

Some Sorption Characteristics of Poly(trimethylene terephthalate) with Disperse Dyes

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ABSTRACT: Sorption characteristics, such as sorption kinetics and isotherms, relation between dye sorption and shade development of poly(trimethylene terephthalate) (PTT) and their comparison with poly(ethylene terephthalate) (PET), were reported. Results from two different dyeing rate studies, dyeing rate under constant temperature and under changing temperature, were examined to obtain the common rate constants, and to obtain information for the

design of dyeing temperature profile and holding time. Rate constants of PTT were compared with that of PET. Sorption isotherms of disperse dyes on PTT were also studied. Both Nernst and Langmuir models were examined. The dye uptake ability of PTT was compared with PET. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 223–229, 2002

Key words: kinetics; polyester; adsorption

INTRODUCTION

As a “new” textile fiber, PTT, poly(trimethylene terephthalate), has attracted quick attention from both fiber and textile industries. This is mainly because of the unique properties of PTT. It has some of the characteristics of both polyester and nylon. One such characteristic is its atmospheric disperse dyeability with excellent colorfastness and natural stain resistance. No pH adjustment, carrier, or high-pressure dyeing machine is necessary for the disperse dyeing of PTT. Under certain circumstances, desirable fabric properties can be obtained with higher temperature or pressure.

General dyeing behaviors of PTT and PTT/poly(ethylene terephthalate) (PET) blends have been reported.^{1–4} However, research on sorption characteristics, such as sorption kinetics and isotherms, the relation between dye sorption and shade development of PTT and their comparison with PET, were not reported. A better understanding of these pieces of information are important to understand the dyeing behavior of PTT and to design the dyeing process more appropriately for the textile industry.

Results from two different dyeing rate studies, dyeing rate under constant temperature and under changing temperature, were examined to obtain the common rate constants (from constant temperature study) and to obtain information for the design of dyeing

temperature profile and holding time (from changing temperature study). Rate constants of PTT were compared with those of PET reported in literature. Sorption isotherms of disperse dyes on PTT were also studied. Both Nernst and Langmuir models were examined. The dye uptake ability of PTT was compared with the dye uptake ability of PET.

EXPERIMENTAL

Materials

The dyes used for this study were C.I. Disperse Red 60, 82, and 167:1, and Blue 56, and 79. The dyes were selected based on their coverage of the major chemical structures, energy levels, and their popularity in industry. Fabric used for most of the dyeing studies was single knit from 100% PTT yarn, which was plied from two staple yarns. Single knit fabrics used for the comparison between PET and PTT sorption isotherm and shade development were both from 18/1 count yarns. The PET and PTT yarns were made from 1.0 and 1.7 denier fibers, respectively. A general description of the extrusion conditions for these yarns has been published.⁵ For PTT dyeing at and below 100°C, deionized water was used directly without pH adjustment. The dye bath pH was about 7. For the dyeings at 130°C, both PTT and PET used a buffer system of acetic acid and sodium acetate to adjust pH to 5.

Dyeing

For the dyeing rate study, the dyestuff used was 1.2% owf (on the weight of fabric) except for the study on

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holding at different temperatures, where 0.5% owf was used. The liquor-to-goods ratio was 100:1. A long liquor ratio decreased the effect of removing a small quantity of the liquid for dye sorption measurement during the course of dyeing on dyeing conditions. For the constant temperature dyeing rate study, the dye bath was heated to the dyeing temperature (100°C) before the addition of the fabric. For the study of the temperature profiles, dyeing started at ambient temperature. The temperature profiles are discussed below.

For the isotherm study, up to 20 % owf of initial dye concentrations were used with a liquor ratio of 10:1. Dyeing started at ambient temperature. Temperature was raised to the dyeing temperature at a rate of 3°C/min and held at the dyeing temperature for 150 minutes. After dyeing, the fabrics were rinsed until there was no further dye bleeding

Dyeing measurement

The shade depth of the dyed fabric was measured by the K/S value obtained from a BYK Gardner spectrophotometer based on the Kubelka–Munk equation,

$$K/S = \frac{(1 - R)^2}{2R} \quad (1)$$

where R equals the decimal reflectance value measured from the wavelength giving fabric the maximum absorption.

The dye sorption data used for the dyeing rate and isotherm study were calculated from the concentration changes of the dye bath during dyeing. The concentration of the dye bath was calculated from the light absorbance of the bath based on the Beer–Lambert Law. The light absorbance of the dye bath was measured at the visible wavelength with the maximum light absorption by the FIAstar Model 5023 spectrophotometer using 50% by weight of DMAc (*N,N*-dimethylacetamide) aqueous solution as solvent.

Dyeing rate parameters

Three commonly used dyeing rate parameters were obtained in this study for the dyeing of PTT with disperse dyes. They were dyeing rate constant (k), the diffusion coefficient (D), and the half dyeing time ($t_{1/2}$). There are many different approaches for the calculation of dyeing rate constant and diffusion coefficient. Many of them are complex and have too many restrictions. For the convenience of industrial applications, the complexity of fiber size and fabric structures in real fabric dyeings, and for relatively good correlation, Vickerstaff's hyperbolic rate equation⁶ and Crank's rate equation for the early stage of dyeing,^{7,8}

were selected for the calculation of the dyeing rate constant and diffusion Coefficient, respectively.

$$k \cdot t = \frac{1}{C_\infty - C_t} - \frac{1}{C_\infty} \quad (2)$$

where k is the rate constant, C_∞ is the % dye adsorption at equilibrium, and C_t is the % dye adsorption at time t .

$$\frac{C_t}{C_\infty} = 4 \left[\frac{D \cdot t}{\pi \cdot r^2} \right]^{1/2} \quad (3)$$

where D is the diffusion coefficient, and r is the radius of the fiber if the rate study is for the single cylindrical fibers.

In this work, D/r^2 is treated as a constant without attempting to give a rough estimation of the radius of various fibers in the fabrics studied, although all were moderately close. In practice, D/r^2 is often used in the literature as a parameter to describe the diffusion of dyes in the fiber for the same reason. Both k and D/r^2 were calculated from the regression (least squares fit) of the experimental data using eqs. (2) and (3). The parameters thus obtained had less experimental error than those calculated using only one set of C_t and t . Due to the fact that Crank's rate equation [Eq. (3)], was only valid for the early stage of dyeing, D/r^2 values reported in this work were from the regression of the data from the initial 3 min of dyeing.

The half dyeing time, the time required to dye the material half the shade depth of that from equilibrium dyeing, was calculated from the regression of the experiment data using Eq. (2), based on the definition given by

$$t_{1/2} = t | C_t = \frac{1}{2} C_\infty \quad (4)$$

where $t_{1/2}$ is the half dyeing time, which is used to describe the dyeing rate.

Dye sorption isotherm

Two sorption isotherms commonly used for dyeing were examined, i.e., Nernst and Langmuir sorption isotherms, shown in Eqs. (5) and (6), respectively.

$$[D]_f = K_N [D]_s \quad (5)$$

$$[D]_f = \frac{K_L [S]_f [D]_s}{1 + K_L [D]_s} \quad (6)$$

where $[D]_f$ and $[D]_s$ are the dye concentrations on fiber and in solution, respectively; $[S]_f$ is the saturated dye concentration on fiber; and K_N and K_L are the con-

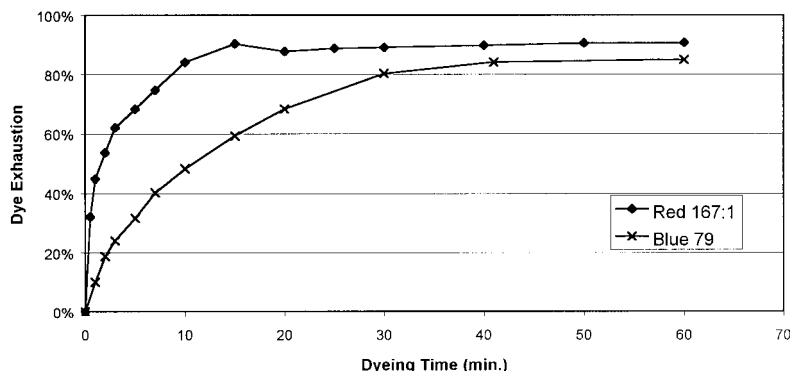


Figure 1 Rate of dyeing of PTT with 1.2% owf disperse dyes at 100°C.

stants for Nernst and Langmuir isotherms, respectively.

RESULTS AND DISCUSSION

Rate of dyeing

The rate of dyeing was studied using both constant and changing temperature profiles. Rate study using constant temperature provides kinetic information on dyeing. Two typical rate of dyeing curves from a constant temperature (100°C) are shown in Figure 1. Depending on the dye structures, dyeing equilibrium could be approached in less than 20 min (e.g., Disperse Red 167:1) or in 1 h (e.g., Disperse Blue 79). The kinetic parameters of some disperse dyeings, i.e., rate constant (k), diffusion coefficient (D/r^2) and half dyeing time ($t_{1/2}$), were summarized in Table I. The dye with highest rate constant had the lowest half dyeing time and highest diffusion coefficient. The rate of dyeing was not related to the energy level of the dyes. The high energy level Disperse Red 167:1 dye had a much higher dyeing rate than the low energy level Disperse Red 60 and Blue 56 dyes. The size and numbers of the single dye molecules and the small particles, rather than the energy level that influenced the dyeing rate, could explain this. The two low-energy dyes examined were both anthraquinone dyes. The rigid anthraquinone structure made it easier for these dyes to form crystals and agglomerates than the relatively more flexible azo dyes. The less the single molecules and small dye agglomerates, the lower the rate of dyeing.

However, azo disperse dyes do not necessarily have a higher dyeing rate than anthraquinone dyes. As listed in Table I, Disperse Blue 79 had the slowest dyeing rate in the dyes examined, although it was an azo dye. This was probably due to its large molecular size. Although the dye is a mono-azo dye, just like Disperse Red 167:1 and Red 82, it has three substituents on each of the benzene rings in addition to the azo group, whereas the other two dyes have only one or two substituents on each ring. The large size of this molecule, and therefore its decreased mobility, might be the reason of the low dyeing rate of Disperse Blue 79. This explanation is supported by the good correlation between diffusion coefficient and dyeing rate constant in Table I. The larger the diffusion coefficient, the larger the dyeing rate constant, indicating the dyeing rate was probably controlled by the diffusion of the dye into the fiber.

Table II compares the rate constants and percent exhaustion of the dyes on PTT at 100°C with the same parameters obtained from ref. 9 on PET at 130°C. The dyeing rate of the disperse dyes on PTT was somewhat lower than that on PET. This was possibly due to the lower dyeing temperature of PTT. At lower dyeing temperature, dye molecules had low kinetic energy, and therefore they penetrated more slowly in the boundary layer and inside the fiber. Although the rate of dyeing was relatively low for PTT at 100°C, the percent dye exhaustion at equilibrium on PTT was the same or slightly higher than on PET. A possible explanation for this is the exothermic process of dye

TABLE I
Some Kinetic Parameters for PTT Dyed with Disperse Dyes at 100°C

C.I. disperse dyes	Energy level	Structure	MW	$t_{1/2}$ (min)	$k \times 10^3$ (min ⁻¹)	$D/r^2 \times 10^3$ (min ⁻¹)
Red 60	Low	Anthraquinone	332	4.9	2.08	5.4
Red 82	High	Azo	439	4.3	2.54	8.5
Red 167:1	High	Azo	506	1.0	11.42	27.4
Blue 56	Low	Anthraquinone	305	4.6	2.47	8.2
Blue 79	High	Azo	639	7.5	1.53	4.5

TABLE II
Comparison of Some Kinetic Parameters between PTT (100°C) and PET (130°C) Dyed
with Disperse Dyes (PET Data were from Ref. 9)

C.I. disperse dyes	$k \times 10^3$ (min ⁻¹) (PTT/PET)	$t_{1/2}$ (min) (PTT/PET)	% dye exhaustion (PTT/PET)
Red 60	2.08/4.95	4.9/2.1	99/97
Red 82	2.54/4.81	4.3/2.6	91/81
Blue 56	2.47/7.49	4.6/1.4	89/94
Blue 79	1.53/2.95	7.5/4.2	88/80

sorption. The relation between dyeing temperature, dye concentration, equilibrium dye sorption, and color yield is discussed below.

Although much information could be obtained from dyeing rate parameters, such information was not enough to direct the production dyeings. This is mainly because dyeing must start at a temperature much lower than 100°C to control the levelness. To obtain information for the design of appropriate temperature profiles for industrial dyeing, dyeing rate with changing temperatures were investigated. Figure 2 shows the rate of dyeing of PTT with Disperse Blue 56. Table I shows the dyeing rate of Disperse Blue 56 was neither too high nor too low; therefore, the study on temperature profile with Disperse Blue 56 should be a good representation. As shown in Figure 2, there was little dye sorption when the temperature was below 60°C. Dyeing rate increased remarkably when the temperature exceeded 80°C. Within 20 min of holding time at 100°C, 90% or more of the dye, which would be sorbed at equilibrium, was already sorbed. Based on the information from Figure 2, a temperature profile for batch dyeings could be recommended. The initial dye bath temperature may be raised quickly before 60°C, e.g., 3–5°C/min. After 60°C, temperature should be raised slowly. A rate of 1–3°C/min from 60 to 80°C, and 1°C/min from 80 to 100°C might be appropriate. The recommended holding time at 100°C

dyeing temperature was 30–60 min. This was based on the fact that most of the dyes studied had 99% or higher exhaustion within 60 min in the constant temperature study. Using the temperature profile recommended, there were another 27–40 min for dye sorption while temperature was raised from 60 to 100°C. After holding at 100°C, a 2–3°C/min rate was recommended to decrease the bath temperature to 50°C before dropping. Due to the relatively low glass transition temperature, a hot drop at high temperature followed by a cold rinse may cause the loss of some stretch ability of PTT textiles. Since disperse dyeing is an exothermic process, some additional dye could be taken up by the fabric during the cooling process. A controlled cooling rate results in more even and higher dye uptake. Figure 3 shows an example of a PTT batch dyeing procedure. The conditions listed in Figure 3 are only for reference. The appropriate dyeing conditions depend on the properties and treatment history of the textile materials, properties of dyes, dyeing auxiliaries, dyeing machines, and the requirement of the end product.

Figure 4 shows the dye sorption with a temperature profile different from that in Figure 3. Temperature was increased at 2°C/min and held for 10 min at 40, 60, 75, 85, and 95°C. Dye uptakes after holding at each temperature are shown in the figure. Dye uptakes after 30- and 60-min holdings at 95°C are also in-

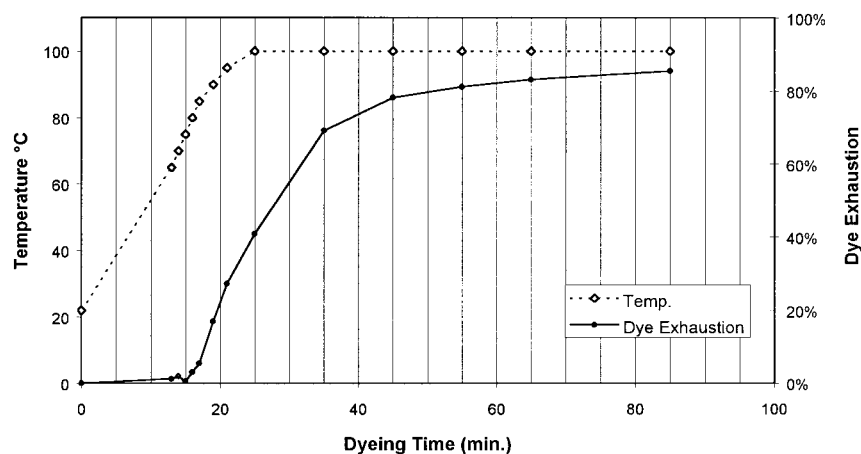


Figure 2 Rate of dyeing of PTT with 1.2% owf Disperse Blue 56 (dyeing started at 22°C and the temperature was raised to 100°C).

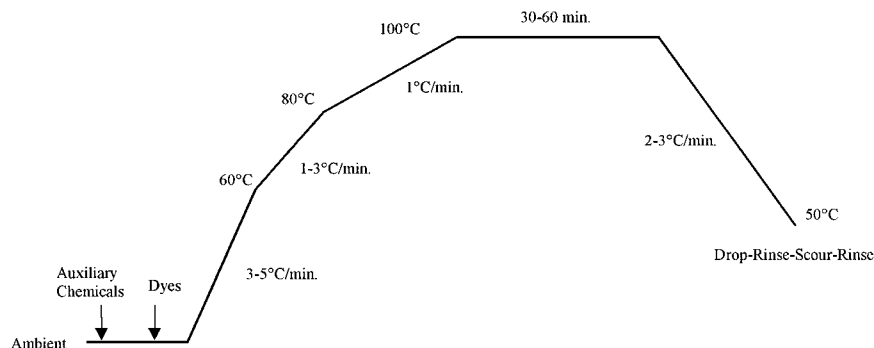


Figure 3 A reference PTT batch dyeing procedure. *Note:* (1) Possible auxiliary chemicals include dispersant, lubricant, chelating agent, defoamer/deaerator, leveling agent. The use of these chemicals depends on the dyeing machines, water, and dye properties, and the end-product requirement. Use only if they are necessary. (2) No pH adjustment is necessary. Suitable dyeing pH at 95–°C is between 4 and 9. (3) Pre-scour before dyeing may be considered if the fabric is not pretreated.

cluded. As shown in Figure 4, holding at 60°C did not result in much dye sorption. However, holding between 75 and 85°C contributed to more than 50% of the total dye exhaustion. This indicated once again that temperature change, especially above 70°C, was very critical to dyeing. Results in Figure 4 suggested that holding at 75–85°C for several minutes might improve levelness of dyeing for the fabrics which were not otherwise easily dyed.

Dyeing equilibrium

The sorption isotherms of C.I. Disperse Red 167:1 and Blue 56 at 100°C are shown in Figure 5. The isotherms were similar to the PET/disperse dye sorption isotherms. Disperse dye sorption on PTT could be described by the stage linear or the Langmuir isotherms, as demonstrated in Figure 5. Most people used the linear isotherm (Nernst Isotherm) for the disperse dyeing of PET. The dyeing mechanism was described as the distribution of disperse dyes in the water phase and the solid “solution” of the fiber, similar to the distribution of a solution in two immiscible solvents. The reason was that it is believed that there are no specific dyeing sites in polyester for the disperse dyes; dyes are “dissolved” in polyester.

Langmuir isotherm is used to describe the dyeing mechanism with specific dyeing sites on the fiber, such as the amine end groups of nylon for the acid dyes. If the Langmuir approaches in Figure 5 were closely examined, it could be found that in the bath concentration range of about 1–4 mg dye/mL, the Langmuir isotherm always gave higher than actual dye sorption values. Because of the lack of the support from the dyeing mechanism and the poor description of the dye sorption in certain concentration ranges, it seemed that the stage linear isotherm was a better description of PTT dyeing, although Langmuir isotherms also mathematically fitted the sorption well ($R^2 > 0.99$).

The stage linear sorption indicated that there could be two to three dyeing zones with different energy levels. The zones in the fiber with the highest surface energy level sorbed the dyes first at the lowest bath concentration, shown as the first stage. Once these areas were occupied, dye molecules would be sorbed to the areas of the fiber with lower surface energies if the driving force or the chemical potential of the bath was high enough. The dye sorption in the areas of the fiber with low energy levels was described by the lines of the following stages with small slopes.

Figure 6 shows the sorption isotherms of PTT and PET with Disperse Blue 56. As shown, when dye sorption on fiber was less than 20 mg/g, all three curves were overlapped, implying the dye sorption ability of PTT at 100°C was the same as PET at 130°C. The isotherms were obtained at a liquor ratio of 10:1. Therefore, if the dyeing was under 2% owf (i.e., light to medium shade depth), dyeing temperature above 100°C did not increase the dye uptake. This was probably because most of the dye initially added to the bath was sorbed by the fiber even at 100°C, as shown in Figure 6. Although increasing temperature in-

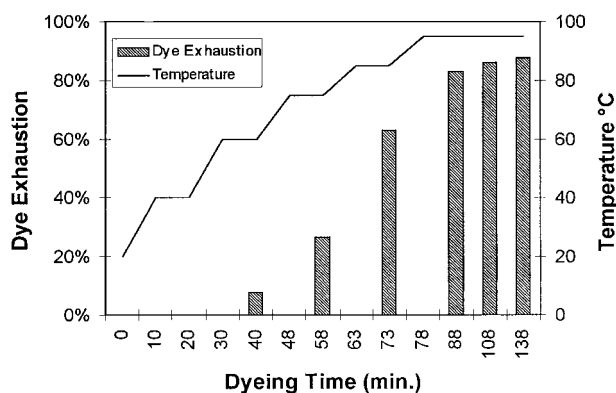


Figure 4 Effect of holding at different temperatures on PTT dyeing with 0.5% owf Disperse Blue 56.

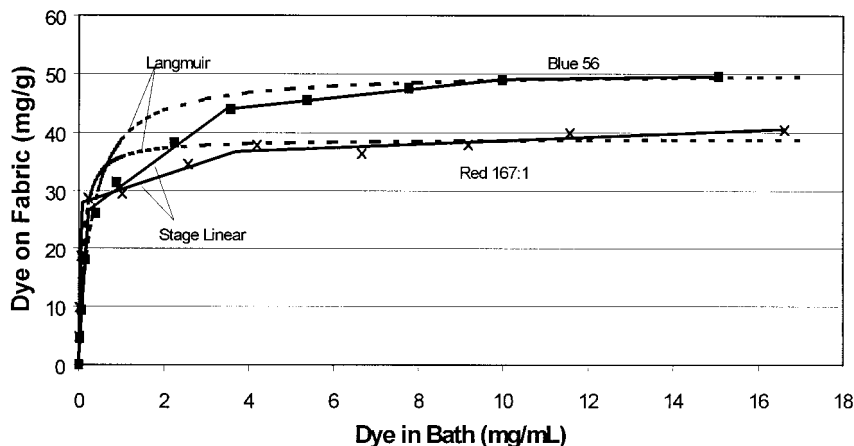


Figure 5 Stage linear and Langmuir sorption isotherms of PTT with disperse dyes at 100°C.

creased the dye-accessible areas in PTT, no dye was available in the bath. Therefore, increasing temperature did not increase dye uptake. When dye concentration increased, i.e., more than 2% owf of the initial dye was used, PTT dyed at 100°C sorbed less dye than PET dyed at 130°C. If dyed at 130°C, PTT sorbed slightly more dye than PET. Therefore, for the dyeing of heavy shade, a temperature above 100°C would increase the dye exhaustion. If high temperature dyeing equipment is available, and if the savings from the increase of the dye sorption are considerable, a dyeing temperature above 100°C may be beneficial, especially for the dyeing of heavy shades.

Figure 7 shows the relation between K/S and dye sorption on PTT at two different temperatures, 100 and 130°C. One interesting phenomenon was that two curves, 100 and 130°C dyeing, almost overlapped. This indicated that dyeing at 100°C did not have any negative effect on the color yield of PTT. Although dye uptake at 100°C was less than that at 130°C if the shade depth was higher than 2%, the dye being sorbed

was still evenly distributed into the fiber. If low temperature caused poor dye penetration, uneven dyeing would occur. Uneven dyeing of the fiber would then result in lower shade depth of the dyed goods.¹⁰⁻¹²

CONCLUSIONS

The dyeing rate of PTT with disperse dyes at 100°C was slightly lower than that of PET at 130°C. This was probably due to the lower kinetic energy of the dye at a lower temperature. Very good correlations existed among kinetic parameters of the disperse dyeing of PTT. Those parameters were rate constant (k), diffusion coefficient (D/r^2) and half dyeing time ($t_{1/2}$). The good correlation between the diffusion coefficient and dyeing rate indicated that the dyeing rate was probably controlled by the diffusion rate of the dye into the fiber. Therefore, the dyes with smaller molecular structure and/or less tendency to form agglomerates and crystals should have a higher dyeing rate. The

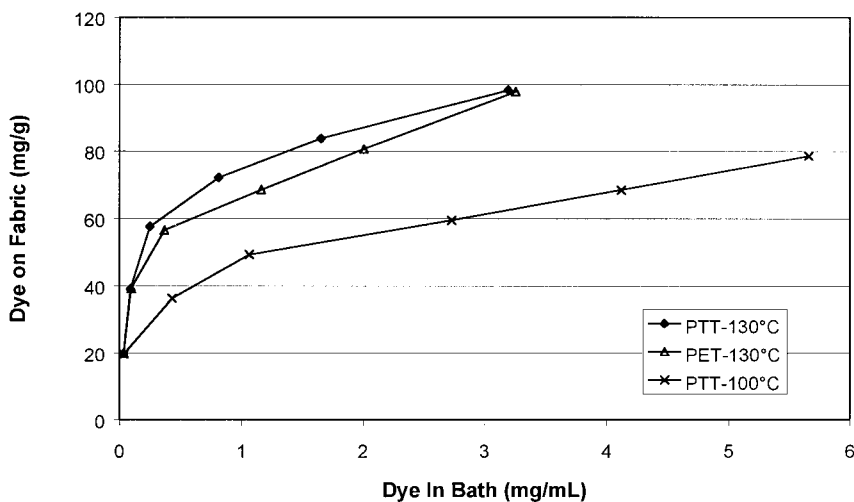


Figure 6 Sorption isotherms of Disperse Blue 56 on PTT and PET.

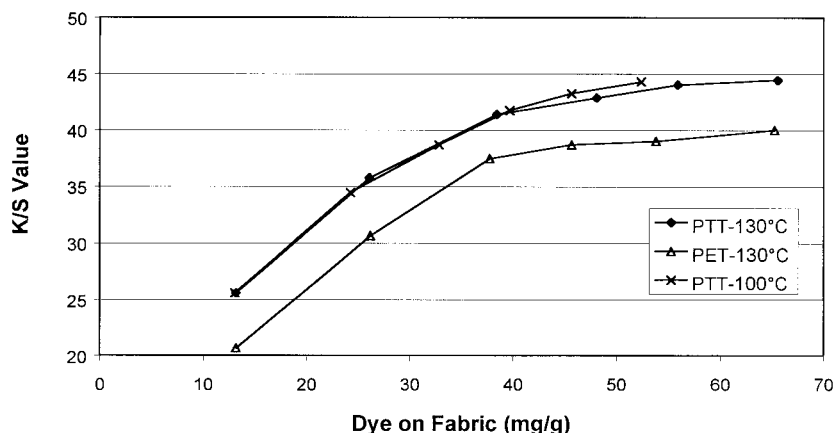


Figure 7 Relation between shade depth (K/S) and dye uptake at different dyeing temperatures with Disperse Blue 56.

dyeing rate was not necessarily related to the energy level of the dye.

Based on the rate studies, the temperature profiles for PTT dyeing were recommended. Raising the dyeing temperature should be strictly controlled when the temperature is above 70°C . Due to the quick and large quantity of dye sorption, uneven dyeing results may occur if the temperature is raised too quickly.

Sorption isotherms of disperse dyes on PTT were similar to that on PET. Both the Langmuir and stage linear isotherms could be applied. However, the stage linear isotherms seemed to fit the sorption data better than the Langmuir isotherms, especially when the equilibrium dye concentrations in the bath were between 1 and 4 mg/mL. The stage linear sorption indicated that there could be two to three dyeing zones with different energy levels in the fiber.

When the initial dye concentration was less than 2% owf, PTT dyed at 100°C sorbed the same amount of the dyes as PET at 130°C . If more than 2% owf of the dye was used, PET sorbed more dye than PTT. However, if both fibers were dyed at 130°C , they sorbed approximately the same amount of the disperse dye.

K/S vs dye sorption curves of PTT dyed at 100 and 130°C overlapped. This indicated that the disperse color yield on PTT at 100°C was the same as that at 130°C . Such an overlap also indicated that at 100°C , no ring dyeing occurred. This supports the recommendation of 100°C dyeing temperature for PTT.

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