

Trial the Microscopic Images for Determination of Diffusion Behavior of Dyes in Fibrous Material

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ABSTRACT: A new technique is presented for determination of the diffusion behavior of dyes in fibrous materials. Polyamide 6.6 in filament form has been dyed with an acid dye in different temperatures and times. The microscopic images of the cross sections of dyed samples are captured and the RGB color images of the surfaces are converted to gray scale intensity data. Then, the variations of intensities within the fiber diameter, from the surface to the center of fiber, are analyzed. A linear relation is assumed between the concentration and the intensity for

each pixel. The concentration-distance curves are plotted and the pseudo-diffusion coefficient of dye is predicted by using the error function relation between the normalized intensity and diffusion coefficient. According to the results, the index is constant for the samples dyed in different times and changes significantly by temperature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1030–1036, 2009

Key words: diffusion; dyes/pigments; fiber; imaging; polyamides

INTRODUCTION

Dyeing is one of the most important finishing processes in the textile industry and having a successful dyeing need a good knowledge of textile chemistry and fiber science. Generally, four stages have been recognized in dyeing processes:

- i. Migration of dyes from the dye bath toward the surface of fiber,
- ii. Adsorption of dyes on the fiber,
- iii. Diffusion of dyes into the fiber, and
- iv. Fixation of diffused dyes inside the fiber.

The rate of dyeing is affected by the slowest stage, i.e., the diffusion rate of dye molecules inside the fiber.^{1,2}

The pore and the free-volume models have been suggested for analyzing of diffusion of dyes in fibers.^{1,2} The efforts have been made to explain the scope of each model. The pore theory is characterized with small activation energy. The amount of this energy maintain constant over a large range of temperature. In fact in such system, the dye molecules are absorbed by the fiber by means of pores filled by water and are fixed on the surface of the pores or absorbed by the macromolecular mass without interference of polymer chains in the diffu-

sion process. On the other hand, the free-volume model supposes that diffusion occurs due to the exchange of position of dye molecule with holes resulting from continues redistribution of free volume. It is assumed that the free volume is caused by the thermal fluctuations of the polymer chains. This model is supported by the very low diffusion rate of dyes in fibers below the glass-transition temperature of the fiber. The Williams, Landel, and Ferry (WLF) equation is more valid for the temperature dependence of such dyeing system in comparison to simple Arrhenius equation.^{1,2}

Different methods have been presented to investigate the diffusion behavior of dyes into the fibers. Using microdensitometric method,^{3,4} multilayer technique^{3,5–8} and laser scanning confocal microscope (LSCM) technique^{9–13} has been recommended for determination of the diffusion behavior of dyes. An index called the diffusion coefficient is normally used to express the rate of diffusion of dyes into fibrous materials. To determine the diffusion coefficient, the variation of dye concentrations against the distance from the surface of the fiber is usually plotted. Then, a suitable equation would be selected to interpret the experimental data. Thus, finding the plots, i.e., verifying the concentration of dye at a given position in the cross section of dyed fiber is the key point in the aforementioned methods.

The simplest practice for determination of diffusion coefficient is the multilayer technique.^{5–7} This technique suffers from serious drawbacks. The assembled film could not be considered as a homogeneous unit layer and the existence of air between

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noncontinuous layers makes the set unreliable and leads to some types of deviations. Besides, the thickness of film is divided into a limited number of layers, hence the concentration is limited to discrete distances.⁹ Because of these types of disadvantage, researchers have tried more reliable techniques to determine the concentration-distance profiles in the more practical conditions. Peter et al.⁴ used the microdensitometer technique for illustration of concentration profiles of the cross sections of dyed polymer films with different dyes. However, the technique needs the instrument which is too expensive and has not been widely welcomed. Recently, a technique based on laser has been used by several researchers to determine the concentration of dye inside the fibers and films.⁹⁻¹³ In this method, a cross section of dyed fiber was prepared and the laser scanning confocal microscope technique, abbreviated by LSCM, was implemented for determination of the concentration of dye in different points of cross section. Hence, the method yields the concentration-distance profile which can be used for later mathematical processing.¹⁰⁻¹³

By determination of dye concentration distance profile, the suitable equation could be implemented to determine the diffusion coefficient. Hill's equation for cylindrical materials (such as fibers) was widely employed¹⁰:

$$\frac{C_t}{C_0} = 1 - Ae^{-BK} - Ee^{-FK} - Ge^{-HK} \dots \quad (1)$$

where, A, B, E, F, G, H, \dots are numerical constants. $\frac{C_t}{C_0}$ is the ratio of dye concentration at the time t and in equilibrium, $K = Dt/r^2$, where D is the diffusion coefficient, t shows the dyeing time and r illustrates the radius of the fiber.

Alternatively, the error function, abbreviated by erf, has been suggested for determination of diffusion coefficient of films^{4,7,13}:

$$\frac{C_t}{C_0} = 1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (2)$$

where, x is the distance of the diffused dye into the layer from the surface. Equation (2) was also used in cylindrical materials, such as fibers, without serious problem.^{12,13}

In this study, a simple optical microscopic method is used to obtain the concentration-distance profiles. A common optical microscope device equipped with CCD still camera was implemented for capturing RGB color images from the cross sections of dyed fibers. By supposing linear responses of camera's CCD against the light intensity, the concentration-distance profiles of dyed fibers are estimated for different samples dyed in different dyeing conditions.

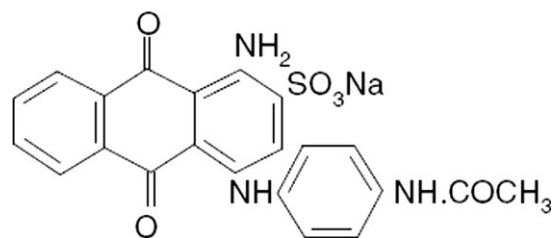


Figure 1 The chemical structure of C.I. Acid Blue 40.

EXPERIMENTS

Materials

Polyamide 66 in the form of yarns (tire cord) produced by a local supplier named Nakheh Zanjan was collected from the producer and used in this study. The fiber diameter was 24 μm . An anthraquinone acid dye (C. I. Acid Blue 40) named Tectilon Blue 4G from Ciba Specialty Chemicals was selected as the diffusant, i.e., the dye moving in the fibers by diffusion. The chemical structure of the applied dye is shown in Figure 1.

Dyeing procedure

Samples were scoured in warm water (50°C) for 10 min with a commercial nonionic detergent named Hostapal CV from Clariant, followed by washing in running water prior to dyeing. Dyeing procedure took place using simple laboratory equipment in a buffer of acetic acid and sodium acetate. Fibers were dyed with 0.5% (on the weight of fiber, owf) of Tectilon Blue 4G in 80°C at different durations, i.e., 30, 50, 70, and 120 min. In addition, to verify the effect of temperature on the diffusion behavior of the applied colorant, dyeings were also performed for 3 and 60 min in 100°C. To grant the semi-infinite dyeing baths, the liquor to goods ratio (L : G) was kept at 150 : 1. The dyed samples were rinsed with cold water and dried in ambient temperature.

Microscopic preparation

To prepare the samples for microscopic study, the dyed fibers were immersed in blocks which were filled with unsaturated polyester resin. The embedded fibers were cut by microtome to prepare suitable cross section samples for microscopic observation.

For capturing of images from the cross sections of fibers, an optical microscope manufactured by Reichert (Austria) was used. The instrument was equipped with a suitable still camera. The instrument was set at 63 \times objective magnification, numerical aperture (NA) equal to 0.8 and 12.5 eyepiece. To capture reproducible images and consistent data, the

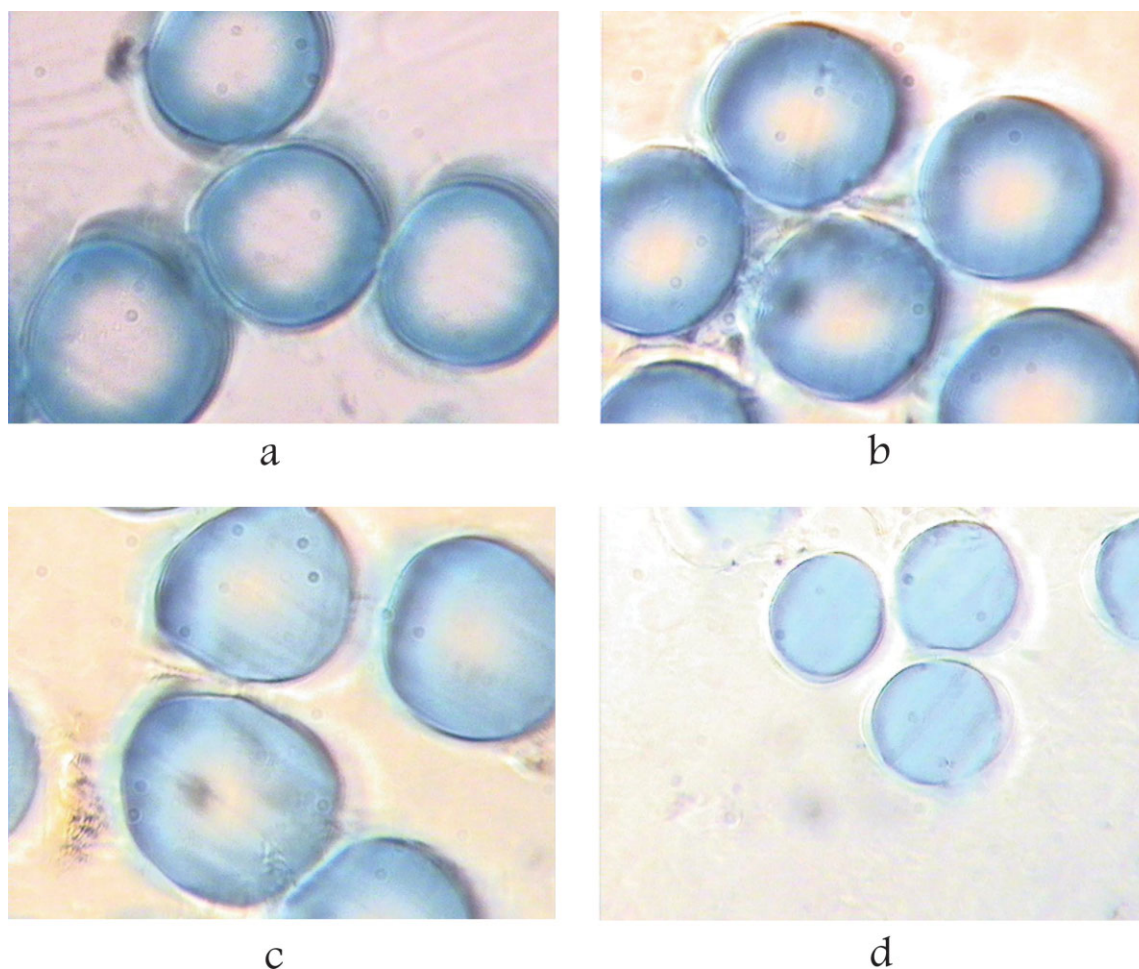


Figure 2 The cross section of dyed fibers (dyeings were carried out in 80°C at different dyeing times, (a) 30, (b) 50, (c) 70, and (d) 120 min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

microscope as well as the CCD camera were tuned and fixed during the microscopic sequences.

Image processing technique

Four images were taken from the cross sections of fibers dyed in particular dyeing conditions. Matlab¹⁴ from Mathworks was employed as programmable software to analyze the captured images. The procedure can be summarized as follows:

- i. Converting of color images to intensity ones,
- ii. Separating the images of cross section of fiber, appeared as circle in the images from the background,
- iii. Determination of the center of the extracted circle,
- iv. Formation of the concentric circles with specified radius around the predetermined center, and
- v. Calculation of the mean of intensity for each sector between the adjacent circles. These values were plotted against the distance to obtain the intensity-distance profile.

RESULTS AND DISCUSSION

The images of the cross sections of dyed fibers were used to analyze the diffusion behavior of applied dye in the given conditions. Figure 2 shows some selective images of the cross sections of dyed fibers in different dyeing durations.

The main subject of this study was obtaining the concentration-distance profiles from the captured images. Therefore, the RGB values of images were saved and processed for this goal. It was claimed that the intensity of each pixel is proportional to the emitted light from that pixel and could be related to the dye concentration.¹¹ Thus, as mentioned earlier, the colored images were firstly converted to the gray scale level images and it was assumed that the intensity of each pixel is a linear function of dye concentrations. A computer program was written to take out the circular cross section of the dyed fibers from the surrounding area in each image while, the centers of circles were determined by suitable program. In brief, the RGB values of selected parts of images (cross sections of dyed fibers) were

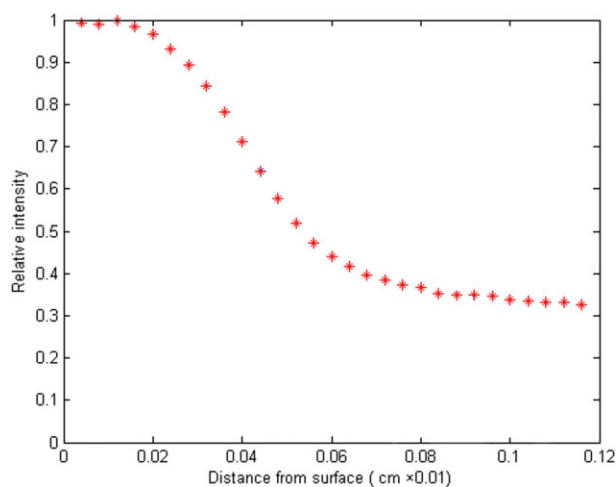


Figure 3 Intensity-distance profile of sample shown in Figure 2(a). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

converted to intensities data and the values of intensities were normalized. It was supposed that the intensity values are proportional to dye concentration in each pixel. Hence, the $\frac{I}{I_0} = \frac{C}{C_0}$ was considered as a key factor for determination of concentrations. Figure 3 shows an intensity-distance profile which was determined for image "a" showed in Figure 2.

Figure 3 shows a nonlinear behavior of $\frac{C}{C_0}$ against the distance from the surface of fiber. Similar to work published by Clerck et al.,^{12,13} an error function equation seemed suitable for fitting the experimental data. Thus, eq. (2) was implemented and the value of diffusion coefficient was determined in a manner to give the minimum difference between the experimental data and those resulted from eq. (2).

Figure 2 demonstrates the cross sections of dyed fibers. As expected, the amount of diffused dye in the interior parts of fiber increased with increasing the dyeing time. As showing in Figure 2(a), the dye concentration decreases sharply by moving from the surface to the interior parts of the fiber, whereas Figure 2(d) demonstrates a flat distribution of dye molecules inside the fiber. The averages of $\frac{C}{C_0}$ values of four measurements of mentioned samples were plotted against the distance from the surface of the fiber and are demonstrated in Figure 4. The experimental results are marked by "*" sign, whereas the solid line shows the best fit of error function equation with optimum diffusion coefficient values.

As Figure 4 shows the intensity values were normalized and vary between 0 and 1, so as Figure 4(d) shows the value of 1 (or close to 1) of $\frac{C}{C_0}$ for different quantity of x refers to complete diffusion.

As plots in Figure 4 illustrate the degrees of fitness between the theoretical and experimental data are completely different. Deviations between the experimental data and those which have been calcu-

lated by model are more significant for the short dyeing times (30 and 50 min), whereas it becomes negligible for the longer dyeing durations. The differences between the experimental and theoretical data could be divided into two segments, i.e., "out" and "in" parts in the plots. These terms were also discussed in some papers.^{12,13} This type of division suggests that the experimental diffusion is different from the theoretical diffusion of dyes. Differences between the theoretical and experimental curves for the outer part show that the actual diffusion near the surface of fiber is higher than those obtained from theoretical calculations. On the other hand, the actual diffusion in the inner part is less than those achieved theoretically. However, this phenomenon becomes less important by increasing the dyeing time. The occurrence could be explained by dye-fiber bond formation. Acid dyes could be kept in polyamide fibers by ionic as well as Van der Waals bonds. In the starting steps of dyeing, the chance of formation of ionic bonds is higher and the positive amino group sites in fiber could be saturated during the passing of dye toward the interior parts. Hence, movement of dyes to the central part of the fiber could be stopped due to dye-fiber fixation force. Therefore, the amount of dye is practically higher in comparison with those obtained theoretically. Prolonging the dyeing process makes the migration of dyes possible and the dyes move to the inner parts of the fiber. These achievements were reported in recent works by employing different instrument.^{12,13}

Hence, the camera sensors do not linearly respond to light intensity, the calculated intensities as well as the concentrations could be considered as a pseudo-intensity. Consequently, the calculated diffusion coefficients are called pseudo-diffusion coefficient and shown in Table I for the samples which are shown in Figures 2 and 4. The standard deviations of determined pseudo-diffusion coefficients are also demonstrated in this table.

According to Table I, the pseudo-diffusion coefficients of dye for the samples dyed in 30, 50, and 70 min are tolerated between about 1×10^{-7} cm²/s to 4×10^{-7} cm²/s. Although the value of diffusion coefficient for 30 min dyeing is higher than others, it is clear that dyeing time could not have a significant effect on the diffusion coefficient. On the other hand, the pseudo-diffusion coefficient reported for 120 min dyeing is abnormal and completely different from others. It was definitely emphasized that this sample could not be suitable for determination of diffusion coefficient, since the concentration-distance profile, which was achieved in this condition, is not appropriate.^{12,13} In fact, the achievement of uniform dye diffusion makes this sample unsuitable for this method. Thus, it could be concluded that the diffusion coefficient is independent of the dyeing time,

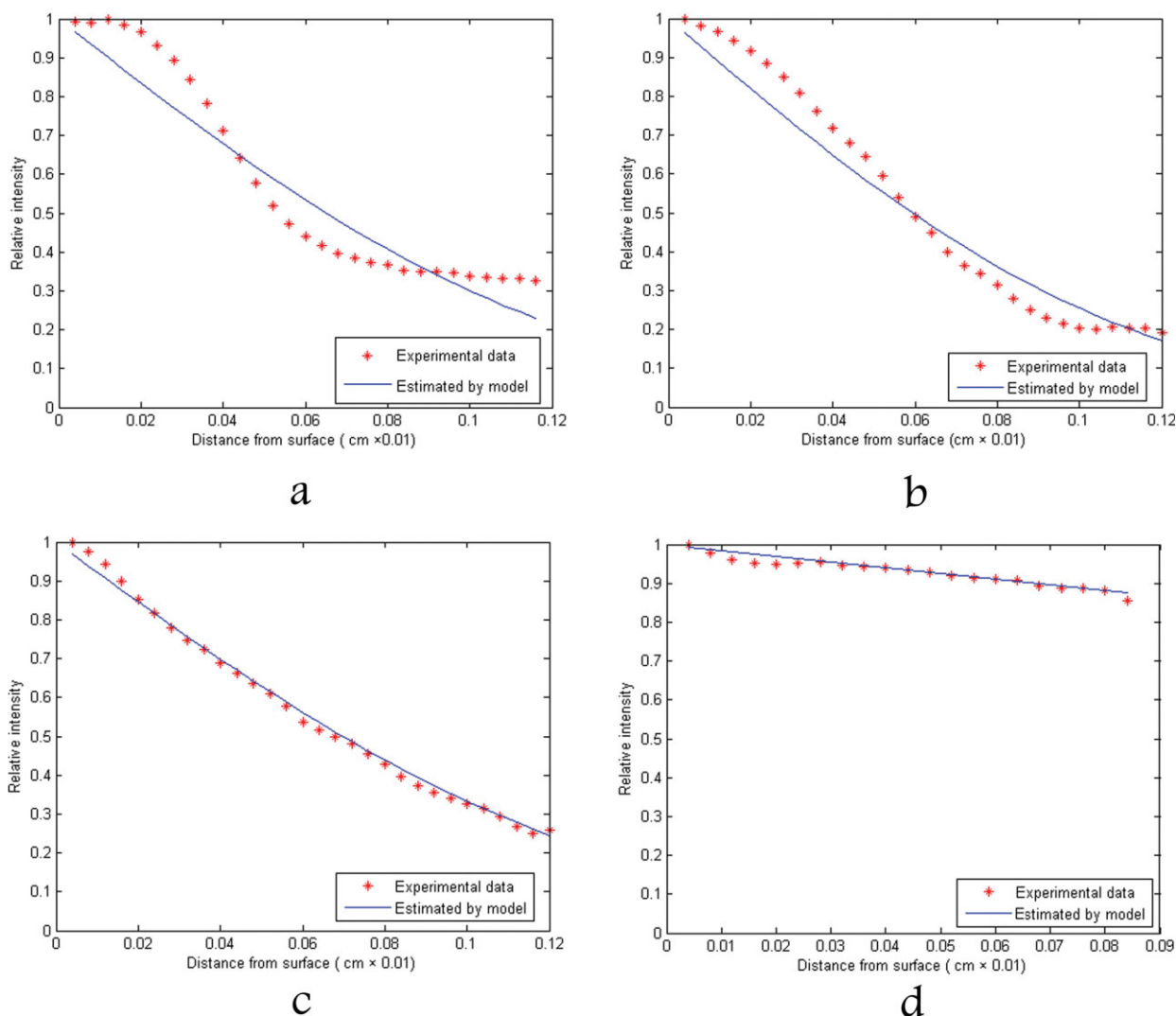


Figure 4 Intensity-distance profile of images shown in Figure 2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

but finding the suitable concentration-distance profile is a key point in this method and leads to more accurate results. The values of standard deviations also confirm this conclusion. In fact, the reproducibility of suggested method is obviously better in more stable dyeing condition, i.e., 50 and 70 min dyeing, whereas the insufficient diffusion in the cen-

TABLE I
Pseudo-Diffusion Coefficient of Tectilon Blue 4G
Obtained from Different Dyeing Times

Dyeing time (min)	Average pseudo-diffusion coefficient (cm^2/sec)	Standard deviation ($\times 10^{-7}$)
30	3.8945×10^{-7}	2.26
50	1.1840×10^{-7}	0.12
70	1.2826×10^{-7}	0.22
120	254.8000×10^{-7}	51.62

tral region of fibers and the limitation of data to the narrow zone near to surface of fibers could lead to problem in achievement of reproducible results.

The images of cross section of dyed fibers with Tectilon Blue 4G in 100°C are shown in Figure 5. This figure shows the key role of dyeing temperature on the diffusion behavior of dyeing system. The intensity of these samples is shown in Figure 6.

Figure 6 indicates that the sample dyed at 100°C for 60 min produces uniform diffusion and could not be used for determination of diffusion coefficient. In fact, complete diffusion occurred in 60 min dyeing time at this temperature; hence, the achieved data was not applicable for further analyzing. So, the image captured from short dyeing time was selected for determination of pseudo-diffusion coefficient. Hence, the index was determined by using data obtained from 3 min dyed sample. The pseudo-diffusion coefficient for this sample was $350.07 \times$

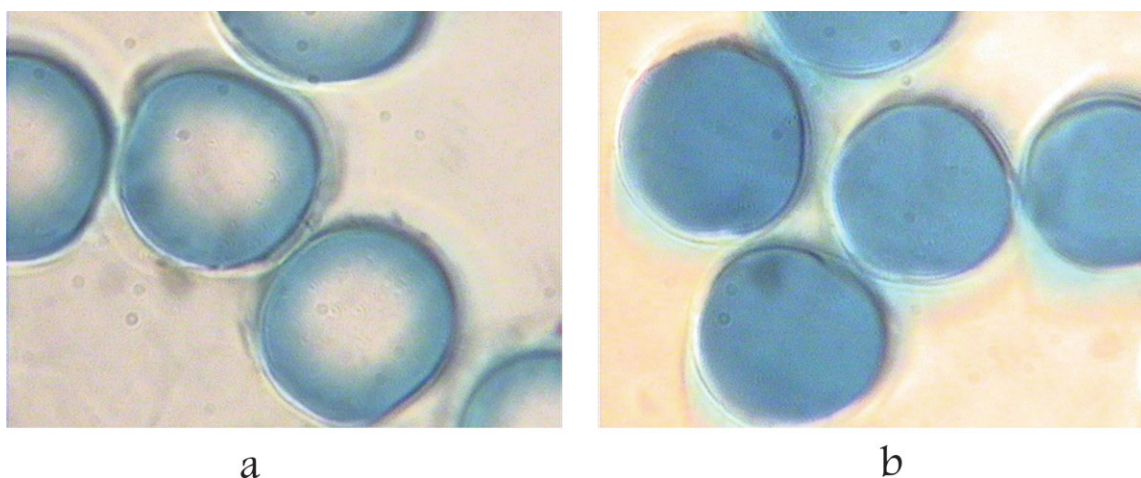


Figure 5 The cross section of dyed fibers at 100°C. (a) dyed for 3 min and (b) dyed for 60 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

10^{-7} cm²/s which is significantly higher than that obtained for samples dyed at 80°C. The results noticeably indicate to the importance of temperature in the diffusion phenomenon.

CONCLUSIONS

A novel method based on analyzing of microscopic images of the cross sections of dyed polyamide fibers was introduced for determination of diffusion behavior of dyes into the fibrous material. The technique led to good and reliable results to study the diffusion index of dyes into textile materials. The proposed method analyzed the RGB color data of

dots in the cross section of dyed fibers and determined concentration-distance profiles of samples. The experimental data, obtained from image analysis of captured data, were employed for drawing the concentration-distance curves while an error function equation was employed to fit them with minimum error. Then, the pseudo-diffusion coefficient was simply determined.

To examine the applicability of method, the effects of dyeing time as well as temperature on diffusion behavior of dye into the fiber were investigated by employing of this technique. Results revealed that dyeing duration could not affect the pseudo-diffusion coefficient, whereas the dyeing temperature increased it significantly.

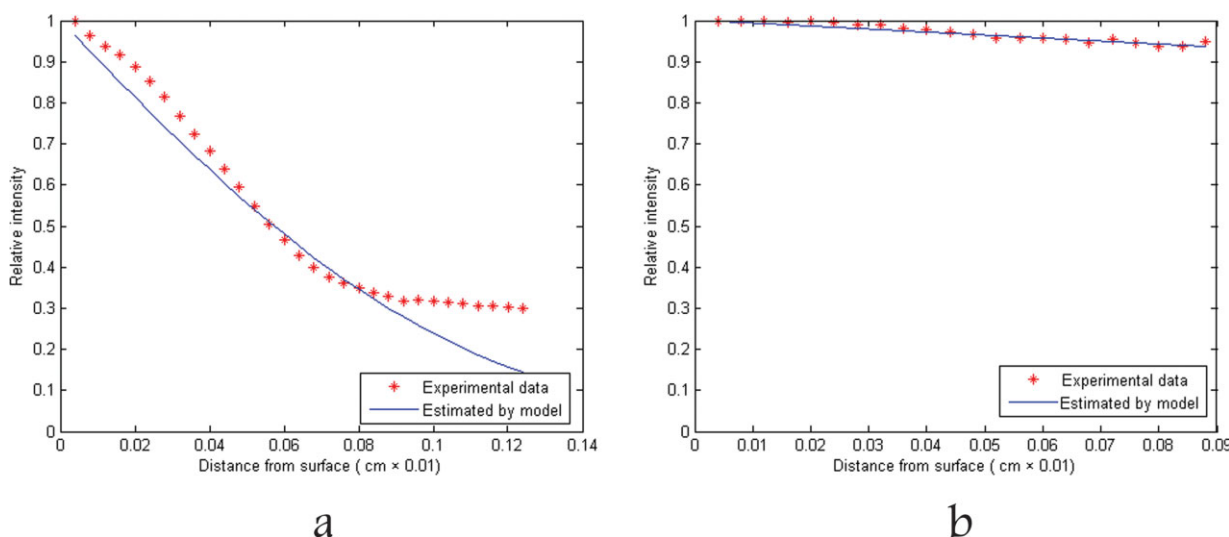


Figure 6 Intensity-distance profile for images shown in Figure 5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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