"Science Stays True Here"
Biological and Chemical Research, 1-10 | Science Signpost Publishing

Dyeing of Stockings of Spandex/nylon Core Yarns with Disperse Dyes in Supercritical CO_2 Fluid

Li Zhenhua, Zheng Guanghong, Wu Kun, Ren Jianhua, Zheng Xiong, Bo Yan, Li Guoli, Huang Jun

Chengdu Textile College, Chengdu, China; postcode: 611731

Received: November 01, 2017 / Accepted: December 02, 2017 / Published: January 25, 2018

Abstract: In the paper the dyeing of stockings made from spandex/nylon core yarns in supercritical carbon dioxide fluid (SCF) with disperse dyes that are affinitive to both components of the yarns is discussed. Dyeing result shows SCF functions well as a detergent in the stockings' pretreatment including oil cleaning and inner-stress relief. As a medium, SCF can dissolve the dye and levelly add color onto the stockings at a relatively high yield with a given color fastness under a proper control of dyeing temperature, pressure and time. Color yield and fastness are subject to the dye applied. Color fastness can also be improved by removing unfixed dye from the stockings with SCF. The SCF dyeing method, which is water-free and environmental-friendly, is applicable and presents a good prospect in the dyeing of stockings made from spandex/nylon core yarns.

Keywords: spandex/nylon stockings, dyeing, supercritical CO_2 fluid, disperse dye, dyeing conditions and quality

1. Introduction

Supercritical carbon dioxide fluid (SCF) dyeing method has been developed fast because of its zero wastewater discharge, easy separation of dye from carbon dioxide after dyeing, dye recycle and other green, environment-friendly features，which meet modern society's requirement and are attractive to dyeing industry that has been troubled by wastewater emission for a long time [1]. Research reports show SCF performs well for synthetic fibers dyeing such as polyester, polypropylene and polyamide duo to the good solubility of disperse dyes in SCF [2].

Stockings, which are made from the core yarns consisting of spandex inside and nylon outside, are

Corresponding author: Li Zhenhua, Chengdu Textile College, Chengdu, China; postcode: 611731

referred to as "female's second skin" because of their excellent elasticity and flexibility. The stockings take a large proportion in today's market. Both spandex (polyurethane fiber with a Tg (glass transition temperature) ranging from 50°C to 70°C) and nylon (polyamide fiber with a Tg between 40°C and 50°C) can combine with disperse dyes by Van der Waals forces and/or hydrogen bonds [3] at relatively low temperature, which is helpful to keep the stockings' elasticity and flexibility. Core structure of the yarns also apparently reduces the stockings' color difference caused by different color yields between the two fibers. On the other hand, SCF well dissolves oil and plasticates the fibers [4]. SCF can be applied to the stockings' pretreatment, which is a necessary step before dyeing to relax fibers and remove the oil brought in during spinning and weaving process. SCF dyeing's in-batch operation is suitable to the stockings. The plastification assists the stockings to absorb dyes at a relatively low temperature. So, the stockings have the essentials suitable to the SCF dyeing method. Study in this regard will make it hopeful to produce colored spandex/nylon stockings in a water-free and environment-friendly way, which generates good socioeconomic benefits.

2. Experiment

2.1 Stockings, dyes and auxiliaries

Stockings: supplied by China Bonus Group, including:

Thick pantyhose: made from spandex/nylon 2070 core yarn, in which nylon: 92.4%; spandex: 7.6%.

Thin pantyhose: whose crotch part made from spandex/nylon 2015FDY core yarn, leg part from 2030DTY; both yarns consist of nylon at 86.8%, spandex at 13.2%.

Dyes: which were refined disperse dyes, including: Blue 79#; Orange 30# and Red 167#; supplied by Zhejiang Runtu Chemical Ltd.

Auxiliaries: Carbon dioxide, Fixing Agent R (supplied by Shenzhi Chemical Ltd.)

2.2 Dyeing machine and operation

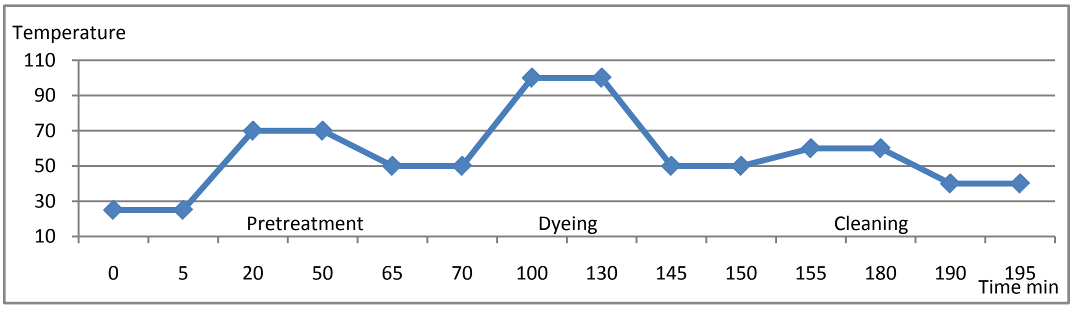
2.2.1 Dyeing machine:

Which was a 5L-capacity sample machine made by Deyang Sichuang Technology. The machine was equipped with a loop control system and able to provide two SCF circulations, among them one was between dye vessel and dyeing vessel, running directly and reversely; another between dyeing vessel and separator in one way.

2.2.2 Operation:

After stockings were loaded in dyeing vessel and dyes in dye vessel, operation was carried out in accordance with the following sequence: pretreatment – dyeing – cleaning, as shown in Figure 1:

Figure 1. Operation sequence and heating curve of SCF dyeing process.



Pretreatment: which started at room temperature with pumping carbon dioxide into dyeing vessel, and then heated up to 70°C, followed by a circulation of CO_2 fluid between dyeing vessel and separator at a given pressure and temperature for 30min.

Dyeing: which started at 50°C with carbon dioxide pumped from dye vessel into dyeing vessel up to a given pressure, then circulated alternatively in direct and reverse orientation between the two vessels for 30min, and then heated up to a maximum temperature, at which directly and reversely circulated for another 30min between the two vessels, finally, cooled to 50°C and discharged into separator from where dye residue is recycled and carbon dioxide is recovered.

Cleaning: whose operation included: at 50°C fresh carbon dioxide was pumped into dyeing vessel to a given pressure, and heated up to 60°C, and then circulated for 30min between dyeing vessel and separator, where dyes was separated from carbon dioxide. After the circulation and separation, temperature decreased to 40^0C, carbon dioxide was discharged and recycled, and then stockings were unloaded.

2.3 Test instrument and method

Deoiling effect: which was the result by assessing self-made oil-stained stocking samples treated with SCF in accordance with China's Gray Scale for Assessing Change in Color on Textiles, GB/T251-2008, in which grade 5 was the best and grade 1 was the worst.

K/S value: which was the result of measuring dyed stocking using E620-G645/4G Color Measuring and Matching Instrument made by Fangzheng Wenxiang Ltd.

Rubbing fastness: which was measured using YB-571B Textile Rubbing Fastness Tester made by Wenzhou Darong Textile Instrument Ltd in accordance with GB/T 3920-2008 Textiles-Tests for color fastness-Color fastness to rubbing, China.

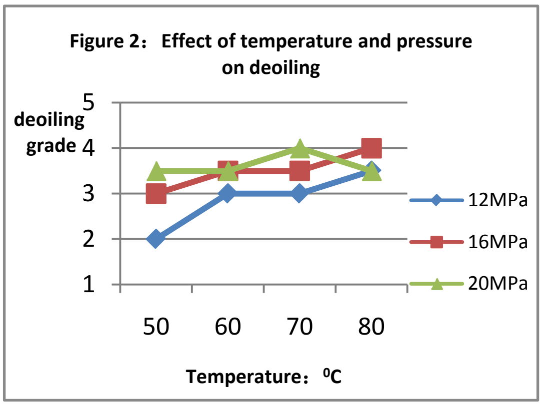
Washing fastness: which was measured using SW-12B Wash Fastness Tester made by Nantong Sansi Electromechanics Ltd. in accordance with GB/T 3921-2008 Textiles-Tests for color fastness-Color fastness to washing, China.

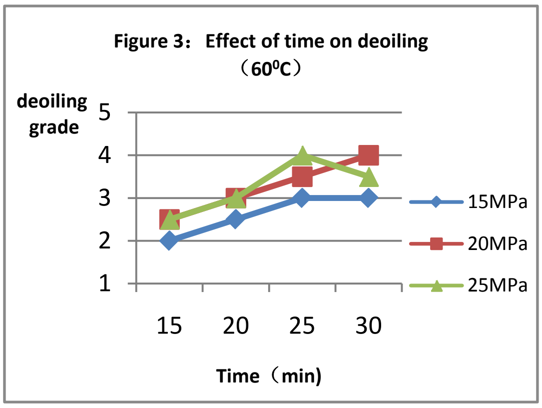
3. Result and discussion

3.1 Pretreatment

The pretreatment aimed at ensuring a uniform dyeing by releasing fiber inner stress and removing from the stockings the oil and stains incurred during spinning and knitting process. It was found that pressure, temperature, time and circulation of SCF were the factors that impacted deoiling effect. Deoiling grade increased with the increase of pressure as shown in Figure 2, due to the increase of solubility of oil in SCF with the increase of SCF density. Heating speeded up the dissolution of oil in SCF, but may decrease the solubility of oil in SCF, leading to deoiling grade no longer increase with the increase of temperature after a maximum point. Influence of time on deoiling grade was shown in Figure 3. In a closed vessel dissolution of oil in SCF would soon reach an equilibrium at which oil no longer dissolved in SCF. In order to break the equilibrium, a circulation between dyeing vessel and separator was introduced, including the change of carbon dioxide fluid from supercritical state to none-supercritical one in which oil solubility greatly reduced. Based on the state change it was available to separate oil from SCF. Test result showed the circulation was effective in oil removing.

Inner stress of the fibers was released by the action of heating and the plasticization of SCF during the pretreatment process.





3.2 Dyeing

SCF dyeing, like other conventional methods, needed to ensure a uniform coloration. Apart from the circulation between dye vessel and dyeing vessel that produced a uniform dye solution and kept dye absorption by fibers in a uniform way, temperature, pressure and dyeing time were the factors that influence dyeing result, in particular, the color yield. The influences of the factors were discussed as below:

3.2.1 Influence of temperature on color yield

Temperature had a significant influence on the K/S value of the stockings dyed in SCF [5]. Figure 4, 5 and 6 shows the K/S values increased fast with the increase of temperature within the range of 60°C to 90°C, then slowly from 90°C to 110°C. The influence reflected that above the Tgs of polyurethane and polyamide fibers there was a fast dye up take during dyeing process. So, in order to have the stockings dyed uniformly, proper temperature control was needed, as well as other leveling measures such as having a uniform solution of dye in SCF. The dyeing process was designed to be starting with a low initial temperature at which carbon dioxide was pumped through dye vessel into dyeing one, and circulated between the two vessels for 30 min, aiming at having a uniform dye solution and an uniform absorption on the fibers, then heated up at a given rate to a maximum dyeing temperature at which circulated for another 30min. Heating at a given rate was aimed at dye's up-take control, and circulation at maximum dyeing temperature at dye's exhausting. The maximum dyeing temperature ranged from 95°C to 100°C, higher than which, the stockings' performance such as elasticity would be deteriorated.

Figure 4: Influence of temperature on K/S value of thick stockings

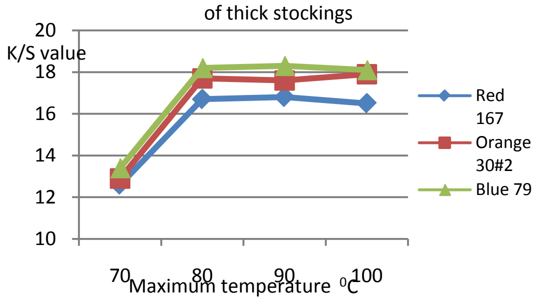


Figure 5: Influence of temperature on K/S value of crotch part of thin stockings

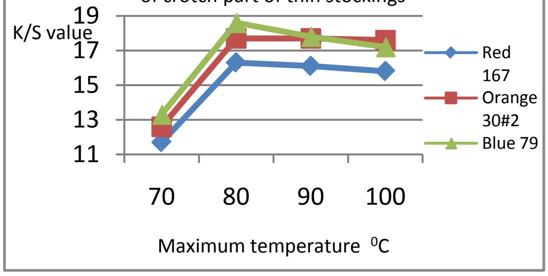


Figure 6: Influence of temperature on K/S value of leg part of thin stockings

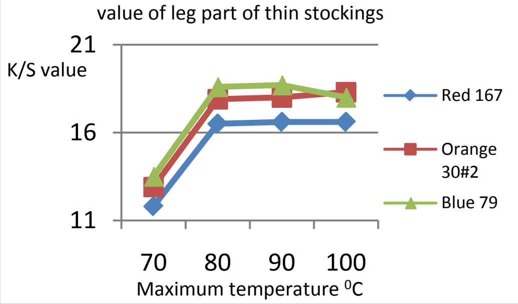
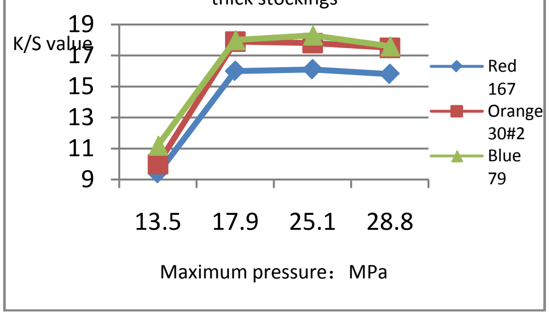


Figure 7: Influence of pressure on K/S value of thick stockings



3.2.2 Influence of pressure on color yield

Effect of pressure on K/S value of the stockings dyed in SCF was shown in Figure 7, 8 and 9. All figures indicate that there was a pressure range that was not wide but produces the highest K/S value. Before reaching the range K/S value increased with the increase of pressure. After the range K/S value slightly decreased with the increase of pressure. The variation of K/S value reflected that dye solubility increased with the increase of SCF density, which was the result of the increase of pressure. In a dyeing vessel, with the increase of pressure more and more dyes were dissolved in SCF until exhausted [6]. After the exhaust, excessive increase of SCF density or pressure leaded to excessive dye solubility. The Excessive solubility not only meant the need of excessive power consumption but the move of dyeing equilibrium towards dye dissolution from stockings. So, it was necessary to determine an optimized pressure range (18-25 Mpa, for example) in SCF dyeing.

Figure 8: Influence of pressure on K/S value of crotch part of thin stockings

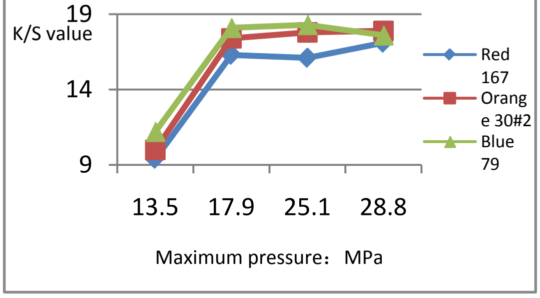
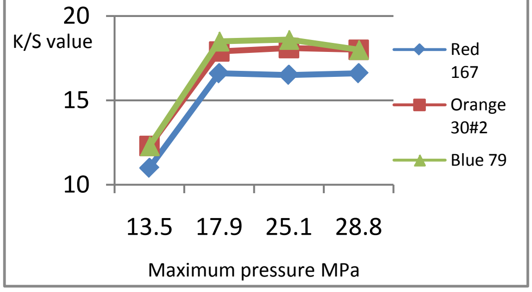


Figure 9: Influence of pressure on K/S value of leg part of thin stockings



3.2.3 Influence of time on color yield

Experiment results show at the maximum temperature the dyeing was able to reach its equilibrium in 20 min as shown in Figure 10, 11 and 12. The dyeing speed was relatively quick. SCF was of the characteristics including excellent dissolving capacity for dyes, low viscosity, good penetrability, weak bond force with dye molecules, thin diffusion layer formed on fiber, which formed a circumstance in favor of dye absorption and diffusion on fiber [7]. On the other hand, holding for sometimes the equilibrium, in which dye absorption and desorption carried on simultaneously, was benefited to a leveling dyeing. So, a bit extension of dyeing time, for instance, keeping the maximum temperature for 30min, was proper.

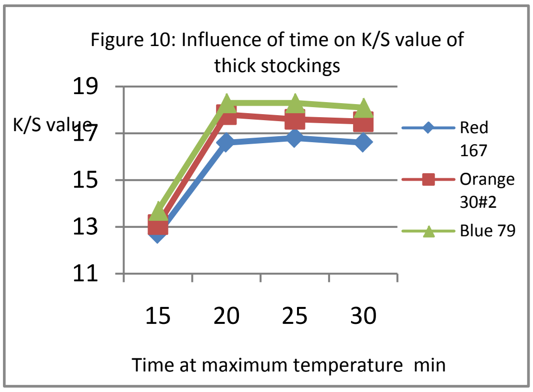


Figure 10: Influence of time on K/S value of thick stockings

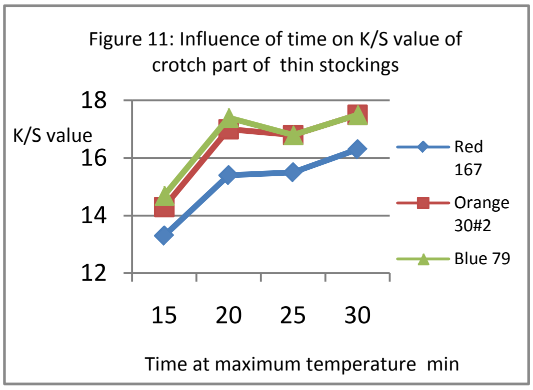


Figure 11: Influence of time on K/S value of crotch part of thin stockings

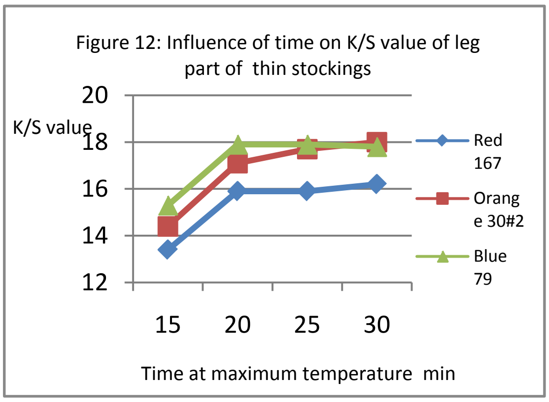


Figure 12: Influence of time on K/S value of leg part of thin stockings

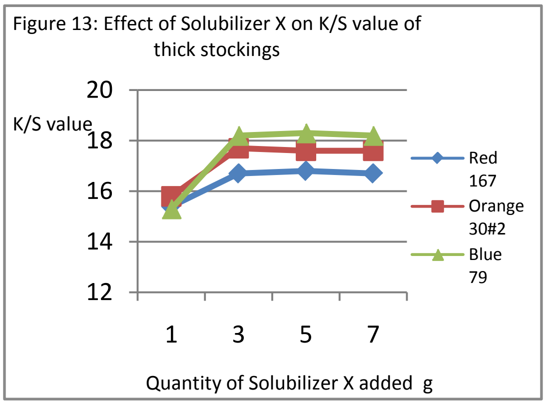


Figure 13: Effect of Solubilizer X on K/S value of thick stockings

3.3 Color fastness and Fixation

Table 1 and 2 shows the problem that color fastness of nylon dyed with disperse was lower than that of polyester fabrics still existed in SCF dyeing, in particular, the FDY and DTY much lower. Measures to improve the color fastness had to be applied, including:

Dye selection: in which it was found that some of the disperse dyes, for example, Orange 30#2, provided a good color fastness with the stockings. Orange 30#2 had a bigger molecular mass than others, resulting in stronger intermolecular forces with fibers.

Cleaning: which was another measure to improve color fastness with the use of SCF to remove unfixed dye from the stocking fibers. Circulation between dyeing vessel and separator attached a very importance to the cleaning process as it provided a good unfixed-dye washing-out tool to the closed system.

Table 1. Washing fastness of the stockings

Fastness / Disperse dye	Fastness to wash					
	Before cleaning			After cleaning		
	Thick stockings	Crotch part of thin stockings	Leg part of thin stockings	Thick stockings	Crotch part of thin stockings	Leg part of thin stockings
Red 167	3.0	2.5	2.5	3.5	3.0	3.0
Orange 30#2	3.5	3.0	3.0	4.0	3.5	3.5
Blue 79	3.0	2.5	2.5	3.5	3.0	3.0

Table 2. Dry and wet rubbing fastness of the stockings

Fastness / Disperse dye	Dry rubbing fastness						Wet rubbing fastness					
	Before cleaning			After cleaning			Before cleaning			After cleaning		
	Thick stock-ings	Crotch part of thin stock-ings	Leg part of thin stock-ings	Thick stock-ings	Crotch part of thin stock-ings	Leg part of thin stock-ings	Thick stock-ings	Crotch part of thin stoc-kings	Leg part of thin stock-ings	Thick stockings	Crotch part of thin stock-ings	Leg part of thin stock-ings
Red 167	3.0	2.5	2.5	3.5	3.0	3.0	2.5	2.0	2.0	3.0	2.5	3
Orange 30#2	3.5	3.0	3.5	4.0	3.5	3.5	3.5	3.0	3.0	4	3.5	3.5
Blue 79	3.0	2.5	2.5	3.5	3.0	3.0	2.5	2.5	2.5	3.5	3	3

Fixation: which is an aqueous solution treatment inserted in the setting process of the stockings. After dyeing, the stocking is treated with a modified cationic polyurethane solution of 20g/L, then dewatered, dried and set. The treatment is able to improve color fastness by half to one grade in general as shown in Table 3 and 4, because the cationic polyurethane is of the function groups, which react with the hydroxies and acylaminoes of disperse dye or polyamide fiber, polyurethane fiber; forming a polymer film to seal the dye in the stockings.

Table 3. Washing fastness of the stockings

Fastness / Disperse dye	Fastness to wash					
	Before fixation			After fixation		
	Thick stockings	Crotch part of thin stockings	Leg part of thin stockings	Thick stockings	Crotch part of thin stockings	Leg part of thin stockings
Red 167	3.5	3.0	3.0	4.0	3.5	4.0
Orange 30#2	4.0	3.5	3.5	4.5	4.0	4.0
Blue 79	3.5	3.0	3.0	4.0	3.5	4.0

Table 4. Dry and wet rubbing fastness of the stockings

Fastness / Disperse dye	Dry rubbing fastness						Wet rubbing fastness					
	Before fixation			After fixation			Before fixation			After fixation		
	Thick stock-ings	Crotch part of thin stock-ings	Leg part of thin stock-ings	Thick stock-ings	Crotch part of thin stock-ings	Leg part of thin stock-ings	Thick stock-ings	Crotch part of thin stoc-kings	Leg part of thin stock-ings	Thick stockin gs	Crotch part of thin stock-ings	Leg part of thin stock-ings
Red 167	3.5	3.0	3.0	4.0	3.5	4.0	3.0	2.5	3	3.5	3.5	3.5
Orange 30#2	4.0	3.5	3.5	4.5	4.0	4.0	4	3.5	3.5	4.5	4.0	4.0
Blue 79	3.5	3.0	3.0	4.0	3.5	3.5	3.5	3	3	4.0	3.5	3.5

4. Conclusion

1. Stockings made from spandex/nylon core yarns were dyeable with disperse dyes in SCF.
2. SCF was able to play a role not only as a dyeing medium, but as an agent for pretreatment and post-dyeing cleaning.
3. It was an effective way to remove oily stains or unfixed dyes from the stocking using SCF circulation combined with separation.
4. Exact control of temperature and pressure was needed to have a uniform dyeing with good color yield.

5. Color fastness can be improved by selecting proper dyes and post-dyeing cleaning.
6. An additional aqueous fixation step was required, which can be inserted in the stockings' setting process, along with the use of reactive polyurethane fixing agent.

Reference

[1]. Zhu Yongren, Wang Xunming, Research Progress of Supercritical Carbon Dioxide Dyeing Technology, Chemical Industry and Engineering Progress, 2012, No. 31: 1891-1897.

[2]. Shinoda T, Tamura K, Solubility of C.I. Disperse Red 1 and C.I. Disperse Red 13 in Supercritical Carbon Dioxide [J], Fluid Phase Equilibria, 2003, 213 (1-2): 115-123.

[3]. Song Xinyuan, Structure, Property and Dyeing of Polyamide Fiber, China Dyeing and Finishing, 2002, No.11: 30-35, No.12: 31-35; 2003,No. 1: 31-37.

[4]. Ma Yueqi, Long Jiajie, Zhao Jianping, Cheng Ankuang, Effects of Supercritical CO_2 Fluid on Polyamide-6 Fibers, Silk Monthly, Sep. 2010, No. 09: 4-10.

[5]. Tusek L, Golob V, Knez Z, The Effect of Pressure and Temperature on Supercritical CO_2 Dyeing of PET-dyeing with Mixture of Dyes [J], Journal of Polymer Material, 47 (4): 657-665.

[6]. Tabata I, Lyu J, etc, Relationship between the Solubility of Disperse Dyes and the Equilibrium Dye Adsorption in Supercritical Fluid Dyeing [J], Coloration Technology, 2001, 117 (6): 346-351.

[7]. Kraan M van der，Cid M V Fernandez，Woerlee G F，Dyeing of natural and synthetic textiles in supercritical carbon dioxide with disperse reactive dyes [J]． Journal of Supercritical Fluids, 2007, 40: 470-476．