The Effect of Oil and Air Annealing on the Structure of Drawn Poly(ethylene terephthalate)

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Oil annealing produces changes in fibre structure of drawn PET not found in air annealing. The results are similar to those found in drawn nylon 66 but there are some differences especially in the effect of annealing on the small-angle intensity. It is suggested that the shrinkage of drawn PET in oil is due to chain folding, or fold regularization of crystals, and to relaxation in the non-crystalline regions.

STATTON[1] has shown that the long period of a single crystal polyethylene mat can be greatly increased by immersion for short times (<1 minute) in hot ethylene glycol. Samples heated in air required 15 hours to reach the same long period. Recently, it has been reported that large changes in the structure of drawn nylon 66 yarns could be achieved by treatment in hot coconut oil[2] or silicone oil[3]. It has also been found that a heat treatment in air requires much longer times to produce the same change that occurs during a one minute heat treatment in silicone oil[4]. The purpose of this note is to demonstrate that a similar difference in structure can be observed for drawn poly(ethylene terephthalate), PET, heated in air or in silicone oil.

EXPERIMENTAL

Spun PET of low crystallinity (<2 per cent by X-ray diffraction[5]) was drawn to a draw ratio of 5X over a hot pin at 80°C. Two types of annealing procedures were used:

(1) Five metre lengths of yarn, in a wire mesh basket, were immersed in silicone oil for one minute, and (2) two and one half metre lengths of yarn were immersed in a test tube of heated air for ten minutes. These annealing times were chosen to obtain maximum shrinkage. All samples were quenched into carbon tetrachloride at room temperature after annealing was completed. The shrinkage S was calculated from the formula

$$S = \frac{\text{Initial length} - \text{Final length}}{\text{Initial length}}.$$

Crystallinity measurements were made with a Norelco X-ray diffractometer, which was also used to obtain the crystallite orientation from scans[5] on the ($\bar{1}05$). The orientation parameter employed was f_c given by

$$f_c = \tfrac{1}{2}\,(3\,\overline{\cos^2 \varphi} - 1)$$

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where $\overline{\cos^2\varphi}$ is the mean-square cosine of the angle, φ, between a ($\bar{1}05$) plane normal and the fibre axis.

Small angle X-ray data were obtained with a Kratky camera (slit collimation). Integrated intensities of the long period maximum were derived from the areas under the maxima after a linear background had been subtracted. Crystallite and amorphous lengths in the direction of the fibre axis were calculated by the method of Tsvankin[6] with the characteristic parameters $\beta/\alpha = 0.4$ and $\epsilon = 0.2$.

Birefringence measurements were made using a compensator. The birefringence values were combined with crystallinity and crystallite orientation measurements to give the orientation of the non-crystalline regions[7]. Tenacity and modulus measurements were made on single filaments using an Instron testing machine.

RESULTS

Shrinkage, crystallinity and orientation results are given in *Table 1*. The shrinkage of the oil annealed yarns increases rapidly with increase in annealing temperature while the increase for the air annealed yarns is much more moderate. On the other hand the crystallinity of the air annealed yarns in-

Table 1. Shrinkage, crystallinity and orientation data for 5X PET heated 10 minutes in air or 1 minute in oil

Sample		Shrinkage (%)	X-ray crystallinity (%)	f_c	f_{am}
5X PET					
in oil at	100°C	8	38	0·94	0·81
	150°C	23	34	0·91	0·71
	175°C	31	38	0·91	0·67
	200°C	43	39	0·86	0·68
	225°C	60	39	0·86	0·48
	240°C	75	34	—	—
5X PET					
in air at	100°C	8	31	0·93	0·84
	150°C	20	34	0·93	0·75
	175°C	24	40	0·93	0·75
	200°C	30	38	0·92	0·73
	225°C	35	38	0·92	0·68
	240°C	44	40	0·93	0·68

creases with temperature while that of the oil annealed samples remains approximately constant and even decreases at an annealing temprature of 240°C. The crystallite orientation remains constant with increases in annealing temperature for the air annealed samples but there is a definite decrease in orientation for the oil annealed samples as the temperature increases. The orientation of the yarn annealed at 240°C in oil could not be measured accurately due to the severely crimped nature of the sample. The overall orientation, as measured by birefringence, decreases with increase in annealing temperature for both oil and air annealed series but the decrease is most marked for the oil annealing. The orientation of the non-crystalline regions shows the same trend as the birefringence in that there is a decrease in orientation with increase in annealing temperature. The decrease is

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much greater for the oil annealed samples and it appears that the non-crystalline regions have little, if any, orientation for an annealing temperature of 240°C.

Table 2 gives the small-angle results. The intensity under the small-angle maximum is nearly the same for both series and increases with annealing temperature. The decreased intensity of the sample annealed at 240°C in oil is probably a reflection of the decrease in crystallinity. The long period increases with annealing temperature but at a greater rate for the oil

Table 2. Small-angle X-ray data for 5X PET heated 1 minute in oil or 10 minutes in air

Sample	Intensity	Long period (Å)	Crystal length (Å)	'Amorphous' length (Å)
5X PET				
in oil at 100°C	8	124	77	40
150°C	47	122	77	37
175°C	76	124	82	32
200°C	147	147	96	41
225°C	214	167	110	44
240°C	132	195	133	45
5X PET				
in air at 100°C	13	132	80	45
150°C	52	120	75	38
175°C	76	120	78	33
200°C	127	132	89	36
225°C	172	140	93	37
240°C	212	151	98	42

annealed yarns. The crystallite lengths show the same trend as the long period. The 'amorphous' lengths remain relatively independent of the annealing temperature and are almost the same for both series.

Table 3 gives the tenacity and tensile modulus values. It was found that for annealing temperatures above 200°C the samples heated in oil developed crimp. This crimp was removed by application of a small load before the

Table 3. Instron data for 5X PET heated 1 minute in oil or 10 minutes in air

Sample	Modulus (g/d)	Tenacity (g/d)	Sample	Modulus (g/d)	Tenacity (g/d)
5X PET			5X PET		
in oil at 100°C	66	6·7	in oil at 100°C	77	7·1
150°C	48	5·8	150°C	51	5·8
175°C	35	4·8	175°C	44	5·3
200°C	27	3·7	200°C	46	4·6
225°C	12	2·2	225°C	32	3·7
240°C	14	1·9	240°C	36	4·1

modulus measurement. The air annealed yarns did not develop crimp at any temperature. The tenacity and modulus values decreased with increase in annealing temperature for both series but the largest decrease was for the oil annealed samples.

DISCUSSION

The results indicate that the use of silicone oil as a heating medium can produce changes not found for the times of heating in air employed here. For example, the shrinkage of oil annealed samples is much greater than the shrinkage of air annealed yarns. In this respect, PET behaves in the same way[4] as drawn nylon 66. However, the results also show that the small-angle intensity is nearly the same for both air and oil annealing which is contrary to the nylon 66 results in which oil annealing produced the larger increase in intensity. According to Dismore and Statton[2] the intensity increase may be attributed to chain folding; the chain folding will also produce the concomitant shrinkage. In PET, then, the implication is that chain folding occurs to about the same extent in both the oil and the air annealing, for this will explain the small-angle intensity results. To explain the difference in shrinkage it is necessary to invoke a second shrinkage mechanism, namely disorientation of the non-crystalline region, which occurs in oil but not in air annealing. There is some support for this from the orientation data which show that the non-crystalline regions have a lower orientation in the oil annealed than in the air annealed samples. It might be expected that the long periods of the oil annealed samples would be smaller than the long periods of the air annealed yarns, due to the greater relaxation of the non-crystalline regions in oil annealing. This is not borne out by the results; in fact the opposite effect is found. It may be noted that the non-crystalline lengths, i.e. the lengths between crystal boundaries, are almost the same for both series of yarns. It is not known how significant this result is, however, because of a certain arbitrariness in the way the Tsvankin analysis was applied. Earlier it was stated that characteristic parameters of $\beta/\alpha = 0.4$ and $\epsilon = 0.2$ were chosen. It has been found[8] that the crystallite length obtained is independent of the choice of parameters but that the amorphous length does depend strongly on this choice. It is possible that the oil and air annealed series each require a different choice of characteristic parameters (different crystal size distribution).

The difference between air and oil annealing also shows up in the Instron results where it is found that the tenacity and modulus are much lower for oil annealed samples. At the highest annealing temperature this is a reflection of the loss of orientation.

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