X-ray diffraction study of solvent-induced crystallization in polyester filaments *

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The present paper attempts to characterize the solvent–fibre interactions in oriented poly(ethylene terephthalate) filaments from measurements of the degree of crystallinity using wide-angle X-ray diffraction. It is shown that the solvent-induced crystallinity is dependent on the solubility parameter of the solvent. An increase in temperature has a favourable effect on the solvent-induced crystallization for most solvents. The degree of solvent-induced crystallinity is linearly related to the shrinkage of filaments. However, the crystallization of PET molecules can occur even if the shrinkage of filaments has been prevented.

INTRODUCTION

Solvent finishing of polyester or polyester–cotton blend textiles is currently in vogue[1]. The interaction between polyester and organic solvents has considerable relevance to non-aqueous dying and finishing of synthetic textiles. For instance, it is known[2] that pretreatment of poly(ethylene terephthalate), PET, with organic solvents, leads to an increase in dye uptake and the rate of dying. Surface oligomers are also believed to be removed in this process[3].

The interaction between the polyester fibres and various organic solvents has been studied by a variety of techniques, such as the load–extension behaviour[4], critical dissolution time[5], shrinkage[6], surface structure[7], etc. It has been reported[8,9] that the interaction shows a bimodal character when expressed as a function of the total solubility parameters of the solvents, indicating specific solvent interactions with the aromatic and aliphatic parts of PET molecules.

Solvents are able to penetrate and swell the PET matrix, and lead to structural pore formation and a plasticization of structure by lowering the temperature at which the glass transition occurs. Solvents thus promote the crystallization of amorphous regions in PET filaments. The solvent-induced crystallinity in PET has been studied by the techniques of scanning electron microscopy[7,10], density[11], infra-red spectroscopy[12], and light scattering[10]. The present work attempts to study solvent-induced crystallization in semicrystalline, oriented PET filaments from X-ray diffraction measurements of the degree of crystallinity in untreated and solvent-treated filaments. The induction of crystallinity has been studied at 65°C and also at the boiling temperatures of various solvents. The PET–solvent interaction has been characterized by crystallinity and shrinkage measurements.

EXPERIMENTAL

Material

Poly(ethylene terephthalate) used in this work was obtained from J. K. Synthetics Ltd, Kota. It was in the form of commercially drawn 24 denier multifilament with 76 filaments and zero twist.

The organic solvents were of reagent grade and were freshly distilled. The solubility parameter values for the materials have been reported elsewhere[13].

Treatment

About 0.5 g of the PET filament made into a small skein and weighed accurately was placed in a stoppered conical flask containing an organic solvent and equilibrated in an oil thermostat set at a desired temperature. The amount of the solvent in the flask was sufficient to cover the PET sample and to remove the spin finish from the latter completely. The flask was continuously shaken mechanically. The filaments were allowed to remain with the solvent in a relaxed state for a definite period of 2 h‡ at a given temperature in case of all solvents. The solvent-treated PET sample was rinsed with some fresh solvent and centrifuged in order to remove the adhering solvent. The occluded solvent was further removed from the sample by keeping it for 2 days in a continuously evacuated potassium hydroxide desiccator provided with a fine air leak. The sample was then kept under a high vacuum for two days.

For treatment at constant length, the filaments were mounted parallel on a device having two brass discs, one with a threaded brass rod fixed at its centre and the other moving coaxially on the latter. The entire device with the filaments wound on it could be immersed in the solvent, contained in a loosely stoppered wide glass jar. After the treatment, the adhering solvent was removed from the sample while still being maintained at constant length.

Another variation of treatment was given by keeping the PET filaments in a slack state during the solvent treatment and stretching them to their original length after removing the solvent.

The filaments were heat treated with silicone oil in a slack state. Most of the silicone oil was removed from the sample

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[‡] This treatment time was chosen on the basis of the observation that the PET filament reaches a near shrinkage equilibrium in all the solvents used here, even at the lowest temperature of treatment employed. Hence this duration of treatment was assumed to be sufficient to allow maximum structural changes in the polymer due to the treatment.

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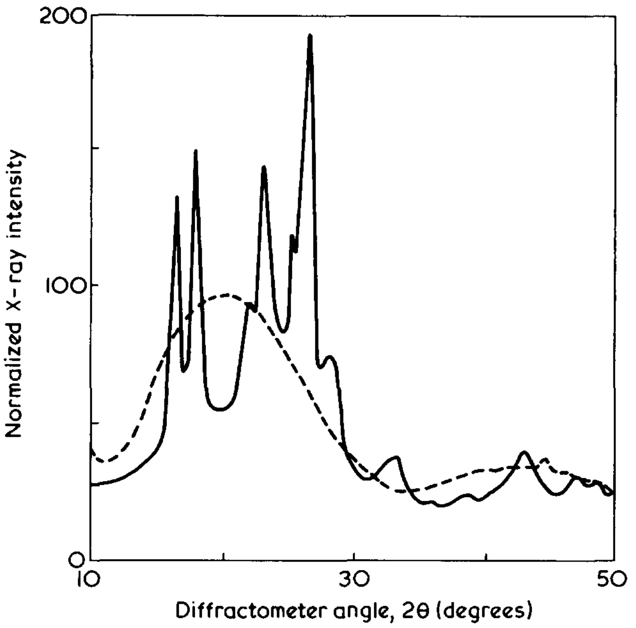

Figure 1 Powder X-ray diffractograms of the reference 'crystalline' and 'amorphous' standards for poly(ethylene terephthalate)

by centrifuging but the remaining traces were eliminated by washing the sample with small amounts of chilled n-hexane in which the silicone oil is highly soluble and which is practically inert[4] to PET.

Shrinkage

The apparatus employed for the measurement of equilibrium isothermal shrinkage of PET filaments in the organic solvents was similar to the one described earlier[6]. A small steel weight of 51 mg was attached to the lower end of the PET filament yarn, producing a stress of 6.71×10^{-4} gpd. The oil thermostat was controlled to within ±0.1°C and the filament length was measured by means of a cathetometer.

X-ray diffraction

Equatorial and powder X-ray diffractograms of PET filaments were studied in a transmission set-up, employing CuKα radiation. Equatorial diffractograms were obtained from a parallel bundle of filaments, mounted on a specimen holder designed especially for this purpose. Powder diffractograms were obtained from pellets prepared from a finely cut powder of filaments. Filaments were chopped into small pieces and powdered using a Wiley mill. A 150 mg portion of the cut material was pressed under a pressure of about 200 kg/cm^2 into a pellet of 11 mm diameter. This pellet could be mounted in the specimen holder of the diffractometer in the usual manner and rotated in its own plane by means of a motor. The X-ray diffraction from filaments and powders was studied on a vertical Philips diffractometer (PW 1050) equipped with a curved crystal focalizer (PW 1075) and aligned in a transmission set-up. The diffracted beam was monitored by a scintillation detector, used in conjunction with a Philips pulse height discriminator (PW 1355) to monochromatize the diffracted intensity. The slit system used was: divergence slit 4°, receiving slit 0.3 mm, and no scatter slit.

The degree of crystallinity was measured by the correlation method due to Wakelin *et al.*[14] which was applied to poly(ethylene terephthalate) by Statton[15]. This method involves a comparison of the powder diffraction of a given sample with diffraction from the reference 'crystalline' and 'amorphous' standards, over a wide range of diffraction angles. The powder X-ray diffractograms of the reference standards are shown in *Figure 1*. The crystalline standard was obtained by annealing PET at 260°C while the amorphous standard was obtained from a freshly spun tow of filament. A computer program was written for the estimation of the degree of crystallinity with an IBM 360 computer. Intensity data read at intervals of 0.5° in 2θ formed the input for the program The details of this procedure have been discussed in a recent review[16].

The procedure outlined above was used to obtain the overall crystallinity values for untreated polyester filaments, filaments treated with organic solvents at different temperatures, and also for filaments which were heat-set in silicone oil at different temperatures, varying from 40° to 160°C. Measurements of crystallinity were made at room temperature (27°C) under ambient conditions. The solvent-induced crystallinity (C_S) at any given temperature was obtained by subtracting the thermally-induced crystallinity (C_T) from the overall crystallinity (C) of the solvent-treated polyester:

$$C_S = C - C_T$$

Since the silicone oil does not chemically interact with PET, the estimates of C_T were obtained from a plot of crystallinity of PET filaments heat-set in the silicone oil as a function of temperature (*Figure 2*).

RESULTS AND DISCUSSION

Figure 2 illustrates a plot of the heat-induced degree of crystallinity of PET filaments as a function of temperature. The crystallinity of PET increases with initial rise in temperature up to 50°C and then drops at the onset of the glass transition. The crystallinity of PET reaches a minimum value at 90°C, which is even lower than the crystallinity of the control sample. Above 95°C, the crystallinity shows a steady increase with rising temperature. From the crystallization minimum (*Figure 2*) it is seen that the glass transition temperature for the PET control sample lies in the vicinity of 90°C.

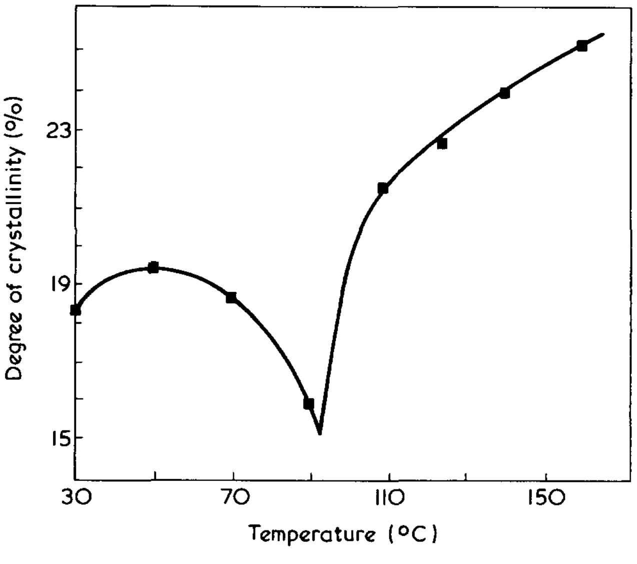

Figure 2 Plot of the degree of crystallinity vs. temperature for PET filaments heat treated in silicone oil

Equatorial X-ray diffractograms of untreated and solvent-treated PET filaments are shown in *Figure 3*. The interaction of nitrobenzene and s-tetrachloroethane with PET at 65°C leads to the growth of lateral crystallite dimensions, as is evident from the improvement in the resolution of equatorial peaks (*Figure 3*). However, no new peaks appear in the diffraction pattern thereby indicating that the untreated and solvent crystallized PET filaments have the same crystalline unit cell. The solvents thus serve only as plasticizing agents and the presence of stoichiometric amounts of solvent of crystallization in the lattice can be ruled out on the basis of present evidence.

The effect of temperature on the solvent-induced crystallization of PET is demonstrated by the powder X-ray diffractograms in *Figure 4*. It is readily seen that the diffractograms of PET filaments treated with nitrobenzene and benzyl alco-

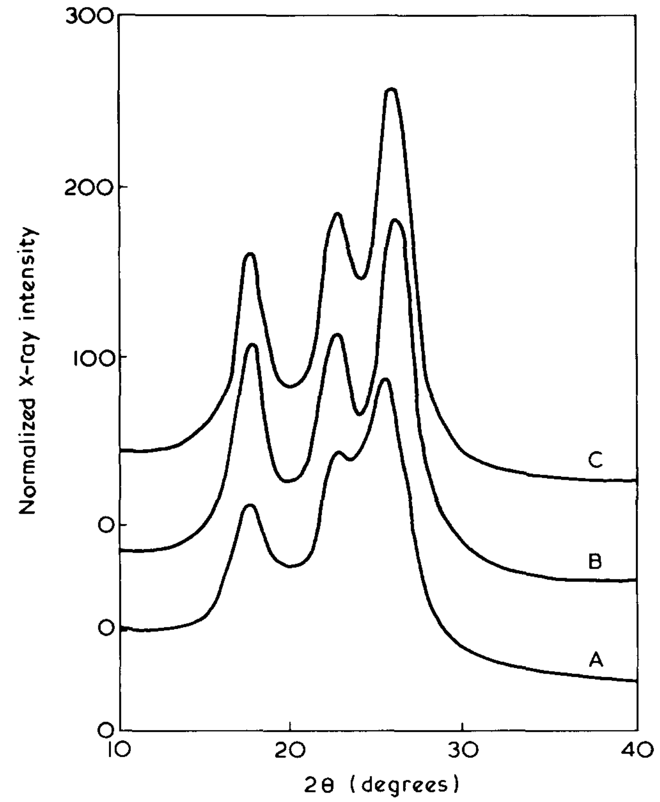

Figure 3 Equatorial X-ray diffractograms of PET filaments: A, untreated; B, treated with s-tetrachloroethane at 65°C and C, treated with nitrobenzene 65°C

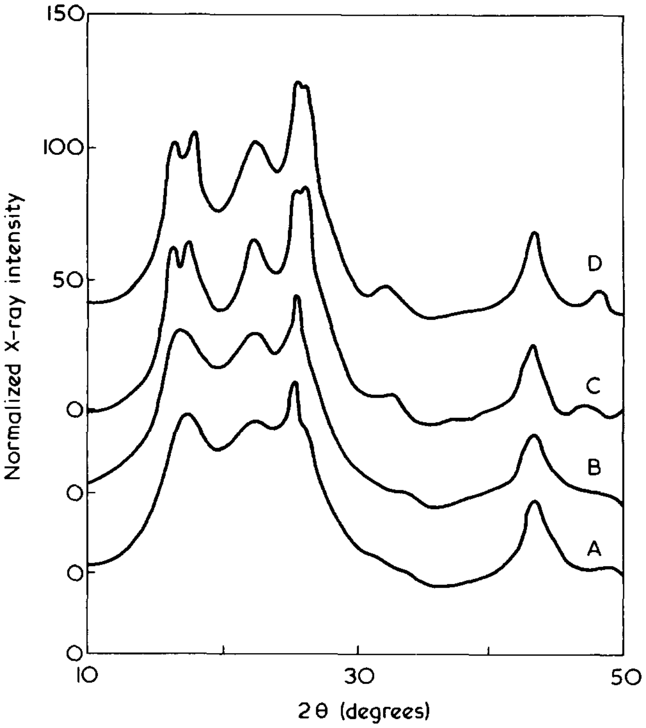

Figure 4 Powder X-ray diffractograms of PET filaments: A, untreated control; B, heat treated with silicone oil at 140°C; C, treated with benzyl alcohol at 140°C and D, treated with nitrobenzene at 140°C

Table 1 Solvent-induced crystallization in poly(ethylene terephthalate) at different temperatures

Serial No.	Organic Solvent	Abbreviation	Solubility parameter (δ)	Interaction temperature T(°C)	Degree of crystallinity (%) Total C	Thermally induced C_T	Solvent-induced $C_S = (C - C_T)$
1	Control	C	10.7	30	18.4	18.4	–
2	Water	WA	23.4	65	19.9	18.9	1.0
3	Water	WA	–	100	22.3	19.4	2.9
4	Acetone	AC	9.62	56	22.0	19.3	2 7
5	1,1,1-Trichloroethane	TE	9.88	65	19.1	18.9	0.2
6	Perchloroethylene	PER	9.36	65	23.3	18.9	4.4
7	Dioxane	DX	10.13	107	36.2	21.1	15.1
8	Trichloroethylene	TRI	9.16	65	24.1	18.9	5.2
9	Trichloroethylene	TRI	9.16	87	28.7	16.6	12.1
10	Dimethylformamide	DMF	11.79	65	25.0	18.9	6.1
11	Dimethylformamide	DMF	11.79	140	42.3	24.0	18.3
12	Chlorobenzene	CB	9.67	65	28.2	18.9	9.3
13	Chlorobenzene	CB	9.67	132	32.7	23.5	9.2
14	s-Tetrachloroethane	TCE	9.85	65	29.2	18.9	10.3
15	s-Tetrachloroethane	TCE	9.85	100	41.7	19.4	22.3
16	Nitrobenzene	NB	10.0	65	30.0	18.9	11.1
17	Nitrobenzene	NB	10.0	140	43.7	24.0	19.7
18	Benzyl alcohol	BZA	12.05	65	30.2	18.9	11.3
19	Benzyl alcohol	BZA	12.05	140	45.8	24.0	21.8
20	Methyl salicylate	MS	10.2	65	32.1	18.9	13.2
21	Methyl salicylate	MS	10.2	140	39.4	24.0	15.4

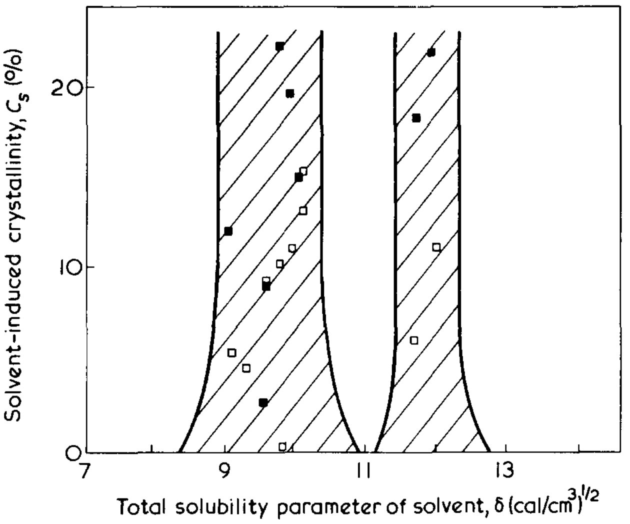

Figure 5 Plot of solvent-induced crystallinity against solubility parameter of solvents at different interaction temperatures: □, 65°C; ■, boiling points

Table 2 Effect of stretch on the crystallinity of solvent-treated PET filaments. Solvent, nitrobenzene; temperature, 65°C

Serial No.	Conditions of treatment	Degree of crystallinity (%)
1	Filaments slack treated	30.0
2	Filaments slack treated and stretched to original length	28.5
3	Filaments treated at constant length	29.0

hol at 140°C are sharper and better resolved than the diffractogram of filaments heat treated in silicone oil at 140°C. Thus solvents induce appreciable crystallization at higher temperatures, over and above that caused by heat alone.

Table 1 summarizes the results of measurement of solvent-induced crystallinity in PET at 65°C and also at various temperatures corresponding to the boiling points of different solvents used in the present study. It can be seen that the interaction between PET and organic solvents occurs to different extents. Water, acetone and trichloroethane do not have much effect on the crystallinity of PET. At 65°C, trichloroethylene, perchloroethylene and dimethylformamide cause only a moderate increase in the crystallinity of PET, whereas chlorobenzene, s-tetrachloroethane, nitrobenzene, benzyl alcohol and methyl salicylate interact strongly with PET and induce a much higher level of crystallization. The solvent-induced crystallization increases with a rise in temperature in case of most of the solvents. This may be attributed to the increase in solvent power of solvents at higher temperatures. However, from the data given in *Table 1* it is evident that the crystallinity of solvent-treated PET never exceeds 45% and is therefore much lower than the maximum crystallinity attainable by heat treatment. A comparison of X-ray diffractograms of *Figures 1* and *4* serves to establish this point, if it is kept in mind that the 'crystalline' standard is prepared by the heat treatment of PET.

Figure 5 shows a plot of solvent-induced crystallinity in PET as a function of the solubility parameter (δ) of different solvents. It is seen that there is appreciable solvent-induced crystallization in the regions of solubility parameter around δ = 10 and 12. For PET, δ = 10.7. The vertical lines and the shaded areas confined between them (*Figure 5*) represent Hildebrand solubility parameter distributions[8] of the interaction of non-aqueous solvents with oriented semicrystalline PET filaments. The solvent-induced crystallization at δ values of 10 and 12 is assocaited with specific interactions of solvents with the aromatic ($-CO-C_6H_4-$) and aliphatic ($-O-CH_2-O-CO-$) parts of the PET molecules, respectively.

The effect of stretch during the solvent treatment on the degree of crystallinity attainable is shown in *Table 2*. It is apparent that the level of crystallization attained by PET molecules is unaffected by the fact that the shrinkage of filaments has not been allowed to occur. This confirms the earlier findings of Knox[9] that the interaction between solvents and PET takes place at the molecular level only and is largely unaffected by the molecular chain orientation and the morphology of PET.

The relationship between the solvent-induced crystallinity and the solvent-induced shrinkage of PET filaments is shown in *Figure 6*. It is seen that an increase in crystallinity is associated with a proportionate increase in the shrinkage of filaments. Although the relationship between crystallization and shrinkage appears to be linear, the data points for various solvents seem to fall on two different straight lines (*Figure 6*). It is very interesting to observe that all data points corresponding to aromatic solvents fall close to the same line. Thus it might be possible that these lines distinguish aromatic solvents from the aliphatic ones and represent interactions of solvent with the aromatic and aliphatic parts of the polyester molecule, respectively. Since the aliphatic ester segment of PET is more flexible than the aromatic residue, interaction with the former results in a greater induced shrinkage than with the latter (*Figure 6*).

CONCLUSIONS

It is shown in the present work that X-ray crystallinity is a property which can characterize the PET–solvent system very well. Solvents are able to induce crystallization in PET,

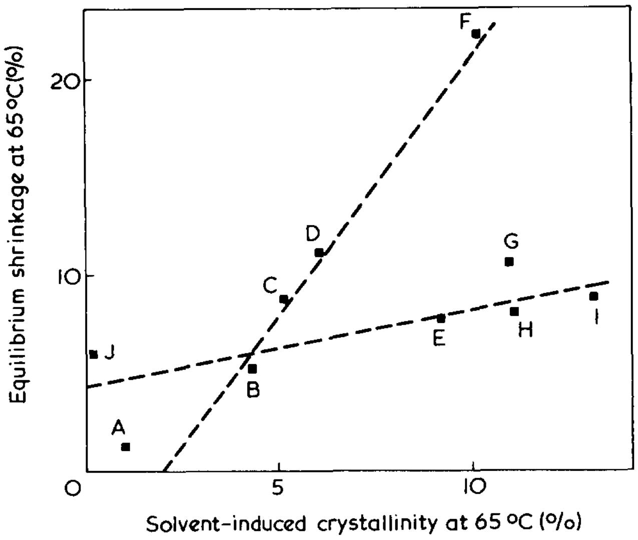

Figure 6 Relationship between the solvent-induced shrinkage and the solvent-induced crystallization: A, Water; B, perchloroethylene; C, trichloroethylene; D, dimethylformamide; E, chlorobenzene; F, s-tetrachloroethane; G, nitrobenzene; H, benzyl alcohol; I, methyl salicylate; J, 1,1,1-trichloroethane

even when the filaments are not allowed to shrink during the treatment. The extent of solvent-induced crystallization is greater at higher temperatures. The solvent-induced crystallinity can be conveniently interpreted in terms of the solubility parameter concept. The relationship between the solvent-induced crystallinity and the shrinkage of PET filaments may be useful in providing information regarding the (aromatic/aliphatic) sites of interaction between PET and solvents. The X-ray diffraction method thus offers considerable potential in characterizing the solvent finishing of polyester based textiles.

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