKNOWLEDGEMENTS

APPENDIX

Angular Dependence of the Coefficient of Linear Thermal Expansion

Let α_x and α_y be the coefficients of linear thermal expansion parallel and perpendicular, respectively, to the slow optic axis of an orthotropic film. (In Section III-A, α_x and α_y are designated by $\alpha_\parallel$ and $\alpha_\perp$, respectively.) Consider now a line segment of length L at temperature T that emanates from the origin of cartesian coordinates whose x axis is parallel to the slow optic axis. It follows that

$$L_x^2 + L_y^2 = L^2 \qquad\qquad (A-1)$$

where L_x and L_y are the components of the line segment on the x and y axes. Differentiation of the equation with respect to T gives

$$L_x dL_x/dT + L_y dL_y/dT = LdL/dT \; . \qquad\qquad (A-2)$$

The coefficient of thermal expansion at temperature T is defined precisely by $L^{-1}dL/dT$. Hence, substitution of $dL_x/dT = \alpha_x L_x$, etc., in Eq. (A-2) gives

$$\alpha_x L_x^2 + \alpha_y L_y^2 = \alpha(\theta)L^2 \qquad\qquad (A-3)$$

where $\alpha(\theta)$ is the expansion coefficient along the line that makes an angle θ with the slow optic axis. Because $L_x = L \cos \theta$ and $L_y = L \sin \theta$, it follows that

$$\alpha_x \cos^2\theta + \alpha_y \sin^2\theta = \alpha(\theta) \qquad \text{(A-4)}$$

or

$$(\alpha_x - \alpha_y) \cos^2\theta + \alpha_y = \alpha(\theta) \qquad \text{(A-5)}$$

To test whether experimental values of $\alpha(\theta)$ conform to Eq. (A-5), $\alpha(\theta)$ can be plotted against $\cos^2\theta$, as illustrated in Fig. 2. The straight line that best represents the data on such a plot should yield the most reliable values of α_x ($\equiv \alpha_{\parallel}$) and α_y ($\equiv \alpha_{\perp}$) to use in Eq. (A-5) to calculate the dependence of $\alpha(\theta)$ on θ.

Although θ changes with temperature, the change is negligible. The rate of change is given by

$$\frac{d\theta}{dT} = \frac{d \tan^{-1}(L_y/L_x)}{dT} = \frac{(L_y/L_x)(\alpha_y - \alpha_x)}{1 + (L_y/L_x)^2}. \qquad \text{(A-6)}$$

As $L_y/L_x = \tan\theta$, it follows that

$$d\theta/dT = (1/2)(\alpha_y - \alpha_x) \sin 2\theta . \qquad \text{(A-7)}$$

This derivative is a maximum when $\theta = \pi/4$.

For the PET films discussed in this report, the largest value of $(\alpha_y - \alpha_x)$ is about 1.5×10^{-5}/°C. Hence, when $\Delta T = 30°C$, for example, the maximum change is θ is 2.3×10^{-4} radian, or $0.013°$.

TABLE I

Dependence of Extinction Angle on Position in
Sheets of Films Studied

Film	Thickness, mils	Width of Sheet, inch	Angle (Counterclockwise) Between Machine Direction and Slow Optic Axis at			
			W[a]	2W/3	W/3	~0
XM-648	1.97	14	54	53	50	49
Mylar-D	3.03	14	55	53	50	48
Celanar-4500	3.01	14	56	55	53	52
JTS-118	3.44	11	57	70	84	48
Melinex-0	3.03	14	59	60	57	61

[a] W is the width of sheet.

TABLE II

Birefringence, Density, and Crystallinity of Films

Film	$\Delta n \times 10^2$ [a]	Density, g/cm^3 [b]	Weight % Crystallinity [c]
XM-648	3.95	1.3980	50.7
Mylar D	4.03	1.3982	50.8
Celanar-4500	2.91	1.3999	52.1
JTS-118	1.83	1.4006	52.6
Melinex-0	2.62	1.4016	53.3

[a] The birefringence Δn was determined only at position "W" (see Table I) on each film; $\Delta n = n_{\parallel} - n_{\perp}$ where $n_{\parallel}$ and $n_{\perp}$ are the refractive indices parallel and perpendicular, respectively, to the slow optic axis.

[b] Determined in a water-zinc chloride density-gradient column.

[c] Calculated from the density by considering that the densities of the amorphous and crystalline phases are 1.331 and 1.470 g/cm^3, respectively.[12]

TABLE III

Data Obtained by Heating Specimens at 5°C per Minute to 190°C,
Followed by Cooling to 25°C, and then Reheating to 190°C

Sample	θ [a]	T_i, [b] °C	Shrinkage, [c] %	$\alpha_1(25)$ [d] $\times 10^5$/°C	$\dfrac{\alpha_2(25)}{\alpha_1(25)}$ [e]	$\alpha_2(130)$ [f] $\times 10^5$/°C
Celanar-4500	0	75	2.53	0.97	0.92	6.09
	45	73	1.38	1.52	1.10	4.35
	65	---	---	1.69	---	---
	90	70	2.80	1.90	1.12	3.66
	110	---	---	1.90	---	---
	135	77	2.76	1.48	1.18	5.12
Melinex-O	0	82	1.80	1.06	1.46	5.23
	45	80	1.68	1.35	1.19	4.92
	90	68	2.65	1.76	1.14	3.62
	135	70	1.99	1.13?	---	4.45
	165	---	---	1.21	---	---
JTS-118	38	70	2.08	1.57	1.06	4.75
	78	72	1.78	1.57	1.16	4.25
	90	70	1.94	1.86	0.93	3.98
	118 [g]	74	---	1.70	---	---
	135	68	2.25	1.62	1.02	5.38
	168	74	1.38	1.53	1.09	6.12
XM-648	0	74	1.59	1.12	1.01	7.33
	18	72	1.89	1.07	1.03	6.78
	45	72	2.25	1.90	1.00	4.91
	65	72	2.10	2.01	1.00	4.08
	90	78	2.03	2.51	1.09	3.90
	111 [g]	---	---	2.11	---	---
	135	140	1.22	1.71	1.05	6.11
	155	74	1.59	1.13	1.00	7.46
Mylar D	0	77	1.09	1.17	1.18	7.95
	20	75	1.35	1.10	1.06	7.06
	45	76	2.06	1.89	1.17	5.29
	90	72	1.85	2.70	1.04	3.84
	110	68	1.78	2.34	1.12	4.80
	135	160	0.80	1.97	1.07	6.56

[a] Angle (clockwise) between the slow optic axis and the longitudinal axis of the specimen.

[b] Inversion temperature; i.e., the temperature at which a specimen begins to contract during the first heating period.

[c] Total shrinkage that occurs during the first heating of a specimen to 190°C.

[d] Coefficient of linear expansion from the linear portion of the curve, beginning at 25°C, obtained during the first heating period.

[e] $\alpha_2(25)$ is the expansion coefficient from the linear portion of the curve, beginning at 25°C, obtained during the second heating period.

[f] $\alpha_2(130)$ is the expansion coefficient from the linear portion of the curve, centered about 130°C, obtained during the second heating period.

[g] Specimen heated only to about 75°C.

TABLE IV

Expansion Coefficients[a] Parallel and Perpendicular to Slow
Optic Axis Evaluated by Fitting Data to Equation (2)

Film	Temp., 25°C			Temp., 130°C			R[b]
	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\alpha_{\perp}/\alpha_{\parallel}$	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\alpha_{\parallel}/\alpha_{\perp}$	
Celanar	0.96	1.95	2.03	6.01	3.57	1.68	0.83
Melinex	1.11	1.68	1.51	5.45	3.84	1.42	0.94
JTS-118	1.50	1.74	1.16	6.32	3.62	1.75	1.51
XM-648	1.04	2.41	2.32	7.50	3.63	2.07	0.89
Mylar	1.05	2.67	2.54	7.70	4.15	1.86	0.73

[a] Coefficients are given here in units of $10^{-5}/°C$.

[b] $R \equiv (\alpha_{\perp}/\alpha_{\parallel})^{130}/(\alpha_{\parallel}/\alpha_{\perp})^{25}$ where the superscripts 25 and 130 denote the
temperatures at which the ratios were evaluated.

TABLE V

Quantities Derived from the Coefficients of Linear and Volumetric
Expansion Below and Above the Glass Temperature

Film	α_t[a] $\times 10^5/°C$		α_t/α_v		$(\alpha_{\parallel} + \alpha_{\perp})/\alpha_v$	
	25°C	130°C	25°C	130°C	25°C	130°C
Celanar	16.1	26.4	0.85	0.73	0.15	0.27
Melinex	16.2	26.7	0.85	0.74	0.15	0.26
JTS-118	15.8	26.1	0.83	0.73	0.17	0.28
XM-648	15.6	24.9	0.82	0.69	0.18	0.31
Mylar	15.3	24.2	0.81	0.67	0.20	0.33
Isotropic[b]	6.3	12.0	0.33	0.33	0.67	0.67

[a] $\alpha_t = \alpha_v - \alpha_{\parallel} - \alpha_{\perp}$ where α_t is the coefficient of linear expansion in the
thickness direction. The coefficients of volumetric expansion below
and above the glass temperature are 19×10^{-5} and $36 \times 10^{-5}/°C$,
respectively.

[b] Properties of isotropic PET whose crystallinity is about the same as
that of the biaxially oriented PET films.

TABLE VI

Effect of Thermal History on the Inversion Temperature, the Shrinkage, and the Expansion Coefficient of Mylar D*

Heating Cycle	Final Temp., °C	T_i, °C	Shrinkage, %	$\alpha(25)$ $\times 10^5/$°C	$\dfrac{\alpha_2(25)}{\alpha_1(25)}$
First	90	70	0.10	1.40	---
Second	190	90	1.42	1.40	1.00
First	120	72	0.45	1.43	---
Second	190	135	1.16	1.45	1.00
First	160	72	0.65	1.44	---
Second	190	155	1.08	1.43	0.99
First	190	70	1.88	1.48	---
Second	190	~190	0.02	1.59	1.07

*The longitudinal axis of each of the four specimens was approximately parallel to the slow optic axis, i.e., $\theta = 0°$.

Symbols in the above table are defined beneath Table III.

TABLE VII

Effect of Tensile Stress and Thermal History on the Inversion Temperature, Shrinkage, and Expansion Coefficient of Mylar D*

Heating Cycle	Stress, psi	T_i, °C	Shrinkage, %	$\alpha(25)$ $\times 10^5/$°C	$\alpha_2(130)$ $\times 10^5/$°C
First	10	72	1.85	2.70	---
Second	10	190	0	2.82	3.99
First	50	145	0.85	2.93	---
Second	10	188	0	2.54	3.26
First	100	148	0.79	2.77	---
Second	10	182	0	2.96	2.65
First	200	145	0.70	3.09	---
Second	10	165	0	2.89	1.43

*Specimens cut perpendicular to the slow optic axis, i.e., $\theta = 90°$.

During each cycle, each specimen was heated at 5°C per minute to 190°C.

TABLE VIII

Properties of Biaxially Oriented PET Film (Not Heat-Set) Prepared by
Stretching an Amorphous Film Radially

Orientation of Specimen[a]	$\alpha(25)$ $\times 10^5/°C$	T_i, °C	Shrinkage,[b] %
22.5°	2.61	63	21.4
67.5°	2.52	62	21.2
90°	2.53	61	22.9
145°	2.70	60	22.0

[a] Specimens cut from near the center of the sample at the indicated angles to an arbitrary line.

[b] Shrinkage produced by heating a specimen to 190°C at 5°C per min.

TABLE IX

Properties of Heat-Set Biaxially Oriented PET Film Prepared by
Stretching Amorphous Film Radially

r[a] inch	Orientation of Specimen[b]	$\alpha_1(25)$ $\times 10^5/°C$	T_{i1},[c] °C	T_{i2},[c] °C	T_{i3},[c] °C
0	25°	1.63	77	112	174
	70°	1.66	77	116	173
	115°	1.69	77	113	172
	175°	1.73	75	114	171
0.50	150°	1.80	80	114	176
2.25	3°	1.78	73	116	171
	10°	1.61	74	117	171
	40°	1.65	72	116	170
	90°	1.68	74	110	171
	130°	1.76	74[d]	---	---
	145°	1.62	75[d]	--	---
3.25	90°	1.63	72	114	177

[a] Specimen cut at distance r from the center of the circular film.

[b] Angle between longitudinal axis of specimen and an arbitrary line.

[c] Inversion temperatures defined as shown in Fig. 8.

[d] Specimen heated only to 80°C.

TABLE X

Temperature of Endotherms Obtained from DSC Curves[*]

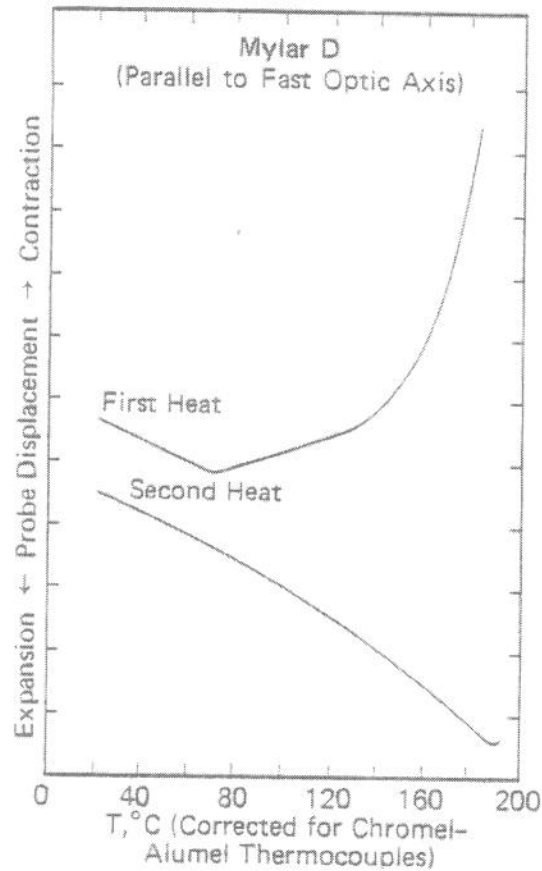| Film	T_m^2, °C	T_m^1, °C
XM-648	237	256
Mylar D	–	254
Celanar-4500	–	254
JTS-118	221	252
Melinex-0	222	256

[*]Heating rate, 5°C per minute

Figure 1. Typical curves that show the expansion and contraction of a specimen during the first heating period and the expansion during the second heating period.
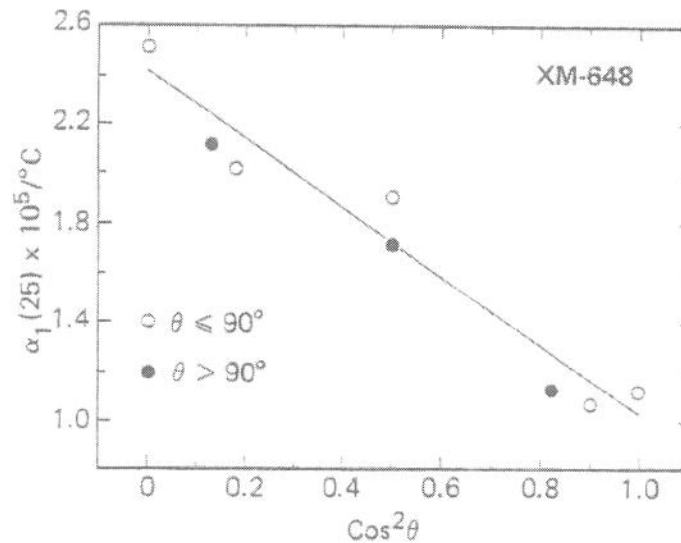

Figure 2. Expansion coefficient obtained near 25°C from the first heating of specimens plotted against $\cos^2\theta$, where θ is the angle between the slow optic axis and the longitudinal axis of a specimen.
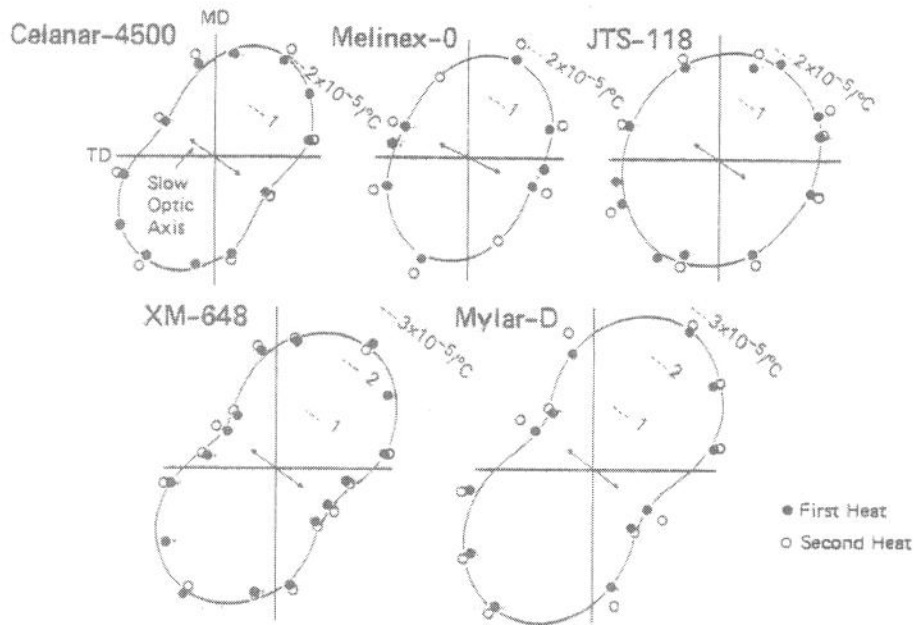
Figure 3. Expansion coefficients obtained near 25°C from the first (solid circles) and the second (open circles) heating of specimens plotted against the angle between the slow optic axis and the longitudinal axis of a specimen. Curves were calculated from Eq. (2) and data in Table IV.
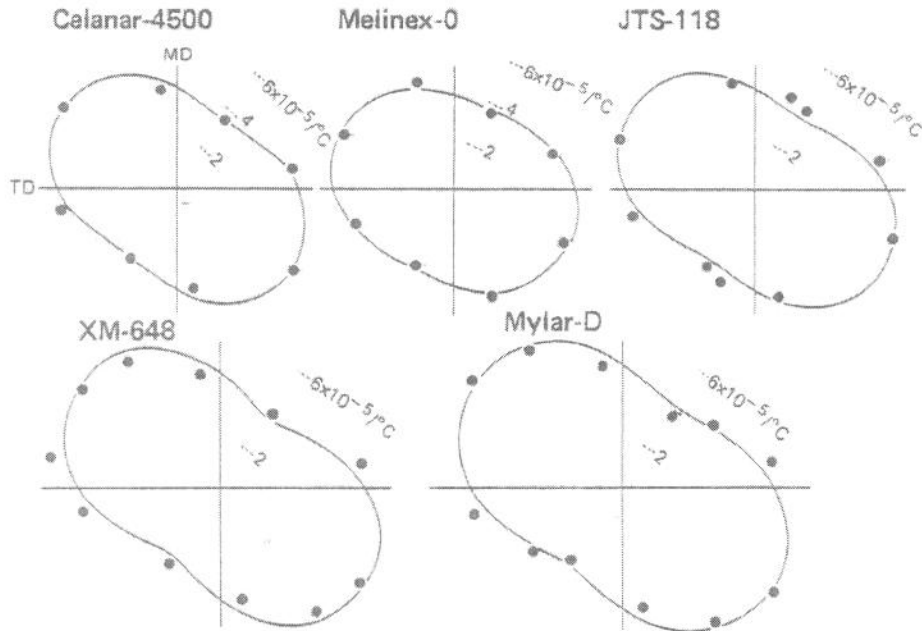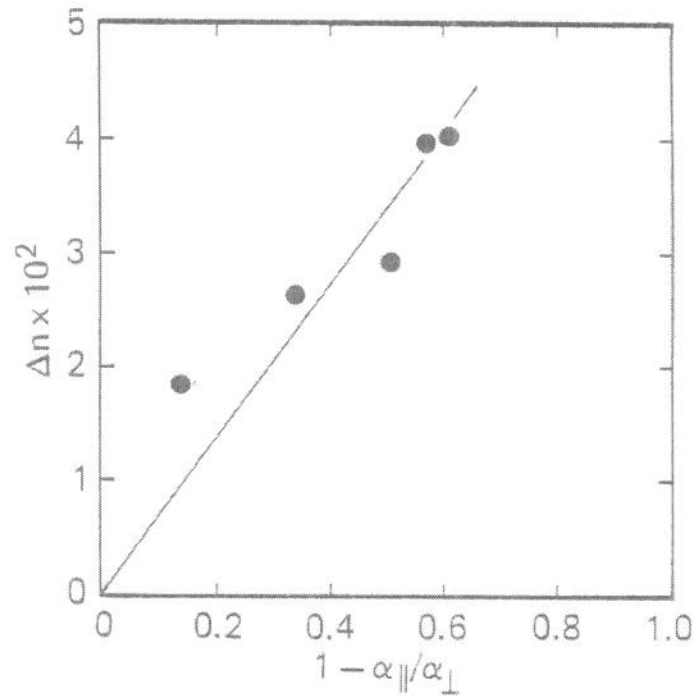

Figure 4. Expansion coefficients obtained near 130°C from the second heating of specimens plotted against the angle between the slow optic axis and the longitudinal axis of a specimen. Curves were calculated from Eq. (2) and data in Table IV.

Figure 5. Birefringence of PET films (Table II) plotted against $(1 - \alpha_{\parallel}/\alpha_{\perp})$, where the values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ are at 25°C and from Table IV.
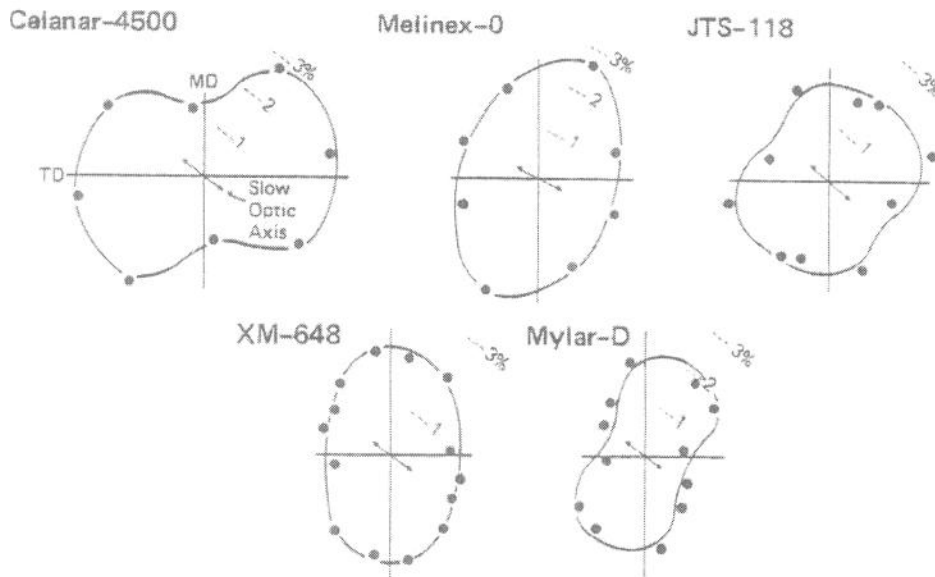

Figure 6. Shrinkage during the first heating of films to 190°C plotted against the angle between the slow optic axis and the longitudinal axis of a specimen.
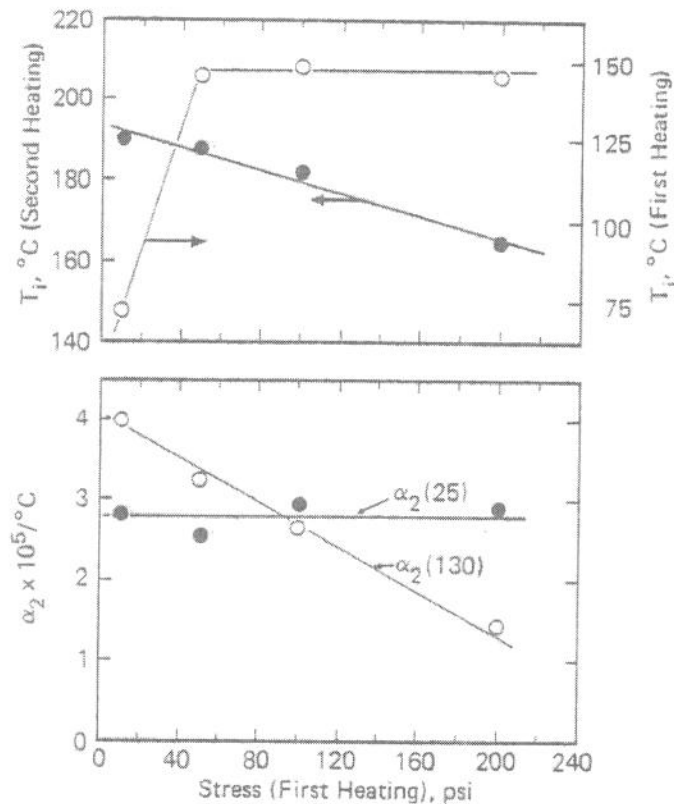
Figure 7. Upper panel shows the inversion temperature T_i of Mylar D obtained during the first and second heating of specimens to 190°C. The stress applied during the first heating is shown on the abscissa; the stress applied during the second heating was 10 psi. The lower panel shows the expansion coefficients obtained at 25° and 130°C during the second heating. (Data are from Table VII.)
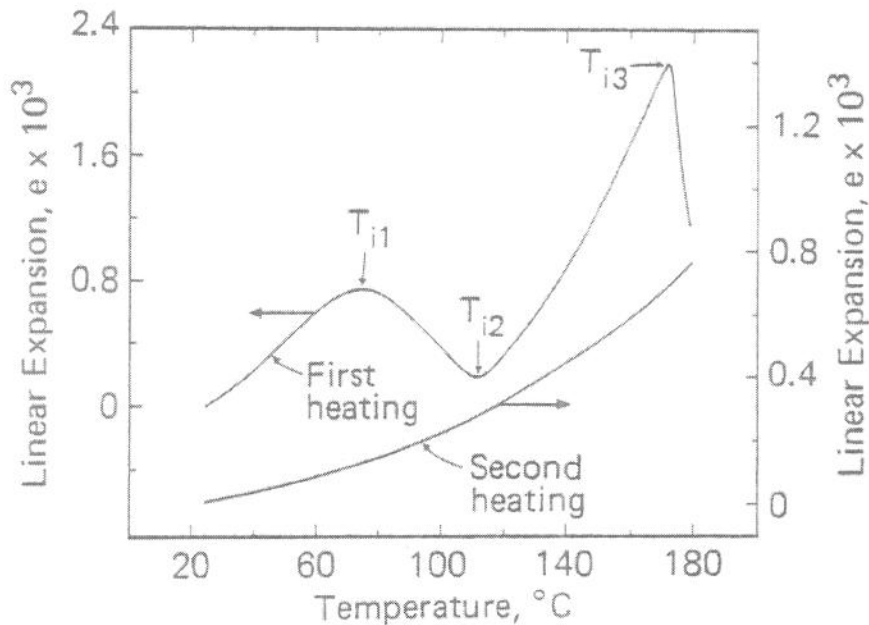

Figure 8. Temperature dependence of the linear expansion during the first and second heating of a biaxially oriented PET film prepared by stretching radially an amorphous film.

REFERENCES

1. C. J. Heffelfinger, Polym. Eng. Sci., 18, 1163 (1978). Also,
    C. J. Heffelfinger and K. L. Knox, Polyester Films, in "The Science and
    Technology of Polymer Films," Vol. II, O. J. Sweeting, Ed.,
    Wiley-Interscience, New York, 1971, Chapt. 14.

2. W. H. Chu and T. L. Smith, Rodlike Superstructures in and Mechanical
    Properties of Biaxially Oriented Polyethylene Terephthalate Film, in
    "Polymer Science and Technology, Vol. I, Structure and Properties of
    Polymer Films," R. W. Lenz and R. S. Stein, Eds., Plenum Press, New
    York, 1973, pp. 67-79.

3. E. M. Barrall and J. A. Logan, "Some Physical Properties of Biaxially
    Oriented Poly(ethylene terephthalate)", IBM Research Report, RJ1223,
    May 21, 1973.

4. E. A. Bartkus and R. L. Price, "PET Films I. Long-Term Dimensional
    Changes", IBM Technical Report, General Products Division, TR44.0244,
    June 15, 1973 (Confidential).

5. B. F. Blumentritt, IBM J. Res. Develop., 23, 56 (1979).

6. O. Ishai, T. Weller, and J. Singer, J. of Materials, 3, 337 (1968).

7. E. A. Bartkus, IBM General Products Division, memorandum "Variation
    of PET Film Properties with Web Position", dated January 16, 1974 and
    sent to T. L. Smith (Confidential).

8. H. J. Greenberg, "Dimensional Stability of Flexible Disks --
    Experimental Results", IBM Research Report, RJ1676, October 16, 1975
    (Confidential).

9. H. J. Greenberg, R. L. Stephens, and F. E. Talke, Experimental
    Mechanics, March 1978, pp. 115-120.

10. R. Stephens, San Jose Research Laboratory, memorandum to file "Long Term Effects of Temperature and Humidity on Flexible Substrates", dated Steptember 29, 1975 (Confidential).

11. S. P. Lee, recent unpublished work (IBM Research, San Jose).

12. W. H. Cobb, Jr. and R. L. Burton, J. Polymer Sci., <u>10</u>, 275 (1953).

13. I. Uematsu and Y. Uematsu, Report on Progress in Polymer Physics in Japan, Vol. III, 1960, p. 102.

14. E. L. Lawton and D. M. Cates, Crystallization of Poly(ethylene terephthalate), in "Analytical Calorimetry," R. S. Porter and J. F. Johnson, Eds., Plenum Press, New York, 1968, pp. 89-97.