Dyeing of Polypropylene Fibers with Disperse Dyes by Supercritical Carbon Dioxide

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Abstract

Polypropylene fabrics were dyed under various conditions by supercritical carbon dioxide technology. Amounts of dye absorbed by polypropylene fibers were calculated from the visible spectrum and penetration of dye was observed by microscopy. The result showed dye had diffused into fibers and dye uptake values of carbon dioxide dyeing obtained from visible analysis were much higher than that of water. X-ray and DSC analysis indicated that dyeing behavior of polypropylene with disperse dyes obeyed the free volume model. No obvious damage had happened while fabrics dyeing at 120°C in accordance with the TGA and mechanical properties test. Wash fastness was the major problem to be necessary to overcome on this dyeing method.

Keyword: Polypropylene, Disperse dye, Supercritical carbon dioxide, Free volume.

1. Introduction

Polypropylene has grown rapidly in polymer market is due to its some attractive properties such as low density, high toughness and resilience, excellent chemical and abrasion resistance. These properties make it quite common in home furnishing and industrial applications.^[1] However, poor moisture adsorption and the lack of dyeing properties make polypropylene unapplicable in apparent aspect.^[2] Hence, many studies on improving the dyeability of polypropylene had been reported. These methods included: (a) fiber chemical treatment by chlorination or bromination to dye fibers with cationic dyes^[3,4] (b) adding polar additives to polypropylene and spinning to form acid-dyeable fibers^[5-7] (c) copolymerizing polypropylene with acrylate series by irradiating initiation made polypropylene as suitable copolymers to be dyed with basic, disperse, reactive or acid dye.^[8-13] In recent years, A. Seves and Jiri Akerman et al. had tried to blend polypropylene with either hydrogenated oligocyclopentadiene or wool to study their dyeing results.^[14,15] Although these ways had increased the dyeability of polypropylene, their sensitivity to

light and possible reduction on mechanical properties, and the most of all, the expensive cost made them hard to be commercialized.

Supercritical carbon dioxide dyeing technology had developed by Saus Wolfgang on dyeing hydrophobic fibers in 1990s because of the economic efficiency and excellent leveling result.^[16-18] As carbon dioxide was used, no any additives were necessary for dyeing hydrophobic polyester. Besides, good compatibility between carbon dioxide and disperse dye can give satisfactory result. Hence this technology was populous in recent years. Regarding the hydrophilic natural fibers, A.S. Ozcan and D.M. Lewis et al. had also dyed modified cotton fibers with disperse dyes. The dyeing results also showed very encouraging when cotton fibers were treated by benzoilation.^[19] Because carbon dioxide is a hydrophobic and low viscosity gas, it can penetrate into polypropylene fibers much easier than water. This concept had also been proved by Y.T. Shieh et al. in their report.^[20] If supercritical carbon dioxide was used in dyeing polypropylene, the results should be expectable due to the excellent permeability of carbon dioxide.

As description stated above are concerned, we tried to dye

polypropylene with three disperse dyes using carbon dioxide as a solvent and compare the dyeing results with traditional water dyeing specimens by visible spectrum and fastness tests. X-ray, DSC and microscopy analysis were also made to study the relation between dyeing result and fiber structure variation.

2. Experiment

2.1 Material

The $\frac{45 \times 36}{50tex / 103f \times 56tex / 110f}$ 2/2 weave isotactic polypropylene fabric used in filtration was supplied by Chong-Yi trade company. Three kinds of dyes, C.I. Disperse Red 60, C.I. Disperse Orange 76 and C.I. Disperse Yellow 3, were purchased from Yi-Whia and supplied by Yong-Kuang company respectively. Their structures were shown in Figure 1. Before the dyeing was carried out, These dyes were purified by extraction and recrystallization using acetone as a solvent. Element analysis of three dyes were listed in Table1.

Figure 1: Structure of disperse dyes used in this experiment

Table 1: Element analysis results

dyes	Elemental analysis value (%)				
		C	H	O	N
C.I. Disperse Red 60	calculated	72.50	3.93	19.33	4.23
	observed	67.91	4.04	15.82	4.36
C.I. Disperse Yellow 3	calculated	66.91	5.58	11.90	15.56
	observed	62.86	4.34	11.55	20.05
C.I. Disperse Orange 76	calculated	52.04	3.83	8.16	17.86
	observed	44.19	2.48	9.44	22.45

2.2 Dyeing and fastness tests

Dyeing apparatus used in this experiment was shown in Figure 2. The maximum pressure it can withstand was 400bar. About 3.5g (6cm×15cm) polypropylene fabric was put into the dye vessel and suitable amount of dye was put in the container before dyeing. The fabric was winded to a circle form. Then the apparatus was sealed and heated to the dyeing temperature we selected while carbon dioxide was pumped simultaneously to the settled pressure. Each of dyeing was maintained for 10 minutes and then released the pressure step by step. At each step, 2.5 MPa of pressure was reduced and temperature still kept at dyeing temperature for 2 minutes until the pressure down to atmosphere. As dyeing process was completed, polypropylene fabric was washed with 2g/l Sunwet S40 detergent at 60℃ for 20 minutes, bath ratio 1:50 and then rinsed with water. For calculating the dye uptake, we cut 1.5g fabric and extracted this colored fabric with 50% v/v pyridine solution and obtained the dye amount by spectrophotometer UV 3000 measurement. Wash and light fastness was tested in accordance with ISO 2 and ISO 105 B05 standard. Instrument of light fastness test was made from James H. Heal company. Fastness grade was decided by ICS Gain Macbeth 20/20 plus spectrophotometer and personal computer.

Figure 2: Diagram of supercritical carbon dioxide dyeing technology

2.3 Analysis and mechanical property test

X-ray diffraction test was carried out by SIEMENS D5000 apparatus to see the micro structure variation of polypropylene fiber. Thermal properties were obtained by using Seiko SSC 5000 DSC and Du Pont 2000 TGA 2050 model. Mechanical property test of warp yarn of fabric was performed by Tختهchno H.Stein 050 apparatus and load cell 100N, preload 0.10cN/tex , draw ratio 300mm/min and

gauge length 100mm.

3. Results and Discussion

3.1 Microscopy analysis

The observation of fibers cross section from the optical microscopy shown in Figure 3 indicated that dye particles have penetrated thoroughly into fibers. Thus, dyeing polypropylene fabrics with carbon dioxide as a medium was quite feasible. Comparing the dyeing ability of carbon dioxide with that of water in Table 2, dye uptake value of C.I. Disperse Red 60 and C.I. Disperse Orange 76 at 120°C by using carbon dioxide as medium were 11.106 and 15.538 $\mu\text{mol/g}$ respectively, which were 3.78 and 18.9 times higher than in water. Although the dye uptake value from carbon dioxide was not high enough at 100 °C , the dyeing performance was still better than water. At 120°C, however, the difference of dyeing between carbon dioxide and water was very clear. Because of the low viscosity and hydrophobic nature of carbon dioxide, it can dissolve disperse dye effectively. Dye particles can penetrate into polypropylene fibers much easier in carbon dioxide than in water. Most of all, there was no any auxilliary needed in this supercritical carbon dioxide dyeing process. The cost of waste treatment and energy consumption will be greatly reduced. Hence, it not only can overcome the dyeing difficulty of polypropylene fibers but shows economic as well.

Figure 3: Optical microscopy analysis of fibers cross section
Table 2: Comparison of dye uptake values from carbon dioxide and water dyeing

method	dyeing temperature	Dye uptake ($\mu\text{mol/g}$)		
		Red 60	Orange 76	Yellow 3
Dyeing with CO ₂	100°C	3.256	6.193	0.991
	120°C	11.106	15.538	2.028
dyeing with water	100°C	1.548	0.930	0.700
	120°C	2.932	0.822	1.007

3.2 Dyeing and Instruments analysis

Dye uptake value varied with pressure was shown in Figure 4. Temperature was kept at 120°C for 10 minutes with 2% o.w.f dye amount. From the diagram, we found dye uptake value increased as pressure was raised up to 25 MPa, then it decreased significantly at higher pressure (30 MPa). Because the density of carbon dioxide was greatly increasing as it was compressed, the dye can be dissolved more as pressure was increased. When pressure was higher than 25 MPa, however, the density of carbon dioxide changed a little and that the dye migrated back to the carbon dioxide phase easier lead to the decrease in dye uptake. Generally speaking, better leveling result can be got at higher pressures because dye particle can be dissolved more thoroughly but also moved back to fluid phase easier.

Figure 4: Relations between dye uptake values and pressures

The relation between dye uptake and temperature was shown in Figure 5 in which the dye uptake value increased with the rising of temperature. The reason was that the molecular chain of polypropylene turned to be more mobile at higher temperature and it made the free volume of polypropylene increasing. From the X-ray diffraction curve and pattern shown in Figure 7, four peaks in the diffraction curve became sharper, but arc length of 2θ of 13° and 16° increased as temperature was raised up. Hence our finding was that crystal region has been changed and recrystallization was taken place as polypropylene fibers immersed in carbon dioxide while temperature was set from 100 to 120 °C , but molecular chain orientation was decreasing. Melting heat calculated by DSC analysis was shown in Table 4, phenomena of thermal shrinkage during the dyeing process demonstrated this conception as well.

Thus, higher dye uptake at higher temperature was mainly due to the decrement of molecular orientation that can lead to the free volume increment. Nevertheless, the results of mechanical property test shown in Table 3 indicated that strength of polypropylene wasn't reduced and shrinkage of yarn was limited (only 5%) at 120°C. TGA analysis in figure 9 also indicated only 1% of weight was lost while fibers were heated to 200°C. Hence, the damage of fiber was slight and tolerable when these specimens were dyed at 120°C. If adequate heat set process had been done onto fiber, the problem of shrinkage and structure change could be minimized. At 130°C, the crystal region of polypropylene showed clear change and fibers also became harsher. Thus, polypropylene can't be dyed properly at this temperature.

Figure 5: Relations between dye uptake value and temperature for three dyes

The dye uptake value vs. the dye amount was shown in Figure 6, in which dye uptake increased as dye amount was increased, and then reached to a saturated state. About 2% o.w.f dye amount seemed to be optimum. Comparing the dyeing performance among three dyes, C.I.Disperse Yellow 3 was the worst one for polypropylene. It's low affinity to polypropylene was probably resulted from the existence of amino acetate group in it. C.I.Disperse Red 60 has the best penetration behavior because of its anthraquinone planar structure which has lower hindrance. So that it can penetrate into fibers easier than the other two dyes. In another aspect, it also migrated easier than C.I.Disperse Orange 76 dye, hence the dye uptake was lower than C.I.Disperse Orange 76.

Figure 6: Variation of dye uptake values in accordance with the change of dye amount

Figure 7(1): X-ray diffraction pattern of polypropylene fabrics(a: untreated raw fabric, fabric dyed at (b:100°C c: 120 °C, d:130°C) with 250bar CO₂)

Figure 7(2): X-ray diffraction pattern of polypropylene fabrics(a: untreated raw fabric, fabric dyed at (b:100°C c: 120 °C, d:130°C) with 250bar CO₂)

Table 3: Mechanical test results of warp yarn of polypropylene fabric used in this experiment

dyeing conditions	mechanical properties		
	Strength (g/d)	Elongation (%)	shrinkage (%)
untreated yarn	5.38±0.14	94.20±4.48	—
yarn dyed treated at 120 °C with 250bar CO ₂	6.06±0.08	52.41±2.86	5.02

Figure 8: DSC analysis of polypropylene fabrics (a: untreated raw fabric, fabric dyed at (b:100°C c: 120°C, d:130°C) with 250bar CO₂)

Figure 9: TGA analysis of polypropylene fiber after it was treated at 120°C with 250 bar CO₂ for 10 minutes

Table 4: Melting heat calculated by DSC analysis

dyeing conditions	melting heat (mJ/mg)
untreated fiber	72.5
fiber dyed at 100°C with 250bar CO ₂	74.3
fiber dyed at 120°C with 250bar CO ₂	79.9
fiber dyed at 130°C with 250bar CO ₂	61.5

3.3 Fastness analysis

Fastness results showed in Table 5 indicated that all three dyes performed only poor to moderate wash fastness but adequate light fastness. C.I. Disperse Red 60 dye showed better wash fastness but lower light fastness due to its anthraquinone planar structure which gave it better penetrative property and showed more sensitive to light. This is due to the heat effect made the free volume of polypropylene fibers changed, and only physical force

existed between dye and fibers. Should supercritical carbon dioxide dyeing technology be used for polypropylene, color fixation after treatment must be considered.

Table 4: Wash and light fastness of polypropylene fabrics

conditions	C.I. Disperse Red 60		C.I. Disperse Yellow 3		C.I. Disperse Orange 76	
	wash	light	wash	light	wash	Light
300bar×120℃×2%×10min	3	3	1	5	2	5
250bar× 90℃×2%×10min	3—4	3—4	1	3-4	3	4-5
250bar×100℃×2%×10min	2	5	1	4-5	3	5
250bar×120℃×2%×10min	2—3	5—6	1—2	5	3	5-6
250bar×120℃×2%× 1min	3—4	3	3	6	1—2	5-6
250bar×120℃×2%× 2min	2—3	6	2	6-7	1—2	5-6
250bar×120℃×2%× 5min	1—2	6	3	6-7	1—2	6
250bar×120℃×2%×30min	2	4—5	3—4	6-7	2	6
250bar×120℃×1%×10min	3	4—5	1—2	6	2	6
250bar×120℃×4%×10min	1—2	5—6	1	6	2	5-6
250bar×120℃×6%×10min	2—3	5—6	2—3	6	2	5-6
250bar×130℃×2%×10min	2—3	6	1	3-4	3	6-7
200bar×120℃×2%×10min	3—4	4—5	1	5-6	3	5
150bar×120℃×2%×10min	3—4	3—4	1	5	2	5
100bar×120℃×2%×10min	2	3	1	5	2—3	5-6
Water dyeing×120℃×45min	3—4	3—4	1—2	3-4	2	3
Water dyeing×100℃×45min	2—3	2—3	1	3-4	2—3	3

4. Conclusion

Dyeing of polypropylene fibers with disperse dye by supercritical carbon dyeing technology was quite feasible because of the excellent permeability of carbon dioxide into polypropylene and its good compatibility with disperse dye. These characters made dye particles penetrate into fiber easier than the usage of water as medium. X-ray diffraction and DSC thermal analysis results demonstrated that recrystallization was produced as polypropylene fibers were dyed in carbon dioxide at 120℃. Orientation decrement of polymer chain was the main factor which can influent the dyeing results. Free volume increment from X-ray and DSC analysis proved that disperse dye could dye polypropylene. Increasing pressure could dissolve dye well and higher temperature (near 120℃) made polypropylene be dyed more easier due to the increment of molecular chains free volume. From our study, the optimal dyeing conditions were suggested that polypropylene was dyed with 2% o.w.f dye for 10 minutes as pressure near 250 bar and temperature up to 120℃.

The result of TGA analysis and tensile test indicated damage of polypropylene fiber was limited when

temperature raised up to 120℃. Wash fastness could be the main problem on this process. If suitable fixation after treatment had been adopted, this problem should have been limited. Consider about these conceptions described above, dyeing polypropylene fabric with carbon dioxide need further study to improve the wash fastness problems. And then, the diffusion behavior will be able to be understood. Thus the feasibility of dyeing polypropylene should be solved economically without any risks in fiber damage.

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