Structural Changes in Partially Oriented Polyester Yarns Subjected to Dry and Wet Heat

J. O. WARWICKER and S. G. GRAHAM, *Textile Products Division, Shirley Institute, Didsbury, Manchester M20 8RX, England*

Synopsis

An examination by X-ray, birefringence, and infrared methods was carried out on partially oriented polyester yarns subjected to dry and wet heat under varying tensions that allowed shrinkage and extension processes to occur. The results can be interpreted in terms of a two-phase morphology in which one phase is a network and the other crystalline. On this basis the evidence suggests that the crystalline phase is composed of extended chains and the network of randomly folded chains with cohesion points randomly distributed between them.

INTRODUCTION

An examination of the dimensional changes brought about, and the changes in mechanical properties, in partially oriented polyester yarns subjected to dry and wet heat was described in the first part.[1] It was suggested that the theory of two phases of morphology of polyester as proposed by many authors[2–4,13] was adequate to interpret the changes noted. In this article, further justification of the two-phase theory is provided by an examination by X-ray, birefringence, and infrared methods of the same yarns as used in part I.[11]

EXPERIMENTAL

Heat Treatment

The partially oriented (PO) yarns were experimental samples supplied by Viscosuisse Ltd and were produced at 3000, 3500, 4000, and 4500 m/min, which for simplicity will be referred to as WS3000, etc. The dimensional changes during heating and the mechanical properties of these PO yarns, as well as derived yarns, have been given by Warwicker and Vevers.[1]

Dimensional changes of a tensioned loop of yarn was observed[1] in dry heat at 100, 180, and 210°C and in water with and without 3.0 g/L Palanil A (Dye Carrier, BASF) at 95°C. Three main stages were recognized in the process: (1) initial contraction; (2) reextension, after the initial contraction, under the same tension to an equilibrium position at which the final length of the loop was less than the original length; and (3) for some tensions, extension to beyond the initial length sometimes occurred without the initial contraction stage.

To investigate the structural processes occurring during these stages of dimensional change, X-ray diagrams were taken, birefringences were determined, and infrared measurements carried out.

Journal of Applied Polymer Science, Vol. 26, 3045–3064 (1981)

CCC 0021-8995/81/093045-20$02.00

TABLE I
X-Ray Data of Structural Changes in Partially Oriented Polyester Yarn Heated at 180°C[a]

l, cm[b]	Change in length, %	X-Ray diagram
62.5	−37.5	NC (1) similar to control PO yarn
68.0	−32.0	NC (1) + weak C (2)
87.7	−12.3	C (3) on NC (1) background
91.1	− 8.9	C (3) on weaker NC (1) background
100	0	C (3) on weak NC (1) background
109.3	+ 9.3	C (3) on very weak NC (1) background

[a] Tension: 0.16 g/tex; POY: WS 3000 m/min; C = crystalline; NC = noncrystalline. The number in parenthesis refers to the type of diagram as illustrated in Figures 1–4.

[b] Based on a length of 100 cm as the original length.

X-Ray Diagrams

X-Ray diagrams were taken of samples of yarn at various stages of dimensional change under different conditions. These diagrams were taken with a semicylindrical camera (R = 5.73 cm) and with nickel-filtered copper radiation. Typical diagrams are shown on Figures 1 to 4, and a summary of the observations is given in Tables I to V. The term noncrystalline background indicates a background similar to the diffraction from the noncrystalline PO yarn (Fig. 1). The term disoriented crystalline pattern implies different degrees of biaxial orientation (see text) and not complete disorientation into a powder pattern, unless so stated (Figs. 2 and 3). Figure 4 represents a well-oriented polyester fiber X-ray diagram.

For descriptive purposes, C refers to crystalline and the number in parenthesis refers to the type of X-ray diagram as illustrated in Figures 2 to 4. NC refers to a noncrystalline background scatter and is similar to Figure 1, but the amount of orientation displayed depends on the experiment. The angle ψ is the angle subtended by the potential equatorial reflection to the center; for a well-oriented crystalline diagram, $\psi = 0$. The fact that $\psi > 0$ in many cases shows that a biaxial orientation process is involved.

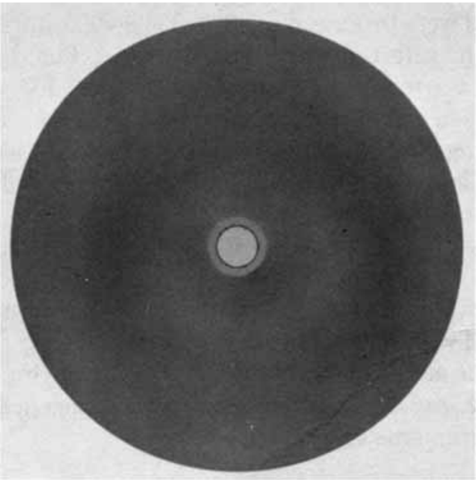

Fig. 1.

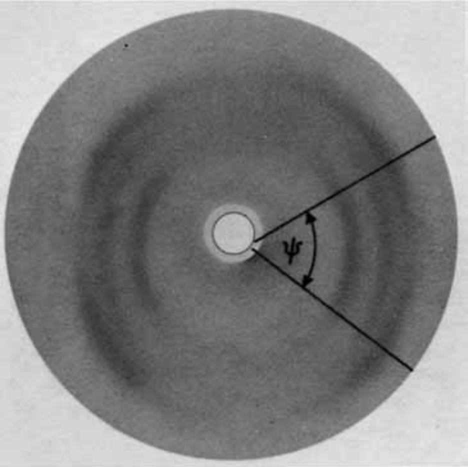

Fig. 2.

Birefringence

The birefringence of the original PO yarns and a selection of shrunk yarns was obtained with a microscope by measuring the path difference by a Berek compensator and the diameter by reference to an eyepiece graticule calibrated against a stage micrometer.

Results are shown in Table VI together with the length of yarn before and after treatment based on a control length of 100 cm.

Infrared Measurements

Infrared measurements were made with fiber grids immersed in liquid paraffin and mounted in a Grubb–Parsons infrared spectrometer Mark II similar to the method described by Wilson.[4] By turning the polarizer, it was possible to take measurements with the electric vector parallel and perpendicular. Since there is an inherent perpendicular polarization in the instrument, it was possible by

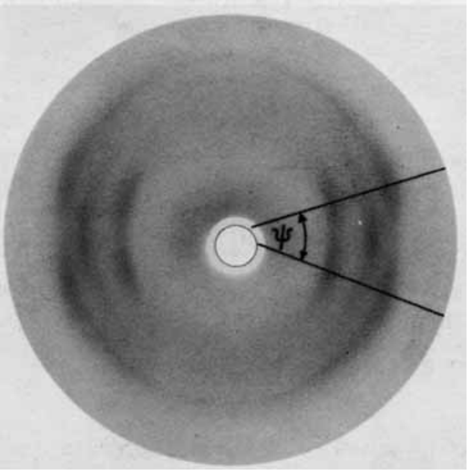

Fig. 3.

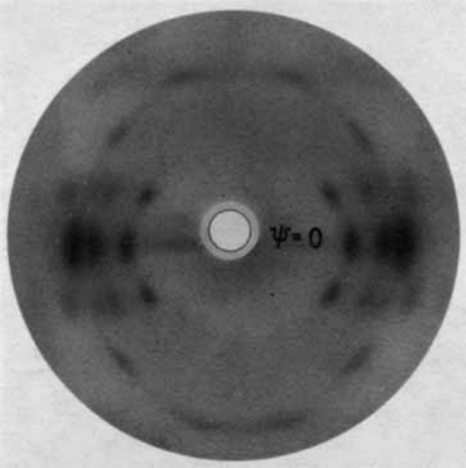

Fig. 4.

turning the specimen to 45° and taking the mean absorbance in the two possible positions to find an approximate isotropic absorbance.

To measure the absorbance, pseudobaselines were drawn in the same way as given by Ward et al.[5] for poly(ethylene terephthalate) infrared spectra. For calibration purposes, the band at 795 cm^{-1} was chosen.[6,7] The absorbance or relative intensity of the bands was therefore given as

$$\text{absorbance } (E) = \frac{\text{absorbance of the band}}{\text{absorbance of the 795 cm}^{-1}\text{ band}}$$

where the absorbance is $\log I_0/(I_0 - I_p)$, where I_p is the peak height from the pseudobaseline and I_0 is the initial intensity.

The band assignments used are shown below and are those given by Miyake[6]:

Band, cm^{-1}	Assignment	
848	CH_2 rocking frequency	trans
896	CH_2 rocking frequency	gauche
973	C—O stretching frequency	trans
1042	C—O stretching frequency	gauche
875	orientation-sensitive bands	
795	independent of structural effects	

Table VII lists the mean absorbance for the position E (45°). The isotropic absorbance is defined by Baranova et al.[8] as

$$E_0(\text{iso}) = \frac{E(\text{parallel}) + 2E(\text{perpendicular})}{3}$$

and the dichroic ratio quoted is defined as

$$R = \frac{E(\text{parallel})}{E(\text{perpendicular})}$$

The sample length is quoted in Table VII as a percentage of the standard control length. The small letters *c* and *e* refer to the direction of motion of the fiber either in contraction and extension, respectively.

TABLE II
Data from X-Ray Diagrams of Partially Oriented Polyester Yarn Heated at 100°C

Tension, g/tex	Change in length, %	Initial contraction X-ray diagram	Change in length, %	Equilibrium position X-ray diagram
WS 3000 m/min				
0.02	−61.2	NC (1) + very weak C (2)	−57.6	C (2) on weak NC (1) background
0.16	−37.3	NC (1) + faint powder C pattern	− 2.0	C (2) on weak NC (1) background
1.60		—	+62.7	C (4) poor lateral order on weak NC (1) background
WS 3500 m/min				
0.02	−56.1	NC (1) + very weak C (2)	−48.2	C (2) on weak NC (1) background
0.18	−33.5	NC (1) + very weak C (2)	− 9.0	C (3) on weak NC (1) background
1.83		—	+41.3	C (4) poor lateral order + weak NC (1) background
WS 4000 m/min				
0.02	−40.5	NC (1) + weak C (2)	−26.8	C (3) on NC (1) background
0.21	−17.0	NC (1) + weak C (3)	− 5.3	C (3) on weak NC (1) background
2.07		—	+24.0	C (4) poor lateral order + weak NC (1) background
WS 4500 m/min				
0.02	− 4.8	C (4) on weak NC (1) background	− 3.5	C (4) on very weak NC (1) background
0.24	− 2.3	C (4) on weak NC (1) background	− 1.6	C (4) on very weak NC (1) background
2.37		—	+10.2	C (4) on very weak NC (1) background

TABLE III
Data from X-Ray Diagrams of Partially Oriented Polyester Yarn Heated at 180°C

Tension, g/tex	Change in length, %	Initial contraction X-ray diagram	Change in length, %	Equilibrium position X-ray Diagram
		WS 3000 m/min		
0.02	−60.4	NC (1) + faint C (2)	−56.5	*C (2) on weak NC (1) background
0.08	−48.9	NC (1) + very faint C (2)	−28.0	*C (2) on weak NC (1) background
0.16	−36.8	NC (1) as PO yarn	+11.0	*C (3) + faint NC (1) background
1.60		—	+66.1	C (4) + very faint NC (1) background
				* ψ progressively becomes smaller
		WS 3500 m/min		
0.02	−56.6	Weak C (2) on NC (1) background	−48.9	* C (2) + weak NC (1) background
0.09	−48.1	NC (1) + very faint C (2)	−26.4	* C (2) + very weak NC (1) background
0.18	−37.1	NC (1) + very faint C (2)	− 3.6	* C (3) + very faint NC (1) background
1.83		—	+44.5	C (4) + very faint NC (1) background
				* ψ progressively becomes smaller
		WS 4000 m/min		
0.02	−43.6	C (2) + NC (1) background	−27.0	* C (3) + weak NC (1) background
0.21	−20.8	NC (1) + faint C (2)	− 1.0	* C (3) + very weak NC (1) background
2.07		—	+26.8	C (4) + very faint NC (1) background
				* ψ progressively becomes smaller
		WS 4500 m/min		
0.02	− 5.5	C (4) + weak NC (1) background	− 2.9	C (4) + very weak NC (1) background
0.24	− 2.8	C (4) + weak NC (1) background	− 1.1	C (4) + very weak NC (1) background
2.37		—	+13.4	C (4) + very weak NC (1) background

TABLE IV
Data from X-Ray Diagrams of Partially Oriented Polyester Yarn Heated at 210°C

Tension, g/tex	Change in length, %	Initial contraction X-ray diagram	Change in length, %	Equilibrium position X-ray diagram
		WS 3000 m/min		
0.02	−61.3	NC (1) + weak C (2)	−55.7	C (2) + weak NC (1) background
0.16	−37.6	NC (1) similar to control	+15.1	C (3) + weak NC (1) background
1.60			+70.1	C (4) + weak NC (1) background
		WS 3500 m/min		
0.02	−58.7	C (2) on weak NC (1) background	−46.7	C (2) on weak NC (1) background
0.18	−36.8	NC (1) + weak C (2)	+ 0.3	C (3) on very weak NC (1) background
1.83			+50.4	C (4) on very weak NC (1) background
		WS 4000 m/min		
0.02	−44.4	C (2) on NC (1) background	−26.1	C (3) + weak NC (1) background
0.21	−21.8	NC (1) with faint C (2)	− 0.7	C (3) + weak NC (1) background
2.07			+30.9	C (4) very little NC (1) background
		WS 4500 m/min		
0.02	− 5.0	C (4) on weak NC (1) background	− 3.3	C (4) on weak NC (1) background
0.24	− 2.8	C (4) on faint NC (1) background	− 0.7	C (4) on faint NC (1) background
2.37			+19.2	C (4) on slight NC (1) background

TABLE V
Data from X-Ray Diagrams of Partially Oriented Polyester Yarn Heated in Water at 95°C

Tension, g/tex	Change in length, %	Initial contraction X-ray diagram	Change in length, %	Equilibrium position X-ray diagram
		WS 3000 m/min		
0.02	−52.5	NC (1) + very weak C (2)	−49.6	C (2) on weak NC (1) background
0.16	−29.0	NC (1) + very weak C (2)	− 6.3	C (2) on weak NC (1) background
1.60			+64.5	C (4) on NC (1) background
		WS 3500 m/min		
0.02	−44.9	NC (1) + C (2)	−35.3	C (2) on weak NC (1) background
0.18	−23.0	NC (1) + C (2)	− 7.9	C (3) on weak NC (1) background
1.83			+42.4	C (4) on weak NC (1) background
		WS 4000 m/min		
0.02	−35.3	C (2) on NC (1) background	−27.5	C (3) on weak NC (1) background
0.21	−15.9	C (3) on NC (1) background	− 7.6	C (3) on weak NC (1) background
2.07			+23.3	C (4) on very weak NC (1) background
		WS 4500 m/min		
0.02	− 5.3	C (4) on weak NC (1) background	− 4.0	C (4) on very weak NC (1) background
0.24	− 2.3	C (4) on weak NC (1) background	− 1.6	C (4) on very weak NC (1) background
2.37			+10.1	C (4) on faint NC (1) background

TABLE VI
Birefringence of PO Yarns Shrunk at 210°C

Sample WS, m/min	Tension, g/tex	Birefringence		Length of yarn, cm	
		Initial contraction	Equilibrium	Initial contraction	Equilibrium
3000	Control:	0.0356		100	
	0.02	0.0046	0.0070	38.7	44.3
	0.08	0.0084	0.0629	49.8	76.7
	0.16	0.0127	0.1124	62.4	115.1
	0.32	0.0305	0.1449	92.5	131.0
	1.60	—	0.1720	—	170.1
3500	Control:	0.0476		100	
	0.02	0.0239	0.0749	41.3	53.3
	0.09	0.0216	0.1152	52.1	79.4
	0.18	0.0369	0.1339	63.2	100.3
	0.37	0.0459	0.1564	95.9	116.9
	1.83	—	0.1731	—	150.4
4000	Control:	0.0678		100	
	0.02	0.0377	0.1386	55.6	73.9
	0.10	0.0389	0.1451	64.0	89.2
	0.21	0.0786	0.1538	78.2	99.3
	0.41	0.1012	0.1587	97.7	108.4
	2.07	—	0.1707	—	130.9
4500	Control:	0.0783		100	
	0.02	0.0953	0.1488	95.0	97.7
	0.12	0.1055	0.1518	96.1	98.0
	0.24	0.1075	0.1521	97.2	99.3
	0.47	0.1167	0.1559	99.0	102.2
	2.37	—	0.1663	—	119.2

DISCUSSION

X-Ray Diagrams

The X-ray diagrams of the partially oriented yarns have been shown to be of two types, one noncrystalline with some evidence of orientation, and the other crystalline with some noncrystalline component. The noncrystalline type of diagram is given by the yarns WS 3000–4000 (Fig. 1), but the partially oriented yarn WS 4500 shows a distinct oriented crystalline pattern similar to Figure 4 on a weak noncrystalline scatter background.

According to diffraction theory, parallel chains aligned with some degree of two-dimensional order would give streak layer lines and very diffuse reflections on the zero layer line (equator) of the diagram. The PO yarns WS 3000–4000 give X-ray diagrams that have SX features which suggest that this ideal diffraction situation is to some extent present together with a large portion of randomly arranged.material. At the higher winding speed of 4500 m/min, the partially oriented yarn apparently has a sufficiently oriented fraction to crystallize; but since there is still evidence of a noncrystalline background, probably there remains a fraction of material similar to that found in the other PO yarns. Since these structures are being formed under stress and strain conditions it seems plausible that the crystalline portion is composed of straight chains, and

TABLE VII
Infrared Data for PO Yarn WS 3000 Heated at 180°C under Tension of 0.16 g/tex/Thread

Sample length	Infrared measurement	Measurements at bands					
		848 cm^{-1}	896 cm^{-1}	973 cm^{-1}	1042 cm^{-1}	875 cm^{-1}	795 cm^{-1}
Control	E(45°)	1.060	1.200	1.315	2.077		
100	E(iso)	1.014	1.146	1.327	2.693		
	R	0.830	1.024	0.738	0.363	0.589	1.795
98.6 *c*	E(45°)	1.392	0.883	1.195	1.129		
	E(iso)	1.232	1.041	0.898	0.904		
	R	0.401	0.558	1.792	0.576	0.160	2.161
91.0 *c*	E(45°)	1.203	0.764	1.200	0.760		
	E(iso)	1.124	0.879	0.915	0.975		
	R	0.426	0.617	2.038	0.715	0.229	1.46
83.5 *c*	E(45°)	1.275	0.868	1.226	0.876		
	E(iso)	1.040	0.975	0.826	0.850		
	R	0.468	0.756	2.108	0.791	0.282	1.444
79.0 *c*	E(45°)	1.474	0.693	1.587	0.619		
	E(iso)	1.242	0.632	1.053	0.803		
	R	0.420	0.811	2.007	0.724	0.244	1.409
75.0 *c*	E(45°)	1.535	0.898	1.339	0.880		
	E(iso)	1.270	0.956	1.049	0.768		
	R	0.351	0.612	2.146	0.661	0.166	1.478
72.0 *c*	E(45°)	0.848	1.009	0.999	1.075		
	E(iso)	0.826	1.060	0.848	0.815		
	R	0.570	0.918	1.710	1.068	0.567	0.996
63.3 *c*	E(45°)	1.389	0.733	1.325	0.704		
	E(iso)	1.320	1.056	0.998	0.808		
	R	0.422	0.729	1.630	0.608	0.206	1.716
62.5 *c*	E(45°)	1.374	0.892	1.470	0.667		
(fully	E(iso)	1.176	0.916	1.348	0.642		
contracted)	R	0.545	1.134	1.670	1.248	0.186	1.523
68.0 *e*	E(45°)	1.047	0.738	1.357	0.944		
	E(iso)	0.926	1.050	0.811	0.870		
	R	0.694	0.942	1.494	0.842	0.518	1.173
74.0 *e*	E(45°)	0.985	1.023	1.210	1.322		
	E(iso)	0.958	1.199	0.914	1.203		
	R	0.850	0.954	1.773	0.836	0.635	1.088
81.7 *e*	E(45°)	1.180	0.749	1.403	0.926		
	E(iso)	1.104	0.946	1.033	0.934		
	R	0.549	0.680	1.837	0.871	0.275	1.390
87.5 *e*	E(45°)	1.788	0.806	1.554	1.074		
	E(iso)	1.768	0.985	1.363	1.026		
	R	0.367	0.700	2.331	0.743	0.140	1.554
93.8 *e*	E(45°)	1.299	0.697	1.496	0.965		
	E(iso)	1.275	0.984	1.182	0.974		
	R	0.511	0.594	2.355	1.246	0.240	1.192
100 *e*	E(45°)	1.582	0.760	1.371	1.005		
(return	E(iso)	1.662	0.929	1.206	1.029		
to length)	R	0.384	0.679	1.888	0.559	0.137	1.961
109.1 *e*	E(45°)	2.378	0.764	2.104	0.847		
	E(iso)	2.508	1.034	1.904	0.817		
	R	0.361	0.959	1.511	0.403	0.142	1.876

similarly the oriented noncrystalline portion that precedes crystallization must have mainly straightened chains. The random noncrystalline portion is visualized as having randomly folded and kinked chains probably with cohesive points or regions similar to the situation in noncrystallized rubber. As a generalization, it is thus possible to visualize the polyester structure in terms of two phases, a noncrystalline and a crystalline phase. But this is an oversimplification, since the noncrystalline phase can have degrees of order and the crystalline phase degrees of disorder as well as different orientations in relation to each other.

The formation of such a structure with different arrangements of the two phases was investigated by taking X-ray diagrams of the PO yarns at different stages of shrinkage and extension. This is illustrated by the data given in Table I for PO yarns WS 3000 heated under tension of 0.16 g/tex at 180°C. The original yarn gives a typical X-ray diagram of an amorphous substance similar to Figure 1, with little or no concentration of the amorphous scatter at the equator. When first introduced into the oven at 180°C, this yarn contracts 37.5% ($l = 62.5$ cm); and if arrested at this stage and an X-ray diagram is taken, the contracted yarn shows no sign of crystallization. This is remarkable in that the conditions are such that chain folding and crystallization, if they are going to occur, should be detected. A sample of yarn that had been through this initial contraction at 180°C and reextended under the same tension to a length of 87.7 cm (compared to 100 cm original sample length) showed a distinct pattern similar to Figure 3 on a noncrystalline background. Prior to this stage, samples indicated weak crystallization with an orientation similar to Figure 2. After this stage, up to attaining the original length and beyond, the orientation of the crystalline part remained substantially constant but became more intense in relation to the noncrystalline background scatter. The nature of the changes in the X-ray pattern indicated that the orientation process is biaxial, and in these experiments the uniaxial stage is not attained. A practical way of indicating this process can be furnished by measuring the angle ψ subtended by the two 100 arcs either side of the equator on one half of the X-ray diagram (see Figs. 2 and 3) and the reciprocal of the half-breadth at half-maximum intensity ($1/\phi_{1/2}$) around the 100 arc taken as an indication of axial orientation (but not necessarily directly proportional to it). When $\psi = 0$, most of the orientation is axial orientation and is related to $1/\phi_{1/2}$.

In the experiment under discussion, $\psi \approx 45°$ at a length of 87.7 cm but does not change even though the length eventually reaches 109.3 cm. But, as already pointed out, the noncrystalline background to the X-ray diagrams weakens in relation to the crystalline diffraction as this extension is taking place.

Experiments were carried out at three different dry temperatures (100, 180, and 210°C) with all the PO yarns under different tensions; the X-ray results from these experiments are summarized in Tables II, III, and IV. At 100°C under a very low tension, a slight crystallization takes place with the WS 3000 yarn during the initial contraction, but further crystallization takes place on extension to the equilibrium position for this particular tension. It is somewhat surprising that under a higher tension (0.16 g/tex) no crystallization takes place on contraction but does on extension back almost to the original length. The employment of a tension that causes extension immediately on application results in a well-oriented (like Fig. 4) X-ray diagram on a weak noncrystalline background. Similar results are found for yarns WS 3500 and WS 4000, the amount of crystallization and orientation increasing with the winding speed of the yarn used. The main point is again emphasized that crystallization is mainly evident only during extension of the yarn. With the WS 4500 yarn, which is crystalline initially, the same tendencies are seen but are mainly confined to changes in the background scatter.

Raising the temperature to 180°C (Table III) does not substantially alter the facts. On initial contraction, very little crystallization takes place. Indeed, under 0.16 g/tex tension, the WS 3000 yarn contracts 37% and still gives an X-ray diagram similar to that of the original PO yarn. On reextension, crystallization takes place and orientation improves as the extension becomes greater. Again the observations for the WS 4500 yarn are mainly confined to the background, which weakens in intensity on extension of the yarn suggesting crystallization of random material on to the crystalline material present. This type of pattern of changes is repeated at 210°C with differences in the degree of orientation or lateral order achieved. In general, there is a greater extension the higher the temperature for any given yarn and tension, and although it was not measured, there appears to be better lateral order in the crystalline regions at the higher temperatures.

Experiments were also carried out in hot water; the results given in Table V should be compared with those in Table II since the temperatures involved are not greatly different. Little difference is found in the results, but there is an impression that the presence of water has aided crystallization to a small extent. Carrier (Palanil A) added to the water did not appear to cause any marked change in the results.

The X-ray diagrams have shown that during the shrinkage experiments biaxial orientation takes place, the (100) plane being the main plane to be preferentially oriented. The (100) plane must therefore be one of the most extended planes of the crystalline array, and the nature of the molecular orientation in this plane must be of importance to the crystallization process. The simplest mechanism to allow an extended (100) plane would be a structure constructed of extended chains, but the X-ray evidence alone cannot be advanced to prove such a structure. If regular chain folding is a mechanism of crystallization, it seems strange that under the influence of heat and under the relaxation conditions of initial contraction, extensive crystallization does not take place but does take place during extension conditions not favourable to chain folding.

Birefringence

Further evidence of the orientation of molecules can be obtained from birefringence measurements (Table VI). However, changes in birefringence can be brought about simply by density changes without necessarily involving orientation of chains but such changes are relatively small; major changes in birefringence must imply changes in molecular orientation.

With the WS 3000 yarn during the initial contraction phase, the birefringence falls at all tensions that permitted this phase to occur. Such a fall in birefringence does not necessarily imply that the chains that contributed to the birefringence of the initial PO yarn are themselves being randomized (although this is possible) but that the aggregations involving these chains are becoming randomly oriented. Of course, due to the shrinkage, density changes may also be playing a part in the fall of birefringence since the changes are relatively small. What is important with this yarn is that even with a small shrinkage, the birefringence reduces slightly from that of the control. On extension after initial contraction, the birefringence rapidly increases even though the tension is insufficient to draw the yarn back to the initial length; and when the initial length is exceeded, the birefringence is that of a well-oriented yarn especially when the length has exceeded the initial length by some 70%.

If these birefringence measurements are compared with the X-ray indications of orientation, it will be seen that the main changes on extension are associated with the crystallization process and the orientation of the crystallites. In really well-oriented polyester fibers, birefringences of 0.22 have been recorded so that the orientations achieved under the present experimental conditions are not optimum.

The WS 3500 yarn shows somewhat similar features; but another factor is becoming evident, and that is the influence of the original winding speed used for the PO yarn. As expected, the original birefringence is higher for WS 3500 than WS 3000 yarns and depends on the orientation of the molecules imparted during the spinning operations. In the initial contraction region, the birefringence does not fall to zero but does vary with the applied tension. The forces operative in this phase are an elongation tendency due to the tension and an entropy factor that leads to a relaxation of the network regions. The tension will tend to keep molecules aligned and the entropy will tend to randomize molecules, the birefringence indicating a balance between these factors. On extension even under the lowest tension, there is an increase in birefringence over that of the original, although the length of yarn is almost half that of the original. When the yarn is virtually back to length (tension = 0.18 g/tex), the birefringence is high (0.1339). And although finally under the highest tension the yarn is only extended about 50% beyond the original length, the birefringence is higher ($\Delta n = 0.1731$) than for a corresponding experiment with the WS 3000 yarn ($\Delta n = 0.1720$), where the extension was 70% beyond the original length. Such results can easily be explained on the assumption of a network phase and a crystalline phase, both contributing to the birefringence but only the network phase contributing to the dimensional changes with the ratio and interaction of the two phases varying in a complex way.

With the WS 4000 yarn, even during the initial contraction phase the birefringence increases over that of the control with the higher tensions used with that phase. On extension even under the smallest tension, there is a marked increase in birefringence even though the yarn is still at a reduced length. Under the highest tension used, the yarn extends some 30% above the original length, but the birefringence is again 0.1707, near the values found under corresponding conditions despite the lower extension. Again, reference to a two-phase structure can explain such a result.

The yarn WS 4500 presents a special case because it is crystalline initially and shrinks only about 5% with the smallest applied tension. At this stage, the birefringence is greater than that of the original yarn despite the shrinkage, and high birefringences are given for shrunk yarn under higher tensions. On extension, the birefringence increases but does not reach 0.17 even with the highest tension employed. Thus, with a tension of 2.37 g/tex, the extension is almost 20%, but the birefringence is 0.1663, less than found with the other yarns under corresponding conditions. It would seem therefore that the network phase must have cohesion points that limit the full extension and orientation possible with this yarn. Presumably to some lesser degree depending on the original orientation, such cohesion points are present in the network phases of the other yarns and are probably not crystalline in nature.

These data suggest therefore that a pattern of orientation and cohesion points is built into the morphology of the PO yarns, depending on the mechanism and thermal history of the yarns. This pattern then has a part to play in all subsequent mechanical and thermal treatments of the yarns.

Infrared

The absorption bands of poly(ethylene terephthalate) are of two types[7]: those that are structure and orientation sensitive, and those that are only sensitive to orientation, the latter being used for calibration with respect to the thickness of the specimen. Of the bands chosen for study, the 848, 896, 973, and 1042 cm^{-1} bands are both structure and orientation sensitive, while the 795 and 875 cm^{-1} bands are orientation sensitive only. The 795 cm^{-1} band was used for calibration purposes.

Since the absorption of the structure-sensitive bands is a complex of the effects of both structure and orientation, the effects of orientation can be eliminated by either the use of the mean absorbance in the two 45° positions or by the use of the isotropic absorbance as defined by Baranova et al.[8] as

$$E(\text{iso}) = \frac{E(\text{parallel}) + 2E(\text{perpendicular})}{3}$$

a formula similar to that used for the isotropic birefringence. The orientation effects could be partly investigated by the dichroic ratio of the 795 and 875 cm^{-1} bands, which are assigned[9] to the in-plane and out-of-plane frequencies of the phenyl group of the polyester molecule. Only the orientation of the phenyl part of the molecule can be obtained in this way and not the orientation of the molecular axis, which has to be inferred by reference to other data.

Although the spectra were examined carefully, no evidence of the so-called regular fold band[10] at 998 cm^{-1} was detected in any of the specimens. This band has been detected in other experiments with poly(ethylene terephthalate) by the use of the same technique but was absent in the present series.

Figure 5 shows the plot of the dichroic ratio of the 795 and 875 cm^{-1} bands at different stages of the contraction–extension process at 180°C under a tension of 0.16 g/tex/thread. By the definition of the dichroic ratio, it can vary from unity for complete randomness to infinity for in-plane vibrations (band 795 cm^{-1}) or to zero for out-of-plane vibration (band 875 cm^{-1}) of the phenyl group for complete orientation. It is seen therefore that in the region of maximum contraction (specimen length region 67.4 to 74 cm) the state of random orientation is approached. In extension from a specimen length of 74 to 100 cm, orientation of the phenyl group occurs but does not improve much on extension beyond the original length. It is difficult on this evidence alone to assess the general orientation of the molecular axis. But since the specimen length is also increasing, it is inferred that the molecular axis orientation is also taking place, which is also supported by the birefringence evidence already discussed.

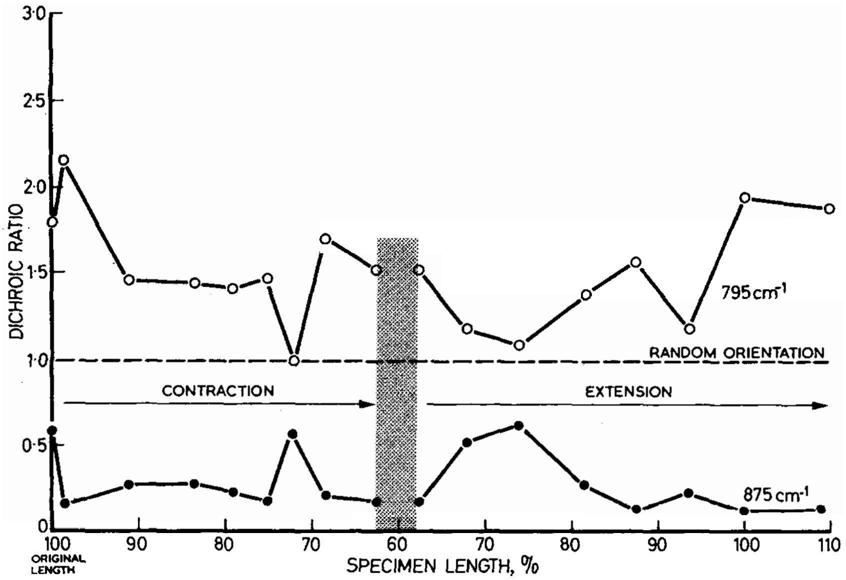

Fig. 5.

Figures 6–9 show the plot of the E(mean 45°) and E(iso) absorbances vs. the specimen length for the bands at 848, 896, 973, 1042 cm^{-1}. The plots of E(mean 45°) and E(iso) vs. specimen length for corresponding bands are remarkably similar and differ only in details for the trend of results. This might be expected since the E(mean 45°) and E(iso) absorbances represent the concentration of the given structural factors in a sample measured in two ways. In consequence, only the E(iso) results will be discussed, the E(mean 45°) results serving as confirmatory evidence.

The 848 and 896 cm^{-1} bands have been assigned[6] to the CH$_2$ rocking mode

Fig. 6.

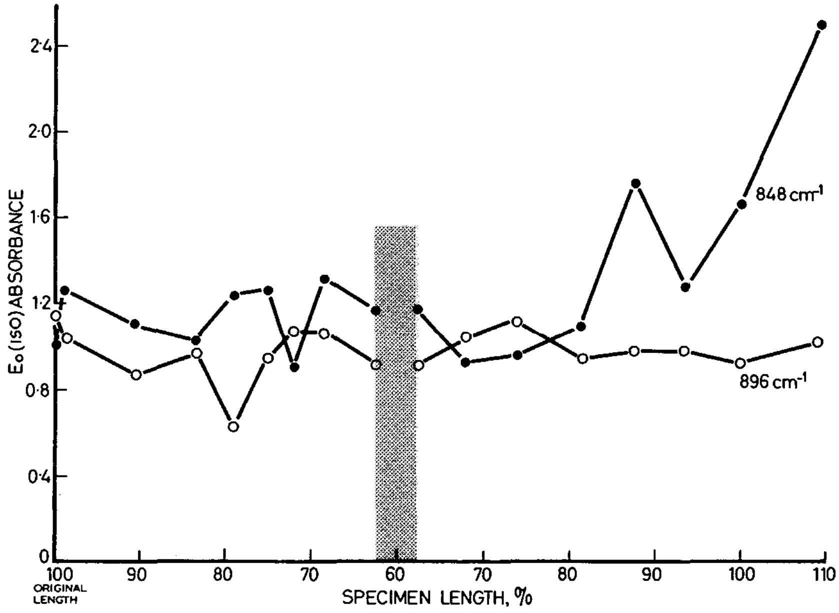

Fig. 7.

in the trans and gauche configurations, respectively. Figures 6 and 7 show the absorbancies of these bands vs. specimen length during the contraction–extension process at 180° under a tension of 0.16 g/tex/thread. There does not seem to be any general trend in the results during contraction; but in extension beyond a length of 74 cm, the intensity of the trans configuration markedly increases

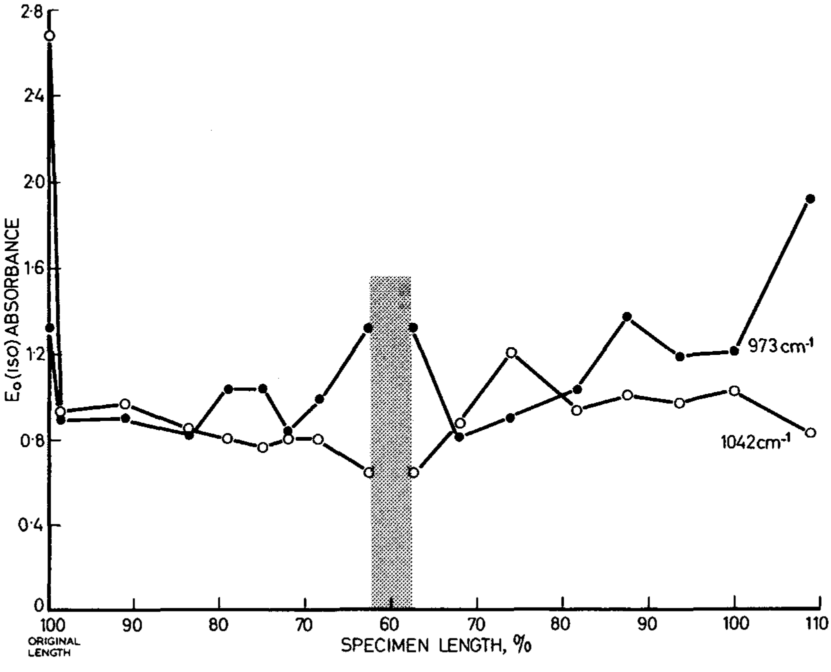

Fig. 8.

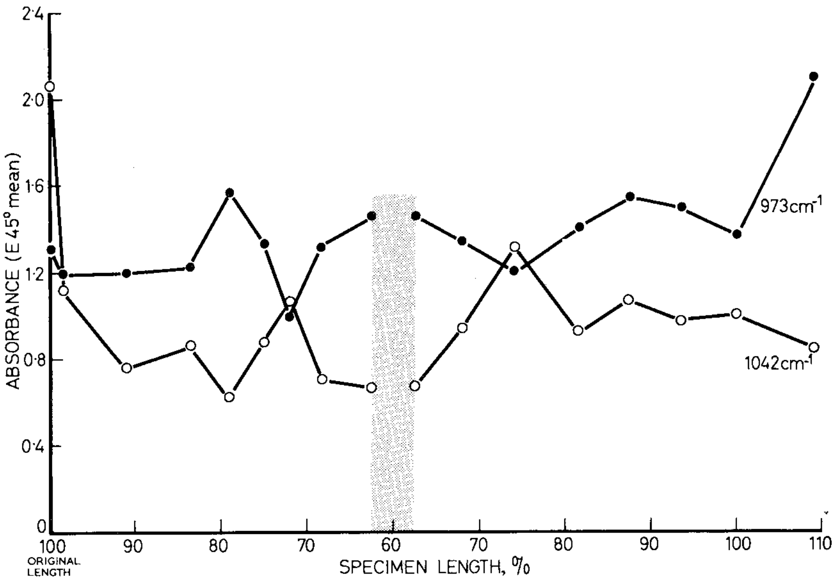

Fig. 9.

while the concentration of the gauche configuration hardly changes. Similar effects have been found by Baranova et al.[8,11] and have been attributed to intermediate configurations of the glycol group being present which do not contribute to either the trans or gauche band intensities but do so on transformation into these configurations. The conclusion to be drawn from these results is that chain extension is taking place during the extension process since the trans configuration is consistent with extended chains. The X-ray evidence shows that it is in this same region of specimen length that crystallization starts to occur and increases as the specimen elongates. Furthermore, the birefringence must also increase rapidly in this region to account for the high birefringence found for extended specimens and the extremely low birefringences of contracted samples. It therefore can be concluded that the crystalline regions are formed from extended chains.

Somewhat similar evidence can be deduced by consideration of the infrared absorbances of the 973 and 1042 cm^{-1} bands. These bands have been assigned[6] to the trans and gauche configurations of the C—O stretching mode. Figures 8 and 9 show the variation of E(iso) and E(mean 45°) vs. specimen length of these bands during the contraction–extension experiment at 180°C. There is a remarkably large drop in the intensity of the gauche band (1047 cm^{-1}) at the commencement of shrinkage without any corresponding increase in the intensity of the trans band (973 cm^{-1}), which seems to imply that intermediate configurations can form that do not contribute to the intensity of either band. Since free rotation around the CH_2—CH_2 bond is expected, such intermediate states at higher potential energies than the preferred states are not unlikely. At maximum contraction, there is a rise in the intensity of the trans band and a fall in the intensity of the gauche band, but this is virtually eliminated on slight extension: the significance of this is not clear. On extension above a specimen length of 74 cm leads to an increase in the trans configuration typical of extended chains and a slight fall in the gauche configuration. When the original length

(100 cm) of the specimen was exceeded, there was a more marked increase in the trans configuration and decrease in the gauche configuration. This evidence again supports extended-chain crystalline regions in the polyester.

The infrared results therefore indicate that during extension of the sample back to its original length after initial contraction, chain extension takes place, and that when back to its original length, chain extension is quite marked. In the conditions of the experiments, it might be questioned whether the polyester yarn was at the temperature of the oven. Since the contraction process took at least 1 min and the extension process took up to 15 min, it can be expected that, at least in the extension cycle, the yarn was at the temperature of the oven. This implies that temperature alone does not crystallise the yarn but a positive tension is required as well, which is consistent with the formation of extended chains during the extension process as indicated by the experimental evidence. If the band at 988 cm^{-1} is interpreted as evidence of regular folded chains, then its absence in the infrared spectra of all these specimens must support extended chains as suggested.

The interpretation of the 988 cm^{-1} infrared band as a regular fold band is however called into doubt by the type of evidence given here. Koenig and Hannon[10] did not detect this band in highly stretched polyester film but did so after annealing under tension at 200°C. They recorded that before annealing the band at 973 cm^{-1} (C—O stretching frequency trans configuration of the glycol group) was intense and increased in intensity during annealing. The experiments described in the first part[1] suggest that such annealing took place under a high tension due to restrained shrinkage, the conditions for causing better lateral order in the crystalline phase as has been shown in other work,[12] and not those under which chain folding could occur. Indeed, these are the conditions under which modification of infrared bands would be expected due to induced crystalline coupling as put forward by Miyake[6] who attributed the 988 cm^{-1} band to this effect. The fact that the 988 cm^{-1} band also occurs in the infrared spectra of the crystalline linear trimer[6,10] where folding is impossible confirms this assignment. It is artificial to expect a different explanation in a polymer of the 988 cm^{-1} band from that in a definite crystalline material, especially since the data from the polymeric material are also caused by crystallization. Thus, the experimental evidence given by Koenig and Hannon as the basis for regular chain folding can readily be interpreted in terms of a two-phase polyester structure and crystalline coupling causing the 988 cm^{-1} band to appear on close packing of the crystalline regions.

In other work on polyester yarn heated to 230°C under tension, it was found that the 988 cm^{-1} band could be detected by the same technique as employed here. X-Ray diffraction carried out on this yarn showed it to be highly oriented and with a high lateral order in the crystalline phase. The interpretation of the 988 cm^{-1} band as a crystalline coupling band is more consistent with these results than an interpretation based on chain folding and thus offers some confirmation that this interpretation of the 988 cm^{-1} band is more logical.

CONCLUSIONS

The partially oriented yarns WS 3000, 3500, and 4000 have been shown by X-ray diffraction to be noncrystalline. If these yarns are allowed to shrink at different temperatures up to 210°C under small tensions, the shrinkage is found to be high (30–40%), and yet little or no crystallization takes place at this stage despite the fact that the yarn has been heated long enough to reach the temperature of the oven. The shrinkage appears to be mainly an entropy effect of a rubberlike network of chains and therefore probably involves random folding and kinking of chains as in rubber. Such conditions should be favorable to regular chain folding and crystallization if this is the mode of crystallization in poly(ethylene terephthalate), but in fact the X-ray evidence shows that little or no crystallization takes place. The birefringence is consistent with a largely amorphous network of chains, and the infrared evidence shows that a mixture of trans and gauche configuration of the glycol group is present. No so-called regular chain fold band at 988 cm^{-1} was detected in the infrared spectra.

Only on extension from the contracted position is there evidence of extensive crystallization and orientation. The birefringence values increase rapidly, and an increase in the trans configuration of the glycol grouping is also shown by the infrared evidence.

The simplest explanation of such phenomena is that straight-chain crystallization takes place which from the X-ray evidence appears to be most extensive in the (100) plane giving rise to a biaxial orientation process. Complete crystallization does not take place since there is still evidence of a noncrystalline portion being present even when the original length of the specimen has been exceeded. The concept that polyester exists in two phases, one a network phase and the other a crystalline phase, can readily explain these data if it is assumed that it is possible for some of the network to be transformed to the crystalline phase during the extension process.

The sample of partially oriented yarn WS 4500 is a special case because it is crystalline in the first place yet perfectly capable of being drawn, even by hand, in the cold. Its shrinkage behavior can be treated in the same way as that of the other PO yarns if it is assumed that the shrinkage and extension behaviour is confined to the network phase only, the crystalline phase moving only in consequence of its relationship with the network phase. The evidence both from the X-ray and infrared data seems to justify this conclusion. The shrinkage does not destroy the crystallization phase. If anything, there is some evidence of a slight increase of crystallization during shrinkage. Shrinkage therefore appears to be a function of the network phase, the extent being a function of the type of network, which will also control the shrinkage forces involved. Extension appears to result in some transformation of the network phase to the crystalline phase as well as contributing to the general orientation of both phases.

In the first part[1] it was noted that the shrinkage force was greatest during the initial contraction stage, but this force decayed, as was shown also in more detailed experiments by Pinnock and Ward.[2] A partially oriented yarn held to length while being heated crystallises as shown by subsequent X-ray diffraction experiments. The same yarn heated freely with a small tension does not crystallize in the fully shrunk state, so that it is implied that the molecules in the restrained state must orient along the line of stress in such a way that crystallization is possible. From the evidence already discussed, such crystallization would be expected to involve extended chains. This type of crystallization might be expected from all the PO yarns during shrinkage if any internal or external restriction is encountered. Internal steric factors such as random kinking of chains might cause local stresses to be set up by this effect and induce a limited amount of crystallization even under free shrinkage. However, a small tension allowing some of these internal stress concentrations to be removed by causing small rotations of the glycol parts of the chain could limit the crystallization during shrinkage as has been found.[1]

The general scheme of shrinkage is not dissimilar to that envisaged by Wilson[4] in that the shrinkage is attributed to the dimensional changes in the network phase and not in the crystalline phase of the polymers. The preferred interpretation of the 988 cm^{-1} infrared band as a crystalline coupling band can also be applied successfully to the results of Wilson, thus obviating the necessity of involving regular chain folding in the crystallization stage. The fact that the 988 cm^{-1} band decreases in intensity on restretching as found by Wilson[4] can be seen as a decoupling due to stress in the crystalline regions together with the effects of peak overlap phenomena caused by an increase in the intensity of the 973 cm^{-1} band relative to the 988 cm^{-1} band.

The experiments described confirm the general two-phase structure of polyester[2–4,13] and strongly suggest that the crystalline phase is composed of extended chains.

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Received September 2, 1980
Accepted February 18, 1981