Some Studies on Thermal Treatments of Polyester Fibers: Structural Changes

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ABSTRACT: The development of the changes of structure during thermal treatment of polyester fiber is studied. Critical dissolution time (CDT) was evaluated to trace the changes in crystallinity and crystal morphology of polyester fibers. CDT increased as the time of thermal treatment was increased. The change in CDT was less effective for samples thermally treated at temperatures up to 160°C, which may indicate a nucleation tendency of tiny crystals. CDT of polyester treated at 200°C in air was found to be relatively high, while silicon oil medium can affect both amorphous and crystalline regions, increasing the structure disorder. The effect of treatment under constant length revealed smaller CDT values than those attained by samples treated in free conditions. An indication to crystal size increase was traced by a decrease in peak width in X-ray diffraction pattern. Thermal treatment increased the crystallinity of polyester fibers up to 160°C. Dry air medium was more effective in increasing the disorder in amorphous regions than silicon oil medium. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2773–2780, 1997

Key words: polyester fibers; thermal treatment; polymer structure; critical dissolution time; X-ray diffraction

INTRODUCTION

In thermal treatment, thermoplastic polymers are brought up to a certain temperature called annealing temperature. The material is usually kept at this temperature for a definite period of time, then slowly or rapidly cooled to room temperature. The thermal treatment followed by cooling is defined as annealing technique.[1] The main effect of annealing is to increase the density, which improves heat resistance, impact strength, and prevents crazing and cracking. Annealing may also bring about changes in the nature of the crystalline state which, in turn, is governed by the nature of the crystal structure, degree of crystallinity, size, and orientation.[1]

It is necessary to follow the crystallization process of the polymeric fiber in order to show how the processing conditions affect its morphology. The final microstructure after a long-term annealing was related to the processing conditions.[2] Studies on the kinetics of crystallization of polymeric fibers have demonstrated that most of the transformation takes place at annealing times of the order of tens of milliseconds.[3–5] Microstructural changes can then be monitored at room temperature, using various characterization methods such as X-ray scattering, specific gravity, birefringence, and shrinkage.[2]

Lipp-Symonowicz[6] studied the structural changes of polyester fibers during heat treatment in different media. The crystallinity, molecular orientation, and molecular cohesive energy of polyester fiber were determined after heating in water, dry air, moist air, and superheated steam. The type of medium was found to be important

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for changes in molecular orientation. The nonproportional increase in critical dissolution time in relation to changes in crystallinity of fibers heated to higher temperatures indicated that during the heat process, a specific rebuilding of the fiber structure occurred into a mosaic block structure, causing increases in the molecular cohesion energy of the fiber.[6]

The present investigation is forwarded to study the development of fiber structure during the thermal treatment of polyester fiber. It aims to follow the changes in the microstructure during the crystallization process and to show the extent of variation of the processing conditions on the morphology of the fibers. A trial is performed to characterize the morphological changes induced in the fiber such as critical dissolution time and the X-ray diffraction patterns.

EXPERIMENTAL

Materials

Polyester Fiber

White polyester fabric (78 d tex and 34 filaments) was soaped at 40°C for $\frac{1}{2}$ h, thoroughly washed, and air dried at room temperature.

Chemicals

Chemicals and reagents of pure grade were used in this study. These are ethyl alcohol, phenol, acetone, ethylmethyl ketone, and acetic acid. Pure silicon oil was used as a heating medium.

Thermal Treatment

Treatment in Dry Air

Thermal treatment was carried out in dry closed oven at various temperatures (60°C–220°C) for different time intervals (1–60 min). The treatment was done under two conditions: (1) the samples were free to relax (slack condition), and (2) the samples were held at constant length (taut condition). As soon as the samples were thermally treated, they were quenched in cold water, squeezed, and air dried.

Treatment in Silicon Oil

Polyester samples were thermally treated in silicon oil bath maintained at a fixed temperature within ±3°C. The thermal treatment was carried out under the same condition as in the case of dry air. Instead of water quenching, the oil treated samples were quenched and stirred in cold silicon oil at 20°C. The treated samples were then subjected to vacuum drying to remove excess oil and then washed several times with ethyl alcohol, and finally rinsed with water and dried at room temperature.

Critical Dissolution Time

Critical dissolution time was performed using the Galil method.[7] The yarn loops of ~ 6.0 cm length were mounted on brass clamps and suspended from a brass hook fixed to a perforated cork stopper. A 1-g weight was attached to the loops. The yarn was placed in a tube containing pure phenol and covered with the cork stopper. The phenol was thermally controlled at 60°C. The time of dissolution was determined by the fall of the weight. The average of 20 readings was taken for each sample.

X-ray Diffraction

X-ray diffraction was carried out with a modified Shimadzu (Japan) XRD-610 diffractometer. The diffractometer employs a $CuK_{\alpha i}$ tube with a wavelength $\lambda = 1.54051$ Å. The diffractograms were recorded over $2\theta = 5-100°$ continuous scanning at a scan rate of 8/min. The computer output was recorded using software system DP61.

Crystallinity

The crystallinity can be defined as a peak area crystallinity, being the ratio of the normalized scatter under the resolved peaks to the total scatter under the unresolved normalized trace. The peaks resolution were described elsewhere.[8]

Crystallite Dimension

In order to estimate any change in crystallite dimensions with thermal treatment, the Scherrer equation can be used.[9]

$$t_{hkl} = \frac{K\lambda}{B \cos \theta_{hkl}}$$

where λ is the wavelength of the X-ray, t is the crystal dimension perpendicular to the (hkl)

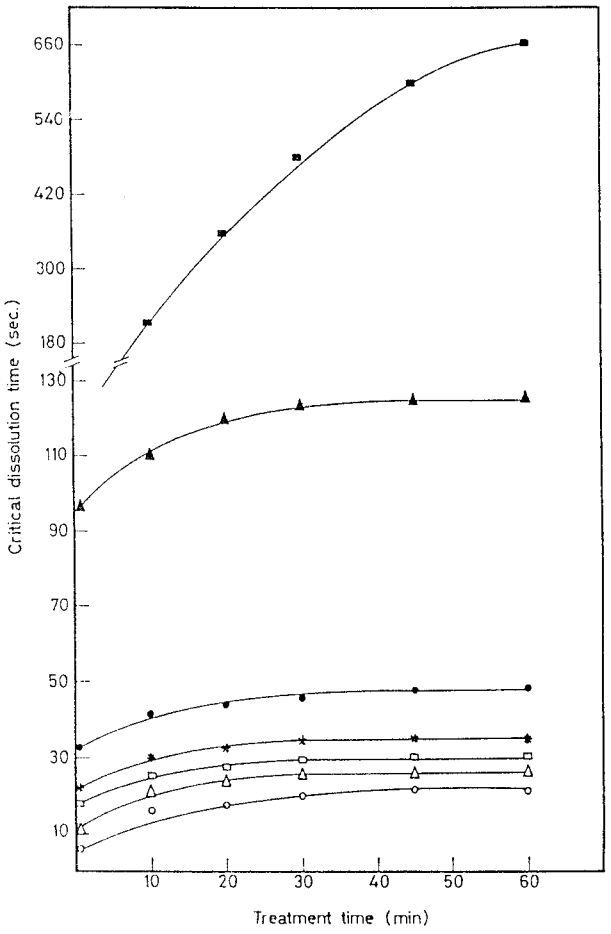

Figure 1 Effect of treatment time on the CDT of polyester fabric thermally treated at different temperatures in dry air (slack). (○—○) 60°C; (△ — △) 80°C; (□ — □) 100°C; (∗ — ∗) 120°C; (● — ●) 140°C; (▲ — ▲) 160°C; (■ — ■) 180°C.

plane, θ_{hkl} is the Bragg's angle of (hkl) plane, B is the width at the half-maximum intensity in radians, and K is a constant equal unity.

RESULTS AND DISCUSSION

Critical Dissolution Time

Changes in crystallinity and crystal morphology of polyester fiber were traced by the determination of critical dissolution time (CDT). The method was used by Galil[7] in studying the thermally induced changes in polyester fiber morphology. This method is based on the assumption that the crystallinity and crystal morphology are the determining parameters in the solubilization of the fiber. The interpretation of the CDT was based on the assumption that the time of solubilization of polyester fibers reflects the overall state of crystallinity and the size and stability of crystallites.

Treatment Time and Temperature

Critical dissolution time was measured for a large number of thermally treated polyester samples at different times and temperatures. Figures 1 and 2 show the dependence of the critical dissolution time of thermally treated polyester in dry air in the free state (slack condition) on time and temperature of treatment, respectively. The critical dissolution time was found to increase as the time of thermal treatment increased (Fig. 1). The change in CDT with treatment times became less effective after 30 min of treatment for samples thermally treated at temperatures up to 160°C; deviation from this value at higher temperatures (at 180° and 200°C) was observed.

Figure 2 shows the relation between treatment temperature (for different periods of time) and CDT. There is a gradual increase in CDT values with increase of treatment temperature up to 140°C, after which a very high increase in the CDT is observed. The increase in CDT values with increasing the treatment temperatures is suggested to be due to increase in crystallinity and to change in the crystalline structure of the fibers.[10]

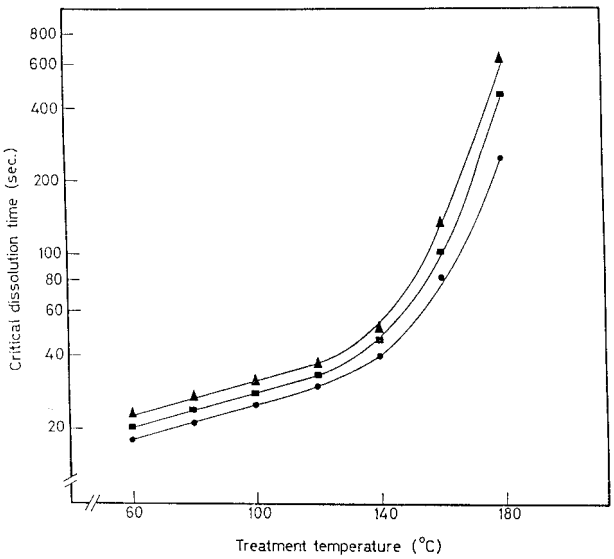

Figure 2 Effect of treatment temperature on CDT of polyester fabric thermally treated in dry air (slack). (● — ●) 10 min of treatment; (■ — ■) 30 min of treatment; (▲ — ▲) 60 min of treatment.

It seems that at higher treatment temperatures, melting of smaller crystallites occurred followed by formation of larger crystallites. The larger crystallites would be expected to have a major retarding influence on the dissolution of polyester structure in phenol. These results go parallel with the dyeing characteristics where the degree of crystallinity is believed to be one of the factors affecting the dyeability beside the size and number of crystallites.

The change in CDT values may also indicate a nucleation tendency or formation of tiny crystals at such specific temperature (160°C), where conditions are suitable for growth of crystal size.

Effect of Media

Figures 3 and 4 show the changes induced in CDT values due to thermal treatment in silicon oil medium. The CDT values of polyester samples treated in silicon oil were found to be smaller than those attained in dry air treatment. This may be attributed to the additional effect of the thermal treatment in air due to partial oxidation and possibility of formation of some type of crosslinks. If this occurred, the CDT could be largely affected. The CDT of polyester treated at 200°C in air is very high, and exceeded 90 min. On the other hand, the silicon oil treatment can affect both amorphous and crystalline regions, increasing the disorder in the polymer structure.[11]

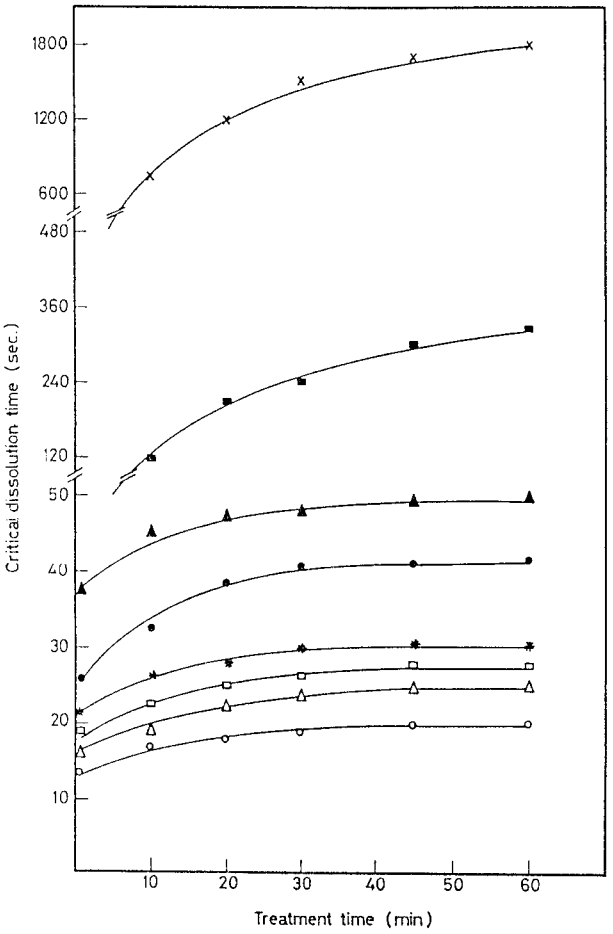

Figure 3 Effect of treatment time on the CDT of polyester fabric thermally treated at different temperatures in silicon oil (slack). (○ — ○) 60°C; (△ — △) 80°C; (□ — □) 100°C; (∗ — ∗) 120°C; (● — ●) 140°C; (▲ — ▲) 160°C; (■ — ■) 180°C; (× — ×) 200°C.

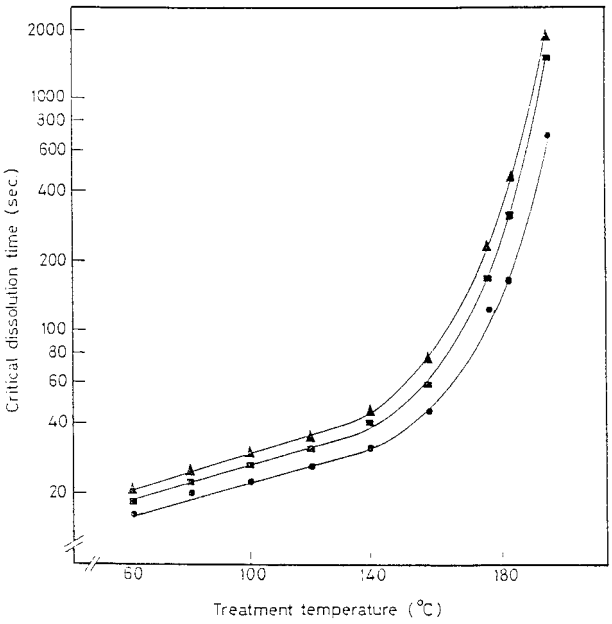

Figure 4 Effect of treatment temperature on CDT of polyester fabric thermally treated in silicon oil (slack). (● — ●) 10 min of treatment; (■ — ■) 30 min of treatment; (▲ — ▲) 60 min of treatment.

Effect of Tension

A comparative study between thermally treated samples under free state (slack condition) and samples treated under constant length (taut condition) are given to show the effect of these treatments on CDT values. Figures 5–9 show the change of CDT values treated under constant length in dry air and in silicon oil, respectively. The CDT values increased with the increase in the time of treatment. Longer time of treatment has nearly no effect on CDT; similar trends are observed in cases of thermal treatment under free conditions. Thermal treatment in dry air under constant length gave, as in the case of free condi-

tions, higher CDT values than those of silicon oil treatment.

The effect of treatment under constant length gave smaller CDT values than those attained by treated samples in free conditions. This can be ascribed to the change in polymer chain structure under constant length, which cannot be freely moved, and the crystallite structure was formed in an incomplete manner with defects. These defects may generate voids in the structure as well as increase the voids volume per crystallite, facilitating the penetration of the solvent molecules into the polymer chains and greatly weaken the polymer intermolecular forces.[12]

X-ray Measurements

Figures 10–12 present the X-ray diffraction patterns before resolution. The peak areas' crystallinity were measured in the angle range 10°–34° (2θ). It can be seen that the peak height increased and the peak width decreased as the treatment temperature increased. The decrease in the peak width may give an indication to the increase in crystallite size. There was nearly no enhancement in the crystallinity up to a treatment temperature of 120°C, when a slight increase in the crystallinity takes place (Fig. 10). The initial fall in crystallinity, below 120°C, indicated the release of strains previously formed in the polymer chains[13] during industrial processes. It can be seen from Figure 10 that the samples treated in dry air at 140° and 160°C in free conditions have three peaks for the three different crystallites formed at higher angles (2θ), i.e., at

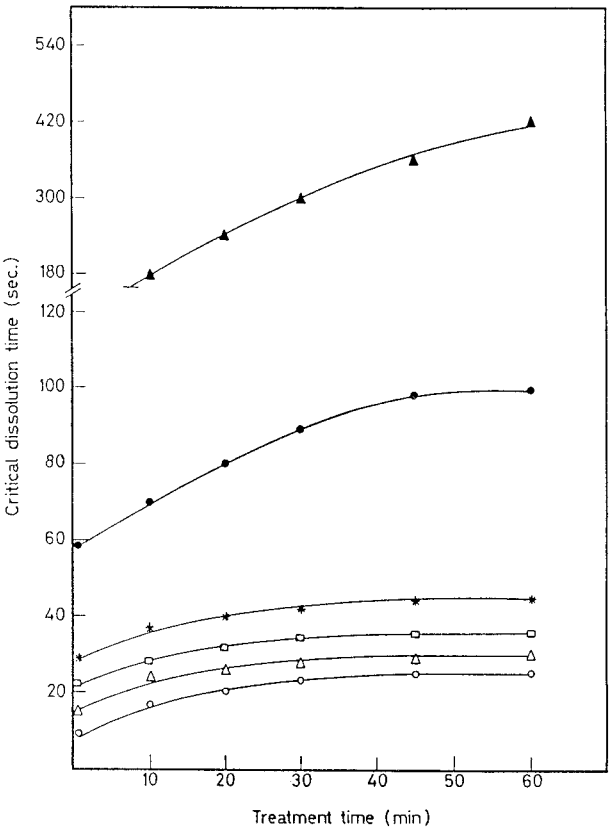

Figure 5 Effect of treatment time on the CDT of polyester fabric thermally treated at different temperatures in dry air (taut). (○ — ○) 80°C; (△ — △) 100°C; (□ — □) 120°C; (∗ — ∗) 140°C; (● — ●) 160°C; (▲ — ▲) 180°C.

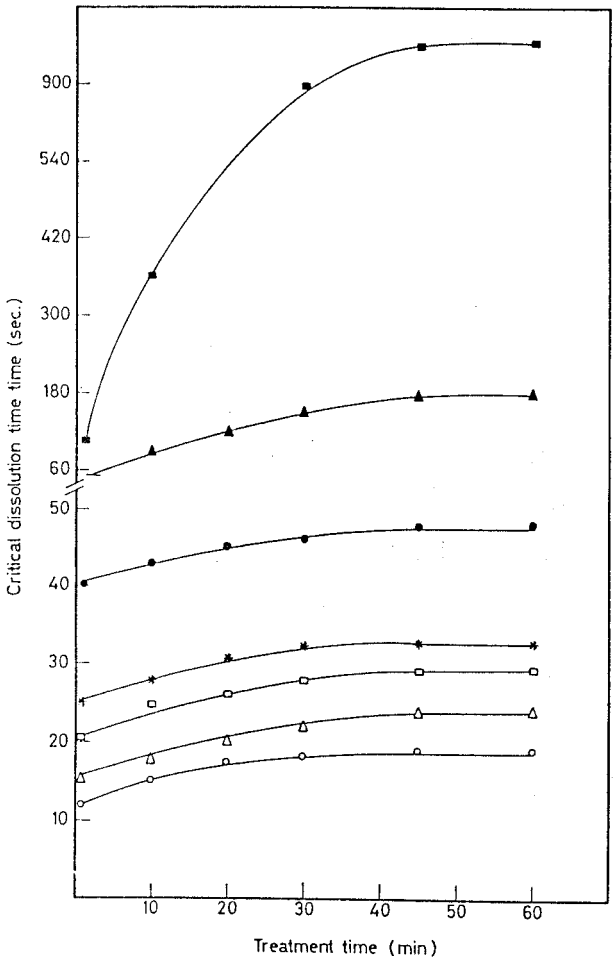

Figure 6 Effect of treatment time on the CDT of polyester fabric thermally treated at different temperatures in silicon oil (taut). (○ — ○) 80°C; (△ — △) 100°C; (□ — □) 120°C; (∗ — ∗) 140°C; (● — ●) 160°C; (▲ — ▲) 180°C; (■ — ■) 200°C.

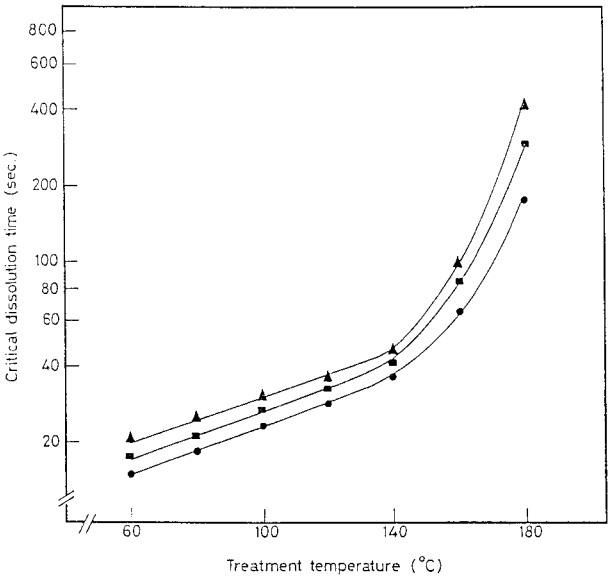

Figure 7 Effect of treatment temperature on CDT of polyester fabric thermally treated in dry air (taut). (● — ●) 10 min of treatment; (■ — ■) 30 min of treatment; (▲ — ▲) 60 min of treatment.

smaller interplanner distance. These crystallites disappeared at higher treatment temperatures. The tiny and small crystallites, which have disappeared, are added (or reformed) to other crystallites to form bigger and more well defined crystallites.

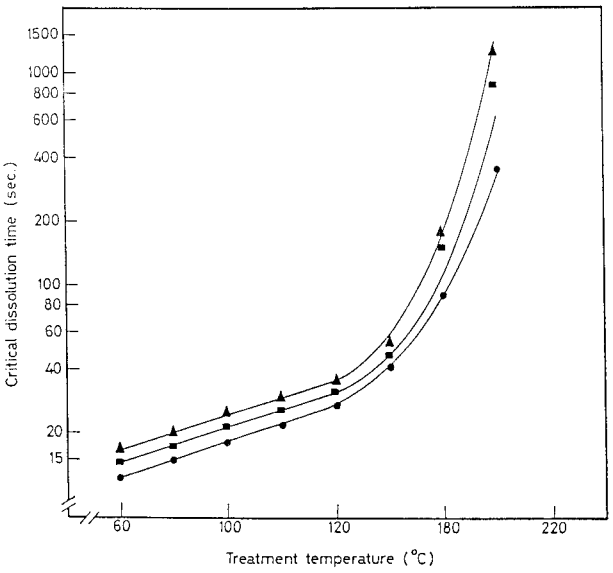

Figure 8 Effect of treatment temperature on CDT of polyester fabric thermally treated in silicon oil (taut). (● — ●) 10 min of treatment; (■ — ■) 30 min of treatment; (▲ — ▲) 60 min of treatment.

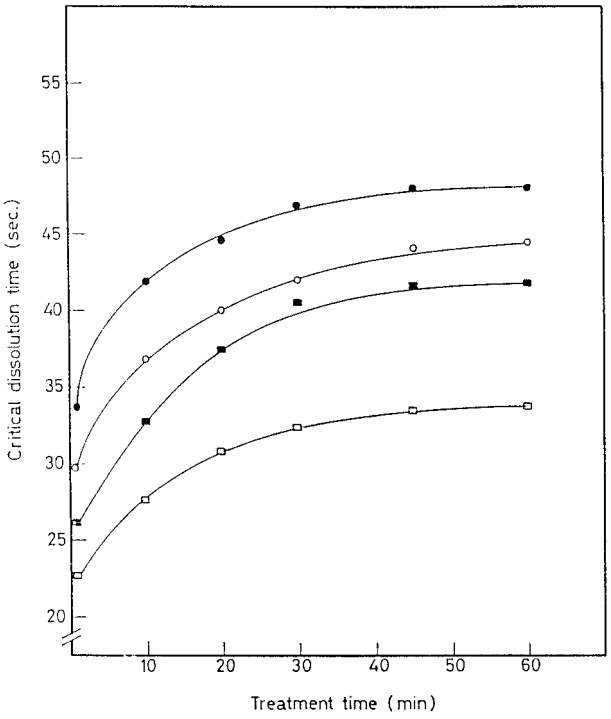

Figure 9 Effect of treatment time on CDT of polyester fabric thermally treated at different conditions. (□ — □) silicon oil treated at 140°C (taut); (■ — ■) silicon oil treated at 140°C (slack); ○ — ○ air treated at 140°C (taut); ● — ● air treated at 140°C (slack).

Crystallinity

A selection of the most significant characterization parameters derived from the resolution of the peaks is given in Table I. Regarding crystallinity

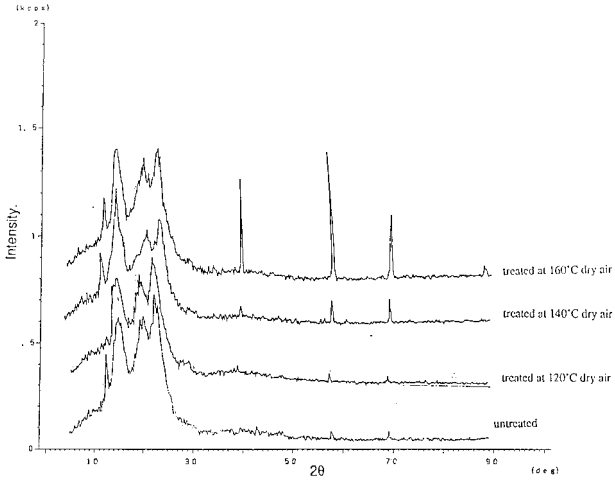

Figure 10 X-ray diffraction patterns of polyester fabric thermally treated at different temperatures.

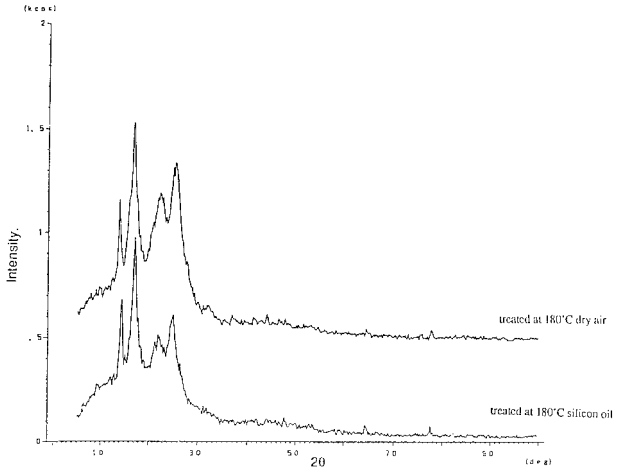

Figure 11 X-ray diffraction patterns of polyester fabric thermally treated at different heating media.

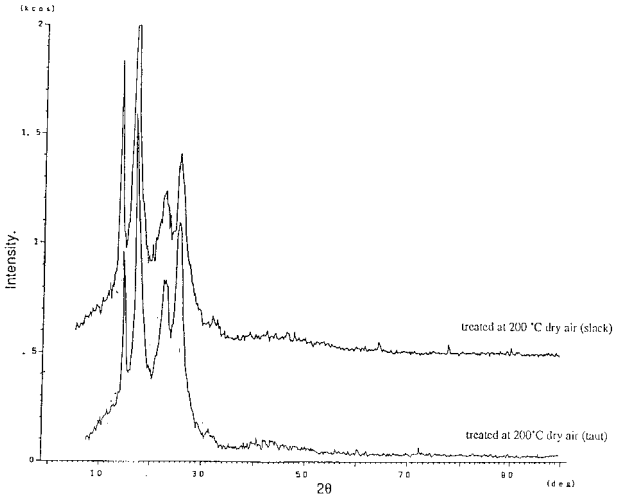

Figure 12 X-ray diffraction patterns of polyester fabric thermally treated at different conditions.

percentage, it can be deduced that the crystallinity of the thermally treated polyester samples is higher than that of untreated ones. It can be observed that the crystallinity increased upon increasing the treatment temperature at a constant rate up to ~ 160°C. At treatment temperature higher than 160°C, the peak at $2\theta = 14°$ became higher and sharper. This peak may indicate the so-called "amorphous component."[14]

The effect of media on treatment is also shown in Table I. The sample treated in dry air at 180°C gave higher crystallinity values than that treated in silicon oil at the same temperature. This indicates that the thermal treatment in dry air effectively increased the crystallinity more than the disorder in the amorphous part. The situation was found to be reversed in case of treatment in silicon oil. Table I also shows the effect of treatment under constant length on the extent of crystallinity of samples treated at 200°C.

Comparison between these samples and those treated under free conditions (slack) showed that crystallinity of the constant length treated sample was slightly lower than that of free condition. This may explain why the CDT values were slightly smaller in case of thermal treatment under constant length, as compared with slack conditions.

Crystallite Size

Table I shows the effect of thermal treatment on the crystallite size. The thermal treatment increased the crystallite size. It can be seen that treatment in dry air gave larger values than treatment in silicon oil. The treatment in silicon oil

Table I X-ray Characterization Parameters after Peak Resolution of Thermally Treated PET Fibers

Thermal Treatment Conditions	Crystallinity (%)	Crystallite Size (Å)		
		010	110	100
Untreated (blank)	25	35.5	47.8	48.6
Air treated at 120°C (free)	26	38.7	48.1	58.3
Air treated at 140°C (free)	30	50.1	56.4	64.8
Air treated at 160°C (free)	39	52.2	63.4	70.1
Air treated at 180°C (free)	51	54.3	64.1	66.0
Air treated at 200°C (free)	66	61.5	68.5	72.5
Silicon oil treated at 180°C (free)	41	59.4	45.6	60.8
Air treated at 200°C (taut)	64	52.3	64.5	70.0

Treatment time, 30 min.

affected the amorphous region at the expense of the neighboring crystallite size. Table I shows that treatment under constant length gave smaller crystallite size than treatment in the slack condition. The treatment under constant length created defects and voids in the crystallite, and hence gave deformed or incomplete crystallites.

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