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Dyeing Study on DMF-Modified Polyesters for Morphology Characterization

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Abstract

Morphology of polyester fiber was physically modified by solvent treatment. PET fiber was treated with N,N-dimethylformamide (DMF) at 100, 120, 140 ℃ for 10 minutes without tension. The structural changes in the morphology of DMF-induced modified PET fiber were FTIR and SEM analysis. Also dyeing behavior of DMF-treated polyester fibers with various disperse dyes was studied to detect changes of amorphous area in fine structure. DMF treatment resulted in increases in total void content, degree of crystallinity, trans isomer content, chain folding, segmental mobility and molecular packing, but it resulted in decreases in amorphous orientation, intermolecular forces and individual void size through longitudinal shrinkage, lateral welling and removal of oligomers. Void-size distribution could be estimated from the dye uptake with various sizes of disperse dyes. In contrast to the large increases in dye uptake with small dye molecules, there is no and little dye uptake with the bulkiest dye, which means that void size is bigger or smaller than the volume of each dye. Diffusion rates of dye molecules showed increases. This dyeing study revealed that the disperse dyeing is very effective method for characterizing the internal morphology of polyester fiber.

Key words: disperse dye, morphology, modification, amorphous, void structure.

I. Introduction

Poly(ethylene terephthalate), PET, is very important to the fiber industry due to its desirable physical and chemical properties. It still has problems to be overcome with regard to its textile use, due to its chemical inertness, hydrophobicity, chain compactness and high crystallinity. These defects give problems in the areas of dyeing, comfort, and static properties.

Therefore, many studies have been done to improve the undesirable properties of PET. Solvent treatment is one of the effective methods to modify the PET physically. Using various solvents, the fiber properties based on internal morphology of PET can be controlled and modified through the formation of open structure. Many strongly interacting solvents and solvent mixtures have been recommended for the swell-

[1] Y.-L. Hsieh, C. Pugh, and M. S. Ellison, "The Effect of Selected Organic Solvents on the Polymerization of Acrylic Acid to Poly(ethylene Terephthalate) by Grow Discharge", *Journal of Applied Polymer Science*, 29 (1984): 3547-3560.

[2] Kuwabara, S., "Dyeing of Poly(ethylene terephthalate) Pre-treated with Solvents", *Sen-I Gakkaishi*, 34(9) (1978): 56-64.

ing of PET, especially, DMF has been revealed as one of the most effective solvents interacting with PET[1~10].

The solubility parameter of DMF is 12.14 $(cal/cm^3)^{1/2}$ which is very close to that (δ = 12.1) of aliphatic segments in PET molecule, which allows DMF to disrupt strong dipole -dipole interactions between adjacent carbonyl groups in PET molecules. DMF treatment on PET results in solvent-induced secondary crystallization as well as the opening up of the polymer chains, leading to the irreversible modification of fiber structure[11].

Many researchers have modified PET by DMF pretreatment, usually prior to dyeing or grafting, and characterized each structural parameter in the internal morphology of modified-PET. Depending on the DMF treatment temperature, treatment time, tension for the constant length of polymer and the nature of the solvent, treatment can affect fiber modification quite differently. This physical modification of PET by DMF treatment also results in the changes in the molecular structure and intermolecular organization of the fiber.

These are defined in this work as the internal morphology including chain orientation, molecular conformation, intermolecular forces, degree of crystallinity, molecular packing, void structure, and segmental mobility, which is an important factor influencing its dyeing properties. The internal morphology and properties of solvent -induced modified PET has been studied extensively, however, the effect of the internal morphology of DMF-induced modified PET on the properties has not been elucidated yet.

The possibility of use of disperse dyeing was suggested as a effective method for studying the internal morphology of polyester fiber. Significant changes in color and depth of shade in dyed polyester fibers depended on differences in fiber amorphous morphology. Since disperse dyes are known to be extremely sensitive to changes in internal morphology of polyester

[3] S. Lenka, and I. B. Mohanty, "Photo-induced Graft Copolymerization: XIV-Graft Copolymerization of methyl Methacrylate onto Nylon-6 Using Acriflavine as the Photoinitiator", *Polymer Photochemistry*, 7 (1986): 285-298.

[4] Y.-J. Lim, M. Tahara, T. Takagishi, N. Kuroki, and T. Wakida, "Dyeing Behavior of Polyester Fiber Treated with Solvents: Relationship between Dyeability and Structure of Disperse Dyes", *Sen-I Gakkaishi*, 40(6) (1984): 88-92.

[5] H. L. Needles, and C. Walker, "Characterization of the Internal Morphology of Heat- and Solvent-Modified Polyester Fibers", *Journal of Applied Polymer Science: Applied Polymer Symposium* 47 (1991): 249-262.

[6] V. H. Patel, and N. V. Bhat, "Effect of Solvent Pretreatment on Dyeability and Morphology of Poly(ethylene terephthalate), *Indian Journal of Textile Research*, 11 (1986): 181-187.

[7] T. Takagishi, T. Wakida, and N. Kuroki, "Changes in Fine Structure and Dyeing Behavior of Polyester Fiber Treated with Organic Solvent/Water", *Sen-I Gakkaishi*, 34(12) (1978): 48-56.

[8] T. Wadanabe, M. Miyoshi, T. Takahashi, and I. Tsujimoto, "Crystallization of Poly(ethylene terephthalate) in Organic Solvent", *Sen-I Gakkaishi*, 33(5) (1977): 35-42.

[9] H.-D. Weigmann, M. G. Scott, A. S. Ribnick, and L. Rebenfeld, "Interactions of Nonaqueous Solvents with Textile Fibers, Part VII: Dyeability of Polyester Yarns After Heat and Solvent-Induced Structural Modifications", *Textile Research Journal*, 46 (1976): 574-587.

[10] H.-D. Weigmann, M. G. Scott, A. S. Ribnick, and R. D. Matkowsky, "Interactions of Nonaqueous Solvents with Textile Fibers, Part VIII: Mechanism of Dye Diffusion in Solvent-Treated Polyester Yarns", *Textile Research Journal*, 47 (1977): 745-752.

[11] Y. Avny, L. Rebenfeld, and H.-D. Weigmann, "The *In Situ* Polymerization of Vinyl Monomers in Polyester Yarns", *Journal of Applied Polymer Science*, 22 (1978): 125-147.

fibers and are not particularly dependent on the nature of the functional groups in the polymer, the studies on disperse dyeing behavior of polyester fibers has been used to detect changes in its internal morphology. Also diffusion of dye molecules is accepted as occurring in the amorphous region only, hence dyeing studies allow detection of changes in amorphous structure.

Dye uptake is not always governed by the total amount of amorphous areas but by the total volume and size of accessible area (voids) in amorphous region. Diffusion rate is controlled by the segmental mobility, total void amount and void size. Thermodynamic equilibrium is influenced by the crystallinity and amount of voids. Disperse dyeing behavior for solvent-modified polyester have been studied tremendously. However, the relationship between their dyeing properties and fiber morphology is still not elucidated.

Therefore, in this study the specific aim is to characterize the morphology of the DMF-induced modified PET fibers and investigate the influence of the morphology on the selected fiber properties. The dyeing characteristics and resultant colour properties of modified polyester were examined and compared. Disperse dyes were used as molecular probes in polyester fibers.

Ⅱ. Experimental

1. Material and Chemicals

Dacron Type 54 polyester fabric (catalog #767 from Test Fabrics, Inc.) was used. It consists of semicrystalline, oriented spun fibers. N,N,-dimethylformamide (DMF) and phenol were reagent grade from Fisher. DMF was used after distillation.
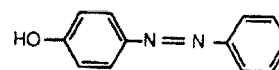
2. Disperse Dyes

The four disperse dyes were chosen due to their structural differences in size and shape: p-Nitroaniline(MW=138.13, 225 cubic Å, Solvent Yellow 7 (p-phenyl azophenol, MW=198.23, 335
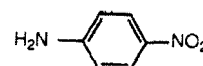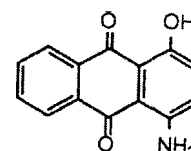

⟨Fig. 1⟩ Chemical Structure of Dyes.
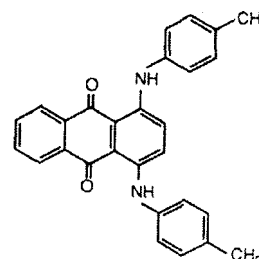
cubic Å, Disperse Red 15 (1-amino-4-hydroxyanthraquinone, MW = 238.23, 450 cubic Å, and Solvent Green 3 (MW=418.50, 4200 cubic Å. Dye size was approximated as the volume in cubic Angstroms of the smallest box that would contain a particular dye molecule[12]. All dyes were above 95% pure as the reagent grade and obtained from Aldrich Chemical Co. The four disperse dyes were purified by recrystallization from the solutions of suitable solvents. Chemical structure of dyes is shown in ⟨Fig. 1⟩.

3. DMF Treatment Procedure

1) DMF Treatment Conditions

The polyester fabrics (10×20 cm^2) were immersed in DMF at 100, 120, and 140℃ for 10 minutes without tension. After treatment, DMF-treated fabrics were air-dried or oven-dried in

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[12] H. L. Needles, and C. Walker, op. cit., pp.249-262.

the vacuum oven at 60℃ for 48 hours.

2) Weight Loss Measurement
The weight loss of DMF-treated samples was determined by weighing the conditioned specimens before (W_1) and after DMF treatment (W_0) and expressed as a percentage as follows: Weight loss(%) = $(W_1 - W_0)/W_1 \times 100$

3) Longitudinal Shrinkage Measurement
Longitudinal shrinkage of DMF-treated samples was calculated by length differences before (L_1) and after DMF treatment(L_0) at room temperature and expressed as a percentage as follows: Shrinkage(%) = $(L_1 - L_0)/L_1 \times 100$

4) Yarn Tex Measurement
Ten yarn specimens were prepared by unraveling the warp yarn from the DMF-treated fabrics. The length and weight of the yarns were measured and represented in g/1000m. Four replicas were made and the results were averaged.

5) Fiber Diameter Measurement
Fiber diameters of DMF-treated PET samples were measured through use of a calibrated optical microscope. Fifty replicas were made and the results were averaged.

4. Characterization Methods

1) Dyeing and Dyeing Measurement

(1) Dyebath Conditions
Each sample (5×5 cm^2) of the untreated, DMF-modified, and grafted PET fabrics was dyed in an infinite dye bath of an aqueous medium at 100℃ for 1/2 hour and 6 hours without any dispersing agents and carriers. The liquor ratio was 100:1 (o.w.f.). The dyed fabrics were washed with hot water.

(2) Dye Concentration Determination
The dyes were extracted from the each dyed sample using 10 % phenol in DMF and the dye concentrations were measured photometrically with a Hitachi U-2000 Spectrophotometer. Dye concentrations were calculated from absorbance with interpolation of their concentration from calibration curves. Dye concentrations were expressed in μmole/1g of dry fabric.

(3) Diffusion Coefficient Calculation
Diffusion coefficients were calculated using the following Crank equation: $C_t/C_\infty = 4(Dt/\pi r^2)^{1/2}$ where, Ct is the dye concentration in the fiber at time t, C_∞ is the maximum dye concentration (in this study taken as the dye uptake after 6 hours dyeing), D is the diffusion coefficient, and r is the fiber radius. Also Hill equation was used: $C_t/C_\infty = 1-Ae^{-By}-Ce^{-Ey}$- where, $y = Dt/r^2$; D = diffusion coefficient; r = fiber diameter; t = dyeing time; and A, B, C, D, etc, are constants. Thus C_t/C_∞ is related to Dt/r^2. Because the Hill equation is complicated, readily available solutions in the form of tables[13] were used. The value C_t/C_∞ was calculated, and the corresponding value for Dt/r^2 was read from the table, then D could be calculated.

(3) Color and Color Difference Measurement
The CIE color coordinates (x, y and z for the color and Y for the depth of shade) for the dyed samples were measured using a Macbeth MS -2000 spectrophotometer. From the standard sample, color difference (ΔE), depth of dyeing (ΔL^*) and overall shade (Δa^*, Δb^*) at each modification level were calculated automatically using the light source of illuminant C and the CIE lab color formula of Adams-Nickerson[14].

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[13] C. H. Giles, A Laboratory Course in Dyeing, Third Ed., *The Society of Dyers and Colourists*, (1974): 137.

[14] Commission Internationale l'Elcairage in Siddiqui, S. A., E. Sanders, and H. Needles, "Color Relationship of Nylon and Polyester Dyed with 1,4-Disubstituted Anthraquinones", *American Dyestuff Reporter*, 70 (1981): 26-40.

2) Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The variations in stereochemistry and spatial arrangement of the sample fibers were investigated with the vibrational spectrum of PET in the range of 4500 to 500 cm^{-1}, especially 1100 to 600 cm^{-1} region, using a FTIR (Perkin-Elmer model 1600 series). For quantitative analysis of molecular orientation, the amounts of trans and gauche conformation were determined by the relative intensity of the 973 and 875 cm^{-1} infrared absorption band, respectively. The intensity of the 973 and 875 cm^{-1} bands (C-O stretching mode of the ethylenedioxy linkage in the trans and gauche conformation, respectively) relative to the intensity of the 795 cm^{-1} band (a normal mode of the p-benzenoid linkage, used to correct for thickness variations) were measured. The fold conformation of polymer chains at the surface of folded chain was detected by the 988 cm^{-1} absorption band[15,16]. The degree of crystallinity was calculated with the relative intensity of trans conformation according to following equation[17]: $X = 12.13 - [265.00/\{(A_{973} \text{ cm}^{-1}/A_{795} \text{ cm}^{-1}) + 21.26\}]$ where, X is crystallinity, A_{973} cm^{-1} and A_{795} cm^{-1} are absorbance at wavelength 973 and 795 cm^{-1}, respectively.

3) Scanning Electron Microscopy Examination

Scanning Electron Micrographs (SEM) of samples were obtained through use of an International Scientific Instrument model DS130 Microscope. Before scanning, fiber samples were sputter coated with gold.

III. Results and Discussion

1. General Fiber Features of DMF-treated PET

Both of the chemical action from the solvent DMF and thermal energy from the DMF treatment temperature take part in changing the fiber features. As shown in ⟨Table 1⟩, great changes in macro structure of the fiber occur after DMF treatment, such as axial shrinkage, increased diameter, and weight loss of the fiber. This alters fiber features and implies significant changes in its micro structure.

Surface morphology was examined and scanning electron micrographs of the untreated PET and DMF-modified PET fiber are represented in ⟨Fig. 2⟩. It shows a great number of tiny particles on the surface of untreated PET fiber assumed to be oligomers. The particles are not found on DMF-treated PET fiber but some vertical slashes are found. Surface cavitation is not found in oriented fibers used in this study, which was shown in an unoriented amorphous PET film or fiber treated with DMF by Durning et al.[18], Góźdź and Weigmann[19], and Jameel et al.[20]. They observed varying surface morphol-

[15] A. Cunningham, and I. M. Ward, "An Infra-Red Spectroscopic Study of Molecular Orientation and Conformational Changes in Poly(ethylene Terephthalate), *Polymer*, 15 (1974): 749-756.

[16] L. D'Esposito, and J. L. Koenig, "Application of Fourier Transform Infrared Spectroscopy to the study of Semicrystalline Polymers: Poly(ethylene terephthalate)", *Journal of Polymer Science: Polymer Physics* Ed. 14 (1976): 1731-1741.

[17] Kuwabara, S. *op. cit.*

[18] C. Durning et al., "Solvent-Induced Crystallization. II. Morphology", *Journal of Polymer Science: Part b: Polymer Physics*, 24 (1986): 1341.

[19] A. S. Góźdź, and H.-D. Weigmann, "Surface Characterization of Bimorphic PET Filaments by Inverse Gas Chromatography", *Textile Research Journal*, 54 (1984): 9-17.

[20] H. Jameel, H. D. Noether, and L. Rebenfeld, "The Effect of Orientation and Crystallinity on the Solvent-Induced Crystallization of Poly(ethylene Terephthalate). II Physical Structure and Morphology", *Journal of Applied Polymer Science*, 27 (1982): 773-793.

⟨Table 1⟩ Physical Characteristics of DMF-treated PET Samples

Treatment	Weight Loss (%)	Yarn Axian Shrinkage (%)	Yarn Tex (g/km)	Fiber Diameter* (μm)
Untreated	–	–	33.5	12.75(0.97)
DMF-treated at 100 ℃	1.5	12.7	35.9	13.17(0.78)
120 ℃	1.8	17.7	37.7	13.54(0.75)
140 ℃	2.4	23.6	40.0	14.19(1.14)

* Standard error in parentheses.

(a)   (b)
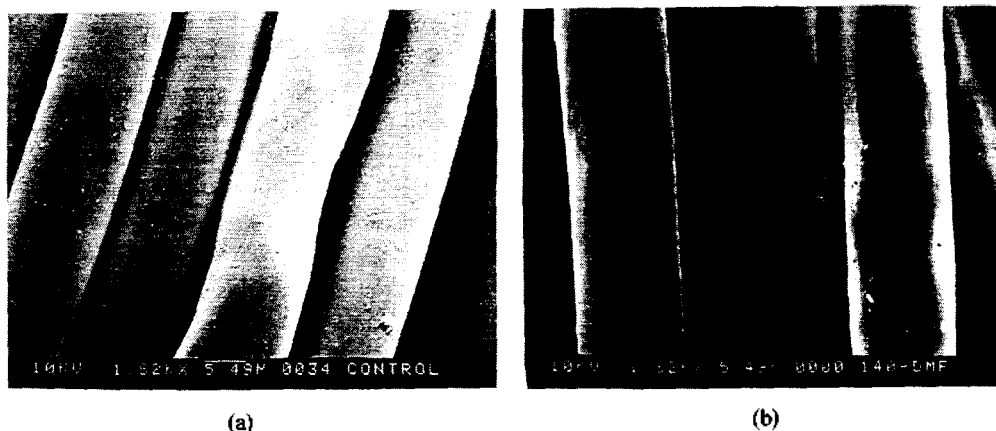
⟨Fig. 2⟩ SEM Photographs of Untreated (a) and DMF-treated (b) PET Fibers.

ogy after DMF treatment from spherulitic surface cavitation with PET of amorphous or low draw ratio to a smooth surface with PET of higher draw ratios.

2. Effect of DMF Treatment on Fine Structure

The molecular conformation, chain orientation and crystallinity of DMF-modified PET was determined through FTIR spectroscopy. The FTIR scans for the untreated PET and DMF-treated PET fibers with the band assignments of trans and gauche isomers are shown in ⟨Fig. 3⟩, and the FTIR scans with chain folding

bands are shown in ⟨Fig. 4⟩. The content of chain folding and trans and gauche isomers were calculated from these scans and listed in ⟨Table 2⟩.

The trans conformation is greater than gauche conformation for all fibers and it increases with increasing DMF treatment temperature. The crystals become larger and more perfect by chain rearrangement[21] to stabilize the shortened fiber, which causes an increase in the trans isomer formation. Usually the trans content has been determined for the drawn PET fibers. The stretched PET fibers have been shown to have an excellent correlation between total trans

[21] J. T. Guthrie, M. Ryder, and F. I. Abdel-Hay, "The Photochemically-Induced Grafting of Styrene onto Cellulose in the Homogeneous Styrene/Cellulose/D.M.S.O/HCHO System", Polymer Bulletin, 1 (1979): 501-508.
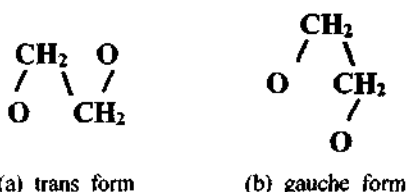
[22] K. K. Mocherla, and J. P. Bell, "Morphology of Uniaxially Oriented Poly(ethylene Terephthalate)", Journal of Polymer Science: Polymer Physics Edition, 11 (1973): 1779-1791.

<Table 2> FTIR Analysis of Relative Intensity and Concentration of Trans, Gauche & Chain Fold in DMF- treated PET Fibers
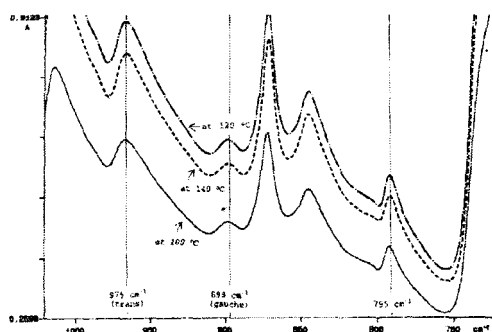
Treatment	Trans	Gauche	Chain Fold	% Trans	% Gauche	Crystallinity (%)
Untreated	1.261	0.391	**	76.3	23.7	36.3
DMF-treated						
at 100 ℃	1.605	0.326	*	83.1	16.9	54.0
120 ℃	1.571	0.310	*	83.5	16.5	52.0
140 ℃	1.865	0.324	*	85.2	14.8	67.0

* observable but not calculable.
** not apparent.

(a) trans form   (b) gauche form

<Fig. 3> Molecular Conformation of Ethylene Glycol Units in PET Molecules.

<Fig. 4> FTIR Scans with Band Assignments of Trans and Gauche Conformation in Untreated PET and DMF-treated PET Fibers.

content and overall molecular orientation[22,23], however, in the case of spun fibers, used in this study, correlate of amorphous orientation to the overall orientation is seen[24]. In contrast to the above results, DMF-treated PET fibers show an inverse relationship between trans content and amorphous orientation.

The spectra of the untreated PET has no or little indication of the 988 cm^{-1} absorption band, and the spectra of DMF-modified samples treated at 100 and 120°C have a little, whereas that of DMF-modified samples treated at 140°C shows a distinct 988 cm^{-1} absorption band. The higher the DMF treatment temperature, the greater the extent of chain folds in fibrils in crystalline area that are formed. The extended state in the drawn polymer is favored to revert to the folded form in DMF, when the temperature is raised, by thermal and kinetic energies. Chain folding occurs to make the stable form of the polymer chains during recrystallization in the contracted fiber. It must be one of the reasons of fiber shrinkage after DMF treatment consequently lowers the amorphous orientation. The chain folding content is well correlated with the trans isomers content.

The chain disorientation can be explained by the irreversible dimension fiber changes with increasing treatment temperature, irreversible contraction in fiber length (12.7~23.6%) and irreversible expansion in fiber diameter (3.3~11.3%) as shown in <Table 1>.

[23] M. Yazdanian, and I. M. Ward, "An Infra-red Study of the Structure of Oriented Poly(ethylene Terephthalate) Fibers, Polymer, 26 (1985): 1779-1789.

[24] H.-D. Weigmann, and A. S. Ribnick, "Interactions of Nonaqueous Solvents with Textile Fibers. Part IV: Effects of Solvents on the Mechanical Properties of Various Textile Yarns", Textile Research Journal, 44 (1974): 165-173.

The mechanism of shrinkage of the oriented semicrystalline PET fiber used in this study in DMF on heating and the changes in internal morphology of DMF-treated PET can be interpreted both in thermodynamic and in kinetic terms based on the observed experimental data and literature data suggested by several researchers[25~27] as follows: i) the original stress in oriented noncrystalline regions would be removed by breaking down the internal molecular bonds between neighboring extended chains on heating above the glass transition temperature and chain molecules would retract to be free or loosened, ii) crystallization of noncrystalline regions would occur after shrinkage. In the crystalline region, recrystallization of imperfect crystalline domains occurs by chain folding (in Table 2) to stabilize the crystalline form. When existing small crystals melt[28], shrunken chains may be recoiled.

In contrast to chain stretching, chain contraction shows decreases in the overall chain orientation through chain loosening, folding and coiling during DMF treatment. However, a temperature effect is not found in the overall chain orientation, which suggests chain orientation in two different regions: crystalline orientation and amorphous orientation. However, It is not available to know which region is affected in chain orientation by the birefringence method. Many researchers have shown that crystals in the crystalline region rearrange to become

fewer, larger and more perfect[29,30], and remain oriented after DMF treatment, which rises the possibility of disorientation in the noncrystalline region.

The degree of crystallinity of DMF-treated PET fibers was calculated from equations based on the content of trans isomers from the FTIR analysis. The crystallinity increases with increasing DMF treatment temperature. With the increasing trans content, the degree of crystallinity increases, also increased chain-folded crystals certainly causes an increase in crystallinity. Many researchers have reported similar results [31,32]. Recrystallization and chain rearrangement occur to stabilize the swollen structure. The greater crystallinity values indicate the higher molecular packing in the DMF-modified PET fibers. DMF-induced recrystallization and chain rearrangement results in the chain compactness in the crystalline region,

3. Effect of DMF Treatment on Void Structure

1) Disperse Dyeing and Void Structure

Disperse dyeing behavior of DMF-treated PET fibers was studied to detect changes in void structure. The color differences and color lightness after DMF treatment of PET fibers are given in ⟨Table 3⟩. Dye uptake by concentration is listed in ⟨Table 4⟩.

Color changes and dye uptake of four dis-

[25] W. E. Morton, and J. W. S. Hearl, Physical Properties of Textile Fibers, The Textile Institute and Butterworth & Co. (1975)

[26] A. S. Ribnick, "The Thermal Shrinkage of an Oriented Polyester Yarn as a Function of Time, Temperature, and Stress", Textile Research Journal, 39 (1969): 742-749.

[27] A. S. Ribnick, and H.-D. Weigmann, "Interactions of Nonaqueous Solvents with Textile Fibers. Part III: The Dynamic Shrinkage of Polyester Yarns in Organic Solvents", Textile Research Journal, 43 (1973): 316-325.

[28] J. T. Guthrie, M. Ryder, and F. I. Abdel-Hay, op. cit., pp.501-508.

[29] H. L. Needles, and C. Walker, op. cit., pp.249-262.

[30] T. Takagishi, T. Wakida, and N. Kuroki, op. cit., pp.48-56.

[31] T. Wadanabe, M. Miyoshi, T. Takahashi, and I. Tsujimoto, op. cit., pp.35-42.

[32] H.-D. Weigmann, M. G. Scott, A. S. Ribnick, and L. Rebenfeld, op. cit., pp.574-587.

⟨Table 3⟩ Color Difference and Lightness for DMF-treated PET Fibers Dyed with Disperse Dyes

A) Color Difference (ΔE)

Treatment \ Dye Dyeing Time(hr)	p-nitro		Sol Y 7		Dis R 15		Sol G 3	
	1/2	6	1/2	6	1/2	6	1/2	6
Untreated	–	–	–	–	–	–	–	–
DMF-treated								
at 100°C	3.5	2.7	2.6	2.7	7.2	7.9	1.9	4.6
120°C	5.4	4.6	3.5	4.4	12.1	11.1	3.9	6.8
140°C	7.7	7.2	5.3	6.3	19.2	12.6	4.6	11.1

B) Depth of Shade (Y)

Treatment \ Dye Dyeing Time(hr)	p-nitro		SolY-7		Dis R 15		Sol G 3	
	1/2	6	1/2	6	1/2	6	1/2	6
Untreated	68.6	67.5	44.7	42.4	5.6	3.1	56.9	31.0
DMF-treated								
at 100°C	67.3	64.5	42.6	40.5	4.5	2.8	59.8	36.5
120°C	66.9	64.7	42.2	39.3	4.2	2.7	59.8	36.5
140°C	66.7	64.0	41.8	38.1	3.6	2.7	64.1	44.7

⟨Table 4⟩ Dye Concentration and Relative Dye Uptake of DMF-treated PET Fibers

Treatment \ Dye Dyeing Time(hr)	p-nitro		SolY-7		Dis R 15		Sol G 3	
	1/2	6	1/2	6	1/2	6	1/2	6
untreated	111.1 (1.00)	148.5 (1.00)	169.2 (1.00)	203.8 (1.00)	23.4 (1.00)	70.9 (1.00)	0.505 (1.00)	3.841 (1.00)
DMF-treated								
at 100 °C	136.5 (1.21)	179.4 (1.21)	193.1 (1.14)	213.6 (1.05)	30.6 (1.31)	96.1 (1.36)	0.007 (0.01)	1.182 (0.31)
120 °C	144.1 (1.22)	181.4 (1.22)	200.6 (1.19)	223.7 (1.10)	34.6 (1.48)	104.6 (1.48)	0.000 (0)	0.657 (0.17)
140 °C	155.7 (1.22)	180.8 (1.22)	199.2 (1.18)	252.4 (1.24)	37.6 (1.61)	95.9 (1.36)	0.000 (0)	0.000 (0)

* ( ) relative dye uptake: ratio of dye uptake for DMF-treated PET to untreated PET.
** dye concentration: μmole × 10^2 / 1 g of dry fabric.

perse dyes, chosen due to their structural differences in size and shape, give a greater understanding of the void structure, total void content and void size within the DMF-modified fibers. Already the possibility of void creation has been noticed based on the weight loss (1.5 %~2.4%) of the fiber after DMF treatment. PET oligomers dispersed throughout the fiber

were extracted. Dyeing properties of DMF-treated PET fibers are compared with the untreated sample as a standard.

The depth of shade(Y) for the DMF modified samples, which is given in 〈Table 3〉, increases with increasing DMF treatment temperature for the three small and less bulky disperse dyes, p-Nitroanline, Solvent Yellow 7 and Disperse Red 15 lowering Y values (darker), but decreases for the bulkiest dye, Solvent Green 3 (brighter). Overall shifts in color differences are shown for the dyed samples as DMF treatment temperature increases. Needles et al.[33~35] explained these phenomena producing color shift with the several factors involving location, orientation and aggregation of the dyes and the nature of physical interactions between dye and polymer. DMF treatment caused the changes in the inherent morphology of PET fiber, which changes dye-substrate interactions and leads to the alteration of color properties.

2) Dye Uptake and Total Void Volume

Dye uptake for short times (C_t) and maximum dye uptakes (C_∞) were determined by measuring the dye concentration of the dyed samples and a percentage of initial dye uptake, the ratio of C_t/C_∞ were calculated and listed in 〈Table 5〉. It shows the same trend as color changes for the four dyes.

Dye uptake of small disperse dyes in DMF-treated PET fibers is not influenced by the volume fraction of the noncrystalline region, into which dye molecules only can penetrate. Dye uptake is always correlated with the total void volume in the noncrystalline region. There-

〈**Table 5**〉 Initial Dye Uptake of DMF-treated PET Fibers

Treatment	p-nitro	Sol Y 7	Dis R 15	Sol G 3
Untreated	0.7481	0.8302	0.3300	0.1315
DMF-treated				
at 100 ℃	0.7609	0.9040	0.3184	0.0059
120 ℃	0.7944	0.8967	0.3308	0
140 ℃	0.8612	0.7892	0.3921	0

* Initial dye uptake: the ratio of dye uptake for 1/2 hour to 6 hours.

fore, the differences between these two regions, the accessible dye sites (voids) in the amorphous region and the noncrystalline fraction should be distinguished elucidating the internal morphology of the fiber and its diffusion properties.

From the considerable maximum dye uptake of the smallest-sized dye molecules, it is assured that DMF treatment creates voids in the fiber, and that more voids are formed at higher temperatures. Short-term dye uptake is more sensitive to changes in the void content. The weight loss from the DMF-treated fibers suggested in advance the possibility of the void formation by the removal of oligomers. Oligomers are defined as the low molecular weight members of a homologous series from PET polymer that could be removed with DMF and boiling water during treatment.

Without using the void conception, Yonetake et al.[36] studied structural changes in the amorphous area by disperse dye sorption with rod -like dye molecules. The long rod-like dye

[33] H. L. Needles, S. Holmes, and M.-J. Park, "The Dyeing and Color Characteristics of Disperse-Dyed Alkali-treated Polyester", Journal of the Society of Dyers and Colorists, 106 (1990): 385-388.

[34] H. L. Needles, A. C. Laidlaw, and S. Polak, "The Effect of Heat Setting and Dyebath Concentration of the Color Properties of Anthraquinone Disperse-Dyed Polyester", Book of Papers, 1984 National Technical Conference, American Association of Textile Chemists and Colorists (1984).
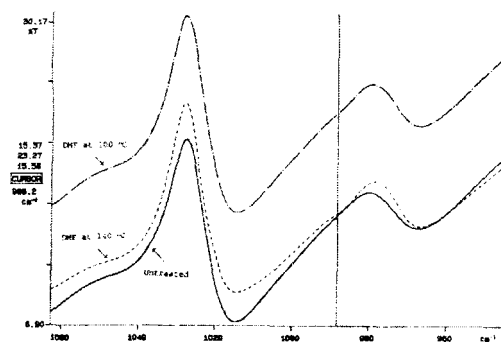
[35] H. L. Needles, A. T ai, and H. Bluen, "The Effect of Dye Interactions on Color", Textile Chemist and Colorists, 15 (1983): 205-208.

[36] K. Yonetake, T. Masuko, K. Takahashi, and M. Karasawa, "Equilibrium Sorption of Disperse Dye in Isotactic Polypropylene Films Treated with Organic Solvents", Sen-I Gakkaishi, 40(4) (1984): 294-303.

⟨**Table 6**⟩ Diffusion Coefficients of DMF-treated PET Fibers   (x 10^{-9} cm²/sec)

Dye / Equation / Treatment	p-nitro		SolY-7		Dis R 15		Sol G 3	
	Crank	Hill	Crank	Hill	Crank	Hill	Crank	Hill
Untreated	6.20	15.82	7.63	21.94	1.21	2.24	0.19	0.32
DMF-treated								
at 100 ℃	6.84 (1.10)	17.74 (1.12)	9.66 (1.26)	32.92 (1.50)	1.20 (1.00)	2.21 (0.99)	0.0004 (0.002)	0.001 (0.003)
120 ℃	7.88 (1.27)	21.39 (1.35)	10.05 (1.32)	33.50 (1.53)	1.37 (1.14)	2.54 (1.13)	0 (0)	0 (0)
140 ℃	10.18 (1.64)	31.13 (1.97)	8.55 (1.12)	23.01 (1.05)	2.11 (1.76)	4.06 (1.81)	0 (0)	0 (0)

Numbers in parentheses below diffusion coefficients (D) are the relative diffusion coefficients, which are the ratio $D_{sample}/D_{control}$

⟨**Fig. 5**⟩ FTIR Scans with Band Assignments of Chain Fold Conformation in Untreated PET and DMF-treated PET Fibers.

molecules, such as Solvent Yellow 3 in this work, tended to bind tightly by dispersion forces between dye molecules and polymer chains due to their parallel alignment with the tie chains, loosening of fold faces, cilia chains and molecular chains in the amorphous side region.

Relative dye uptake, the ratio of dye concentration for DMF-treated PET fibers to that of untreated fibers given in ⟨Table 4⟩ of the rod-like

dye molecule is lower than that of p-Nitroaniline after DMF treatment. Similar to the suggestions of Yonetake et al.[37], it is assumed without considering the void concept that the fold loops are tightened up, tie chains are reduced, and cilia chains are shortened due to the larger and perfect crystallite formation in recrystallization process during the DMF treatment. Also, dye sorption in the region located parallel to the chain axis between crystallites might be reduced.

3) Dye Size and Void Size

Even as the total void content increases, the individual void size certainly becomes smaller after DMF treatment. Void-size distribution could be estimated from the dye uptake with various sizes of disperse dyes in ⟨Table 4⟩. In contrast to the remarkable increases in dye uptake with p-nitroaniline, Solvent Yellow 3 and Disperse Red 15 after DMF treatment, there is no and little dye uptake with the bulkiest dye of Solvent Green 3, which means that void size is bigger than dye volume of Disperse Red 15

[37] K. Yonetake, T. Masuko, K. Takahashi, and M. Karasawa, *op. cit.*, pp.294-303.

[38] Y.-J. Lim, M. Tahara, T. Takagishi, N. Kuroki, and T. Wakida, *op. cit.*, pp.88-92.

(approximately 450 cubic Å but smaller than that of Solvent Green 3 (approximately 4200 cubic Å. DMF treatment results in the most increase in the relative dye uptake of the larger dye Disperse Red 15. Lim et al.[38] has compared saturation dye uptake values using a series of anthraquinone dyes (which are smaller than Solvent Green 3) and has suggested that larger or more bulky dyes is more accessible to the DMF-treated PET fiber. This would occur only when the voids are larger than the dyes in size. The voids should have sufficient space for the larger-sized dye molecules to penetrate into the fiber, but the void size of DMF-treated fibers presumably is too small to permit diffusion of Solvent Green 3.

IV. Summary and Conclusions

Morphology of polyester fiber was physically modified by solvent treatment. PET fiber was treated with N,N,-dimethylformamide (DMF) at 100, 120, 140 ℃ for 10minutes without tension. The structural changes in the morphology of DMF-induced modified PET fiber were FTIR and SEM analysis. Also dyeing behavior of DMF-treated polyester fibers with various disperse dyes was studied to detect changes of amorphous area in fine structure.

DMF treatment resulted in increases in total void content, degree of crystallinity, trans isomer content, chain folding, segmental mobility and molecular packing, but it resulted in decreases in amorphous orientation, intermolecular forces and individual void size through longitudinal shrinkage, lateral swelling and removal of oligomers. Void-size distribution could be estimated from the dye uptake with various sizes of disperse dyes. In contrast to the large increases in dye uptake with small dye molecules, there is no and little dye uptake with the bulkiest dye, which means that void size is bigger or smaller than the volume of each dye. Diffusion rates of dye molecules showed increases. This dyeing study revealed that the disperse dyeing is very effective method for characterizing the internal morphology of polyester fiber.

References

Avny, Y., L. Rebenfeld & Weigmann, H. -D. 1978. The In Situ polymerization of vinyl monomers in polyester yarns, *Journal of Applied Polymer Science*, 22.

Commission Internationale l'Elcairage in Siddiqui, S. A., Sanders, E. & Needles, H. 1981. Color relationship of nylon and polyester dyed with 1,4-disubstituted anthraquinones, *American Dyestuff Reporter*, 70.

Cunningham, A. & Ward, I. M. 1974. An infra-red spectroscopic study of molecular orientation and conformational changes in poly(ethylene terephthalate), *Polymer*, 15.

D'Esposito, L & Koenig, J. L. 1976. Application of fourier transform infrared spectroscopy to the study of semicrystalline polymers: poly(ethylene terephthalate), *Journal of Polymer Science: Polymer Physics Ed.* 14.

Durning, C et al., 1986. Solvent-induced crystallization. II. morphology, *Journal of Polymer Science: Part b: Polymer Physics*, 24.

Gd, A. S. & Weigmann, H.-D. 1984. Surface characterization of bimorphic PET filaments by inverse gas chromatography, *Textiles Research Journal*, 54.

Giles, C. H. 1974. A laboratory course in dyeing, third ed., The Society of Dyers and Colourists.

Guthrie, J. T., Ryder, M. & Abdel-Hay, F. I. 1979. The photochemically-induced grafting of styrene onto cellulose in the homogeneous Styrene/Cellulose/D.M.S.O/ HCHO System, *Polymer Bulletin*, 1.

Hsieh, Y.-L., Pugh, C. & Ellison, M. S. 1984. The effect of selected organic solvents on the polymerization of acrylic acid to poly (ethylene Terephthalate) by grow discharge, *Journal of Applied Polymer Science*, 29.

Jameel, H., Noether, H. D. & Rebenfeld, L. 1982. The effect of orientation and crys-

tallinity on the solvent-induced crystalli-zation of poly(ethylene terephthalate). II Physical structure and morphology, *Journal of Applied Polymer Science*, 27.

Kuwabara, S. 1978. Dyeing of poly(ethylene terephthalate) pre-treated with solvents, sen -I *Gakkaishi*, 34.

Lenka, S. & Mohanty, I. B. 1986. Photo-in-duced graft copolymerization: XIV-Graft copolymerization of methyl methacrylate onto nylon-6 using acriflavine as the pho-toinitiator, *Polymer Photochemistry*, 7.

Lim, Y.-J., Tahara, M., Takagishi, T., Kuroki, N. & Wakida, T. 1984. Dyeing behavior of polyester fiber treated with solvents: rela-tionship between dyeability and structure of disperse dyes, Sen-I *Gakkaishi*, 40.

Mocherla, K. K. & Bell, J. P. 1973. Mor-phology of uniaxially oriented poly(ethylene terephthalate), *Journal of Polymer Science: Polymer Physics Edition*, 11.

Morton, W. E. & Hearl, J. W. S. 1975. Phys-ical properties of textile fibers, The Textile Institute and Butterworth & Co.

Needles, H. L., T. ai, A. & Bluen, H. 1983. The effect of dye interactions on color, *Textiles Chemist and Colorists*, 15.

Needles, H. L., Laidlaw, A. C. & Polak, S. 1984. The effect of heat setting and dye-bath concentration of the color properties of anthraquinone disperse-dyed polyester, Book of Papers, 1984 National Technical Confer-ence, American Association of Textile Chemists and Colorists.

Needles, H. L., Holmes, S. & Park, M.-J. 1990. The dyeing and color characteristics of disperse-dyed alkali-treated polyester, *Jour-nal of the Society of Dyers and Colorists*, 106.

Needles, H. L. & Walker, C. 1991. Charac-terization of the internal morphology of heat- and solvent-modified polyester fibers, *Journal of Applied Polymer Science: Ap-plied Polymer Symposium*, 47.

Patel, V. H. & Bhat, N. V. 1986. Effect of solvent pretreatment on dyeability and mor-phology of poly(ethylene terephthalate), *Indi-an Journal of Textile Research*, 11.

Ribnick, A. S. 1969. The thermal shrinkage of an oriented polyester yarn as a function of time, temperature, and stress, *Textile Research Journal*, 39.

Ribnick, A. S. & Weigmann, H.-D. 1973. Interactions of nonaqueous solvents with textile fibers. part iii: the dynamic shrinkage of polyester yarns in organic solvents, *Textile Research Journal*, 43.

Takagishi, T., Wakida, T. & Kuroki, N. 1978. Changes in fine structure and dyeing behav-ior of polyester fiber treated with organic solvent/water, Sen-I *Gakkaishi*, 34.

Wadanabe, T., Miyoshi, M., Takahashi, T. & Tsujimoto, I. 1977. Crystallization of poly (ethylene terephthalate) in organic solvent, Sen-I *Gakkaishi*, 33.

Weigmann, H.-D., Scott, M. G., Ribnick, A. S. & Rebenfeld, L. 1976. Interactions of nonaqueous solvents with textile fibers, part vii: dyeability of polyester yarns after heat and solvent-induced structural modifica-tions, *Textile Research Journal*, 46.

Weigmann, H.-D. & Ribnick, A. S. 1974. In-teractions of nonaqueous solvents with tex-tile fibers. part iv: effects of solvents on the mechanical properties of various textile yarns, *Textile Research Journal*, 44.

Weigmann, H.-D., Scott, M. G., Ribnick, A. S. & Matkowsky, R. D. 1977. Interactions of nonaqueous solvents with textile fibers, part viii: mechanism of dye diffusion in solvent -treated polyester yarns, *Textile Research Journal*, 47.

Yazdanian M. & Ward, I. M. 1985. An infra -red study of the structure of oriented poly (ethylene Terephthalate) Fibers, *Polymer*, 26.

Yonetake, K., Masuko, T., Takahashi, K. & Karasawa, M. 1984. Equilibrium sorption of disperse dye in isotactic polypropylene films treated with organic solvents, Sen-I *Gakkaishi*, 40.