Dye Leveling in PET Fibers. I. The Effect of Fiber Morphology and Carrier

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Synopsis

Migration of dye from darker fibers to lighter ones was quantitively studied by placing fibers dyed to equilibrium with undyed ones in a common bath, measuring dye concentrations in the fibers as a function of time. 2X, 4X, and 6X fibers were heat-set and boiled before the experiment. Disperse red 15 was the dye, and 13 g/L benzoic acid was used as a carrier in some of the tests. Structural measurements indicated a glass transition temperature reduction of ca. 20°C in the presence of the carrier, with a large corresponding increase in dye diffusivity and migration rate. At long times (7–22 h) however, the diffusivity decreased because of a 4–5% increase in crystallinity. The rates of leveling corresponded to the diffusivities, confirming that leveling for a given dye is controlled by polymer molecular mobility. It was possible to reverse the carrier effect by boiling the fibers in a bath containing no carrier. Pretreatment of the fibers with carrier was ineffective; it was necessary for carriers to be present in the leveling bath. In the absence of carrier, the T_g was above the dyeing temperature and diffusion and migration were very slow. Voids formed by the previous presence of carrier, observed by small angle X-ray scattering, tended to collapse. This resulted in migration behavior similar to fibers not exposed to benzoic acid.

INTRODUCTION

Leveling is defined as the ability of a dye–polymer system to even out concentration differences, which frequently appear during a dyeing process.[1] One of the main objectives in dyeing is the production of a yarn or fabric in which no irregularities of color can be detected. Several factors have been suggested as causes for unlevelness,[1-5] but no one has treated the problem in relation to the basic fiber morphology.

The migration of the dye within the fiber substrate is of interest. The migration of dyestuffs can be assessed by placing dyed and undyed bundles of fibers in a clear blank bath under standardized conditions. In other words, the initially undyed fibers absorb dye which was released by other fibers which were initially dyed to equilibrium. Such an analysis can be used to calculate the migration factor *M*, i.e., the ratio at time *t* of the amount of dye on the formerly undyed material to the amount of dye on the formerly dyed one. This quantity can be used to predict a leveling time, i.e., when $m = 1$, the amount of dye in the undyed fiber equals the amount of dye in the dyed one. The dyed fiber–undyed fiber system is regarded as being "finite," i.e., the amount of dye in the system (bath plus substrate) is fixed. By defining the initial and boundary conditions, mathematical solutions

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can be obtained and the diffusion coefficients can be estimated. Analytical solutions for diffusion in geometrical systems with diffusion from or diffusion to cylinders are given by several authors.[5-11]

In the present work qualitative relationships between dye leveling and PET morphology are developed. In the following article, a mathematical model is proposed for the combined desorption and absorption process, and the predictions from the model are compared with the experimental leveling data.

EXPERIMENTAL

Sample Preparation

Bright PET carpet yarn fibers of different draw ratios (2x, 4x, 6x) were initially heat set for 7 h at 130°C in an evacuated oven under slack condition, i.e., the fibers were free to relax. An additional 1 h treatment in boiling water was given in order to avoid structural modifications due to water presence during the dyeing process. Other structural details of these fibers have been reported previously.[12a]

DYEING

Dyeings were carried out in presence and absence of carrier (benzoic acid) to equilibrium in an "infinite" dyebath within a controlled temperature and shaking bath. The shaking was in the horizontal direction (70 cycles/min), and the dyeing temperature was 100°C. The dye solution was prepared by adding 4.5 g of dye to 3 L of distilled water. Fiber samples weighing between 0.100 and 0.300 g were placed in a 250-mL flask containing 125 mL of dye solution. For the dyeings in presence of carrier, a concentration sufficient to give 13 g/L of benzoic acid was added to the dye bath.

The dye used was 1-amino 4-hydroxy-anthraquinone (C.I. disperse red 15). Dye concentrations on the fibers were determined by extraction with dimethyl formamide (DMF) at 95°C. Three extractions of 15 min each were necessary to completely remove the dye from the fibers. The optical density of the extract was measured by UV spectrophotometry and the percent of dye on the fiber was calculated by the expression below[13]:

$$\% \text{ dye} = \frac{\text{optical density} \times \text{extracted vol} \times \text{dilution factor} \times 100}{\text{dye extinction coeff.} \times \text{dyed sample weight} \times 1000}$$

Migration

The migration test consisted of exposing fibers, dyed to equilibrium, to an equal weight of similar undyed fiber in a blank dyebath at the normal dyeing temperature, and determining the time required for the two groups of fibers to become the same shade (the same dye concentration).

The migration factor m is defined by the following expression:

$$m(t) = \frac{\text{amount of dye on originally undyed material}}{\text{amount of dye remaining on originally dyed material}}$$

when $m = 1.0$, it can be said that levelness has been reached.

The migration experiments were carried out in presence and basence of carrier (benzoic acid, 13 g/L of solution). In the case where the originally dyed fibers were dyed in the presence of carrier, the corresponding originally undyed fibers were also treated in benzoic acid solution, using the experimental conditions of the dyeing experiments.

The fibers (dyed and undyed) were placed in a cylindrical 100 mL bottle. A stainless steel net of very fine mesh was used to separate the dyed fibers from the undyed ones. The bottles were closed firmly and placed in a controlled shaking and temperature oil bath. The temperature and shaking conditions were the same as in the dyeing procedures.

Structural Measurements

Density and crystallinity measurements were made using density gradient column and differential scanning calorimetry (DSC) methods. The liquids used in the density gradient column were n-heptane and carbon tetrachloride.[12b]

Swelling measurements were made through the changes in the diameters of the fibers, measured by optical microscopy.[14]

The Rheovibron direct reading viscoleastomer, Model DDV-II (Toyo Measuring Instruments Co., Japan), was used for measuring the dynamic mechanical properties of the PET fibers. The frequency used for the measurements was 11 cps and the temperature range was from room temperature to 260°C. The readings of E' and tan δ were taken at 5°C intervals, with smaller intervals (2°C) near the transition region. Samples were allowed to equilibrate for 5 min at each temperature before taking the measurements. The measurements were made at 100% relative humidity in order to better represent the fiber properties during dyeings.

Small angle X-ray scattering measurements were made with pinhole collimation, with a specimen to film distance of 29 cm. Ni-filtered CuKα radiation was used. During the exposure time, vacuum was maintained to avoid air scattering. The long period was calculated using the Bragg law.

RESULTS AND DISCUSSION

Dye Leveling and the Fiber Morphology

In the migration experiment, the blank fibers are absorbing the dye released from the originally dyed ones. The resulting curves for the migration experiments are shown in Figures 1, 2, and 3.

Figure 1 represents the experiment in absence of carrier. In Figure 2, although the medium (bath) was free of carrier, the originally dyed fibers
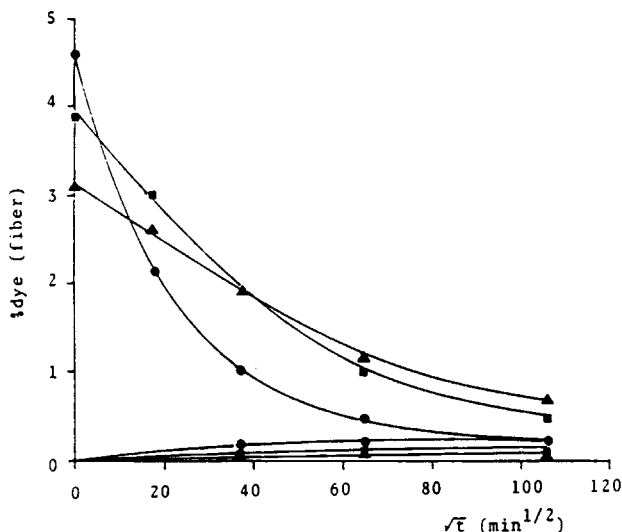
Fig. 1. Percent of dye on fiber vs. (time)$^{1/2}$ for migration experiment in absence of benzoic acid. No carrier; disperse red 15; (●) 2x; (■) 4x; (▲) 6x.

were dyed in the presence of carrier and the originally undyed fibers were also pretreated in this same carrier. The conditioning time was the time required for the dyed fiber to reach equilibrium during the dyeing process in the presence of benzoic acid.

Figure 3 represents the case where the medium also contained carrier; the fibers had the same conditioning treatment as in Figure 2.

In all figures the decendent curves represent the dye desorption by the originally dyed fibers and the ascendent curves represent the dye absorption
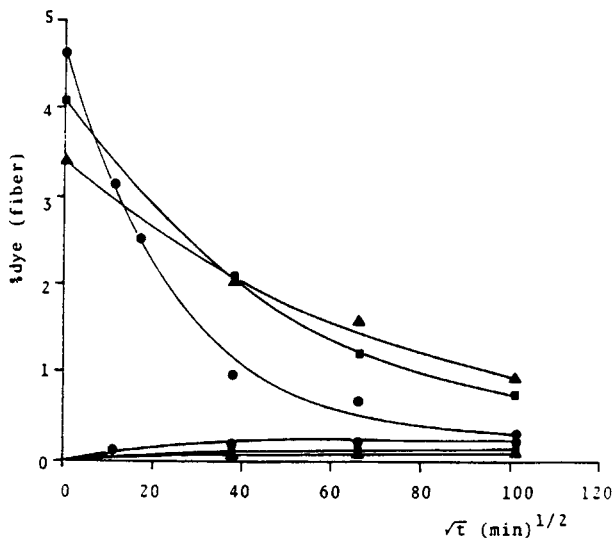

Fig. 2. Percent of dye in the fiber vs. (time)$^{1/2}$ for migration experiment in the absence of carrier; fibers initially pretreated in benzoic acid (concn 13 g/L). Disperse red 15; bath free of carrier; (●) 2x; (■) 4x; (▲) 6x.
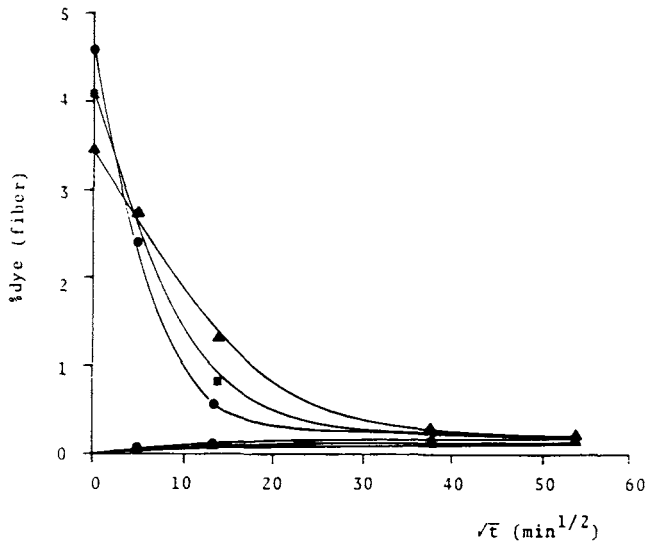
Fig. 3. Percent of dye on fiber vs. (time)$^{1/2}$ for migration experiment in presence of benzoic acid. (●) $2x$; (■) $4x$; (▲) $6x$; disperse red 15; carrier (concn 13 g/L).

by the blank fibers. In order to better understand the desorption and absorption mechanism involved in the migration experiments, the following discussion of the structural measurements is of interest.

The diameter and density changes after benzoic acid treatment at different concentrations for 2 h are shown in Figures 4 and 5, respectively. Figure 4 shows that swelling is much more significant for the $2x$ sample.
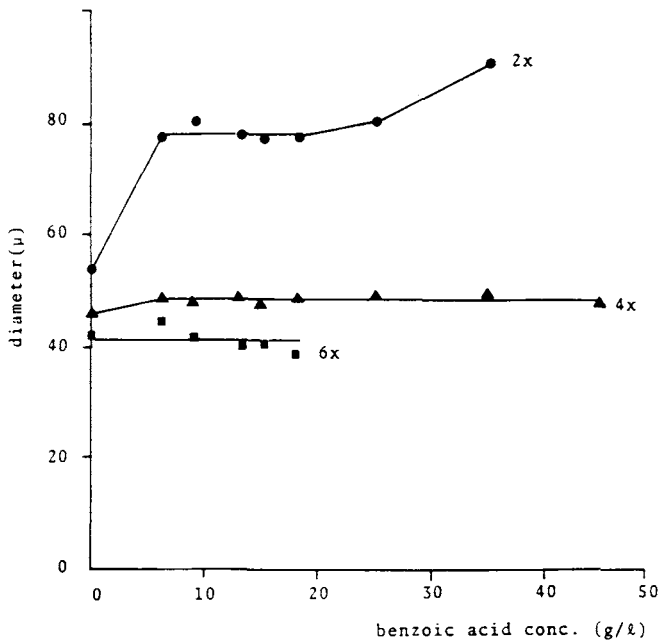

Fig. 4. Diameter vs. benzoic acid concentration used to pretreat the fibers. Treatment time: 2 h.
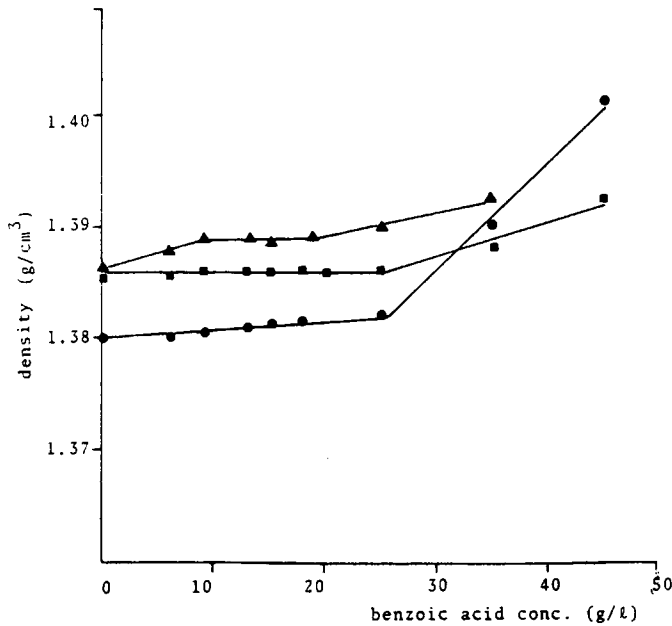
Fig. 5. Density vs. benzoic acid concentration used to pretreat the fibers; treatment time 2 h: (●) 2x; (■) 4x; (▲) 6x.

Changes in density (Fig. 5) are observed only at high concentrations of benzoic acid for this 2 h treatment time, perhaps due to an increase in crystallinity, particularly in the 2x sample.

The crystallinites for the control and for the samples treated in benzoic acid solution, at a concentration of 13 g/L for the time necessary to reach equilibrium during dyeing experiments, are given in Table I. Table I reveals an increase of apparent crystallinity, attributable to the benzoic acid, of from 4 to 5% for all samples at these treatment times.

The results from dynamic mechanical analysis are shown in Figures 6–12.

The plasticizing effect of the benzoic acid treatment in the heat set fibers is shown by comparing Figures 6 and 7, 8 and 9, and 10 and 11. The temperatures where the E''_{max} occurs (T_g) are shifted to lower values for all of the benzoic acid treated samples.

TABLE I
The Effect of Benzoic Acid Pretreatment upon Crystallinity

Benzoic acid concn (g/L)	2× (% Cryst.)[a]	4× (% Cryst.)[b]	6× (% Cryst.)[b]
0.0	33.98	38.50	39.40
13.0	37.36	43.52	44.80

[a] DSC method: pretreatment time 7 h.
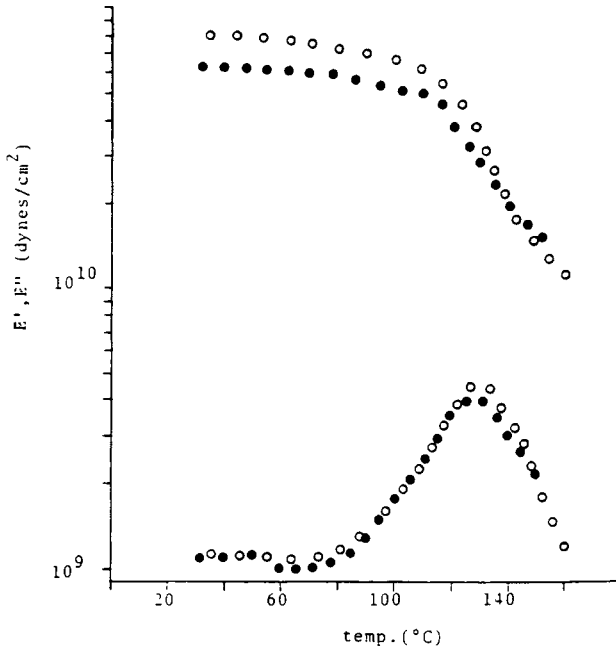[b] DSC method: pretreatment time 22 h.

Fig. 6.   Dynamic and loss modulus vs. temperature; 2x: (○) 0% relative humidity; (●) 100% relative humidity.
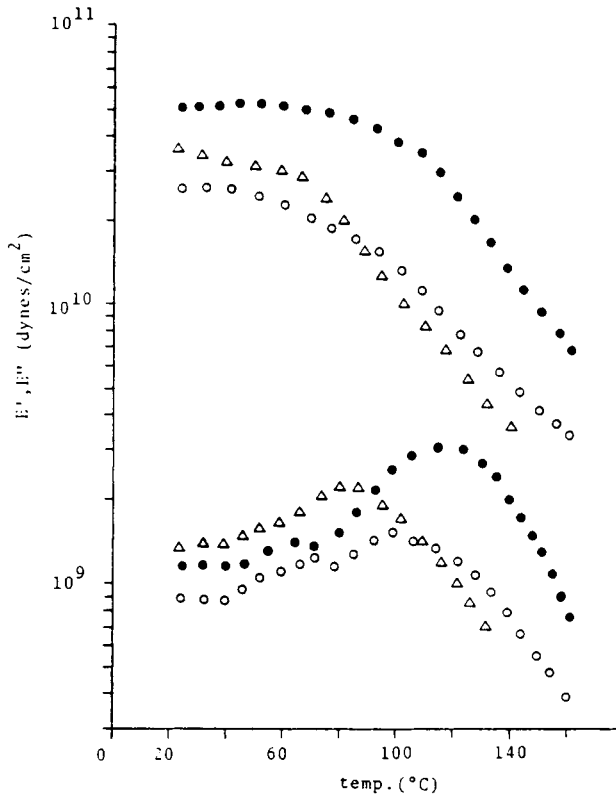

Fig. 7.   Dynamic and loss modulus vs. temperature for the 2x fiber treated at benzoic acid concentration of 13 g/L: (△) 2 h; (○) 7 h; (●) 7 h, 1 h boiling.
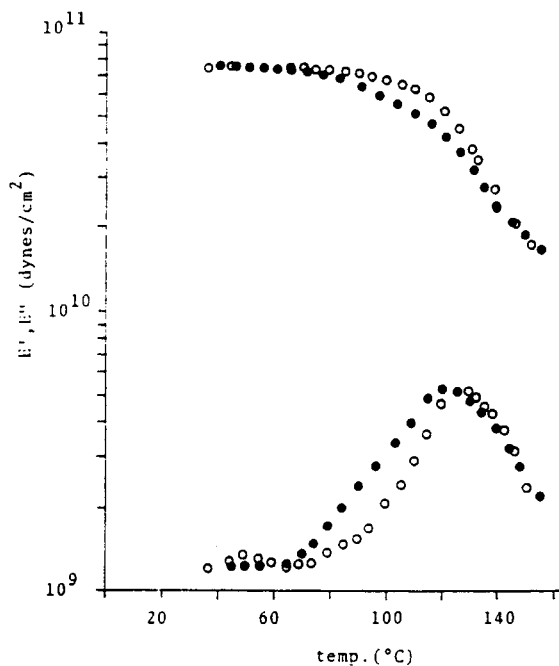
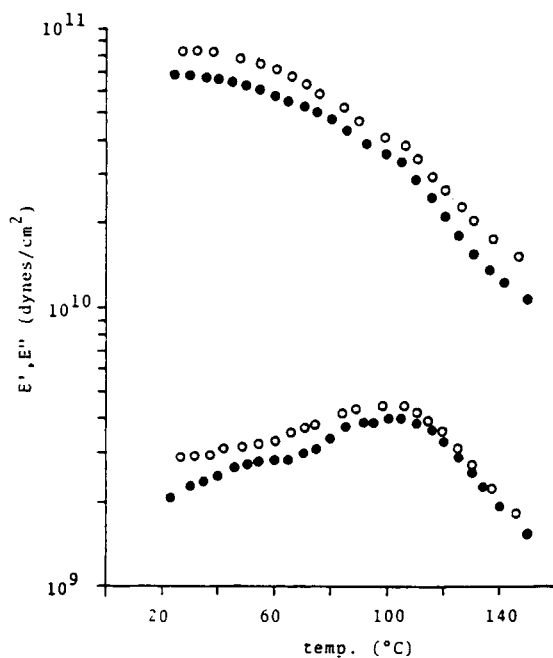**Fig. 8.** Dynamic and loss modulus vs. temperature; 4x: (○) 0% relative humidity; (●) 100% relative humidity.

Fig. 9. Dynamic and loss modulus vs. temperature for the 4x fiber treated at benzoic acid concentration of 13 g/L: (○) 2 h; (●) 22 h.
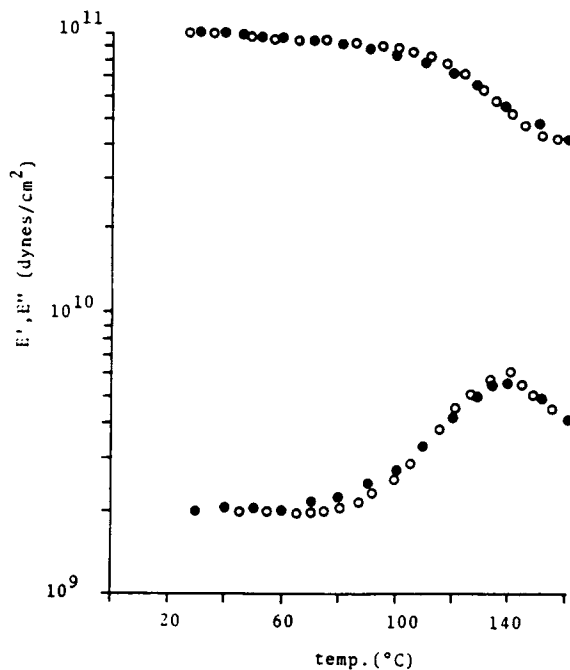
Fig. 10.   Dynamic and loss modulus vs. temperature; 6x: (○) 0% relative humidity; (●) 100% relative humidity.
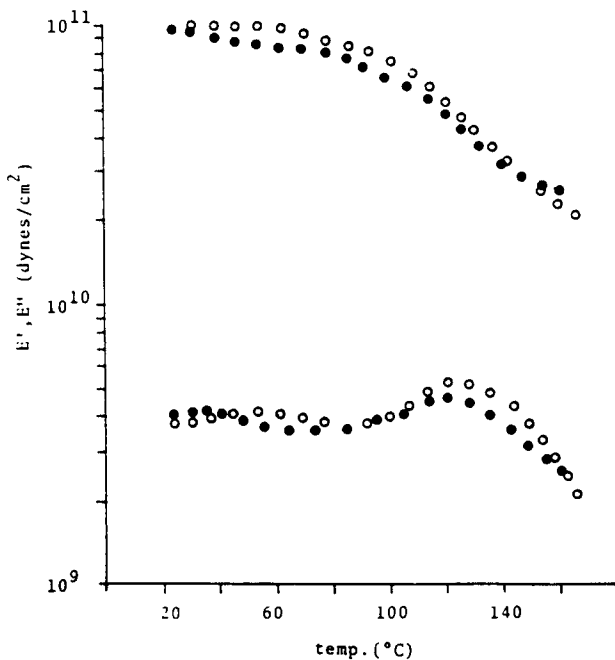

Fig. 11.   Dynamic and loss modulus vs. temperature for the 6x fiber treated at benzoic acid concentration of 13 g/L: (○) 2 h; (●) 24 h.
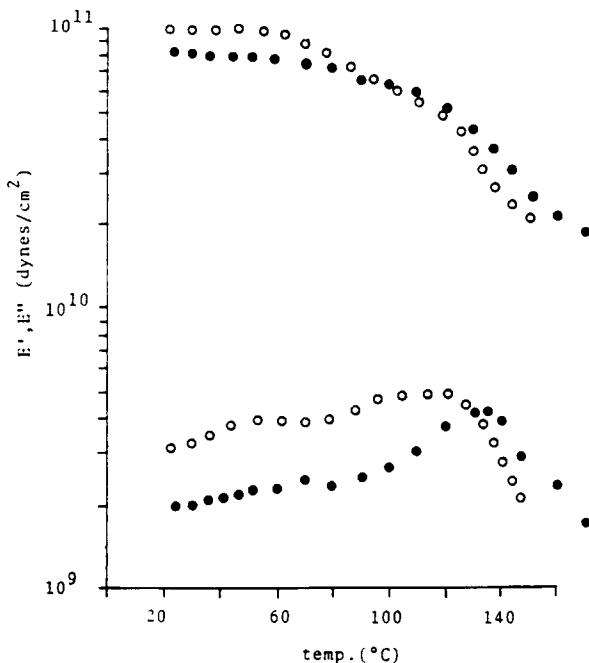
Fig. 12. Dynamic and loss modulus vs. temperature for the 6x fiber treated at benzoic acid concentration of 13 g/L. (○) 22 h; (●) 24 h, 1 h boiling.

After treatment in benzoic acid, a second peak or shoulder is observed at a temperature of about 50°C, prior to the major α-dispersion peak. The appearance of this shoulder has been associated[15] with the presence of residual amounts of the solvent used to treat the fiber, which would be expected to shift the α-dispersion peak to lower temperature. This shoulder is independent of the treatment time, as it was present for several different treatment times. Also, it has been observed that this shoulder can be easily removed and the α-dispersion is returned to its original position when a subsequent rinse in boiling water for one hour is applied. This effect is shown in Figures 7 and 12. These data are in agreement with the work of Weigmann et al.,[15] where PET fibers were treated in presence of DMF. Subsequent boiling water treatment also showed effectiveness in the DMF removal.

Table II shows a slight decrease in the E''_{max} values for the fibers of draw ratios 4x and 6x after benzoic acid treatments. However, a much steeper decrease is observed for the sample of lower draw ratio. The swelling effect is one possible cause for this decrease. Another suspected factor is the increase in crystallinity, especially after prolonged times of treatment. The increase in crystallinity after 7 h of treatment in benzoic acid solution shifted the T_g from 85°C to 100°C.

In the case of the fibers drawn 4x and 6x, the increase in crystallinity does not seem to be the major contributing factor for the decrease in the E''_{max} value. The dynamic modulus E' did not increase after prolonged treatment times in benzoic acid (Figs. 9 and 11), and T_g has not increased. Therefore, the interaction of benzoic acid solution with these heat-set fibers

TABLE II
The Effect of Benzoic Acid Treatment upon E''_{max}

Sample draw ratio	Time of treatment (h)	E''_{max} (dyn/cm^2)	T_g (°C)
2x	0	3.9 × 10^9	120
	2	2.20 × 10^9	85
	7	1.50 × 10^9	100
	7 + 1 h (b.w.)[a]		
4x	0	5.2 × 0^9	120
	2	4.01 × 10^9	100
	22	4.38 × 10^9	100
6x	0	5.6 × 10^9	135
	2	5.22 × 10^9	120
	24	4.52 × 10^9	120
	24+1 h (b.w.)[a]	4.07 × 10^9	125

[a] Samples which subsequent boiling water treatment were applied.

was not strong enough to promote large changes in their structure. The decrease in the E''_{max} value seems to be due to the benzoic acid plasticizing effect only.

The existence of voids in these fibers after benzoic acid treatment is revealed in the SAXS pictures (Figs. 13–15). The swelling effect, especially in the case of the 2x draw ratio fiber, caused a considerable amount of voids formation; the voids are responsible for the diffuse patterns obtained. The collapse of voids after subsequent boiling water treatment is shown in Figures 13(d), 14(c), and 15(c), where a less diffuse pattern and a decrease in intensity is observed. Table III gives the diffusion coefficients (D) calculated for the samples undergoing desorption in the migration experiment. The calculation of the diffusion coefficients is described in detail in Part II of this series, concerning the mathematical model.

As expected, the diffusion coefficients decrease as the fiber draw ratio increases. Also, Table III shows that the presence of benzoic acid in the medium is essential to improve the dye desorption process.

The samples which were given pretreatment in benzoic acid before undergoing the desorption process in a medium free of benzoic acid, presented diffusion coefficients very close to the diffusion coefficients of the samples which had experienced no benzoic acid treatments at all.

This result is in agreement with the structural data already discussed. In the case of the samples that had no prior carrier treatment, the dye molecules have to find their way out of the fiber substrate primarily through voids, microvoids, and cracks, since the T_g's of these fibers are above the working temperatue (100°C).

The benzoic acid pretreatment plasticizes these fibers, but, since the medium of transport is free of carrier, the dye desorption will follow the same process as described in the prior case. It has been demonstrated that benzoic acid is removed from a fiber substrate undergoing boiling water treatment. The same behavior will occur for these samples, since the medium is free of carrier. The benzoic acid will, however, be desorbed at a faster rate than the dye molecules, causing a deplasticizing effect, i.e., increase in T_g and
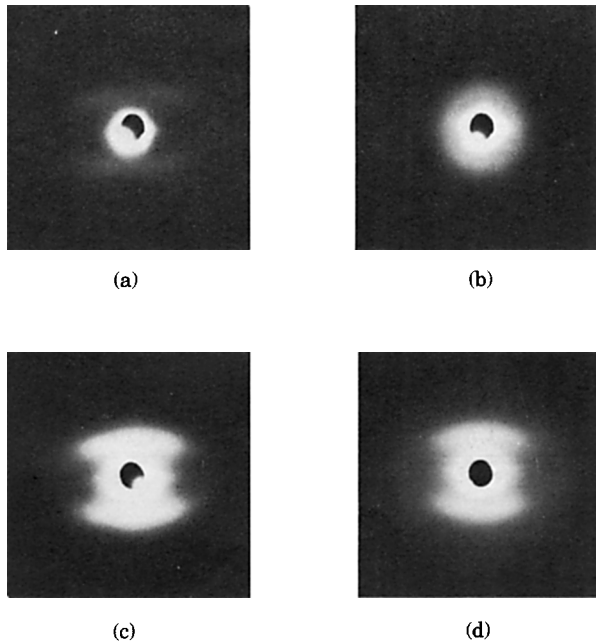
Fig. 13. SAXS for the fiber drawn $2x$: (a) control; (b) carrier concn 13 g/L, 2 h; (c) carrier concn 13 g/L, 7 h; (d) carrier concn 13 g/L, 7 h + 1 h boiling.

decrease in chain flexibility. Also, there will be collapsing of voids that had been formed by the benzoic acid treatment, closing up the originally more open structure. Consequently, the dye desorption rate will decrease, and the dye molecules will have to find their way out of the fiber substrate as if no prior plasticization had occurred.

The presence of carrier in the medium will maintain the equilibrium of the system, i.e., benzoic acid molecules will not be desorbing. In this situation the plasticizing effects of the carrier will be the dominant factor in the dye desorption.

The relationship between dye diffusion coefficients and loss modulus E'' is well known[13,16] when chain flexibility is involved or when the working temperature is above T_g. The diffusivity depends on the difference between the dyeing temperature and the glass transition temperature (T_g). For a
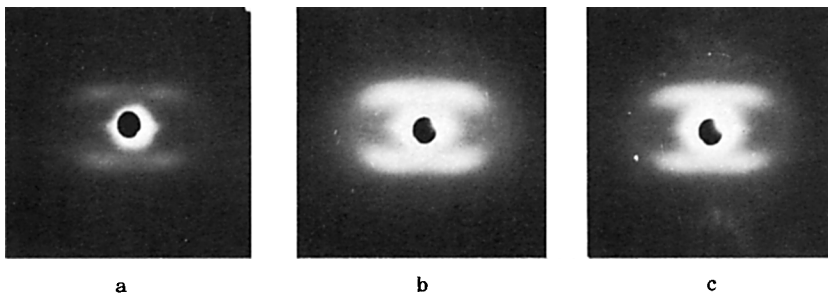

Fig. 14. SAXS for the fiber drawn $4x$: (a) control; (b) carrier concn 35 g/L, 2 h; (c) carrier concn 35 g/L, 2 h + 1 h boiling.
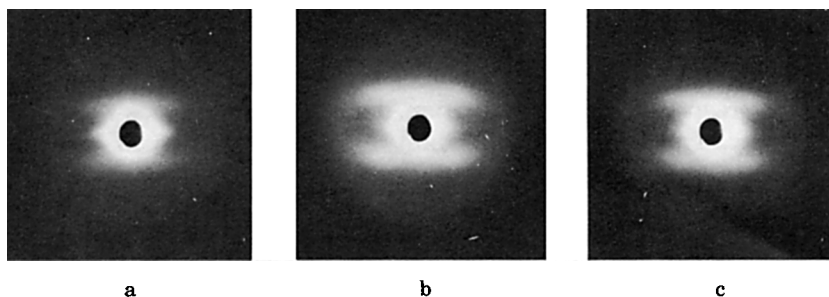
a   b   c

Fig. 15.   SAXS for the fiber drawn 6x: (a) control; (b) carrier concn 13 g/L, 22 h; (c) carrier concn 13 g/L, 22 h + 1 h boiling.

fixed dyeing temperature, D is dependent on the structure of the fiber, since T_g depends on orientation, crystallinity, and other structural parameters. Usually an increase in orientation or crystallinity will increase T_g. But, as already demonstrated, T_g may be decreased by the use of carriers in the dye bath, and such a change can be considered equivalent to an increase in the dyeing temperature. Different concentrations of carrier will give different diffusivities since they will affect T_g in accordance with the concentration used. Obviously, T_g will not always decrease, since a carrier can promote structural changes such as an increase in crystallinity, as already demonstrated.

Table III shows that the diffusivity D was much higher when carrier was present in the dye bath. From the curves E'' vs. temperature it can be seen that, after the maximum, the curves fall quite steeply. This means that at higher temperatures, lower values of E'' are obtained and consequently a high value of D. Thus use of carrier in these experiments decreased T_g approximately 20°C for all samples. This fact would correspond to an increase of temperature of above 20°C in the experiment without carrier, i.e., a working temperature of 120°C. Checking the E'' values at this temperature in Figures 6, 8, and 10 it can be seen that these values correspond to the values close to the E'' for the 2x and 4x samples. Comparing the E''_{max} values in Table II (at zero and 22 h of treatment in benzoic acid, respectively), it is observed that the values are very close to one another in the case of the 4x sample. In the case of the 6x sample, E''_{max} at 120°C (Fig. 10) is equal to 4.21 × 10⁹ dyn/cm², which can be considered equal to the value found after 24 h of treatment in 13 g/L of benzoic acid solution, or 4.25 × 10⁹ dyn/cm² (Fig. 11).

TABLE III
Diffusion Coefficients for PET Fibers from Desorption Data

Sample draw ratio	D (cm²/min)		
	No carrier[a1]	No carrier[b]	Carrier
2x	2.53×10^{-9}	2.54×10^{-9}	3.60×10^{-8}
4x	2.52×10^{-10}	2.80×10^{-10}	5.55×10^{-9}
6x	1.18×10^{-10}	1.16×10^{-10}	1.33×10^{-9}

[a] Fiber and medium free of carrier.
[b] Medium free of carrier only.

The sample of lower draw ratio (2x) presented a much lower value of E''_{max} after treatment for 7 h in benzoic acid solution, when compared with the E''_{max} at zero concentration. The reason for this discrepancy is the swelling and corresponding voids formation. The presence of voids will decrease E''_{max} steeply. The increase in dyeability of dye desorption in this fiber is attributed to not only chain flexibility but also to the presence of a substantial amount of voids.

But, for all cases it is possible to affirm that in presence of carrier, the chain segments achieved more freedom of movement, allowing easier penetration of the dye molecules.

The above discussion explains the relationship between the leveling process and the fiber structure. It is evident that decreasing the T_g and consequently increasing the chain mobility is a general requirement for improvement in either dye desorption or absorption, and this mobility has been the major factor in the different curves obtained, i.e., Figures 1–3. However, other factors, such as the presence of voids in the fiber substrate, may be important after long times of heating. Voids may collapse and consequently make the dye migration process difficult. This effect was especially important in the case where carrier was not present in the medium of transport. For that experiment the chain flexibility was very poor, and the migration process depended mainly on presence of voids and microvoids in the fiber substrate. Consequently, leveling cannot be easily obtained at temperatures below the T_g of fibers.

The presence of carrier in the medium will give increased chain flexibility, but this increased flexibility can also, after long times of heating, result in some degree of structural modifications, such as an increase of crystallinity. These changes make the levelling process slower. Obviously the degree of structural modification will depend on the structural stability of the fibers at the constant dyeing temperature.

Also, Figures 1 and 2 reveal that the desorption curves representing the fibers of higher draw ratios have a common point at adsorption time of about 24 h (1440 min). The crossover results from the combination of the higher initial dye concentration of the lower draw ration samples, because of lower crystallinity and orientation, and their higher desorption rate, because of higher chain mobility. Although the dry T_g's of these fibers are above the working temperature of 100°C, somewhat lower values can be expected when the samples are immersed in water (e.g., Fig. 8). The T_g's will be somewhat closer to the working temperature. Therefore, although still working below T_g, the breadth of the transition permits a certain degree of chain flexibility; this degree of chain flexibility will depend upon the draw ratio of the fiber.

In the case where the migration experiment was carried out in presence of carrier (Fig. 3), it can be observed that all desorption cruves meet at a common point at the same desorption time of the experiments mentioned above (24 h).

Finally, it can be observed in Figures 1–3 that the amount of dye taken up by the originally undyed fibers is very small when compared with the amount of dye desorbed by the originally dyed fibers. This is consistent with the observation that the concentration of dye in the water, although

small, increased steadily. This is expected since we are working with a well-stirred, finite dyebath system where the concentration of dye involved is very small, and the ratio of water to fibers is very large. Therefore, although the concentration of dye in the water is homogeneous at all times, the amount of dye surrounding the originally undyed fiber will be very small.

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