

# MODELING OF THE DIFFUSION DURING POLYESTER DYEING - A SURVEY -

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## ABSTRACT

A common goal of all dyers is to achieve the correct shade as early as the first dyeing. However, the disperse dyeing process is very complex, being characterized by the diffusion-controlled sorption of dyes that depends on several physicochemical parameters such as dye concentration and temperature of dyebath solution.

The literature reveals no equation that expresses the influence of experimental and measurable parameters on the diffusion coefficient value. Thus, a mathematical model describing the evolution of this diffusion coefficient for disperse dyes as a function of time, initial dye concentration, temperature and the nature of the dyebath (finite, infinite) is proposed.

This model applies to the dyeing of conventional polyester fibers and microfibers with disperse dyes. The critical discussion is developed dealing with the possibility of the model industrial application and its effectiveness.

## INTRODUCTION

Many papers have dealt with the kinetics of dyeing but the problem is to know whether the equations that have been proposed represent the real physical mechanism. Generally, the dye diffusion into a fiber is described mathematically by Hill and Wilson's equations (or their approximations) which compare the diffusion into a textile fiber with the diffusion into a cylinder of infinite length (Etters 1980; Inoue and Suda 1968; Johnson 1989; Kilby 1960; Shibusawa 1979; Tsuda 1962; Urbanik 1974; Urbanik 1976; Vickerstaff 1954). This approach is based on the second Fick's law. Moreover, these models consider that the diffusion coefficient is constant during the entire dyeing process and thus neglect the dye concentration and the dyebath temperature influence on the diffusion. A new mathematical model taking into account the initial dye concentration influence has been developed in our previous works (Casetta et al. 1999; Casetta et al. 2001; Koncar and Casetta 2001). In our recent research studies we have improved the method used to compute the

diffusion coefficient evolution as a function of time. Then, the temperature variations influence on the diffusion coefficient value has been introduced and modeled. Finally, we have validated this model by making an experiment with a given initial dye concentration and a temperature profile that implies the diffusion coefficient variation (Casetta and Koncar 2001; Koncar et al. 2000). The dyeing uptake rate results coming from the previous experiments are compared to simulation results obtained from our diffusion model and dyeing kinetics model.

Discussion introducing the growing economical interest of polyester fibers and specially the interest of microfibers involved in many new high performance textile products is developed at the end of this paper.

The organization of the paper is as follows: in the next section, we will introduce some elementary dyeing properties of conventional polyester fibers and microfibers. These may be regarded as a general framework for diffusion coefficient modeling. We will present results of modeling and identification based on the genetic algorithms method tracking problems in the next section. Then the discussion and comments will be exposed in the and finally the conclusion and future investigations will be given. The organization of the paper should optimize the readability.

## DYEING PROPERTIES OF CONVENTIONAL POLYESTER FIBERS AND MICROFIBERS [Burkinshaw 1995; Lallam et al. 1997; Shin and Bide 2000]

On immersion of a fiber into dye liquor disperse dyeing process comprises four stages:

- Some of the dye dissolves in the dyebath
- Dye molecules are transferred from the bulk of the liquor to the fiber surface
- The solution in the dyebath is replenished by the dissolution of more solid material from the dispersion
- Single molecules of the adsorbed dye diffuse into the polymer itself

The fourth process is generally considered to be slower than the others and may be taken to be the rate-determining step in dyeing.

A microfiber is defined as a fiber or filament of linear density of less than 1 dtex (the dtex is the mass in grams of 10 km of fiber).

The reduction in the filament linear density is also accompanied by an increase in the surface area per unit volume of the filament, the specific surface increasing markedly with decreasing filament linear density.

Compared to conventional fibers, microfibers exhibit several important differences, even if there is no difference in the chemical structure or morphology. These differences apply both to the properties of the final dyeing, and the dyeing process itself.

In the context of dyeing, the increase in surface area that accompanies a decrease in filament linear density serves firstly to increase the extents of both dye adsorption and desorption, these two effects resulting in, respectively, an increase in the rate of dyeing and often decreased wet and light fastness and secondly, to reduce the visual and instrumental depth of shade obtained.

Disperse dyes exhibit a faster rate and greater extent of uptake on polyester microfibers than on conventional fibers: microfibers can absorb 2 to 3 or even 4 to 5 times as much disperse dye, the magnitude of this differential dye uptake depending on dye structure as well as fiber fineness and cross-sectional shape. A difference between the amorphous zones of polyester microfibers and conventional fibers has also been invoked to explain this behavior. Fully penetrated dyeings are more rapidly attained on microfibers than on coarser fibers and, as a result, shorter times are required under high temperature dyeing conditions to achieve good dye penetration. The temperature range over which dye adsorption occurs as well as the time required to achieve dyebath exhaustion and fully penetrated dyeings depends on the fineness of the fibers.

As a consequence of disperse dyes exhibiting a faster rate and greater extent of uptake on polyester microfibers than on conventional fibers, the leveling behavior of the dyes on microfiber is often poorer than that on conventional fibers. To improve leveling, microfiber dyeing usually begins at a lower temperature than that employed for conventional fibers. Furthermore, a lower rate of rise of temperature up to the top dyeing temperature is usually used.

More dyestuff is required to achieve a given visual depth of shade on microfibers, with the greater surface area of microfiber providing a greater surface reflectance.

Disperse dyes display lower fastness to light on microfibers than on conventional polyester fibers because of the greater fiber surface area that is exposed to light.

However, dyeings on microfiber do exhibit lower wet fastness than comparable dyeings on conventional fibers, especially in heavy depths, due to inadequate after treatment and when thermally treated. The lower wet fastness of disperse dyes on microfibers can be attributed to the greater amount of dye present within the fiber and to the greater specific surface from which dye desorption can occur. The fastness of dyeings to sublimation on microfibers are lower than on conventional fibers, this

phenomenon being due to the greater amount of dye on microfibers.

## DIFFUSION COEFFICIENT $D$ MODEL

### Existing models

A model describing the influence of initial dye concentration and time on the diffusion process has been developed recently (Casetta et al. 1999; Casetta et al. 2001; Koncar and Casetta 2001). However, this model cannot be applied to commercial dyeing systems because the dyeing process is not an isothermal one. Instead of using the average value of  $D$  in order to compute the dyeing uptake rate, we know that temperature influences the diffusion process.

In the literature, several models exist that describe the diffusion coefficient evolution whether as a function of the temperature or as a function of dye concentration.

A number of attempts have been made to choose dye exhaustion profiles for the optimal control of dyeing process. All these approaches have been based on the theoretical isothermal dye-uptake curve, although the dyeing process is not an isothermal one (Popescu and Segal 1984).

According to Crank, the apparent diffusion coefficient can be represented by:  $D = 418 (1 + 2.4 C) \text{ cm}^2/\text{min}$  in contrast to Garvie and Neale's conclusion that it was a simple power function:  $D = D_0 C^{0.5}$  (Vickerstaff 1954).

Narebska et Ostrowska (Ostrowska and Narebska 1980) have stated that for the polymer-dye system they investigated, the relation between  $D$  (diffusion coefficient) and  $C$  (dye concentration in the fiber) is of the form:  $D(C) = D_0 \exp(\delta C)$  where  $D_0$  and  $\delta$  are constants.

A semi-empirical equation that describes the variation of viscoelastic properties of amorphous polymers with temperature has been proposed by Williams, Landel and Ferry (Williams et al. 1955). Fumita (Fumita et al. 1960) has demonstrated that the variation of diffusion coefficients can be related to these viscoelastic properties. The combination of these two relationships leads to the equation (1).

$$\log \frac{D_T}{D_{T_g}} = \frac{A(T - T_g)}{B + (T - T_g)} \quad (1)$$

where  $T_g$  is the glass transition temperature,  $D_T$  is the value of the diffusion coefficient at temperature  $T$ ,  $D_{T_g}$  is the value of the diffusion coefficient at  $T_g$  and where  $A$  and  $B$  are constants. For almost all polymers  $A = 17.44$  and  $B = 51.6$ .

A large number of polymers have been found to conform to the WLF relationship over the temperature range from  $T_g$  to  $T_g + 100$  ( $^{\circ}\text{C}$ ).

## Modeling

After an extensive study of experimental curves giving the diffusion coefficient evolution against time obtained from the dyeing results, the mathematical model is obtained (equations (2) and (3)). Our reflection was also based on the diffusion coefficient models already existing.

- Infinite bath

$$D_{inf-bath}(t, C_0, T) = a_i t^{b_i} \exp(-c_i t^{d_i}) \quad (2)$$

- Finite bath

$$D_{f-bath}(t, C_0, T) = a_f t^{b_f} \exp(-c_f t^{d_f}) \quad (3)$$

where:  $t$ : time (s)  
 $C_0$ : initial dye concentration (g/L)  
 $D$ : diffusion coefficient (cm<sup>2</sup>/s)  
 $T$ : temperature (°K)  
 $P_i = [a_i, b_i, c_i, d_i]$ : infinite bath parameters;  $P_i$  depends on  $C_0$  and  $T$ .  
 $P_f = [a_f, b_f, c_f, d_f]$ : finite bath parameters;  $P_f$  depends on  $C_0$  and  $T$ .

## Identification

The diffusion coefficient values obtained from the model and those computed from experimental  $\frac{M_t}{M_\infty}$  values and

Shibusawa's approximations of Wilson and Hill's equations are compared.

For instance, the curves obtained for a 4% initial dye concentration and temperatures of 135°C, 130°C, 125°C and 120°C are given in Fig. 1 to 4.

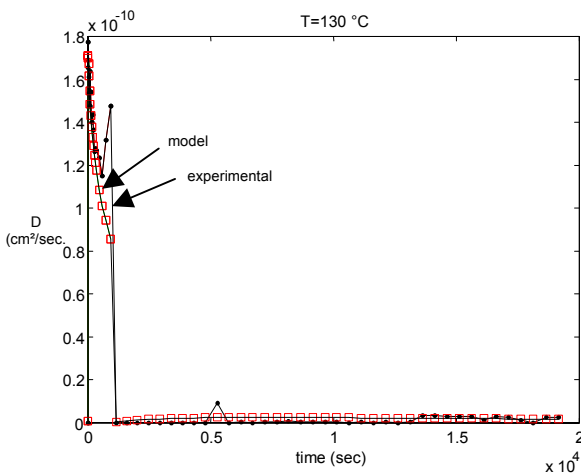


Figure 1: Apparent diffusion coefficient for 4.14% initial dye concentration and 135°C.

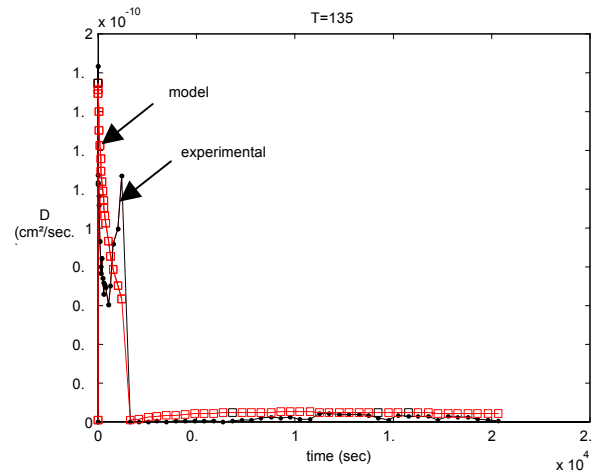


Figure 2: Apparent diffusion coefficient for 4.22% initial dye concentration and 130°C.

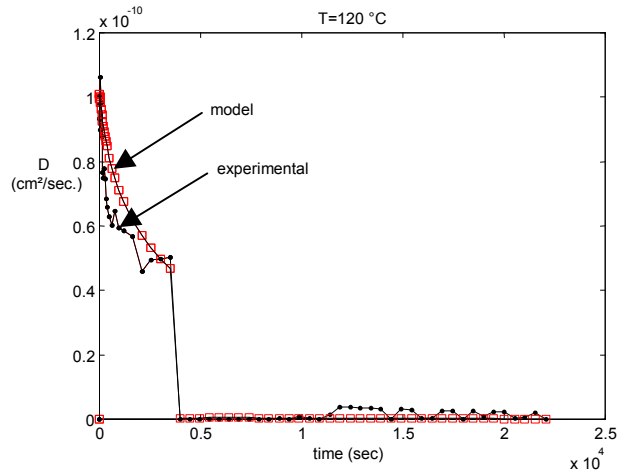


Figure 3: Apparent diffusion coefficient for 3.94% initial dye concentration and 125°C.

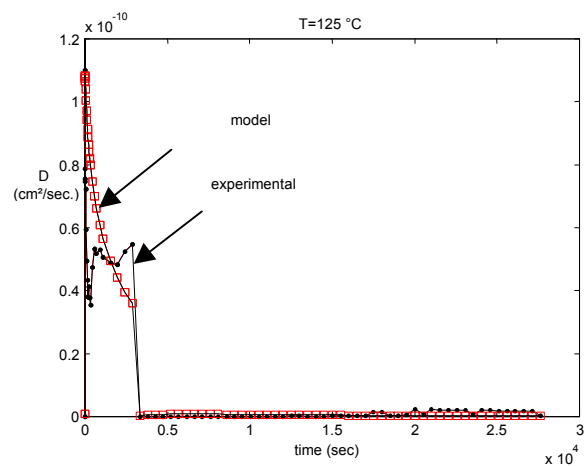


Figure 4: Apparent diffusion coefficient for 4.03% initial dye concentration and 120°C.

Then, the genetic algorithms based optimization program is used to identify  $P_i$  and  $P_f$ . This optimization method is

applied for all combination couples of initial dye concentration and dyeing temperature.

The parameters analysis shows that  $c_i$  and  $c_f$  parameters are independent of the initial dye concentration if the temperature is unvarying. Moreover, for a given initial dye concentration,  $b_{i,f}$  and  $d_{i,f}$  parameters do not vary, whatever the temperature of application.

Equations describing the evolution of each parameter as a function of the initial dye concentration  $C_0$  and the temperature  $T$  are obtained by minimizing the sum of quadratic errors between the identified parameter equation values and the same parameter table values.

Expressions giving the identified parameters functions toward measured temperature and initial dye concentration are given below, in the tables 1 and 2:

Table 1:  $P_i$  and  $P_f$  Vectors Analysis

Initial dye concentrations $C_0$	Parameter as a function of $C_0$	Correlation Coefficient between Parameter Function and Real Parameter Data
$C_0 > 0.8045\%$ (infinite bath)	Power Fit: $b_i = 0.0292 C_0^{-0.9266}$	Correlation coefficient: 0.992
$C_0 > 0.8045\%$ (infinite bath)	Power Fit: $d_i = 0.4349 C_0^{-0.0678}$	Correlation coefficient: 0.970
$C_0 < 12.8045\%$ (finite bath)	Linear Fit: $b_f = 2.4204 - 0.5461 C_0$	Correlation coefficient: 0.966
$C_0 < 12.8045\%$ (finite bath)	Linear Fit: $d_f = 0.3381 - 0.0452 C_0$	Correlation coefficient: 0.964

Table 2:  $P_i$  and  $P_f$  Vectors Analysis

Initial dye concentration $C_0$	Parameter as a function of $T$	Correlation Coefficient between Parameter Function and Real Parameter Data
$C_0 > 0.8045\%$ (infinite bath)	Linear Fit: $c_i = -0.6524 + 0.0017 T$	Correlation coefficient: 0.988
$C_0 < 12.8045\%$ (finite bath)	Linear Fit: $c_f = 4.4086 - 0.0097 T$	Correlation coefficient: 0.997

## Global model

The main objective of our study is to develop a global model including both the dye diffusion and the dye concentration evolution into polyester. The diffusion is described by the diffusion coefficient  $D(t, C_0, T)$  and the dye concentration into polyester fibers by the  $\frac{M_t}{M_\infty}$  ratio

where  $M_t$  is the dye concentration into the fiber at time  $t$  and  $M_\infty$  the dye concentration at the equilibrium state.

In its final configuration, the proposed model is defined in the form of a non-linear state space model (4).

$$\begin{aligned} \dot{X}(t) &= f(X(t), U(t), t) & \text{state equation} \\ S(t) &= g(X(t)) & \text{output equation} \end{aligned} \quad (4)$$

( $S(t)$  is the color of the textile product at time  $t$ )

$$\begin{aligned} \text{where: } X(t) &= \begin{bmatrix} \frac{M_t}{M_\infty} \\ D(t, C_0, T) \end{bmatrix} & \text{system state} \\ U(t) &= \begin{bmatrix} T \\ C_0 \end{bmatrix} & \text{system input} \end{aligned}$$

The exogenous parameters relative to the dyeing process are fiber dimension, polyester properties, dyes properties and the dyeing machine properties. These parameters influence dyeing models parameters equations that have to be identified for each set of exogenous parameters.

A fine analysis of the equations is given in order to highlight the complexity of the observed phenomena.

The nature of the dyeing process (batch under high pressure), the  $S(t)$  output measured with the spectrophotometer (measurement by reflection) is accessible to measurement only at the end of the dyeing, on the dried products (yarn bobbin or fabric). The diffusion coefficient  $D(t, C_0, T)$  cannot be measured directly. The output equation model,  $g(\cdot)$ , is not the object of this article.

The objective of modeling is to establish the direct relation between the product's final color and the measurable parameters during the dyeing like the dyebath temperature and the initial dye concentration and indirectly throw the model parameters involving exogenous parameters.

The functions  $f(\cdot)$  and  $g(\cdot)$  thus characterize at the same time the dye/polyester system and the dyeing machine properties by including the physicochemical phenomena knowledge.

Therefore, the global model of the dyeing process can be expressed as follows (equation (5)).

$$\begin{bmatrix} \frac{d\left(\frac{M_t}{M_\infty}\right)}{dt} \\ \frac{dD(t, C_0, T)}{dt} \end{bmatrix} = \begin{bmatrix} \sum_{n=1}^{\infty} \frac{4}{r^2} [D + t.D] \exp\left(-\frac{\beta_n D(t, C_0, T).t}{r^2}\right) \\ \left(\frac{b_i}{t} - c_i . d_i t^{d_i-1}\right) D(t, C_0, T) \end{bmatrix} \quad (5)$$

The dyebath temperature and the initial dye concentration appear through the parameters  $b_i$ ,  $c_i$  and  $d_i$ . The first and second expressions of equation (5) are the differential equations whose solutions are respectively Hill's model and our diffusion model. In that second case, the initial condition is as follows:  $D_{(t=0)} = a_i$ .

To simplify the presentation, we only developed in this demonstration the global dyeing model in the case of the infinite bath with a sufficient flow rate (Hill's equation). In the case of the finite bath and/or insufficient flow rate, the global model varies in connection with the approaches of Wilson or also Crank or Newman for insufficient flow rates (Shibusawa 1985).

## DISCUSSION AND COMMENTS

### Model

Two equations describing the diffusion coefficient evolution according to the dyebath nature (infinite or finite) have been obtained, each containing four parameters.  $b_{i,f}$  and  $c_{i,f}$  parameters are independent of the dyeing temperature whatever the initial dye concentration. Moreover, the results obtained after the optimization step show that parameters  $c_{i,f}$  depend only on the temperature. Parameters  $a_i$  and  $a_f$  are much more difficult to explain. In fact, the part corresponding to finite bath conditions is not easy to model as the  $a_f$  values are close to the limit of MATLAB precision. This is why the  $a_f$  value is constant ( $10^{-16}$ ) whatever the dyebath temperature and the initial dye concentration. As for parameter  $a_i$ , variations can be observed not only according to the dyebath temperature but also to the initial dye concentration. Several assumptions can be made to explain this phenomenon.

The small variations of  $a_i$  against initial dye concentration can be due to the possible change in the quantity of dye dissolved in the bath during the dyeing. However, we can notice that the  $a_i$  values are very close for initial dye concentrations of 6, 8 and 16% whereas the difference is marked for 2 and 4%. For these two last concentrations, the transition between infinite and finite bath occurs 10 to 20 minutes after the beginning of the dyeing experiment. We can thus wonder whether this time is sufficiently long

for the  $\left(\frac{M_t}{M_\infty}\right)_{transition}$  value to be defined with sufficient precision.

### Economical interest and industrial application

Since the last two decades, the "right-first-time" production has become more and more important to dyeing industry. When the resultant shade obtained does not match the target color, a shade correction or even re-dyeing process must be carried out to correct the failed shade until it passes quality examination. It is not unusual that an off-shade dyeing requires two or more additional shading processes before approval. However, this situation does not meet the demands of dyeing industry as shade correction or re-processing will consume labors, energies,

materials and time. Therefore, the re-dyeing process is not welcome in dyeing industry.

Our study focused on the dyeing of polyester fibers for which the choice of dyes is limited, being confined to the disperse dye range. However, the economical interest of this type of dyes is very important.

## CONCLUSION AND FUTURE INVESTIGATIONS

The modeling procedure resulted in two equations describing the diffusion coefficient evolution as a function of time, initial dye concentration and temperature. Each equation is applied according to the bath nature: infinite or finite; the transitional bath corresponds to the combination of these two equations.

This model contains, for infinite and finite dyebaths, four parameters  $a_{i,f}$ ,  $b_{i,f}$ ,  $c_{i,f}$  and  $d_{i,f}$ :  $b_{i,f}$  and  $d_{i,f}$  depend only on the initial dye concentration and  $c_{i,f}$  varies according to the temperature. Thus, the advantage of this model is that each parameter depends on a unique experimental variable.

Finally, we proved that this model is well adapted to the dyeing process of conventional polyester fibers and microfibers.

The future research works will be basically oriented toward diffusion model area of validity (all dye types and synthetic fibers).

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