

Studies on Dyeing and Structural Behavior of Chemically Treated Polyester Yarns

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SYNOPSIS

The dyeing behavior of poly(ethylene terephthalate) based flat, high twist, and spun yarns pretreated with trichloroacetic acid–methylene chloride (TCAMC) reagent was studied. Disperse dyes having two different energy levels were employed for the dyeing work. The effect of time, temperature, and dye diffusion transition temperature (T_D) on dye uptake was analyzed. A considerable increase in equilibrium dye uptake and decrease in T_D of all the treated yarns were observed. The variations in dye diffusion behavior of higher and lower molecular weight dyes and the difficulties encountered in calculating the diffusion coefficient of the dyes are discussed. The structural and morphological changes effected by the pretreatment were also investigated using XRD and SEM, respectively. The increase in lateral order of the treated yarns was noted. The possible reason for an unusual relationship between the increase in lateral order and increase in dye uptake was explained. The cross-sectional shape and swelling and the smoothening out of the fiber surface were evidenced by SEM. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In an earlier article¹ the tensile behavior of various polyester yarns modified by the trichloroacetic acid–methylene chloride (TCAMC) solvent system was discussed. It is inferred from the study that the changes in tensile properties of poly(ethylene terephthalate) based polyester fibers reflect the structural modifications induced by TCAMC treatment. An improvement in dye uptake of fibers is connected with structural changes. Several researchers^{2–9} studied this effect. The dyeing characteristics of thermally modified polyester yarns are quite different from those of chemically modified polyester yarns.^{3–13} In the former a decrease in dye uptake is observed at lower heating temperature, and the subsequent increase in treatment temperature showed reversal in trend^{11,12}; in the latter only the increase in dye uptake, in most instances, resulted. This improvement in dye diffusion is due to the increase in

segmental mobility of the polymer and the creation of more microvoids, cracks, etc. in the polymer structure.³ On the other hand, combined heat and solvent treatments produce varying degrees of changes in dye absorption.^{3–6,10} This article deals with the dyeability characteristics of TCAMC pretreated polyester yarns. In addition, the structural changes due to the TCAMC treatment are also reported.

EXPERIMENTAL

Materials

Flat filament yarn (FFY; 5OD/36) obtained from Orissa Synthetics (Dhenkanal, India), high twist filament yarn [HTFY; 40D/27; $2200 \pm 5\%$ twist per meter] and spun polyester yarn (SPY; Ne 20/1) supplied by Reliance Industries Ltd. (Bombay, India) were used. All the aforementioned polyester yarns are of the poly(ethylene terephthalate) type.

Chemicals

All chemicals used were laboratory grade (LR): TCA, MC (dichloromethene), and acetone.

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Dyes

The disperse dyes used were CI disperse blue 183 (MW 473) and CI disperse red 91 (MW 355). The former is an azo type and the latter is an anthraquinoid type. The structures are illustrated in Figure 1.

Treatment Procedure

The yarn samples in the form of skeins were treated with TCAMC reagent at various concentrations for 5 min at ambient temperature of about 30°C. The treatments were carried out in a relaxed state in a closed rectangular trough. The material to liquor ratio was maintained at 1 : 100. After the treatment, the samples were rinsed with pure MC followed by acetone to remove any adhering reagent. Because the final rinsing solvent acetone can be easily removed by ambient drying or with hot air for a few seconds, there was no solvent retention on the treated yarns. The dried and conditioned [65% relative humidity (RH) \pm 2%; 27 \pm 2°C] samples were used for experimental work.

XRD

A Philips X-ray generator fitted with a texture goniometer attachment was utilized for calculating the X-ray order factor of both untreated and treated yarns. The samples were scanned in the transmission mode and reflection mode. In the transmission mode an equatorial scan from a well parallelized bundle of filaments was taken; in the reflection mode the yarn was cut into fine powder, passed through a 300 mesh, and made into a 100 mg circular pellet with a special die. All the patterns were run under the same experimental conditions of instrumental setting.

Birefringence

A polarizing light microscope fitted with a Berek compensator was used for determining the molecular orientation of the yarns. A retardation method described elsewhere¹⁴ was followed for birefringence measurement.

SEM Topography

The SEM observations were carried out on the samples after mounting them on specimen stubs and coating with Au-Pd in a vacuum fine coat ion sputter (JFC-1100). The thickness of the coating and time were optimized before the samples were examined in a Jeol SEM (T 330A-368). A micron reader provided in the instrument was used for measuring the distance between two points (horizontal and vertical) of the cross-sectional video image of the samples. The specimen tilting facility available was also utilized for accurate measurement. An average of 10 readings in each case is reported.

Dyeing Procedure

The dyes in the form of crude dry powder without any diluents and dispersing agents were used as received. The purity of dyes was checked at the laboratory before commencing the dyeing. No carrier was added in the dye bath because the presence of carrier can alter the structure of the yarns and diffusion behavior of the dyes causing the interpretation of results to be complicated. However, a little dispersing agent (0.2 g/L) was added to promote the dissolution of dyes. The higher material-liquor ratio of 1 : 600 was maintained. The dyeing was conducted in a laboratory model Ahiba polymat dyeing machine. Dyeings were made at different temperatures

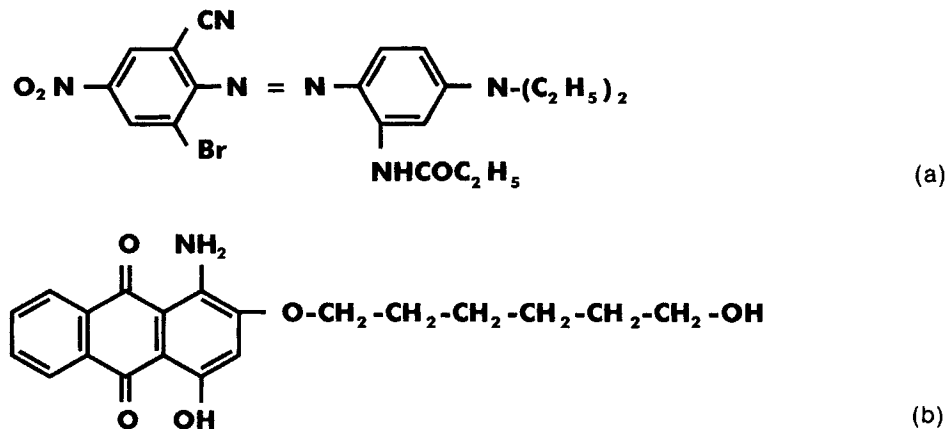


Figure 1 Structure of dyes: (a) CI disperse blue 183 and (b) CI disperse red 91.

from 85 to 130°C for varying lengths of time up to 960 min, namely saturation. After the predetermined dyeing period, the samples were taken off and washed under running water to remove the adhering dye. The free surface deposited dye was eliminated by rinsing several times in acetone until the last rinse was colorless. The dyed samples were then dried at ambient conditions and taken for extraction work.

Analysis of Dye Content

Because the determination of the amount of dye absorbed by the yarn is one of the main criteria in interpreting the results, greater care was taken to select and optimize the test procedure. The dye content of any dyed substrate can be determined either by dissolving the dyed sample in a suitable solvent or extracting the dye from the dyed ones.¹⁵ A trial and error method was done employing those methods because both have some merits and demerits. The extraction method proposed by Kissa,¹⁶ which

makes use of stabilized and acidified dimethyl formamide (DMF) as an extractant, was finally adopted.

About 0.2 g of dyed yarn was placed in an extraction flask containing 10 mL of DMF stabilized with an antioxidant (2,6-di-*t*-butyl-4-methylphenol) and acidified with a nonvolatile acid (*p*-toluenesulfonic acid) to adjust the apparent pH to 4. The flask was heated at 140°C for 2 min and the extract was immediately transferred into a 100-mL standard volumetric flask cooled in ice water. This procedure was repeated twice for the sample dyed at lower temperature and thrice for the higher temperature dyed ones. The extracted sample was inspected to ensure complete desorption of dye.

Spectrophotometric Evaluation

The OD of the dye extract was measured using a Milton Roy double beam color graph. Previously, a linear correlation between OD and dye concentration was established by measuring the OD of a series of dye solutions of known concentrations. The dye

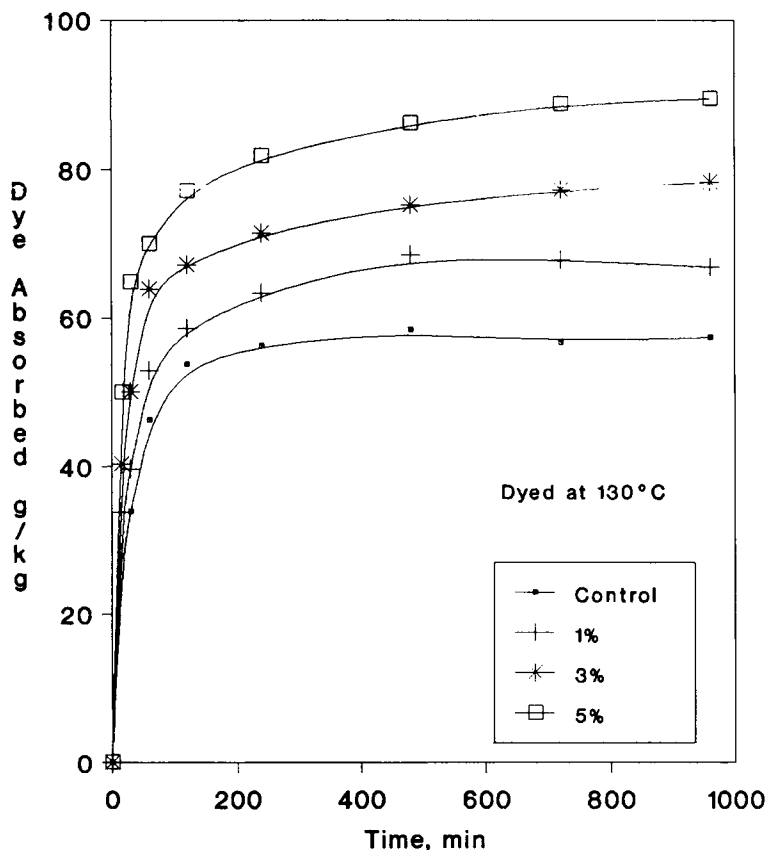


Figure 2 Dyeing kinetics of flat yarn with CI disperse blue 183.

uptake in grams per kilogram of yarn was estimated from the calibration chart.

Effect of Pretreatment on Dyeing Behavior

The FFY, SPY, and HTFY samples treated with 1, 3, and 5% TCAMC for 5 min were dyed with medium and high energy level disperse dyes at 85, 100, 115, and 130°C for 15, 30, 60, 120, 240, 360, 480, and 960 min. Each time the respective untreated yarn was also dyed simultaneously under identical conditions for comparison. Some typical plots of the amount of dye absorbed by the yarn at the dyeing temperature of 130°C vs. different times are shown in Figures 2-7. The equilibrium dye uptake was taken as the dye in the yarn after 16 h of dyeing. In some cases, especially samples dyed at lower temperatures, although equilibrium values require a much longer dyeing time, a period of 16 h may be considered reasonable because the dye uptake curves became asymptotic in this region. The saturation dye uptake

values are given in Table I. It can be seen that all the treatments led to increased dyeability compared to that observed for the respective control sample. Both the rate of dyeing and the uptake of dye at equilibrium were observed to increase with treatment concentration. The steeper the curve, the greater the rate of dyeing and it drops to zero as the dyeing approaches the saturation level. These changes in dyeing behavior reflect changes in fiber structure effected by TCAMC treatment. The major changes in fiber structure depend on the extent of interaction between the polymer and the reagent. As a result of this interaction, a significant effect on the dyeing behavior takes place. The interpretation of dyeing phenomena during the transportation of dye molecules from the dye bath to the interior of the fiber is discussed in detail elsewhere.¹⁷ The improvement in dye uptake observed in the treated yarns, irrespective of their nature, is probably from the large increase in available free volume and thereby greater segmental mobility of polymer molecules, a decrease in glass transition temperature (T_g), formation of microvoids, cracks, and so on.^{3,4} In addition, there are two main hypotheses dealing

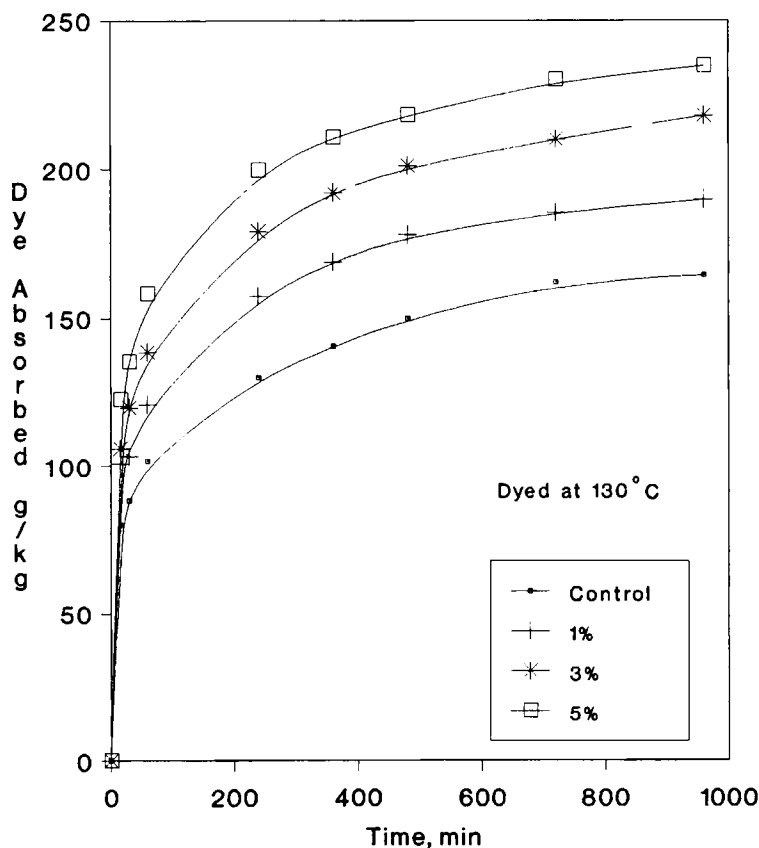


Figure 3 Dyeing kinetics of flat yarn with CI disperse red 91.

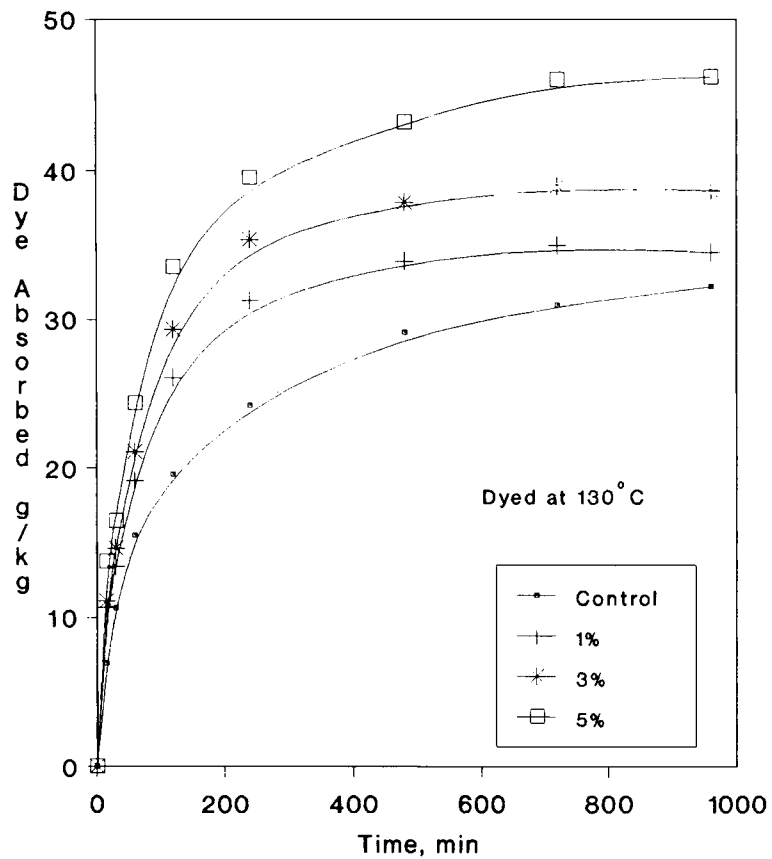


Figure 4 Dyeing kinetics of spun yarn with CI disperse blue 183.

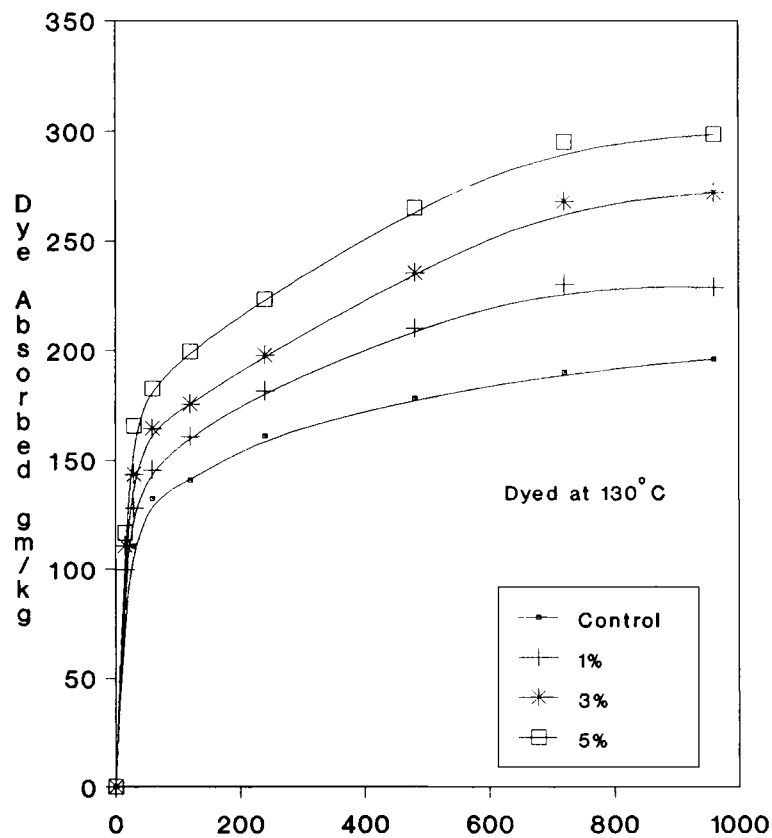


Figure 5 Dyeing kinetics of spun yarn with CI disperse red 91.

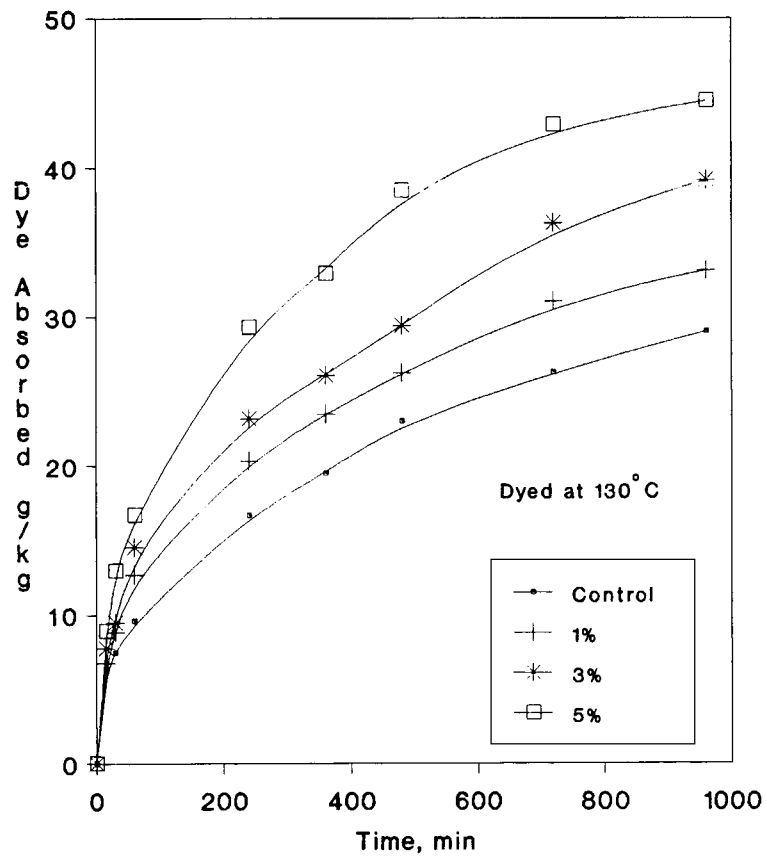


Figure 6 Dyeing kinetics of high twist yarn with CI disperse blue 183.

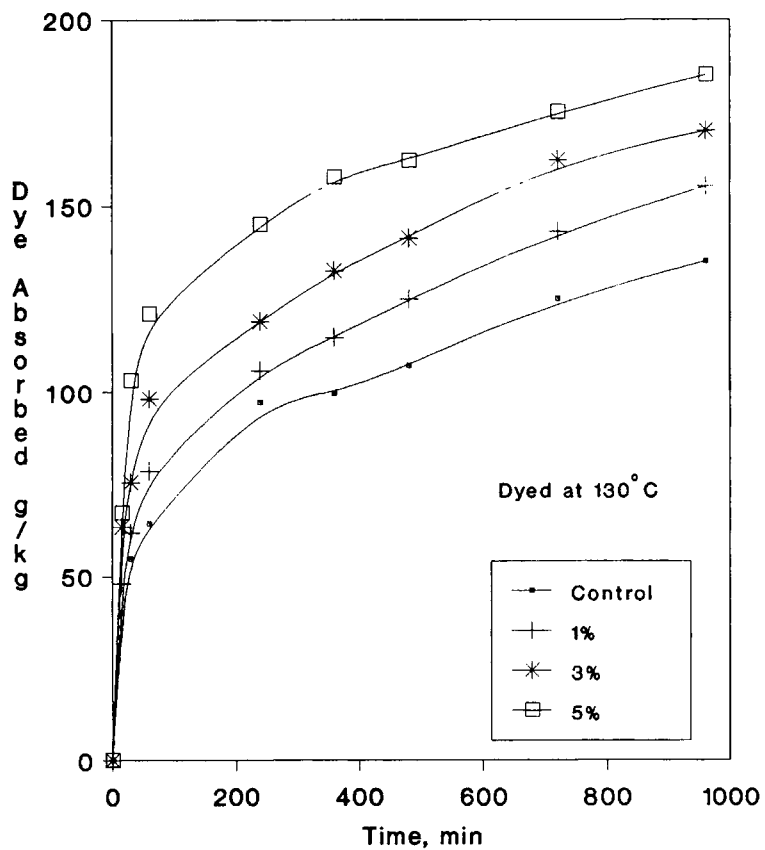


Figure 7 Dyeing kinetics of high twist yarn with CI disperse red 91.

Table I Effect of Pretreatment on Equilibrium Dye Uptake of Polyester Yarn

Percent Concn (w/v)	Dyeing Temp. (°C)	Equilibrium Values for Yarns (g/kg)					
		Flat Filament		High Twist Filament		Spun	
		CI Disperse Blue 183	CI Disperse Red 91	CI Disperse Blue 183	CI Disperse Red 91	CI Disperse Blue 183	CI Disperse Red 91
0	85	3.49	6.45	1.23	4.52	1.57	3.32
1	85	3.98	11.05	1.41	5.23	1.67	5.65
3	85	4.59	13.68	1.54	5.61	2.30	6.52
5	85	6.01	20.07	1.66	6.15	3.17	10.95
0	100	12.96	32.11	3.76	21.93	4.22	14.17
1	100	17.02	46.64	3.92	22.84	5.33	22.02
3	100	20.41	54.79	4.74	25.45	6.33	26.27
5	100	32.96	66.56	5.77	28.74	12.59	41.98
0	115	42.60	58.94	16.82	44.92	15.80	42.23
1	115	53.33	74.28	17.95	46.88	19.49	47.36
3	115	63.06	87.42	18.94	48.03	24.88	50.84
5	115	82.36	98.35	23.19	48.35	38.05	65.05
0	130	57.40	164.48	29.01	135.13	32.22	195.97
1	130	66.85	189.80	33.11	155.25	34.51	228.78
3	130	78.32	218.01	39.15	170.25	38.65	272.02
5	130	89.53	234.73	44.46	185.25	46.15	298.73

with the influence of solvent treatment on dye uptake. According to the first hypothesis,¹² the solvent treatment increases the amorphous volume per crystallite in the amorphous region of the polymer. This increases the higher segmental mobility of the molecules in the polymer and facilitates higher dye absorption. The crystalline phase is not at all involved in dyeing. The second hypothesis¹⁸ states that the noncrystalline region in the polymer is further divided into completely oriented (anisotropic) and completely unoriented (isotropic) regions. The interaction of solvent with the polymer results in the disorientation of anisotropic domains yielding a more open structure.

The above discussions show that the TCAMC reagent influences the polyester polymer for secondary crystallization. The well-known thermal treatment (heat setting) also induces the secondary crystallization in the polymer.¹⁹ However, there are some differences in dye diffusion behavior between solvent induced crystallization and thermal induced crystallization. In the former the dye uptake is found to increase with the increase in solvent induced crystallinity; the latter involved a reduction in dye uptake at lower heating temperature and after about 170°C, the trend was reversed. This less receptivity for dye at lower heating temperature of thermal treatment is due to the increase in the degree of

crystallinity; and as the heat treatment temperature increases, the polymer has loosening of the structure by disorientation and as a result the receptivity for dye increases. It appears that the TCAMC reagent increases the freedom of motion of polymer molecules by reducing the attractive forces between them. Because of this, a much faster rate of diffusion of dye through the fiber takes place. It is observed in Figures 2-7 that the magnitude of increase in dye uptake of treated yarns at a given dyeing temperature and time is found to be in the order of FFY > SPY > HTFY. The least dye uptake is observed in HTFY samples. This may be attributed to the fact that penetration of TCAMC reagent into the polymer is restricted due to the compact structure of the yarn and hence the insufficient structural modification induced in the polymer. It is also observed that the molecular weight of dyes plays an important role in dye diffusion behavior. The dye uptake of yarns, irrespective of their state, dyed with high energy level dye is lower than the medium energy level dyed ones. This difference in diffusivity of dye may be due to the differences present in the structure of the dye and the shape of the molecules. The larger dye molecules are restricted in their movement at the fiber surface and also within the fiber. Therefore, the diffusion property of dye into the polymer is diminished with an increase in mo-

lecular weight. However, there are some studies in which the opposite occurs.²⁰

Diffusion Coefficient

Most researchers follow the practice of using diffusion equations to calculate the rate of diffusion of dyes in a dyeing system. The greater the magnitude of diffusion coefficient, the more rapidly can the dye molecules penetrate into the fiber structure. Of course, the diffusion coefficient is not only used to predict the relative dyeing speed but is also used to study the structural changes effected in the fiber by various agencies. However, several workers^{21,22} observed that diffusion equations are not widely used because of the complexity involved in solving the formula. Etters²³ made greater efforts and proposed a simplified formula to determine the diffusion coefficient of dyes. In spite of that, several researchers found contradictory observations in interpreting the results of diffusion coefficient of disperse dyes. For instance, the results of Needles and Walker⁵ are consistent with that of Gupta et al.²⁴ but in opposition to those of Weigmann et al.²⁵ The probable

reason for this is the use of two different formulae for calculating the diffusion coefficient. The former used the Hill's equation²⁴ whereas the latter used the Crank's equation.²⁵ Besides, there are some essential prerequisite conditions required in the dyeing operation for the possible application of conventional diffusion coefficient equations. Some of the prerequisites are that the substrate should have infinite cylinders, be morphologically stable, and have uniformly accessible homogeneous fibers.²³ However, so far no diffusion equation is derived for fibers possessing noncircular cross sections. (J. N. Etters, private communication).

In the light of the above discussions and because the FFY and HTFY yarns used in this study possess noncircular cross sections (trilobal) and the other cylindrical yarn (SPY) is of discontinuous length, the study on the diffusion of dyes making use of conventional diffusion equations was not conducted.

Effect of Transition Temperature on Dye Uptake

Figures 8 and 9 show the temperature dependence of the uptake of high energy level CI blue 183 and

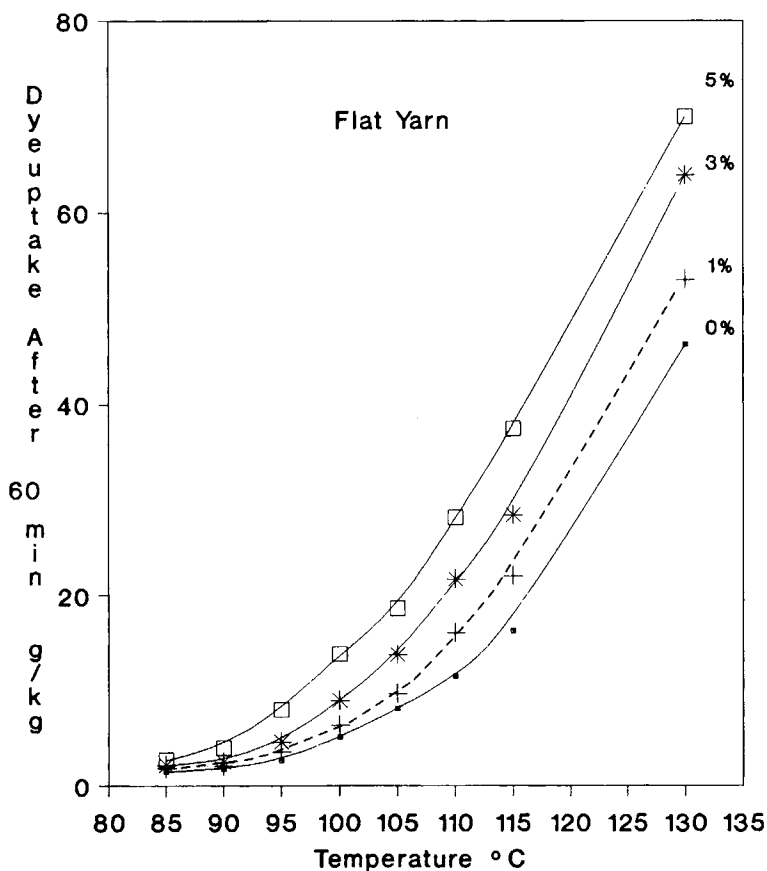


Figure 8 Effect of temperature on dye uptake with CI disperse blue 183.

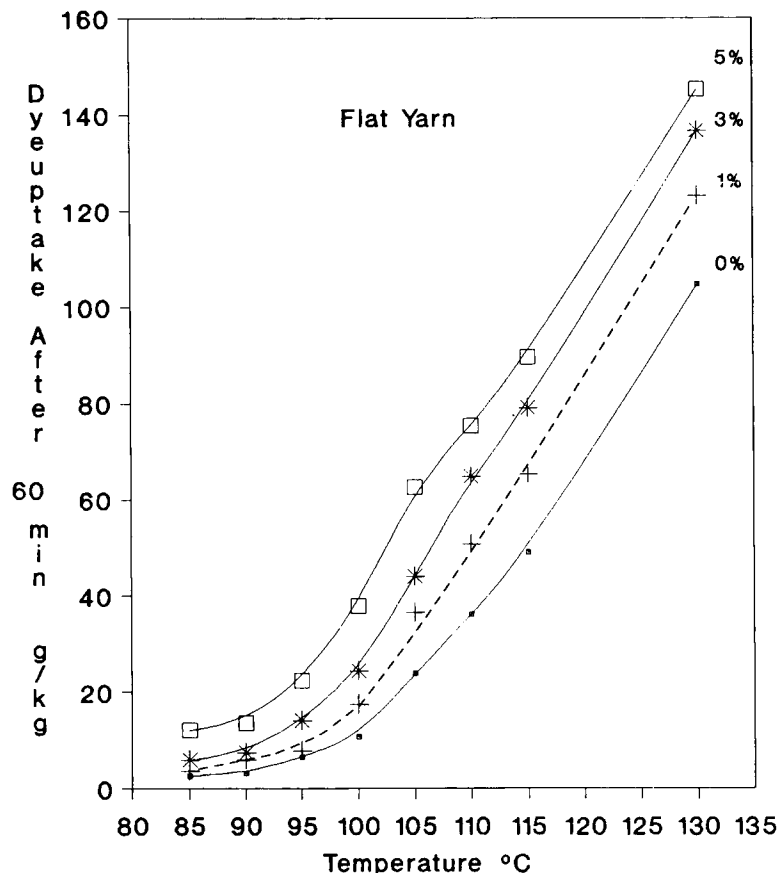


Figure 9 Effect of temperature on dye uptake with CI disperse red 91.

medium energy level CI red 91 dyes, respectively, by TCAMC treated FFY samples for dyeing times of 60 min. As expected, the amount of dye absorbed by the yarn increases with an increase in dye bath temperature. The magnitude of dye uptake also increases with an increase in pretreatment concentration of TCAMC reagent. The fundamental reason for this is the increase in kinetic energy of the dyes. At higher temperatures, the movement of dye molecules is much faster from the dye bath to the fiber and they take less time to diffuse into the interior of the fiber.

The temperature at which the dyeing begins to occur more rapidly is called as the transition temperature (T_D). The plots of temperature dependence on dye uptake (Figs. 8 and 9) show that at certain temperature (T_D) the dye uptake or the dye diffusion starts suddenly. The T_D values of this temperature obtained by drawing the best straight line through the linear portion of the curves and extrapolating the line to the abscissa of the graph are presented in Table II.

Generally, it has been considered that the diffusion of dyes starts at or above the glass transition temperature (T_g). The segmental mobility of polymer molecules can be increased considerably by solvent-polymer interaction at temperatures well below T_g .²⁶ The changes in T_D would reflect comparable changes in T_g .²⁷ The relationship between T_D and T_g has been studied by many workers and a linear

Table II Effect of Pretreatment on Transition Temperature of Flat Filament Polyester Yarn

Percent Concn (w/v)	Transition Temp. (°C)	
	CI Disperse Blue 183	CI Disperse Red 91
0	106	101
1	103	96
3	100	93
5	97	89

Table III X-Ray Order Factor and Birefringence of Polyester Yarn

Percent Concn (w/v)	Flat Filament Yarn		High Twist Yarn		Spun Yarn		Birefringence
	Transmission Mode	Reflection Mode	Transmission Mode	Reflection Mode	Transmission Mode	Reflection Mode	
0	0.32	0.26	0.43	0.33	0.43	0.31	0.1754
1	0.57	0.38	0.44	0.34	0.46	0.36	0.2017
3	0.52	0.41	0.44	0.35	0.47	0.39	0.1967
5	0.57	0.42	0.45	0.36	0.48	0.41	0.1975

relationship between the two^{28,29} was found. Consequently, it may be mentioned that both T_D and T_g reflect the structural modification of polymers effected by the interacting chemical system.

XRD and Birefringence Studies

All the yarn samples were scanned by both the symmetrical transmission method and the reflection method and the results obtained are presented in Table III. The principle suggested by Goppel and Arlaman³⁰ was utilized by various workers for developing a simplified method for determining the crystallinity index of polymers. The problem associated with the measurement of crystallinity of polymers by conventional method using X-rays is discussed elsewhere.³¹ A simple method proposed by Manjunath et al.³² was used to calculate the lateral

order factor of the samples. The proposed formula for determining the resolution factor (R) for an equatorial scan containing three peaks is given by

$$R = \frac{m_1 + 2m_2}{h_1 + h_2 + h_3},$$

where $h_1, h_2,$ and h_3 represent the heights of maxima and m_1 and m_2 denote the heights of minima of the peaks from the base line pattern. The R tends to be zero when the resolution is maximum and it tends to be 1 when the resolution is completely lost. Therefore, R is inversely related to lateral order. The X-ray order factor is calculated by subtracting from 1, namely $(1 - R)$. The order factor is directly related to the crystallinity.

It can be seen (Table III) that the FFY treated yarns show an increase in order factor. The larger increase in order factor is more pronounced at 1% treatment and, thereafter, the effect is maintained

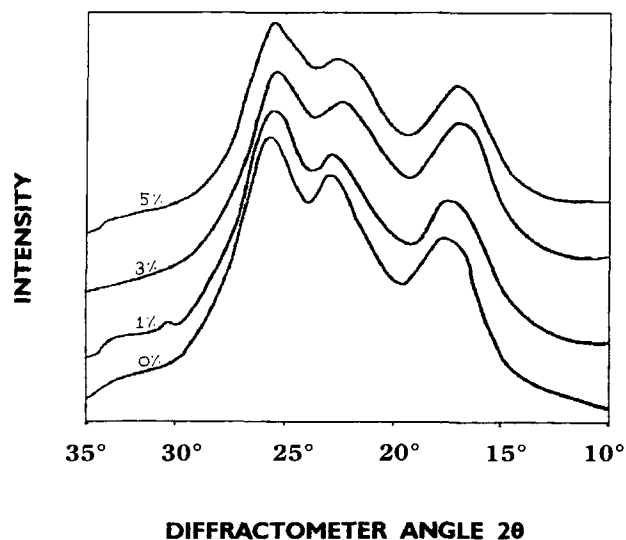


Figure 10 X-ray diffractograms of flat yarn.

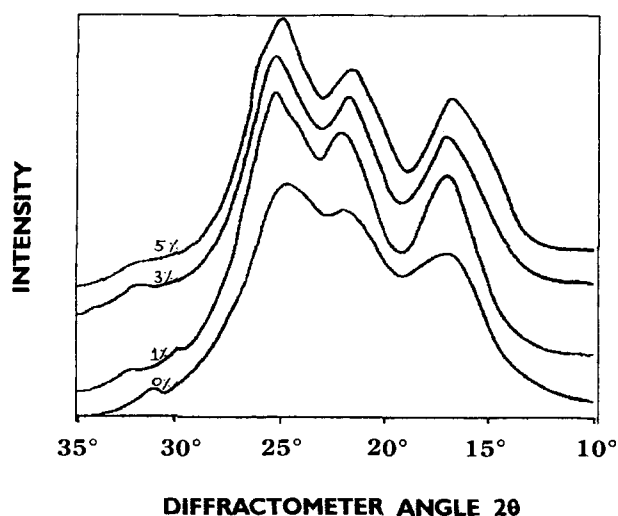


Figure 11 X-ray diffractograms of spun yarn.

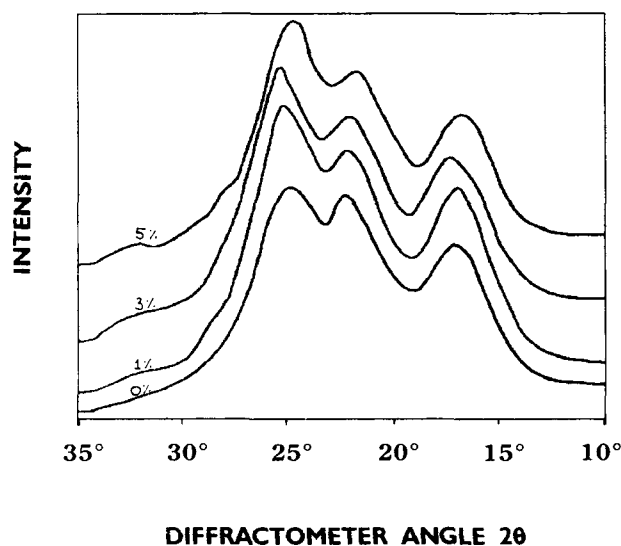


Figure 12 X-ray diffractograms of high twist yarn.

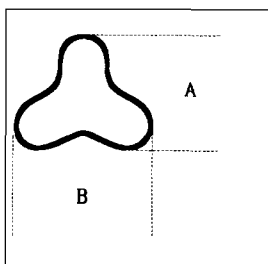
at higher concentration treatments of 3 and 5%. However, there is no appreciable increase in the order factor of HTFY treated samples. The changes in lateral order are marginal in SPY treated samples. These changes reveal that the TCAMC treatment influences the crystallinity of polyester polymers, thereby indicating structural modification. Naturally, the degree of crystallinity depends on the nature of the polymer, extent of interaction between

the polymer and the reagent, concentration of the reagent, and the time of treatment. The structural modification effected in the HTFY yarns due to the treatment is not varied much by the restriction of penetration of reagent into the yarn because of more compactness.

It was noted that the degree of crystallinity as well as the dye uptake increases due to the treatment. Presumably the increase in order of the crystalline phase accompanies a decrease in order in the amorphous domains that facilitates higher dye uptake. Another possible reason for the increase in dye uptake, in spite of an increased crystallinity, could be the increase in void volume that leads to higher porosity. The typical equilibrium scans of FFY, SPY, and HTFY are shown in Figures 10–12, respectively. The figures show the sharpening of the intensity at $2\theta = 24.8^\circ$ ($1\bar{1}0$) and 17° (010) after TCAMC treatment. This indicates that the crystallite size increases in the direction of these planes. The birefringence of the treated SPY samples was measured to observe the changes in overall molecular orientation (Table III). An increase in birefringence is observed, as expected, because of the increase in crystalline value. The birefringence of the other two samples (FFY and HTFY) could not be measured because they possess noncircular cross sections that posed a problem in getting the Becke line in the polarizing microscope.

Table IV Effect of Pretreatment on Cross-Sectional Swelling of Polyester Yarn

Percent Concn (w/v)	Diameter of Yarn Fibers ($\mu\text{m} \times 10^{-3}$)				
	Trilobal Flat Filament		Trilobal High Twist Filament		Circular Spun Yarn (Cylindrical)
	A	B	A	B	
0	6.09	5.09	6.80	6.17	4.68
1	6.47	5.41	7.13	6.37	4.84
3	6.86	6.11	7.46	6.78	5.55
5	7.15	6.21	7.61	6.81	5.78



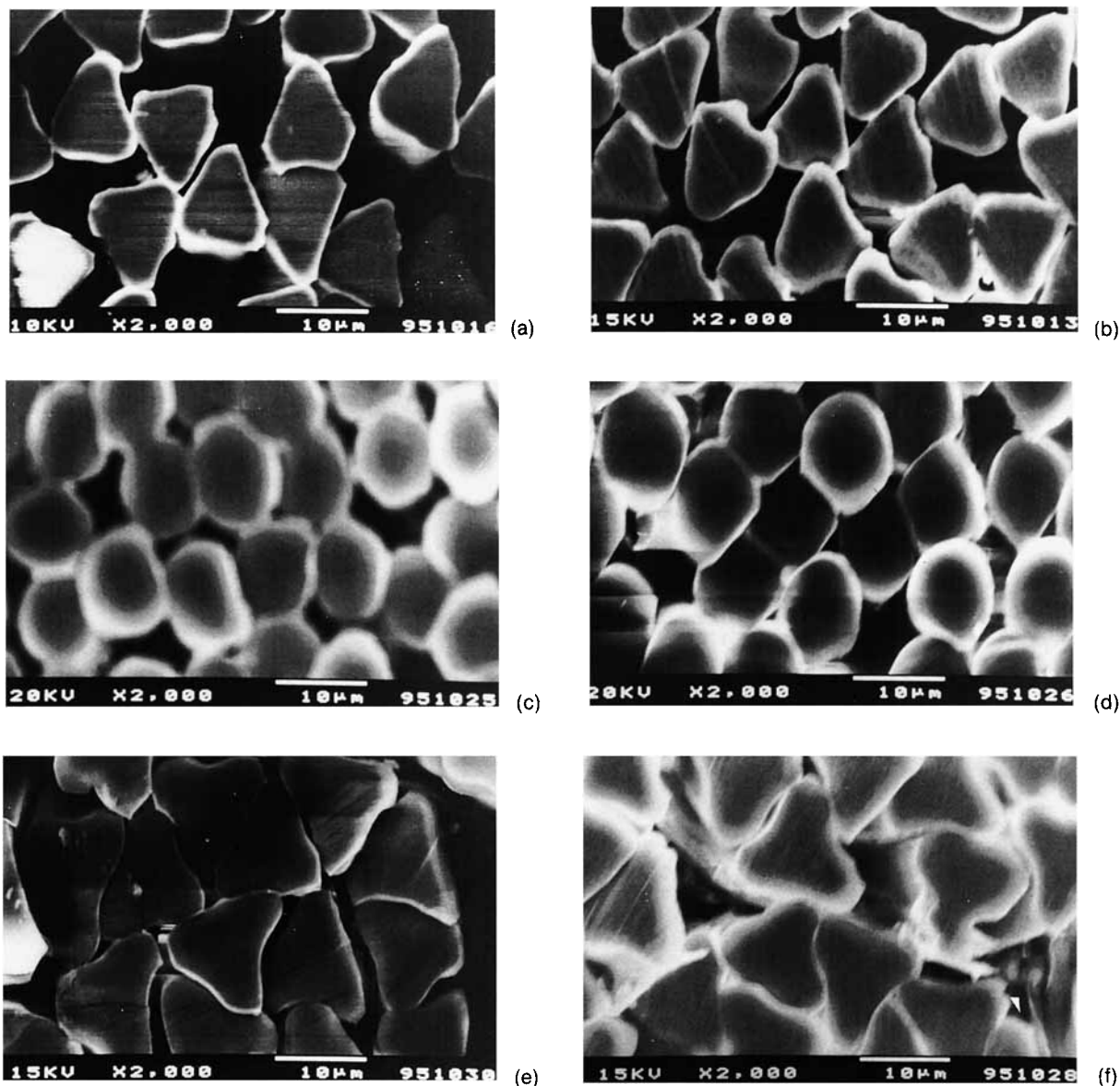


Figure 13 SEM micrographs of: (a) untreated flat yarn, (b) treated flat yarn (5% TCAMC), (c) untreated spun yarn, (d) treated spun yarn (5% TCAMC), (e) untreated high twist yarn, (f) treated high twist yarn (5% TCAMC).

Changes in Surface Topography

Scanning electron micrographs of cross sections of FFY, SPY, and HTFY treated samples (5%) along with their respective untreated controls are presented in Figure 13(A–F). It is seen from the micrographs that SPY samples possess round cross sections, whereas FFY and HTFY hold a trilobal shape. It is also seen that the fibers swell significantly due to the treatment, indicating detectable morphological changes. The extent of cross-sectional swelling as measured in the SEM is given in Table IV. The

results show that the extent of swelling depends on the treatment concentration. The 1% treatment swells the SPY fiber by 3.5%; on the other hand 3 and 5% produce 18.5 and 23.5% swelling, respectively. A similar trend lengthwise and widthwise is also seen in FFY, but there is marginal cross-sectional swelling in the HTFY. The longitudinal view of the samples was also viewed under SEM, and it was observed that the fiber surface of the treated yarns were smoother than the respective untreated ones. The smooth surface of the fiber is perhaps from the increase in perfection of the crystals. This ob-

servation is consistent with the findings of Subramanian and Venkataraman³³ in which they found that the swelling treatment of nylon 6 polymer with phenol swelling agent changes the crystal structure and increases the lateral order. Another possible reason for the smoother surface of treated yarn could be the capability of TCAMC reagent to remove the delusturing agents and the low molecular weight compounds (oligomers) from the polyester. It may be noted that certain solvents are known for their ability to dismiss the oligomers from polyester fibers.³⁵

CONCLUSIONS

The capability of TCAMC reagent to modify the structural and morphological characteristics of polyester yarns was evidenced by the dyeing study. A significant increase in the rate of dyeing and the equilibrium dye uptake of the treated yarns, irrespective of their types, was noticed. The magnitude of increase in dye uptake depends on the type of yarn used and the extent of interaction between the polymer and the reagent. The treated yarns exhibited lower dye diffusion temperature (T_D) than the untreated ones. An increase in crystallinity was observed in all the treated yarns. The probable reason for an increase in dye uptake, in spite of an increase in crystallinity, was the decrease in order in the amorphous domains and creation of pores in the polymer structure. The fibers of the treated yarns showed smoother surfaces. A steady increase in cross-sectional swelling with treatment concentration was observed.

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