Effect of Microencapsulation on Dyeing Behaviors of Disperse Dyes Without Auxiliary Solubilization

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ABSTRACT: Microencapsulated disperse dye can be used to dye hydrophobic fabric in the absence of auxiliaries and without reduction clearing. However, little available information for dyeing practice is provided with respect to the effect of microencapsulation on the dyeing behaviors of disperse dyes. In this research, disperse dyes were microencapsulated under different conditions. The dyeing behaviors and dyeing kinetic parameters of microencapsulated disperse dye on PET fiber, e.g., dyeing curves, build up properties, equilibrium adsorption capacity C_∞, dyeing rate constant K, half dyeing time $t_{1/2}$, and diffusion coefficient D were investigated without auxiliary solubilization and compared with those of commercial disperse dyes with auxiliary solubilization. The results show that the dyeing behaviors of disperse dye are influenced greatly by microencapsulation. The diffusion of disperse dyes from microcapsule onto fibers can be adjusted by the reactivity of shell materials and mass ratios of core to shell. The disparity of diffusibility between two disperse dyes can be reduced by microencapsulation. In addition, the microencapsulation improves the utilization of disperse dyes due to no auxiliary solubilization. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 484–491, 2011

Key words: microencapsulation; disperse dyes; diffusion; kinetic parameters

INTRODUCTION

The traditional dyeing of hydrophobic fibers such as PET is usually performed with commercial disperse dyes in the presence of dispersant.[1] The auxiliary solubilization increases the solubility of disperse dye by forming micelles.[2] But auxiliary solubilization also causes environment problems by increasing the color, the COD (Chemical oxygen demand) and BOD (Biochemical oxygen demand) value of the effluent.[3] Many new methods are developed successfully to treat the dyeing wastewater of disperse dye, such as novel coagulant,[4] newly isolated *Bacillus sp.* VUS,[5] UV/TiO_2/H_2O_2 process,[6] TiO_2-catalyzed UV system,[7] and *Bacillus fusiformis*.[8] However, these methods are still in laboratory scope, but not industrially available.

Reduction clearing is a necessary step to remove the disperse dyes from the surface of PET fibers, because disperse dyes aggregate and deposit at the surface of the fiber when dyeing medium to heavy shades.[9] While the bath of reduction clearing contains a large amount of reducing agent and alkali, it will damage disperse dyes with azo groups and generate the aromatic amine. For the disperse dyes with anthraquinone, surface dyestuff can be reduced to an almost colorless, water-soluble leuco-form, which has no substantivity for the hydrophobic polyester and will remain in the reducing bath. Therefore, traditional reduction clearing of disperse dye leads to high COD, BOD, and TOC (Total organic carbon).[10,11]

Microcapsules provide a vehicle of packaging, separating, and storing materials in microscopic scale for later release under controlled conditions. Microencapsulation can introduce important new qualities to textile products, such as enhanced stability and controlled release of active compound. A considerable number of microcapsule-based commercial products have appeared in the textile industry since the 1990s, such as fire retardant textiles, antimicrobial textiles, temperature control textiles, sunscreen, antioxidants textiles, etc.[12–14] However, in these cases only the increase in additional value of the textiles is focused on, but the impact on environment is ignored. Few literatures on microcapsules application in textile industry are related to environmentally friendly dyeing.

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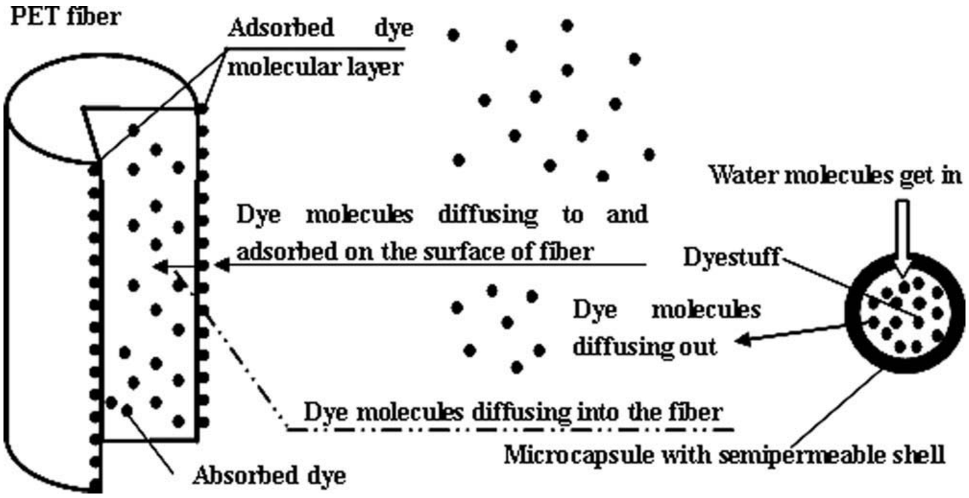

Figure 1 Dyeing process using microencapsulated disperse dyes.

In our previous work, it was found that microencapsulated disperse dye could be used to dye PET or nylon fabric in the absence of auxiliaries and without reduction clearing.[15–17] The dyeing process using microencapsulated disperse dyes is illustrated in Figure 1 and is described as follows:

At the dyeing temperature, water molecules get into microcapsules easily and dissolve the dye forming a dye solution with relatively high concentration. Under the function of driving force, i.e., a disparity in dye concentrations between the inside and outside of the microcapsule, the dissolved dye molecules in the microcapsule diffuse out into the bulk water phase and form a very thin solution of dye. The PET fiber will adsorb dye molecules forming a monomolecular layer on the surface of the fiber. Part of the adsorbed dye molecules will be absorbed by the fiber. In such a dye system, the composition of the dyeing liquor is very simple compared to the traditional dyeing process. There are only water, dye molecules, and the fiber.[18] The effluent can be reused several times after being simply filtered and can be used as solvent for scouring, which results in zero effluents.[19] But some further studies on the relationship between microencapsulation and the dyeing behaviors of disperse dye are still required.

In this research, disperse dyes were microencapsulated with different shell materials and ratios of core to shell. The dyeing behaviors and some dyeing kinetic parameters of microencapsulated disperse dye on PET fiber were investigated without auxiliary solubilization. As comparison, the dyeing behaviors and some dyeing kinetic parameters of commercial disperse dye with auxiliary solubilization were also discussed.

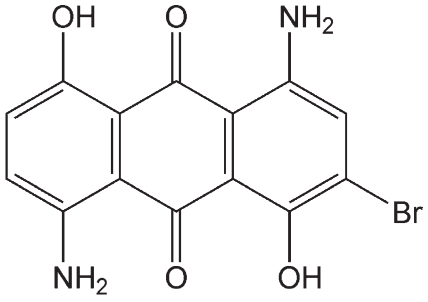

Figure 2 C.I. disperse blue 56.

EXPERIMENTAL

Materials

Melamine prepolymers with different reactivity (trimethylol- and hexamethylol- melamine) supplied by Xinguang Chemical Factory (Shanghai, China) were used as shell materials in this study. C.I. disperse blue 56 (Fig. 2) and C.I. disperse red 73 (Fig. 3) with different structures were selected as core materials. The disperse dyes without any additive and the commercial products were obtained from Longsheng Chemical Co. (Zhejiang, Shangyu, China). The ammonia product of alternating copolymer of maleic anhydride and styrene (MS) was used as emulsifier and was provided by Xinguang Chemical Factory (Shanghai, China). The foregoing related chemicals were adopted in industrial grade. All other chemicals (acetic acid, ammonia, sodium hydroxide, sodium hydrosulphite, acetone, and dimethylbenzene) were reagent grade.

PET fabric (plain weave, warp 45dtex, weft 45dtex, fabric weight 60g m^{-2}, fiber radius 4.91×10^{-6} m) was obtained from Shenghong group (Jiangsu, Wujiang, China).

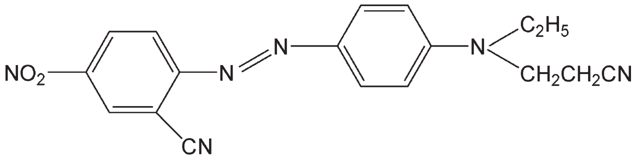

Figure 3 C.I. disperse red 73.

Preparation of microencapsulated disperse dyes with different shell materials and mass ratios of core to shell

Disperse dye microcapsules were prepared by in situ polymerization. Disperse dyes (C.I. disperse red 73 or C.I. disperse blue 56, no any additives, 1 g) and MS aqueous solution (1% w/w, 100 mL) were mixed by high-speed emulsifier (10,000 rpm) for 5 min. The pH of the mixture was adjusted to 4–5 using acetic acid solution (50% v/v). The mixture was then put immediately into a flask with stirring (250 rpm). Designated amount of shell material (1 g, 2 g, 3 g, 4 g, trimethylolmelamine or hexamethylolmelamine) was added at ambient temperature. After being stirred uniformly, the reaction system was heated to 65°C (heating rate 1°C/min) and maintained for 120 min to form microencapsulated disperse dyes with different mass ratios of core to shell (1 : 1, 1 : 2, 1 : 3, 1 : 4 w/w). Subsequently, the reaction system was cooled down and its pH was adjusted to 7–8 using ammonia. The microencapsulated disperse dyes were then separated by air pump filtration and rinsed by distilled water. The prepared samples were dried in a vacuum oven at 40°C for 4 h.

Characterization of microencapsulated disperse dyes

Surface morphology of microencapsulated disperse dyes were observed by JSM-5600LV scanning electron microscope (JEOL, Tokyo, Japan).

Thermogravimetric analysis (TGA) of microcapsule shells prepared with trimethylolmelamine and hexamethylolmelamine were performed with a Model TGA-7 system (Perkin-Elmer, Waltham, Massachusetts) and heated from 25°C to 500°C at a rate of 10°C/min under constant nitrogen flow.

Particle size and particle size distribution of microencapsulated disperse dyes were measured using a LS 13,320 Particle Size Analyser (Beckman Coulter, Brea, California).

Dyeing process

Dyeing was carried out in an IR dyeing machine (Rapid, Taipei, Taiwan) at the liquor-to-goods ratio of 30 : 1 with exhaustion procedure. PET fabric was performed with the recipe 2% owf disperse dyes, 1 mL/l anionic dispersing agent (no necessary when dyeing with microencapsulated disperse dyes), pH 5–6. Dyeing started at ambient temperature, which was subsequently raised to the dyeing temperature at a rate of 2°C/min and held at the dyeing temperature 130°C for 30 min. After dyeing, the dyed fabrics were rinsed with cold tap water. The reductive cleaning process of PET fabrics dyed with commercial disperse dyes was conducted for 15 min at 80°C, using 2 g L^{-1} sodium hydroxide and 2 g L^{-1} sodium hydrosulphite at a liquor ratio of 20 : 1.

For the dyeing kinetic study, 2% owf of dye concentration was used with a liquor ratio of 300 : 1 at the dyeing temperature 130°C for 10, 20, 40, 80, 120, 160, 200, 240, 280, 320, and 360 min.

Dyeing behaviors

Dyeing curves were used to assess the diffusibility of disperse dyes and obtained by parallel tests. The relative color strength of dyed fabrics was represented by *K/S* value based on the Kubelka–Munk equation:

$$K/S = (1 - R)^2/2R \tag{1}$$

where R is the decimal reflectance value measured from the wavelength giving fabric the maximum absorption.

The *K/S* values of each dyed fabrics were measured every 5 min when the temperature rose from 70°C to 130°C, while tests were carried out every 10 min after the temperature reached 130°C. The *K/S* values were tested by Datacolour SF600PSUS tester (Datacolour, Lawrenceville, New Jersey) at $\lambda_{\max}$ with illuminant D65 and 10° observer.

The build-up properties were investigated by measuring *K/S* values of dyed fabrics at various dye concentrations (0.5%, 1%, 2%, 4% owf).

Determination of dye absorbed on the fabrics

The dyed fabrics were washed by acetone to remove loose color. The absorbed dyes on the fabric were then extracted by dimethylbenzene using Soxhlet extractor (flask volume 250 mL) at 140°C until the fabric became colorless. The absorbance of dye solution was determined at the $\lambda_{\max}$ (C.I. disperse red 73: 493 nm, C.I. disperse blue 56: 626 nm) on U-3310 spectrophotometer (Hitachi, Tokyo/Japan). The quantity of dye absorbed on the fabrics was estimated from the absorbance of dye solution and the calibration curve. The regression equation for the calibration curve of C.I. disperse red 73 is $A = 91.104C$ (g L^{-1}), $R^2 = 0.9994$. The regression equation for the calibration curve of C.I. disperse blue 56 is $A = 55.641C$ (g L^{-1}), $R^2 = 0.9996$.

Dyeing kinetic parameters

In this research, the equilibrium dye uptake (C_∞), the dyeing rate constant (k), the half dyeing time ($t_{1/2}$), and the diffusion coefficient (D) were used to evaluate the disparity of diffusibility between microencapsulated and commercial disperse dyes.

The dyeing rate was determined based on Vickerstaff's hyperbolic equation[20,21]:

$$\frac{t}{C_t} = \frac{1}{C_\infty} \cdot t + \frac{1}{k \cdot {C_\infty}^2} \tag{2}$$

where k is the dyeing rate constant, C_∞ is the equilibrium dye uptake, and C_t is the dye uptake at time t.

According to equation (2), the relationship of (t/C_t) and t is linear. If b is the intercept of the straight line, the dyeing rate constant and the half dyeing time can be calculated as follows:

$$k = \frac{1}{b \cdot {C_\infty}^2} \tag{3}$$

$$t_{1/2} = \frac{1}{k \cdot C_\infty} \tag{4}$$

The diffusion coefficient values D for the dyes in polyester fiber were calculated using equation[22]:

$$D = \frac{\pi r^2}{16t}\left(\frac{C_t}{C_\infty}\right)^2 \tag{5}$$

where r is the radius of the fiber, t is the dyeing time, C_t is the dye uptake at time t, and C_∞ is the equilibrium dye uptake.

Plots of c_t/c_∞ versus the square root of time were linear and diffusion coefficients D were obtained from their slopes.

RESULTS AND DISCUSSION

Characterization of microencapsulated disperse dyes

The microcapsules shown in Figure 4 are nearly spheric with rough surface and irregular pores on the surface. It can be observed that the surface of microcapsules prepared by hexamethylolmelamine is much looser than the surface of microcapsules produced by trimethylolmelamine. The morphology features of microcapsules plays an important role in their release performance. The more looser microcapsule shell is, the faster release rate it will be. For the *in situ* polymerization, all reactions occur in the continuous phase, i.e., aqueous solution. The prepolymer of shell material is dissolved in the continuous phase, while the polycondensate precipitates in the aqueous solution and deposits at the surface of core material. Trimethylolmelamine has the higher reactivity because of the higher accessibility of hydroxyl. The higher steric hindrance of hexamethylolmelamine leads to the larger aggregates of polycondensates, which arrange incompactly on the surface of core materials and form the shell.

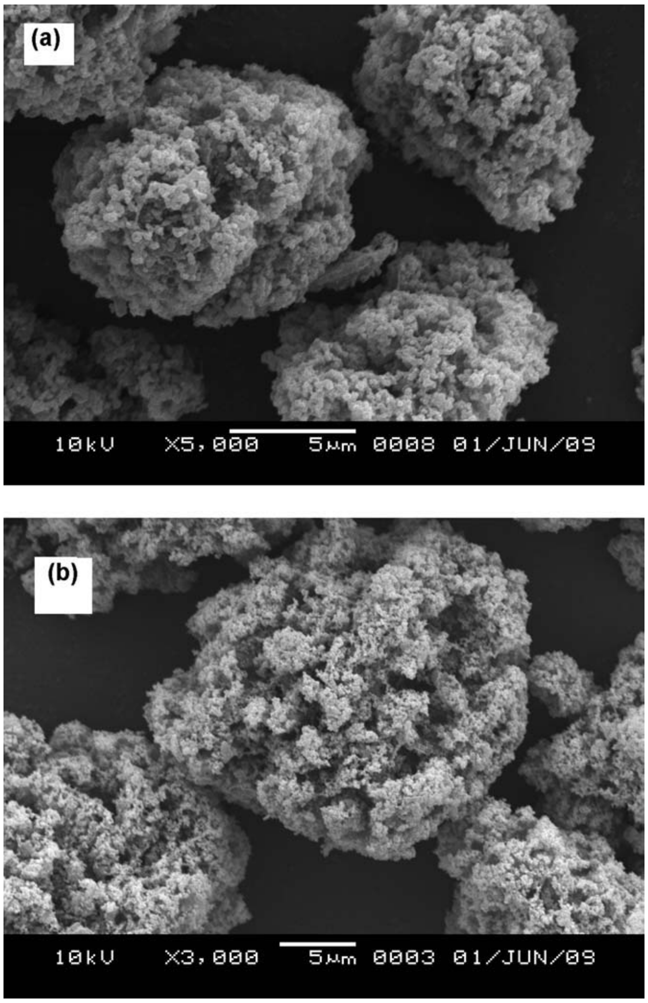

Figure 4 SEM micrograph of microencapsulated disperse dyes: (a) Core material, C.I. disperse red 73; shell material, trimethylolmelamine; mass ratio of core to shell, 1 : 2; (b) core material, C.I. disperse blue 56; shell material, hexamethylolmelamine; mass ratio of core to shell, 1 : 2.

Thermogravimetric analysis results of microcapsule shells prepared with different materials are given in Figure 5. Melamine resin as a thermosetting polymer exhibits good thermalstability below 250°C. Due to possessing more hydroxyl groups, hexamethylolmelamine shows more severe weight loss than trimethylolmelamine above 250°C.

The particle size distribution of microencapsulated Disperse dyes are shown in Figure 6. The mean size of C.I. disperse red 73 microcapsules prepared by trimethylolmelamine is 8.9 µm. While the mean size of C.I. disperse blue 56 microcapsules prepared by hexamethylolmelamine is 11.5 µm. Two microcapsule samples reveal relatively concentrated particle size distribution.

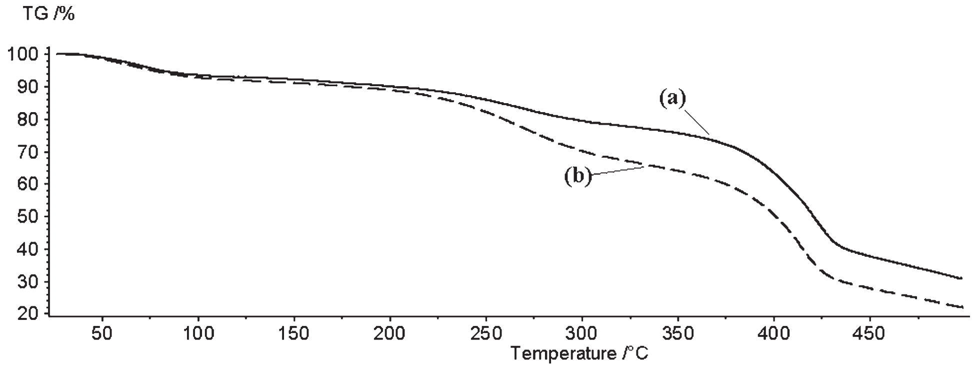

Figure 5 TGA curves of microcapsule shells prepared with different materials (a) trimethylolmelamine; (b) hexamethylolmelamine.

Effect of microencapsulation conditions on diffusibility

Dyeing curves of disperse dyes under different microencapsulation conditions, i.e., shell materials with different reactivity and different mass ratios of core to shell, are presented in Figure 7. The diffusibility of disperse dyes can be adjusted by shell materials and ratios of core to shell. Compared to the fabrics dyed by hexamethylolmelamine microcapsules, the fabrics dyed by trimethylolmelamine microcapsules exhibit lower relative color strength (*K/S* value). In addition, the *K/S* value of dyed fabrics increases with the increase of mass ratios of core to shell. Because the hexamethylolmelamine formed relatively incompact microcapsule shell, it was relatively easy for the dye molecules to penetrate through. Besides the type of shell material, the quantity of shell material also affects the release behavior of microcapsules. More shell materials lead to thicker microcapsule shell, and create further resistance to diffusing of dye molecules. After microencapsulation, it is possible that two dyes with significant difference in diffusion rate achieve almost the same diffusion rate.

Figure 8(a) shows the dyeing curves of two commercial disperse dyes. Figure 8(b) displays the most similar dyeing curves of microencapsulated disperse dyes that are selected based on the results of Figure 7. Microencapsulated C.I. disperse red 73, which was encapsulated in trimethylolmelamine with core to shell ratio of 1 : 2, exhibits very close dyeing performance to the microencapsulated C.I. disperse blue 56, which was encapsulated in hexamethylolmelamine with core to shell ratio of 1 : 2. It confirms that two dyes with different dyeing behaviors can behave almost the same dyeing performance after being microencapsulated. The *K/S* values of dyed samples with C.I. disperse red 73 decreases greatly by using trimethylolmelamine microencapsulated dyes. While the *K/S* values of dyed samples with C.I. disperse blue 56 decreases slightly by using hexamethylolmelamine microencapsulated dyes. Thus, the dyeing behaviors of C.I. disperse red 73 and C.I. disperse blue 56 can be adjusted to similar level by microencapsulation.

Effect of microencapsulation on build-up properties

Figure 9 illustrates the K/S values of dyed PET fabrics depended on dye concentration (% owf). The build-up properties of C. I. disperse red 73 and C. I. disperse blue 56 become similar after being microencapsulated, while the exhaustion of the microencapsulated dyes on PET is lower than that of the same commercial dyes on PET. This is mainly due to the controlled release property of microcapsule. The water molecules can get through the shell, which is

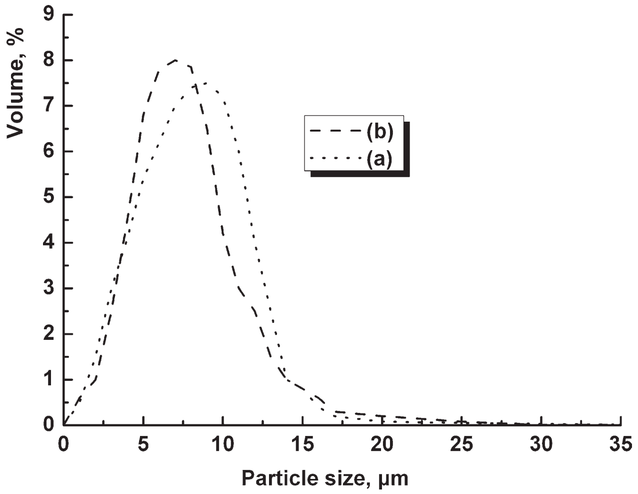

Figure 6 Size distribution curves of microencapsulated disperse dyes: (a) core material, C.I. disperse red 73; shell material, trimethylolmelamine; mass ratio of core to shell, 1 : 2; (b) core material, C.I. disperse blue 56; Shell material, hexamethylolmelamine; mass ratio of core to shell, 1 : 2.

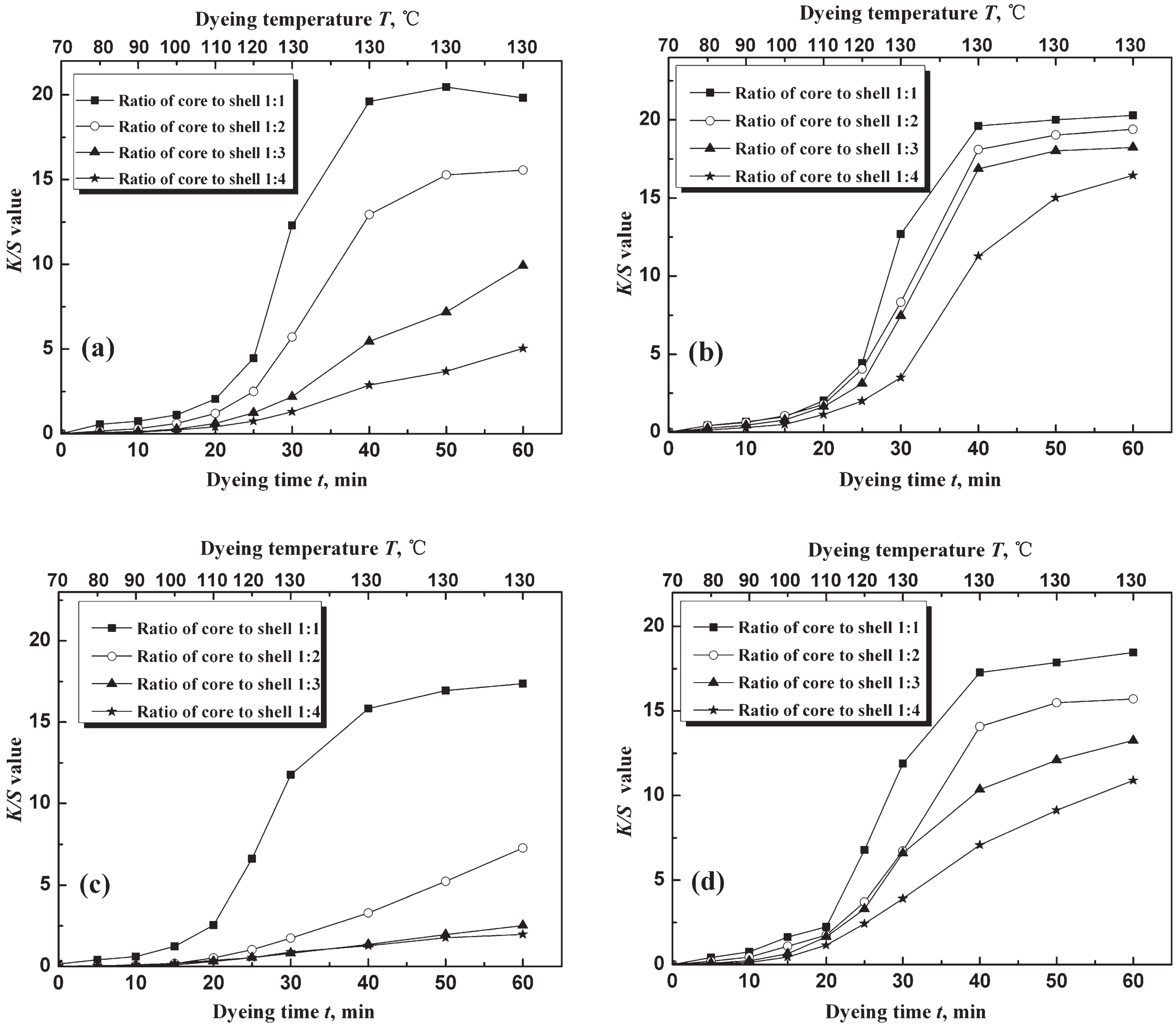

Figure 7 Dyeing curves of disperse dyes under different microencapsulation conditions: (a) Core material, C.I. disperse red 73; shell material, trimethylolmelamine; (b) core material, C.I. disperse red 73; Shell material, hexamethylolmelamine; (c) core material, C.I. disperse blue 56; shell material, trimethylolmelamine; (d) core material, C.I. disperse blue 56; shell material, hexamethylolmelamine.

a permeable membrane, and dissolve dye molecules under certain conditions. The dissolved dye then penetrates through the membrane slowly. The shell prepared with different material has different controlled release profile, and they release disperse dye with different quantity at the same time.

Effect of microencapsulation on kinetic parameters

The rate of dyeing curves for disperse dyes on PET fabric are shown in Figure 10. The results indicate that the equilibrium adsorption capacity of fabric dyed by microencapsulated disperse dyes is higher than that of fabric dyed by commercial disperse dyes. It is mainly due to the auxiliary solubilization. Disperse dyes are nonionic aromatic compounds with a relatively low molecular weight, and have an extremely low solubility in water. To maintain the dye in a finely divided state and assist in dispersion in the dyebath, large quantity of auxiliaries is added into the commercial products. Auxiliary solubilization can form micelles and prevent aggregation of the dye particles and their adherence to the surface of the fabric. However, the increase of the dye into the dyebath causes the decrease of the dye on the fiber. When dye PET using microencapsulated disperse dyes, the solubilization effect could not occur because of the absence of auxiliary. Thus, microencapsulation improve the utilization ratio of disperse dyes without auxiliary solubilization.

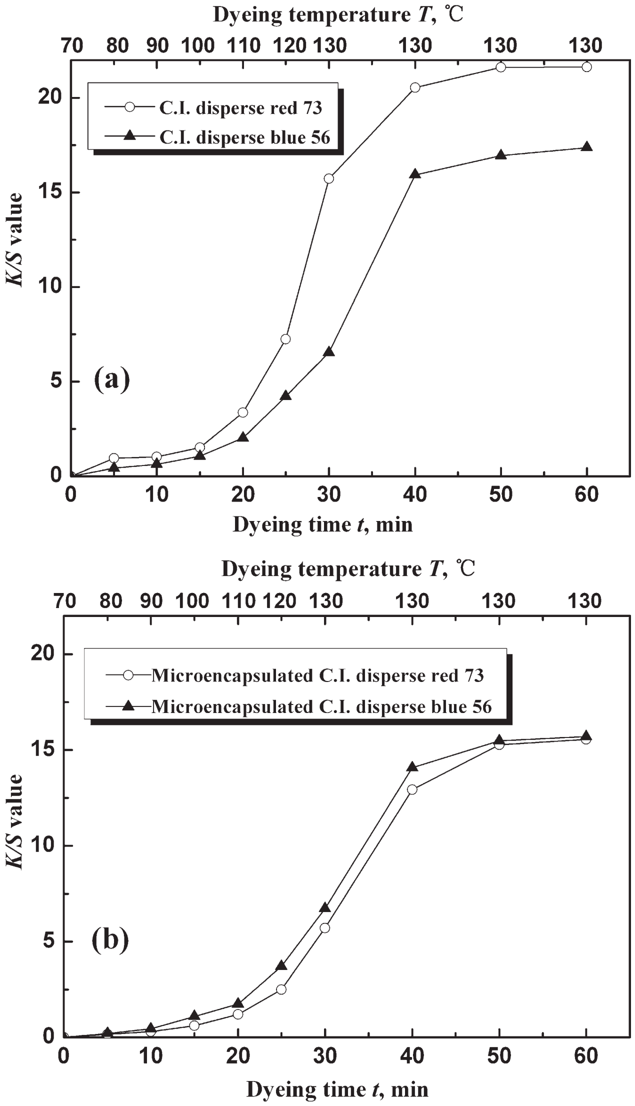

Figure 8 Dyeing curves of commercial and microencapsulated disperse dyes: (a) Commercial disperse dyes; (b) microencapsulated disperse dyes (microencapsulated C.I. disperse red 73: trimethylolmelamine as shell material, mass ratio of core to shell 1 : 2; microencapsulated C.I. disperse blue 56: hexamethylolmelamine as shell material, mass ratio of core to shell 1 : 2).

Some kinetic parameters, i.e., the dyeing rate constant (K), half dyeing time ($t_{1/2}$), and diffusion coefficient (D) are listed in Table I. It is found that microencapsulated disperse dyes have the lower dyeing rate constant, the longer half dyeing time, and the smaller diffusion coefficient than commercial disperse dyes.

The rate of dyeing is primarily dependent upon the rate of diffusion of the disperse dyes into amorphous regions of the fibers. However, in some cases, the number of single dye molecules available is small due to the low solubility of the dye. During the dyeing process of microencapsulated disperse dyes, the disperse dyes diffusing out of the shell dissolve in the dyebath and form saturated solution with very low concentration. The dye molecules then are absorbed by fiber immediately. On the other hand, the dyeing process of microencapsulated disperse dyes is involved in three more steps than that of commercial disperse dyes, i.e., diffusion of water into microcapsules, dissolution of dye in microcapsules, and diffusion of dye in the solution. Hence, the total time that microencapsulated disperse dyes diffuse from the dyebath into the fiber is longer, and the total diffusion rate is lower than commercial disperse dyes.

Table I also shows that the disparity of diffusibility of two disperse dyes can be reduced, indicating that the compatibility of two disperse dyes become closer by microencapsulation.

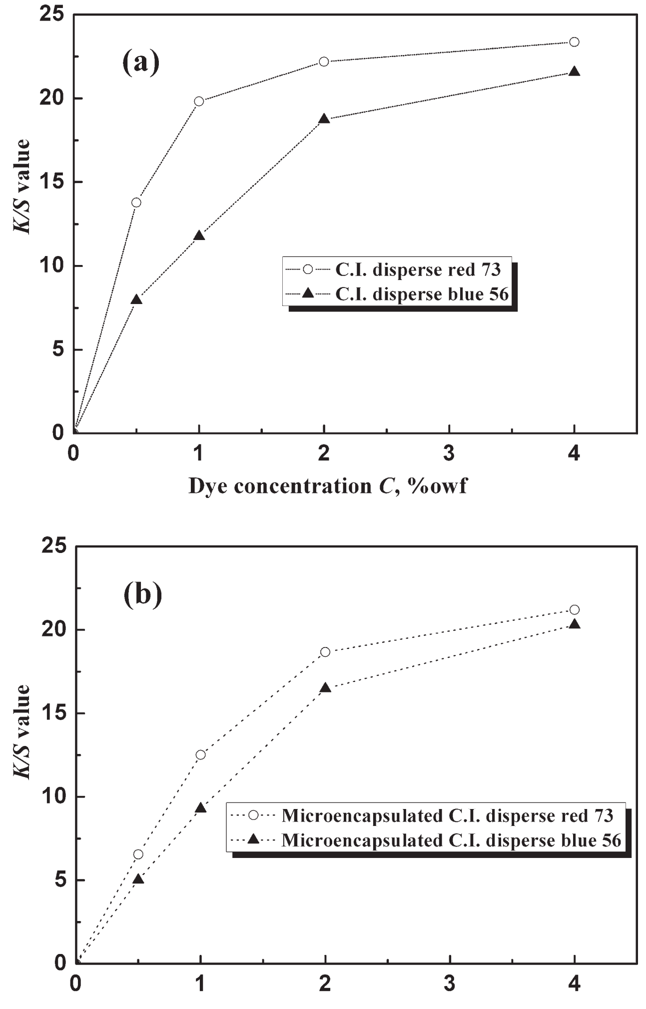

Figure 9 Build-up properties of disperse dyes on PET fabric: (a) commercial disperse dyes; (b) microencapsulated disperse dyes (microencapsulated C.I. disperse red 73: trimethylolmelamine as shell material, mass ratio of core to shell 1 : 2; microencapsulated C.I. disperse blue 56: hexamethylolmelamine as shell material, mass ratio of core to shell 1 : 2).

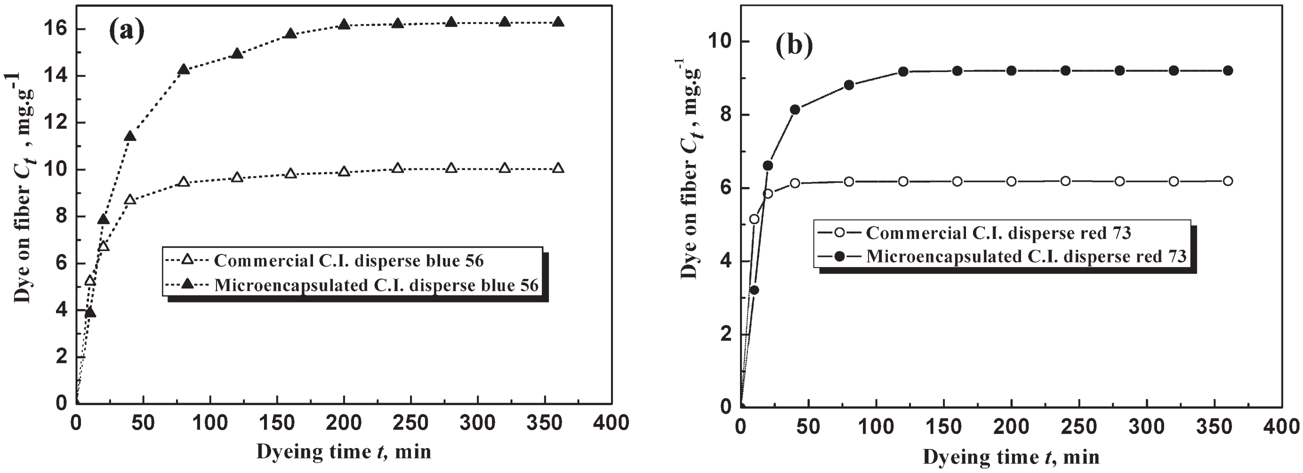

Figure 10 Rate of dyeing curves for disperse dyes on PET fabric: (a) C.I. disperse blue 56; (b) C.I. disperse red 73.

TABLE I
Some Kinetic Parameters for PET Dyed with Disperse Dyes

Dye type	C.I. disperse dyes	C_∞ (mg g^{-1})	$K \times 10^2$ (g mg^{-1} min^{-1})	$t_{1/2}$ (min)	$D \times 10^6$ (mm^2 min^{-1})
Commercial dyes	Red 73	6.188	8.16	1.98	0.117
	Blue 56	10.030	1.83	5.45	0.055
Microencapsulated dyes	Red 73	9.208	1.42	7.65	0.047
	Blue 56	16.260	0.49	12.55	0.025

CONCLUSIONS

The dyeing behaviors of disperse dye are influenced greatly by microencapsulation. The disperse dyes penetrate more easily through the microcapsule shell produced by hexamethylolmelamine, which has looser microcapsule shell. Melamine resin as a thermosetting polymer exhibits good thermalstability below 250°C. The diffusibility of disperse dyes can be adjusted by shell materials and ratios of core to shell during the encapsulation process. The dyeing curves and the build-up properties of C. I. disperse red 73 and C. I. disperse blue 56 become similar after being microencapsulated. The equilibrium adsorption capacity of fabric dyed by microencapsulated disperse dyes is higher than that of fabric dyed by commercial disperse dyes. Therefore, microencapsulation improve the utilization ratio of disperse dyes without auxiliary solubilization. Microencapsulated disperse dyes have the lower dyeing rate constant, the longer half dyeing time, and the smaller diffusion coefficient than commercial disperse dyes. The disparity of diffusibility of two disperse dyes can be reduced by microencapsulation, indicating that the compatibility of two disperse dyes become closer.

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