Dynamic Mechanical Analysis of Fibers. II. Estimation of Fiber Orientation and Characterization of Heat Set PET Yarns

Y. P. KHANNA,* T. J. TAYLOR, and R. KUMAR†

Allied Corporation, P.O. Box 1021R, Morristown, New Jersey 07962-1021

SYNOPSIS

A drawn PET yarn was heat set (annealed) at temperatures between 110°C and 245°C in an unconstrained mode and the samples characterized by dynamic mechanical analysis (DMA). A method for estimating the fiber orientation factor (α) is proposed using DMA and shown to be more sensitive than the crystalline orientation (x-ray diffraction) or total orientation (birefringence) measurements of the heat set yarns. The extension/shrinkage behavior of the heat set yarns has been discussed in the light of morphological changes, e.g., degree of orientation and the micro-crystallite formation. Unlike in the unconstrained mode, heat setting under constraint does not lead to the formation of micro-crystallites as revealed by differential scanning calorimetry. As a consequence, although the modulus and degree of orientation increase upon constrained annealing, the thermal stability, i.e., loss of orientation (reflected by shrinkage) could not be improved.

INTRODUCTION

In our previous paper[1] in this series, we reported that the modulus of a flexible chain fiber at temperatures around or above the T_g, increases with an increase in pre-tension. We termed this reversible phenomenon as elastic orientation under force (EOF). In this paper not only do we wish to reaffirm the same for PET but also extend the use of high pre-tension DMA to obtain an orientation factor. The available literature[2,3] and references therein suggest the formation of micro-crystallites during unconstrained heat setting (annealing). The present work indicates the absence of micro-crystallite formation when the yarns are annealed under a pre-tension. The purpose of this paper is to report (1) a DMA-based method to estimate the fiber orientation factor and (2) thermal/mechanical property changes upon heat setting under constraint and without constraint.

* To whom correspondence should be addressed.

† Present address: Union Carbide Corporation, P.O. Box 670, Bound Brook, NJ 08805.

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EXPERIMENTAL

Material. A drawn PET yarn (multifilament, ≃ 1030 denier) was used throughout this study.

Heat treatment. The control yarn was heat treated for about 30 sec at various temperatures between 110 and 245°C in an oven in an unconstrained mode, i.e., free to relax. In addition, two samples were thermally treated at 180°C/15 min, with and without a constraint of 6 N, directly in the mechanical analyzer.

Dynamic mechanical analysis. Polymer Laboratories (UK) dynamic mechanical thermal analyzer (DMTA) unit was operated in an argon atmosphere using a tensile deformation mode, 3°C/min heating rate, 1 Hz frequency, and 0.16% strain. Measurements were made using a constant force probe which applied a constant pre-tension of either 1 N or 6 N. The DMTA unit also provided us with the fiber displacement (extension/shrinkage) values which went into the computation of true modulus, reported in this study. Also, after a particular heat treatment, the cross-sectional area of the yarn was calculated and the value used in modulus computations.

Birefringence measurements. Ten filaments were selected randomly from each bundle. Fiber diameters were measured directly and fiber birefringence was determined using the method of compensation by means of a 25 order Berek compensator. Due to the phenomenon of dispersion observed in PET which results in anomalous retardation colors, we used the "purple" extinction band to determine the birefringence.

X-Ray diffraction. XRD scans (fast-rotational and azimuthal) were obtained using a Philips APD-3600 diffractometer in transmission mode with Cu Kα radiation. A crystalline index (CI) and an index of crystallite size and perfection (CSP) for the 29.1° 2θ peak (an approximate correction for instrumental broadening was done by subtracting 0.2° 2θ from the FWHM) were calculated from profile fits of the fast-rotational scans using a curve resolver. The degree of orientation (f_c) was calculated from the azimuthal scans at 48.2° 2θ.

RESULTS AND DISCUSSION

Before discussing our results on PET yarns, we wish to recall our previous study[1] which pointed out that the modulus of fibers at temperatures around or above their T_g, increases with an increase in pre-tension. Such an increase in modulus due to pre-tension has been termed as elastic orientation under force due to the reversible nature of this phenomenon.[1] Consistent with our previous study on an experimental fiber and a polyethylene yarn, PET exhibits similar stiffening under load as revealed in Figure 1. Having defined the role of pre-tension on the modulus, the effect of morphological variables on fiber properties can be evaluated.

Heat Setting Under No Constraint

In the fiber industry, the yarns are heat set to stabilize yarn twist, increase wrinkle resistance, obtain durable creases and pleats, and impart dimensional stability.[4] Heat setting operations are normally carried out at a temperature between the T_g and T_m for a time scale of $\leq$ 30 min without any significant constraint. During the heat setting process, the yarns develop a crimp and morphological changes are known to occur which subsequently affect the yarn behavior, e.g., PET[2] and nylon 6.[3,5,6] In this paper we present the changes in PET yarns during the heat setting operation as studied by DMA.

Figure 2 reveals that at a pre-tension of 1 N, the "control"—highly oriented sample undergoes shrinkage while the 245°C treated yarn—least oriented, undergoes extension beginning at the T_g

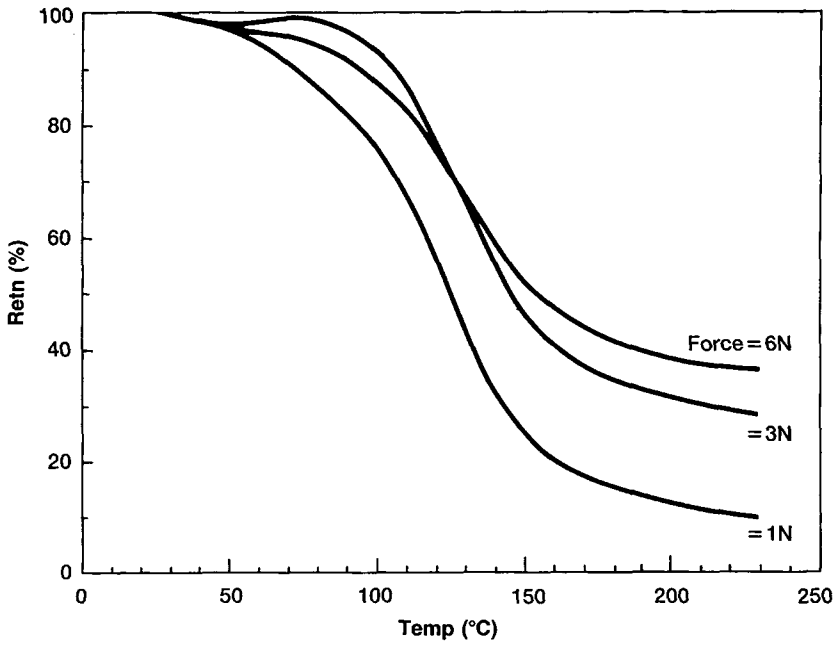

Figure 1 Effect of pre-tension (force) on the modulus retention vs. temperature of an oriented PET yarn.

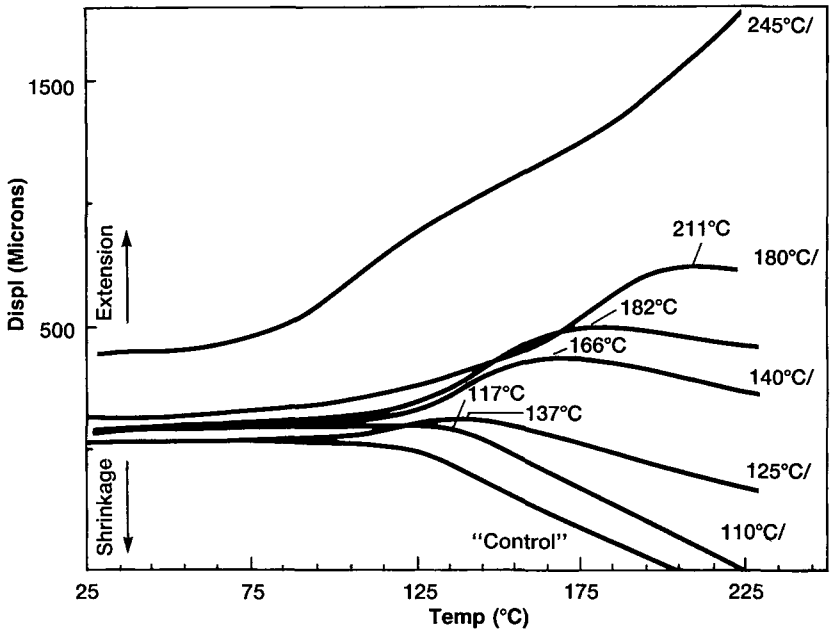

Figure 2 DMA of PET yarns heat set at various temperatures for 30 sec (analysis @ a pre-tension of 1 N).

(note: 1 N pre-tension, approximately, represents the force in Newtons, needed to produce the strain to be imposed on the sample during the dynamic mechanical experiment). The intermediate samples first exhibit extension and then shrinkage at a certain characteristic temperature. The explanation is that during the heat setting at a temperature T ($T_g < T < T_m$), the oriented yarn undergoes a partial disorientation[2] and develops micro-crystallites in the amorphous phase which melt at T + (10–30°C).[2,3] As a consequence, the heat set yarn first undergoes extension corresponding to the partially disoriented phase, and the remaining shrinkage (disorientation) occurs when the micro-crystallites melt, i.e., at T + (10–30°C). This forms the basis of a linear correlation between the shrinkage onset temperature and the heat setting temperature (Fig. 3). An increase in the heat setting temperature can be expected to yield an increased level of disorientation (e.g., see "control" in Fig. 2) such that the higher temperature heat set yarns will exhibit a lesser disorientation (shrinkage). At a pre-tension of 10 N, no shrinkage is shown even by the control–highly oriented PET yarn. This is partly due to the masking of shrinkage by an increased level of extension and partly due to a reduced shrinkage at such a high pre-tension.

In addition to the dimensional changes, profound changes occur in modulus characteristics due to heat setting (Table I). In general, the modulus of a fiber should increase with an increase in the degree of orientation.[7] As the heat setting temperature increases, there is an increase in the disorientation, and as a consequence the modulus should decrease. In fact, this has been shown for PET yarns heat set between 140°C and 220°C.[2] In our present work, we

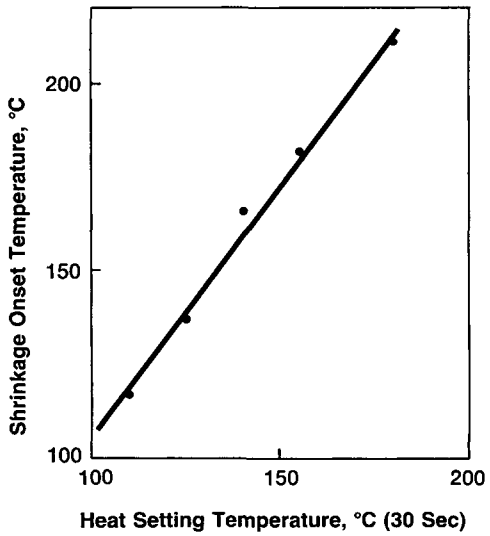

Figure 3 Shrinkage onset temperature by DMA vs. the heat setting temperature (analysis @ a pre-tension of 1 N).

Table I Characterization of Unconstrained Heat Set PET Yarns

Thermal Treatment 30 sec. @	X-ray Diffraction				Tensile Properties			Dynamic Mechanical Analysis		
	Crystallinity (%)	Index of Crystallite Size and Perfection	Degree of Orientation	Birefringence ($\times 10^{-3}$)	Modulus GPa	Strength GPa	Elongation (%)	Modulus @ 30°C GPa	Extension μm (30–200°C)	Orientation Index (α)
Control	35	40	0.989	245 ± 28	14.4	0.910	13.8	13.2	269	0.93
110°C	32	43	0.987	239 ± 8	10.8	0.836	13.3	13.1	365	0.90
125°C	31	35	0.986	246 ± 12	11.3	0.836	15.9	12.0	581	0.85
140°C	33	35	0.984	233 ± 14	9.5	0.825	21.0	11.7	924	0.75
155°C	37	35	0.986	232 ± 10	8.0	0.815	23.3	11.2 ± .3*	1129 ± 53*	0.70 ± .02*
180°C	35	35	0.984	212 ± 7	7.2	0.720	28.3	10.0	1673	0.44
245°C	36	48	0.965	182 ± 6	1.6	0.360	77.7	6.1	3751	—

* Standard deviation based on 5 measurements.

have covered a wider range of heat setting temperatures, i.e., between 110–245°C and used the DMA data to obtain an orientation factor.

Estimation of Orientation Factor

Thermomechanical analysis (TMA) of the control-highly oriented PET yarn shows a shrinkage of > 20% prior to melting. As a consequence of shrinkage, the heat set yarns have a "crimped" appearance. At a normal pre-tension of 1 N, the sample crimp creates uncertainty in obtaining reliable extension data. At a very high pre-tension of 10 N, some of the high-temperature heat set yarns may not be strong enough for the DMA experiment. Thus, an intermediate pretension of 6 N was selected which still eliminated the shrink-induced "crimp" of the yarn. The increase in extension (Δu) under these conditions is the least for the control-highly oriented yarn and the highest for the 245°C yarn-least oriented (Fig. 4). We can define an orientation factor (α) of a fiber sample as follows

$$\alpha = 1 - \frac{\Delta u \text{ sample}}{\Delta u \text{ unoriented}}$$

A perfectly oriented fiber can be expected to show nearly zero Δu such that $\alpha = 1$. On the other hand, an unoriented sample will exhibit a very high Δu such that $\alpha = 0$. Thus, by measuring the Δu of a fiber, its degree of orientation can be described within the limits of $0 < \alpha < 1$. By heat setting the control-highly oriented PET yarn at various temperatures, we have been able to prepare PET yarns differing in the degree of orientation. We have assumed that the 245°C (solid ↔ melt region) treated sample is the least-oriented PET yarn that one can obtain by heat setting. In this manner, we can use the orientation index (α) for monitoring the changes in yarn orientation during heat setting. Using this approach we obtain an $\alpha = 0.93$ for the control-highly oriented PET yarn and this gradually decreases to $\alpha = 0.44$ for the 180°C heat set yarn (Table I).

The importance of our approach can be realized by comparing the DMA information with the x-ray diffraction (XRD) and birefringence results. Shrinkage during heat setting (e.g., > 20%) followed by a loss in tensile properties (Table I) implies a loss in orientation upon heat setting.[2] Measurements of crystalline orientation by XRD reveal only small changes up to an annealing temperature of 180°C (Table I). We wish to mention that although XRD did not indicate any major differences in crystalline

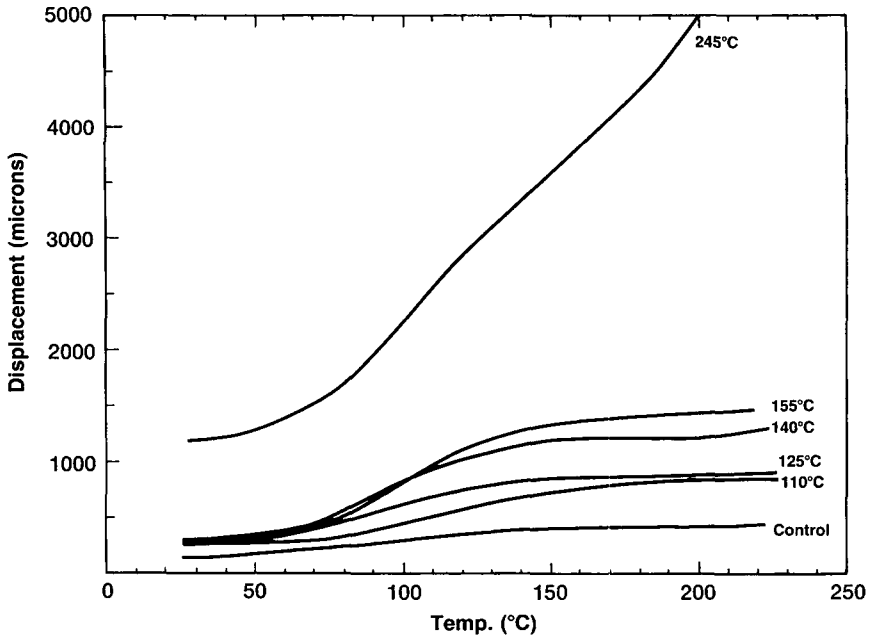

Figure 4 DMA of PET yarns heat set at various temperatures for 30 sec (analysis @ a pre-tension of 6 N).

orientation, there might be differences in amorphous orientation; the latter could be a subject of future study. Birefringence, a measure of total orientation (amorphous + crystalline) differentiates between the control and the heat set fibers except for the 125°C treated sample, but nonuniformities between fibers give rise to large standard deviations (note: birefringence values are to be used only for relative purposes due to uncertainties in accurately measuring the cross-sectional area of the heat-treated yarns which appeared to be somewhat deformed). In contrast, DMA orientation index (α) provides a much

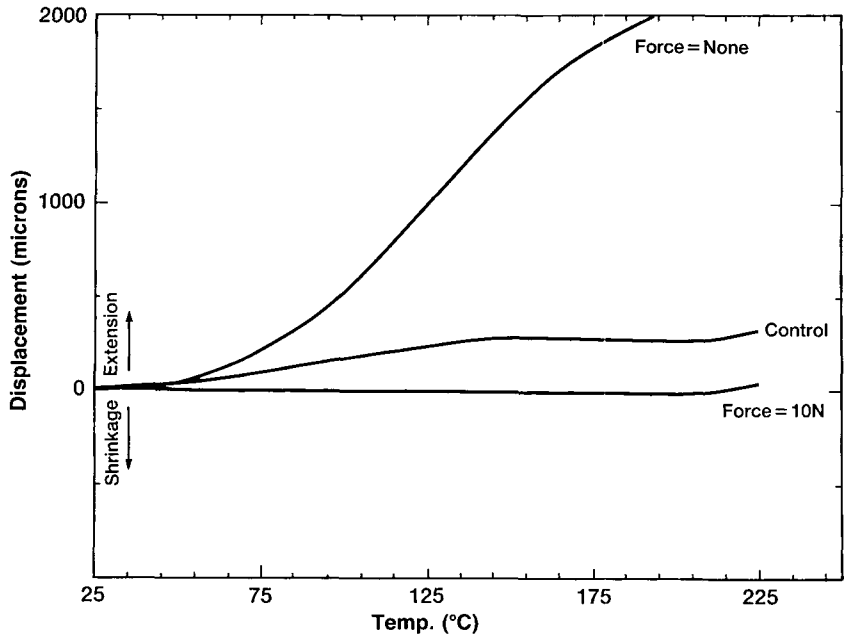

Figure 5 Comparative DMA thermograms of "control" and heat set (180°C/15 min, unconstrained vs. constrained @ 10 N) PET yarns at a pre-tension of 6 N.

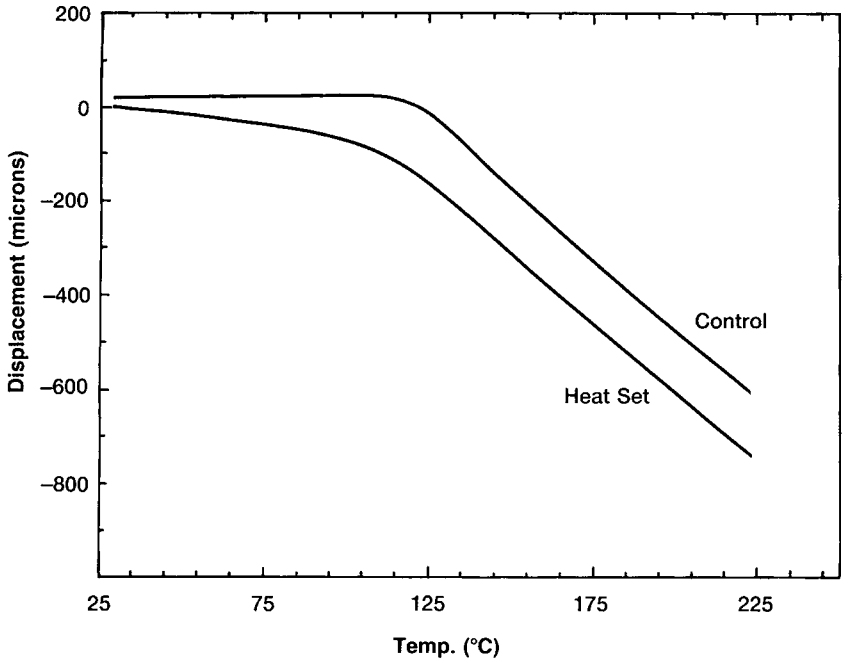

Figure 6 DMA thermograms of "control" and heat set (180°C/15 min, constrained @ 6 N) PET yarns at a pre-tension of 1 N.

wider range for the heat set yarns with a standard deviation of ± 5%. For the yarn annealed at 180°C/15 min under a pre-tension of 10 N, the degree of orientation (α) increases from 0.93 to ~ 1.0 which can be expected due to the molecular extension at a high temperature and a high force.

Regarding the significance of α, we must mention that it signifies molecular extension and provides a sensitive means of ranking the heat set yarns. This parameter should be used for following the relative changes in molecular extension upon heat setting and should not be confused with the absolute degree of orientation. As an example, the 245°C treated yarn has been assumed to be the least-oriented PET

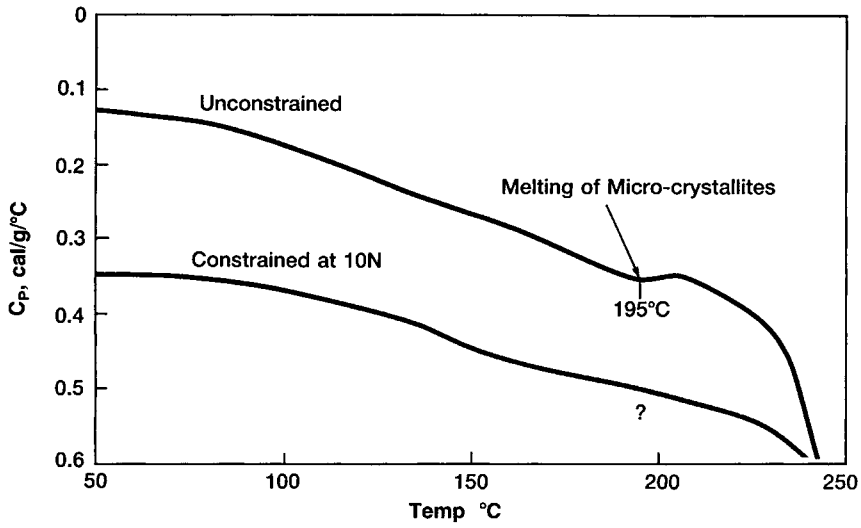

Figure 7 DSC thermograms of PET yarns heat set at 180°C/15 min under unconstrained and constrained (10 N) conditions.

but certainly, we do not imply that it is unoriented. Therefore, the advantage of our orientation index (α) is in relative evaluations.

Heat Setting Under Constraint

We attempted to heat set the control-highly oriented PET yarn under a pre-tension with the intention of further orienting the yarn and stabilizing the oriented amorphous phase through the formation of micro-crystallites; the latter originating from the heat treatment.[2,3] As shown in Figure 5, the yarn treated at 180°C—under no constraint, undergoes extension because of the disorientation caused during the heat treatment. On the other hand, the yarn treated at 180°C—under a pre-tension, undergoes lower extension than the control which is attributable to the enhanced degree of orientation. The changes in modulus follow the orientation factor (α) for the yarns heat set under constraint and under no constraint (Fig. 5).

We had hoped that the higher orientation and higher modulus achieved by the heat treatment under tension would be locked-in up to at least the heat treatment temperature, as a consequence of micro-crystallite formation, i.e., up to $\sim$ 180°C in this case. However, the shrinkage profile in Figure 6 clearly reveals that such is not the case. To date, the bulk of the studies on micro-crystallites appear to have been done on unconstrained samples.[2,3] Based on the differential scanning calorimetric (DSC) studies, we are finding that the micro-crystallites did not form when the sample was annealed under a high level of pre-tension (Fig. 7). This finding explains why we lose the orientation (reflected by shrinkage) of the constraint-annealed yarn at temperatures below the annealing temperature.

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