Research on Sustainable Textile Production: Waterless Dyeing of PET and Recycled PET Fabrics

Raziskave o trajnostni proizvodnji tekstila: brezvodno barvanje poliestrskih in recikliranih poliestrskih tkanin

Abstract

Due to water limitations and the growing global demand for raw materials, manufacturers and consumers are seeking more environmentally friendly alternatives. Polyester, a non-biodegradable fibre derived from petroleum, can be replaced with recycled polyester (r-PET), a sustainable alternative that reduces environmental impacts through the reuse of materials. The textile finishing industry, known for its high water and energy consumption, is calling for the development of low-water-consumption technologies. One innovative approach involves waterless dyeing procedures using a supercritical carbon dioxide (scCO₂) medium that is particularly suitable for dyeing synthetic fibres. To assess its effectiveness, a study compared traditional water dyeing with scCO₂ medium dyeing on woven fabrics made from both polyester (PET) and recycled polyester (r-PET) fibres with varying weights. After conducting tests on the dyed fabrics, the data revealed that r-PET fabrics dyed using a supercritical carbon dioxide (scCO₂) medium appeared darker than fabrics dyed using traditional water dyeing techniques. Moreover, r-PET fabrics demonstrated better colour fastness. Notably, the K/S_{sum} values (measurement of colour intensity) of r-PET fabrics were at least as good as those of PET-based fabrics in all cases of dyeing, while the fastness values were similar for both PET and r-PET fabrics.

Keywords: supercritical carbon dioxide medium, polyester fabric, recycled polyester fabric, dyeing, sustainable
1 Introduction

Two of the most important problems for the textile industry are industrial waste and water consumption [1]. Given the chemicals they contain, the water they consume and the associated drying processes, traditional water dyeing processes cause a significant amount of energy and resource consumption. The byproducts of dyeing do not degrade and cannot be recycled [2]. Dyeing processes in a supercritical medium involve a solution that can be applied to reduce this energy and resource consumption. No water is used for dyeing in supercritical environments. Preferred instead, is CO$_2$, which readily adapts to the supercritical medium. CO$_2$ is not a flammable substance, is non-toxic and is reasonably priced. It can easily reach the critical pressure ($P_c = 7.38$ MPa) and critical temperature ($T_c = 31.1$ °C) [3]. Supercritical carbon dioxide dyeing (scCO$_2$) has come to the fore in recent years among dyeing processes with its short dyeing time, easy recovery, high dye uptake and zero waste emission. Similar to the dyeing processes used for synthetic fibres, studies have been carried out in the dyeing of natural fibres in recent years [4, 5].

Polyester (PET) fibres have long been widely used in the textile industry due to their good mechanical properties and excellent dyeability. According to statistics, PET constitutes approximately 50% of the fibre market and growth is expected to increase in the coming periods [6]. Polyester also currently accounts for around 49% of the world’s apparel, while estimates indicate that this proportion will nearly quadruple by 2030. It is thought that this increase in dependence on polyester textiles will bring environmental problems [7]. The use of recycled polyester (r-PET), as a textile raw material produced using various methods (physical or chemical), has alternative applications to virgin polyester [8, 9]. The use of recycled polyester instead of virgin polyester reduces dependence on petrochemicals, and creates advantages such as reduced energy consumption and fewer carbon dioxide emissions. It has been found that the production of r-PET yarns requires 50% less energy than virgin polyester yarns, while carbon emissions are reduced by more than 55% and water consumption is reduced by 20% [10].

While investigating research in literature, it was found that polyester fibre is successfully dyed in scCO$_2$ medium without using any water, whereas the traditional polyester dyeing process uses high amounts of water, energy and chemicals [11−15]. Supercritical carbon dioxide dyeing was reported to offer an environmentally friendly alternative with results comparable to synthetic fibre dyeing, while eliminating water consumption and reducing air pollution [16]. Polyester fabrics are dyed using disperse dyes and, in traditional dyeing processes, dispersants are used to achieve uniform dispersion and stability [17]. However, the fact that disperse dyestuffs have plasticizing and swelling properties against hydrophobic polymers, and dissolve in a scCO$_2$ medium without a co-solvent, make this technology important [18].

Although there are many studies on the dyeing of PET fabrics in literature, no experimental study was found in terms of comparing the traditional water dyeing method of PET and r-PET fabrics and the dyeing processes in a scCO$_2$ medium. In this study, traditional water dyeing and scCO$_2$ medium dyeing were performed to compare the dyeing performances of woven fabrics produced from PET and r-PET fibres in different weights. The colour performance,
fastness values and strength values of the fabrics were compared.

2 Experimental

2.1 Materials
In the study, 100% polyester and 100% recycled polyester plain woven fabric, manufactured by Berteks A.Ş., were utilized. The warp and weft densities of the fabrics were 20 warp/cm and 20 weft/cm, respectively. Fabrics were produced from two spun yarns of Ne 30/1 (20 tex) and Ne 30/2 (20 tex). Ne 30/1 fabric weights were 63 g/m² and 60 g/m² for PET and r-PET fabrics, respectively. Ne 30/2 fabric weights were 96 g/m² and 99 g/m² for PET and r-PET fabrics, respectively. Two colours, Dianix Rubin S-2G (C.I. Disperse Red 167) and Dianix Yellow S-6G (C.I. Disperse Yellow 114) were chosen to be used in dyeing. In traditional dyeing, acetic acid (C₂H₄O₂), sodium hydrosulphite (Na₂S₂O₄), sodium hydroxide (NaOH) produced by Merck and dispersant produced by Onan Kimya were used.

2.2 Traditional dyeing
Traditional dyeing was carried out at dyestuff concentrations of 0.1% and 1% in a solution ratio of 1:30, 1 ml/L dispersant and 1 ml/L acetic acid bath at 120 °C for 60 minutes [14]. After the samples were dyed, they were post-washed with 2 g/L NaOH and 2 g/L Na₂S₂O₄ at 80 °C (Figure 3).

2.3 Supercritical CO₂ chemical reaction and dyeing apparatus
The waterless dyeing processes of polyester fabrics were carried out in a device manufactured by DyeCoo, in a container with a volume of 290 mL. The prepared containers were kept in a Vestel SD 200 model deep freezer for cooling, and carbon dioxide was added to the container. The fabrics were wrapped in mesh and placed inside the container, and steel balls were placed inside. The prepared containers were placed in an oil bath containing polyethylene glycol in a Rapid Xiamen Model H-12 device manufactured by DyeCoo for scCO₂ treatment. Dye ratios of 0.1% and 1% were chosen. The experiments were carried out at 120 °C under 25 MPa pressure for 60 minutes [15, 19, 20]. The amount of CO₂ needed was calculated from http://webbook.nist.gov/chemistry/ according to the pressure and temperature values. After the process, the samples were post-washed with acetone.

Figure 1: Molecular structure of Disperse Yellow 114

Figure 2: Molecular structure of Disperse Red 167

Figure 3: Dyeing diagram
2.4 Characterization of the dyed textiles

**Colour strength**

After dyeing, the \(K/S\) values of the samples were calculated from the reflectance values of the maximum absorbance (\(\lambda_{\text{max}}\)) at the appropriate wavelength using a Konica Minolta CM3600D spectrophotometer under illuminant D65 using a 10° standard observer. The \(K/S_{\text{sum}}\) values of the specimens (obtained by summing all \(K/S\) values measured at 10-nanometer intervals within the measurement wavelength range) were assessed.

**Colour fastness to washing and rubbing**

Washing fastness tests were carried out using TEST Laboratory Equipment 412 NB HT according to the ISO105:C06-B2S test method. Rubbing fastnesses were determined according to TS EN ISO 105-X12 standards. The results were measured in a reflectance spectrophotometer and the values were recorded.

**Colour fastness to light**

Light fastness tests were carried out in accordance with the ISO 105-B02:2014 standard. Light fastness refers to the ability of a dye to resist fading when exposed to light. Textile dyes are classified for light fastness on a scale from one to eight. The measurement of light fastness often involves the use of a Xenotest150S Arc device. At the end of the light fastness test, which lasted for three days (72 hours), the colour fading of the fabrics was observed and the colour values of the fabrics measured in the reflectance spectrophotometer were recorded.

**FTIR (Fourier-transform infrared spectroscopy) analysis**

The structure of PET and r-PET fabrics was analysed using FTIR spectroscopy (Shimadzu, IRSpirt) at room temperature. Samples were scanned in the range of 400 cm\(^{-1}\) and 4000 cm\(^{-1}\).

**Tensile strength**

Tensile strength tests were performed using a SHIMADZU Model AG-Xplus (Kyoto, Japan) test device in accordance with the ISO 13934-1 standard, and the results were recorded.

**Scanning electron microscope (SEM) analysis**

The surface characteristics of the raw fabric, and scCO\(_2\)-dyed, and traditionally dyed samples were studied through SEM analysis. Employing an in-house method, the images were captured at a magnification of 30x and 1000x to magnify the morphological features.

3 Results and discussion

This experimental investigation encompassed two distinct dyes, namely red and yellow, utilized at dye concentrations of 0.1% and 1%.

3.1 Dyeing with C.I. Disperse Red 167

The \(K/S_{\text{sum}}\) values related to Disperse Red 167 dyeing are presented in Figures 4 and 5. When reviewing these figures, it is clear that elevating the dyeing concentration leads to an augmentation in \(K/S_{\text{sum}}\) values for both PET and r-PET fabric types in both traditional and waterless dyeing processes. This outcome could be attributed to intensified dye molecule absorption onto the fibre surface with increasing concentration, resulting in surface layer formation. A comparison between dyeing methodologies conducted in aqueous solutions and in a scCO\(_2\) medium, as depicted in Figures 4 and 5, reveals that scCO\(_2\) dyeing yields more intense colours than traditional dyeing. The same dye concentration produces deeper shades when employed in scCO\(_2\) dyeing. Mechanical recycling stands as the predominant approach for repurposing polyester fabrics. Remarkably, this technique does not alter the molecular structure of polyester fibres, thus rendering the dyeability of both PET and r-PET fabrics quite similar [21, 22]. When evaluating fabric components, it is clear that the colour strength of r-PET fabrics surpasses that of PET fabrics. Figure 6 illustrates visual representations of PET and r-PET fabrics subjected to Disperse Red
167 dyeing, employing both traditional and scCO₂ methods. The images underscore the darker hues attained for both PET and r-PET-based fabrics in the scCO₂ medium.

![Figure 4: K/S\textsubscript{sum} values of dyeing with Disperse Red 167 (Ne 30/1 Fabric)](image)

Analysis of dyeing effectiveness should take into account both colour fastness and colour strength. According to Table 1 for the red dyestuff, commercially acceptable, high washing fastness values (4/5 grey scale values). In addition, there was no significant difference in washing fastness values between PET and r-PET fabrics. The observed rubbing fastness were in the range of 4–5.

The lightfastness of dyed textiles is inherently linked to both the chemical structure and physical attributes of the fibres themselves. When assessing the lightfastness data, it is evident that for the red dyestuff applied to fabrics through a scCO₂ medium, the fabrics dyed using traditional techniques display superior fastness characteristics. Enhanced dispersion of the dye within the fibre matrix corresponds to reduced fading effects. In this context, it can be inferred that dye molecules achieve better entrapment within the fibre structure when used in fabrics dyed through a scCO₂ medium [23]. Lightfastness values typically increase when the dyestuff concentration is increased [24], a trend corroborated by the findings presented below. When reviewing Table 2, no notable distinction in lightfastness values emerges between PET and r-PET fabrics.

![Figure 6: Images of Ne 30/1 fabrics and Ne 30/2 fabrics dyed with Disperse Red 167](image)
Table 1: C.I. Washing and rubbing fastness values of fabrics dyed with Disperse Red 167

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye concentration (%)</th>
<th>Method</th>
<th>Washing fastness</th>
<th>Rubbing fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>WO&lt;sup&gt;a&lt;/sup&gt;</td>
<td>PAC&lt;sup&gt;b&lt;/sup&gt;</td>
<td>PES&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ne 30/1 Fabrics PET</td>
<td>0.1</td>
<td>Traditional</td>
<td>4–5</td>
<td>4–5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>scCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4–5</td>
<td>4–5</td>
</tr>
<tr>
<td>Ne 30/1 Fabrics r-PET</td>
<td>0.1</td>
<td>Traditional</td>
<td>4–5</td>
<td>4–5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>scCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4–5</td>
<td>4–5</td>
</tr>
<tr>
<td>PET</td>
<td>1</td>
<td>Traditional</td>
<td>4</td>
<td>4–5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>scCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4–5</td>
<td>4–5</td>
</tr>
<tr>
<td>Ne 30/2 Fabrics r-PET</td>
<td>1</td>
<td>Traditional</td>
<td>4</td>
<td>4–5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>scCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4–5</td>
<td>4–5</td>
</tr>
<tr>
<td>PET</td>
<td>1</td>
<td>Traditional</td>
<td>3–4</td>
<td>4–5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>scCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4–5</td>
<td>4–5</td>
</tr>
<tr>
<td>r-PET</td>
<td>1</td>
<td>Traditional</td>
<td>4</td>
<td>4–5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>scCO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4</td>
<td>4–5</td>
</tr>
</tbody>
</table>

<sup>a</sup> wool; <sup>b</sup> acrylic; <sup>c</sup> polyester; <sup>d</sup> polyamide; <sup>e</sup> cotton; <sup>f</sup> acetate

Table 2: C.I. Light fastness values of fabrics dyed with Disperse Red 167

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye concentration (%)</th>
<th>Fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Traditional method</td>
</tr>
<tr>
<td>Ne 30/1 Fabrics PET</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>r-PET</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>PET</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>r-PET</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

| Ne 30/2 Fabrics PET | 0.1 | 3 | 4 |
| r-PET | 0.1 | 2–3 | 3–4 |
| PET | 1 | 2–3 | 4 |
| r-PET | 1 | 3 | 4–5 |

3.2 Dyeing with C.I. Disperse Yellow 114

Figures 7 and 8 illustrate the $K/S_{\text{sum}}$ values associated with Yellow 114 dyeing. A detailed analysis of these figures reveals an increase in $K/S_{\text{sum}}$ values for both PET and r-PET fabrics, whether subjected to traditional water dyeing or waterless dyeing, when dyeing concentrations were increased. This observation aligns with the notion that higher dye concentrations lead to increased absorption of dye molecules onto the fibre surface, culminating in the formation of a surface layer, as discussed earlier. Taking into account the dye concentration, it is evident that the colour potency of Disperse Yellow 114 dyestuff is more pronounced in scCO<sub>2</sub> dyeing processes than in traditional methods, which is in line with the trend noted for Disperse Red 167 dyestuff. It is evident from Figures 7 and 8 (although the $K/S_{\text{sum}}$ values...
of r-PET fabrics conventionally dyed with Disperse Yellow 114 are generally lower than PET fabrics) that the colour strength of r-PET fabrics in dyeing in a scCO$_2$ medium was much higher than PET fabrics. This observation underscores the notable advantages of employing a scCO$_2$ medium for dyeing r-PET fabrics.

Shown in Figure 9 are images depicting fabrics of Ne 30/1 and Ne 30/2 varieties, both dyed with Disperse Yellow 114 dyestuff. These dyeing results align with the patterns depicted in the K/S$_{sum}$ graphs, as apparent from the visual examination of the images.

The washing fastness values pertaining to dyeing carried out using Disperse Yellow 114 dyestuff are presented in Table 3 below. Notably, the obtained results exhibit washing fastness values that are commercially acceptable and of a high standard (rated as 4/5). The observed rubbing fastnesses were in the range of 4–5. Furthermore, when comparing the scCO$_2$ dyeing approach with the traditional method, it is evident that the scCO$_2$ process yields values that are either on par with or exceed the performance of the traditional method, with instances where the scCO$_2$ process even outperforms the traditional method. When the data is thoroughly analysed, it can be concluded that the fabric type, whether PET or r-PET, does not exert any discernible influence on the washing fastness values.
The light fastness test results are given in Table 4. As previously stated, the distribution of the dyestuff into the fibre and the amount of fading are inversely proportional. When the findings were compared to the traditional method, dyeing performed using a scCO2 medium showed higher light fastness values. Additionally, when the results from Table 4 light fastness values between PET and r-PET materials are compared, there is no apparent difference.
3.3 Analysing FTIR results

The FTIR results showed that PET and r-PET fibres produced peaks that were consistent with available literature [25‒27]. The 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) peaks are compatible with the asymmetric and symmetric stretching of the CH\(_2\) groups from the ethyl chains in the fibre. The peak at 1712.7 cm\(^{-1}\) is associated with the C=O bond. While the 1408 cm\(^{-1}\) stretching vibration is attributed to the aromatic ring, it is associated with the peak CH\(_2\) groups found at 1338.5 cm\(^{-1}\) [26]. Peaks of 1242.1 cm\(^{-1}\) and 1095.5 cm\(^{-1}\) are attributed to the stretching vibrations of the C—O groups. Finally, the peak at 721.3 cm\(^{-1}\) is usually associated with the deformation peak originating from the benzene rings in the fibre chains of the C—H groups [27].

When analysing the FTIR results (Figure 10), it is evident that both the dyeing process and the chosen dyeing medium have no discernible impact on PET and r-PET fabrics. The fact that dyeing processes in a scCO\(_2\) medium do not damage the molecular structure and that the fibre structure is preserved can be understood from the results.

![Figure 10: a) Untreated PET fabric, b) Untreated r-PET fabric, c) Traditional dyed PET fabric, d) Traditional dyed r-PET fabric, e) ScCO\(_2\) dyed PET fabric, f) scCO\(_2\) dyed r-PET fabric](image-url)
3.4 Tensile strength analysis
The effects of dyeing and traditional dyeing processes in a supercritical medium on the tensile strength of PET and r-PET fabrics were investigated. Maximum force (N) values were measured as shown in Figures 11, 12 and 13. When the results were evaluated, it was observed that the maximum strength values of PET and r-PET fabrics are close to each other; however, the strength values of PET fabrics are generally higher. This situation was comparable with studies in literature [28]. It was observed that the maximum strength values of the samples dyed in a scCO₂ medium, in both colours, are generally higher than the traditional water dyeing process. The thickness of the fabrics strengthens the structure of the fabric, as stated in literature, and causes the fabric to be more durable [29]. For this reason, it was observed that the maximum strength values of thick fabrics were higher for both colours. It was observed that the strength values of dyed fabrics are generally higher than the raw fabric strength values for both colours. Compared to the other samples, the samples dyed with a scCO₂ medium have the highest strength values.

![Figure 11: Strength values of raw fabrics](image1)

![Figure 12: Maximum force values of dyeing with Disperse Red 167](image2)

![Figure 13: Maximum force values of dyeing with Disperse Yellow 114](image3)
3.5 SEM analysis

SEM images of the most intensely coloured sample are presented in Figure 14. Based on this, it can be observed that samples dyed in a scCO$_2$ medium and the raw sample exhibit similar SEM images. In contrast, the sample dyed using the traditional method displays a slightly more intricate structure, with fibres appearing more prominently on the surface. This is believed to be a result of the mechanical effects induced by the movement of the dye bath in the traditional dyeing method. It was thus presumed that samples dyed using the scCO$_2$ method cause less damage to the fibre structure.

![SEM images](image)

Figure 14: SEM images of samples: a & d) raw fabric; b & e) scCO$_2$ dyeing; c & f) traditional dyeing

4 Conclusion

As conventionally understood, polyester fabric is typically dyed using traditional aqueous dyeing methods at temperatures of around 130 °C, often necessitating the inclusion of auxiliary chemicals [30, 31]. Interestingly, a notable observation emerges, wherein higher K/S$_{sum}$ values are achieved in a scCO$_2$ medium, characterized by lower dyeing temperatures and an absence of additional chemicals beyond dyestuffs. This holds true when comparing the dyeing outcomes of a scCO$_2$ medium to those of the traditional water-based dyeing method. Furthermore, the achievement of effective dyeing for r-PET fabrics in a waterless medium bears significant importance in today’s context, where resource depletion underscores the significance of recycling efforts. Notably, the K/S$_{sum}$ values attributed to r-PET fabrics generally surpass those of PET fabrics when subjected to dyeing in scCO$_2$ mediums. This is in line with existing literature where studies also provide support for this trend [21]. It was understood that the highest K/S values occurred in a scCO$_2$ medium at 120 °C and a 1% dyestuff concentration. This phenomenon can be attributed to the higher proportion of amorphous regions in r-PET fabrics compared to PET fabric, resulting in dye molecules becoming entrapped within these amorphous regions [32]. The used of less dyestuff during the scCO$_2$ dyeing process for r-PET fabrics, as opposed to PET fabrics, highlights a noteworthy advantage in terms of both conserving raw materials and energy resources. This presents a beneficial prospect for sustainability. Despite the absence of a significant divergence
in terms of washing and light fastness properties between PET and r-PET fabrics, the fastness values of materials dyed in scCO$_2$ mediums are generally better than those obtained through water-based methods. FTIR analysis corroborates that scCO$_2$ dyeing processes do not compromise the molecular structure of PET and r-PET fabrics, preserving their chemical composition without alteration. Although the mechanical attributes of r-PET fabrics may slightly lag behind those of PET fabrics, the disparity is not substantial enough to impede their use. Additionally, dyeing carried out in scCO$_2$ mediums typically yields enhanced tensile strength values. In light of these findings, it is reasonable to conclude that scCO$_2$ mediums establish a more protective environment for fabrics. Based on the experimental findings, r-PET fabrics hold the potential to serve as a viable alternative to PET fabrics in waterless dyeing processes. Given the imperative to curb waste and judiciously exploit limited resources, dyeing r-PET-based fabrics in scCO$_2$ mediums is emerging as a promising and forward-looking solution.

**Conflict of Interests**

The authors declare that they have no conflict of interest.

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