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Change in crystal width on axial stretching of poly(ethylene terephthalate) yarn

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Drawn multifilament poly(ethylene terephthalate) yarn was heat-set isothermally at temperatures between 180 and 258°C in the slack and taut conditions. The apparent crystal widths of these samples in the undeformed state and when axially stretched by 5–40% were monitored by X-ray diffraction. Significant reduction of crystal width occurred in the [010] direction in samples heat-set at high temperatures. Also, while this reduction in width commenced at low extension in the taut-annealed samples, it occurred at relatively higher extension in the slack-annealed yarns. These differences in behaviour have been attributed to the differences in the mechanisms of deformation that become operative on stretching the two sets of samples, and their structural origins have been examined.

(Keywords: poly(ethylene terephthalate); crystal width; axial stretching)

Introduction

There is considerable interest in establishing the links between macroscopic deformation in oriented polymers and identifiable molecular processes. To explain the low strain mechanical anisotropy of as-drawn and heat-set oriented low-density polyethylene sheets, Gupta and Ward[1,2] postulated three deformation mechanisms, namely interlamellar shear, *c*-axis shear and movement of twins. Detailed studies, with the help of X-ray diffraction, on the structural changes that occur on deformation of oriented polyethylene were made by Keller and Pope[3], Young *et al.*[4] and Pope and Keller[5], and interlamellar slip, intralamellar or chain slip and lamellar separation were identified as the principal deformation mechanisms, the term slip being used in the same context as shear. Gupta *et al.*[6] monitored the structural changes occurring during elongation up to fracture of uniaxially drawn, heat-set poly(ethylene terephthalate) (PET) film samples by rapid scanning Fourier transform infra-red (*FT*i.r.) spectroscopy and identified chain uncoiling (lamellar separation) in the amorphous regions and longitudinal slip in the crystalline regions as the main deformation mechanisms in these samples. More recently, Van Den Heuvel *et al.*[7] identified molecular uncoiling by *gauche–trans* transitions as the major deformation mechanism when a technical PET yarn was axially stretched.

The present investigations have been made on oriented PET multifilament yarns in the as-drawn and heat-set states. The crystal widths of these yarns were measured in the undeformed and deformed states with the help of X-ray diffraction. The results have been explained on the basis of different deformation mechanisms which become operative when the yarn is stretched axially. The structural characteristics of the samples relevant to the present investigation have also been obtained and they assist in providing the structural basis for the proposed deformation mechanisms.

Experimental

The starting material was conventional two-stage PET yarn of 76 denier, 36 filaments and zero twist. It had been spun at 800 m min^{-1} and then drawn to a draw ratio of 3.92 at a wind-up speed of 642 m min^{-1}. This control sample was subjected to isothermal heat-setting in a silicone oil bath for 5 min at temperatures of 180, 230 and 250°C while free to shrink (designated as free-annealed or FA), and at temperatures of 180, 230 and 258°C while held taut at constant length (taut-annealed or TA).

The crystallinity and crystallite orientation were determined from X-ray diffraction measurements on the samples using methods described elsewhere[8,9]. The amorphous orientation factor was determined by making i.r. measurements[10] and then combining them with the structural parameters obtained from X-ray studies. Sonic modulus was measured[11] with the help of a pulse propagation meter operating at 5 kHz. The degree of series and parallel coupling between the crystalline and amorphous regions was determined with the help of the Takayanagi model[12] using the procedure described in an earlier publication[13].

The change in crystal width on axial deformation of the yarn was studied by measuring the apparent crystal sizes corresponding to the (010) and (100) planes. The yarn sample was carefully wound over a metal frame to form a 20 mm × 15 mm parallel layer. The frame was transferred to a specially designed stretching device, which could be fitted into the base of an X-ray powder diffractometer. The sample was stretched axially to between 5 and 25% in the case of TA samples and 5–40% for FA samples, and equatorial scans in the range $2\theta = 10$–$35°$ were recorded at each of the selected strain levels. The apparent crystallite width perpendicular to

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the (010) and (100) planes were estimated from the half-widths of these planes using the Scherrer equation, as described in an earlier publication[9]. No attempt was made to separate crystallite size-broadening from strain-broadening for the following reason. The equatorial scans of the as-stretched samples showed a slight shift of the diffraction peak to higher angles, apparently due to the contraction of the unit cell in the lateral direction, indicating that the crystallites are uniformly strained. When the strain is uniform, the principal contribution to line-broadening arises from the small size of the crystallites.

Results and discussion

The structural and related data are presented in *Table 1*, from which the following noteworthy observations may be made: (a) the control sample is highly oriented with predominantly parallel coupling between the crystalline and amorphous phases; (b) on heat-setting, crystallinity increases in all cases while crystallite orientation decreases slightly in the case of FA samples and remains almost unchanged for the TA samples; (c) the amorphous orientation decreases in all cases, the decrease being relatively more for the FA samples; and (d) the sonic modulus decreases appreciably in the case of FA samples and only slightly for TA samples.

The measured crystallite widths perpendicular to the (010) and (100) planes, namely t_{010} and t_{100}, are plotted for the various samples in *Figures 1* and *2*, respectively, as functions of percentage extension. From an examination of the data presented in these figures, some noteworthy observations are made, as described below.

Undeformed samples. On heat-setting of the control sample, the crystal widths t_{010} and t_{100} increase, the increase being much more pronounced in samples heat-set at 230°C and above. Low-angle X-ray scattering studies on these samples, reported elsewhere[13], found that neither the control nor the 180°C heat-set samples showed any discrete low-angle patterns, indicating an imperfect lamellar structure with lack of distinct phase separation. On the other hand, samples heat-set at 230°C and above showed distinct low-angle patterns. Also, i.r. studies showed[14] that in the control and 180°C treated samples, chain folding could not be detected whereas samples heat-set at 230°C and above showed the presence of some chain folds.

Huisman and Heuvel reported[15] that on heat-setting of oriented PET yarn, t_{010} registers a greater increase than t_{100}. They explained this by stating that the observed direction of the strongest growth is the one in which the intermolecular interaction between ester dipoles exists,

Table 1 Structural and related data on control and heat-set PET yarns

Parameter	Control	FA 180°C	FA 230°C	FA 250°C	TA 180°C	TA 230°C	TA 258°C
X-ray crystallinity (%)	34.1	47	55.3	58.9	47	52.5	59
Hermans crystallite orientation factor	0.94	0.92	0.88	0.86	0.95	0.94	0.94
Hermans amorphous orientation factor	0.58	0.43	0.20	0.04	0.47	0.42	0.28
Sonic modulus (10^{11} dynes/cm^2)	1.60	0.77	0.57	-	1.60	1.52	1.38
Coupling parameter							
Series	0.31	1.0	-	-	0.53	0.60	0.69
Parallel	0.93	0.44	-	-	0.88	0.87	0.85

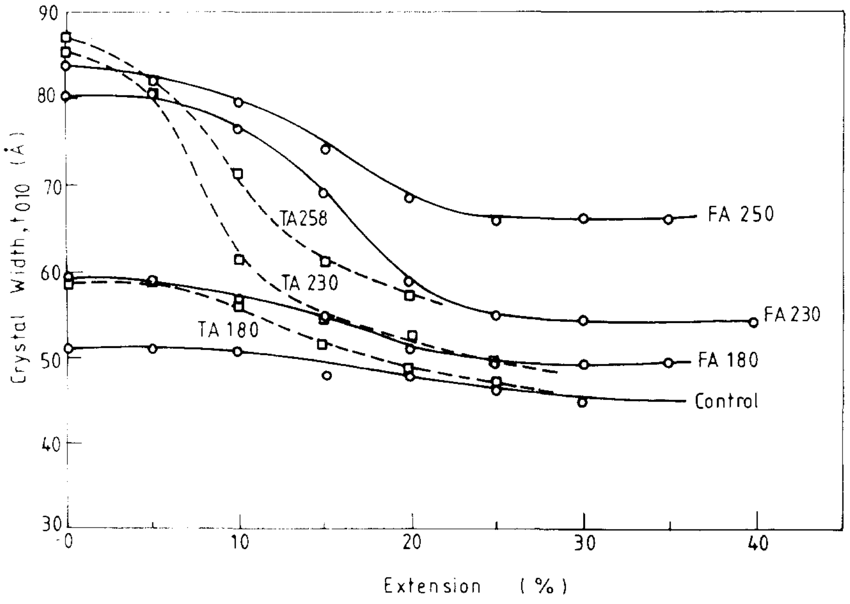

Figure 1 Crystal width in the [010] direction as a function of extension for the control, taut-annealed (TA) and free-annealed (FA) samples

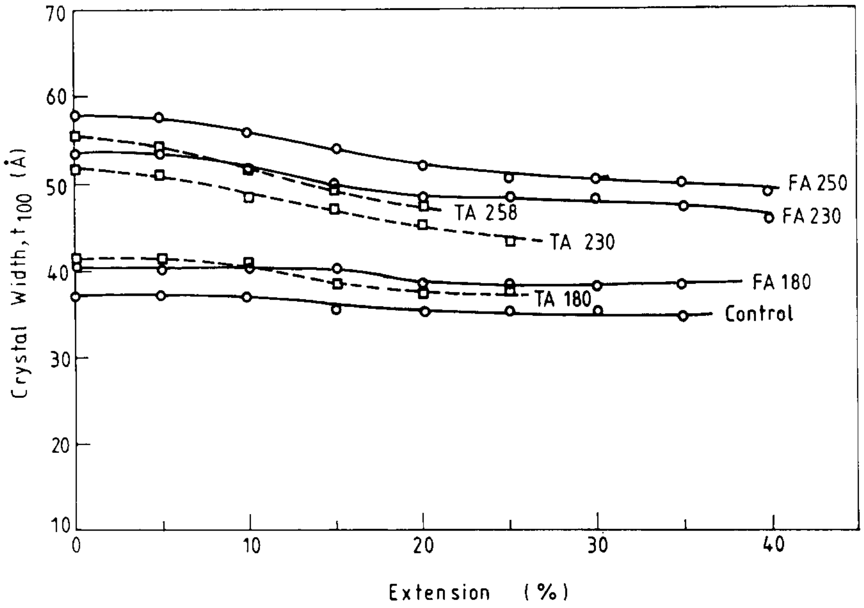

Figure 2 Crystal width in the [100] direction as a function of extension for the control, taut-annealed (TA) and free-annealed (FA) samples

namely along the [010] direction. The present data also show a similar effect and can be attributed to the same factor.

Deformed samples. It is interesting to observe that, broadly speaking, significant reduction in crystal width occurs on stretching the yarns axially. A closer examination of the data leads to the following specific observations.

(i) The reduction in crystal width, in t_{010} and t_{100}, in the control and 180°C annealed samples on stretching is relatively less in comparison to the reduction that occurs in samples annealed at 230°C and higher temperatures. It may be recalled that during heat-setting at the higher temperatures, significant crystal growth occurs through chain folding, and this provides greater scope for crystal size reduction by chain slip or by unfolding of the folded chains. Chain unfolding was actually observed when PET film heat-set at 220°C was axially stretched on an *FT*i.r. instrument and its spectra recorded simultaneously.

(ii) For samples heat-set at 230°C and above, the reduction in t_{010} on stretching the yarn is relatively greater than the reduction in t_{100}. This observation is consistent with the statement made earlier that chain folding occurs predominantly in the [010] direction, since it would be expected that chain slip and chain unfolding would occur in the direction in which the chain had initially folded.

(iii) There are significant differences between the FA and TA samples in the way in which crystal width changes with percentage extension in the two cases, and these are particularly clear for t_{010} for samples heat-set at the higher temperatures. It is noteworthy that while in the TA samples the reduction in crystal width occurs all through the uniaxial deformation, for the FA samples the reduction occurs mainly in the 10–20% extension range. To explain this observation, it may be recalled from the data presented in *Table 1* that the TA samples are characterized by a greater degree of parallel coupling between the crystalline and amorphous phases, and higher amorphous orientation. As a result, there would be more efficient load sharing by the two phases and longitudinal slip processes such as chain slip and chain unfolding would therefore be expected to operate even at low strains and may thus result in a reduction of the crystal width. Previous work has indeed shown that in a film sample taut-annealed at 220°C, chain unfolding occurs over the whole range of deformation until break for the sample. The FA samples, on the other hand, have a greater degree of series coupling and low amorphous orientation. As a result, the initial deformation of the yarn mainly involves uncoiling of the chains in the amorphous regions which results in lamellar separation. This may result in lateral contraction and bending of the lamellae[5], which can also lead to a reduction in crystal width. Once the chains in the amorphous regions are oriented, crystal deformation through chain slip and chain unfolding can occur. *FT*i.r. studies on a similar free-annealed PET film sample showed[6] a similar sequence of events when the film was stretched to failure.

The results of the investigation presented in this communication are consistent with the earlier studies on axially stretched PET films. It is instructive to compare the present results with those reported[5] on deformation of oriented low-density polyethylene, which showed that samples annealed at low temperatures containing small, imperfect lamellae deform mainly by chain slip whereas samples annealed at higher temperatures with a more pronounced lamellar structure deform mainly by lamellar slip and lamellar separation. The results on PET are partially consistent with this observation in that the TA samples annealed at the higher temperatures with significant parallel coupling have a more imperfect lamellar structure compared to the FA samples; it is therefore not surprising that the TA samples deform mainly through chain slip and chain unfolding. Pope and Keller[5] further pointed out that, of the various deformation processes, chain slip, in which case elastic energy must be stored on the surfaces of the lamellae and other amorphous regions, is the most reversible deformation process and is not impaired, as is lamellar separation, by broken tie chains and pulled-out folds.

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