Structure-Dyeability Relationship of Heat Set Poly (ethylene Terephthalate) Filament Yarns (I)

열고정된 PET 필라멘트사의 구조와 염색성간의 상관연구(I)

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<Contents>

<Abstract>

PET 필라멘트사를 건조열을 이용해 여러 온도에서 열고정 시킨 후, 섬유의 염색성 및 결정화도가 연구되었다. 그리고 두 변인 간의 상관성이 규명되었다.

섬유의 내부구조 변인으로 사용된 결정화도는 밀도 측정법으로 얻어졌으며, 염색성은 염색된 시료를 m-cresol에 완전히 용해시킨 후 스펙트로포토미터를 이용하여 염료 흡착량을 측정하였다.

열고정된 PET의 결정화도는 처리온도가 증가함에 따라 증가하였으나, 염색성은 온도가 증가함에 따라 감소하였다. 일반적으로 열고정된 PET 필라멘트사의 염색성은 시료의 결정화도에 의한 예언율이 높았다.

I. Introduction

It is well known[2,23,25~27] that during heat setting processes, structural changes take place which affect the subsequent dyeing behavior of the treated yarns and fabrics. The processes change the molecular arrangement within fibers and consequently bring about altered physical properties, dyeability as well as dimensional stability.[11]

The simplest form of heat setting consists of heating an assembly of filaments so as to relax the stresses incurred during the manufacturing processes and to establish a new equilibrium state for the fiber assembly.[2] At an elavated temperature, the cross links between the molecules in the fiber break and reform in the equilibrium positions for the new configuration, and then remain in the structure and tend to bring the fiber back to the same form.[19]

However, improper heat setting brings about certain undesirable results such as wrinkles

introduced during the washing and drying processes. If fabrics which are improperly heat treated are washed at temperatures above or even close to the glass transition temperature, wrinkles develop throughout. These wrinkles do not disappear on drying and the fabrics require ironing to improve their appearance; thus the easy care properties which synthetic fabrics ought to possess are not realized in practice.

Optimum heat setting involves proper control of four basic factors: the initial high temperature to which the material has to be raised, the length of time for heat setting, the tension on the material and the rate of cooling. The importance of each of these factors can not be underestimated.[25]

The literature on heat setting treatments illustrates that the materials are usually heat set in the slack condition[4,8,10,12,13], under constant tension[2,6,25~27] or at a constant length[8,10,25,28] to vary the amount of tension given. If refolding and shrinkage are permitted during the heat treatment, subsequent shrinkage forces are greatly reduced. And, when greater tension is applied, careful heat setting process control is needed.

Haet setting of polyester can be done by the use of steam or dry heat. If steam is used, some hydrolysis of the ester groups within the polyester fiber can occur resulting in a possible loss of strength. Therefore, dry heat setting is nearly always used for polyester.[16]

Polymer molecules in the solid state have a tendancy to aggregate in to a semicrystalline state. The presence of crystallinity in polymers strongly influences their properties. Since the polymer chains are more tightly packed in the crystalline areas and are in close and regular contact over relatively long distances in the crystallites, the net forces holding them together are far greater than in the amorphous areas.[15]

If thermoplastic fibers are heat set, they experience such effects as variation in crystallinity, orientation and fluid-like segmental motion. High temperature heat treatments, in general, increase the crystallinity whenever synthetic fibers are heat treated at temperatures above that of their previous treatment.[11]

Density is the most basic macroscopic quantity of a crystalline material.[29] Polyester increases in density when heated; thus extent of crystallinity also increases with density.[8,15,26] This suggests that a more closely packed fine structure is formed as the result of heat setting.

It is assumed that a semi-crystalline polymer consists of two separate and distinct phases: a purely amorphous phase and a purely crystalline phase. Experimental values of the den sities of semi-crystalline polymers lie somewhere between the crystalline and amorphous densities. On the basis of the two-phase assumption, semi-crystalline density can be expressed as the sum of contribution from each phase in proportion to its weight fraction.[29]

The dyeing of polyester fibers with disperse dyes has attracted considerable attention. Disperse dyes are a class of water-insoluble dyes, originally introduced for cellulose acetates, usually applied from fine aqueous suspensions.

In dyed fibers, the disperse dyes are present chiefly in the monomolecular state.[14] The disperse dyeing process can be described as follows[20]:

- some of the dye dissolves in the water of the dyebath,
- molecules of dye are transferred from solution to the surface of the fiber,
- the solution in the dyebath is replenished

by the dissolution of more solid material from the dispersion,

· the adsorbed dye diffuses monomolecularly into the fiber.

Heat treatment of fibers can greatly influence the rate of dye absorption and the location of dye in the fiber.[22] Changes in dyeing rate are attributed to differences in the internal morphology of the fiber such as the ratio of crystalline to amorphous areas and in the glass transition temperature.[18,21]

According to Warwicker,[26] the uptake of disperse dyes by heat-set polyester initially decreased as the temperature of preheating was raised. But, at higher temperatures, the dye uptake increased with a rise in temperature and could be greater than that of the untreated control. Similar effects were noted for other polyesters and dyes by a couple of other researchers.[9,17]

The temperature of the dyebath is important in the study of dyeability using heat treated samples. According to Weigmann et al.,[28] the dyeing temperature should be based on the assumption that the temperature would be appropriate to reveal the effects of structural modifications on dyeing behavior and therefore would be suitable for comparative evaluations.

Prolonged dyeing times can result in a change in the structure of the fiber and this change might obscure the structural effects of the original heat treatment.[26] Therefore, such a comparison should be based on a dye uptake after a predetermined and constant dyeing time.

Amount of dye uptake of fibers can be estimated spectrophotometrically. According to Bouguer, Lambert and Beer, the absorption of light in passage through any medium is proportional to the number of absorbing molecules in its path. The term called absorbance or optical density has a linear relationship with the molar concentration of the absorbing substance.[7]

In summary, it can be seen that heat treatment provides better-defined crystalline regions to polyester fibers. Structural changes of fibers due to heat treatment can produce changes in dyeability of polyester fibers. Therefore, it is essential to understand and control the structural changes which are brought about by the heat treatment of fibers.

The purpose of this research was to investi gate the effect of heat setting on the dyeability of polyester filament yarns which were treated at varying high temperature with dry heat while in the constant length condition, a treatment analogous to some setting treatments. Furthermore, it aimed to relate the dyeability to the structural changes caused by the heat treatment.

Ⅱ. Experimental

2-1. Test specimen

Polyester multifliament yarns(Dacron® 100/34) were used which were commercially available drawn yarns furnished by E.I. du Pont de Nemours & Company. The filaments had round cross section and were semidull.

2-2. Heat Treatment Method

Lengths of multifilament yarns were wound with minimum tension on a wooden frame at constant length so that each turn was separate from its neighbor. Each frame contained approximately 47.0 ± 0.01 m (0.52 ± 0.005 g) yarn.

The frame was placed in the previously heated oven at the desired temperature for 3 minutes. Upon removal from the oven, the

yarns were cooled at the standard atmosphere for textile testing before they were removed from the frame.

The different oven temperature settings were: 150, 165, 180, 195, 210, 225, 235°C.

A specimen on the frame with heat treatment represented a sample; several subsamples were obtained from the sample. For a given temperature, two replications were obtained by repeating the heat treatment. The order of oven temperature in which the frame was placed was determined randomly.

2-3. Dyeing Experiments

The disperse dye used was Intrasperse Orange 2RN Ex. (C.I. Disperse Orange 3, 11005), a commercial dyestuff manufactured by the Crompton and Knowles Corporation. The dyebath contained 0.5 g dye and 10 ml 30% acetate acid made up to 1 liter.

Prior to dyeing, 0.25 g samples were scoured in a solution composed of 2 g sodium carbonate, 1 g nonionic detergent and 1 liter distilled water. The scouring was done at 50°C for 30 minutes.

Each specimen (0.25 g) was dyed using the dyeing machine (Ahiba Texomat TC 101). The specimens were introduced into the dyebath at a starting temperature of 50°C. The temperature was increased to 90°C at a rate of 2°C per minute, then dyeing was continued for 90 minutes.

The dyeing conditions were such that dyeing took place in an infinite dyebath. Since only a total of 0.25 g of yarn was held loosely in place in each dyebath, and the uptake was small, the dyebath would be virtually an infi nite one.

At the end of the dyeing, each specimen was rinsed thoroughly under running distilled water. Then it was rinsed 5 times in 20 ml portions of aceton for 5 seconds at room temperature to remove the remainder of the free surface-held dye. Following the final aceton rinse, the dyed yarns were rewashed with distilled water. The specimens were dried in the oven at 80°C for 4~5 hours and then put into a desiccator to cool for at least 3 hours.

2-4. Estimation of Dye Uptakes of Samples

A weighed amount (0.01 g) of dyed fiber was dissolved in 5 ml of m-cresol. The solvent m-cresol used was vaccum-distilled several times (BP=90°C/0.1 Torr) until the distillate was nearly colorless. The amount of dye uptake was estimated spectrophotometrically at 428.7 nm wave length.

The Lambert and Beer relationship between concentration and absorbance of well-mixed suspensions of the dye in the solvent was obtained in a 10 mm path-length cuvette. The spectrophotometer used was spectronic 2,000 (Bausch & Lomb) connected to a personal computer (Apple $\mathrm{II_e}$).

For each dyed sample, two different solutions were prepared. From each solution, two readings were made and an average value was calculated.

2-5. Density Measurements

The fiber density of each specimen was measured according to the recommended ASTM procedure[1]. The mixtures were ethanol (ρ= 0.789 g/cm^3) and carbon tetrachloride (ρ= 1.544 g/cm^3). A density gradient was set up by a continuous filling method with liquid entering the gradient column becoming prograssively more dense. The mixture of the heavy and the light solvent proportioned so as to have a maximum density of 1.5135 and

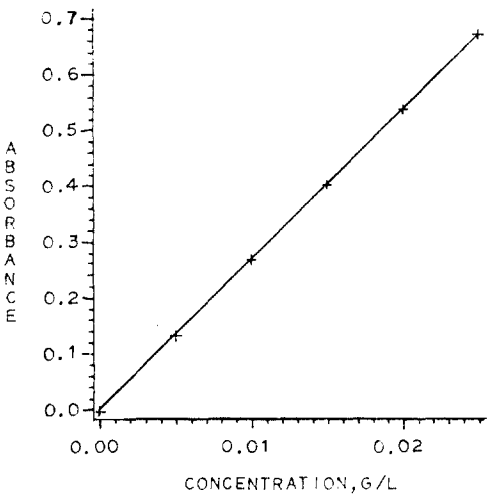

Fig. 1. Concentration-Absorbance Curve of Disperse Orange 3 in m-cresol.

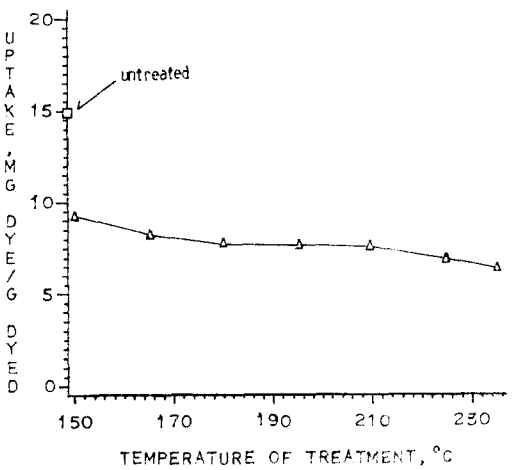

Fig. 2. Effect of Heat Setting on the Uptake of Dye by PET Filament Yarns.

the minimum of 1.2720. The gradient was determined with calibrated beads which had density values of 1.335, 1.355, 1.375, 1.395, and 1.415 g/cm³.

After the gradient was established, small portions of fibers knotted into various shapes for identification were dropped into the column and the flotation level measured after an extended period of time (72 hours).

Table 1. Uptake of Dyes by Heat Set PET Filament Yarns

Temperature °C	Dye Uptake mg of dye/g of dyed fiber
Untreated	14.92
150	9.12
165	8.20
180	7.66
195	7.62
210	7.55
225	6.82
235	6.36
Standard error	0.28

Ⅲ. Results and Discussion

3-1. Dyeability of Heat Set PET Filament Yarns

The Lambert and Beer relationship between concentration and absorbance of well-mixed suspensions of the Disperse Organge 3 in m-cresol is shown in Fig. 1. The regression equation of the curve was:

absorbance $= -0.0006 + 26.84 \times$ concentration

The standard deviation of the regression was 0.0011 and the correlation coefficient was 0.9999.

The experimental results for the dyeability of PET filament yarns are shown in Table 1. The amount of dye taken up by the untreated PET filament yarns was 14.92 mg of dye/g of dyed fiber. When the fiber was heat set at 150°C, the amount of dye uptake was reduced severely and within the treated fibers the uptake decreased moderately as the heat setting temperature increased (Fig. 2).

Acc ording to the contrasts (Table 2), polye-

Table 2. Contrast Analyses for Dye Uptake of PET Filament Yarns

Contrast	df	ms	F-value	p-value
Control vs treated	1	184.76	631-94	0.0001
Linear trend	1	17.85	60.42	0.0001
Quadratic trend	1	0.07	0.26	0.6274

ster showed only a linear decreasing trend (p-value<0.0001), not a quadratic, between temperature and dye uptake. The untreated fiber was excluded from the analysis to see the temperature and the dye uptake relationship.

Dumbleton[5] and Warwicker[26] showed that the dye uptake initially decreased as the temperature of heat setting was raised. And at higher temperatures the rate of dye uptake increased with increasing temperature and could be greater than that for the untreated control.

The present study, however, did not show any sharp increase in dye uptake at higher temperatures. Generally, under normal setting conditions, the aqueous dyeability of heat set fibers within the range of 200~249°C could show a sharp increase. But, it may be different according to the heat set condition and fiber type.

3-2. Effect of Heat Setting on Crystallinity

From the fiber density, sample crystallinity was calculated using the weight fraction percent crystallinity

$$\beta=\frac{\rho_c(\rho-\rho_a)}{\rho(\rho_c-\rho_a)}\times 100$$

where ρ_a : density of 100% amorphous material

ρ_c : density of 100% crystalline material

ρ : density of sample.

Table 3. Density and Degree of Crystallinity of Heat Set PET Filament Yarns

Temperature °C	Density g/cm³	Crystallinity %
Untreated	1.380	39.6
150	1.384	43.6
165	1.385	44.4
180	1.301	48.8
195	1.393	50.7
210	1.395	52.9
225	1.397	54.5
235	1.399	56.0
Standard error	0.003	0.0

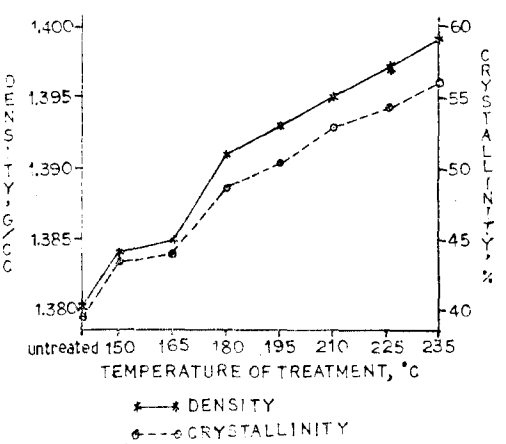

Fig. 3. Effect of Heat Setting on the Density and Crystallinity of PET Filament Yarns.

The densities of 100% amorphous material and 100% crystalline material were taken as 1.335g/cm² and 1.455g/cm², respectively[3,24].

Table 4. Constrast Analyses for Density and Crystallinity

Contrast	df	ms	F-value	p-value
Density				
Control vs treated	1	0.0008	224.51	0.0001
Linear trend	1	0.0011	317.46	0.0001
quadratic trend	1	0.0000	2.56	0.1534
Crystallinity				
Control vs treated	1	0.0581	260.74	0.0001
Liner trend	1	0.0811	363.84	0.0001
Quadratic trend	1	0.0006	3.13	0.1200

The results including those for the density experiments are listed in Table 3. Density of untreated PET yarns was 1.380g/cm³ and the degree of crystallinity was 39.6%. When the yarns were heat set at 150°C, the density and the degree of crystallinity increased, and as the treatment temperature increased the two values increased progressively (Fig. 3).

Based on contrast analyses for density and crystallinity, which are listed in Table 4, polyester showed a significant linear trend (p-value<0.0001) in the density-temperature relationship. Trend for crystallinity was exactly the same as for density.

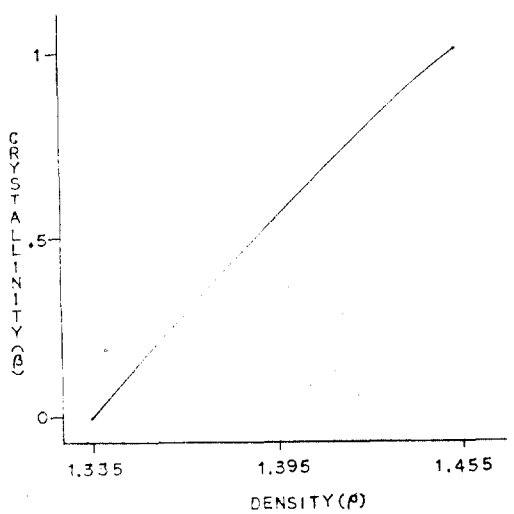

Fig. 4. Relationship Between Degree of Crystallinity and Density for PET Filament Yarns.

Since the degree of crystallinity is an increasing function of density, there is no doubt that crystallinity also increased as density increased (Fig. 4).

Heat setting, in general, above a particular temperature increases the degree of crystallinity. Therefore, it can be seen that the portion of amorphous regions in the fiber structure apparently decreases at higher temperatures. The results for PET filament yarns are in agreement with those of Venkatesh et al.[25] and Warwicker[26].

3-3. Relationship of Dyeability and Crystallinity

For studying the relationship between the amount of dye absorbed and the degree of crystallinty, correlation coefficient was obtained between dye uptake and crystallinity. Similarly, to document the relationship, plot was drawn between variables.

The amount of dye uptake by heat set polyester fibers was interrelated with the amount of crystallinity developed by the treatment. Regression analyses were used to secure a

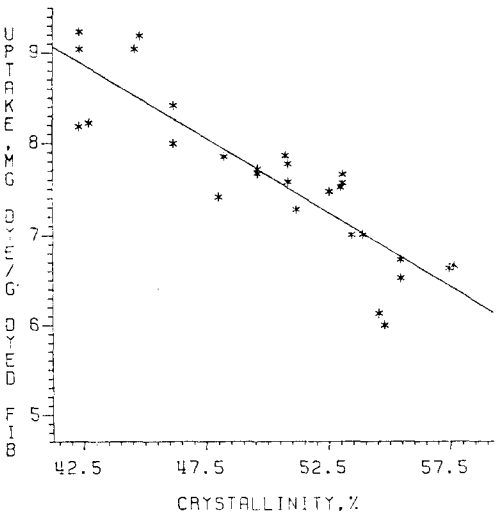

Fig. 5. Plot of Dye Uptake vs Crystallinity for PET filament Yarns.

possible equation to predict the degree of crystallinity when the amount of dye uptake of the fiber would be given or vice versa.

According to the correlation coefficient for treated polyester yarns, dye uptake was negatively correlated with crystallinity ($r=-0.88$), and plot of dye uptake versus crystallinity delineated a negative relationship clearly (Fig. 5).

The regression model for predicting dye uptake from crystallinity was as follows:

$$\text{dyeability} = 15.75 - 0.16 \times \text{crystallinity}$$

where the R-square value was 0.78.

Since dye molecules chiefly locate in the amorphous regions, the increased crystallinity in PET yarns decreases the amount of dye absorbed by the fibers.

In terms of the two-phase theory of structure involving a crystallinity and an amorphous region, two opposing factors play a part in the dye uptake of the heat set fibers. The dyeing properties were quite consistent with the two phase theory of structure. An increase in the degree of crystallinity resulted in a reduction of the uptake.

Because the changes in the overall crystallinity were considerable, the net effect was a decrease in the dye uptake. In practice, the dyeability of heat set fibers could be explained in terms of structure, especially in terms of degree of crystallinity.

Ⅳ. Conclusions

This study was undertaken to investigate how heat treatment affected the degree of crystallinity and the amount of dye uptake of polyester filament yarns and to find out how the degree of crystallinity was related with the dyeability of heat set polyester filament yarns.

Dye uptake of polyester showed a decreasing tendency as temperature increased. Degree of crystallinity for polyester gradually increased with temperature.

Dye uptake and crystallinity were highly correlated for polyester. The increased crystallinity of the treated fibers was accompanied by decreased dye uptake. In other words, crystallinity was an important contributor to change dyeability. Therefore, dye uptake would be a fair way to measure changes in crystallinity.

The information obtained in this study may serve as a basis for the further investigation of heat treatment of thermoplastic fibers and in the interpretation of the structural changes which take place during heat treatment. This study indicates a need for further investigation in the areas of the degree of orientation which may affect the dyeability.

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