Diffusion of disperse dyes into microfibres and conventional polyester fibres

K H Park, M Casetta and V Koncar*

GEMTEX/ENSAIT, 9 rue de l'Ermitage, BP 30329, 59056 Roubaix, Cedex 01, France
Email: keun-hoo.park@ensait.fr; mathilde.casetta@ensait.fr; vladan.koncar@ensait.fr

Coloration Technology

Society of Dyers and Colourists

The dyeing properties of polyester microfibres are quite different from those of conventional polyester fibres. In this paper, the sorption isotherms, the diffusion coefficients and the amount and rate of dye uptake into the fibres are compared for both conventional fibres and microfibres. Shibusawa's approximation of Hill's equation is used to compute the diffusion coefficient, which depends on the initial dye concentration, the time and the fibre count for a fixed temperature (130 °C). The kinetic properties are analysed only under infinite bath conditions. The sorption isotherms and diffusion coefficients as functions of time for conventional polyester fibres and microfibres are compared by considering the surface area and the diffusional boundary layer influence.

Introduction

A microfibre is defined as a fibre or filament of linear density of less than 1 dtex.† 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 [1]. Compared to conventional fibres, microfibres 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 [2–4].

In the context of dyeing, the increase in surface area that accompanies a decrease in filament linear density serves, firstly, to increase the extent 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 microfibres than on conventional fibres; microfibres can absorb 2–3, or even 4–5, times as much disperse dye, the magnitude of this differential dye uptake depending on dye structure as well as fibre fineness and cross-sectional shape. A difference between the amorphous zones of polyester microfibres and conventional fibres has also been invoked to explain this behaviour [3,4]. Fully penetrated dyeings are more rapidly attained on microfibres than on coarser fibres 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 fibres.

† The unit 'dtex' expresses linear density as the mass in g/10 km of fibre

As a consequence of disperse dyes exhibiting a faster rate, and a greater extent, of uptake on polyester microfibres than on conventional fibres, the levelling behaviour of the dyes on microfibres is often poorer. To improve levelling, microfibre dyeing usually begins at a lower temperature than that employed for conventional fibres. Furthermore, a slower rate of increasing the temperature up to the desired level is usually used.

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

Disperse dyes display lower fastness to light on microfibres than on conventional polyester fibres because of the greater fibre surface area that is exposed to light. However, dyeings on microfibres do exhibit lower wet fastness than comparable dyeings on conventional fibres, especially in heavy depths. The lower wet fastness of disperse dyes on microfibres can be attributed to the greater uptake of dye within the fibre and to the greater specific surface from which dye desorption can occur. The fastness of dyeings to sublimation on microfibres are lower than on conventional fibres, this phenomenon being due to the greater uptake of dye on microfibres.

Theory

Most theoretical equations describing the rate of dyeing have been derived by assuming that the overall dyeing rate is determined by the dye diffusion rate within a fibre [5–10].

Diffusion of dyes into polyester fibres can occur under both infinite and finite dyebath conditions during the dyeing procedure. In the case of infinite dyebaths, the dye concentration in the dyebath does not change during the sorption process, whereas for finite dyebaths, the dye concentration at the fibre surface continuously decreases during the sorption process until equilibrium between the dye concentration within the fibres and in the dyebath is achieved [11].

The diffusion rate of dye molecules into polyester fibres

from a well-stirred solution is expressed by Wilson's equation for a finite dyebath (Eqn 1). Eqn 1 is reduced to Hill's equation (Eqn 2) when fractional exhaustion E_∞ = 0, i.e. describing the dyeing rate from an infinite dyebath.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1+\alpha)\exp[-q_n{}^2(D_f t / r^2)]}{4 + 4\alpha + \alpha^2 q_n{}^2} \quad (1)$$

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{\beta_n{}^2}\exp[-\beta_n{}^2(D_f t / r^2)] \quad (2)$$

where M_t and M_∞ are amounts of dye taken up by a fibre of radius r at time t and at equilibrium, respectively, the q_n values are positive (non-zero) roots of $\alpha q_n J_0(q_n) + 2J_1(q_n) = 0$, where J_0 and J_1 are zero and first-order Bessel functions, D_f is the diffusion coefficient of dye in the fibre (cm^2/s), the parameter α corresponds to $(1 - E_\infty)/E_\infty$, where E_∞ is the fractional equilibrium exhaustion, and the β_n values are positive (non-zero) roots of $J_0(\beta_n) = 0$.

The diffusion coefficient is computed from M_t/M_∞ experimental dyeing results for microfibres and conventional fibres. In the case of high initial dye concentrations, this infinite dyebath condition is maintained during the entire dyeing process. In the case of lower initial dye concentrations, two different dyeing configurations are possible: transitional dyebath (first infinite and then finite dyebath); or only finite dyebath. As shown previously [12,13], the dye diffusion into the fibre is more important during the infinite dyebath enabling fast increase of M_t values. The fact is that the most important and efficient phase of a dyeing process is during the infinite dyebath condition. Therefore, in this paper, the diffusion coefficient is analysed only for the infinite dyebath configuration for microfibres and conventional fibres.

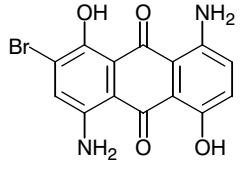
This paper discusses the differences between microfibres and conventional fibres in the sorption isotherms, dye uptake evolution (M_t) and diffusion coefficient results obtained from M_t/M_∞ experimental values, and the results are analysed and compared.

Experimental

Materials

Three polyester multifilament yarns were used in this study and were obtained from Hyusuing Inc., South Korea. Two of these were microfibres [0.22 dtex (77 dtex/300 fil) and 0.56 dtex (83 dtex/144 fil)] and one was a conventional fibre [1.46 dtex (292 dtex/200 fil)].

Dyeing of all polyester yarns was carried out with CI Disperse Blue 56 (**1**), which was obtained from Ciba and used without further purification.



1

Dyeing procedure

Polyester yarn (14 g) was dyed in a well-stirred dyebath (Ahiba Turbocolor dyeing machine) at a liquor ratio of 50:1. The initial dye concentration was fixed (at either 2, 4 or 16% owf) and the dyeings were carried out at a constant temperature (130 °C) in order to fulfil the conditions of Hill's equation. Initially, the yarn was placed in a dyebath at a temperature of 90 °C. This was then heated up as quickly as possible (*ca.* 4 min) to 130 °C and maintained at this temperature for several hours. During this isothermal dyeing, dyebath samples were obtained regularly using the dyeing machine sampling device and any particulate dye still present in these samples was dissolved with dimethyl formamide. The absorbance of the dye solution samples was determined using a Datacolor SF 600 PLUS spectrophotometer in order to evaluate the dye concentration in the dyebath in real time (applying the Beer–Lambert law). Then, from these results, the dye concentration within the fibre was computed.

Crystallinity index measurements

The crystallinity index (X) was determined by differential scanning calorimetry (DSC) measurements using a TA Instruments DSC 2920CE machine. Samples were examined at a rate of 10 °C/min up to a temperature of 300 °C. After that, samples were put in ice and the measurement procedure was repeated in order to obtain the glass transition temperature.

For the crystallinity index, the DSC curve was used to obtain the enthalpy values for the melting point and this value was divided by the theoretical enthalpy value for 100% crystalline polyester [14,15].

Sorption isotherms

Sorption isotherms depend on the presence of dispersing agents, the dyeing temperature, the dye structure and fibre types. Generally, sorption isotherms of disperse dyes on polyester fibres have been reported as Nernst-type linear distribution isotherms in the presence of a constant concentration of dispersing agent [11,16].

However, in the absence of dispersing agent, the sorption isotherms of disperse dyes on polyester fibres have more complex shapes. It has been reported that a dual-mode sorption model that is composed of both Nernst and Langmuir sorption models, or a more complex sorption model which has one Nernst type model and several Langmuir sorption models, may be more appropriate [17]. The simple dual-mode sorption model is usually expressed by Eqn 3:

$$C_f = C_P + C_L = K_P C_b + \frac{K_L S C_b}{1 + K_L C_b} \quad (3)$$

where C_f and C_b are the equilibrium dye concentrations on the fibre and in the dyebath, and C_P and C_L are the equilibrium concentrations of dye on the fibre sorbed by Nernst-type partitioning and Langmuir sorption, respectively; S is the saturation value for Langmuir sorption; K_P is the partition coefficient; and K_L is the Langmuir constant. However, this dual-model also depends on the dye structure and on the dyeing temperature. Therefore,

the selection of the sorption isotherm model for polyester disperse dyeing depends on dyeing and material conditions [17–19].

In our study, the disperse dye isotherms and their sorption models were determined for the microfibres and conventional polyester fibre at a dyeing temperature of 130 °C.

Diffusion coefficient computation

Each initial dye concentration during the dyeing process was expressed as the M_t/M_∞ ratio in order to compute the diffusion coefficient (D_f) for an infinite dyebath by applying Shibusawa's approximation of Hill's equation. The diffusion coefficient is often considered as constant in the literature. In Hill's and Wilson's equations it is also considered as constant. In fact they have used the mean value of D_f during the whole dyeing process. On the other hand, this diffusion coefficient depends on the dyebath temperature, on the dye concentration and on the fibre count.

It is agreed that the value of D_f can be considered as constant but only for a short period of time (sampling period) when the temperature and the dye concentration variations are small. Therefore, Hill's equation is then used during these sampling periods to compute the diffusion coefficient considered as constant. This procedure is repeated for each sampling period. Thus, the diffusion coefficient varies at each sampling time.

In order to compute the diffusion coefficient by using Shibusawa's approximation of Hill's equation and to compare the differences between microfibres and conventional fibres, the experimental parameters were determined as shown in Table 1. The fibre radius of each fibre depends on its count. The fibre surface area decreases strongly with an increase in fibre count, as expected. The crystallinity index remains stable for all the fibres.

Table 1 Experimental parameters[a] for the various yarn types[b]

	Parameter		
Yarn	r (cm)	A (cm^2/g)	X (%)
0.22 dtex	0.254×10^{-3}	7.26×10^3	47
0.56 dtex	0.375×10^{-3}	4.21×10^3	44
1.46 dtex	0.490×10^{-3}	2.11×10^3	45

a r = fibre radius; A = fibre surface area; X = crystallinity index
b Temperature = 130 °C; liquor ratio = 50:1

The influence of the different fibre counts on D_f values, was investigated by calculating the values of D_f/r^2. In this study the infinite bath duration and the D_f/r^2 magnitude variations were compared for the different fibre counts (0.22 and 0.56 dtex microfibres and 1.46 dtex conventional fibre) and various initial dye concentrations (2, 4 and 16% owf) at the same dyebath temperature (130 °C).

Results and Discussion

Differences in the sorption isotherms (Langmuir sorption model)

As already mentioned, there are reports in the literature on studies of dual-mode sorption models that have been carried out for low dyeing temperatures (between 60 and 120 °C) [17–19]. These models change with dyeing conditions or dye structure and many results show that the contribution of the Langmuir sorption isotherm to the dual-mode sorption model increases with an increase in dyebath temperature and a decrease in the dye molecules [17–19].

The sorption isotherm for this present study, for the two microfibres and conventional fibre at a standard dyeing temperature of 130 °C, are shown in Figure 1. The sorption parameters are given in Table 2.

The results in Figure 1 were obtained using the Langmuir sorption equation and it is clear that the experimental results fit well to the Langmuir model. However, the model expressed by Eqn 3 (the dual-model sorption isotherm) did not fit the experimental results. Thus, the conclusion concerning the fitness of the Langmuir model under high temperature dyeing conditions is confirmed. It is also clear from Table 2 that parameters K_L and R increase as the fibre count decreases. This means that the Langmuir sorption isotherm is more appropriate for microfibres than for conventional fibres.

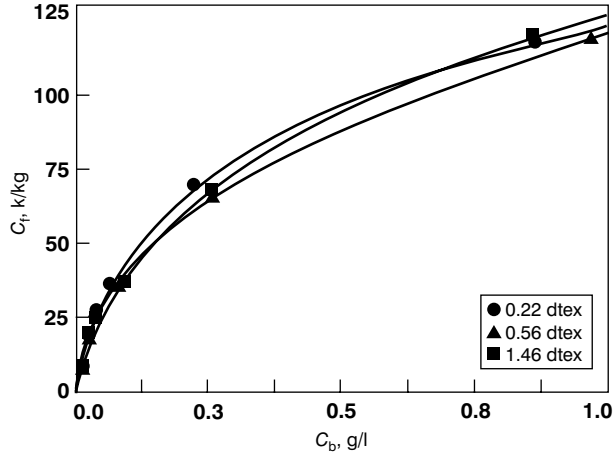


Figure 1 Sorption isotherms for the microfibres (0.22 and 0.56 dtex) and the conventional fibre (1.46 dtex) at 130 °C

Table 2 Sorption parameters[a] for the microfibres (0.22 dtex and 0.56 dtex) and conventional fibre (1.46 dtex) at 130 °C

	Sorption parameter		
Yarn	K_L (l/g)	S (g/kg)	R (%)
0.22 dtex	4.927	142.78	99.63
0.56 dtex	3.976	146.98	99.16
1.46 dtex	3.699	154.25	99.14

a K_L = Langmuir constant; S = saturation value for Langmuir sorption; R = degree of correlation between experimental results and Langmuir sorption curve

Differences of dye uptake

The rate of dye uptake by the different fibres over the dyeing period was investigated for initial dye concentrations of 2, 4 and 16% owf and the results are compared in Figure 2. The differences between the dyeing properties of the microfibres and the conventional fibre are made easier to detect because the experimental values have not been divided by the equilibrium dye concentration value M_∞. This way of comparing the dyeing properties avoids the minimisation of differences. In fact, they are amplified in order to understand the fibre count influence on dyeing properties.

It is clear from Figure 2 that there are two stages in the dye uptake of the fibres.

Initial stage

It is clear that the dye uptake at time t (M_t) increases faster for microfibres than for conventional fibres for lower initial dye concentrations. This is particularly obvious for 2% initial dye concentration (Figure 2a). For the 4 and 16% owf dyeings (Figures 2b,c), the plots are almost superimposed for all the fibres.

This phenomenon can be explained by the larger surface area A exposed to dye molecules for 0.22 and 0.56 dtex microfibres than that for 1.46 dtex conventional fibre and by the fact that at 2% initial dye concentration, the diffusional boundary layer is not important. Therefore, this diffusional boundary layer does not disturb the adsorption of dye molecules onto the surface of the microfibres or conventional fibre.

It is also important to note the considerable deviation of the dyeing kinetics from theoretical behaviour for 16% owf. This deviation could be explained by the fact that a process of dye dissolution is interfering with dyeing kinetics. This phenomenon could also partly explain the superimposition of dyeing kinetics for 0.22, 0.56 and 1.46 dtex fibres.

Equilibrium state (final stage)

It is also clear from Figure 2, for the equilibrium state, that increasing the initial dye concentrations leads to further increased differences in dye uptake between the microfibres (particularly 0.22 dtex) and the conventional fibre (see insets in Figures 2a–c).

It is considered that this phenomenon could be explained by the higher dyeing capacity of microfibres than of conventional fibres. The dye molecules are fixed on available dyeing sites. For higher dye concentrations, there are more molecules to be fixed on the available dyeing sites. For example, for 2% initial dye concentration, the microfibre dyeing capacity is higher than the dyebath dyeing capacity (quantity of dye molecules). Therefore, for 2% owf initial dye concentration, there is no difference among equilibrium values of M_t for the three fibres because none of the polyester samples are saturated at this dyebath concentration. On the other hand, for 16% owf initial dye concentration, when the dyebath dyeing capacity is sufficient the difference in the number of dyeing sites between microfibres and conventional fibre is pronounced (Figure 2a).

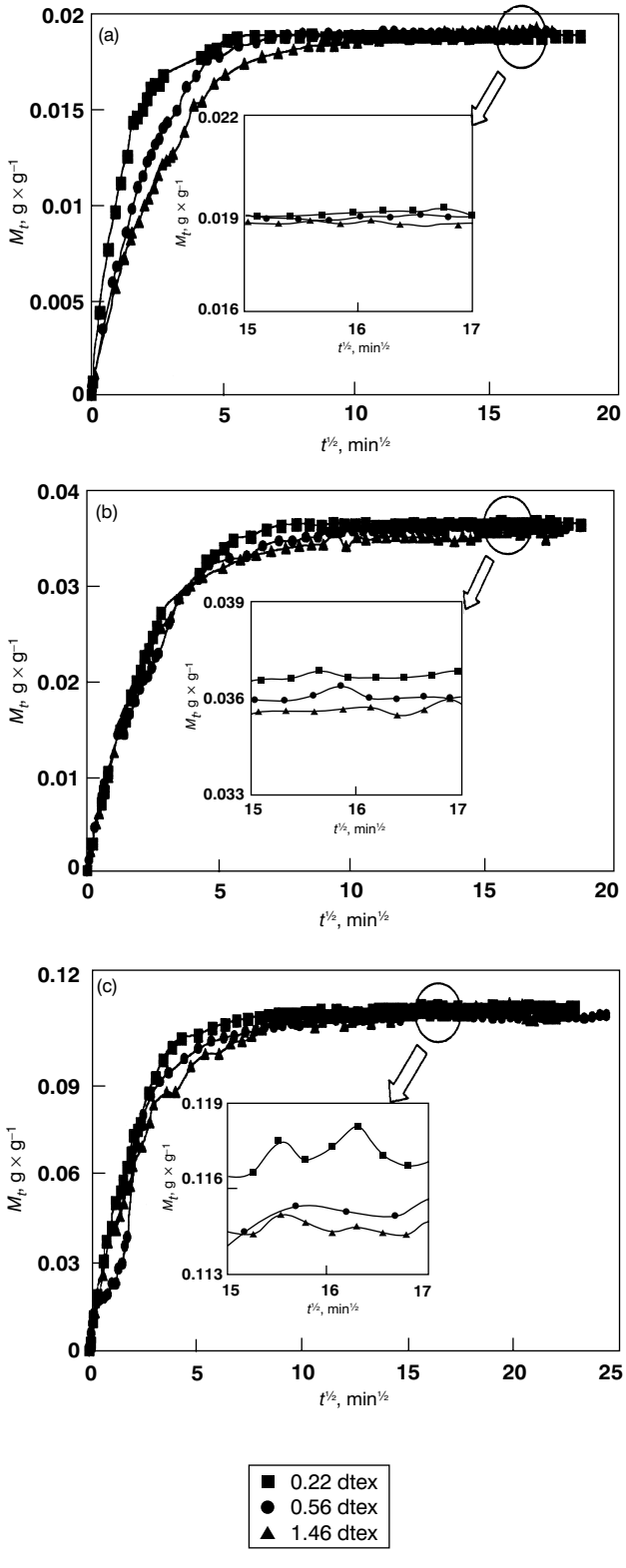


Figure 2 Dye uptake evolution (M_t) for the different fibres at 130 °C and different initial dye concentrations (a) 2, (b) 4 and (c) 16% owf

Diffusion coefficient differences

The diffusion coefficients (D_f) for the microfibres and the conventional fibre were analysed only during the infinite dyebath phase for infinite and transitional dyebaths. The diffusion coefficient for the finite dyebath configuration corresponding to very low initial dye concentrations has not been studied. In fact, the D_f values obtained in the case of the finite dyebath condition are much lower than that obtained previously (infinite dyebath).

The diffusion coefficient differences, measured as D_f/r^2, for the three fibres at difference initial dye concentrations

(2, 4 and 16% owf) are shown in Figure 3. The first observation is that for the same initial dye concentration, the duration of the infinite dyebath phase decreases with a decrease in fibre count. This means that the infinite dyebath phase time length is shorter for microfibres than for conventional fibres. The second observation is that the variations among the D_f/r^2 curves as a function of fibre count are more important for lower initial dye concentrations. In the case of 16% owf initial dye concentration there are no differences among D_f/r^2 curves for all the fibres (i.e. all the D_f curves are superimposed).

It is considered that these two observations are due to the combination of the two main phenomena involving the surface area (A) differences and the diffusional boundary layer influence that changes as the initial dye concentration is increased.

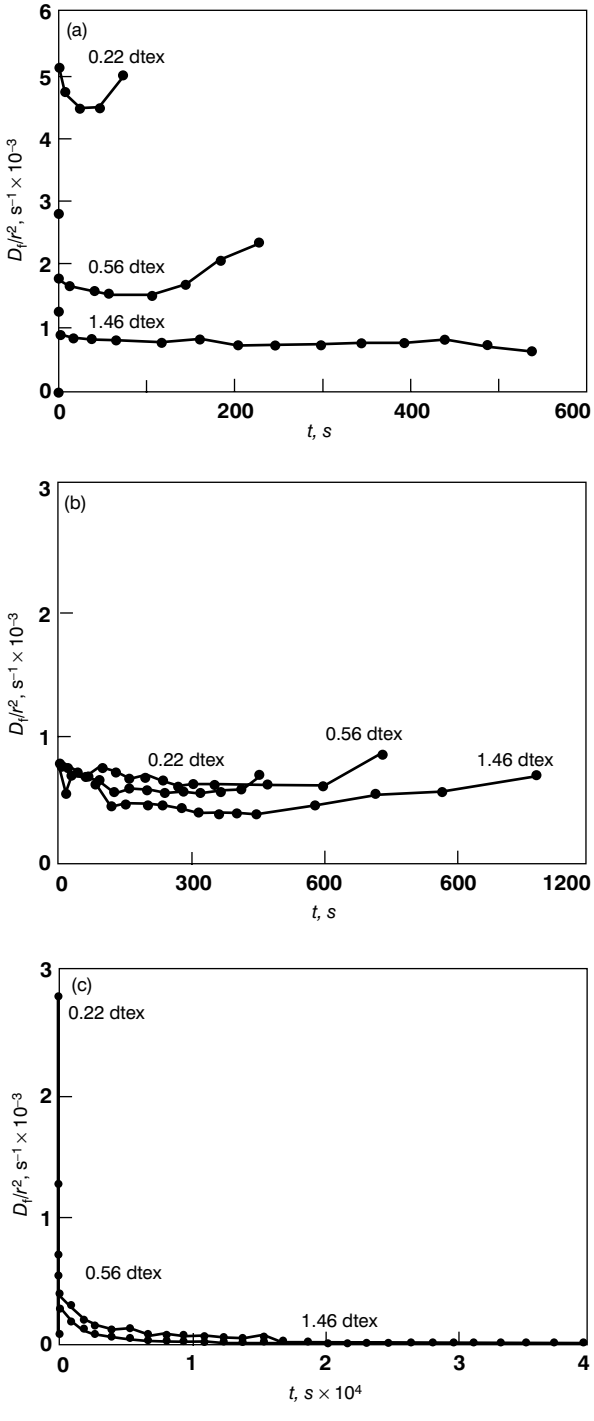


Figure 3 D_f/r^2 values for the different fibres at 130 °C and different initial dye concentrations (a) 2, (b) 4 and (c) 16% owf

Therefore, for low initial dye concentrations the duration of the infinite dyebath is much lower for microfibres because their dyeing capacity largely exceeds the dyebath dyeing capacity. This can be explained by the higher number of dyeing sites in microfibres. Moreover, for low initial dye concentrations the diffusional boundary layer does not disturb the sorption process or, indirectly, the diffusion process.

On the other hand, for high initial dye concentrations, the dyebath dyeing capacity is sufficient and the diffusional boundary layer influence becomes important and disturbs the sorption process. This leads to the diminution of differences among D_f/r^2 curves for all the fibres.

From these results, it is confirmed that differences among D_f/r^2 values between microfibres and conventional fibres are noticeable at lower initial dye concentrations while the differences at high initial dye concentrations are very small. Therefore, in the practical dyeing process of polyester microfibres, the diffusion coefficient of the disperse dye is an important parameter for dyers. Understanding the differences between the diffusion coefficient for microfibres and conventional fibres, as a function of initial dye concentration, should help dyers achieve good dyeing results with microfibres.

Conclusions

The first conclusion that can be reached from the results of this study is that the simple Langmuir sorption isotherm fits well to the experimental sorption isotherms obtained at high dyeing temperatures. The correlation is, however, better for microfibres than for conventional fibres. These results confirm the observations found in the literature about high temperature sorption isotherms.

The second conclusion deals with the variations of dyeing uptake rates observed for different initial dye concentrations and different fibre counts. The surface area and the diffusional boundary layer interdependent variations can explain the changes in the dyeing uptake rates.

Finally, the diffusion coefficients were obtained as a function of time for different fibre counts and initial conditions. It is observed a faster diffusion rate which is greater for low initial dye concentrations and for microfibres.

This initial study has helped to further the understanding of the dyeing properties of polyester microfibres. Further work is now underway to investigate the differences in the dyeing properties of conventional polyester fibres and supermicrofibres for different initial dye concentrations, dyeing temperatures and fibre counts. The main objective is to develop a diffusion coefficient mathematical model, which depends on measurable dyeing parameters, and can be applied to microfibres dyeing.

References

1. M C Tubbs and P N Daniels, *Textile Terms Definitions*, 9th Edn (Manchester: Textile Institute, 1991) 209.
2. S M Burkinshaw, *Chemical Principles of Synthetic Fibre Dyeing* (London: Blackie Academic & Professional, 1995) 194.

3. J Shin and M Bide, *J.S.D.C.*, **116** (2000) 305.
4. A Lallam, J Michalowska, L Schacher and P Viallier, *J.S.D.C.*, **113** (1997) 107.
5. E Cleve, E Bach, U Denter, H Duffner and E Schollmeyer, *Text. Res. J.*, **67** (1997) 701.
6. J Crank, *Philosoph. Mag.,* **39** (1948) 362.
7. J N Etters and A Urbanik, *Text. Res. J.*, **53** (1983) 598.
8. J N Etters, *Text. Res. J.*, **64** (1994) 406.
9. T Shibusawa, *J.S.D.C.*, **101** (1985) 231.
10. A H Wilson, *Philosoph. Mag.,* **39** (1948) 48.
11. W McDowell and R Weingarten, *J.S.D.C.*, **85** (1969) 589.
12. V Koncar and M Casetta, *Int. J. Modell. Simul.*, **21** (2001) 191.
13. M Casetta, V Koncar and C Cazé, *Text. Res. J.*, **71** (2001) 357.
14. W J Sichina, *DSC as Problem Solving Tool: Measurement of Percent Crystallinity of Thermoplastics* (Norwalk, USA: Perkin Elmer, 2000) 1.
15. S B Warner, *Fiber Science* (New Jersey, USA: Prentice-Hall Inc., 1995) 39.
16. M J Schuler and W R Remington, *Disc. Faraday Soc.*, **16** (1954) 201.
17. T Shibusawa and T Nakamura, *J. Polym. Sci. Part B, Polym. Phys.*, **33** (1995) 159.
18. T Nakamura, R B Rama and Y Kamiishi, *Text. Res. J.*, **70** (2000) 961.
19. T Nakamura, S Ohwaki and T Shibusawa, *Text. Res. J.*, **65** (1995) 113.