ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 10, No. 4. 2004

Influence of Morphological Heterogeneity of Wool Fiber on Acid Dye Sorption

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Received 30 August 2004; accepted 18 October 2004

The influence of applied surfactants on dyeing of wool with acid milling dye at low temperature considering its chemical and morphological heterogeneity is examined. The presence of nonionic surfactant molecules reduces surface barrier to dye diffusion into the fiber. Studies show that the intercellular regions and the low sulfur proteins of endocuticle should be considered as dye penetration route into wool fiber at initial stage of diffusion.

Keywords: wool, diffusion barrier, surfactant, dye.

INTRODUCTION

When wool is dyed under standard conditions, its strength is reduced. This has been ascribed to extraction of soluble proteins from the CMC, a breakdown of cystine linkages and under severe conditions hydrolysis of peptides [1 – 3]. Higher-affinity dyes, such as acid milling dyes with larger molecules do not penetrate into the wool fiber at lower temperature and a major problem is ring dyeing. Ring dyeing can give rise to problems such as reduced fastness, shade change, or poor rubbing fastness.

It is established that the rate of dyeing with selected milling acid dyes is markedly increased when sparingly water soluble organic compounds are added to the dye bath, or wool fibers are pretreated before dyeing [1, 4 – 9] and, thus, making lower-temperature dyeing viable.

As a fiber, wool is heterogeneous, both chemically and physically. It is assumed that in the case of the wool without the damage in cuticle cells the dye uptake in early stage of adsorption is subject to the dyeing behaviour of the intercellular regions of cuticle-cuticle (surface) layer [4]. Dye possibly throughout the gaps between the scales of wool fiber penetrates fairly rapidly into the intercellular region of the surface layer and soon becomes to equilibrium with dye in outer solution.

It has been suggested, however, that lipids present at the cuticular junctions may hinder entry of dye into the fiber [10, 11]. The concept of a lipid 'barrier' to wool dyeing located at the fiber surface or near it is supported by the results, which show that extraction of normally scoured wool with lipid solvents increases the dyeing rate [1]. Significant effect on cell membrane complex (CMC), especially on the structure of δ- and β-layers which reduce to the initial dye penetration, and disruption of lipid 'barriers' by using benzyl alcohol or dyeing auxiliaries could favor to dye diffusion into the fiber [4, 6, 10].

Recently Telegin *et al* have indicated that hydrophilic/ lipophilic properties of acid dyes predetermine the mechanism of their interaction with wool fiber [12]. Temperature changes in sorption of hydrophilic dye and high values of affinity of lipophilic dye support the idea that nonkeratinous components control the transport of acid dyes into the fiber.

In present paper we intend to interpret the role of dyeing auxiliaries in the initial stage of acid milling dye sorption assuming that the intercellular region from the underside of cuticle cell and around cortical cell of wool fiber should be the pathway for dye diffusion into cuticle and cortex cell. We used the method of dyeing rate curves analysis applied by Medley and Andrews [13, 14].

THEORY

General experience shows that when the rate of dyeing of an isotropic fiber is studied, a plot of the relative dye uptake against the square root of the dyeing time gives a straight line passing through the origin over most of the dyeing time. The curve in short time of dyeing would reflect the mode of the dye penetration in the surface of the wool fiber and the straight-line the greater part reflect mode of dye penetration in the bulk phase of the fiber [14]. In the case of wool the dyeing curve is initially concave and becomes linear after some time. This lead to the assumption that a 'barrier' with small capacity of dye exists at the fiber surface. The barrier was believed to be responsible for the non-Fickian dyeing isotherms obtained with wool.

As shown in Fig. 1, the asymptote to the curve is extrapolated to intercept the ordinate axis. The slope and the intercept of this line can be used to calculate diffusion coefficient D and the "admittance" factor of the barrier α [1].

C_t / C_∞ in Figure 1 represents dye uptake at time t as a fraction of the equilibrium uptake. This has allowed many workers to examine the effects of various surface modifications on the dyeing of wool, with particular reference to the surface barrier effect. Using this technique and the rate of dyeing equation for cylinders, they were able to show that modifications of wool, which either reduced or removed the surface barrier increased the diffusion coefficient for Orange II in wool [13]. According to Medley and Andrews [14], the "admittance" of the barrier factor $\alpha = D_b C_b / \delta C_\infty$, where D_b is the diffusion coefficient in the barrier, C_b is the equilibrium concentration of dye in the barrier of thickness δ.

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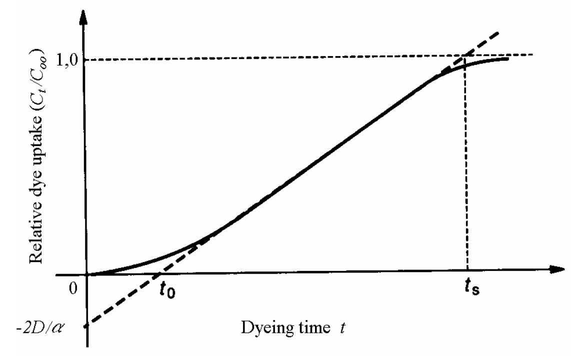

Fig. 1. The surface barrier effect in wool dyeing [1]

If *α/D,* where *D* is the diffusion coefficient in the bulk of fiber phase, is constant, i.e. diffusion coefficient and a barrier to the diffusion of dye molecules during dyeing do not change, the solution for diffusion equation is one formally dealt with equation which is given by Crank and described by Vickerstaff:

$$C_t/C_\infty = 2(D\cdot t/\pi)^{1/2}\,. \tag{1}$$

Equation (1) sometimes with satisfactory results is used in the early stage of diffusion, i.e. it applies in the initial stage of uptake for small time in connection with diffusion and surface evaporation [13]. A plot of C_t/C_∞ against $t^{1/2}$ should therefore be linear with a slope proportional to the square root of the diffusion coefficient.

In the presence of diffusion barrier the solution may be expanded in two forms for describing initial and ultimate behaviour. The equation is given by

$$C_t/C_\infty = 2(D\cdot t/\pi)^{1/2} - D/\alpha + 1/\alpha^2\left(D^3/\pi\right)t^{1/2} + \ldots \tag{2}$$

Equation (2) shows that, once the initial lag due to the barrier effect has been overcome, a plot of C_t/C_∞ against $t^{1/2}$ approaches a line of slope 2 $(D\,t/\pi)^{1/2}$ with an intercept on the sorption axis of $-D/\alpha$.

In the present paper we will concern the early stage of dyeing, which is generally accepted to be responsible for the dyeing rate of fiber and levelness of dyeing. We expressed the dyeing with acid milling dye kinetics with standard $t^{1/2}$ plot. In order to compare the results of dyeing in the presence and in the absence of dyeing auxiliaries we plotted the curves of C_t/C_∞ against $t^{1/2}$. We believed that the $-D/\alpha$ values comprising the "admittance" of the barrier factor will help to appreciate the origin of surface layer barrier and the role of CMC in the mechanism of wool dyeing with acid milling dye.

The dye absorption rate constants were calculated using modified Cegarra-Puente equation suitable to baths with exhaustion [15]:

$$\ln\left[-\ln\left(1 - C_t^2/C_\infty^2\right)\right] = a\ln t + a\ln K \tag{3}$$

where a is a coefficient depending on exhaustion, C_t is the dye concentration in the fiber at the time t, C_∞ is the dye concentration at the equilibrium, K is the absorption rate constant, t is the dyeing time.

EXPERIMENTAL

Materials. The wool fabric used was treated according to ISO 105/F: 1985 (E*).* The average diameter of the merino fibers was 18.9 µm. The dye in this study used was CI Acid Blue 80 dye supplied by Clariant and purified by recrystallization three times: dissolving in hot dimethylformamide, precipitating by acetone and then filtering. Commercial dye was used in this work, also. The percentage of dye in the commercial product was obtained by weighing the extract in dimethylformamide and was used to calculate the dyeing solution recipe and dye sorption. The dyeing auxiliaries nonionic products ethoxylated alkylnonylphenol and dispersing agent mixture recommended for use in low temperature wool dyeing Lanasan LT (Clariant) and alkylaminoethoxylate and glycolic ether mixture Rucogal MSC (Rudolf Chemie) recommended use in wool and polyamide dyeing. The other reagents of analytical grade were used without purification.

Dyeing. Before dyeing samples of fabric were immersed for one hour in 0.1 M acetic acid buffer adjusted to pH 4.2 ± 0.05. We obtained dyeing rates at a dyeing time and initial dye concentration 1.7×10^{-4} mol/l. Dyeing occurred in a laboratory apparatus with magnetic bar stirrer and cylinder to girdle the sample of 10 × 20 cm fabric with dyeing liquor pH 4.2 ± 0.05 and temperature 60 °C or 85 °C. In all dyeing the liquor-to-fiber ratio was 200 : 1. After dyeing, the bath pH was unchanged. Dyeing was carried out in the absence and in the presence of auxiliaries (1.8 % owf) with commercial and purified dye. Conventional dyeing in presence of electrolyte was carried out in presence of 10 % owf sodium sulphate and of 4 % ammonium sulphate. The dye concentration in the dyebath was measured at the start and after 5, 10, 15, 20, 30, 45, 60, 90 min. and up to the dye equilibrium.

Dye sorption was calculated from the difference in dye concentration before and after dyeing time *t.* Dye concentration in liquor was measured in 10 mm cell using the Spectronic Unicom Genesys TM spectrophotometer. On completion of dyeing, wool fabric samples were removed from the dye liquor rinsed in water to remove any loosely adsorbed dye and dried in air.

Colour yield *K*/*S* of dyed samples was measured using Spektroflash SF 450 PLUS (Datacolor) spectrophotometer.

RESULTS AND DISCUSSIONS

In Fig. 2 the isotherms of dye on fibers are presented and Fig. 3 shows the plots of dye uptake C_t against the square root of dyeing time $t^{1/2}$ for dyeing solution without any auxiliaries (A) and in presence of dyeing organic auxiliaries (LAN or MSC) or electrolyte (EL).

Values for the initial kinetic constant *K* in the absence and the presence of auxiliaries are shown in Table 1. It is clear from these results that the use of nonionic surface active agents leads to a considerable increase in the apparent dye uptake and that addition of Lanasan LT (LAN) as well as Rucogal MSC (MSC) renders the whole quantity of dye to penetrate into fiber more readily as suggested by kinetic constant *K*.

It is considered that alkoxytethylated nonylphenol in the dyebath had a significant effect on CMC [6]. This occurs by the way the modification of hydrophobic domains of the CMC and that the lipid disruption and alteration of the internal lipid bilayer structure could favor

Table 1. Kinetic constant (K) and half time dyeing ($t_{1/2}$) in the presence and in the absence of auxiliaries at different temperatures

Auxiliary	60 °C		85 °C	
	K	$t_{1/2}$	K	$t_{1/2}$
A*	1.86	48.4	10	9
LAN	2.45	32.3	16	6
MSC	1.56	46.0	26	4
EL*	0.35	150.0	-	-

*A – in the absence of auxiliaries; EL – electrolyte;
K – kinetic constant, × 10^{-3} min^{-1}, t – time, min.

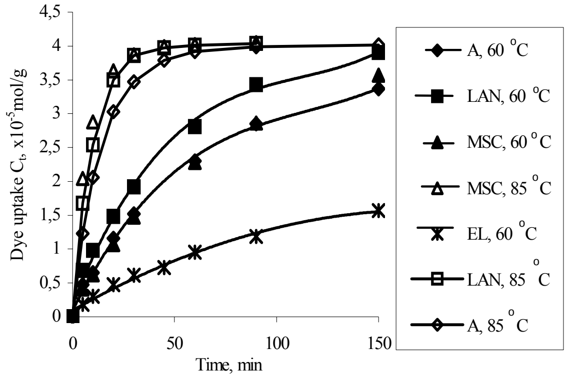

Fig. 2. Dye absorption kinetics

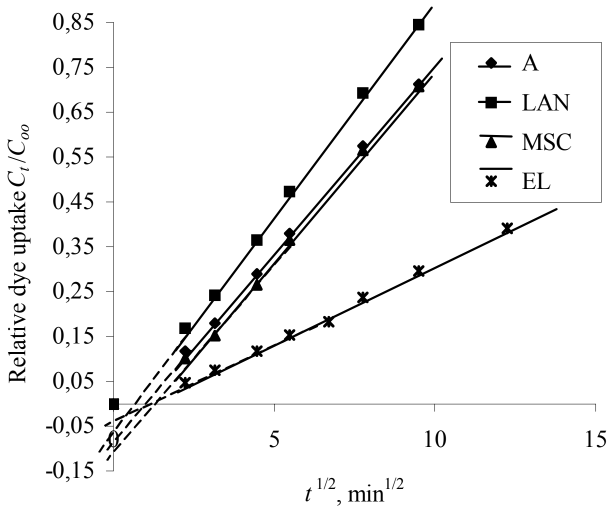

Fig. 3. Relationship of relative dye uptake versus dyeing time ($t_{1/2}$) at temperature of 60 °C

dye diffusion into the fiber. From Figure 2 and Table 1 with LAN at 60 °C temperature can be seen to have the higher increase in total dye absorption and in dyeing rate compared with MSC. Figure 3 shows that the intercept on dye absorption axis in the case of LAN is significantly reduced, while with MSC it did not reduce compared with that of dyeing in the absence of auxiliary. The result was different when dyeing at 85 °C was carried out. In this case MSC in comparison with LAN is produced a higher increase in the dye absorption and dyeing rate, particularly in the early stage of dyeing. It can be seen from Figures 3 and 4 that at the increase of temperature for the dyeing in the absence of auxiliaries a value – D/α remains significant, i.e. the dye diffusion barrier at 80 °C was important as well as for 60 °C.

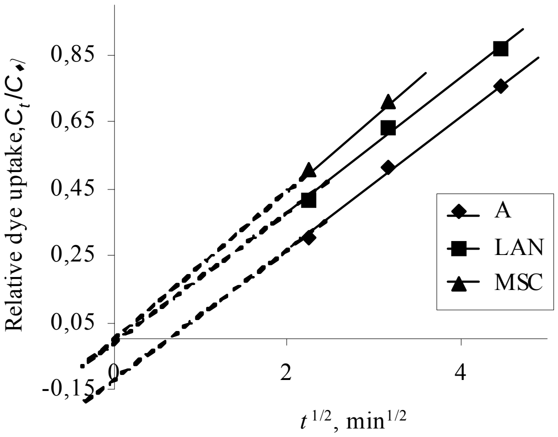

Fig. 4. Relationship of relative dye uptake versus dyeing time ($t^{1/2}$) at temperature 85 °C

Figure 5 shows that in the initial stage of dye absorption, when the concentration of dye in the fiber was about 0.6×10^{-5} mol/g, the values of kinetic constant for LAN were significantly higher compared to those obtained at the dye concentration of $0.8 \times 10^{-5} - 2.0 \times 10^{-5}$ mol/g.

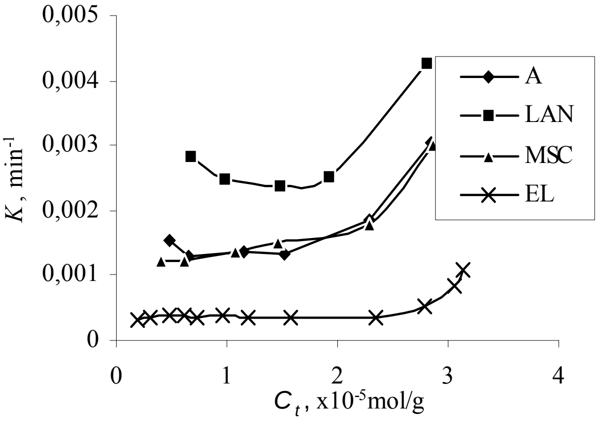

Fig. 5. Relationship of kinetic constant (K) and dye concentration (C_t) on the fiber at time

In general colour yield for dyed samples should be related with amount of dye in a fiber up to a certain dye concentration on the fiber. Colour yield of dyed samples in this study have been measured and results are shown in Table 2. The results show that there is an important variation in the colour yield and the amount of dye in the fiber relationship when fabric samples were dyed at 60 °C temperature. The variation of this relationship was small or disappeared when dyeing occurred at 85 °C temperature.

We have compared colour yield values changes due to the presence of auxiliary for the samples dyed at 60 °C. The values obtained were compared with the increase of kinetic constant. The result was surprising. The relation of kinetic constants values taken from Table 1 $K_{\text{LAN}} / K_{\text{MSC}}$ and the relation of colour yield (K/S) values taken from Table 2 $(K/S)_{\text{LAN}}/(K/S)_{\text{MSC}}$ was almost the same – 1.2.

Table 2. Effect of auxiliaries and temperature on dye exhaustion (E) on colour yield (K/S) of wool fabric

Auxiliary	60 °C			85 °C		
	t, min	E, %	K/S	t, min	E, %	K/S
A*	300	98.7	21.9	150	99.0	28.2
LAN	240	10.0	26.6	90	99.4	28.4
MSC	270	97.0	22.2	90	99.7	29.3
EL*	600	77.3	19.3	360	97.1	26.2

*A – in the absence of auxiliaries; EL – electrolyte

The comparison of kinetic constants and colour yield values for LAN with respect to the corresponding values for dyeing in the absence of auxiliary (K_{A} and $(K/S)_{\mathrm{A}}$ respectively) have shown, that $K_{\mathrm{LAN}} / K_{\mathrm{A}} = 1.3$ and $(K/S)_{\mathrm{LAN}} /(K/S)_{\mathrm{A}} = 1.2$. Thus, above presented results allow assume that the enhanced rate of dye uptake should be considered to be due to the facility of increase on the amount of dye in the surface layer cuticle of wool fiber. The approximative calculation of amount of active sites represented by the basic groups of cuticle proteins should be less than 8.3×10^{-5} equiv/g. In the CMC and endocuticle jointly the amount of basic groups should be less than 3.8×10^{-5} equiv/g. Thus, 4.0×10^{-5} mol/g (see Fig. 2) of dye absorbed in the wool fiber should correspond to a half of the amount of basic groups considered in cuticle or to the amount of basic groups present in CMC and endocuticle.

The experimental results presented in Figure 3 do not allow to judge that the dye could diffuse into exocuticle, when the dye uptake was less than about 3×10^{-5} mol/g or $C_t / C_\infty = 0.75$.

The results suggest that acid milling dye in exhaust dyeing at 60 °C diffuse first through intercellular cement component of CMC and then into the endocuticle. The results presented in Table 2 allow assume that when dye sorption equilibrium is established, dye is transferred from endocuticle rather to the sulphur-rich exocuticle than into the cortex.

CONCLUSIONS

The dyeing properties of wool at low temperature have been evaluated using acid milling dye and nonionic auxiliaries agents.

The presence of nonionic surfactant molecules during dyeing with acid milling dye reduces surface barrier in the initial stage of diffusion into the wool fiber. It should be considered that acid milling dye at 60 °C in the exhaust dyeing diffuse first through intercellular cement component of CMC and then into the endocuticle. When dye sorption equilibrium is established dye is transferred from endocuticle rather to the sulphur-rich exocuticle than into the cortex.

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