Dyeing of microdenier polyester fabric in supercritical carbon dioxide

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Supercritical fluid dyeing technology has been used to dye microdenier polyethylene terephthalate fibres at elevated pressure and temperature simultaneously. It is observed that the dye speck disappears when pressure increases beyond 200 bar and dye uptake increases when pressure increases above 250 bar. Temperatures above 120°C are found to be suitable for the dyeing of polyester fabrics. As the pressure releases step by step, a deeper shade is obtained because of the incremental mixing of the fluid, dyestuff and substrate. Disperse Red 60, which own anthraquinoid structure, could be dissolved more easily in supercritical fluid system. Reduction cleaning is not required and the fastness properties of dyed samples still meet commercial requirements. The results also show that the dye uptake could be raised with solvents such as dimethyl formamide and dimethyl sulfoxide in combination with dyestuffs. DSC and X-ray analyses also indicate no obvious damage when polyester fabrics are dyed at 250 bar pressure and 120°C temperature for 10 min in supercritical fluid carbon dioxide.

Keywords: Dyeing, Microdenier fabric, Polyethylene terephthalate, Supercritical fluid

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1 Introduction
Polyethylene terephthalate (polyester) must be dyed with disperse dyes because it has no hydrophilic group which can react with other dyes and these dyes can diffuse only at high temperatures using assistant agents such as surfactants. Supercritical fluid, which is indistinguishable as liquids or gases, is defined as the fluid processed beyond the critical point. Supercritical carbon dioxide dyeing method has several benefits, such as nonflammable, nontoxic, easy to use, economical and environmentally acceptable. The study became attractive since Saus et al., Schmidt et al., and Ozcan et al. studied the dyeing of polyester and modified natural fibres with disperse dyes in supercritical carbon dioxide. Then, Beltrame et al., Schmidt et al., and Ozcan et al. studied the dyeing of cotton and modified cotton in supercritical carbon dioxide. They reported that the temperature and pressure are the main factors which could affect dyeing performance. It has been demonstrated that the supercritical carbon dioxide is a good medium for hydrophobic polymer dyeing, but some factors which affect the results, such as pressure, temperature, dye concentration, pH value and addition of assistant agents, still need to be studied. In the present study, supercritical fluid dyeing technology has been used to dye microdenier polyester fabric in a 180 ml capacity dye pot by raising pressure and temperature simultaneously.

Dyeing theory for polyester is accepted in accordance with free volume theory. When a fibre is heated up to glass transformation temperature, the thermal activity of molecular chains is more vigorous which increases the free volume of molecules and dye diffusion. As the temperature is reduced, dyestuffs are fixed inside the molecular chain and stay in the fibre. Disperse dyes dissolved in dyeing systems diffuse rapidly because of the low viscosity of supercritical fluid which shortens the dyeing time. Dye is preserved in the resealing procedure. The density of carbon dioxide can be controllable upon changing pressure. Raising pressure increases the solubility and high temperature increases the diffusion of dye. Polyester can be dyed without vigorous convection, and the carbon dioxide can be reused with a recycling process with no pollution. It has been demonstrated that the supercritical carbon dioxide is a good medium for hydrophobic polymer dyeing, but some factors, such as addition of organic solvent, still need to be understood. Solubility of disperse dyes in supercritical carbon dioxide was also measured.
2 Materials and Methods

2.1 Materials

2/1 drill microdenier polyester woven fabric (warp: 90 threads/inch, 75 denier, and 72 filaments; and weft: 100 threads/inch, 150 denier and 288 filaments) was used for the study. The commercial dyes, namely C.I. Disperse Red 60, C.I. Disperse Yellow 3 and C.I. Disperse Orange 76, were purchased from Yi-Whia and supplied by the Yong-Kuang company. Their structures are shown in Fig. 1. The dyes were purified by extraction and recrystallization. Firstly, each dye was dissolved in saturated sodium chloride solution which was boiled for 1 h. Secondly, the dispersing agent was removed using a filtration step, and dried for 24 h at 50°C, then extracted with acetone to get pure dye. The fabrics were separately impregnated with different solvents, namely acetone, 2-methoxy ethanol, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), all of extra grade. Industrial grade perchloroethylene and a commercial reagent (carrier SP) were also used.\textsuperscript{13-15}

The dyed sample's apparent colour yield (K/S) was tested with an ICS Gain spectrophotometer. Dyed materials were also tested for the reflectance (R) and apparent color yield using a color matching system and the following formula:

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

The dye uptake was measured using DMF by extractive method. Fastness testing was subjected to a simulated ISO 2 and ISO 105 B05 standards before and after reducing wash. The colour fastness was measured by an ICS Gain Macbeth 20/20 plus spectrophotometer. To observe the microstructure variation in microdenier polyester fibre, an X-ray diffraction pattern was observed using a SIEMENS D5000 apparatus. Thermal properties were observed using a Seiko SSC5000 DSC.

2.2 Dyeing Procedure

The specifications of the dyeing apparatus, manufactured by Zaar Technical Company, have been reported in a previous publication\textsuperscript{16}. The dyeing apparatus can be compressed and heated up to 400 bar and 200°C respectively. A measured amount of dye was placed into a dye vessel and a microdenier polyester fabric was cut to a 40mm x 200mm size and wound on an iron wire before dyeing. Then, the fabric was put into the dye speck and the tubes were sealed to make a closed system. In the dyeing procedure, pressure and temperature were raised at the same time with 4°C/min rate. The dyeing was carried out for 10 min and then pressure was released step by step. At each step, 25 bar of pressure was reduced and the temperature was still kept at dyeing temperature for 2 min until the pressure comes down to atmosphere. As the dyeing process was completed, reducing wash was performed. For reducing wash, specimen was treated with 2g/L sodium hydroxide and 2g/L sodium hydrosulfite solution at 80°C for 10 min and then dried at 60°C.

2.3 Solubility of Dye

Dye dissolved in carbon dioxide was extracted by dimethyl formamide in solvent container as carbon dioxide passes through it. Dye particles deposited in tube were also washed with dimethyl formamide and collected in solvent container. Second solvent container was cooled with ice to reduce the volatility of dimethyl formamide. Finally, the volume of carbon dioxide, collected over the water container, was detected by wet flow meter to calculate the mole of...
carbon dioxide in accordance with the following formula \(^{17, 18}\):

\[
\frac{n_{\text{CO}_2}}{RT} = \frac{(P_{\text{sat}} - P_{\text{H}_2O} - P_{\text{sol}})}{RT} \cdot V_{\text{CO}_2}
\]

where \(n_{\text{CO}_2}\) is the mole of carbon dioxide; \(P_{\text{sat}}\), the pressure of atmosphere; \(P_{\text{H}_2O}\), the saturated vapour pressure of water in water container; \(P_{\text{sol}}\), the saturated vapour pressure of solvent (dimethyl formamide) in solvent container; \(V_{\text{CO}_2}\), the volume of carbon dioxide detected by wet flow meter; \(R\), the gas constant; and \(T\), the absolute temperature of wet flow meter.

Vapour pressure of dimethyl formamide and water was calculated using the following formula:

\[
\log P^o = A - \frac{B}{T} + C
\]

where \(P^o\) is the vapour pressure of dimethyl formamide or water; \(A\), the constant (dimethyl formamide: 6.03823, water: 7.61171); \(B\), the constant (dimethyl formamide: 1393.225, water: 1948.271); and \(C\), the constant (dimethyl formamide: 195.722, water: 249.201).

The mole of dye \((n_{\text{dye}})\) may be determined by visible spectra. Hence, the solubility of dye was calculated from the following formula:

\[
x_{\text{dye}} = \frac{n_{\text{dye}}}{n_{\text{CO}_2} + n_{\text{dye}}}
\]

where \(x_{\text{dye}}\) is the solubility of dye expressed in mole fraction.

The solubility of disperse dyes in carbon dioxide was tested using the apparatus shown in Fig. 2.

3 Results and Discussion

3.1 Microscopic Analysis

The woven microdenier polyester fabric was wound into the dyepot, the apparatus was sealed and then heated to 120°C, whilst carbon dioxide was pumped at the pressure of 250bar. The temperature was maintained at 120°C with 4% (owf) dyes for 10 min separately. The cross-section of dyed microdenier polyester fibres observed by the optical microscopy is shown in Fig. 3. The figures indicate that the dye particles have penetrated thoroughly into fibres within 10 min when carbon dioxide is the transport medium. Thus, dyeing of microdenier polyester fibres in supercritical fluid is feasible.

3.2 Dye Solubility

The solubility of disperse dyes in supercritical carbon dioxide was measured. (Table 1) Disperse Red 60 shows better solubility than the others. Besides, comparison of solubility of dyes indicates that the dyes have better solubility in supercritical fluid than in water. \(^{19}\) Both Disperse Yellow 3 and Disperse Red 60 dyes have similar solubility parameter or dye's density. Both Disperse Orange 76 and Disperse Red 60 dyes have similar \(E\) value. Hence, the Disperse Red 60 can be dissolved more easily. On the other hand, anthraquinonid based disperse dye shows higher solubility than azo based disperse dye.

3.3 Dyeing Analysis

Comparative account of dye uptake at different pressures using temperature of 120°C and dye concentration of 4% (owf) is shown in Fig. 4. Results show that the specimens dyed at higher pressures have increased dye uptake, especially at pressures above 200bar. At pressures exceeding 275bar, the dye uptake becomes lower but more even. As soon as the carbon dioxide reaches its supercritical state, disperse dye begins to dissolve and stain the fabric. It is uneven because dye particles are not dispersed evenly and most of the dye particles precipitate to the bottom of the fabric to form a deeper shade at the bottom and dye spots. This phenomena can be observed on the specimen dyed at low pressure (<150bar). When pressure is raised above 200bar, the particles staining the fabric dissolve into the fluid state and penetrate into the fibres. Leveling efficiency is greatly improved as pressure rises above 250bar. Higher
pressures dissolve dye more efficiently which makes the dye uptake greater. But at pressures greater than 275bar, superior solubility allows dye particles in stains to be dissolved back into the fluid. When the system is released, the dissolved dyed particles excluded out into the dyeing system and this reduces the dye uptake.

In second set of experiment, the dyeing was carried out at different temperatures (50, 70, 90, 110, 120 and 130°C) using 250bar pressure and 4% (owf) dye concentration. Fig. 5 shows that the dye exhaustion increases upon reaching the glass transition temperature of 80°C and reaches maximum at 120°C-130°C, which is similar to the traditional water dyeing method. But at 90°C, supercritical fluid dyeing methods get better results than water dyeing methods at the same temperatures. It is known that the fluid density of carbon dioxide in supercritical field is dependent on temperature when pressure is constant. When the temperature is higher, the fluid density will be lower. This shows that the Disperse Red 60 and Disperse Yellow 3 have better dye uptake at 90°C than that at 100°C. It is obvious that the dyes would be released from the interior of the fibre when dyeing temperature is raised, except showing the good compatibility. As shown in Table 1, Disperse Orange 76 has solubility parameter close to that of fibre. In

Table 1—Solubility of disperse dyes in supercritical carbon dioxide

<table>
<thead>
<tr>
<th>Dye</th>
<th>Density g/cm³</th>
<th>ε value⁺ L/cm-mole</th>
<th>Solubility parameter (cal/cm³)⁰⁰⁰</th>
<th>Solubility in CO₂ (x₃), mole/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.I. Disperse Red 60</td>
<td>1.24</td>
<td>12768</td>
<td>14.77</td>
<td>1.28×10⁻⁵</td>
</tr>
<tr>
<td>C.I. Disperse Yellow 3</td>
<td>1.26</td>
<td>21611</td>
<td>14.89</td>
<td>1.03×10⁻⁶</td>
</tr>
<tr>
<td>C.I. Disperse Orange 76</td>
<td>1.38</td>
<td>12987</td>
<td>13.22</td>
<td>4.95×10⁻⁶</td>
</tr>
</tbody>
</table>

⁺Characteristic of dye at the specified wavelength (λmax) according to Beer-Lambert law (Dye was dissolved in dimethyl formamide).
other words, there is more compatibility between Disperse Orange 76 and microdenier polyester fibre. Disperse Orange 76 dyed microdenier polyester fibre shows the highest uptake. Only at temperatures beyond 110°C, the leveling efficiency satisfies our requirements. Using the results from the sublimation fastness test, it is found that the samples which are dyed above 90°C have the same grade of fastness. It is believed that the supercritical carbon dioxide can plasticize the polymer and makes it dyeable at 90°C, but this phenomenon is limited and temperature is the major factor affecting fibre swelling and dye diffusion.

In third set of experiment, dye concentration was varied from 1.0% (owf) to 8.0% (owf) using 250bar pressure and 120°C temperature to observe the dyeing results. As shown in Fig. 6, the dye uptake increases as the dye concentration increases. Dye shades can be controlled using dye concentration adjustments. Dyers can also change pressure under suitable conditions simultaneously to get a satisfactory results.

3.4 Effects of Solvent
Perchloroethylene is thought to be the best choice in solvent dyeing because it can swell polyester to increase the diffusion rate of dye particles and hence indicates the dye ability of the fibre. Carrier SP is also used in dyeing processes for polyester which acts like perchloroethylene. Both the perchloroethylene and carrier SP show the solubility parameters 9.3 (cal/cm³)^(1/2) and 11.1 (cal/cm³)^(1/2) respectively which is near to polyester solubility parameter 10.0 (cal/cm³)^(1/2) (refs 19-21). Table 2 shows some data of solvent and assistant agent. In the experiment, the dyeing was carried out at 250bar×120°C×10min in supercritical fluid, using the concentration of 4% (owf) and carrier SP/water mixture of 1:1 ratio. The results show that the carrier SP and acetone reduce the dyeing efficiency. The solvents 2-methoxyethanol, DMF and DMSO give better colour yield (Fig. 7). These results can be attributed to the excellent dispersion of dye

<table>
<thead>
<tr>
<th>Solvent/fibre</th>
<th>Boiling point/melting point °C</th>
<th>Solubility parameter (cal/cm³)^(1/2)</th>
<th>Solubility x10⁻³ g dye/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td>255</td>
<td>10.0</td>
<td>—</td>
</tr>
<tr>
<td>Perchloroethylene</td>
<td>121.0</td>
<td>9.3</td>
<td>—</td>
</tr>
<tr>
<td>Carrier SP</td>
<td>245.0</td>
<td>11.1</td>
<td>—</td>
</tr>
<tr>
<td>Acetone</td>
<td>56.1</td>
<td>9.8</td>
<td>40.0</td>
</tr>
<tr>
<td>2-methoxyethanol</td>
<td>124.5</td>
<td>10.1</td>
<td>7.11</td>
</tr>
<tr>
<td>DMF</td>
<td>152.8</td>
<td>12.1</td>
<td>34.3</td>
</tr>
<tr>
<td>DMSO</td>
<td>189.0</td>
<td>12.9</td>
<td>9.4</td>
</tr>
</tbody>
</table>
particles which causes the molecules to penetrate well. Solvents, like acetone, will vaporize under dyeing conditions and then reduce the solubility power.

3.5 Fibre Analysis

The curves obtained from DSC analysis and X-ray diffraction of microdenier polyester fibres are shown in Figs 8 and 9 respectively. It is observed that the melting temperature variation is not clear for the treatment conditions 250bar×120°C×dye4%×10min in supercritical fluid. The melting point calculated by DSC is found to be 253.0-253.1°C but the X-ray diffraction curves show a little change in crystal

| Parameter                  | Fastness to
<table>
<thead>
<tr>
<th></th>
<th>Dry heating</th>
<th>Washing</th>
<th>Organic solvent</th>
<th>Rubbing</th>
<th>Xenon arc lamp light</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-reduction cleaning</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>5</td>
</tr>
<tr>
<td>Reduction cleaning</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>5</td>
</tr>
</tbody>
</table>
degree. Untreated raw polyester fibre shows 41.5% degree of crystal, fibre treated at 250bar x 120°C x dye4% x 10min in supercritical fluid shows 38.3% degree of crystal, fibre treated with DMF at 250bar x 120°C x dye 4% x 10min in supercritical fluid shows 36.2% degree of crystal, and fibre treated with DMSO at 250bar x 120°C x dye 4% x 10min in supercritical fluid shows 37.8% degree of crystal.

3.6 Colour Fastness
Data on colour fastness to dry heating, washing, organic solvent, rubbing, xenon arc lamp light are shown in Table 3. For all the above fastness conditions, specimens show the same fastness for non-reduction and reduction cleaning. The residual solution after reducing wash was also measured using a Milton Roy 3000 spectrophotometer. Table 4 shows the dye quantity in the residual solution after reducing wash. The dye quantity of the washing solution is found to be ≤0.3% above 120°C. This indicates that the post-treatment is not necessary in the supercritical fluid dyeing processes.

4 Conclusions
It is observed that the dyeing conditions for microdenier polyester fabric are suitable at 250bar, 120°C and with suitable dye concentration by using decompress-compressing procedure. The solvents DMF and DMSO could be the better choice as their boiling points are greater than dyeing temperature with better solvolysis power to selected dye. The DSC and X-ray analyses indicate no obvious damage for fabrics dyed at 250bar x 120°C x 10min in the supercritical fluid. Dye fastness is satisfactory and reducing wash is not necessary. The proposed processes have the potential for substantial energy savings and waste reduction as compared to existing methods. It is evident that these researches are still a long way from the performance of existing process. The potential benefits of another hydrophobic material’s dyeing are great and the combination of materials and application techniques needs to be explored.

Acknowledgement
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References

<table>
<thead>
<tr>
<th>Parameter</th>
<th>90°C</th>
<th>100°C</th>
<th>120°C</th>
<th>140°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye quantity μmol/g</td>
<td>0.044</td>
<td>0.026</td>
<td>0.030</td>
<td>0.027</td>
</tr>
<tr>
<td>Per cent</td>
<td>0.63</td>
<td>0.34</td>
<td>0.29</td>
<td>0.25</td>
</tr>
</tbody>
</table>

*Dye quantity in residual solution / dye quantity on fibres)x100%