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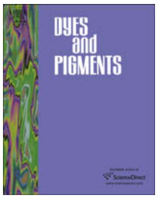

The crystal morphology of C. I. Disperse Blue 79 in supercritical carbon dioxide

Aiqin Hou*, Jinjin Dai

National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, 2999 North Renmin Road, Songjiang, Shanghai 201620, China

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ABSTRACT

The crystal growth and morphological changes of C. I. Disperse Blue 79 in supercritical CO_2 were investigated using scanning electron microscopy, X-ray diffraction and differential scanning calorimetry. Crystals of the undissolved dye grew in the supercritical fluid and the melting point and crystallinity of this undissolved dye increased with increasing temperature and pressure.

1. Introduction

In recent years, supercritical fluids as solvents have attracted considerable attention in many fields; such fluids display high solute diffusivity and low viscosity. Owing to its unique properties, supercritical carbon dioxide is a very popular supercritical fluid, as it is low cost and recyclable. Carbon dioxide is obtained as a by-product from fermentation and ammonia synthesis [1,2].

Dyeing with supercritical carbon dioxide (SCD) has been developed to completely avoid the use of water during dyeing, thus creating no pollution. No other chemicals are used in the process, and residual dye can be recovered in a reusable form with this novel technique [3,4]. Research on dyeing of synthetic fibers in supercritical fluid has been reported [5–9], and the effect of SCD dyeing conditions on the morphology of fibers has been investigated [4,10,11]. The research reveals that the crystal size and melting point (T_m) of PET fiber after treatment with SCD do not significantly change, but the crystal index decreases. Treatment with SCD at higher temperatures causes surface morphological changes of PET fiber. The solubility of disperse dyes in SCD has also been reported [12–18]: the solubility varies significantly for different dyes. However, up to now no information has been available on the influence of supercritical carbon dioxide on crystal growth and morphological changes of dye powder.

C. I. Disperse Blue 79 is a commercially important disperse dye capable of dissolving in SCD over a wide range temperature and pressure [19]. In the present work the sample of C. I. Disperse Blue 79, was placed in a dye autoclave and exposed to supercritical CO_2 under conditions representing a typical supercritical CO_2 dyeing cycle. Scanning electron microscopy, X-ray diffraction and differential scanning calorimetry were used to characterize morphological changes of the dye. The recrystallization of the dye from the supercritical fluid was also investigated.

2. Experimental

2.1. Materials

C. I. Disperse Blue 79 was obtained as powder from Hangzhou Jihua Chemical Company (Zhejiang, China) and used without further treatment. The dye powder did not contain any additives, such as dispersing agents and surfactants, and it is press cake. The molecular structure of the dye is shown in Fig. 1.

2.2. Treatment of the dye powder with supercritical CO_2

The principle of the supercritical CO_2 dyeing pilot plant is shown in Fig. 2. The disperse dye was placed on the sintered metal plate in the dye autoclave. The system was heated to the desired temperature, CO_2 was then introduced into the liquid phase from a cylinder and isothermically compressed to the working pressure (shown in Fig. 2a). When the system reached the desired temperature (80, 100, 120 or

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* Corresponding author. Tel.: +86 216 779 27 22; fax: +86 216 779 27 28.
E-mail address: aiqinhou@dhu.edu.cn (A. Hou).

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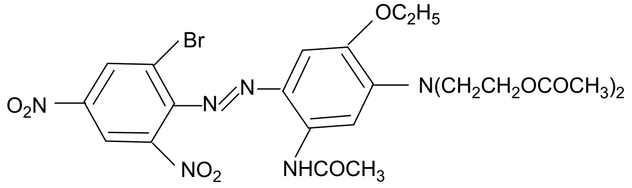

Fig. 1. Chemical structure of C. I. Disperse Blue 79.

130 °C) and pressure (14 or 20 MPa), the fluid was passed through the dyeing autoclave and the dye autoclave with the circulation pump (the same as the dyeing procedure, shown in Fig. 2b). After 40 min, the dyeing and dye autoclaves were cooled as rapidly as possible. After the pressure was gradually reduced to atmospheric pressure via a separating vessel (Fig. 2c), the disperse dye sample was removed from the dye autoclave.

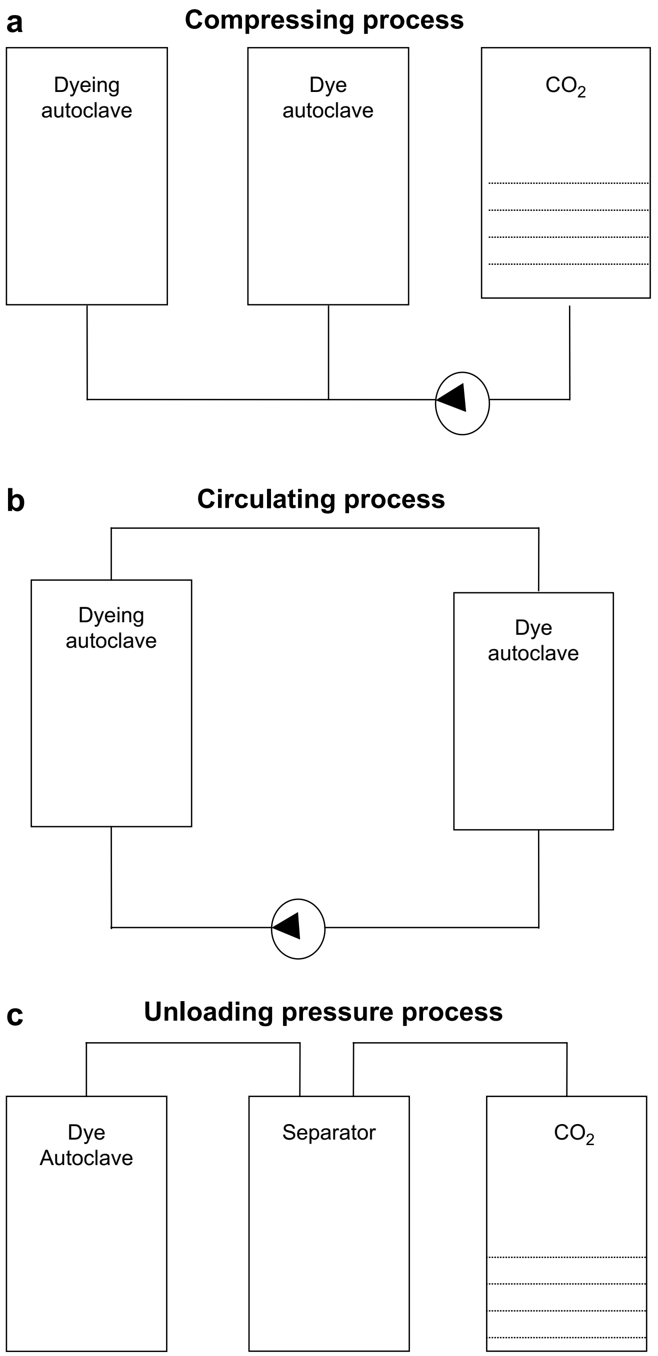

Fig. 2. Supercritical CO_2 dyeing diagram: (a) compressing process, (b) circulating process, (c) unloading pressure process.

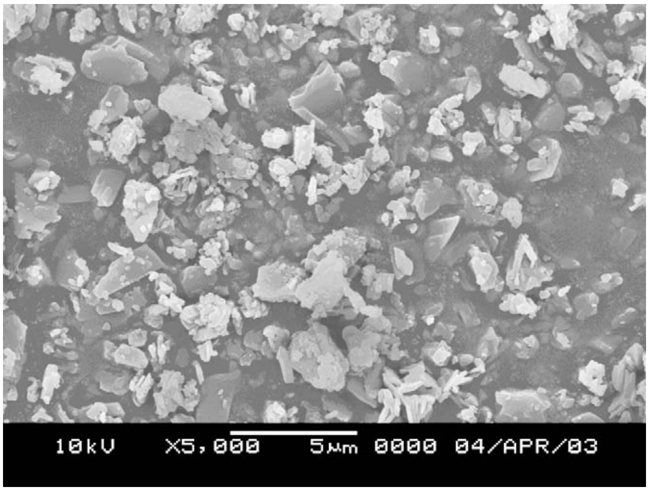

Fig. 3. SEM micrograph of the untreated dye.

2.3. Scanning electron microscopy (SEM)

For SEM analysis, the disperse dye samples were sputter-coated with gold and examined using a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

2.4. X-ray diffraction

X-ray diffraction patterns of the disperse dye were recorded using a D/MAX-B X-ray diffractometer (Rigaku, Japan), with a Ni-filtered Cu K_α target at 40 kV and 40 mA.

2.5. Differential scanning calorimetry (DSC)

A DSC822e differential scanning calorimeter (METTLER TOLEDO, Switzerland) was used, for disperse dye samples of about 5 mg heated in a DSC pan from 25 to 300 °C at a scanning rate of 10 °C min^{-1}, in a constant flow of dry nitrogen.

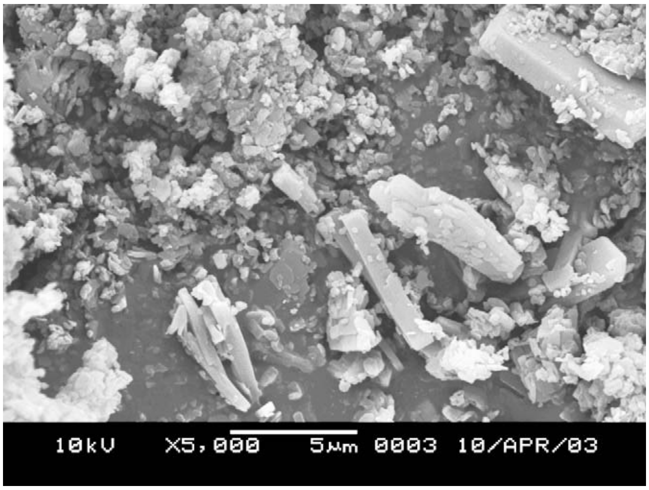

Fig. 4. SEM micrograph of the dye treated at 80 °C and 20 MPa, for 40 min.

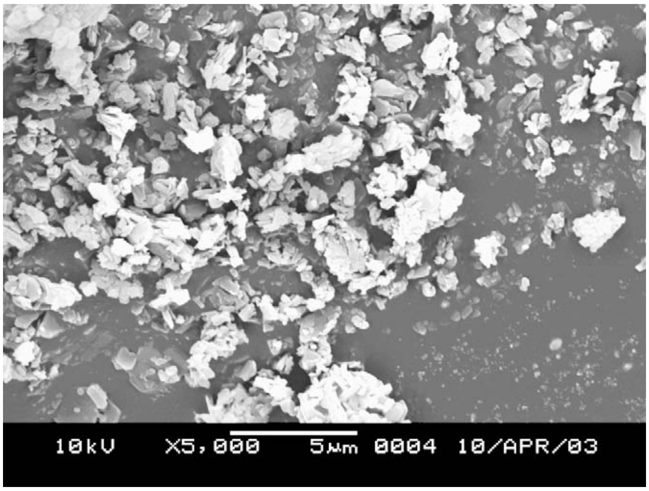

Fig. 5. SEM micrograph of the dye treated at 100 °C and 20 MPa for 40 min.

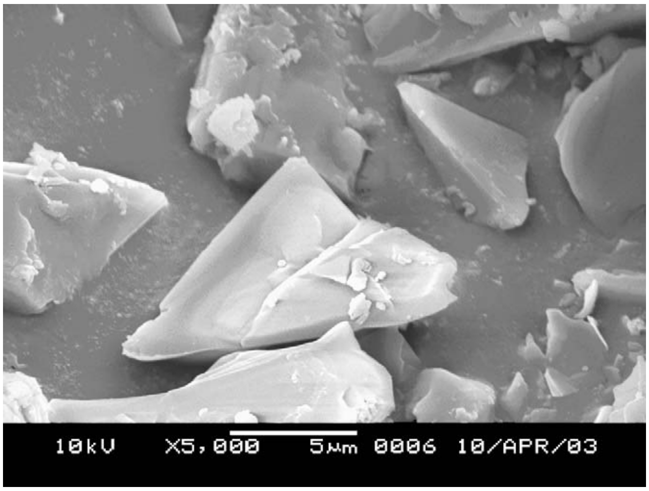

Fig. 7. SEM micrograph of the dye treated at 130 °C and 20 MPa for 40 min.

3. Results and discussion

The crystallinity of disperse dyes may change during storage or treatment under different environmental conditions, and affect dyeing properties [1,15]. Supercritical CO_2 is a high temperature and pressure system. The principal objective of this study was to characterize the crystal changes of the disperse dye powder in supercritical CO_2. This is very important for potential applications of supercritical CO_2 in dyeing.

3.1. SEM analysis

The disperse dye was placed in the dye autoclave, and supercritical CO_2 was passed through the dye autoclave with a circulation pump. A small amount of the disperse dye dissolved in supercritical CO_2 and the solubility of it in SCD is similar to that of it in water [17–19]. It was thought that after a period of dissolution the crystallinity and morphology structure of the undissolved dye powder could change. Representative SEM micrographs, taken at a magnification of 5000× of the untreated and treated dye samples under different supercritical conditions, are shown in Figs. 3–8. Fig. 3 is the micrograph of the untreated dye powder and Figs. 4–7 are the micrographs of the disperse dye treated in SCD at 20 MPa and 80, 100, 120 and 130 °C. With increasing temperature, the crystalline grains of the disperse dyes gradually grew. Figs. 7 and 8 indicate that the grains of the dye also grew with increasing pressure at 130 °C.

The SCD system was circulated for 40 min at 130 °C and 20 MPa, resulting in partial dissolution of C. I. Disperse Blue 79 dye. After the pressure of the SCD system was rapidly reduced to atmospheric pressure, the small amount of dissolved disperse dye recrystallized. The SEM micrograph in Fig. 9 shows that the recrystallized dye formed long stick-like crystals.

3.2. DSC analysis

DSC was performed on the samples to determine percent crystallinity, and qualitatively characterize melting behavior of the dye before and after treatment with SCD. The melting temperature (T_m) and enthalpy of melting (ΔH) data from DSC scans are summarized in Tables 1 and 2.

The change in T_m of the treated and untreated dyes was calculated from

$$\Delta T = T_{m1} - T_{m0}$$

where T_{m1} and T_{m0} are the melting temperatures of the SCD treated and untreated dyes, respectively.

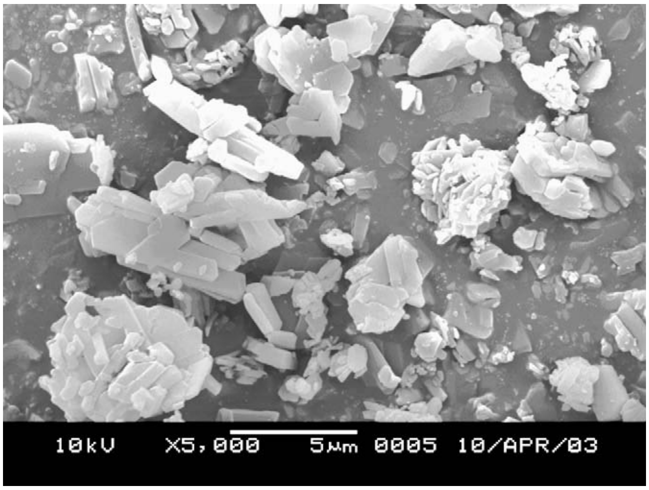

Fig. 6. SEM micrograph of the dye treated at 120 °C and 20 MPa for 40 min.

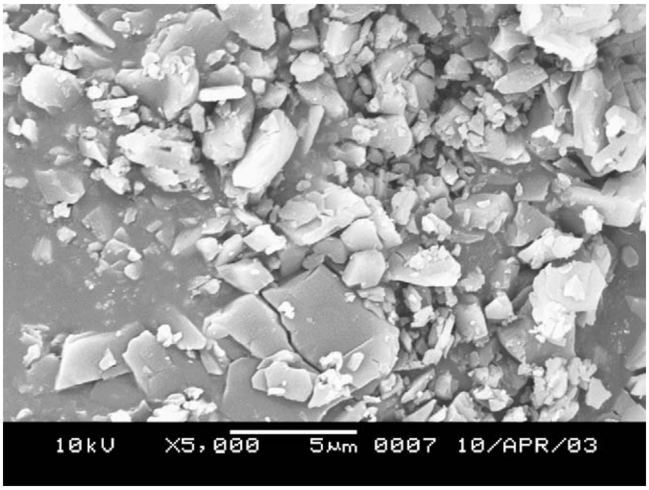

Fig. 8. SEM micrograph of the dye treated at 130 °C and 14 MPa for 40 min.

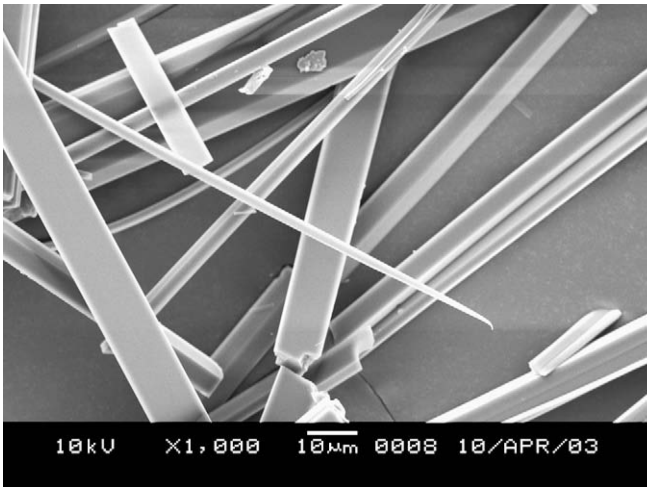

Fig. 9. SEM micrograph of the dye recrystallized from SCD at 130 °C and 20 MPa for 40 min.

Table 1 shows that ΔT increased with increasing temperature as T_m of the treated samples increased from 80 to 130 °C at 20 MPa. Table 2 shows that T_m of the treated samples increased with increasing pressure from 14 to 20 MPa at 130 °C. These trends indicate that disperse dye further crystallized in supercritical CO_2.

The powder of C. I. Disperse Blue 79 was recrystallized from acetone: the recrystallized sample was regarded as completely crystalline, and the enthalpy of melting, ΔH_0, of the recrystallized dye was determined by DSC as 95.16 J g^{-1}.

The relative crystallinity index X_c was calculated from the following equation [20]:

$$X_c = \frac{\Delta H}{\Delta H_0}$$

where ΔH is the measured enthalpy of melting of the dye sample, obtained from the DSC scan. The crystallinities of the untreated and treated dye samples are listed in Tables 1 and 2. The crystallinity of the disperse dye treated with SCD increased more with increased temperature and pressure, compared with the untreated dye. In the SCD system, increase of temperature and pressure made the disperse dye crystals grew.

3.3. X-ray analysis

To determine the effect of SCD on the crystalline structure of the disperse dye, the untreated and treated dyes were characterized by X-ray diffraction. The X-ray diffraction analyses are given in Tables 3 and 4. There were many diffraction peaks in each diffraction pattern of the untreated and treated dye samples, and the shapes, relative locations and intensities of diffraction peaks did not significantly change after SCD treatment. Consequently, the crystalline structure of the disperse dye treated with SCD did not change as a result of the treatment.

Table 1
DSC data for untreated sample, and samples treated at 20 MPa and 80–130 °C.

Treating temperature (°C)	T_m (°C)	ΔT (°C)	ΔH (J/g)	X_c (%)
Untreated dye sample	145.26	0	79.54	83.58
80	145.90	0.64	84.63	88.93
100	146.61	1.35	84.64	88.94
120	148.87	3.61	81.74	85.90
130	150.02	4.76	93.11	97.84

Table 2
DSC data for untreated sample, and samples treated at 14–20 MPa and 130 °C.

Treating pressure (Mpa)	T_m (°C)	ΔT (°C)	ΔH (J/g)	X_c (%)
Untreated dye sample	145.26	0	79.54	83.58
14	147.68	1.92	80.01	84.08
20	150.02	4.76	93.11	97.84

Table 3
Main XRD peaks of the untreated dye sample.

2θ (°)	d	Half-peak breadth (Å)	Relative intensity	Integral intensity
5.950	14.842	0.050	34	46.806
8.950	9.872	1.100	30	896.772
10.800	8.185	1.500	43	1749.689
18.050	4.910	0.700	31	586.785
19.550	4.537	1.200	28	929.038
21.200	4.187	0.600	54	872.431
23.700	3.751	0.600	99	1606.172
24.550	3.623	0.600	63	1019.486
25.400	3.504	0.600	51	825.064
27.200	3.276	0.600	51	829.878
28.550	3.124	0.800	28	604.433
29.550	3.020	3.00	25	2028.347
33.100	2.704	2.700	22	1622.026
37.200	2.415	2.700	25	1814.906

Table 4
Main XRD peaks of the dye treated at 120 °C and 20 MPa, for 40 min.

2θ (°)	d	Half-peak breadth (Å)	Relative intensity	Integral intensity
6.100	14.477	0.050	33	61.631
9.050	9.763	0.700	26	686.943
10.900	8.110	1.200	39	1704.726
18.200	4.870	0.800	27	811.659
19.650	4.514	0.700	27	689.112
21.300	4.168	0.600	54	1185.446
23.800	3.736	0.400	99	1454.288
24.700	3.601	0.500	66	1203.062
25.500	3.490	0.500	52	956.625
27.350	3.258	0.700	54	1384.996
28.650	3.113	0.800	27	806.565
29.700	3.006	1.000	25	925.433
33.200	2.696	1.000	25	943.061
37.300	2.409	1.000	27	995.687

4. Conclusions

The morphology of C. I. Disperse Blue 79 changed after treatment with supercritical CO_2. With increasing temperature and pressure the dye crystal grains grew in the supercritical fluid, and T_m and crystallinity of the disperse dye also increased. The dye crystals recrystallized from supercritical CO_2 showed long stick-like morphology. The crystalline structure of the disperse dye did not change after treatment with supercritical carbon dioxide.

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