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The Kinetics of the Dyeing and Fading of Coloured Poly(ethylene-2,6-naphthalenedicarboxylate) Fiber

Ping Yueh Wang & Jin Feng Ma

Department of Textile Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan 10772, Republic of China

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ABSTRACT

The kinetic behavior of CI Disperse Blue 79 on poly(ethylene-2,6-naphthalenedicarboxylate) fiber was investigated. The dye uptake, time of half dyeing, diffusion coefficient, activation energy and dyeing rate were determined. The dyeability, light fastness, fading characteristics and the fading rate constant at the different dyeing temperatures and dye bath concentrations were also evaluated. The obtained results indicated that the free volume in a polymer–dye (diluent) system is the main factor determining the kinetic data under investigation. The rate of dyeing is closely related to the diffusion behavior of dyes on PEN fiber. The dyeing rate increases with increasing diffusion coefficient of the dye. In addition, the fading process follows first-order kinetics. © 1998 Elsevier Science Ltd

Keywords: dyeing, fading, poly(ethylene-2,6-naphthalenedicarboxylate).

INTRODUCTION

Poly(ethylene-2,6-naphthalenedicarboxylate) (PEN) is a new high performance polyester that exhibits physical and chemical properties superior to those of poly(ethylene terephthalate) (PET). The naphthalene moiety in PEN provides stiffness to the linear polymer backbone, leading to improved thermal resistance and excellent mechanical properties such as tensile properties and dimensional stability [1–3]. PEN can be prepared from commercially available dimethyl-2,6-naphthalenedicarboxylate (DM-2,6-NDC) and ethylene glycol (EG) by means of an ester-interchange reaction to form a mixture of oligomers, followed by a polycondensation to obtain the PEN prepolymer. The preparation of PEN was first described in 1948 [4]. Later on, several other patents [5–9] were disclosed dealing with the preparation and applications of PEN. Like PET, PEN is a clear resin that can be used to produce films, containers, and industrial fibers. Despite its established use and growing popularity, relatively few publications have concerned the dyeing and fading of PEN. In this paper, we present a study on the dyeability, lightfastness and fading characteristics. The dye uptake, time of half dyeing, diffusion coefficient, activation energy, dyeing rate and fading rate constant were measured.

EXPERIMENTAL

Materials

PEN fiber (breaking tenacity: 4.46 g d^{-1}, elongation at break: 13.1%, 1,60 d) was supplied by Industrial Technology Research Institute, CI Disperse Blue 79 by Allied Industrial Corp., Ltd, and a commercial sample of coloursol ACE-65, a dispersing agent, was supplied by Chen Yee Chemical Co. All other reagents were of general purpose grade.

Dyeing

PEN knitted fabric was dyed with CI Disperse Blue 79 by the conventional exhaustion method, using Coloursol ACE-65 as dispersing agent in the dyeing bath at a liquor ratio 1:50. The dyeing process was carried out for 5–120 min at a temperature of 90–120°C. The dyed samples were washed in a bath containing 2 g l^{-1} of NaOH and 2 g l^{-1} of $Na_2S_2O_4$ at 80°C for 20 min. The dyeing process is shown in Fig. 1.

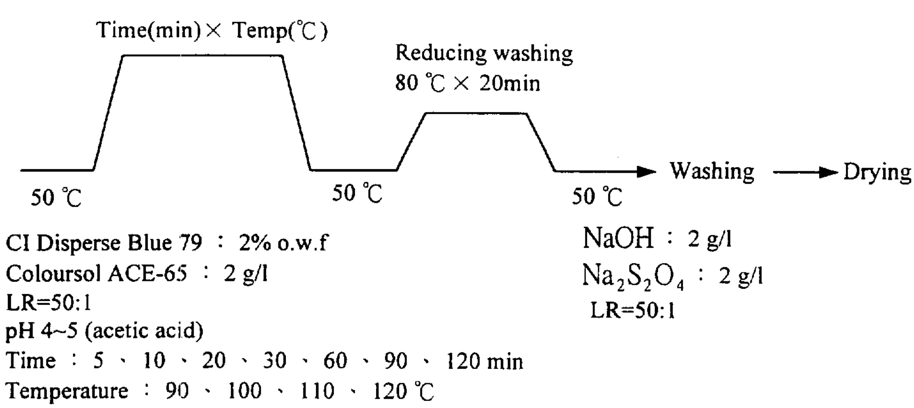

Fig. 1. Dyeing method for CI Disperse Blue 79.

Dye diffusion
A dye solution was used for dyeing PEN fiber at various time intervals (5, 10, 20, 30, 60, 90, 120 min) and different temperatures (90, 100, 110 and 120°C). The samples were removed from the dyebath immediately after each time interval and were washed thoroughly with 25 ml of distilled water, which was then added to the remaining dyeing liquor. The concentrations of both the dye solution and the amount of dye on the samples, taken as optical densities, were estimated spectrophotometrically from their absorption spectra in the visible range (400–700 nm) using a Shimadzu Spectrophotometer UV-240.

Spectrophotometric measurements
The dyed samples were irradiated in Xenotest 150 Sun light Fastness Fade-Ometer for different periods varying from 5–160 h at a temperature of 25 ± 2°C and relative humidity of 60 ± 5%. The reflectance values of the dyed samples before and after different exposure times were measured using an applied colour system (ACS-CS-5) interfaced to a digital PC under illuminate D65, using a 10° standard observer with specular component excluded and UV component included. The K/S values were derived from the reflectance values at the λ_{max} of the dye.

RESULTS AND DISCUSSION

Dyeability characteristics

In Fig. 2, it is evident that the dye uptake (g kg^{-1}) of CI Disperse Blue 79 on PEN fabric increases with increasing dyeing time and temperature. The dye is firstly adsorbed on the surface of the polymer and then an equilibrium occurs between adsorbed and diffused dye inside the pores. The affinity of the dye to the fiber increases with rise in temperature.

The diffusion coefficient (D) was calculated from Fick's equation [10, 12] and the rate of dyeing (K_t) was determined from the following equation [11]:

$$K_t = \frac{1}{c_\infty - c_t} - \frac{1}{c_\infty} \qquad (1)$$

Table 1 shows the diffusion coefficient (D) and dyeing rate (K_t) at different dyeing temperatures and times, and also the activation energy values (E). The results show that D and K_t increase with the increment of dyeing time and increase with rise of temperature, which may be explained in terms of the free volume theory [12–15]. The rate of dyeing depends on the existence of a

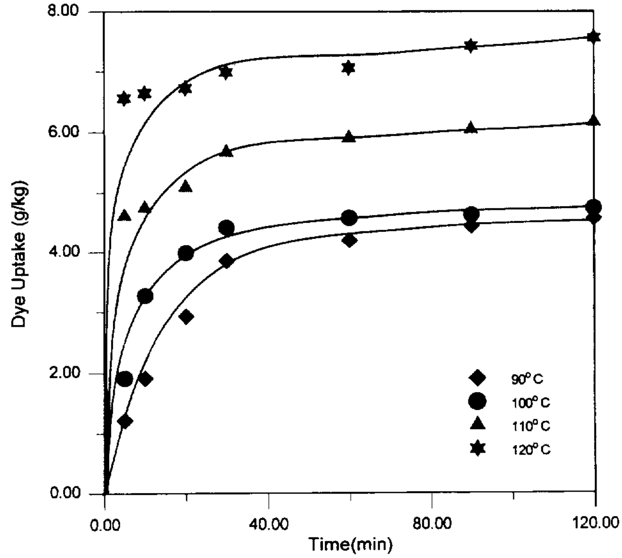

Fig. 2. Dye uptake (g kg^{-1}) of the examined PEN fabric at different dyeing times.

TABLE 1
Diffusion Coefficient (D), Dyeing Rate (K_t) and Activation Energy (E) for PEN Samples at Different Temperatures and Times

Temp. (°C)	*D(cm² min⁻¹) ×10⁻⁸*	*Dyeing rate (K_t)*					*Activation energy (kJ mol⁻¹)*
		5	10	20	30	60	
90	0.90	0.079	0.158	0.390	1.189	2.483	
100	1.46	0.143	0.474	1.122	2.914	4.039	
110	4.82	0.483	0.542	0.772	1.878	3.684	85.557
120	6.49	0.878	0.966	1.072	1.622	1.868	

sufficient number of holes between polymer chains which are large enough to accommodate dye molecules, and that a direct relationship exists between the available number of holes, i.e. the free volume, and the glass transition temperature (T_g). At the higher temperature, the larger the free volume, the greater is the probability that suitable voids will open up periodically through which the dye molecules move. At the T_g, the polymer chains are in the viscoelastic state, causing dye molecules to diffuse easily into the amorphous regions of the fiber. When the values of log (D) were plotted against ($1/T$), straight lines were obtained (Fig. 3), whose slopes gave the values of (E/R), from which the activation energy of diffusion was evaluated; the results are shown in Table 1.

Photofading characteristics

Figure 4 shows the fading kinetic curves of the dyed PEN fabric, which may be presented by first order rate curves, and probably represent the dye present in the monodisperse form [16].

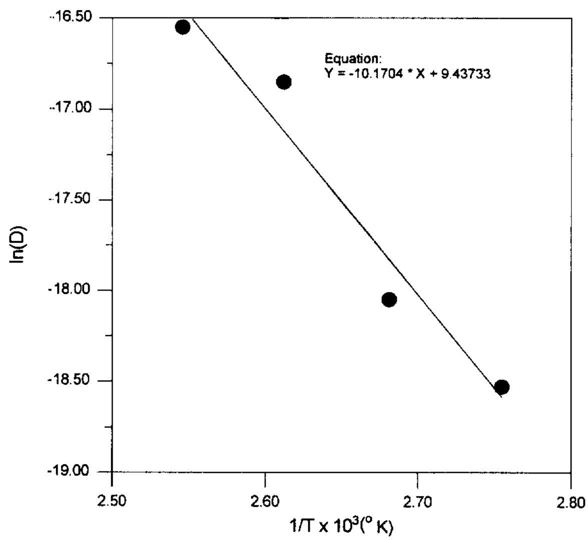

Fig. 3. Values of In (D) at different dyeing temeratures.

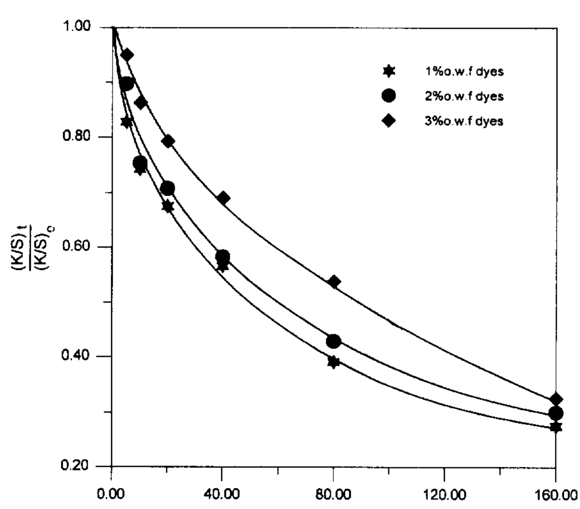

Fig. 4. Fading rate curves of PEN fabric dyed with CI Disperse Blue 79.

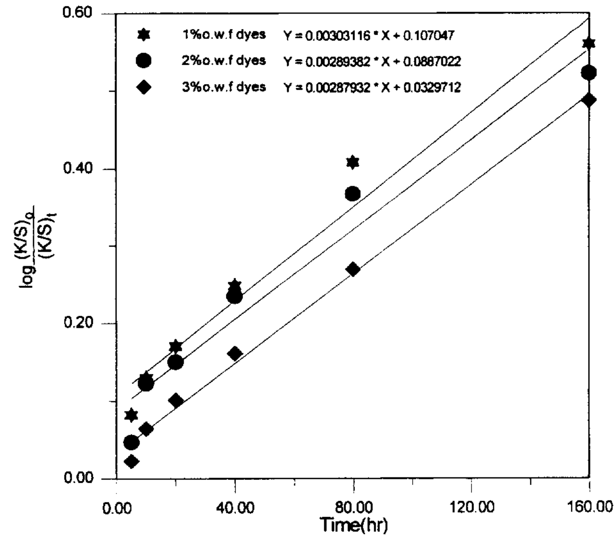

Fig. 5. Rate curves (logorithmic scale) for fading of CI Disperse Blue 79 in PEN fabric.

TABLE 2
Fading Rate Constant (K_o) and the Light Fastness (LF) of the Dyed PEN Fabric at Different Dye Concentrations

Dye concentration (% o.w.f.)	$K_o \times 10^{-3}$	*LF*
1	3.031	3
2	2.894	3–4
3	2.879	4

When log $\left(\frac{(K/S)_o}{(K/S)_t}\right)$ values were plotted against the exposure time (t), straight lines were obtained (Fig. 5), whose slopes gave the fading rate constant (K_o) (Table 2). It is clear from these results that K_o decreases with increase of the concentration of the dye, i.e. the fading rate decreased as the aggregation of the dye particles increased.

CONCLUSIONS

This investigation involved the kinetic behavior of the dyeing and fading of CI Disperse Blue 79 on poly(ethylene-2,6-naphthalenedicarboxylate) fiber. We have found that the free volume in a polymer-dye (diluent) system is the main factor determining the kinetic data. The rate of dyeing is closely related to the diffusion behavior of the dye on PEN fiber. The dyeing rate increases with increasing diffusion coefficient of the dye. In addition, the fading process follows first-order kinetics, and the fading rate constant decreases with increase of the concentration of the dye.

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