In this paper, polyester fibers were dyed with Disperse Red 153 and its crude dye in supercritical CO₂. The effect of dyeing temperature, dyeing time, dyeing pressure, as well as auxiliaries in the commercialized Disperse Red 153 on the dyeing performance of polyester fibers was investigated. The obtained results showed that the dyeing effect of crude dye for polyester was better than that of Disperse Red 153 in the same dyeing condition. The color strength values of the dyed polyester samples were increased gradually with the increase of temperature and pressure since mass transfer of dye was improved. In addition, the mass transfer model of Disperse Red 153 in supercritical CO₂ was also proposed.

Key words: mass transfer, disperse dye, supercritical CO₂, dyeing
Zheng, H.-D., et al.: Mass Transfer of Disperse Red 153 and Its Crude Dye in supercritical CO₂. The effects of different dyeing parameters on the dyeing performance of polyester were investigated. Moreover, mass transfer of Disperse Red 153 and its crude dye in supercritical CO₂ was also analyzed.

Experimental

Materials and dyeing procedure

Polyester fibers (3-D) were purchased from Liaoning Chaoyi Industry & Trade Group, Liaoning, China. Commercialized Disperse Red 153 and its crude dye were supplied from Zhejiang Longsheng Group Co., Ltd., Zhejiang, China. The dyeing of polyester was carried out in the same batch system as described elsewhere [5, 6]. Before dyeing, polyester fibers and Disperse Red 153 were placed into the dyeing vessel and the dye vessel, respectively. Supercritical dyeing experiments were conducted for 20 minutes and 40 minutes at different temperatures (80, 90, 100, 110, 120, 130, and 140 °C) and pressures (17, 19, 21, 23, 25, 27, and 29 MPa). The CO₂ and Disperse Red 153 were then recycled at pressures and temperatures ranging from 4 to 5 MPa and 25 to 40 °C. The mass ratios of dyes to polyester fibers were 1, 2, 3, 4, 5, 6, and 7%, respectively. The chemical structure of Disperse Red 153 was shown in fig. 1.

Color strength assessment

Color strength (K/S value) was measured using a Datacolor SF600 computer color matching instrument. The D65 light source was adopted and the observation angle was 10°. The K/S value was calculated on the Kubelka-Munk equation [7]:

\[ K/S = \frac{(1 - \rho_\infty)^2}{2\rho_\infty} \]  

where \( K \) is the absorption coefficient of object, \( S \) – the scattering coefficient of object, and \( \rho_\infty \) – the reflection of the maximum absorption wavelengths.

Results and discussion

Effect of system temperature and time

As shown in fig. 2, K/S values of the dyed polyester were increased gradually with the raising of system temperature during the same dyeing period. At a constant dyeing temperature, the K/S values were also increased with the time prolonging from 20 to 40 minutes. Moreover, it is observed that the dyeing result of crude dye was better than that of Disperse Red 153 under the same condition, which indicated that the auxiliaries in the commercialized dye presented a negative effect on the dyeing. Theoretically, the macromo-
lecular chains of polyester move slowly at lower temperature. Simultaneously, slower diffusion rate and lower dye-uptake were obtained. With the increase of temperature, macromolecular chains of polyester rotate much faster, forming more cavities in the amorphous region. Furthermore, diffusion rate of dye increases as the dye particles gain more kinetic energy. Thus, excellent dyeing effect was obtained with the improvement of dyes mass transfer at higher temperature.

**Effect of system pressure**

The density of CO₂ fluid is a function of pressure and temperature, and the pressure and the density of supercritical CO₂ are proportional to each other at the same temperature. During dyeing, increasing of pressure can enlarge the dissolution performance of dyes, which is useful to supercritical dyeing process. As depicted in fig. 3, the K/S values of the dyed polyester were increased moderately between 17 and 23 MPa, which indicated more dyes dissolved in supercritical CO₂ because of the increase of the CO₂ fluid density. Moreover, the diffusion rate of the dye and the dye concentration on the fiber surface were increased with the improvement of mass transfer impetus at higher pressure [3]. Therefore, more dyes diffuse into the fiber to promote the dyeing. However, over a certain pressure, the K/S values of the dyed polyester samples remain almost constant with the pressure increasing. Better dyeing effect was also observed for the samples dyed with the crude dye due to the absence of auxiliaries in supercritical CO₂.

**Effect of dye concentration**

It can be seen in fig. 4 that dyeing effect of crude dye was better than that of Disperse Red 153 under the same dye concentration. Furthermore, the K/S values of the dyed polyester samples were increased approximately linearly with the increase of dye concentration between 1 and 4%, which demonstrated that in supercritical CO₂, the dyeing of disperse dyes basically obeyed Nernst distribution law. In supercritical CO₂ dyeing procedure, with the increase of dye concentration, more disperse dye molecules can approach the fiber surface to form a concentration gradient, thereby promoting the dyeing. However, the K/S values of the dyed fiber were increased slowly after the dye concentration arrived at 4%, which proves the balance of the supercritical CO₂ dyeing process.

**Effect of auxiliaries**

Supercritical CO₂ fluid as a non-polar medium displays a higher dissolving ability than water, thus causing dyes to dissolve in a single molecular state and then finish the dyeing
process. However, it is difficult for dispersants to dissolve in supercritical CO₂ because most dispersants are anion type of organic salts. The crystal growth, transformation, and suspension of dyes occurred with the presence of dispersants, which decrease the mass transfer of dyes, and lower the stability of dye molecules.

In addition, supercritical CO₂ can be regarded as an ideal fluid. According to Bernoulli’s equation [8]:

\[ gz + \frac{p}{\rho} + \frac{v^2}{2} = \text{constant} \]  

where \( v \), \( p \), \( \rho \), \( g \), and \( z \) are velocity at a point, pressure, density, acceleration of gravity, and height above an arbitrary reference level, respectively. As depicted in fig. 5, when CO₂ fluid reaches the fiber surface, the pressure at point A arrives at the maximum because the velocity is zero, and the diffusion boundary is formed due to the retardative effect of fiber. Hence, dyes could be quickly adsorbed onto the fiber surface through the diffusion boundary, which greatly improved the dyeing speed, the levelling property, and the permeability. Furthermore, in supercritical dyeing process, CO₂ fluid with high flow rate moved continuously in the whole system. The single disperse dye molecule was carried to dye the fibers dynamically, which reduced the crystal growth of dyes, and improve the uptake rate.

![Figure 5. Mass transfer model of Disperse Red 153 in supercritical CO₂](image)

**Conclusion**

Mass transfer behaviors of Disperse Red 153 and its crude dye were investigated in the supercritical CO₂ dyeing process for polyester. Effects of system temperature, time, pressure, dye concentration, as well as auxiliaries on the dyeing effect of polyester fibers were analyzed. The dyeing results showed that the auxiliaries in the commercialized Disperse Red 153 had significant influence on the supercritical CO₂ dyeing process, and the dyeing effect of crude dye was better than that of Disperse Red 153 at the same dyeing condition. Furthermore, the \( K/S \) values of the dyed polyester were increased gradually, which indicated that mass transfer of dye was improved with the increase of system temperature and pressure. In supercritical CO₂, disperse dye molecule is quickly adsorbed onto fiber surface through the diffusion boundary, thereby improving the dyeing speed, the levelling property and the permeability.

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