

Carrier Effect on Structure and Properties of Heat-Treated Poly(Ethylene Terephthalate) Fibers. II. Dyeing Behavior

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SYNOPSIS

The changes in the morphology of heat-set poly (ethylene terephthalate) (PET) fibers (as spun and 2.8 \times) submitted to benzoic acid action at different concentrations and times were analyzed by wide-angle x-ray scattering and dynamic and mechanical thermal analysis. Also, dyeings in the presence of two different Disperse dyes were performed. Therefore, the calculated diffusivities as well as the dye absorption percentage at equilibrium were related to the morphological changes of the fibers, due to the benzoic acid action. The plasticization effect of the benzoic acid over the as-spun fiber occurs in the first 30 min of exposition and in 24 h for the drawn one. This plasticizing action of the benzoic acid seems to be the commanding factor over the dyeing behavior of the fibers, as demonstrated by an increase of the diffusion coefficient with the increase of benzoic acid concentration. However, the morphological changes due to exposition for long periods of time at increased benzoic acid concentrations are one of the major responsible factors by the observed maxima in the figures of percentage of dye on the fibers at equilibrium versus benzoic acid concentration. Also, changes in the angular coefficient (B) calculated from the free volume theory equation are indicative that factors such as the size of the dye molecules as well as their solubilities in water in addition to the morphological changes may be playing a role in the dyeing behavior. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly (ethylene terephthalate) (PET) fibers are hydrophobic, have a very compact structure, and are semicrystalline. In addition, the stiffness imparted to the chains by the phenyl residues of the terephthalate group results in a relatively high glass transition temperature (T_g). So, the dyeing process at regular dyeing temperatures is somewhat difficult. Among the methods used to improve dyeability, the addition of a "carrier" into the dyebath is a procedure normally used. The "carrier" works as a plasticizer, decreasing the glass transition temperature, allowing the dyeing to be carried out at regular dyeing temperatures, usually in boiling water.

The mechanism of carrier action is not very well understood, and many factors have been postulated

as playing a role.¹ It seems, therefore, that "carriers" act primarily by the virtue of their plasticizing action on the fiber, which allows the chain segments in the polymer to have greater freedom of movement and hence the dye to penetrate more rapidly. Balmforth et al.² showed that there is a "carrier" concentration that gives a maximum dye uptake; any increase beyond this concentration results in a lower dye uptake. They suggested that the optimal concentration would seem to correspond to the amount of carrier needed to saturate the system and any excess of this will be present as a third phase. The solubility and partition characteristics of the components involved would be responsible for this third phase.

Finally, they suggested that benzoic acid, a commonly utilized "carrier" for PET fibers, which does not promote dyeing by increasing the partition of the dye in favor of the fiber, possibly operates by increasing the solubility of the dye in the bath. In another work, Ingamells and Narasimham³ suggested that this maximum dye uptake reported by Balmforth et al.² with increased carrier concentra-

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tion occurs due to the effect of a reduction in the partition coefficient of the dye, due to a change in the morphology of the fiber, or perhaps both. More recently, Simal,¹ in another study involving benzoic acid as a "carrier" for PET fibers, suggested that the maximum dye uptake observed with increased "carrier" concentration was governed mainly by the competition between carrier and dye molecules to enter the fiber substrate and that morphological changes due to benzoic acid action at high concentration might be involved.

Contrary to the work by Balmforth et al.,² the PET fibers utilized by Simal¹ were annealed before dyeing in the presence of benzoic acid at different concentrations. Such conclusions were obtained based on the comparison between the experiments where the fibers were and were not initially in equilibrium with the benzoic acid solution before dyeing. Also the structural measurements show that the highly drawn fibers (4× and 6×) were structurally more stable to the benzoic acid action than were the low draw ratio fiber (2×).⁴

In those experiments, the time of dye absorption in the presence of benzoic acid at different concentrations was fixed in 2 h. At this time, the fibers had not yet reached the equilibrium in the low range of concentrations of benzoic acid (around 10 g/L). Therefore, it was necessary to complete these analyses, studying how these maxima of dye absorption would behave at different times (up to the equilibrium) of exposition in a dye bath solution containing different concentrations of this carrier.

Thus, the preheat-fixed PET fibers with different draw ratios (0×, 2.8×) were submitted to such dyeing in the presence of benzoic acid in different concentrations, up to equilibrium. The same blank fibers were also submitted to treatments in pure solutions of benzoic acid for the same times and concentrations of the dyeing, for structural analysis.

EXPERIMENTAL

Sample Preparation

PET fibers from Rhodia S/A, SP/Brazil, with different draw ratios (as spun and 2.8×) and title of 75 dtex were submitted to two different heat treatments before dyeing. Treatment T1 consisted of 8 h of exposition in boiling water and treatment T2 consisted of 7 h of heat setting in an evacuated oven and inert atmosphere at 130°C followed by 1 h of treatment in the presence of distilled boiling water. The boiling water treatment was necessary to avoid

structural changes due to the plasticization effect of the water during the dyeing experiments.

The dry heat treatment for 7 h has been shown^{1,4} to be sufficient to heat set the fibers. These heat treatments would assure that any structural changes occurring in the fibers during the dyeing would be caused by the benzoic acid action only. After these heat settings, the fibers were submitted to treatment in pure benzoic acid solution at the same concentration and times used for the dyeing experiments.

Dyeing Experiment

Two different and pure disperse dyes from Ciba Geigy S/A, SP/Brazil, were used in this work. The Disperse blue 14 (C.I. 61500) is an anthraquinone type and the Disperse red 1 (C.I. 11110) is chemically a mono-azo type.

The dyeing was performed in a flask containing 60 mL of dye solution (1.5 g/L). The amount of fibers used was enough to assure an infinite dyebath condition and permit the calculations of the dye diffusivities by the Hill equation.⁵

The dyeing was effectuated at different times and in a medium containing different concentrations of benzoic acid: 0, 5, 10, and 20 g/L for the as-spun fiber and 0, 10, 20, and 30 g/L for the fiber drawn 2.8×. The dyeing was performed under constant agitation (shaking bath at 150 rpm) and temperature of 95 ± 2.0°C.

The dye percentage was calculated by a spectrometric method after extraction in the presence of dimethyl formamide (DMF), as described elsewhere.^{4,6} The equation utilized for such an evaluation is the following:

$$\% \text{ Dye} = \frac{o.d. \times V \times f}{\epsilon \times \omega \times 1000} \times 100 \quad (1)$$

where: *o.d.* = optical density, ϵ = extinction coefficient (cm²/mol), *V* = extracted volume (cm³), *f* = dilution factor, and ω = sample weight after dyeing (g).

Structural Measurements

Swelling

Swelling measurements were made by knowing the diameter of the fibers before and after the heat treatments. The swelling percentages were calculated through the following expression:

$$\%S_w = \frac{S_w^o - S_w^f}{S_w^o} \times 100 \quad (2)$$

where S_w^o and S_w^f are the initial and final diameters, respectively. Polarized light microscopy was used in the diameter calculations.

Dynamic and Mechanical Thermal Analysis

Dynamic and mechanical thermal analysis (DMTA) (from Polymer Laboratories) runnings were used to evaluate the dynamic and mechanical properties of the samples through E' , E'' , and $\tan \delta$ measurements. The running conditions were heating rate of $3^\circ\text{C}/\text{min}$ and frequency of 10 Hz. The frequency of 10 Hz was chosen in order to permit, eventually, a comparison between our results and the dynamic and mechanical results obtained by Dumbleton and colleagues,⁷ whose frequency was 11 Hz with Vibron equipment (Model DDV-II). The linear dependence of $\left(\frac{\ln D}{RT}\right)$ versus $\ln \frac{E''}{W}$ was evaluated through the following equation:

$$\left[\left(\frac{\ln D_T}{RT}\right) = -B \ln(E''/W) + C - B \ln\left(\frac{1}{3}\right)\right] \quad (3)$$

where D_T = diffusion coefficient, B and C = constants, W = frequency, and E'' = tensile dynamic loss modulus at frequency W and temperature T .

The validity conditions of this equation have been discussed in the literature^{5,7,8} and therefore this is not the subject of this article. We are interested here in the B value calculations, which seem to be related to morphological parameters, such as orientation and crystallinity, as mentioned in earlier references.^{7,8}

Wide-Angle X-Ray Scattering

The x-ray diffraction method was performed with Carl Zeiss Jena equipment, utilizing Ni-filtered Cu $K\alpha$ radiation and the results were analyzed by the diffractometric method.

Wide-angle x-ray scattering (WAXS) measurements were used to calculate the crystallinity index (CI), crystal size (CS), and lateral order (LO) as described in detail in the literature.⁹⁻¹² Our PET fibers presented a characteristic three-peak equatorial x-ray scattering pattern as described by Cullerton et al.⁹ and Bhat and Naik.¹² The observed peak maxima were: $2\theta_1 \cong 17.5^\circ$, $2\theta_2 \cong 22.5^\circ$, and $2\theta_3 \cong 25.5^\circ$ which correspond to the crystal planes (010), (110), and (100), respectively.¹² Although much more precise

methods for crystallinity determinations can be found in the literature,¹⁰ the method utilized by Cullerton and colleagues⁹ was chosen due its simplicity. This method assumes a two-phase model for the fiber and involves separating the scattering diagram into relative crystalline and amorphous components. The width of the crystalline peak at $2\theta \cong 17.5^\circ$ was considered for the crystal size calculations, through the basic Scherrer equation¹² or:

$$CS = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

where K is a shape factor which varies between 0.9 and 1.1. A value of 1.0 has been considered for our calculations. λ = wavelength of the radiation used (Cu $K\alpha$ = 1,5418 Å), β = half-maximum breadth in radians, and θ = Bragg's angle.

The crystalline size measurement corresponds to the direction perpendicular to the plane (010) chosen for the calculations. The calculated values of the CS should be considered as relative values only, since the necessary corrections for the Scherrer equation¹⁰ were not made.

The LO^{11,12} parameter can be related to several factors at the same time, such as the crystallinity of the samples, perfection, size, and distribution of the crystallites and it was calculated from the following equation:

$$\%LO = (1 - RF) \times 100 \quad (5)$$

where RF is the resolution factor which is given by the following expression:

$$RF = \frac{m_1 + 2m_2 + m_3 + \dots + m_n - 1}{h_1 + h_2 + h_3 \dots + h_n} \quad (6)$$

where m_1, m_2 , etc., are the heights of minima from the appropriate baseline, and h_1, h_2 , etc., are the heights of maxima from the same baseline. Therefore, this resolution factor for our PET fibers can be written as follows:

$$RF = \frac{m_1 + 2m_2}{h_1 + h_2 + h_3} \quad (7)$$

where m_1 and m_2 correspond to the minima between the planes (010) and (110) and between the planes (110) and (100), respectively. The variables h_1, h_2 , and h_3 are the observed maxima diffraction peaks corresponding to be planes (010), (110), and (100).

When the resolution is absent, RF tends to be 1, and RF tends to be zero, when the resolution is max-

imum. Thus, RF is inversely related to the LO .¹¹ Some authors^{11,12} have used this parameter in substitution for the CI measurement. In this case, it is being considered the total order rather than the absolute crystallinity. In our study, it was considered both parameters.

Fourier Transform Infrared

Fourier Transform Infrared (FTIR) from Bomem-Michelson 102 equipped with a polarizer from Perkin Elmer was used to evaluate the ratio between the trans and gauche content in the PET fibers. The trans conformation can be present in both regions, amorphous and crystalline, and is related to the straight parts of the molecule. The gauche conformation can be present in the amorphous region only and is related to the bended or distorted parts of the molecule.¹³ The changes in the absorption ratio between the trans and gauche conformers can be used to quantify the conformational changes during the crystallization process due to heat treatments. The bands near 1473, 1343, 973, and 848 cm^{-1} have been referred to in the literature¹⁴ as vibrational modes of the trans ethylene glycol segment of the polymer chain, and the bands near 1453, 1372, 1042, and 898 cm^{-1} refer to the vibrations of the gauche ethylene glycol segment of the polymer chain.¹⁴ For this study, the bands 973 cm^{-1} and 898 cm^{-1} ¹³ were chosen to calculate the structural absorbances (A_o) of the trans and gauche conformations, respectively, in accordance with the following expression.¹⁵

$$A_o = \frac{A_{//} + 2A_{\perp}}{3} \quad (8)$$

The structural absorbance was determined in order to remove the effects of orientation concerning the spectra of the samples with cylindrical symmetry.¹⁵ All of the calculated structural absorbances can be corrected by an internal reference,¹³ which is necessary to compensate for the sample thickness. This correction is particularly important for quantitative calculations of the content of a particular band (trans or gauche conformers) and the calculation of the dichroic function (DF), as expressed by the following equation¹⁵:

$$DF = \frac{R - 1}{R + 2} \quad (9)$$

where R is the dichroic ratio defined as the quotient of the extinction values of an absorption band for

parallel ($A_{//}$) and perpendicular (A_{\perp}) vibration directions of the infrared spectrum.

The dichroic function has been mentioned in the literature¹⁵⁻¹⁷ to represent orientation data, due its proportionality to the orientation function.¹⁵ This approach is particularly useful in the case of uncertainty about the exact transition band, which is necessary for the calculation of the orientation function¹⁵ as expressed by the following equation:

$$f = \left(\frac{R - 1}{R + 2} \right) / \left(\frac{R_o - 1}{R_o + 2} \right) \quad (10)$$

where $R_o = 2 \cot^2 \alpha$ ¹⁸ represents the dichroic ratio of the absorption band ideally oriented, and α is the angle between the transition moment and the molecular axis. Therefore, equation 10 can be reduced to equation 9 when the analyzed band is a π type, where $R_o = \infty$ and $\alpha < 54.7^\circ$.¹⁸ In this study, equation 9 was applied to estimate the orientation of the amorphous region of our PET fibers through the 898 cm^{-1} band,¹⁷ which is a π -type band and representative of the gauche conformation.

The internal reference band utilized for the calculations was the 1506 cm^{-1} ¹⁶ band, with π polarization and designated to the vibrational mode of the benzoic ring.^{18,19} The reference band chosen might be a band independent of changes in physical structure, such as those representing trans, gauche, and folded conformations. Therefore, the most suitable specie is the benzene part of the molecule.¹⁸

RESULTS AND DISCUSSION

The Dyeing Behavior

The plasticizing effect with increased benzoic acid concentration can be visualized in Figures 1–4. Also, Table I shows the calculated diffusion coefficients for the different dyes and concentrations of benzoic acid studied.

It is possible to verify in Table I that the undrawn fibers (0 \times) presented a higher diffusion coefficient for the dye Disperse red 1 than for the Disperse blue 14 with lower molecular weight (314.45 and 266.30 g/mol, respectively). This situation is inverted for the drawn fibers (2.8 \times). These facts suggest that factors other than the dye molecular size are playing a role in the dyeing process. Such additional factors could be the different solubilities of the dyes in water (4.8 mg for the blue 14 and 10.8 mg for the red 1 at 90°C⁵) and the different dye abilities to form agglomerates in solution.

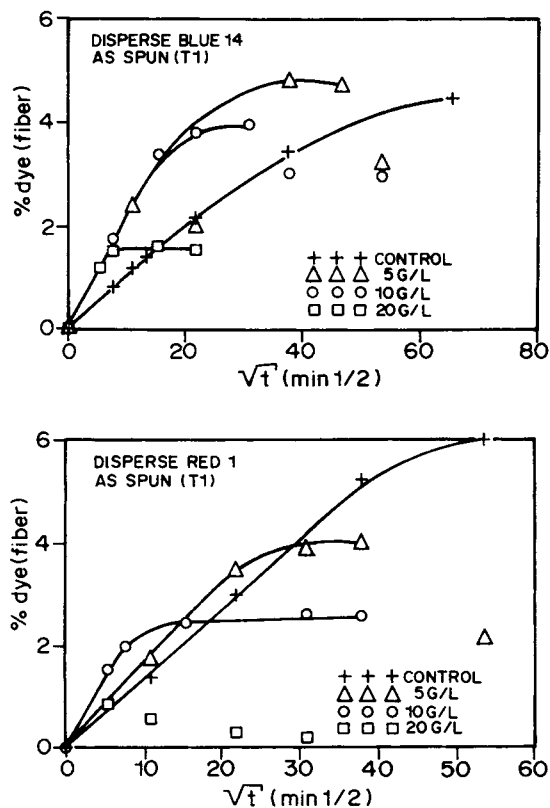


Figure 1 Percentage of dye on the as-spun fiber (heat treatment T1) versus $(\text{time})^{1/2}$ in the presence of benzoic acid at different concentrations (0, 5, 10, and 20 g/L): (a) Disperse blue 14 and (b) Disperse red 1.

The diffusion coefficients are lower for the drawn fibers independent of the applied heat settings (T1 or T2). As expected, this fact reflects the difficulty of dye penetration into a more compact structure of the drawn fibers. Also, the diffusivities for the fibers heat set for 8 h in boiling water (treatment T1) are higher than the calculated values for the dry heat-treated ones followed by 1 h in boiling water (treatment T2).

Some authors²⁰ have suggested that the dye absorption percentage in fibers with a porous structure depends on the internal surface of the fibers and/or the ability of the dye molecules to form agglomerates within the pores. As will be discussed later, the boiling water treatment (T1) for 8 h generates a more open structure in the studied fibers. Also, an increase of benzoic acid concentration in the dyebath promoted an accentuated increase of the dye diffusion coefficient in the fiber substrates. Again, this result might be associated with an increase of this "carrier" on the surface of and within the fiber substrate, as

well as with the possibility of morphological changes due to its plasticizing action.^{4,20-22}

Also, it is clear from Table I that the time to reach equilibrium depends on the benzoic acid concentration in the dyebath. The higher the "carrier" concentration, the lower will be the time to reach the equilibrium. However, the values of the dye absorption maxima do not present a direct relationship with the benzoic acid concentration, but reveal the possibility of being related to the morphological modifications in the fibers.

When the dye absorptions at equilibrium time are plotted as a function of the benzoic acid concentration, the resulting curves are shown in Figure 5.

The curves for the as-spun fibers dyed in the presence of Disperse blue 14 [Fig. 5(a)] show an accentuated decay after a benzoic acid concentration of 5 g/L, while for the curves obtained for the dyeings in the presence of Disperse red 1 [Fig. 5(b)], this decay starts at zero concentration of benzoic acid

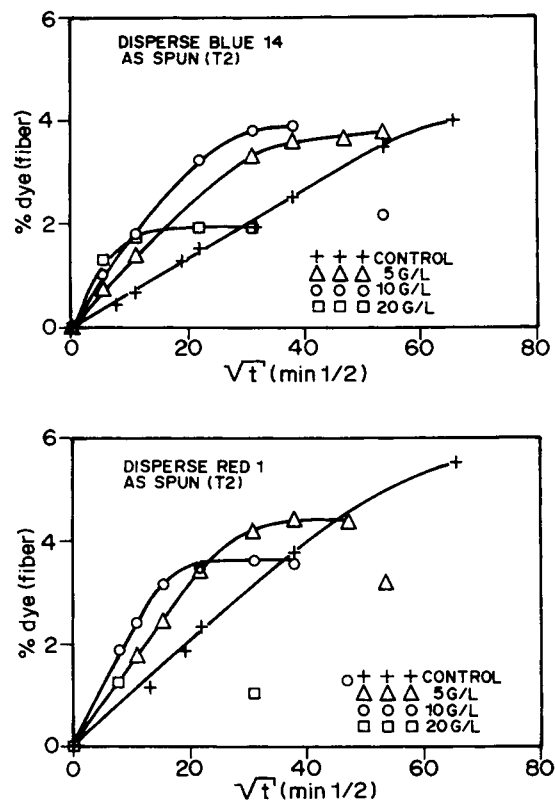


Figure 2 Percentage of dye on the as-spun fiber (heat treatment T2) versus $(\text{time})^{1/2}$ in the presence of benzoic acid at different concentrations (0, 5, 10, and 20 g/L): (a) Disperse blue 14 and (b) Disperse red 1.

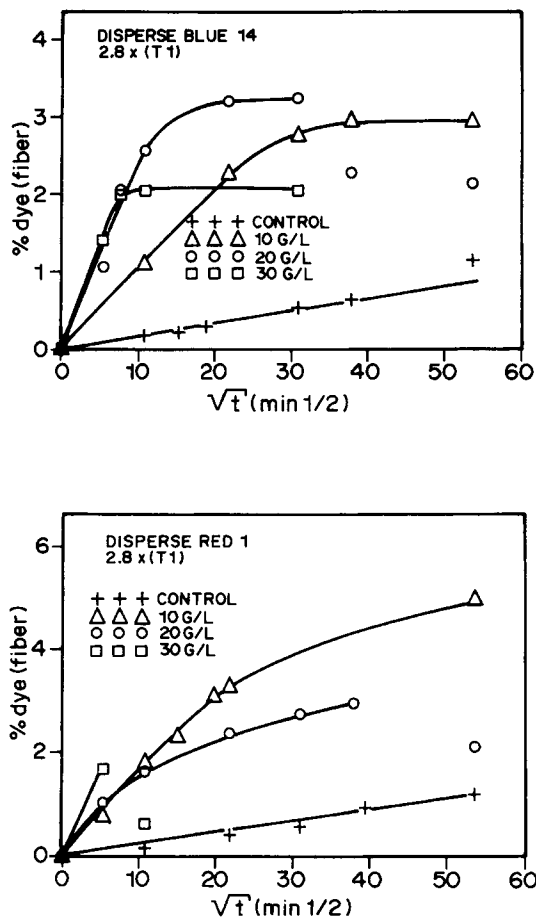


Figure 3 Percentage of dye on the $2.8 \times$ drawn fiber (heat treatment T1) versus $(\text{time})^{1/2}$ in the presence of benzoic acid at different concentrations (0, 10, 20, and 30 g/L): (a) Disperse blue 14 and (b) Disperse red 1.

(dye bath free of "carrier"). Therefore, two behaviors can be observed, a plateau-like region up to 5 g/L of benzoic acid concentration for the Disperse blue 14 and a maximum around 0 g/L of benzoic acid concentration for the Disperse red 1. Also, the absorption maxima values at the equilibrium time in the above-cited regions are different for both dyes. The disperse blue 14 presented lower values than the disperse red 1 in these regions. Here, two factors are contributing to such behaviors: the sizes of the dye molecules and their solubilities in water. The size of the dye molecule might be related to the point where the decay of the curves starts and the dye solubilities might be related to the dye absorption values at these regions. The Disperse blue 14 has a smaller molecular weight and a lower solubility in water than the Disperse red 1. It is clear also in these figures that the different heat settings applied to the fibers interfere in the absorption values of

the studied dyes. Figure 5(a) shows clearly high absorption values for the fibers heat treated for 8 h in boiling water (treatment T1). The continuous decay after these maxima regions might be related to the morphological modifications due to benzoic acid action at high concentrations and the competition for sites between the dye and "carrier" molecules.¹

The curves for the drawn fibers ($2.8 \times$) show an increase of dye absorption maxima at equilibrium time up to the benzoic acid concentration around 20 g/L, followed by a decrease. This behavior seems to reflect two aspects; the first one would be the predominance of the plasticizing effect that would be controlling the dye absorption up to concentrations of 20 g/L of benzoic acid. After this concentration, the morphological changes and competition between dye and carrier molecules for sites would be the commanding factors, with consequent decrease of the dye absorption maxima. Since the benzoic acid molecules are smaller than the dye mole-

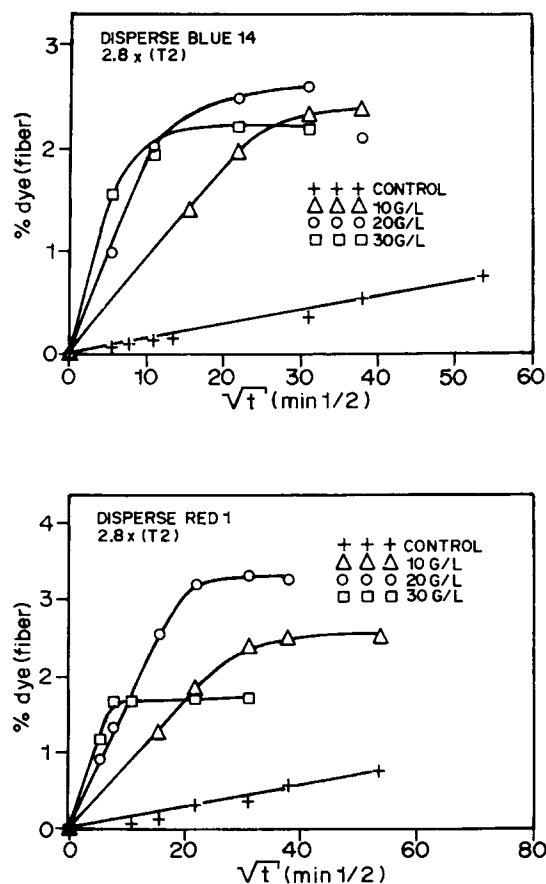


Figure 4 Percentage of dye on the $2.8 \times$ drawn fiber (heat treatment T2) versus $(\text{time})^{1/2}$ in the presence of benzoic acid at different concentrations (0, 10, 20, and 30 g/L): (a) Disperse blue 14 and (b) Disperse red 1.

Table I Diffusion Coefficients for the PET Fibers, Dyed With C.I. Disperse Blue 14 (D_B) and C.I. Disperse Red 1 (D_R), Dye Percentage (%Dye) and Time (t) at Equilibrium

Fibers	Heat Treatment	C (g/L)	$D_B \times 10^{9a}$ (cm ² /min)	% Dye	t (h)	$D_R \times 10^{9a}$ (cm ² /min)	% Dye	t (h)
0x	T1	0	2.6	4.48	72	22.7	5.99	48
		5	10.6	4.81	24	66.4	3.98	24
		10	16.0	3.96	16	453.0	2.58	16
		20	81.8	1.56	2	—	—	—
	T2	0	1.3	4.02	72	1.6	5.54	72
		5	5.6	3.76	48	6.1	4.40	24
		10	8.9	3.89	24	16.5	3.62	16
		20	57.1	1.94	8	—	—	—
2.8X	T1	0	—	—	—	—	—	—
		10	4.7	2.96	24	0.8	4.99	48
		20	14.1	3.26	16	3.2	2.96	24
		30	—	2.04	8	—	—	—
	T2	0	—	—	—	—	—	—
		10	1.2	2.37	24	1.0	2.52	48
		20	4.3	2.58	16	2.2	3.50	24
		30	15.1	2.18	8	13.4	1.72	8

^a Calculated from Hill's equation.⁵

cules and have higher solubility in water at dyeing temperature (95°C), they predominantly would diffuse first into the fiber substrate and would be occupying sites that would be designated for the dye molecules. It is clear that at higher concentrations these effects would occur together with the plasticizing action. The higher chain flexibility due to decreasing T_g and this effect continuing for longer times would result in a morphological change of the fiber substrate, as for example, an increase of crystallinity. In the undrawn fiber with a more unstable structure, this effect is occurring earlier, at lower benzoic acid concentrations.

The Morphological Changes Due to Benzoic Acid Action

In order to achieve a better understanding of the dyeing behavior, as described by the observations of Figures 1–5, the possible morphological changes cited above as a consequence of the plasticizing effect of the benzoic acid after a long time of exposition will be analyzed in the following paragraphs.

Therefore, the annealed fibers (from treatments T1 and T2) were submitted as described in the experimental section to treatments in a flask containing benzoic acid solution in different concentrations and at the same temperature as that for the dyeing. Thus, the obtained structural parameters are presented in Table II and Figure 6.

Figure 6 shows the plasticizing effect of the benzoic acid solution at different concentrations on the fibers. T_g decreases linearly and independently of the originally applied preheat treatments (T1 and T2) and the orientations of the fibers.

The plasticizing effect on the as-spun fiber occurs in the first 30 min of exposition in benzoic acid solution for all of the analyzed concentrations. This effect occurs for longer times of exposition in benzoic acid solution, when the studied fiber is the drawn one (2.8×), i.e., its glass transition temperature decreases continuously up to 24 h of treatment in benzoic acid. This figure shows, for a fixed plasticization time, the quasi-superposition of the curves for the fibers with the same draw ratios but originally submitted to different preheat treatments. It is possible to observe also a quasi-parallelism between the curves for the fibers with different draw ratios.

The described behavior indicates a similar level of plasticization for a fixed time of exposition in benzoic acid for all of the fibers, although as expected, the drawn fiber (2.8×) presented, for all analyzed concentrations, higher values of T_g than the as-spun one. The less stable structure, due to lack of orientation of the as-spun fiber and its more flexible structure, is responsible for its lower values of T_g .

Table II shows the changes in the analyzed structural parameters of the annealed fibers after 24 h of treatment in benzoic acid solution at different concentrations. The time of 24 h was chosen for analysis

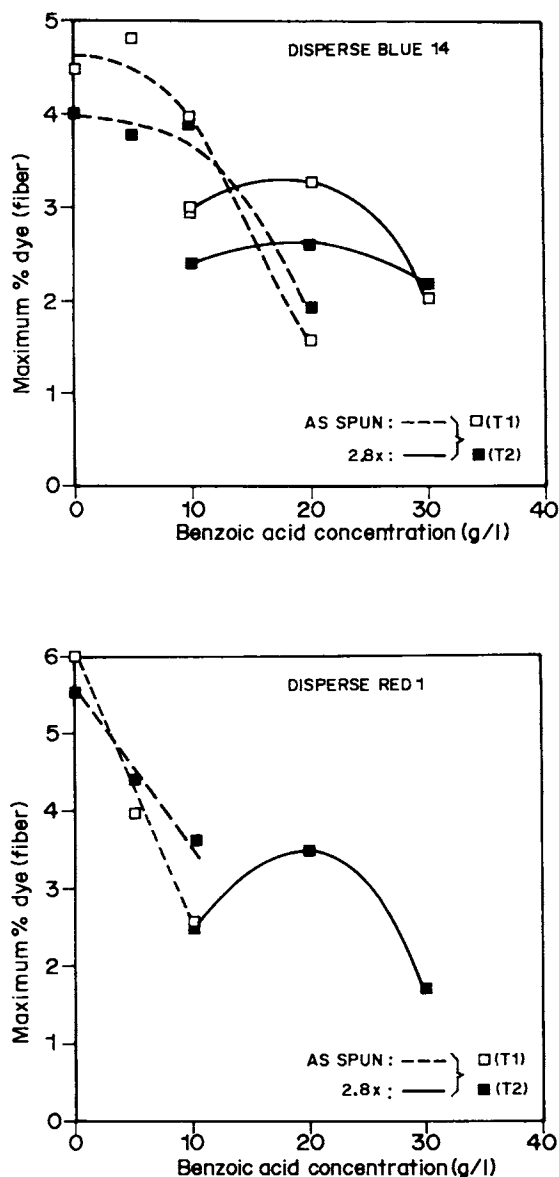


Figure 5 Maximum dye absorption (equilibrium) on the as-spun (---) and 2.8 × drawn fibers (—) versus benzoic acid concentration (g/L); preheat treatments T1 (□) and T2 (■): (a) Disperse blue 14 and (b) Disperse red 1.

because of its representativeness of the equilibrium time (maximum of dye absorption) for most of the fibers/dyebath systems studied. At this time, most of the fibers have already reached the dye absorption maximum (equilibrium) or are very close to it. Also, these structures will correspond closely to the structures at the maxima observed in Figure 5 for both fibers.

Therefore, Table II shows for the analyzed fibers a clear relationship between the parameters DF_a (dichroic function of the amorphous phase) and the

percentage of *T/G* (trans/gauche) ratio and the treatments realized in the presence of benzoic acid at different concentrations and fixed time (24 h). This relationship will depend on the existence of a previous orientation in the fiber and on the type of heat setting applied to the fibers.

The trans conformation has been related^{13,15} to the straight parts of the molecules in the amorphous and crystalline regions, and the gauche conformations have been related to the bended parts of the molecules within the amorphous phase only. Considering this convenient two-phase model, as described elsewhere^{13,15} to represent our fibers, a decrease in the trans/gauche ratio could mean a decrease or increase of the trans conformation in the crystalline region, in the amorphous region, or even in both regions.

Table II reveals that both control fibers (0×, 2.8×), when submitted to treatment T2 (dry treatment followed by 1 h in boiling water) presented higher values of *T/G* ratio and lower orientation values of the amorphous region than the control ones submitted to heat setting T1 (8 h in the presence of boiling water). Therefore, the treatment T2 seems to be less effective in promoting orientation of the amorphous region than treatment T1. Thus, the higher values of the *T/G* ratio observed when the applied heat setting is treatment T2 might be more related to the events occurring in the crystalline regions. As can be seen, the crystalline parameters CS and %LO are reaching higher values for heat setting T2 than heat setting T1 for both fibers. So treatment T2 can be forming bigger and more perfect crystals, which would be increasing the amount of trans conformation of the crystalline regions, due to a closer packing and straightening of the molecules within this region. Also, the higher values of DF_a and *T/G* ratio observed for the 2.8× control fiber for all analyzed heat settings are directly related to its previous orientation.

When the preheat-treated as-spun fiber is submitted to subsequent treatments in the presence of benzoic acid solutions at different concentrations, a decrease of its amorphous orientation is observed as the benzoic acid concentration increases. This disorientation is occurring for both preheat settings (treatments T1 and T2), showing a complete disorientation of these fibers at high concentrations of benzoic acid. Also, it is clear that a more intense disorientation is occurring when the as-spun fiber was previously heat setted by treatment T1. As explained before, this treatment is more effective in promoting the orientation of the amorphous region than treatment T2. Also, a decrease of the *T/G* ratio

can be observed as the benzoic acid concentration increases for both preheat settings applied to this fiber. This behavior can be related to changes in the trans conformation, not only in the amorphous region, but also in the crystalline region as mentioned before.

Analyzing the crystalline parameters for both heat settings as the benzoic acid concentration increases, the CI, CS, and LO increase continuously. However, it seems that these events related to changes in the structural parameters of the crystalline regions are not overcoming the events related to the amorphous region. So the overall T/G ratio might be decreasing mainly due to a decrease in the trans conformation in the amorphous region. Such behavior could be promoted by swelling or even the type of structure being developed due to benzoic acid action. The swelling behavior is a phenomenon related to the amorphous phase. So, any increase of this parameter would be favoring a disorientation of the molecules in this phase. When the applied heat setting is treatment T1, the samples are swelling continuously as the benzoic acid concentration increases. So, the swelling seems to be one of the contributing factors for the disorientation of the amorphous phase of these fibers. In the case of heat setting T2, the swelling data remain practically con-

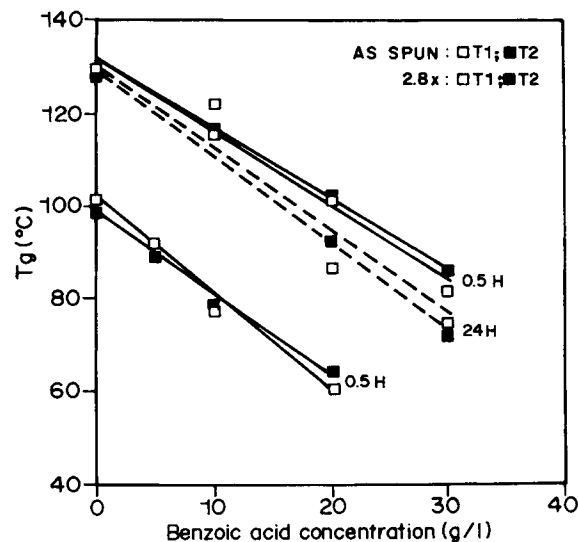


Figure 6 Glass transition temperature versus benzoic acid concentration for the as-spun and 2.8 × drawn fibers at different times of exposition (— 0.5 h and --- 24 h) and after preheat treatments T1 (□) and T2 (■).

stant as the benzoic acid concentration increases. Since this control sample already presented very low values of orientation of its amorphous region, and the subsequent benzoic acid treatments at different

Table II Structural Parameters of the Annealed Fibers Submitted to Benzoic Acid Treatment for 24 h at Different Concentrations

Fibers	Preheat Treatment	Benzoic Acid Concentration (g/L)	T_g^a (°C)	CI (%)	CS (A_o)	LO (%)	S_w (%)	DFa	$\frac{A_o(973)}{A_o(898)}$ (%)
0X	T1	0	102	47	30	20	50	0.20	41.0
		5	94	53	32	25	54	0.05	48.8
		10	79	55	34	28	52	-0.02	36.9
		20	—	58	34	29	59	-0.06	34.9
	T2	0	98	47	32	26	53	0.05	49.7
		5	92	54	34	30	50	-0.09	41.0
		10	79	56	34	28	52	-0.10	39.5
		20	—	58	37	29	—	0.00	31.9
2.8X	T1	0	129	57	34	23	12	0.46	50.5
		10	116	60	37	26	13	0.25	65.9
		20	87	67	41	33	13	0.33	55.8
		30	75	67	41	33	13	0.38	63.5
	T2	0	128	63	41	30	12	0.19	60.3
		10	116	62	37	36	13	0.33	59.6
		20	94	67	45	36	13	0.38	73.0
		30	73	68	45	33	13	0.28	51.4

^a T_g : Glass transition temperature (measured at temperature where E'' is maximum); %C.I.: Crystallinity index (measured by X-Ray diffraction); C.S.: Crystals Size; %L.O.: Lateral Order percentage.

% S_w , swelling percentage; DFa, DF of the amorphous phase for the 898 cm^{-1} absorption band (gauche conformation). $\frac{A_o(973)}{A_o(898)}$, structural absorbance ratio of the 973 cm^{-1} /898 cm^{-1} (trans/gauche) absorption bands (in percentage).

concentrations are not affecting the swelling result, the disorientation of the amorphous regions might be reflecting more the type of structure being formed due to benzoic acid action.

When the analyzed fiber is the drawn one (2.8 \times), Table II reveals that the DF of the amorphous phase (DFa) is presenting a very singular behavior depending on the previous heat setting applied. When the heat setting is treatment T1 the DFa parameter seems to be presenting a minimum at a concentration of benzoic acid of 10 g/L and then increasing. The opposite is occurring when the heat setting is treatment T2. Considering the overall T/G ratio, the tendency is toward higher values, as the benzoic acid concentration increases for both heat settings.

However, as the benzoic acid concentration increases, the crystalline parameters CI, CS, and LO are increasing as well, for both heat settings, reaching higher values of CS and LO for heat setting T2 than for treatment T1. Therefore, the heat setting T2 is more effective in promoting higher and more perfect crystals than treatment T1. The swelling data remain unchanged as the benzoic acid concentration increases for both heat settings, reflecting again the more stable structure of the drawn fiber.

Since the observed increase of the overall T/G ratio is being accompanied by an increase in the DFa parameter for the samples which were submitted previously to treatment T2, it is possible to affirm that the events related to both regions (amorphous and crystalline) are the contributing factors. The chains in the amorphous region might be pulled out by the new crystals which are being developed due to the benzoic acid action. This fact would increase the amount of trans conformation in this region.

This same effect would be occurring only at treatments in the presence of high concentrations of benzoic acid for the samples previously submitted to treatment T1. The initial loosening of the chains in the amorphous region at a concentration of 10 g/L might be related to the type of heat setting applied to this fiber.

Now, recalling the calculated data from Table I and Figures 1–6, it is possible to affirm that the diffusion coefficients are much more related to the plasticization effects of the benzoic acid on the fibers than to the structural transformations as just described. Therefore, the flexibility of the chain segments caused by the benzoic acid action is the commanding factor for the continuous increase of the diffusivities as the benzoic acid concentration increases. This is an expected behavior, since the diffusivities are calculated from the straight parts of the curves of percent dye in the fiber versus the

square root of time, as shown in Figures 1–4. The angular coefficients of these curves increase continuously for all analyzed concentrations of benzoic acid and dyes. Thus, an increase of benzoic acid concentration in the dyebath acts as when we submitted the fibers to increased dyeing temperatures. However, this effect does not explain by itself the observed changes of the dye absorption at equilibrium as a function of benzoic acid concentration (Fig. 5). Therefore it is in the equilibrium point of such curves that the structural changes due to the benzoic acid action start to play a role, or are even commanding this process.

It has been shown in a previous work²² (Part I of these series of papers) from DSC analysis and DMTA that the increase in the CI (global crystallinity from x-ray analysis) is a consequence of an increase of the area under a second premelting peak (around 180–190°C), revealed by the DSC analysis and the main melting peak (around 245–259°C) after the treatments in benzoic acid solutions at different concentrations. It has been suggested²² that this second premelting peak is related to the formation of smaller, but more perfect, new crystals inside the amorphous regions. The DMTA revealed also an α_c relaxation peak related to this second premelting peak, confirming therefore the formation of a new and complex structure due to benzoic acid action. It was concluded in that work that the benzoic acid is not only forming new crystals (related to the appearance of the second premelting peak), but is also altering the original crystalline region formed during the preheat settings (treatments T1 and T2).

The benzoic acid acts by breaking the intermolecular bonds, relaxing the residual orientations and consequently decreasing T_g (increases of chain flexibility). This continued plasticizing effect for long times will result in such complex morphology.

Relationship Between Morphology and Dye Behavior

Comparing the described results of Table II with the results presented in Figure 5, it is possible to delineate the following hypothesis: the increase of CI observed as the benzoic acid concentration increases after 24 h of exposition to this carrier (near the equilibrium time for both fibers) is occurring mainly due to the generation of the new crystallites within the amorphous region,²² which appear as a second premelting peak in DSC analysis as explained above.

In the case of the as-spun fiber submitted to heat settings T1 and T2, the generation of such new

crystallites in the amorphous region might be responsible, in addition to the swelling, for the observed disorientation of its amorphous region, as discussed in the previous section. So, the presence of such crystallites in the amorphous region not only will act as a barrier to the dye molecule movement inside the fiber substrate, but also will act by reducing the amount of sites available for the dye molecules. An increase of crystallinity would imply a reduction in the amount of amorphous phase. Although the T_g values are still decreasing as the benzoic acid concentration increases for the treatments realized for 24 h, this phenomenon by itself is not enough to promote an increase of dye absorption as the benzoic acid concentration increases. The barrier generated by the presence of these new crystallites and the decrease in the amount of amorphous region available for dye diffusion will overcome any increase of flexibility of the chains. This decrease in T_g as the benzoic acid concentration increases might be associated with the increase of size and perfection of the crystals.⁷

The basic differences between the heat settings applied to this fiber are restricted to the swelling behavior as the benzoic acid concentration increases. When the heat setting is treatment T1 (8 h in boiling water), the swelling increases continuously, contrary to heat setting T2, where the swelling remains practically constant for all analyzed benzoic acid concentrations. The additional swelling occurring in the fiber previously heat set by treatment T1, when submitted to additional treatments in the presence of benzoic acid solutions, might be the result of void formation as mentioned before. Simal and Bell⁴ have shown through SAXS (small-angle x-ray scattering) the formation of voids, when their PET fibers were submitted to benzoic acid treatment. So, this fact might be the main reason for the higher dye absorptions present for the as-spun fiber in the equilibrium dye uptake, at low concentrations of benzoic acid, when the initial heat setting is treatment T1 (see Fig. 5 and Table I). When the analyzed fiber is the drawn one the differences are directly related to the presence of a previous orientation in this fiber and its more stable structure.

Figure 5 indicates that the maxima of dye absorption (at equilibrium) for the as-spun fiber is occurring at a lower benzoic acid concentration (around 0 g/L) than for the 2.8 \times fiber (around 10–20 g/L). As already explained, the as-spun fiber permitted a faster plasticizing effect of the benzoic acid (30 min) than the drawn one, with a continued plasticizing effect up to 24 h. It is clear that the more stable structure due to the presence of ori-

entation in the 2.8 \times fiber will result in such behavior.

In the case of the drawn fiber, although the new crystallites are being formed as in the case of the as-spun fiber,²² at lower concentrations of benzoic acid, they are not making the increase of dye absorption difficult. The decrease of T_g due to the plasticization effect of benzoic acid is still favoring an increase of dye absorption, up to the concentration of 20 g/L of benzoic acid. After this concentration the phenomenological aspects concerning the crystalline region, as described for the as-spun fiber, start to overcome the plasticization effect, i.e., reducing the available sites for the dye molecules, due to an increase of crystallinity, and forming a barrier with new crystallites inside the remaining amorphous region, making the absorption of the dye molecules difficult. Obviously, as demonstrated before by Simal and Bell,⁴ the degree of structural modification will depend on the structural stability of the fibers.

The basic differences concerning the heat settings applied to this fiber are now restricted to the dichroic function of the amorphous region (DFa parameter) and the crystalline parameters of the control samples. Heat setting T1 promoted lower values of the crystalline parameters in the control fiber than did treatment T2. Although treatment T1 promoted a higher orientation of the amorphous region for the control fiber, it presents lower crystallinity values, which would facilitate the dye absorption. Also, as the benzoic acid concentration increases, the DFa parameters presented a minimum at a concentration of 10 g/L followed by an increase, reaching a DFa value at a concentration of 30 g/L still below the initial DFa value of the control sample. So, this loosening of chains due to the benzoic acid action in addition to the lower values of the crystalline parameters can be responsible for the higher dye absorption values at equilibrium as compared to the samples heat set by treatment T2. Although the crystallinity is increasing as the benzoic acid concentration increases, the initial loosening of the chains at a lower concentration of benzoic acid is facilitating the absorption of the dye molecules.

In the case of treatment T2 (dry treatment followed by 1 h in boiling water), a different behavior is controlling the dye absorption at equilibrium. As the benzoic acid concentration increases, the DFa parameters are increasing as well. So as already mentioned in a previous section of this paper, the increase of crystallinity might be responsible for the straightening of the molecules in the amorphous region. This fact seems to be one of the contributing

factors for the lower dye absorption reached by the fibers heat set by treatment T2.

It is clear also that the earlier hypothesis concerning the dye solubilities and the competition for sites between the benzoic acid and the dye molecules¹ can be playing a role in such observed behavior. Therefore the dyeing behavior presented in Figures 1–5 is being governed by these phenomena or complex mechanisms.

Relationships Among the Diffusion Coefficient, the Loss Modulus (E''), and the Morphological Changes Due to Benzoic Acid Action

DMTA permitted the loss modulus (E'') determination in the dyeing temperature for all benzoic acid concentrations studied. The relationship between the diffusion coefficient (D) and the value of E'' (equation 3) in the dyeing temperature was used to detect the structural differences through the angular coefficients B_B and B_R of the dyes Disperse blue 14 and red 1, respectively.

The temperatures corresponding to the values where E'' is maximum, and presented in Table II and Figure 6 for the different fibers treated for different times and concentrations of benzoic acid, were not obtained (due to experimental difficulties) in the presence of water, which would better represent the dyeing conditions. It is well known,⁸ that the T_g of the PET fibers can be decreased about 20°C due to the plasticizing effect of the water. Therefore, it is expected that these T_g values in the dyeing conditions are about 20°C lower than the ones presented in Table II and Figure 6. Consequently, the E'' values, which are more representative of the dyeing conditions, would be those taken at temperatures around 115°C or 20°C above the experimental dyeing temperature of 95°C. Therefore, the established conditions for the dyeing and the experimental analysis seem to be within the validity of the free volume theory.⁸

The linearity of the obtained curves (Figs. 7 and 8) for all analyzed dyes, applied heat settings, and fibers are in accordance with the applied theory.⁸ The calculated angular coefficients from these curves are presented in Table III.

The as-spun fibers presented B_B and B_R values lower than those for the 2.8× fibers for all analyzed preheat treatments and times of exposition in benzoic acid. This fact could be indicative of the dependence of the B values on the original orientations of the fibers. Dumbleton and colleagues⁷ found, for PET fibers heat treated under dry conditions at different temperatures and dyed in the absence of

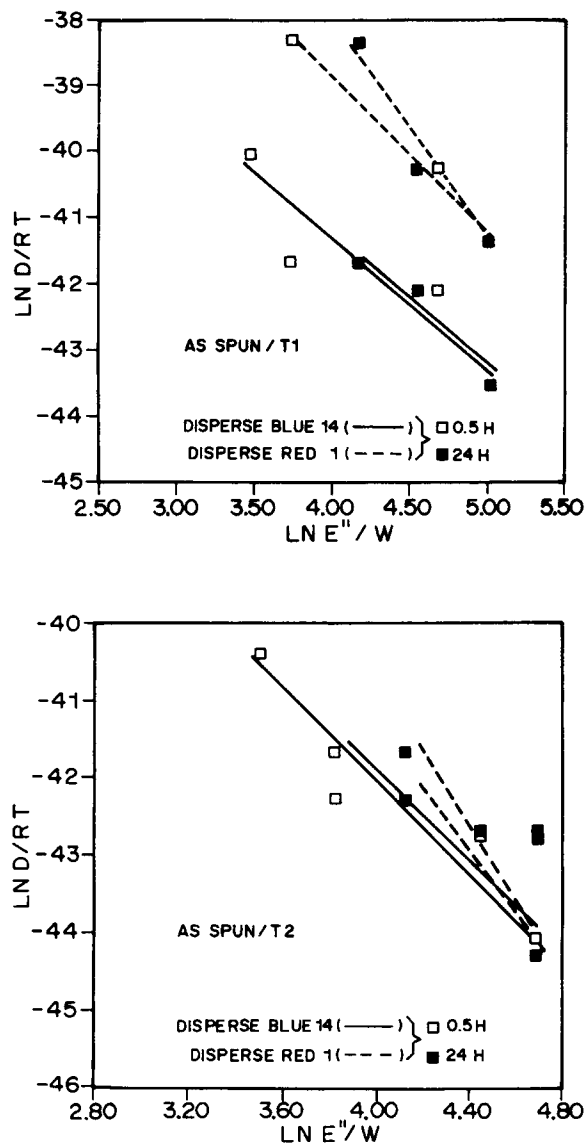


Figure 7 $\ln D/RT$ versus $\ln E''/W$ for the as-spun fiber at different times of exposition in benzoic acid (\square 0.5 h and \blacksquare 24 h) and different dyes (— Disperse blue 14 and - - - Disperse red 1): (a) preheat treatment T1 and (b) preheat treatment T2.

“carrier,” B values equal to 1 for the as-spun fibers and around 4 for the drawn ones (4.25×). For an amorphous and nonoriented system, we could expect B values equal to 1.^{7,8}

Since the B values obtained for the as-spun fiber were around 2 to 3.5, it is possible that structural factors other than differences in the orientation only are playing a role in the dyeing process. Such factors could be the new crystalline structure generated by the benzoic acid treatment, the prior type of heat setting given to the fibers, and the presence of voids.

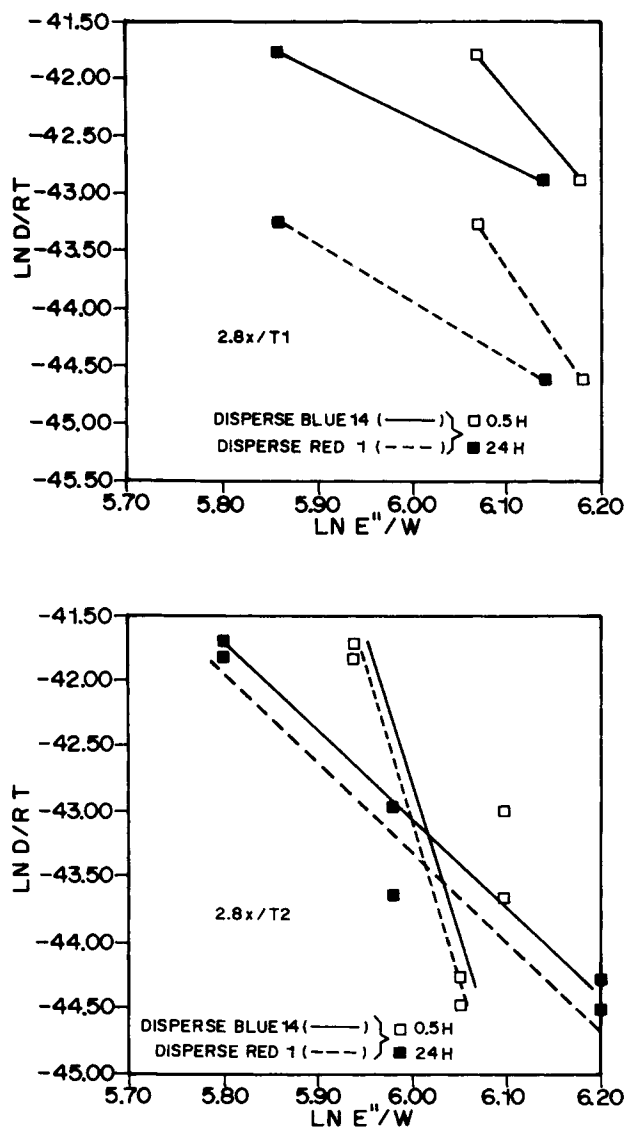


Figure 8 $\ln D/RT$ versus $\ln E''/W$ for the 2.8 drawn fiber at different times of exposition in benzoic acid (\square 0.5 h and \blacksquare 24 h) and different dyes (— Disperse blue 14 and --- Disperse red 1): (a) preheat treatment T1 and (b) preheat treatment T2.

Indirect factors, such as the size of the dye molecules as well as their solubilities in water, may be contributing to the calculated B values, also.

As can be seen in Table III, the obtained B values for the as-spun fiber treatment in benzoic acid solution for half an hour and 24 h are very close to each other for the different dyes studied and applied heat settings.

As already discussed, the observed result of Figure 6, the benzoic acid plasticizing effect over the as-spun fiber, occurs in the first 30 min of treatment. This means that for long times of treatment in a

certain benzoic acid concentration, the T_g value is not being reduced any longer and the morphological changes generated by this treatment do not impose any more chain flexibility reduction (T_g remains practically at the same levels). It can be said that the B values reflect the degree of chain flexibility and consequently the amount of restriction that the morphology of the substrate can induce to the chain movements. The lower the B value, the higher the flexibility.

This discussion becomes more clarified if the results obtained for the 2.8 \times fiber are considered. The calculated B values for the 2.8 \times fiber depend on the time of treatment in benzoic acid solution. The time for an effective plasticizing action of the benzoic acid over this fiber is around 24 h, as already discussed. Although the B values are still very high after 24 h of treatment in benzoic acid solution (around 3.9 to 6.5), they have presented a reduction of about 40–60%, depending on the previous heat setting and disperse dye used.

Another interesting observation related to Figures 7 and 8 is that for the drawn 2.8 \times fiber, a decrease of the dye molecular weight dislocated the straight line to a position above that obtained for a higher molecular weight dye, or the curves obtained for the dye Disperse blue 14 (266.30 g/mol) are above those obtained for the Disperse red 1 (314.4 g/mol). This situation is inverted for the undrawn fiber, when its higher solubility in water and ability to agglomerate in a porous matrix might be influencing such behavior.

CONCLUSIONS

The dyeing behavior in the presence of benzoic acid at different concentrations up to the equilibrium for the analyzed PET fibers was shown to be strongly dependent on several factors such as the original structural characteristics (presence of crystallinity and orientation) which will control the structural stability of the fibers; previous thermal history (type of heat treatments) to fix the structure of the fibers for further treatments in the presence of benzoic acid solutions at different concentrations; the type of structure developed in the fibers due to benzoic acid action, which will depend on the concentration and time of exposition to this carrier, the size and the solubility of the dyes in the dyebath, and the competition for sites between the dye and the carrier molecules.

It has been shown that the observed maxima at certain concentrations in the curves of the dye ab-

Table III Angular Coefficients from Equation (3) for the Different Dyes, Fibers, and Times of Treatment in Benzoic Acid

Fibers	Preheat Treatment	t (h)	B_B^a	B_R^a
0X	T1	0.5	2.7	2.3
		24.0	2.1	3.5
	T2	0.5	2.7	2.5
		24.0	2.1	2.9
2.8X	T1	0.5	9.9	12.2
		24.0	3.9	4.8
	T2	0.5	10.4	13.4
		24.0	6.3	6.5

^a Angular coefficients from the straight lines for the dyes Disperse blue 14 (B_B) and Disperse red 1 (B_R).

sorption at equilibrium versus benzoic acid concentration reflect two main aspects: the first one would be the predominance of the plasticizing effect that would be controlling the dye absorption up to the maxima values. The position of the maxima values will depend on the structural stability of the fibers and the type of heat set applied to them. Second, after these maxima, the morphological changes and the competition between dye and carrier molecules for sites within the fiber substrates would be the commanding factors. The subsequent decrease in the dye absorptions at equilibrium after these maxima and the studies on the morphological changes due to benzoic acid action reinforced such conclusions. All of these effects, the maxima position, and the changes in the structure due to benzoic acid action will occur at lower benzoic acid concentration for the originally undrawn fiber with a more unstable structure. Also, the plots of $\ln D/RT$ versus $\ln E''/W$ helped us to better understand the influence of the structural differences between the fibers on the dyeing behavior through the angular coefficients B_B and B_R , relative to the dyes Disperse blue 14 and red 1, respectively.

The calculated angular coefficients for the undrawn fiber as compared to the drawn one revealed that structural factors other than differences in the orientation only are playing a role in the dyeing process. These factors are the new crystalline structure generated by the benzoic acid treatment, the prior type of heat treatment given to the fibers, and the presence of voids. Other indirect factors, such as the size of the dye molecules and their solubilities in water, may be contributing to the calculated B values, also. Yet it was observed that the B values reflect the degree of chain flexibility

and consequently the amount of restriction that the morphology of the substrate can induce to the chain movement. The lower the B value, the higher the flexibility.

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