DIFFUSION OF DISPERSE DYES INTO SUPERMICROFIBRES

K. H. Park and V. Koncar*

GEMTEX/ENSAIT,
9, rue de l'Ermitage - BP 30329 - 59056 ROUBAIX CEDEX 01 FRANCE
keun-hoo.park@ensait.fr, vladan.koncar@ensait.fr*

Abstract

All dyers share the common goal of achieving the correct shade as early as the first dyeing. But the dyeing process is very complex, being characterised by the diffusion-controlled sorption of dyes that depends on several physicochemical parameters.
Moreover, the dyeing properties relating to microfibres and conventional fibres are caused by different properties such as the exposed surface area and the crystallinity index.
Wilson and Hill developed equations describing the uptake rate of disperse dyes by a cylindrical fibre model as a function of the diffusion coefficient and the nature of the dyebath. The inverse of Shibusawa's polynomial approximation of Hill's and Wilson's equation is used to compute the diffusion coefficient, which depends on the initial dye concentration, the time and the fibre count at a fixed temperature.
In this paper, the sorption isotherms, the diffusion coefficient, the dye concentration evolution into the fibres and the dyeing uptake rate are computed from experimental results for conventional fibres, microfibres and supermicrofibres. The sorption isotherms and the diffusion coefficient evolutions as a function of time, initial dye concentration and temperature for supermicrofibres are discussed by considering the surface area and the diffusional boundary layer's influence. Important differences in the dyeing properties are observed, depending on the fibre count, which should be useful in the optimisation of the supermicrofibre dyeing process. The aim is to provide a tool for dyeing practitioners to increase dyeing reproducibility and to improve the performance of 'right-first-time' production.

Key words:

dyeing, diffusion, supermicrofibres

1. Introduction

A microfibre is traditionally defined as *a fibre or filament of linear density below approximately 1 dtex*. However, even finer fibres of less than 0.3 dtex are produced, these commonly being referred to as supermicrofibres or ultrafine fibres [1].
It is obvious that the physical, mechanical and especially the dyeing properties of these various microfibres are quite different. First, the reduction of filament linear density is also accompanied by an increase in the surface area per unit volume of the filament. In fact, the specific surface increases markedly with the decrease in filament linear density [2, 3].
Moreover, the microfibre production method changes as a function of the filament count. For instance, microfibres are often produced by direct spinning methods, and supermicrofibres in contrast are generally produced by the conjugate spinning method.
Therefore, even if there is no difference in the chemical structure or morphology, various microfibres exhibit several important differences related to dyeing properties. These differences are induced by different surface areas, which has a twofold influence.
First, the diffusion rate of disperse dye molecules into the fibre is different during dyeing; secondly, the visual and instrumental depth of dyed microfibres are also different because of modified light reflection properties depending on the microfibre counts.
Most theoretical equations describing the overall rate of dyeing have been derived by assuming that this is determined by the dye diffusion rate within a fibre [4-9].
Diffusion of dyes into polyester fibres can occur under both infinite and finite dyebath conditions during the dyeing process. In the case of an infinite dyebath, the dye concentration in the bath does not

change during the sorption process. In the case of a finite dyebath, the dye concentration at the fibre surface continuously decreases during the sorption process until equilibrium between the dye concentration into polyester fibres and in the bath is achieved [10].

The diffusion rate of dye molecules into polyester fibres from a well-stirred solution is expressed by Wilson's equation for a finite dyebath (1). Equation (1) is reduced to Hill's equation (2) when fractional exhaustion $E_\infty = 0$, i.e. describing the dyeing rate from an infinite dyebath.

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

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

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 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 (cm²/s), parameter α corresponds to $(1-E_\infty)/E_\infty$, where E_∞ is the fractional equilibrium exhaustion, and the value β_n 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 throughout the dyeing process. In the case of lower initial dye concentrations, two different dyeing configurations are possible: a transitional dyebath (first an infinite and then a finite dyebath) or a finite dyebath only. As shown previously [11, 12], the dye diffusion into the fibre is more important during the infinite dyebath, enabling a rapid increase in 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 infinite dyebath configuration for supermicrofibres, microfibres and conventional fibres at the fixed dyeing temperatures (120 and 130°C).

2. Experimental study

2.1. Fibres and dyeing procedure

The polyester multifilament yarns, 0.07 dtex (Sea-Islands fibre type) 0.22 dtex (77 dtex/300 fil), 0.56 dtex (83 dtex/144 fil) and 1.46 dtex (292 dtex/200 fil) were used. All these fibres were obtained from Hyusung Inc., South Korea. The fibre radius R (cm) and the specific surface area A (cm2/g) were computed for all the fibres and are summarised in the Table 1.

Table 1. Experimental parameters

Parameter	Parameter values			
	0.07 dtex	0.22 dtex	0.56 dtex	1.46 dtex
Q, l/kg	50 / 1	50 / 1	50 / 1	50 / 1
R, cm	0.125×10^{-3}	0.254×10^{-3}	0.375×10^{-3}	0.490×10^{-3}
A, cm²/g	11.78×10^3	7.26×10^3	4.21×10^3	2.11×10^3
X,%	27	32	31	32

Dyeing of all polyester yarns was carried out with C.I. Disperse Blue 56 without further purification. The quantity of 14 g of yarn was used for the dyeing procedure in a well-stirred dyebath, and the liquor ratio (Q) was 50:1. The dyeings were carried out at two different temperatures, 120°C and 130°C, in order to fulfil the conditions of Hill's equation. These temperatures were used in order to analyse the supermicrofibres' dyeing properties as a function of the dyebath temperature. Initially, the yarn was placed in a dyebath at a temperature of about 90°C. This was then heated up as quickly as possible (ca. 4 min) to 120°C or 130°C and maintained at this temperature for several hours (time of dyeing). 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 (by applying the Beer-Lambert law). Then, from these results, the dye concentration within the fibre was computed. The initial dye concentrations range from 1% (on the weight of fibre, o.w.f.) to 16%.

2.2. Crystallinity index measurements

The crystallinity index (X) was determined by differential scanning calorimetry (DSC 2920CE) measurements. Samples were examined with the temperature rate of 10°C/min up to 300°C. After that, samples were put in ice and the measurement procedure was repeated.
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 [13, 14].

2.3. Sorption isotherms

Sorption isotherms of disperse dyes, depending on various parameters (the presence of dispersing agents, the dyeing temperature, the dye structure and fibre types) are reported as Nernst-type linear distribution isotherms in the presence of a constant concentration of dispersing agent [15].
However, in real dyeing conditions, the sorption isotherms of disperse dyes on polyester fibres have more complex shapes. It has been reported that a dual mode sorption model (equation 3), that is composed of both Nernst and Langmuir sorption models, may be more appropriate [16-19].

$$C_f = C_p + \sum_{i=1}^{n} C_{Li} = K_P C_b + \sum_{i=1}^{n} \frac{K_{Li} S_i C_b}{1 + K_{Li} C_b} , \qquad (3)$$

where C_f (g/kg) and C_b (g/L) are the equilibrium dye concentrations on the fibre and in the dyebath, C_P (g/kg) and C_L (g/kg) are the equilibrium concentrations of dye on the fibre sorbed by Nernst type partitioning and Langmuir sorption, respectively. S (g/kg) is the saturation value for Langmuir sorption, K_P (L/kg) is the partition coefficient and K_{Li} (L/g) is the Langmuir constant. This model can be simplified to the simple dual-mode sorption model where $n=1$.
In this study, the disperse dye isotherms and their sorption models were determined for supermicrofibres, microfibres and conventional polyester fibres (0.07, 0.22, 0.56 and 1.46 dtex) at two different dyeing temperatures (120 and 130°C) in order to understand the parameters' evolution.

2.4. Dye uptake rate and diffusion coefficient

In Hill's and Wilson's equations, the diffusion coefficient is considered as constant. In fact, the mean value of D_f (diffusion coefficient) has been used during the whole dyeing process. We consider the value of D_f as constant but only for a short period of time, when the temperature and the dye concentration variations are small. Therefore, an inverse Hill's equation is then used during this short period to compute diffusion coefficient considered as constant. In fact, Shibusawa's approximation of Hill's equation has been utilised to compute the D_f values for the infinite dyebath phase. This procedure was detailed in our previous work [16].
In this article, we have computed the diffusion coefficient evolution for two different dyebath temperatures and for different fibre counts.
The results obtained were then compared and analysed together with the corresponding dye uptake rate. Important differences were observed depending on the dyebath temperature, initial dye concentration and the fibre count. Moreover, several interesting conclusions confirming our previous studies have been made.
The experimental parameters for all experiments carried out during our research work are summarised in Table 1.

3. Results and Discussions

In this section, we present all the results concerning the sorption isotherms, dye uptake and diffusion coefficient differences, together with discussions and an attempt to understand the phenomena that influence the dyeing process.

3.1. Sorption isotherms for different fibres

It has been shown that the sorption isotherms of fibres with counts of 0.22 dtex, 0.56 dtex and 1.46 dtex at a dyebath temperature of 130°C are mostly of the double Langmuir type [19].
Many results in the literature 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 amount of dye molecules [20-22].
Figure 1 shows the sorption isotherms for the supermicrofibre (0.07 dtex) at two different dyeing temperatures (120 and 130°C) in this present study .
All the sorption parameters are given in Table 2 for 120°C and in Table 3 for 130°C respectively, where R (%) is the degree of correlation between the experimental results and the sorption isotherm model.

Table 2. Sorption parameters for 0.07 dtex supermicrofibre, 0.22 dtex and 0.56 dtex microfibres and 1.46 dtex conventional fibres at 120°C

Parameter	Sorption parameter values at 130°C			
	0.07 dtex	0.22 dtex	0.56 dtex	1.46 dtex
K_p, L/g	153	-	-	-
K_{L1}, L/g	14.11	0.38	0.33	0.26
S_1, g/kg	83.87	194.36	278.33	547.52
K_{L2}, L/g	-	10.90	14.73	37.19
S, g/kg	-	76.58	56.39	34.39
R,%	99.89	99.74	99.74	98.97

Table 3. Sorption parameters for 0.07 dtex supermicrofibre, 0.22 dtex and 0.56 dtex microfibres and 1.46 dtex conventional fibres at 130°C

Parameter	Sorption parameter values at 120°C			
	0.07 dtex	0.22 dtex	0.56 dtex	1.46 dtex
K_p, L/g	90.23	-	-	-
K_{L1}, L/g	8.60	13.29	11.41	17.64
S_1, g/kg	80.23	489.49	236.34	617.42
K_{L2}, L/g	-	3.04	0.17	1.69
S, g/kg	-	141.13	71.44	133.96
R,%	99.63	99.94	99.97	99.91
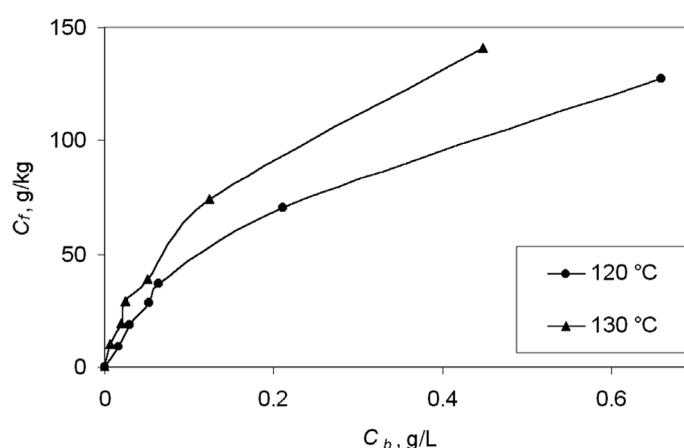
Figure 1. Sorption isotherms for supermicrofibre (0.07 dtex) at two different dyeing temperatures (120 and 130°C)

For the supermicrofibre, the sorption isotherm fits the simple dual mode sorption model composed of the Nernst and the first-order ($n=1$) Langmuir sorption models.
It is interesting to point out that for the supermicrofibre (0.07 dtex), the parameters K_P, K_{L1} and S decrease as the dyebath temperature decreases.

Also, the only Langmuir sorption-based model is not sufficient to describe the supermicrofibres' sorption isotherms. In this case, the sorption isotherms have to be modelled by a simple dual mode Nernst and Langmuir sorption models for 120 and 130°C.

3.2. Dye uptake and diffusion coefficient analysis

The rate of dye uptake (M_t/M_∞) and the sorption value of M_t ($M_\infty = \lim\limits_{t \to \infty} M_t$) were investigated for different fibres, different initial dye concentrations and at two dyebath temperatures (120 and 130°C). These differences have been analysed and discussed in this section. After that, the diffusion coefficients for all the cases were computed and compared. The diffusion coefficient evolution obtained from the inverse Hill's model corresponding to the infinite dyebath phase, describes the dye uptake rate evolution in the first phase of the dyeing process.

The dye uptake rate evolutions for all the fibres (0.07 dtex, 0.22 dtex, 0.56 dtex and 1.46 dtex) at 120°C dyebath temperature and for the initial dye concentrations of 8% o.w.f. are compared in Figure 2. The same structure of dye uptake rates at 130°C is shown in Figure 3.
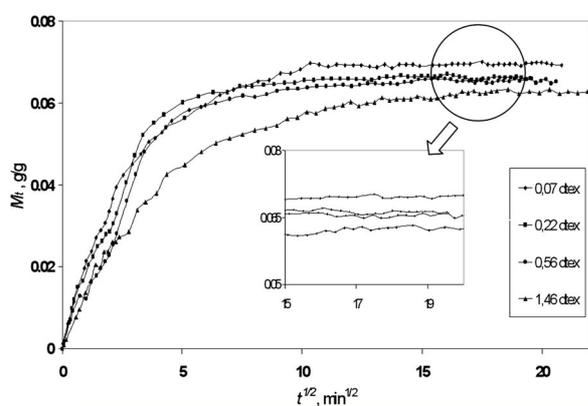
Figure 2. Dye amount evolution (M_t) vs. time for different fibres for 8% initial dye concentration at 120°C
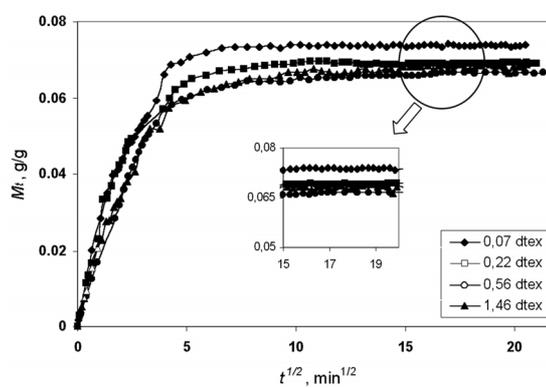
Figure 3. Dye amount evolution (M_t) vs. time for different fibres for 8% initial dye concentration at 130°C

It is clear that the dye uptake rate at time t, before the equilibrium, (M_t) increases faster as the fibre count decreases. This phenomenon is valid for both dyebath temperatures, and it can be explained by the larger surface area exposed to dye molecules for supermicrofibres in comparison to that for microfibres or conventional fibres. However, this rate phenomenon is more important at the lower temperature of 120°C, and can be explained by the contribution of surface area, which is more important at 120°C. At 130°C the importance of dyebath temperature contribution becomes more significant. Therefore, as the diffusion of dye molecules is more important at 130°C, the surface area exposed to dye molecules has less importance and differences in dye uptake rate evolutions (M_t) are smaller.

Another important parameter of the supermicrofibre dyeing process is the saturation value of M_t (i.e. M_∞).

From Figures 2 and 3, it is clear that the M_∞ value increases as the dyebath temperature increases, and especially as the polyester fibre count decreases.

Thus, the statement that supermicrofibres have a higher dyeing capacity than microfibres (and microfibres have a higher dyeing capacity than conventional fibres) due to the quantity of the available dyeing sites is confirmed. For higher initial dye concentrations and higher dyebath temperatures, there are more molecules to be fixed on available dyeing sites.

The diffusion coefficient (D_f) for the supermicrofibres, microfibres and conventional fibres were analysed only during the infinite dyebath phase for infinite and transitional dyebaths. We have not studied the diffusion coefficient for the finite dyebath configuration, which due to their low values correspond to very low initial dye concentrations. In fact the diffusion coefficient for the infinite dyebath configuration illustrates the slope of dye uptake rate during the initial stage. Therefore, the diffusion coefficient measures the intensity of variations of M_t/M_∞, and not the variations of dye quantity into the polyester fibres or microfibres. Thus, the diffusion coefficient is a relative parameter.

Therefore, any given dyeing process is completely defined by the diffusion coefficient D_f and the saturation dye uptake M_∞.

As in our previous work [16], our principal observation is that for transitional baths, the duration of the infinite dyebath phase decreases as the fibre count decreases. This is specially marked for a supermicrofibre, where the dyeing capacity is extremely high and the amount of dye molecules penetrating the supermicrofibres is important at the beginning of dyeing.

Finally, in Figure 4, the case of the supermicrofibre (0.07 dtex) with the 16% o.w.f initial dye concentration (infinite dyebath) at two different dyebath temperatures (120°C and 130°C) is presented. It is evident that the temperature of bath influences the diffusion coefficient. In fact, the diffusion is better at higher temperature. This is verified for all the fibre counts.
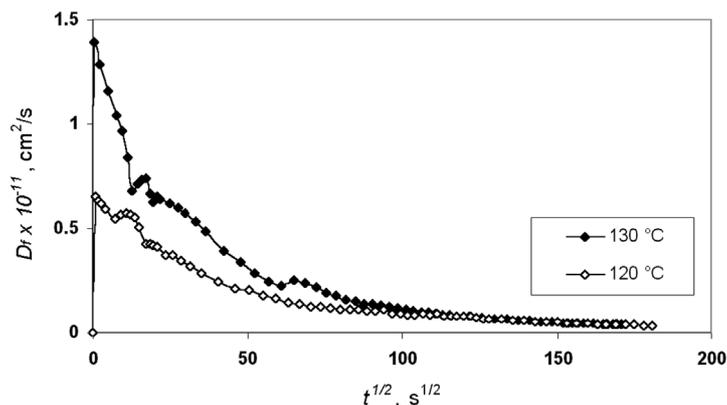
Figure 4. D_f for different dyebath temperatures (120 and 130°C)
at 16% initial dye concentration for supermicrofibre

4. Conclusions

The first conclusion of this study is that the sorption isotherms of supermicrofibres are different from those of microfibres and conventional fibres. This means that the dyeing process of supermicrofibres is different, and that these kinds of fibres have to be dyed with caution.

The second conclusion confirms the results of our previous study. Therefore, the surface area and different dyeing capacities of supermicrofibres explain the changes in the dyeing uptake rates. It is obvious that supermicrofibres can accept more dyes, and that they have to be dyed at higher temperatures.

References

1. *J E McIntyre, P N Daniels, Textile Terms Definitions, 10th ed, (Manchester, Textile Institute, 1995) 209.*
2. *S M Burkinshaw, Chemical Principles of Synthetic Fiber Dyeing (London, Blackie Academic & Professional, Chapman & Hall, 1995) 194.*
3. *J Shin and M Bide, J. Soc. Dyers Colour., **116** (2000) 305.*
4. *E Cleve, E Bach, U Denter, * Duffner and E Schollmeyer, Textile Res. J., **67** (1997) 701.*
5. *J Crank, Philosoph. Mag., **39** (1948) 362.*
6. *J N Etters and A Urbanik, Textile Res. J., **53** (1983) 598.*
7. *J N Etters, Textile Res. J., **64** (1994) 406.*
8. *T Shibusawa, J. Soc. Dyers Colour., **101** (1985) 231.*
9. *A H Wilson, Philosoph. Mag., **39** (1948) 48.*
10. *W McDowell, and R Weingarten, J. Soc. Dyers Colour., **85** (1969) 589.*
11. *V Koncar and M Casetta, International J. of Modelling and Simulation, **21** (2001) 191.*
12. *M Casetta, V Koncar and C Cazé, Textile Res. J., **71** (2001) 357.*
13. *W J Sichina, DSC as Problem Solving Tool: Measurement of Percent Crystallinity of Thermoplastics (Norwalk, USA: Perkin Elmer, 2000) 1.*
14. *S B Warner, Fiber Science (New Jersey, USA: Prentice-Hall Inc., 1995) 39.*
15. *M J Schuler and W R Remington, Disc. Faraday Soc., **16** (1954) 201.*
16. *K H Park, M Casetta and V Koncar, Color. Technol., **118** (2002) 319*

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, Textile Res. J.,* **70** *(2000) 961.*
19. *T Shibusawa, Textile Res. J.,* **66** *(1996) 421.*
20. *T Nakamura, S Ohwaki and T Shibusawa, Textile Res. J.,* **65** *(1995) 113.*
21. *J N Etters, Journal of Applied Polymer Science,* **42** *(1991) 1519.*
22. *T Shibusawa, J. Soc. Dyers Colour.,* **96** *(1980) 293.*
23. *T Shibusawa, J. Soc. Dyers Colour.,* **104** *(1988) 28.*