SUPERCRITICAL CO_2 FOR COLOR GRAPHIC DYEING
Theoretical Insight and Experimental Verification

by

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A novel theory for graphic dyeing is proposed using supercritical CO_2 fluid. Different dyes with different diffusion and anti-dyeing effect are used in experiment. The paper concludes that dyes' mixing ratio has the greatest influence on the color graphics dyeing. The temperature can be used to adjust the dyeing process.

Key words: *supercritical CO_2, graphics dyeing, diffusion, mixed dyes, kinetic*

Introduction

In recent years, CO_2, as a main greenhouse gas, has caused the largest impact on the environment. Its contribution rate on the greenhouse effect is as high as 63% [1]. CO_2 is a gas at room temperature and pressure, and it turns into a liquid and then into a solid with pressure increasing. At a critical point (31.1 °C, 7.3 MPa), CO_2 is in the supercritical state. After CO_2 turns into the supercritical state, its density and solvation capacity are close to liquid, while its viscosity and diffusion coefficient are similar to those of a gas [2-4]. The supercritical CO_2 (SC-CO_2) fluid has been widely accepted as a clean medium for textile dyeing and finishing.

The research mainly focused on the pure color dyeing and could not satisfy people's pursuit of free and abstract patterns. There have been no reports on graphics dyeing in SC-CO_2 fluid so far. Therefore, developing a graphics dyeing for textile in SC-CO_2 is desirable.

In dyeing procedures, the diffusion rate primarily depends on the molecular structures of dyes, the size of fabrics' strapping parts and the fibers' micro-gap. Smaller micro-gap in fibers or larger dye molecules can easily form the mechanical diffusion barriers, thus causing relatively low probability of dye molecules getting through micro-gap. Conversely, smaller dye molecules or larger micro-gap are conducive to the spread of dye molecules. Hence, an approach of graphics dyeing in SC-CO_2 can be achieved using diffusion properties of different dyes and capillary effect.

The aim of present work is to investigate graphics dyeing of polyester fabrics in SC-CO_2 using disperse red 60, disperse red 91, disperse blue 60, and disperse blue 73 with dyes mixing ratio (1:10, 1:5, 1:1, 5:1, and 10:1), temperature (80 °C, 100 °C, 120 °C, and 140 °C), and pressure (18 MPa, 21 MPa, 24 MPa, and 27 MPa) to study the graphics effect. The influence factors of graphics dyeing were also analyzed in SC-CO_2 fluid.

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Experimental

Materials

Polyester fabrics were obtained from Liaoning Chaoyi Industry & Trade Group. Disperse red 60 (≥ 98%), disperse red 91 (≥ 98%), disperse blue 60 (≥ 98%), and disperse blue 73 (≥ 98%) were supplied by Zhejiang Shaoxing fine chemical industry. CO_2 with a purity of 99.99% was purchased from Dalian Guangming Research & Design Institute of Chemical Industry.

Dyeing methods

The bundle method was employed in the experiments to meet the demand of graphics dyeing. Polyester fabrics was folded into fan shape by lengthways and equally wrapped with three cotton fabrics. The weight ratio of dyes and fabric was 4%. Dyeing experiments were then conducted for 30 minutes at 80-140 °C, and 18-27 MPa. After the dyeing procedure was finished, the dyed fabrics were removed, ironed and used for color measurement.

Colorimetric measurements

The blank polyester fabric was chosen as reference sample. Choosing bundle place of dyed fabrics as test boundary, ΔL^*, Δa^*, and Δb^* values of both sides of the border at 3 mm range were measured using a CM-3600d colorimeter (Konica Minolta, Japan). Each data entry was the average of 20 points.

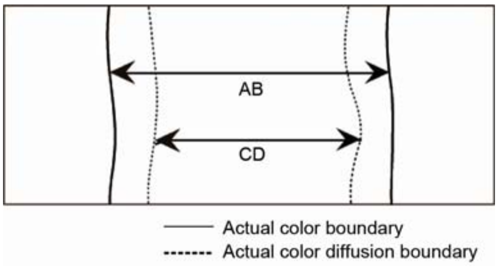

Figure 1. Actual boundaries of patterns

Penetration width measurements

The diffusion width was calculated according to eq. (1). As shown in fig. 1, different parts of the sample were measured ten times to obtain the average values. It can be seen from eq. (1), color effect of dyed polyester fabrics is correlated directly to the penetration width.

$$W = AB - CD \tag{1}$$

where W is the penetration and diffusion width.

Result and discussion

Kinetics of graphics dyeing of polyester fabrics in SC-CO_2

Graphics dyeing of polyester fabrics in SC-CO_2 can be achieved by the different diffusion properties of dyes. A mass of dyes are used in the dyeing procedure, thereby forming infinite loop and approximately infinite dye bath. With the interior and exterior dyeing process of the equipment, dyes can preferably diffuse into the internal of fibers. According to the diffusion equation of Fick’s second law & crank, relationship of dye concentration C_t (sample: g/100 g) in the dyed fabrics is obtained at dyeing time t, balance of dyeing C_∞, and diffusion coefficient D:

$$\frac{C_t}{C_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-D \frac{(2m+1)\pi^2 t}{t^2} \right] \tag{2}$$

where m is a positive constant.

In fact, the calculation of eq. (2) is not very easy due to the equation is endless. Simplification of eq. (3) is based on conditions early in the dyeing. The amount of dye in the fiber at any time is then directly related to the square root of dyeing time [5]:

$$\frac{C_t}{C_\infty} = 2\sqrt{\frac{D_\mathrm{f} t}{\pi}} \tag{3}$$

Table 1. Diffusion coefficient in SC-CO_2

Dyes	Disperse red 60	Disperse red 91	Disperse blue 60	Disperse blue 73
$D\cdot 10^{12}/(\mathrm{m^2 s^{-1}})$	0.5831	1.1812	1.2805	0.547

Polyester fabrics were wrapped in a porous stainless beam. Disperse dyes and the fabrics were put into the coloring matter kettle, and dyeing kettle, respectively. The dyes in fabrics were extracted by acetone after the dyeing procedure was finished. Dye amount on fabrics was then measured by a 722S visible spectrophotometer. A apparent diffusion coefficient shown in tab. 1 was calculated from the slope of C_t/C_∞ against $t^{1/2}$ by eq. (3) [5].

The maximum values of the dye's diffusion coefficient were obtained at temperature 120 °C, pressure 24 MPa by eq. (3). As shown in tab. 1, the largest difference for diffusion coefficient was emerged between disperse red 60 and disperse blue 60, so they were selected as the dyes used. These two dyes were firstly dissolved in acetone with weight ratio (1:10, 1:5, 1:1, 5:1, and 10:1) to ensure fully mix. The mixed dyes were then removed, grinded, and placed in a dryer after the acetone completely evaporated.

The diffusion coefficient D at different temperatures was applied to estimate the activation energy of the adsorption of disperse dyes onto polyester by the Arrhenius equation [6]:

$$\ln D = \ln D_0 - \frac{E}{\mathrm{R}T} \tag{4}$$

where D_0, R, and E refer to the Arrhenius factor, the gas constant, and the diffusion activation energy, respectively.

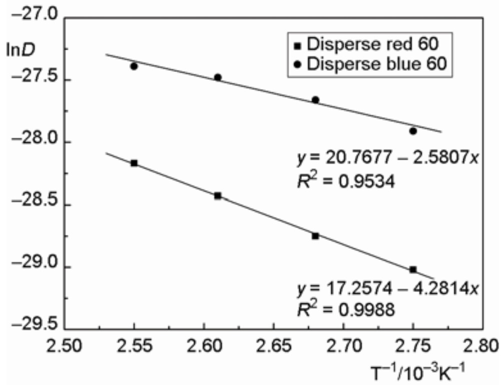

Figure 2. Plot of ln*D* against 1/*T* for determination of diffusion activation energy

The slope of the plot of ln$D$ *vs.* 1/T was used to calculated E as shown in fig. 2. The activation energy for disperse red 60 and disperse blue 60 in SC-CO_2 were 35.6 kJ/mol, and 21.5 kJ/mol by eq. (4), respectively. The higher diffusion coefficient or lower diffusion activation energy indicated a smaller diffusion resistance for dye molecule in the fibers. The value of diffusion activation energy decreased as the diffusion coefficient increased, thereby effectively reducing the diffusing energy resistance of the dye in the fabrics. Furthermore, with the increase of dyeing temperature, the glass transition temperature and the content of amorphous zone of polyester increased [7]. Therefore, a growing number of dye molecules with lower diffusion activation energy in the channel of polyester fibers could enter into fabrics by the capillary effect. Moreover, in the dyeing procedure, SC-CO_2 fluid penetrated into polyester fibers, which generated the plasticizing and swelling effects on the fibers, thus leading to the increase of diffusion and penetration ability of dyes.

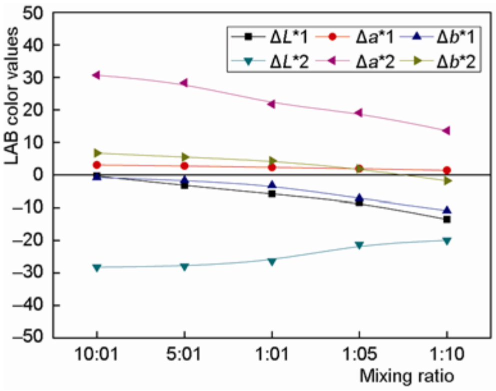

Figure 3. Effect of dyes' mixing ratio (disperse red 60 : disperse blue 60) on CIELAB values (Δ*L1, Δ*a**1, Δ*b**1 – CIELAB values on bundle place within 3 mm from the bundle boundary. Δ*L**2, Δ*a**2, Δ*b**2 – CIELAB values on unbundle place within 3 mm from the bundle boundary)**

Influence of mixing ratio on CIELAB values

An influence of dyes' mixing ratio on the $L^*a^*b^*$ color values of dyed polyester fabrics was investigated at temperature 120 °C, pressure 24 MPa, mass ratio of dyes and fabrics 4% and strapping laps of fabrics 4 with disperse red 60 and disperse blue 60 in SC-CO_2. It can be seen from fig. 3 that values of Δa^*2 and Δb^*2 were greater than zero at non-bundled place. Δa^*2 was decreased significantly from 30.67 to 13.61 with higher mass ratio of disperse blue 60 while only a minor drop appeared for Δb^*2. The hue of non-bundled place was always located in the area of red and yellow light. When the mixing ratio was 10:1, compared with the blank sample, Δa^*1 and Δb^*1 were 3.76 and –0.76 at the bundle place within 3 mm from bundle boundary and color effects could not be formed. However, Δb^*1 was decreased from –0.76 to –10.86 with mixing ratio increasing. The decreasing rate of Δa^*1 was much smaller than Δb^*1, and its hue was biased towards blue-ray direction. Degree of biased blue-ray reached the maximum with the mixing ratio 1:10. Therefore, blue light was increased with the transfer amount of disperse blue 60 increasing at the bundle boundary. Obvious color effect could be obtained.

Mechanism of color graphics dyeing

In the SC-CO_2 dyeing procedure, as shown in fig. 4, solid dyes could be dissolved and gradually flowed close to the interface of fibers with CO_2. As a solvent, SC-CO_2 has the advantages of high diffusion and solubility. Dyes dissolved in SC-CO_2 were mostly in decentralized single molecules state. In this state, dye molecules could be close to the fibers and enter into the dynamic boundary of fibers' interface. These dyes were adsorbed rapidly onto fibers' surface relying on the intermolecular forces after reaching a certain distance. Concentration difference or chemical potential difference of dyes internal and external fibers was then emerged, leading to dyes spreading to the fibers' interior.

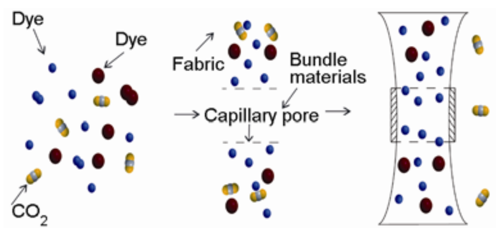

Figure 4. Schematic drawing of color graphics dyeing with one-bath in SC-CO_2
(for color image see journal web-site)

After temperature and pressure reached the required dyeing conditions, the motion of fiber molecular chains could contribute to form larger internal pore. Meanwhile, the expansion of internal fiber channels could be intensified with diffusion and swelling effect of

SC-CO_2. Dyes were driven by chemical potential difference to enter into the internal of fibers until dyeing balance was achieved under these conditions. Due to the blocking effect of anti-dyeing fabrics, few dye molecules could enter into the dynamic boundary layer of bundle place, resulting in failing to adsorb by fibers' surface. In addition, capillary channels were formed at bundle place and organizational structure of fibers. Accordingly, dyes could be carried by SC-CO_2 and diffused to parts of anti-dyeing districts through these capillary channels. Therefore, effect of graphics dyeing in SC-CO_2 was obtained by different transfer rate and quantity of dyes.

Conclusions

Using different diffusion performance of disperse dyes, the capillary effect as well as anti-dyeing effect, color graphics dyeing of polyester was achieved in SC-CO_2 fluid. Dyes' mixing ratio had the greatest influence on the color graphics dyeing. Effect of color graphics dyeing with disperse dyes was improved with the increase of compound proportion. Diffusion amount of disperse dyes to bundle place increased steadily with temperature and pressure increasing. The diffusion coefficients for disperse red 60 and disperse blue 60 on polyester fabrics were calculated to be $0.5831 \cdot 10^{-12}$ m^2/s and $1.2805 \cdot 10^{-12}$ m^2/s at 120 °C in SC-CO_2. The activation energy for disperse red 60 and disperse blue 60 in SC-CO_2 were 35.6 kJ/mol and 21.5 kJ/mol, respectively. In addition, bundle strength had a considerable impact on color graphics dyeing effects. It is difficult to form color graphics dyeing effect with relatively high or low strength. However, specific bundle strength still needs to be further studied.

Acknowledgments

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