

# Structure of Heat-Treated Nylon 6 Fibers.

## II. Structural Stability and Dye Leveling

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### SYNOPSIS

Nylon 6 fibers were submitted to three types of heat treatments at different temperatures and times in order to find the best conditions to achieve structural stability. The boiling water treatment proved to be more effective in promoting profound structural modifications than the other treatments (dry treatment and the dry treatment followed by a 5-h boiling water heat setting). Also, the fibers reached their maximum structural transformations after 1 h of treatment. Thus, a 5-h boiling water treatment was chosen to heat-set the fibers. Then, the heat-set fibers were submitted to dyeing and migration experiments with different disperse dyes. The obtained results demonstrate that the discontinuities observed in the curves of migration factor versus square root of time might be related to the mechanism of the migration experiments. The different solubilities of the disperse dyes in water helped the understanding of this mechanism. Also, this study with nylon 6 fibers reveal that the proposed model can be used for leveling time prediction, and the discontinuities mentioned above can for practical purposes be neglected. © 1992 John Wiley & Sons, Inc.

### INTRODUCTION

Leveling has been defined as the ability of a dye-polymer system to even out concentration differences, which frequently appear during a dyeing process.<sup>1</sup> This subject has been recently treated in terms of the fiber morphology. It has been shown in studies of dye leveling in poly(ethylene terephthalate) (PET) fibers<sup>1</sup> that the use of a carrier such as benzoic acid decreases  $T_g$  and improves consequent dyeability and leveling processes. But, the presence of carrier in the medium may also, after long times of heating, promote some degree of structural modifications such as an increase of crystallinity, and the consequence of these structural modifications is a slower leveling process.

It was indicated also<sup>2</sup> in the curves of migration factor versus square root of time that the steep deviations from the curves constructed through the mathematical model proposed for predicting leveling times were indicative of progressive structural mod-

ifications associated with the plasticizing effect of benzoic acid in the PET fibers under long heating times.

Thus, in order to better understand this phenomenon a fiber was chosen such that the dyeing and leveling experiments would be carried out above  $T_g$  of the fibers but in the absence of carrier. So, in the present work nylon 6 fibers were chosen in order to satisfy these conditions, i.e., to obtain a lower  $T_g$  in the dyeing bath without the use of carrier. Also, the structural stability of these fibers has to be achieved by a heat treatment before submitting them to any dyeing or leveling process. Therefore, the study of structural stability of nylon 6 fibers is of fundamental importance. Once the conditions to achieve structural stability have been found, the leveling process in terms of the mathematical model recently proposed<sup>2</sup> for the leveling time prediction will be discussed.

### EXPERIMENTAL

#### Sample Preparation

The nylon 6 fibers from De Millus S/A (Rio de Janeiro, Brazil) of different draw ratios (3.2x, 3.7x)

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were submitted to three heat treatments under slack conditions. The first one ( $T_1$ ) was realized in an evacuated oven with inert atmosphere for 2 and 5 h at 150, 170, and 190°C. In a second heat treatment ( $T_2$ ), the samples of the first heat treatment were submitted to an additional 5-h treatment in boiling water. The third one ( $T_3$ ), was a boiling water treatment at times of 1, 5, and 15 h.

For the first heat treatment there was an additional temperature of treatment at 100°C for 1, 5, and 15 h in order to permit a better comparison with the samples of the third treatment.

### Structural Measurements

The heat-treated fibers were submitted to the same structural analysis of the Part I of these series of papers.

### Dyeing

Dyeings were carried out in the absence of carrier to equilibrium in an infinite dyebath within a controlled temperature and shaking bath. The shaking was in the horizontal direction (140 cycles/min)

and the dyeing temperature was  $90 \pm 1^\circ\text{C}$ . The dye solution was prepared by adding 4.5 g of dye to 3 L of distilled water. Fiber samples weighing about 0.030 g were placed in 100-mL flask containing 60 mL of dye solution.

Three different pure disperse dyes from Ciba Geigy S/A were used: C.I. disperse yellow 3, C.I. disperse red 1, and C.I. disperse blue 14. Dye concentrations on the fibers were determined by extraction with DMF at 140°C. Three extractions of 10 min each were necessary to completely remove the dyes from the fibers. The optical density (OD) of the extract was measured by UV spectrophotometry, and the percent of the dye on the fiber was calculated by the following expression:

$$\% \text{ dye} = \frac{\text{OD} \times \text{extracted vol.} \times \text{dilution factor} \times 100}{\text{dye extinction coef.} \times \text{dye sample weight} \times 1000} \quad (1)$$

### Migration

The migration test consisted of exposing fibers, dyed to equilibrium, to an equal weight of similar undyed

**Table I** Effects of Heat Treatment on Analyzed Structural Parameters<sup>a</sup>

Heat Treatment	$T$ (°C)	Time (h)	%Cryst.	%CPI	%S	LO	LP (Å)	$\Delta n$ ( $\times 10^{-3}$ )
Control <sup>b</sup>	RT	—	32.9	68.3	—	0.30	72.1	50.59
$T_1^c$	100	1	35.0	72.9	5.4	0.35	72.5	49.60
	100	5	34.3	72.7	5.7	0.33	72.5	50.85
	100	15	34.3	72.0	5.3	0.35	72.5	49.70
	150	2	40.0	73.9	7.0	0.42	74.0	51.90
	150	5	40.0	74.3	7.0	0.40	75.0	52.43
	170	2	41.4	77.6	7.9	0.46	78.0	52.32
	170	5	41.4	81.0	7.1	0.45	79.0	52.74
	190	2	42.1	84.3	8.9	0.59	83.6	54.33
	190	5	42.1	84.3	8.6	0.59	82.9	54.84
	$T_2^d$	150	2	42.9	84.3	1.3	0.53	80.4
150		5	42.9	84.5	1.6	0.53	79.6	52.88
170		2	43.6	80.3	0.6	0.52	79.6	52.51
170		5	43.6	81.8	0.6	0.50	78.0	53.33
190		2	42.9	83.5	0.4	0.57	83.6	55.49
190		5	43.6	85.6	0.1	0.56	83.0	55.49
$T_3^e$	98	1	42.1	89.0	13.4	0.64	83.7	51.45
	98	5	42.9	90.8	13.3	0.64	84.9	51.19
	98	15	42.1	92.8	13.3	0.64	85.5	51.33

<sup>a</sup> Crystallinity percentage, crystalline perfection index (CPI), shrinkage (S), lateral order (LO), long period (LP), and birefringence ( $\Delta n$ ) for the 3.2x fiber.

<sup>b</sup> Control sample: without heat treatment.

<sup>c</sup> Dry heat treatment in an inert atmosphere of  $\text{N}_2$ .

<sup>d</sup> Treatment  $T_1$  followed by a 5-h boiling water treatment.

<sup>e</sup> Boiling water treatment.

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 (same dye concentration).

The fibers (dyes and undyed) were placed in a 100-mL cylindrical bottle containing 50 mL of distilled water. A stainless steel net of very fine mesh was used to separate the dyed fibers from the undyed ones.

The firmly closed bottles were placed in a controlled shaking and temperature oil bath. The temperature and shaking conditions were the same as in the dyeing procedure.

The migration factor  $m$  is defined by the following expression:

$$m = \frac{\text{amount of dye on originally undyed material}}{\text{amount of dye remaining on originally dyed material}} \quad (2)$$

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

The migration factor  $m$  may be theoretically calculated from the mathematical model proposed by

Simal<sup>2</sup> and then compared to the experimental data obtained.

## RESULTS AND DISCUSSION

### Conditions for Structural Stability of Nylon 6 Fibers

Tables I and II show the effects of the three heat treatments on the morphological parameters analyzed for the 3.2x and 3.7x fibers, respectively.

It was shown in the Part I of these series of papers that the effects of the heat treatment  $T_1$  on the analyzed parameters were time independent for both fibers. This same result is demonstrated in Tables I and II for the heat treatments  $T_2$  and  $T_3$ . The very small differences observed are within the expected experimental errors.

Thus, it is possible to affirm that these fibers have reached their maximum structural transformations for all three applied heat treatments after 1 h.

In order to find the best type of heat treatment that would permit the fibers to achieve their maximum morphological transformations, to assure sta-

**Table II** Effects of Heat Treatment on Analyzed Structural Parameters<sup>a</sup>

Heat Treatment	$T$ (°C)	Time (h)	%Cryst.	%CPI	%S	LO	LP (Å)	$\Delta n$ ( $\times 10^{-3}$ )
Control <sup>b</sup>	RT	—	34.3	69.0	—	0.36	72.1	51.11
$T_1^c$	100	1	35.7	75.8	5.5	0.42	72.5	51.14
	100	5	35.7	77.2	6.6	0.42	72.5	50.82
	100	15	35.7	75.9	6.1	0.42	72.5	51.51
	150	2	38.6	74.2	6.8	0.46	76.4	52.58
	150	5	37.9	76.6	7.4	0.45	75.4	53.15
	170	2	40.0	80.8	8.3	0.53	79.1	53.30
	170	5	40.0	80.7	8.0	0.52	79.0	53.67
	190	2	40.7	86.0	10.1	0.63	85.5	55.16
	190	5	40.7	86.2	9.3	0.64	85.5	55.35
	$T_2^d$	150	2	42.1	87.9	1.7	0.62	82.4
150		5	42.4	86.0	1.7	0.62	81.8	53.81
170		2	41.4	83.1	0.7	0.57	80.7	53.39
170		5	42.1	83.5	0.5	0.57	80.7	53.41
190		2	42.1	87.6	0.6	0.62	84.8	55.31
190		5	41.4	88.4	0.6	0.63	85.9	55.25
$T_3^e$	98	1	41.4	90.2	13.5	0.67	83.6	52.63
	98	5	40.7	92.2	13.3	0.67	84.9	52.18
	98	15	41.4	90.9	13.5	0.67	84.2	52.30

<sup>a</sup> Crystallinity percentage, crystalline perfection index (CPI), shrinkage ( $S$ ), lateral order (LO), long period (LP), and birefringence ( $\Delta n$ ) for the 3.7x fiber.

<sup>b</sup> Control sample: without heat treatment.

<sup>c</sup> Dry heat treatment in an inert atmosphere of  $N_2$ .

<sup>d</sup> Treatment  $T_1$  followed by a 5-h boiling water treatment.

<sup>e</sup> Boiling water treatment.

bilization during subsequent dyeing and leveling experiments, heat treatment  $T_1$  will first be compared to treatment  $T_3$ , second to treatment  $T_2$ , and finally treatment  $T_2$  will be compared to treatment  $T_3$ .

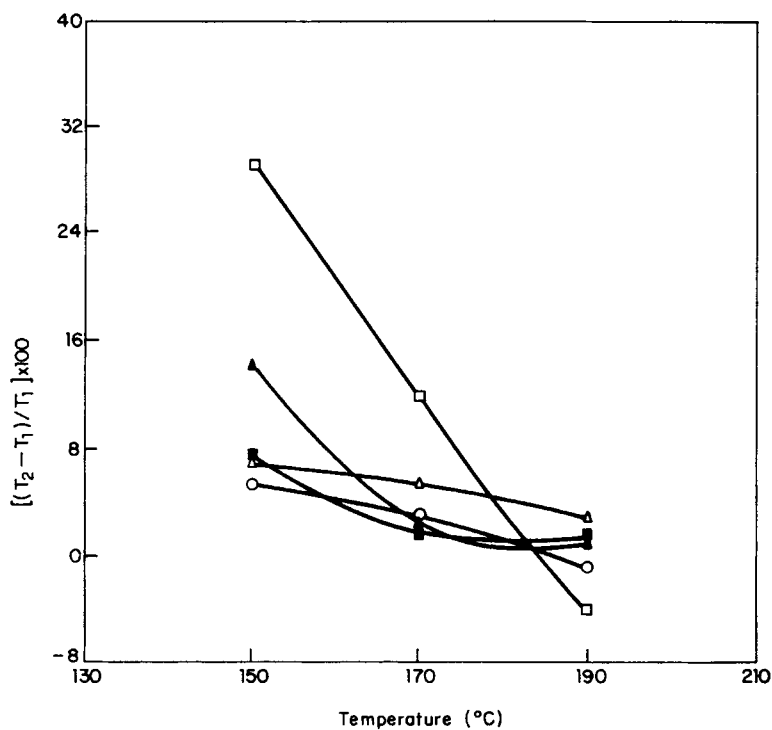
The boiling water treatment ( $T_3$ ) when compared to the dry treatment ( $T_1$ ) at  $100^\circ\text{C}$  proved to be more effective in promoting morphological transformations. This result demonstrates the strong plasticization effect of the water molecules on the fibers. This treatment ( $T_3$ ) demonstrated to be more effective, even when compared to the dry treatment ( $T_1$ ) at higher temperatures ( $170$  and  $190^\circ\text{C}$ ).

The  $T_g$  of the nylon 6 fibers in the presence of water is expected to be reduced to near  $10^\circ\text{C}$ ,<sup>3-5</sup> and this fact can by itself explain the reason for such intense morphological transformations. The plasticization effect of the water increases the chain flexibility promoting more intense relaxation of the existing internal tensions, resulting in a higher percentage of shrinkage (around 30%). The lower values of birefringence observed for the boiling-water-treated ( $T_3$ ) fibers must be related to the higher shrinkage values obtained in this condition of treatment. Also, this is an indication that the crystals in boiling-water-treated fibers are more desoriented than the crystals of the dry-treated fibers.

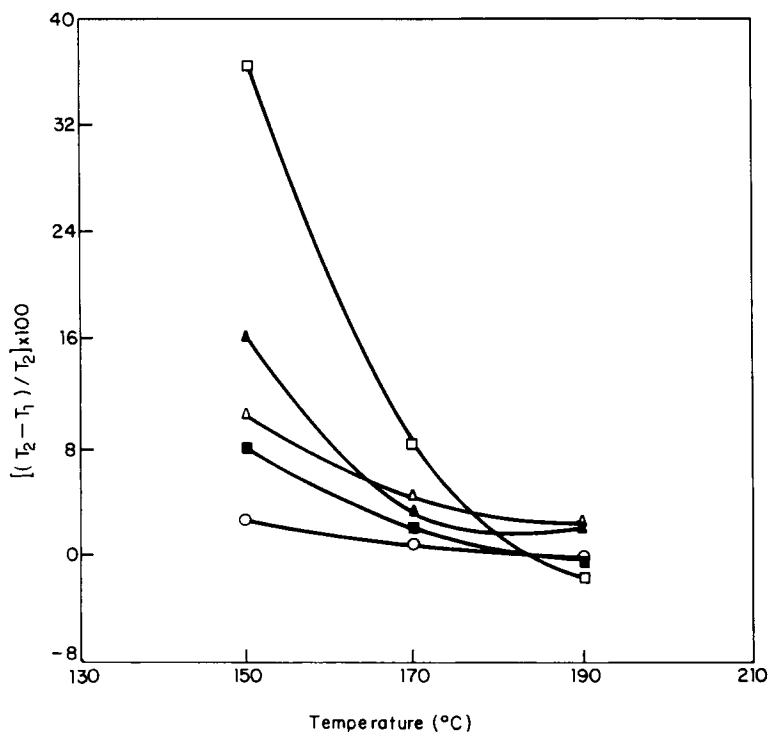
Figures 1 and 2 compare the effects of treatment  $T_1$  and  $T_2$  in the studied parameters for both fibers. These figures reflect the amount of variation over the studied parameters when the dry heat-treated fibers are submitted to a subsequent 5-h boiling water treatment ( $T_2$ ).

The figures show that as the temperature of the treatments increases, the differences between the analyzed parameters decreases. At  $190^\circ\text{C}$  these differences are close to 0%. These results are an indication that as the temperature of the dry treatment ( $T_1$ ) increases, getting closer to the  $T_m$  of the fibers, the level of structural stability also increases. This fact will make additional structural modifications difficult due to the boiling water action in the fibers that were pretreated in the dry condition at higher temperatures. Thus, it seems that these fibers will be reaching their structural stabilization when submitted to dry treatments at temperatures near to their  $T_m$ . Some authors<sup>6</sup> have suggested that dry treatment on nylon 6 fibers would promote formation of stable additional amide-amide bonds, allowing a major proximity among chains.

Finally, when the heat treatment ( $T_2$ ) is compared to the boiling water treatment ( $T_3$ ) for both fibers, it is possible to observe the same behavior



**Figure 1** Percent of variation between the parameter values obtained for the 3.2x fiber when submitted to the heat treatments  $T_1$  and  $T_2$  vs. temperature: (□) lateral order, (▲) CPI, (△) crystallinity, (■) long period, (○) birefringence.



**Figure 2** Percent of variation between the parameters values obtained for the 3.7x fiber when submitted to the heat treatments  $T_1$  and  $T_2$  vs. temperature: (□) lateral order, (▲) CPI, (△) crystallinity, (■) long period, (○) birefringence.

already discussed, i.e., when heat treatment  $T_1$  was compared to heat treatment  $T_3$ . For all analyzed parameters the boiling water treatment ( $T_3$ ) was more severe, i.e., this treatment is capable of promoting in the analyzed fibers more profound structural modifications than treatments  $T_1$  and  $T_2$ , even when these two treatments were realized at higher temperatures. Therefore, the boiling water treatment seems to be the best type of treatment to heat-set the fibers.

Also, the subsequent dyeing and migration experiments would be realized at less severe conditions, i.e., in a water bath at 90°C for times not greater than 10 h.

For convenience, the time of treatment in boiling water in order to heat-set the fibers was chosen to be 5 h, although the structural stabilization was reached after 1 h of boiling water exposition, as discussed before.

Also, for the following experiments the 3.7x fiber with a higher draw ratio was chosen, which has been proven to have a more stable structure as discussed on Part I of this series of papers (the calculated activation energy for this fiber to attain an increase of crystallinity was about 86% higher than the calculated value for the 3.2x fiber).

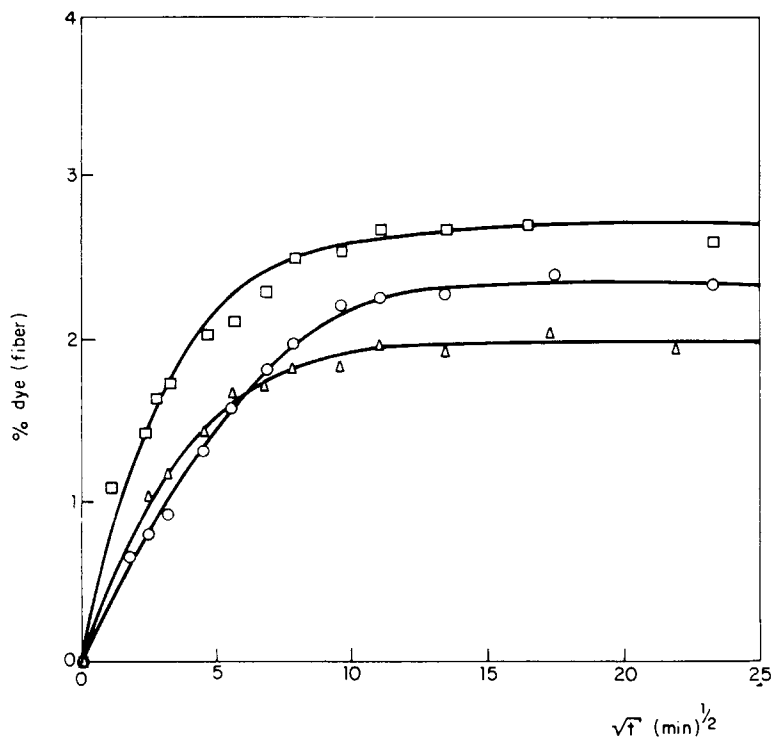
### Mechanism of the Migration Experiment

As described in the literature,<sup>2</sup> to apply the mathematical model proposed for leveling time prediction, it is first necessary to dye the fiber to the equilibrium in an infinite dyebath condition. The results obtained for the 3.7x fiber with the three selected disperse dyes are shown in Figure 3.

The calculated diffusivities through the Hill's equation<sup>7</sup> for the studied disperse dyes are shown on Table III.

Figure 4 shows the results for the migration test applied for the 3.7x fiber with the analyzed disperse dyes as described by Simal and Bell<sup>2</sup> with the descendent curves representing the dye desorption and the ascendent curves the dye absorption by the blank fibers.

The experimental migration factor  $m$  can be calculated from the data of Figure 4 through Eq. (2), and the theoretical calculations were made as described by Simal and Bell.<sup>1,2</sup> The experimental and theoretical results are compared in Figures 5–7 for the analyzed disperse dyes. These figures show good agreement between experimental and calculated data for times up to 64, 61, and 100 min for the disperse yellow 3, blue 14, and red 1, respectively.



**Figure 3** Dye absorption vs.  $(\text{time})^{1/2}$  for the 3.7x fiber from infinite dye bath: ( $\square$ ) disperse yellow 3, ( $\circ$ ) disperse red 1, ( $\triangle$ ) disperse blue 14.

After these times, the experimental data show a deviation from the normal tendency of the experimental curve.

A similar behavior has been described for the PET fiber, carrier, and disperse dye system.<sup>2</sup> It has been suggested for this system that the linearity of this deviation line could be an indication of progressive structural modifications associated with the plasticizing effect of the carrier (benzoic acid) in these fibers under long heating times of the experiment. For the 6x fiber with a higher structural stability, this discontinuity had occurred only after 50 h of experiment.

In the present work, it has been shown that the nylon 6 fibers have reached a stabilized structure

after 1 h of heat setting for all the analyzed heat treatments, where the boiling water treatment demonstrated to be the most effective in order to promote accentuated morphological transformations.

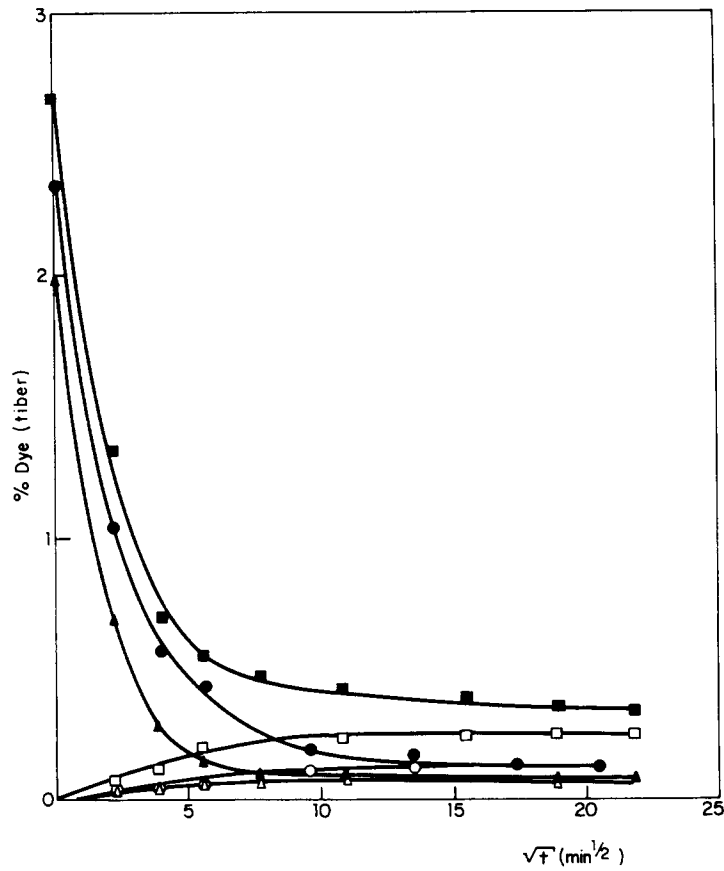
Since the dyeing and migration experiments would be realized at 90°C, and therefore below the heat setting temperature of 98°C (boiling water temperature), the possibility of occurrence of further morphological modifications during the mentioned experiments is expected to be very small or null.

Thus, for the 3.7x nylon 6 fibers, the observed discontinuity observed in the experimental curves of  $m \times \sqrt{t}$  may not be related to morphological transformations. The curves of the migration experiments (Fig. 4) reveal that when the equilibrium

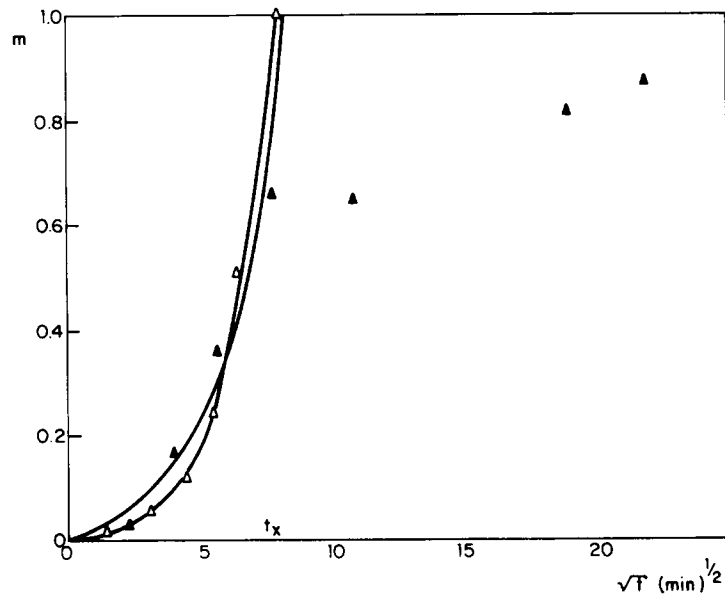
**Table III** Calculated Diffusivities ( $D_1$ ) from Hill's Equation for the 3.7x Fiber in an Infinite Dye bath Condition

Disperse Dye	$D \times 10^6$ (cm/min)	Dye Molecular Weight (g/mol)	% $M_\infty$ <sup>a</sup>	Time to Reach the Equilibrium (h)
Red 1	2.67	314.35	2.33	2.3
Yellow 3	7.97	289.31	2.68	1.35
Blue 14	5.63	266.70	1.98	1.35

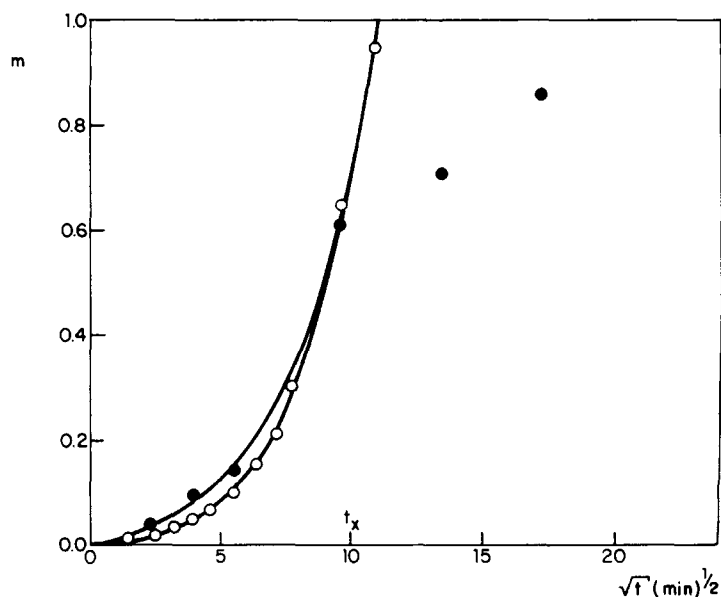
<sup>a</sup> Amount of dye at infinite time.



**Figure 4** Percent of dye on fiber vs.  $(\text{time})^{1/2}$  for the migration experiment (3.7x): Desorption process: (■), (●), (▲) disperse yellow 3, disperse red 1, and blue 14. Absorption process: (□), (○), (△) disperse yellow 3, disperse red 1, and blue 14.



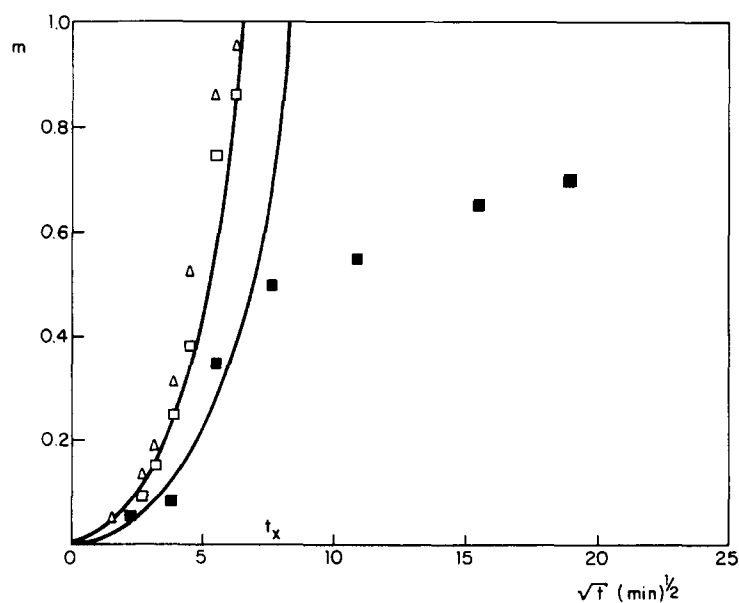
**Figure 5** Migration factor vs.  $(\text{time})^{1/2}$  for the 3.7x fiber with disperse blue 14: (▲) experimental, (△) model.



**Figure 6** Migration factor vs.  $(\text{time})^{1/2}$  for the 3.7x fiber with disperse red 1: (●) experimental, (○) model.

time ( $t_x$ ) has been reached by the desorption and absorption processes, the amount of dye in the originally dyed and blank fibers are not the same, although very close to each other. Also, as the originally blank fibers stops the dye absorption, the originally dyed fiber is still capable of releasing very small amounts of dye. This behavior was observed for all the studied dyes.

It is interesting to note that the points where the discontinuities begin are very close to the equilibrium times ( $t_x$ ) mentioned above. So, the calculations of the migration factor  $m$  by Eq. (2) will become, after this point ( $t_x$ ), a division of a practically constant number (the amount of the dye in the originally blank fiber) by another number that is still decreasing very slowly (due to very small amounts



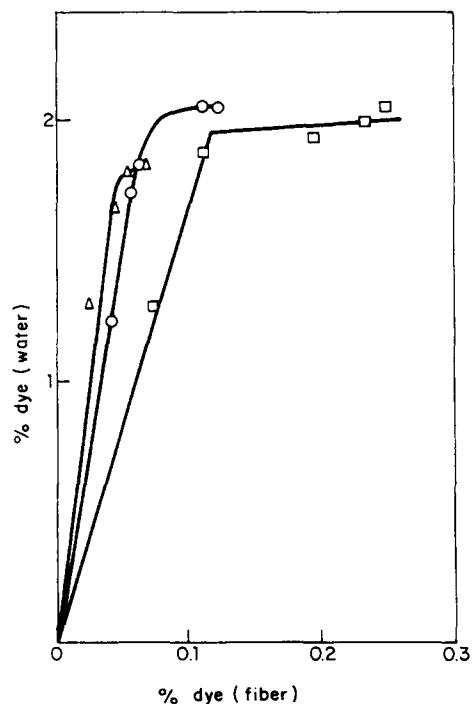
**Figure 7** Migration factor vs.  $(\text{time})^{1/2}$  for the 3.7x fiber with disperse yellow 3: (■) experimental, (□, △) model.



of dye desorption by the originally dyed fiber). It seems that at this point ( $t_x$ ), the iterative process of dye desorption and absorption by the fibers is ceasing, and for practical purposes it is possible to affirm that the equilibrium being reached for both fibers (blank and dyed) involved at this point of the migration experiment. In this experiment the originally blank fiber is absorbing the dye that is being released by an originally dyed fiber through a bath of a constant volume of distilled water.

Figure 8 shows the dye partition between water and the absorbing fiber at different times of the experiment for the three dispersed dyes, which present different solubilities in water (see Table IV).

The partition coefficients are linear for all the analyzed dyes up to the point where the equilibrium is being reached. The linearity regions observed in Figure 8 mean that as the dye is being released to the water the originally blank fiber is absorbing a proportional amount of dye present in the water, and the amount of dye absorbed by the fiber depends on the dye solubility in water. Table IV shows that the percentage of dye in the fiber at equilibrium increases as the dye solubility in water increases. After the equilibrium point the originally blank fiber will be able to absorb dye from its surface only, leaving



**Figure 8** Percent of dye in the water adsorbed by the originally dyed fiber vs. percent of dye in the originally undyed fiber during the migration experiment: ( $\Delta$ ) disperse blue 14, ( $\circ$ ) disperse red 1, ( $\square$ ) disperse yellow 3.

**Table IV** Solubilities of Studied Disperse Dyes in Water

Disperse Dye	Solubility in Water at 90°C (mg) <sup>a</sup>	Dye Percentage at Equilibrium in the Migration Expt.	
		Water	Fiber <sup>b</sup>
Red 1	10.6	2.04	0.120
Yellow 3	31.6	1.90	0.220
Blue 14	4.8	1.81	0.066

<sup>a</sup> From Ref. 8.

<sup>b</sup> The absorbing fiber.

the amount of dye in water practically constant. The very small increases of dye in water observed after this point will be governed by the dye release by the originally dyed fiber.

Therefore, the observed discontinuities of the experimental curves in Figures 5–7 for the nylon 6 fibers seem to be more related to the mechanism of the migration experiments than to the morphological modifications as indicated for the PET-carrier-disperse dye system. However, it is not possible to discard from these studies with nylon 6 the possibility of morphological modifications due to carrier action during long times of experiment with the PET fibers. In the PET case, the observed discontinuity of the experimental curves might be related to the mechanism of the migration experiment as well as to the morphological modifications due to carrier action.

### Leveling Time Prediction

Figures 5–7 of  $m \times \sqrt{t}$  showed the good agreement between the theoretical and experimental results. Also, it was possible to observe that the theoretical curves did not show the discontinuities presented by the experimental curve. Thus, the mathematical

**Table V** Leveling Times

Disperse Dye	Leveling Times (min)		
	Model <sup>a</sup>	$t$ Expt.	Expt. <sup>b</sup>
Red 1	120	100	120
Yellow 3	44	64	67
Blue 14	64	61	64

<sup>a</sup> Calculated from the mathematical model.<sup>2</sup>

<sup>b</sup> From the extrapolation of the experimental curve to  $m = 1$ .

**Table VI Diffusivities Calculated from Simal Equation<sup>9, a</sup>**

Disperse Dyes	$D$ (cm <sup>2</sup> /min)
Red 1	$2.67 \times 10^{-8}$
Yellow 3	$4.60 \times 10^{-8}$
Blue 14	$5.63 \times 10^{-8}$

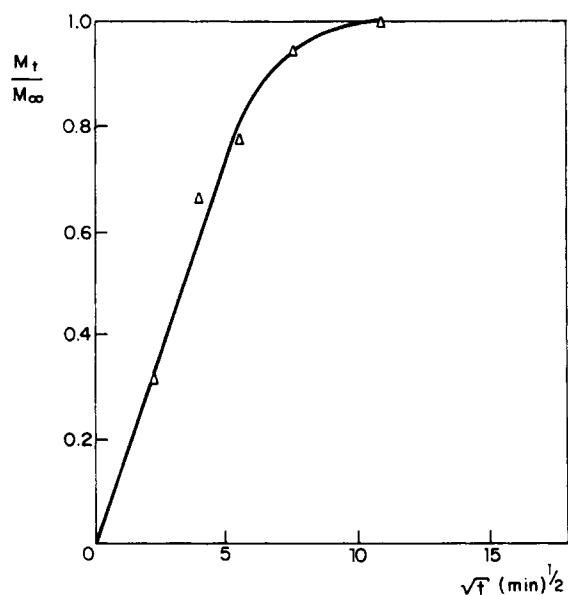
<sup>a</sup> For the absorption process in the migration experiment.

model<sup>2</sup> utilized for the calculation of the theoretical  $m$  values does not take into account the release of small amounts of dyes by the originally dyed fiber after point  $t_x$ , as explained earlier in this work, where the discontinuities begin.

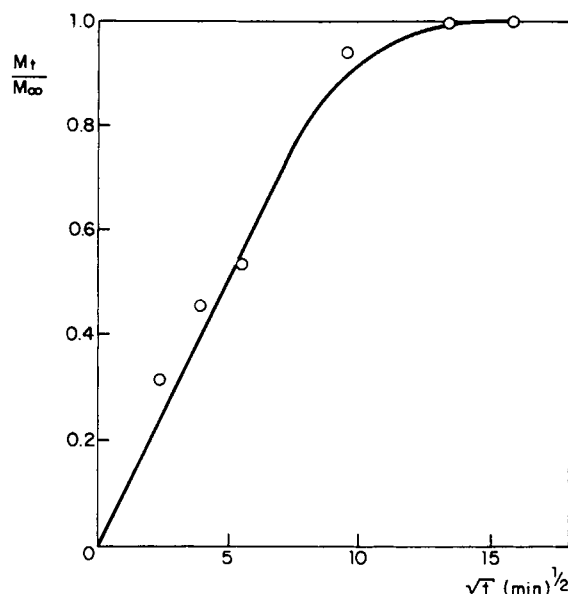
The theoretical curves show that the leveling will be reached for  $m = 1$ , i.e., when the amount of dye in the originally dyed fiber equals the amount of dye in the blank fiber. The theoretical values of  $m = 1$  will be reached at times very close to the times  $t_x$ , i.e., the times where the equilibrium has virtually been reached by both fibers (see Fig. 4).

The theoretical leveling times, the experimental values of  $t_x$ , and the times resulted from the extrapolation of the experimental curves to  $m = 1$  are compared in Table V. The comparison shows that these values are very close to each other for the disperse dyes red 1 and blue 14.

The difference of around 30% observed for the disperse yellow 3, when the experimental values are

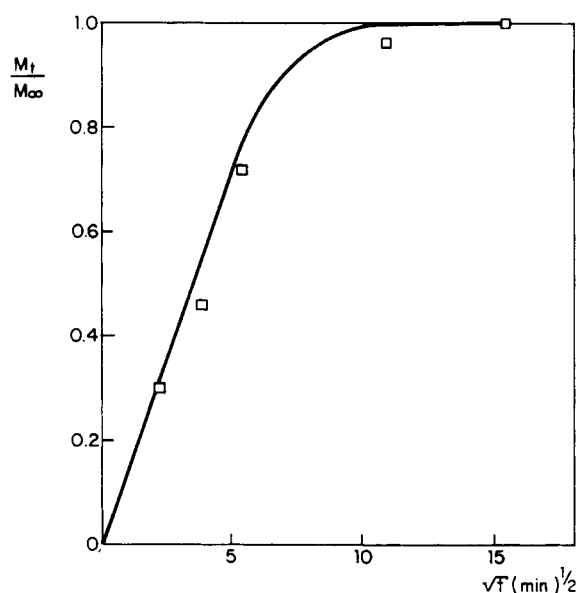


**Figure 9** Dye absorption vs. (time)<sup>1/2</sup> for the 3.7x fiber from a stirred solution of limited volume with disperse blue 14: ( $\Delta$ ) experimental, (-) model.



**Figure 10** Dye absorption vs. (time)<sup>1/2</sup> for the 3.7x fiber from a stirred solution of limited volume with disperse red 1: (O) experimental, (-) model.

compared to the theoretical values, is hard to explain. Probably this difference is associated to experimental errors due to dye extraction. The Simal<sup>9</sup> equation applied to obtain the absorption curve during the migration experiment for this dye promoted a better fitness between theoretical and experimental data for a smaller diffusion coefficient,



**Figure 11** Dye absorption vs. (time)<sup>1/2</sup> for the 3.7x fiber from a stirred solution of limited volume with disperse yellow 3: ( $\square$ ) experimental, (-) model.

i.e.,  $4.60 \times 10^{-8}$  cm<sup>2</sup>/min against  $7.97 \times 10^{-8}$  cm<sup>2</sup>/min as calculated from Hill's equation for an infinite dyebath (compare Tables III and VI).

Also, Tables III and VI show that the diffusion coefficients for the disperse dyes red 1 and blue 14 obtained from the Simal<sup>9</sup> equation for the absorption process during the migration experiment (finite dye bath) are exactly equal to those calculated from the Hill's equation for an infinite dyebath. Figures 9, 10, and 11 show the agreement between theoretical and experimental data for the fiber that is absorbing dye in the migration experiment.

Since disperse yellow 3 has a higher solubility in water than the others dyes, it would expect a higher diffusivity in the fiber, as obtained for the absorption case in the infinite dye bath experiment.

Finally, the results presented in this work reveal once more that the proposed model<sup>2</sup> can be used for the leveling time prediction and the discontinuities observed in the experimental curve of  $m \times \sqrt{t}$  can for practical purposes be neglected.

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