Supercritical Dyeing of Polyester Fibers in a Mini-Plant Possessing Internal Circulator

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Abstract: The polyester fabric (PET) was dyed with C.I. Solvent Blue 35, C.I. Disperse Red 60 and C.I. Disperse Yellow 54 in supercritical carbon dioxide (scCO2) using the apparatus that possesses circulation system. The experimental conditions were optimized to obtain both visibly and spectrophotometrically uniform dye uptake in PET fabric. The staining of the dye was suppressed by addition of stainless mesh and cotton fabrics between the PET specimen and the stainless cylinder settled in the high-pressure column. The visible difference of color depth between the layers of fabric was improved with circulation of the dye bath especially as the scCO2 was released after the dyeing. The spectrophotometric measurements firmly indicated the invisible distinction of dye uptake between the fabric layers, which was inhibited by enhancement of duration in the process of scCO2 release. The 88-97% dye uptake of C.I. Solvent Blue 35 and C.I. Disperse Red 60 was obtained in scCO2 dyeing by the improved procedure.

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1. Introduction

Supercritical fluid is an attractive medium applied to recycling polymer materials [1,2], decomposition of harmful substances [3,4], extraction [5-7] and impregnation [8,9] of target components from/to polymer products. The supercritical water and methanol are highly reactive thus they are used for not only decomposition of substances inducing environmental pollution e.g. poly chlorinated biphenyl (PCB) and dioxin [10], but also recycling of the fibers and other polymer materials [11]. The supercritical carbon dioxide (scCO2) has been applied in the various fields especially polymer processing. It promotes the impregnation of many functional compounds and foaming of polymer products due to its plasticizing effect and high permeability into polymer materials [12]. Furthermore, supercritical carbon dioxide fluids is inactive, cheap, easy to obtain (Tc=31.1°C and Pc=7.28MPa) and more easily recycled as compared to supercritical water and methanol, leading to lower initial cost for the equipments and smaller amount of emission in processes.

Researches on scCO2 dyeing of fibers were sensational launched in 1990 [13], while the scCO2 has been industrially applied to the extraction of caffeine from coffee beans and the essence from hops since 1970s [14]. The supercritical dyeing requires no auxiliaries, no emission because of the recycle of CO2, and no drying process meaning low energy consumption. Moreover, the dye remained in the dye bath is reusable. These are specific advantages of scCO2 and it is difficult to gain such benefits in water dyeing. A lot of fundamental investigations of scCO2 dyeing have been done however only a few trials for practical use were performed so far [15,16]. Previously we conducted elemental investigations of the swelling behavior of polymer materials in scCO2 [17], solubility of dyes into scCO2 [18] and diffusion coefficients of the dyes between scCO2 fluid and the fibers [19], and proposed the mechanism of scCO2 dyeing [20].

For a purpose in developing the scCO2 dyeing to technical scale, an apparatus consisting of 2.2 l column and a circulation system was designed and used for scCO2 dyeing of polyester fabric with commercially available solvent and disperse dyes in the present study. The effects of experimental conditions e.g. flow of the fluid in the dye bath and speed of decompression of scCO2 on the dyeing were investigated.
2. Experimental

2.1 Materials

Poly(ethylene terephthalate) fabric (PET; twill, fabric mass/area: 185 g/m²) was supplied from Toyobo Co., Ltd. C.I Solvent Blue 35, C.I. Disperse Red 60 and C.I. Disperse Yellow 54 without any addition of surfactants and salts were provided by Komatsu Seiren Co., Ltd. The chemical structure of the dyes is given in Table 1. Cotton strings and cotton fabric with a 10% viscose rayon mix (cotton fabric 1) were purchased from Yutaka Make Co., Ltd and the Yamazaki Corporation, respectively. Cotton fabric which side had flannel structure (cotton fabric 2), and mercerized one (cotton fabric 3, density: 130 × 70 yarns/inch, mass/area: 122 g/m²) was supplied from Shikisensha Co., Ltd. Stainless net (18 mesh) provided by Tao kana-ami Co., Ltd was composed of stainless wire with 0.2 mm diameter. Liquid carbon dioxide (≥99.995%) was obtained from Uno sanso Co., Ltd. N,N-dimethylformamide (DMF) was reagent grade from Nacalai Tesque.

2.2 Supercritical Fluid dyeing

The PET fabric was cut in 15×160 cm² using a heat-cutter. The fabric specimen was rolled around a stainless cylinder bearing punched holes (0.5 cm diameter), and fixed with a piece of cotton string. The fabric specimen tied on the cylinder was loaded in the high-pressure column with 2230 ml volume (Fig. 1) and a cotton paper wrapping dye inside was set on the cylinder. The carbon dioxide was pumped up to 25 MPa to obtain supercritical carbon dioxide (scCO₂). The high pressure CO₂ was preheated up to 128 °C and then passed to the column heated at 120 °C. The head of the pump was kept at -5 °C using a cooler. The circulation system was initiated as the pressure of CO₂ reached at 10 MPa. The stream of the fluid was induced using a magnetic drive settled under the column and a stainless impeller. The speed of the magnetic drive was 750 rpm. The fluid was flowed from inside to outside of the cylinder. After the temperature, pressure and speed of the circulation reached at certain stable values, the condition was hold for 30 min in order to dye the fabric. The pressure was then reduced to the atmospheric pressure with control of the speed, and the PET fabric was taken out from the column.

The uptake of the dye was spectrophotometrically determined. The fabric dyed in scCO₂ was cut in 2×3 cm² and dipped in 20 ml DMF at 100°C for 60 min to extract the dye. The UV/Vis spectra of the dye solution were measured with a spectrophotometer (Shimadzu UV-1700) and the dye uptake was estimated at wave length of maximal adsorption (λmax). The λmax of C.I. Solvent Blue 35, C.I. Disperse Red 60 and C.I. Disperse Yellow 54 in DMF were 644 nm, 521 nm and 445 nm, respectively.

Table 1 Chemical structure of dyes used for supercritical dyeing.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.I. Solvent Blue 35</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>C.I. Disperse Red 60</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>C.I. Disperse Yellow 54</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1 Influence of flow in dyeing

The photo images of the PET fabric dyed in scCO\textsubscript{2} are shown in Fig. 2. The staining of the dye was observed on the fabric along the holes, suggesting inhomogeneous dyeing, as the fabric was directly rolled on the cylinder without any addition between the cylinder and specimen fabric ((a) in Fig. 2).

The addition of cotton fabric or metal mesh between the cylinder and the PET fabric was examined to reduce the staining and unevenness of dye adsorption. The condition of the trials and the results are given in Table 2. The staining was still observed although cotton fabrics were loaded between the cylinder and the PET specimen. The use of both metal mesh and cotton fabric 3 improved the homogeneity in dyeing as displayed in Fig. 2. It is presumed that the flow of scCO\textsubscript{2} containing dyes is uniformly distributed via stainless mesh after it is passed though the holes on the cylinder while the scCO\textsubscript{2} penetrates into the cotton fabric resulting in no change of the stream.

3.2 Influence of circulation in decompression of scCO\textsubscript{2}

The staining of dye due to the holes on the cylinder was hindered by addition of stainless mesh and cotton fabrics. However, visible difference of color depth between the fabric layers was still obvious. The effect of circulation of the dye bath during the release of pressure on the dye uptake was investigated.

The fabric was dyed with 2.0 %\textsubscript{owf} dye in scCO\textsubscript{2} at 120 °C and 25 MPa for 30 min, and the pressure was then reduced to the atmospheric pressure (0.1 MPa) in 10 min with circulating the fluid. The dye uptake estimated spectrophotometrically is plotted against the number of layer in Fig. 3. The number of layer was counted from inside to outside of the rolled specimen. The uptake is decreased with increasing the layer number for all dyes although the visible color difference between the layers was very slight. The visible difference of color depth might be retarded in the following manner; the density and temperature of scCO\textsubscript{2} are lowered when the pressure is reduced, leading to reduction of solubility of the dye in scCO\textsubscript{2}. The reduction in the solubility causes precipitation of the dye in the column. The precipitated dye is filtered by the fabric on the cylinder and accumulated inside of the fabric. The accumulation of dye is prevented by circulation of fluid. Consequently, the stirring of the fluid inside to outside of the rolled specimen.

![Fig. 2](https://example.com/image2)

**Table 2** Effects of additional cotton fabrics and stainless mesh on supercritical dyeing of PET fabric.

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Cotton string</th>
<th>Cotton fabric 1 (number of layers)</th>
<th>Cotton fabric 2 (number of layers)</th>
<th>Cotton fabric 3 (number of layers)</th>
<th>Stainless mesh (cm\textsuperscript{2})</th>
<th>Staining of dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>lots</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>lots</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>lots</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>lots</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>lots</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>lots</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>4</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>lots</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>-</td>
<td>15 x 91</td>
<td>much less</td>
</tr>
</tbody>
</table>

The cotton fabrics were loaded between the cylinder and PET specimen. The cylinder was wrapped with cotton fabric 1, cotton fabric 2 and then PET fabric in trial No. 7. In trial No. 8, stainless mesh was put on the cylinder and then cotton fabric 3 and PET fabric were rolled successively. The fabrics were dyed with C.I. Solvent Blue in scCO\textsubscript{2} at 120 °C and 25 MPa for 30 min.
during release of the pressure inhibits the accumulation of dye, which diminishes the difference of color depth between the layers.

The relationships between the dye uptake and the layer number as the mixture of two dyes was used in the scCO₂ dyeing are exhibited in Fig. 4, Fig. 5 and Fig. 6. In these experiments, the scCO₂ was released from the column to the atmosphere with stirring in 10 min after the dyeing. The apparent color difference between the layers of PET fabric was not significant not only when one dye was singly used but also when two different dyes were simultaneously used for the dyeing. However, the dye uptake determined spectrophotometrically is decreased with increase in the number of layer in both cases.

### 3.3 Influence of duration in decompression of scCO₂

The apparent color differences between the layers of PET fabric dyed with solvent and disperse dyes in scCO₂ was minimized by the stirring of the dye bath during the scCO₂ release. However, spectrophotometric analysis suggested uneven dyeing although the dyeing method was improved by the stirring. The influence of duration in the pressure release on the dye uptake was investigated. The fabric was dyed with C.I. Solvent Blue 35 in scCO₂ and then the pressure was reduced to the atmosphere in 20 min with circulating the fluid. Fig. 7 demonstrates the plots of dye uptake against the layer number. The expansion of release time for scCO₂ results in the homogeneous dye uptake in PET fabric. The decrease in the release speed of scCO₂ must promote a migration of the dye in the fabric, causing the even dyeing.

The scCO₂ dyeing of PET fabric was improved by addition of stainless mesh between the cylinder and PET specimen, stirring the fluid and increase of the duration in the process of scCO₂ release. The PET fabric was dyed by this improved method and the dye uptake in PET was spectrophotometrically determined. The results are summarized in Table 3. The uptake of C.I. Solvent Blue 35 and C.I. Disperse Red 60 is 88-97% owf as the initial concentration is 0.5 and 2.0 % owf. These uptakes are sufficient for industrial dyeing in factories. However, the dye uptake of C.I. Disperse Yellow 54 is smaller than that of other dyes. Considering the fact that large amount of yellow dye was left in the column after the dyeing, the small uptake maybe due to the lower solubility of the yellow dye into scCO₂ as compared with that of blue and red dyes. Further experiments are required to find the good yellow dye for scCO₂ dyeing.

### Table 3 Total dye uptake in PET fabric dyed uniformly using supercritical carbon dioxide.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Conc. of dye (%owf)</th>
<th>Dye uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.I. Solvent Blue 35</td>
<td>0.5</td>
<td>95.8</td>
</tr>
<tr>
<td>Blue 35</td>
<td>2</td>
<td>88.8</td>
</tr>
<tr>
<td>C.I. Disperse Red 60</td>
<td>0.5</td>
<td>93.9</td>
</tr>
<tr>
<td>Red 60</td>
<td>2</td>
<td>96.7</td>
</tr>
<tr>
<td>C.I. Disperse Yellow 54</td>
<td>0.5</td>
<td>80.9</td>
</tr>
<tr>
<td>Yellow 54</td>
<td>2</td>
<td>31.7</td>
</tr>
</tbody>
</table>

The fabric was dyed using stainless mesh of 91 cm length and 4 pieces of cotton fabric 3 at 120 °C and 25 MPa for 30 min in scCO₂. The scCO₂ was released from the column to the atmosphere with stirring in 20 min after the dyeing.

### 3.4 A mechanism of scCO₂ dyeing in circulation system

The effects of use of stainless mesh, stirring the dye bath and decrease in release speed of scCO₂ on the dyeing propose a model for a mechanism of scCO₂ dyeing of PET with solvent and disperse dyes using the apparatus with circulation system as shown in Fig. 8. As the specimen fabric is directly located around the cylinder or cotton fabrics are supplied between the cylinder and the specimen (1-(a)), the scCO₂ containing the dye is passed though the holes on the cylinder and the fabric, resulting in the staining of the dye, visible difference of color depth and spectrophotometric difference of dye uptake between fabric layers (1-(d)). The use of the stainless mesh between the cylinder and the specimen leads to the higher fluid distribution (2-(a), 3-(a) and 4-(a)), which makes the fabric dyed without staining but with visible and spectrophotometric differences of color depth (2-(d), 3-(d) and 4-(d)).

No stirring of the dye bath during the release of scCO₂ (2-(b)) causes visible unevenness of dyeing (2-(d)) while the circulation of the bath (3-(b) and 4-(b)) brings the apparently homogeneous dyeing (3-(d) and 4-(d)). This result might be owing to the retardation of accumulation of the dye on the fabric. Additionally, the decrease in release speed of scCO₂ after the dyeing (4-(c)) results in the homogeneous dye uptake both visibly and spectrophotometrically as shown in 4-(d).

Consequently, PET fabric is uniformly dyed with high uptake of especially C.I. Disperse Red 60 and C.I. Solvent Blue 35 in scCO₂ by the improved procedure using stainless net, circulation of dye bath particularly
4. Conclusions

The apparatus essentially consisting of high-pressure pump, heater, high-pressure column and the circulation system was designed and used for scCO$_2$ dyeing of PET fabric with solvent dye and disperse dyes. The staining of the dye was observed and the dyeing was visibly and spectrophotometrically inhomogeneous in the first trial. The apparatus and experimental conditions were modified to acquire the even dye uptake between the fabric layers rolled around a holder. The flow of the dye fluid was during the release of scCO$_2$ and increase in duration for the release of scCO$_2$.
changed by adding stainless net between the specimen and the cylindrical holder, providing less staining. The fabric was uniformly dyed in scCO2 from the visual view when the scCO2 containing dyes were circulated not only during the dyeing but also during the release of scCO2. The circulation prevented the layers of PET fabric from clogging up with the precipitated dye and irregular flow of the scCO2. However, the spectrophotometric measurements clearly indicated the uneven dye uptake between the fabric layers. The dyeing in scCO2 was further improved by altering speed i.e. increase of the duration in the process of scCO2 release, which resulted in spectrophotometrically even dyeing of PET fabric.

Consequently, PET fabric is uniformly dyed with high uptake of especially C.I. Disperse Red 60 and C.I. Solvent Blue 35 in scCO2 by the improved procedure using stainless net, circulation of dye bath particularly during the release of scCO2 and increase in duration for the release of scCO2.

The addition of stainless mesh, the circulation of dye bath during the release of scCO2 and increase in the speed of scCO2 release resulted in even distribution of fluid in the dye bath, the homogeneous precipitation of the dye and even migration of the dye, leading to uniform scCO2 dyeing of PET.

References


