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Dyeability of Heat Treated Synthetic Fibers (1)

—On the Basis of Polyester Filament Yarns—

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열처리된 합성섬유의 염색성에 관한 연구(Ⅰ)*

—폴리에스터 필라멘트사를 중심으로—

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國文抄錄

본 연구에서는 연신정도가 다른 완전배향사(FDY)와 부분배향사(POY)를 열처리시켜 내부구조변화를 유도한 후 염색성을 연구하였고, 염색성과의 관련성을 위해 결정화도 및 복굴절률을 조사하였다.

열처리는 silicone oil 속에서 정장상태로 실시하였으며, 시료의 염색은 Disperse Yellow 42를 이용해 무한염욕상태에서 실시하였다. 그리고, DMF를 이용해 염료를 추출시킨후 spectrophotometer로 염료흡착량을 측정하였다. 결정화도는 밀도-결정화도 관계식으로 구하였으며, 복굴절률은 편광현미경으로 시료의 두께와 retardation을 측정한 후 계산하였다.

FDY와 POY 필라멘트사의 염색성은 열처리시 감소하였으며 POY의 염색성이 FDY보다 우수했다. 결정화도는 열처리시 증가하였으며 열처리되지 않은 POY가 열처리되지 않은 FDY에 비해 낮은 값을 나타냈다. 복굴절률은 열처리시 증가하였으며 열처리되지 않은 POY가 열처리되지 않은 FDY에 비해 낮은 값을 나타냈다. 열처리후에도 POY가 FDY보다 낮은 복굴절률을 나타낸 반면 결정화도는 열처리된 POY가 열처리된 FDY와 비슷한 값을 나타냈다. 염색성은 결정화도와 배향도에 부적인 상관관계 즉 결정화도와 배향도가 증가함에 따라 염색성은 감소하는 관계를 시사했다.

Ⅰ. Introduction

Heat setting of textile materials has developed in importance since the introduction of synthetic fibers. When thermoplastic fibers such as nylon and polyester are heat set, they become dimensionally stable and resist permanent deformation; thus the resulting fabric or garment will retain its shape and keep the creases which have been put in. This process, accordingly, has been stimulated by the demand for easy care textile items by consumers.[1,2]

As discussed in the previous report,[3] heat setting processes bring about structural changes which affect the subsequent dyeing behavior of the treated yarns and fabrics. The reason is that the processes change the molecular arrangement within

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fibers and consequently bring about altered dyeability.

A typical drawn PET fiber has a possible structure where the chains are essentially extended and more or less folded[4] When such a drawn fiber is treated at higher temperatures under unconstrained conditions, more stable intermolecular bonds are formed and the local order (crystallinity) increases by allowing a recrystallization of folded chains to occur.[5] At the same time, degree of orientation of the whole system increases.[1]

High temperature heat treatments, in general, increase the crystallinity whenever synthetic fibers are heat set at temperatures above that of their previous treatment. But, degree of orientation of heat set fibers shows variation according to the tension given during the heat treatment.

According to Venkatesh et al,[6] the overall orientation of the polymer chains decreases on heat setting in the slack condition. When the sample is not allowed to shrink while heating, the birefringence values are unaffected. But, Gupta and Kumar[7] stated that birefringence of samples treated under slack tension decreased and that treated at constant length condition increased.

Nowadays, manufacturers provide Partially Oriented Yarns (POY) with less sensitivity to atmospheric conditions and better thermal stability. It is believed that POY-textured polyester has superior dyeability and a crisp hand.[8]

Heat treatments of polyester at increasing temperatures up to a certain point cause a decrease in the equilibrium dye uptake irrespective of the conditions under which the filaments are heat set. The dye uptake then rises rapidly when the fiber is heat set within the range of 200~248°C because of an increasing tendency for structural changes to occur before actual fusion of the fibers[9~14].

The increase in crystallinity may explain the decrease in dye uptake at lower heating temperatures. Even though the significant increase in the crystallinity of the sample can still be a factor affecting fiber properties, adaptation of measurements of orientation will be a good way to explain heat set fiber properties.

Therefore, in this research, the effect of heat setting temperature on the dyeability of both Fully Drawn Yarns(FDY) and POY polyester filament yarns was investigated. And the degree of crystallinity and orientation by density and birefringence measurements were obtained as the structural changes caused by the heat treatment, and related to the dyeability.

Ⅱ. Experimental

2-1. Test Specimen

Polyester multifilament yarns were used which were commercially available Fully Drawn Yarns (FDY, 75/36) and Partially Oriented Yarns (POY, 116/36). They were furnished by the Kolon company and the filaments had round cross section and were semidull.

2-2. Heat Treatment

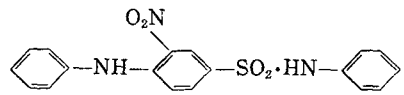
Both FDY and POY were heat treated at constant length condition in a silicone oil bath of which temperature could be maintained at different levels within ±1°C.

After treatment for a predetermined period (3 min), the sample was cooled rapidly in water at room temperature and washed with n-heptane to remove the oil from the fiber surface.

The different temperature settings were:
150, 170, 190, 210, 230°C.

2-3. Dyeing Experiments

The disperse dye used for both FDY and POY was Miketon Polyester Yellow YL, MDW (C.I. disperse Yellow 42, 10338) and the structure was as follows:



Owing to the difficulty of preparing stable dispersions from purified dye, commercial dye was used for the preparation of dyebaths. The dyebath

contained 1 g dye and 10ml 30% acetic acid made up to 1 liter.

Each specimen was dyed using the dyeing machine (Mathis Laboratory Jet dyeing machine, Swiss, Werner Mathis) under infinite dyebath conditions. The specimens were introduced into the dyebath at a starting temperature of 20°C and the temperature was increased to 120°C at a rate of 2.5°C per minute. Then the dyeing was continued for 90 minutes.

At the end of the dyeing, each specimen was rinsed thoroughly with distilled water, and then it was soaped in a solution composed of 2 g sodium carbonate, 1 g nonionic detergent and 1 liter distilled water. The soaping was done at 50°C, for 30 minutes to remove the remainder of the free surface-held dye.

2-4. Estimation of Dye Uptakes of Samples

The dye content of the samples was determined by extracting the dye with DMF (at 90°C) and measuring its concentration by spectrophotometry (Spectronic 21, Bausch & Lomb) at 420 nm wave length. Before extracting, the dyed samples were dried under vacuum at 80°C for 4 hours.

The Lambert-Beer relationship for the purified dye in DMF was found to be linear. The concentration-absorbance relationship of disperse yellow 42 in D.M.F. was:

$$\text{Absorbance} = 0.0246011 + 0.01574 \times \text{Concentration}.$$

Sample dye content was expressed as mg of dye/g of dyed fiber.

2-5. Density Measurements and Calculation of Degree of Crystallinity

The fiber density ρ was measured at 23°C by the same way previously described,[3] using a mixture of n-heptane and carbon tetrachloride.

Weight fraction percent crystallinity β from density was determined using the following equation:

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

where ρ_a, ρ_c and ρ are the densities of the amorphous, the crystalline and the unknown samples. For PET, the density values were taken to be 1.455 and 1.335 g/cm^3 for the 100% crystalline and 100% amorphous materials, respectively.[15,16]

2-6. Birefringence Measurements

Birefringence was measured using a Nikon polarizing microscope and a compensator. It was measured directly by determining the relation of the one principal ray relative to the other. The width of the fiber was measured by means of a micrometer eyepiece and, on the assumption the fiber is cylindrical, this gave a measure of the path-length through the fiber.

Five measurements of retardation and width for each specimen were made and, for each specimen, trimmed mean was obtained as its retardation and width.

From the retardation and width values, birefringence was calculated as follows:

$$\Delta\eta = \frac{r}{w}$$

where $\Delta\eta$, w, and r represent birefrigence, width, and retardation value of the sample, respectively.

Ⅲ. Results and Discussion

3-1. Effect of Heat Setting on Dye Uptake

After the specimens were dyed at 120°C for 90 minutes, the dye uptake of the fibers was measured spectrophotometrically by extracting the dye from the dyed fiber. The comparison of dye uptake by FDY and POY at various temperature settings is shown in Figure 1.

The amount of dye uptake by the untreated FDY was 5.48 mg of dye/g of dyed fiber, and that by the untreated POY was 10.75 mg of dye/g of dyed fiber. POY showed dyeability almost twice as much as FDY for the dyeing condition. When the fibers were heat set at 150°C, the amount of dy taken up was reduced and as the treatment temperature increased, the dye uptake decreased

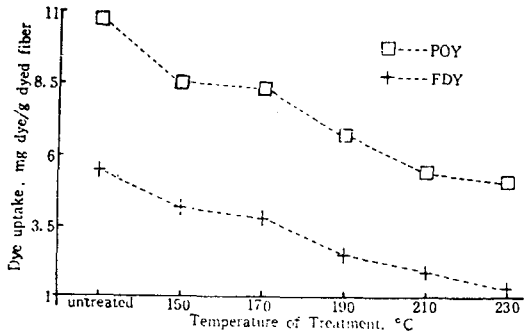


Fig. 1. Comparison of Dye Uptake by Heat Set FDY and POY Filament Yarns

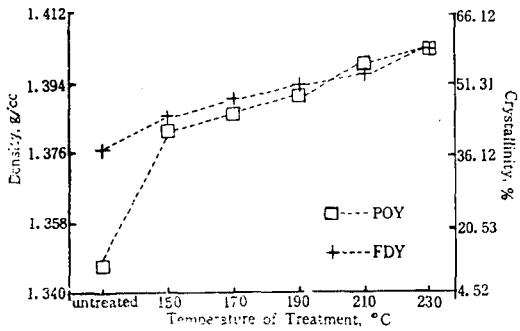


Fig. 2. Effect of Heat Setting on the Density and the Crystallinity of FDY and POY Filament Yarns.

for both FDY and POY.

As expected, the partially oriented yarn showed more dyeability than the fully drawn yarn. And, as the heating temperature increased the dyeability of both FDY and POY decreased. However, there was no sharp increase at higher temperatures. Again, it might be due to the different heat set condition and fiber type. Or, the highest setting temperature adopted in this study might not be high enough to indicate the sudden sharp increase in dye uptake.

3-2. Effect of Heat Setting on Crystallinity

Degree of crystallinity of the yarns was obtained by measuring densities of the samples from a density gradient column. The results, including

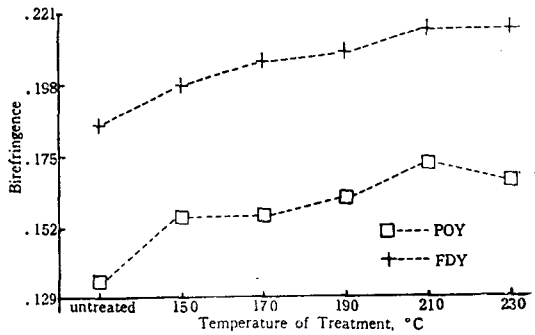


Fig. 3. Effect of Heat Setting on the Birefringence of FDY and POY Filament Yarns.

those for untreated yarns, are shown in Figure 2.

Density of untreated FDY was 1.376 g/cm³ and the degree of crystallity was 36.5% When the FDY filaments were heat set at 150°C, the density increased to 1.384 g/cm³ and the degree of crystallinity to 42.9% POY filaments had a density value of 1.347 g/cm³ and a crystallinity value of 10.4% for the untreated yarns. When the yarns were heat set at 150°C, the density and degree of crystallinity increased drastically and the values were 1.381 g/cm³ and 40.6%.

The degree of crystallinity of the samples treated at various temperatures was very similar in spite of the inherent differences of crystallinity of the untreated FDY and POY yarns. POY increased in degree of crystallinity lot faster than FDY when heat treated at 150°C and within the treated samples, the two yarns showed similar level of crystallinity.

Therefore, it can be said that the degree of crystallinity is more dependent on the treatment temperature than on the drawing condition. Both FDY and POY supported that heat setting, in general, increases the degree of crystallinity and the results were in aggreement with those of several researchers.[3,6,12]

3-3. Effect of Heat Setting on Birefringence

Birefringence of the yarns was obtained by measuring the retardation and the fiber width using a polarizing microscope. The comparison of the

Table 1. Correlation Coefficients among Dye Uptake, Crystallinity and Birefringence

	FDY			POY		
	1	2	3	1	2	3
1. Dye Uptake	—	−0.98	−0.97	—	−0.94	−0.96
2. Crystallinity	—	—	0.97	—	—	0.97
3. Birefringence	—	—	—	—	—	—

Table 2. Regression Parameters for Dyeability as Predicted by Crystallinity and Birefringence

	Intercept	Regression Coefficients		R^2
	β_0	β_1	β_2	
FDY	17.72	−0.15	−36.33	0.97
POY	30.28	−0.01	−140.50	0.92

results for FDY and POY at different temperature settings is shown in Figure 3.

Birefringence of the untreated FDY filaments was 0.185 and that of the untreated POY was 0.135. As the treatment temperature increased, birefringence of both FDY and POY increased as in the case of crystallinity. However, the inherent birefringence differences between FDY and POY were kept unlike crystallinity for the treated samples. In other words, the degree of orientation of the heat set fibers is less dependent on the heat setting temperature than on the drawing condition.

Heat setting decreases the birefringence of samples treated under slack tension.[7,17] On the other hand, heat set fibers treated at constant length condition show increase in birefringence,[7] or show no change.[6] The results for both FDY and POY filaments are in agreement with those of Gupta and Kumar.[7]

3-4. Relationship of Dyeability and Internal Structure

For studying the relationship between the amount of dye absorbed and the degree of crystallinity, and between the amount of dye and the birefringence, correlation coefficients were obtained among dye uptake, crystallinity and birefringence for each fiber type (Table 1). Also, multiple regression analysis was used with the dye uptake as the dependent variable, and the crystallinity and the birefringence as the independent variables (Table 2).

According to the correlation coefficients for the treated FDY filaments, dye uptake was negatively correlated with degree of crystallinity ($r=-0.98$) and birefringence($r=-0.97$). The estimate of the parameters for FDY predicting dye uptake from crystallinity and birefringence can be written as follows:

$$\text{Dyeability}=17.72-0.15X_1-36.33X_2$$

where; X_1=percent crystallinity

X_2=birefringence.

For the treated POY yarns, dye uptake was also negatively correlated with crystallinity ($r=-0.94$) and birefringence ($r=-0.96$). From the regression analysis, dyeability of heat set POY filaments can be written as follows:

$$\text{Dyeability}=30.28-0.01X_1-140.50X_2$$

The increased crystallinity and birefringence of the treated polyester fibers resulted in a decrease of dye uptake due to the decrease in amorphous regions and the increase of orientation. This dyeing property is quite consistent with the two-phase of structure involving a crystalline region and amorphous region.

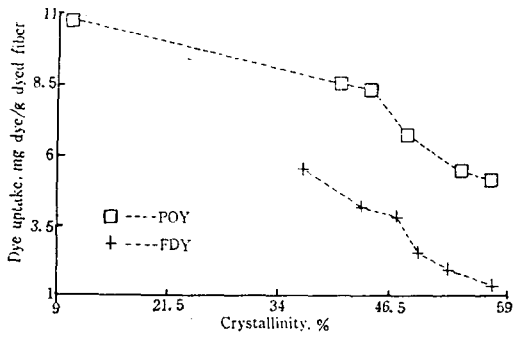


Fig. 4. Plot of Dyeability vs. Crystallinity for FDY and POY Filament Yarns.

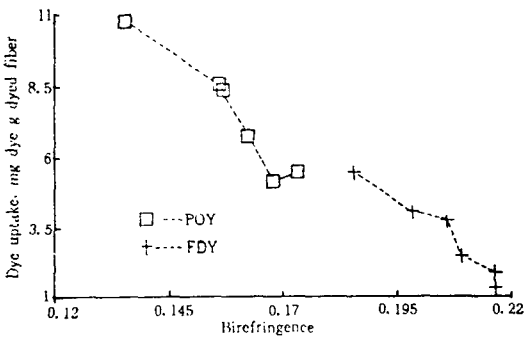


Fig. 5. Plot of Dyeability vs. Birefringence for FDY and POY Filament Yarns.

To document the relationship visually, dyeability was plotted against crystallinity (Figure 4) and birefringence(Figure 5). Looking at the figures, POY yarns showed more dyeability in spite of the similar level of crystallinity for the treated samples. Therefore, the more dyeability of the POY filaments compared with the FDY can be explained by the less birefringence value, that is, the inherent unchanged less degree of orientation.

Ⅳ. Summary and Conclusions

Changes in FDY and POY polyester filament yarns were determined after heat treatment at various temperature under constant length conditions. An attempt was made to relate structural changes and changes in dyeability due to heat setting.

Dyeability of both FDY and POY showed a decreasing tendency as treatment temperature increased. Degree of crystallinity and birefringence of both FDY and POY showed an increasing tendency as treatment temperature increased. Dyeability of both FDY and POY was highly negatively correlated with crystallinity. Also, dyeability showed negative relationship with the birefringence of the polyester yarns. The increased crystallinity and birefringence of the treated fibers was accompanied by the decreased dye uptake.

Degree of crystallinity was dependent on the heat setting temperature. The degree of crystallinity of heat set FDY and POY did not show significant differences. On the other hand, degree of orientation of the treated FDY and POY showed almost the same amount of gaps induced by the drawing condition.

The findings of this study indicate a need for further investigation in the areas of amorphours orientation and crystallite orientation which may explain the dyeability more specifically. Further investigation might well be limited to a more thorough study of a polymer while varying the treatment conditions.

REFERENCES

1) Hearle, J.W.S. and Miles, L.W.C. (Editors), The Setting of Fibers and Fabrics, Watford England: Merrow Publishing Co. Ltd., (1971)
2) Morton, W.E. and Hearle, J.W.S., Physical Properties of Textile Fibers, Manchester: Butterworth & Co. Ltd. and the Textile Institute, (1979)
3) Cho, G., Structure-Dyeability Relationship of Heat Set Poly(ethylene Terepnthalate) Filament Yarns (1), *J. Korean Home Econ. Assoc.*, **23, 3**, 17-26, (1985)
4) Dismore, P.F. and Statton, W.O., Chain Folding in Oriented Nylon 6.6 Fibers, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 133-148, (1966)
5) Koenig, J.L. and Hannon, M.J., Infrared Studies of Chain Folding in Polymers. Ⅱ. Polyethy-

lene Terephthalate, *J. Macromol. Sci., Phys.*, **1**, 119-145, (1967)

6) Venkatesh, G.M., Bose, P.J., Shah, R.V. and Dweltz, N.E., Studies on Heating and Cooling of Synthetic Fibers, Yarns and Fabrics. I. Properties of Nylon and Polyester Filament Yarns on Heat Setting in Silicone Oil, *J. Appl. Polym. Sci.*, **22**, 2357-2377, (1978)

7) Gupta, V.A. and Kumar, S., The Effect of Heat Setting on the Structure and Mechanical Properties of Poly (ethylene Terephthalate) Fiber. I. Structural Cnanges, *J. Appl. Polym. Sci.*, **26**, 1865-1876, (1981)

8) Joseph, M.L., Introductory Textile Science, 4th ed., Holt Rinehart and Winston, 112, (1981)

9) Dumbleton, J.H., Bell, J.P. and Murayama, T., The Effect of Structural Changes on Dye Diffusion in Poly (ethylene Terephthalate), *J. Appl. Polym. Sci.*, **12**, 2491-2508, (1968)

10) Merian, E., Carbonell, J., Lerch, U. and Sanahuja, V., Saturation Values, Rates of Dyeing, Rates of Diffusion and Migration of Disperse Dyes on Heat-set Polymer fibers, *J. Soc. Dyer. Colour.*, **79**, 505-515, (1963)

11) Taylor, A.R. and Fries, R.E., Precise Control Is Necessary in Heat-Setting, *Text. Chem. color.*, **2**, 147-148, (1970)

12) Warwicker, J.O., The Structural Causes of Variations in Dyeing Properties of Terylene Yarn Subjected to Dry and Wet Heat, *J. Soc. Dye. Colour.*, **88**, 142-148, (1972)

13) Warwicker, J.O., and Graham, S.G., The Structural Causes of the Dyeing Variations of Terylene Subjected to the False-Twist Texturing Process, *J. Appl. Polym. Sci.*, **21** 1137-1148, (1977)

14) Weighman, H.-D., Scott, M.G., Ribnick, A.S., and Rebenfeld, L., Interactions of Nonaqueous Solvents with Textile Fibers, Part Ⅷ: Dyeability of Polyester Yarns After Heat and Solvent Induced Structural Modifications. *Tex. Res. J.*, **46**, 574-587, (1976)

15) Dauben, R. dep., Bunn, C.W. and Brown, C.J., The Crystal Structure of Polyethylene Terephthalate, *Proc. R. Soc. London, Ser. A*, **226**, 531-542, (1954)

16) Thompson, A.B. and Woods, D.W. Density of Amorphous Polyethylene Terephthalate, *Nature(London)*, **176**, 78, (1955)

17) Samuels, R.J., Structured Polymer Properties, Wiley, New York, (1974)