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Dyeing Kinetics of Vinylon Modified with β-Cyclodextrin

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Abstract
In this paper, dyeing experiments were performed on vinylon modified with β-cyclodextrin using a reactive dye. The kinetics of the dyeing process for vinylon modified with β-cyclodextrin was researched by measuring the dye uptake, time of half dyeing, dyeing rate constant and the diffusion coefficient. The results show that grafting β-cyclodextrin onto vinylon enables to increase the diffusion and uptake of reactive dyestuffs from a bath, and that the degree of grafting is closely related to the improvement of diffusion and uptake of dyestuffs.

Key words: *dyeing kinetics, β-cyclodextrin, modified vinylon fibres, reactive dyestuff.*

Introduction

Vinylon fibre is an important synthetic fibre that is widely used in industry, agriculture, fishing, and especially in the textile industry because of its relatively high moisture regain, light weight, durability, weather resistance, abrasion resistance, light resistance and corrosion resistance [1]. However, the dyeing of vinylon fibres by the conventional method (with reactive dyestuffs in a dyebath) gives a very low rate of dye-uptake. Vinylon fibre is generally difficult to dye deeply because of its acetalisation, in the process of which a large quantity of hydroxyl groups in the amorphous region of the fibre form a methylene ether link with formaldehyde [2] and the skin-core structure, in which the compact skin of fibres slows down the diffusion rate of dyestuffs [3].

β-cyclodextrin is seven toroidal-shaped cyclic oligosaccharides with a hydrophilic outer surface which can react with reactive dyestuffs and an internal hydrophobic hollow interior which can entrap a vast number of lipophilic compounds in their hydrophobic cavity and yield complexes with many dyestuffs [4], depending on their sizes and molecular structures. Many attempts to utilise β-cyclodextrin and β-cyclodextrin derivatives in textile have been made in the last decade, including deodorant, aroma, antimicrobial, insect repellent, mite repellent finishes, etc [5 - 7].

In our previous work, the chemical grafting of β-cyclodextrin onto vinylon fiber had been investigated and used epichlorohydrin as crosslinking agent and different degrees of grafting β-cyclodextrin on the fiber were obtained (***Table 1***) [8]. It was found that vinylon fibre grafted with β-cyclodextrin has better dyeing properties. Currently there are various theoretical mathematical models (Vickerstaff, Patterson, Sheldon, Crank diffusion equation, Fick diffusion equation, Hill equation) of the diffusion of dyestuff from a solution into a fibre describing the time-dependent dye uptake of vinylon fibre in the dyeing exhaustion process. In this paper, the dye uptake, time of half dyeing, dyeing rate constant and diffusion coefficient were measured, and the influence of grafting β-cyclodextrin on the dyeing kinetics of vinylon modified with β-cyclodextrin using reactive dyestuffs is presented.

Experimental

Materials and chemicals

Vinylon fibre was obtained from Sinopec Sichuan vinylon works (diameter: 18 μm), and C.I. Reactive Red 2 (Reactive Red X-3B) was purchased from Taifentaixing Co. Ltd. β-cyclodextrin epichlorohydrin., sodium carbonate and all other reagents were of analytical grade. The water used was distilled.

The degrees of grafting β-cyclodextrin on vinylon fibre are shown in ***Table 1***.

Dyeing

Vinylon fibres with different grafting degrees and ungrafted vinylon fibres were dyed with C.I. Reactive Red 2 (2% o.w.f) by the conventional exhaustion method at a liquor ratio of 1 : 50. The dyeing process was carried out for 5 - 80 min at a temperature of 40 °C. The dyed fibres were washed thoroughly with distilled water and dried.

Dyeing kinetics determination in the dye exhaustion

Evaluation of the kinetics in the exhaustion process of vinylon fibres is based on the premise that an increased (decrease) concentration of dye in the fibres (in a bath) depends significantly on the dyeing time. The process of dyeing was finished at a certain time interval (5, 10, 20, 40, 60 & 80 min). After removal of the fibres from the dyebath, the dyebath was filled up with ethanol to 25 ml. The quantity of exhausted dyestuff in the fibres was estimated indirectly from the absorption of dye solution measured at its λ_{max} in the equipment (spectro-photometer TU-1901) and from the calibration curve (***Figure 1***, see page 134). In ***Equation 1*** c_∞ is the concentration of dyestuff at the moment of an equilibrium state, which also represents the maximal adsorptive capacity of fibres for dyestuffs. When the values of $1/c_t$ were plotted against $1/t$, straight lines were obtained (***Figure 2***, see page 134), where intercepts gave values of $1/c_\infty$, from which c_∞ in the dyeing

Table 1. *Different degrees of grafting β-cyclodextrin onto vinylon fibre.*

Samples	Degree of grafting, %
S0	0
S1	1
S2	2
S3	3.5
S4	5

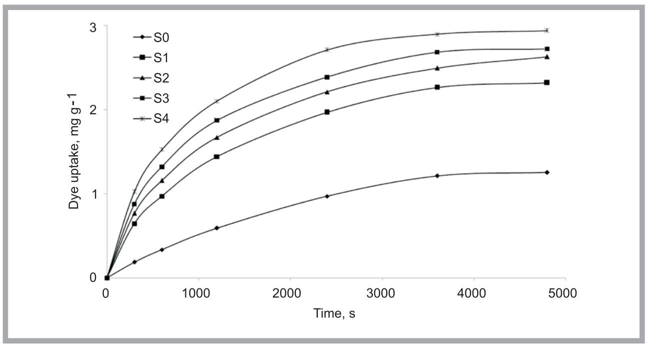

***Figure 1.** Dye uptake of the vinylon fibres examined at different dyeing times.*

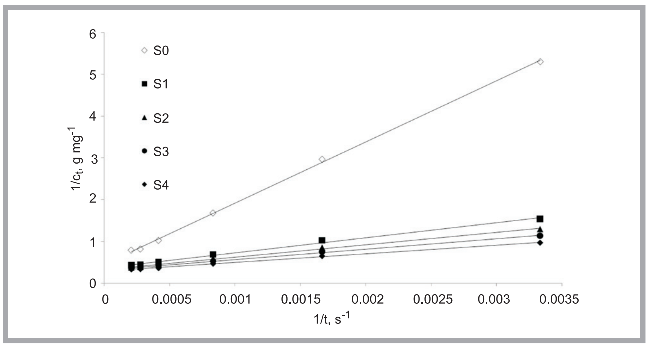

***Figure 2.** Relationship between $1/c_t$ and $1/t$ on c_∞ for vinylon fibres.*

of vinylon fibres with reactive dyestuff was evaluated [9]; the results are given in ***Table 2***.

The dependence of dyestuff exhaustion on time was used for calculating the dyeing rate constant (K). The dyeing rate constant (K) was determined from the following equation [10]:

$$K = \frac{t}{c_\infty - c_t} - \frac{t}{c_\infty} \quad (1)$$

The time of half dyeing ($t_{1/2}$) is that required for the fibre to absorb half the quantity of dyestuff absorbed in the state of equilibrium, which was calculated from hyperbolic Vicker staff's equation [11 - 13]:

$$t_{1/2} = \frac{1}{K c_\infty} \quad (2)$$

The diffusion coefficients (D) were obtained from Hill's empirical equation [10, 14] and calculated by ***Equation 3***:

$$D_{Hill} = 6324 \times 10^{-2}\ K\ c_\infty\ r^2 \quad (3)$$

where r – radius of the fibre in m, t – dyeing time interval in sec, D – diffusion coefficient in m^2s^{-1}, K – dyeing rate constant in s^{-1} from ***Equation 1***, c_t – concentration of the dyestuff in the fibre after time t in mg g^{-1}, c_∞ - concentration of dye at the moment of an equilibrium state in mg g^{-1}.

Results and discussion

Vinylon fibres modified with β-cyclodextrin and different degrees of grafting were dyed by the exhaust process from a bath with C.I. Reactive Red 2. The dyeability of these fibres was evaluated in dependence on the degree of grafting the vinylon fibres, the dyeing kinetics of which were investigated with respect to time (0 - 80 min). The dependence of dye exhaustion on time was used for calculation of the dyeing rate constant (K), the time of half dyeing ($t_{1/2}$) and the diffusion coefficient (D).

The amount of C.I. Reactive Red 2 dyestuff exhausted by vinylon fibres increases over time, as well as the degree of grafting β-cyclodextrin (***Table 2***). At all dyeing time intervals, vinylon fibres modified with β-cyclodextrin appear to have a dye yield several times higher than unmodified ones. Reactive dyestuff is first absorbed on the surface of fibres,then penetrates into fibre pores, and finally attains a state of equilibrium (between absorption and diffusion of dyestuff). The amount of dyestuff exhausted by vinylon fibres and the dye absorption rate depend on the number of active areas, which makes it possible to dye vinylon fibre deeply. The amount of active areas of vinylon fibre increases with an increase in the degree of grafting β-cyclodextrin. At all degrees of grafting vinylon fibres modified with β-cyclodextrin, there is better dyeability (***Table 2***). It is known that β-cyclodextrin has a hydrophilic outer surface composed of twenty-one hydroxyl groups, which can improve the affinity of dyestuff to the fibres, and an internal hydrophobic hollow interior, which can entrap a vast number of dyestuff molecules in its cavity to produce complexes with dyestuff. The dyeing rate constant (K), time of half dyeing ($t_{1/2}$) and diffusion coefficient (D) calculated using the hyperbolic Vickerstaff's and Hill's equations of vinylon fibres dyed with reactive dyestuffs confirm the previous results. The dyeing rate constant (K) and diffusion coefficient (D) increase and the time of half dyeing ($t_{1/2}$) decreases with an increasing degree of grafting β-cyclodextrin (***Table 2***). These results show that the affinity of reactive dyestuff to vinylon fibres is greatly increased with an increasing degree of grafing. Vinylon fibres modified with β-cyclodextrin have a higher diffusion coefficient in comparison with unmodified vinylon fibre.

***Table 2.** Dyeing rate constant (K), time of half dyeing ($t_{1/2}$) and diffusion coefficient (D) of vinylon samples at different degrees of grafting β-cyclodextrin.*

Samples	c_∞, mg g^{-1}	$K \times 10^4$, s^{-1}	$t_{1/2} \times 10^{-3}$, s	$D \times 10^{12}$, m^2s^{-1}
S0	2.17	1.45	317.8	1.61
S1	2.71	3.75	98.4	5.21
S2	2.99	3.76	88.9	5.76
S3	3.15	4.01	79.1	6.48
S4	3.39	4.20	70.2	7.29

Conclusions

In this paper, the dyeability of vinylon fibres modified with β-cyclodextrin as well as the dyeing kinetics were studied. From the results obtained we can conclude the following:

The dye uptake of vinlon fibres modified with β-cyclodextrin dyed by C.I. Reactive Red 2 is evidently improved in comparison with unmodified vinylon fibres. The highest dye uptake was measured for vinylon fibres modified with β-cyclodextrin.

The dyeing rate constant and diffusion coefficient increase and the time of half dyeing decreases with an increase in the degree of grafting β-cyclodextrin.

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