

Dyeing of Polylactide Fibers in Supercritical Carbon Dioxide

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ABSTRACT: Polylactide (PLA) fibers were dyed with Disperse Blue 79 in supercritical carbon dioxide (SC-CO₂). The effects of dyeing conditions such as the temperature, pressure, and time on the dyeing and mechanical properties were discussed in comparison with those in water. A major advantage of dyeing PLA in SC-CO₂ over dyeing PLA in an aqueous medium was its much better retention

of the fiber strength. The loss of the breaking strength of PLA dyed in SC-CO₂ at 120°C for 60 min was 9.22% versus a 44.66% loss in aqueous dyeing at the same temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1903–1907, 2007

Key words: adsorption; biodegradable; polyesters

INTRODUCTION

A sustainable fiber in the textile industry becomes more and more attractive because of the quickly increasing price of petroleum. As the only synthetic fiber from an annually renewable resource, polylactide (PLA) could be an important fiber for the textile industry. However, textile products made of PLA are still very limited. One of the possible reasons for the limited applications of PLA in textiles is its poor resistance to conventional textile processing conditions, such as dyeing and scouring if PLA is blended with cotton. It was reported that dyeing PLA with disperse dyes at 110°C for 90 min resulted in a 35–60% loss in the breaking strength.¹ Another possibility is its low dye uptake. Many disperse dyes that have 95% or higher exhaustion on poly(ethylene terephthalate) (PET) have less than 50% exhaustion on PLA.² Such low dye uptakes cause problems in wastewater treatment and perhaps poor colorfastness.

Studies have shown that the strength loss of PLA during processing is mainly due to the hydrolysis of the polymer.³ Therefore, water-free processes should have advantages for the control of PLA degradation over conventional aqueous processes. The supercritical carbon dioxide (SC-CO₂) process is a water-free technology and has been used to study the dyeing and other treatments of synthetics⁴ and natural fibers^{5–10} for more than 10 years. SC-CO₂ technology is also recognized as a process in favor of chemical

reuse, which should also be in favor of PLA dyeing because a spent dye bath of PLA has high concentrations of disperse dyes.^{2,11,12}

The goal of this study was to explore the possibility of dyeing PLA fibers in SC-CO₂ and to investigate the effect of dyeing conditions on the mechanical properties of the fiber. Disperse Blue 79 was selected for the study because of its popularity and its good exhaustion on PLA fibers dyed in an aqueous medium² and on PET fibers in SC-CO₂.^{13,14} The effects of the temperature, pressure, and time on the dyeing and mechanical properties are discussed and compared with those for aqueous dyeing.

EXPERIMENTAL

Materials

The PLA used for this work was 7.65-dtex staple fibers. The dye was C.I. Disperse Blue 79, which was obtained as a press cake from Hang Zhou Jihua Chemical Co. (China) and used without further purification. The chemical constitution of the dye is shown in Figure 1. The purity of CO₂ was 99.99%.

Dyeing procedure

Supercritical fluid dyeing

The pilot equipment for dyeing in SC-CO₂ is shown in Figure 2, and it was designed and manufactured by this laboratory. It consisted of a stainless steel dyeing autoclave with a 2-L capacity, a dye autoclave with a 0.5-L capacity, a pressurized pump, a circulation pump, and a separator.

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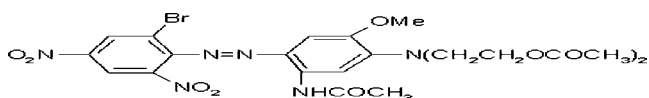


Figure 1 Chemical constitution of C.I. Disperse Blue 79.

PLA staple fibers (ca. 5 g) were spread evenly on a piece of cotton fabric (50 cm × 15 cm) and wrapped around a perforated stainless steel tube, which was then inserted into the dyeing autoclave; a calculated quantity of the dye, 2.0% based on the weight of fibers (owf), was added to the dye container with two sintered metal plates at both ends (the plates could prevent the dye from being entrained to pipelines), and the container was also inserted into the dye autoclave. After the equipment was sealed, liquid CO₂ was charged into the whole system by means of a pressurized pump, and the system was heated (valves 11–13 being kept closed) at the same time. When the system reached the required temperatures (100–130°C) and pressures (8–20 MPa), valves 8 and 9 were opened, valve 10 was closed, and the circulation pump began to operate. After dyeing for an appropriate time, valves 8 and 9 were closed, valve 10 was opened, and the system was cooled. When the temperature dropped below the glass-transition temperature of the fiber, valves 11–

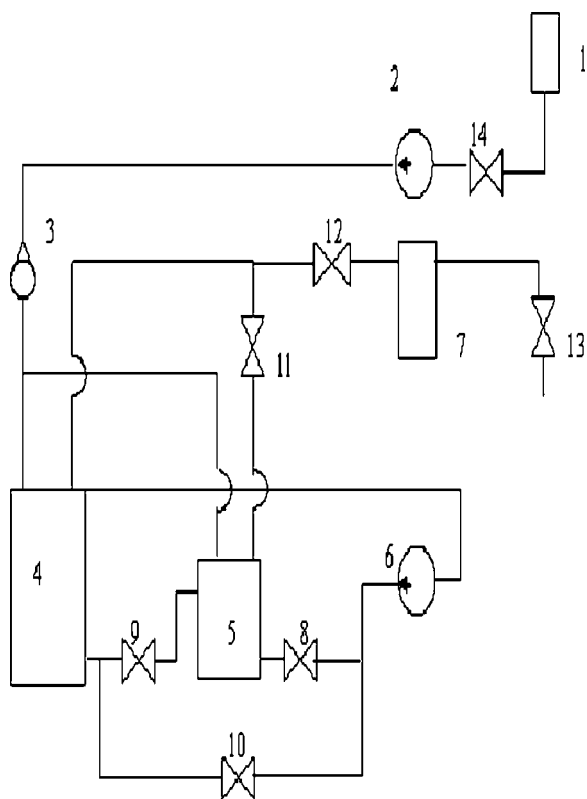


Figure 2 Schematic diagram of the pilot equipment: (1) CO₂ cylinder, (2) pressurized pump, (3) check valve, (4) dyeing autoclave, (5) dye autoclave, (6) circulation pump, (7) separator, (8–10) two-way valves, and (11–14) needle valves.

13 were opened to depressurize the system slowly, and the unused dye was trapped in the separator. After the dyeing procedure was completed, the dyed samples were removed and were ready for the determination of dye uptake and the measurement of the mechanical properties without any washing.

Aqueous dyeing

PLA fibers were dyed with 2.0% (owf) Disperse Blue 79. The pH used for the dyeing of PLA was 4.5, as adjusted by HAC/NaAc. The dyeing was performed in a Roaches dyeing machine in the range of 90–130°C. After dyeing, the samples were reductively cleaned in a bath containing 2 g/L sodium dithionite and 2 g/L sodium carbonate at 65°C for 15 min, then rinsed in water, and dried at room temperature. The dye uptake at temperatures higher than 110°C was not measured because the recommended dyeing temperature in the literature^{2,11,12} was 110°C and an immense loss of fiber strength was encountered in our experiment.

Measurement

Dye uptake

Fibers (0.1 g) were placed in a 100-mL beaker, to which was added 20 mL of *N,N*-dimethylformamide

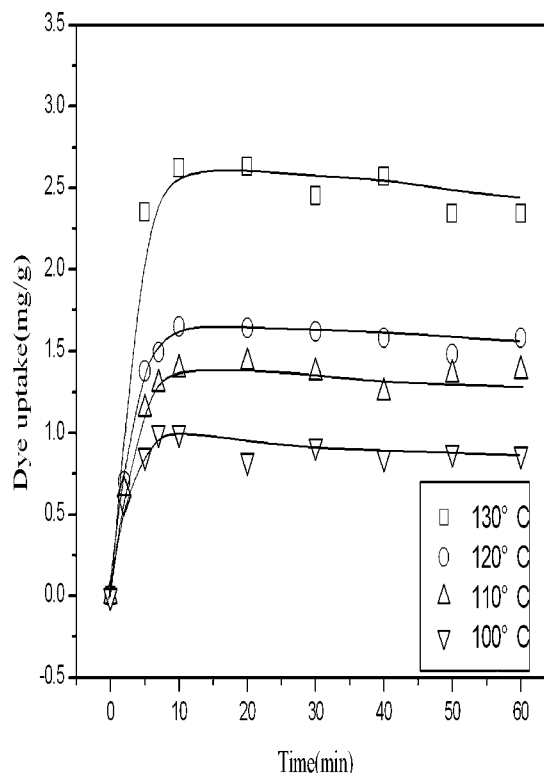


Figure 3 Effect of the dyeing temperature and time on the uptake of Disperse Blue 79 (2.0% owf) on PLA fibers dyed in SC-CO₂ at a dyeing pressure of 20 MPa.

(analytical reagent), and the beaker was heated for 10 min to make the sample dissolve completely. After the solution cooled to the room temperature, it was transferred to a 25-mL volumetric flask, and its absorbency was measured with a spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd.) at 590 nm (λ_{max}) with a reference solution containing the same amount of raw PLA fiber.

Colorfastness

The washing fastness was tested with a Washingtec P A2 launderometer according to ISO 105-C03:1989.

The light fastness was tested with an Atlas Alpha light fastness tester (Atlas Co., United Kingdom) according to ISO 105-B02:1994.

Mechanical properties

The tensile strength was measured with an XQ-1 fiber tensile tester (Donghua University, China) according to ISO 5079-1977. The gauge length for the samples was 20 mm, and the rate of extension was 40 mm/min. Fifty staple fibers were measured for one sample, each sample was repeated twice, and the mean value was taken.

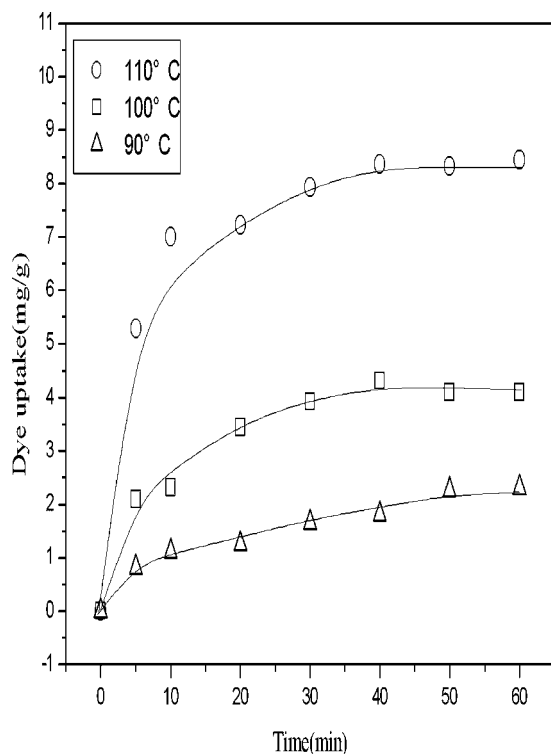


Figure 4 Effect of the dyeing temperature and time on the uptake of Disperse Blue 79 (2.0% owf) on PLA fibers dyed in an aqueous medium.

TABLE I
Effect of the Dyeing Pressure on the Sorption of Disperse Blue 79 (2.0% owf) on PLA Fibers at 100 and 120°C for 40 min in SC-CO₂

Pressure (MPa)	Dye uptake (mg of the dye/g of the fiber)	
	100°C	120°C
8	0.05	0.11
11	0.13	0.74
14	1.22	2.12
17	1.46	2.44
20	0.85	1.58

RESULTS AND DISCUSSION

Effect of the temperature and time on the dye uptake of PLA

The effects of the dyeing temperature and time on the dye uptake from SC-CO₂ and an aqueous medium were determined, and the results are shown in Figures 3 and 4, respectively. Figure 3 shows that when the dyeing temperatures were enhanced from 100 to 130°C, dye sorption increased, especially from 120 to 130°C; this is similar to what happened in a water bath, as shown in Figure 4. It seems that the dyeing behavior of PLA fiber in SC-CO₂ is quite similar to that of PET, which was investigated extensively in this lab.^{13,14}

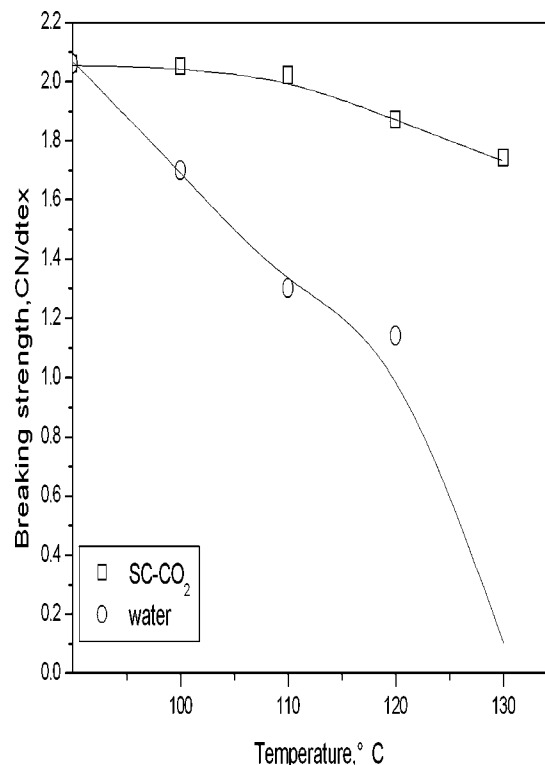


Figure 5 Effect of the temperature on the breaking strength of PLA fibers dyed in both SC-CO₂ and water.

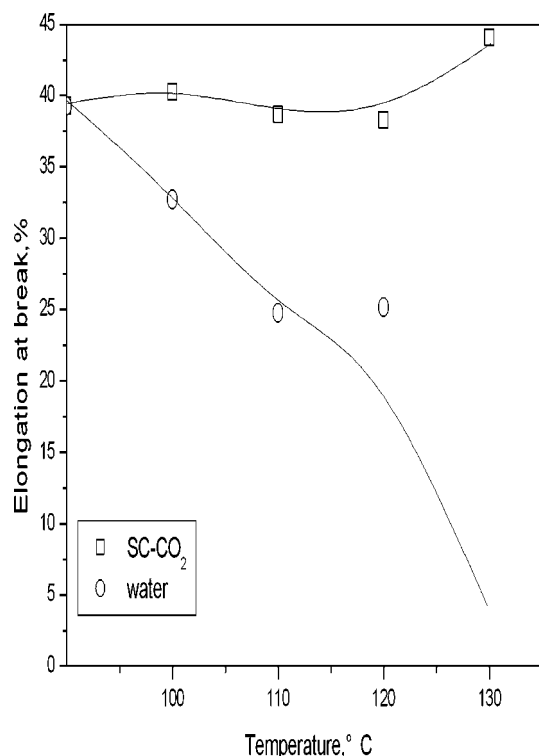


Figure 6 Effect of the temperature on the elongation at break of PLA fibers dyed in both SC-CO₂ and water.

It was also found from Figures 3 and 4 that the dyeing rate in SC-CO₂ was higher than that in water. The equilibrium was reached in about 10 min in SC-CO₂ for all temperatures within the experimental range, but it took about 40–50 min in water.

The equilibrium uptake of the dye on the PLA fiber for Disperse Blue 79 in SC-CO₂ was much lower compared with that in water, that is, one-fourth at 100°C and one-sixth at 110°C. However, this might be a very special case because similar

results were not obtained for other dyes in the following experiments.

Effect of the pressure on the dyeing property of PLA

To estimate the effect of the dyeing pressure on the dye sorption, dyeing at various pressures from 8 to 20 MPa was carried out, and the dye uptakes were determined and are listed in Table I. As shown in Table I, the CO₂ pressure had a remarkable influence on the dye sorption at dyeing temperatures of 100 and 120°C. The dye uptake of the PLA fiber increased as the pressure increased from 8 to 17 MPa, but a decrease was observed when the pressure exceeded 17 MPa. Similar results were also obtained when PET fiber was dyed in SC-CO₂ with disperse dyes.¹⁵

Influence of the dyeing conditions on the mechanical properties of PLA

The effects of the temperature on the breaking strength and elongation at break of the PLA fibers are shown in Figure 5 and 6 and summarized in Table II. As shown in Figure 5, the breaking strength of the PLA fiber decreased with the increase in temperature in both media; when dyeing temperature was lower than 110°C, the breaking strength of the fiber dyed in SC-CO₂ decreased slightly. Above 110°C, the loss of the fiber strength increased considerably, but the loss of strength in SC-CO₂ was much less than that in water at the same temperature, as shown in Table II (a reduction of 9.22% at 120°C vs 44.66% in an aqueous medium); even the loss of fiber strength at 130°C in SC-CO₂ was almost comparable to that in water at 100°C.

These results could be explained by different modes of degradation of PLA in both media. When PLA is dyed in water, an autocatalytic hydrolysis¹⁶ of the fiber will be observed, and its molecular weight exhibits a significant reduction,¹⁷ which leads to a substantial loss of tensile strength. In contrast, when PLA is dyed in SC-CO₂, the water-free medium, it will little affect the mechanical behavior of the fiber,¹⁸ so the thermal degradation is the main

TABLE II
Effect of the Dyeing Temperature on the Tensile Properties of PLA Fibers Dyed in SC-CO₂ [2.0% (owf) Dye, 20 MPa, and 60 min] and in an Aqueous Medium [2.0% (owf) Dye, 40 min, and No Reduction Clearing]

Sample	Breaking strength (CN/dtex)	Loss (%)	Elongation at break (%)	Loss (%)
Control	2.06	—	39.26	—
SC-CO ₂ 100°C	2.05	0.49	40.23	-2.47
110°C	2.02	1.94	38.64	1.58
120°C	1.87	9.22	38.25	2.57
130°C	1.74	15.53	44.06	-12.23
Water 100°C	1.70	17.48	32.50	17.21
110°C	1.30	36.89	25.11	36.04
120°C	1.14	44.66	25.14	35.97
130°C	— ^a	—	— ^a	—

^a The tensile test could not be performed because of the severe degradation of the PLA fibers.

TABLE III
Effect of the Dyeing Time on the Tensile Properties of PLA Fibers Dyed in SC-CO₂ with 2.0% (owf) Dye at 120°C and 20 MPa

Dyeing time (min)	Breaking strength (CN/dtex)	Loss of breaking strength (%)	Elongation at break (%)	Loss of elongation (%)
0 (control)	2.06	—	39.26	—
60	1.87	9.22	38.25	2.57
120	1.82	11.65	42.34	-7.85

TABLE IV
Light and Washing Fastness of Samples Dyed in SC-CO₂ and in Water

Sample	Light fastness	Color change	Staining					
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
SC-CO ₂	6	5	4-5	4-5	4-5	4-5	4-5	4-5
Water	7	4-5	3-4	4-5	2	3-4	4-5	4

reason for the strength loss of PLA due to its low thermal stability. Gogolewski and Mainil-Varlet¹⁹ reported that a loss of the molecular weight was not found when PLA was treated in argon at 135°C for less than 10 h; only a 25% loss of the molecular weight was observed when PLA was treated at 180°C for 60 min in a nitrogen atmosphere,²⁰ and similar results were obtained also by Jamshidi et al.,²¹ which implied that the pyrolysis under our experimental conditions was unremarkable.

It could be concluded from Figure 6 that the effect of SC-CO₂ dyeing on the change in the elongation of PLA was negligible. However, under aqueous dyeing conditions, the elongations were greatly affected, especially when the dyeing temperature was 110°C or greater; the decrease in the elongation reached 36.04%, as shown in Table II. These results could also show that the degrees of degradation of PLA in water were more severe than those in SC-CO₂ because the elongation at break was the parameter most sensitive to the structural changes among the mechanical properties.²²

The breaking strength of the dyed fibers showed a progressive reduction with the dyeing time, as shown in Table III. However, as the dyeing time increased from 60 to 120 min at 120°C and 20 MPa, only an extra loss of 2.43% in the breaking strength was observed, and this further confirmed the previous explanation.

Colorfastness

The light and washing fastnesses of the dyed fiber in SC-CO₂ and in water were also determined, and the results are shown in Table IV. The samples dyed in SC-CO₂ and in water had comparable light and wash fastnesses.

CONCLUSIONS

PLA fibers were successfully dyed with Disperse Blue 79 in SC-CO₂. The dyeing properties of the PLA fibers were affected by the temperature, time, and pressure in the dyeing process. The dye sorption of PLA in SC-CO₂ increased with increasing dyeing temperature, the rate of dyeing in SC-CO₂ was faster, and the dyeing equilibrium was reached in

10 min versus 40 min in water. The dye uptake of the PLA fiber increased before 17 MPa but decreased when the pressure exceeded 17 MPa. PLA fibers dyed in SC-CO₂ had light fastness and wash fastness comparable to those in water.

The tensile strength measurements proved that the SC-CO₂ dyeing technology could successfully protect PLA fibers from severe hydrolysis, which happened in the conventional aqueous dyeing process. There was a 9.22% loss of the breaking strength of PLA fibers after dyeing in SC-CO₂ at 120°C for 60 min versus a 44.66% loss in aqueous dyeing at the same temperature because the thermal degradation of PLA in SC-CO₂ was much less severe than autocatalytic hydrolysis in water. This study showed that dyeing PLA in SC-CO₂ resulted in a much better retention of the mechanical properties and indicated that SC-CO₂ technology is also recommendable for other wet processes for PLA and its blends.

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