LIU, CHENGYANG. Characterization of the Effects of a Pretreatment on Dark Colored Polyester Fabrics. (Under the direction of Dr. Harold S. Freeman and Dr. Lisa Parrillo-Chapman).

Inkjet printing of polyester (PET) fabric requires a pretreatment step that enhances the receptivity of the fabric surface to water-based inks. During the course of printing on dyed fabrics, it was found that application (spraying or padding) of a commercial pretreatment agent often caused a significant color shift when applied to dark colored surfaces. Since the printed area is typically smaller than the pretreated area, this development poses a problem for the printers. Therefore, the goal of this project was to determine the cause of the unwanted color shifts. A solution to this problem was also of interest. As a focal point for this research, the nature of the interactions between the pretreatment and the dyed fabric and the adsorbed dyes was characterized. PET fabrics, before and after the pretreatment, were analyzed spectrophotometrically and compared in terms of color difference against each other. The dyes were then extracted from the printed fabrics to determine which were sensitive to the pretreatment.

Color strength measurement was conducted on 44 pairs of fabrics, to analyze the differences in $L^*a^*b^*$ values between treated and untreated pairs. The results showed that 12 of the 44 untreated fabrics underwent unacceptable color changes following pretreatment, giving $\Delta E_{\text{CMC}}$ values in the 1.65 – 7.89 range with the shifts more pronounced on a back surface.

To characterize interactions between the disperse dye and the pretreatment, dyes were extracted from 22 fabrics before and after pretreatment and analyzed by
Thin Layer Chromatography (TLC) and Ultraviolet-Visible spectroscopy (UV-Vis).

The results showed that none of the dyes were impacted molecularly by the pretreatment agent, and $R_f \lambda_{\text{max}}$ values were unchanged.

The focus of this work was then turned to scanning electron microscopy (SEM) to determine whether the shade differences were physical rather than chemical in nature. SEM analysis showed a heavy white coating of pretreatment agent on the PET surface, which seems to be the source of the color shifts. While it is not surprising that black shades are more sensitive, it is unclear why certain blue shades are much less so.
Characterization of the Effects of a Pretreatment on Dark Colored Polyester Fabrics

by
Chengyang Liu

A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Master of Science

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DEDICATION

To my Dad and Mom.
BIOGRAPHY

Chengyang Liu was born in Nanping, Fujian, China in 1992, and grew up in Shantou, Guangdong, China. He was admitted by Donghua University, in China in 2010 and received his Bachelor of Engineering in Textile Engineering in 2014. During the study in Donghua University, he received the Social Work Scholarship in 2011 and the Outstanding Student Leader in the College of Textiles in 2009 and 2011 respectively. He joined the exchange student program between Donghua University and North Carolina State University in 2013. Following that, he was accepted by the graduate school and began studies towards a Master of Science degree in Textile Engineering under the direction of Drs. Harold S. Freeman and Lisa Chapman.
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### TABLE OF CONTENTS

**LIST OF TABLES**
- ix

**LIST OF FIGURES**
- x

1. Introduction ..............................................................................................................1
2. Literature Review ..................................................................................................2
   - 2.1 Disperse Dyes ...............................................................................................2
      - 2.1.1 Azo dyes ..................................................................................................4
         - 2.1.1.1 Monoazo dyes ..................................................................................4
         - 2.1.1.2 Disazo dyes .....................................................................................5
         - 2.1.1.3 Heterocyclic diazo dyes ....................................................................6
      - 2.1.2 Anthraquinone dyes ..............................................................................7
      - 2.1.3 Disperse dyes with other chromophores ...............................................8
      - 2.1.4 The relationship between structure and color of azo dyes .....................9
      - 2.1.5 Mechanism of dyeing polyester fabric with disperse dyes ....................10
      - 2.1.6 Applications to polyester .......................................................................12
   - 2.2 Polyester and woven polyester fabric ..........................................................16
      - 2.2.1 Overview of polyester ............................................................................16
      - 2.2.2 Synthesis of polyester ............................................................................19
      - 2.2.3 Physical properties of polyester fibers ..................................................22
      - 2.2.4 Chemical properties of polyester fibers ...............................................23
      - 2.2.5 Properties of woven polyester fabric ....................................................24
      - 2.2.6 Applications of woven polyester fabrics in textiles .............................26
   - 2.3 Pretreatment methods of polyester for use in textiles ................................27
      - 2.3.1 Coating ....................................................................................................27
      - 2.3.2 Chemical pretreatments ..........................................................................29
         - 2.3.2.1 Solvent pretreatment .......................................................................30
         - 2.3.2.2 Caustic soda pretreatment ...............................................................30
      - 2.3.3 Plasma treatment ....................................................................................30
   - 2.4 Inkjet printing .................................................................................................32
2.4.1 Overview of inkjet printing ..................................................... 32
2.4.2 Mechanism and process of inkjet printing ............................... 33
2.4.3 Dyes and colorants in inkjet printing .................................... 35
2.4.4 Surface modification of polyester fabrics for inkjet printing ...... 37
2.4.5 Applications of inkjet printing ............................................... 39
  2.4.5.1 Applications in textiles .................................................. 39
  2.4.5.2 Applications in other fields .......................................... 40
2.5 Research plan ........................................................................... 42

3. Experimental ............................................................................... 45
  3.1 Materials ................................................................................ 45
  3.2 Instruments ........................................................................... 46
  3.3 Thin Layer Chromatography (TLC) of dyes ............................... 47
  3.4 Dye extraction and isolation ................................................... 47
  3.5 Surface morphology .............................................................. 49
  3.6 UV-Visible absorption spectroscopy ...................................... 50
  3.7 Mass spectroscopy ................................................................ 50
  3.8 High-performance liquid chromatography (HPLC) spectroscopy ... 51

4. Results and Discussion ................................................................. 52
  4.1 Color measurements .............................................................. 52
  4.2 Dye extraction and isolation ................................................... 64
  4.3 Thin Layer Chromatography (TLC) of dyes ............................... 67
  4.4 Characterization of extracts from Samples 5, 5+, 6, 6+, 8, 8+, and 13,
      13+ ...................................................................................... 69
     4.4.1 UV-Vis spectra .............................................................. 69
     4.4.2 Mass spectra ................................................................. 70
  4.5 Characterization of Sample 16 extract .................................... 73
     4.5.1 Dye separations .............................................................. 73
     4.5.2 The UV-Vis spectra ........................................................ 74
     4.5.3 Mass spectra ................................................................. 80
4.5.4 High-performance liquid chromatography (HPLC) spectra........83
  4.5.4.1 HPLC purification and mass spectra of dye mixture........84
  4.5.4.2 HPLC purification and mass spectra of isolated dyes.....88
4.6 Analysis of commercial disperse dyes with pretreatment agent...96
4.7 SEM analysis...........................................................................105
5. Conclusions.................................................................................107
REFERENCES..................................................................................109
APPENDIX........................................................................................118
  Appendix A: L*a*b* values of 44 pairs of PET samples..............118
  Appendix B: Mass spectrum of Sample 5, 5+, 6 and 6+..............122
  Appendix C: UV-Vis spectra of all selected commercial disperse dyes and organic solvents..................................................126
LIST OF TABLES

Table 2.1 Physical properties of PET fibers.................................................................22
Table 2.2 Chemical resistance of PET fibers .................................................................23
Table 2.3 The list of polyester fabric samples.................................................................43
Table 3.1 Chemicals used in the research.................................................................45
Table 4.1 The color attributes of samples .................................................................58
Table 4.2 The weights of dye extracts of Samples 2-22 and Samples 2+ to 22+.....66
Table 4.3 The weights of isolated dyes of Sample 16 extract.................................74
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>The general structure of aminozobenzene disperse dyes</td>
<td>5</td>
</tr>
<tr>
<td>2.2</td>
<td>Some disperse dye structures based on aminozobenzene disperse dyes</td>
<td>5</td>
</tr>
<tr>
<td>2.3</td>
<td>Examples of disazo disperse dyes</td>
<td>6</td>
</tr>
<tr>
<td>2.4</td>
<td>Examples of heterocyclic diazo disperse dyes</td>
<td>7</td>
</tr>
<tr>
<td>2.5</td>
<td>Examples of anthraquinone disperse dyes</td>
<td>7</td>
</tr>
<tr>
<td>2.6</td>
<td>Examples of disperse dyes with other chromophores</td>
<td>8</td>
</tr>
<tr>
<td>2.7</td>
<td>Examples of disperse dyes</td>
<td>9</td>
</tr>
<tr>
<td>2.8</td>
<td>Some examples of carriers</td>
<td>12</td>
</tr>
<tr>
<td>2.9</td>
<td>Some examples of disperse dyes applied to automotive fabrics</td>
<td>13</td>
</tr>
<tr>
<td>2.10</td>
<td>Chemical structure of polyethylene terephthalate (PET)</td>
<td>17</td>
</tr>
<tr>
<td>2.11</td>
<td>Chemical structure of poly(butylenes terephthalate) (PBT)</td>
<td>18</td>
</tr>
<tr>
<td>2.12</td>
<td>Chemical structure of poly(dihydroxymethylcyclohexyl terephthalate) (PDT)</td>
<td>19</td>
</tr>
<tr>
<td>2.13</td>
<td>The structure of plain weave</td>
<td>25</td>
</tr>
<tr>
<td>4.1</td>
<td>The Munsell circle</td>
<td>52</td>
</tr>
<tr>
<td>4.2</td>
<td>Cylindrical representation of the CIELAB color space</td>
<td>53</td>
</tr>
<tr>
<td>4.3</td>
<td>The colors for Munsell planes with different hues</td>
<td>54</td>
</tr>
<tr>
<td>4.4</td>
<td>2-D graph of a*-L* values of Samples 1-22 and Samples 1+ to 22+</td>
<td>60</td>
</tr>
<tr>
<td>4.5</td>
<td>2-D graph of b*-L* values of Samples 1-22 and Samples 1+ to 22+</td>
<td>61</td>
</tr>
<tr>
<td>4.6</td>
<td>2-D graph of a*-b* values of Samples 1-22 and Samples 1+ to 22+</td>
<td>61</td>
</tr>
<tr>
<td>4.7</td>
<td>2-D graph of a*-L* values of Samples 22-44 and Samples 22+ to 44+</td>
<td>62</td>
</tr>
<tr>
<td>4.8</td>
<td>2-D graph of b*-L* values of Samples 22-44 and Samples 22+ to 44+</td>
<td>62</td>
</tr>
<tr>
<td>4.9</td>
<td>2-D graph of a*-b* values of Samples 22-44 and Samples 22+ to 44+</td>
<td>63</td>
</tr>
<tr>
<td>4.10</td>
<td>The mini-mill used to powder fabric samples</td>
<td>64</td>
</tr>
<tr>
<td>4.11</td>
<td>A powdered fabric sample for dye extraction</td>
<td>65</td>
</tr>
<tr>
<td>4.12</td>
<td>The soxhlet extractor system for dye extraction</td>
<td>65</td>
</tr>
<tr>
<td>4.13</td>
<td>Examples of dye extracts</td>
<td>66</td>
</tr>
</tbody>
</table>
Figure 4.14 TLC plate of Samples 2-14 and Samples 2+ to 14+.................68
Figure 4.15 TLC plate of Samples 15-22 and Samples 15+ to 22+.............68
Figure 4.16 UV-Vis spectrum of Sample 5..............................................69
Figure 4.17 UV-Vis spectrum of Sample 5+.............................................69
Figure 4.18 UV-Vis spectrum of Sample 13..............................................70
Figure 4.19 UV-Vis spectrum of Sample 13+.........................................70
Figure 4.20 Mass spectrum of Sample 5 in negative ESI..........................71
Figure 4.21 Mass spectrum of Sample 5+ in negative ESI.........................71
Figure 4.22 Mass spectrum of Sample 5 in positive ESI............................72
Figure 4.23 Mass spectrum of Sample 5+ in positive ESI.........................72
Figure 4.24 TLC plate from Sample 16 extract.......................................73
Figure 4.25 UV-Vis spectrum of light blue dye from Sample 16...............75
Figure 4.26 UV-Vis spectrum of light blue dye and pre-treatment agent from Sample 16 .................................................................75
Figure 4.27 UV-Vis spectrum of yellow dye from Sample 16.....................76
Figure 4.28 UV-Vis spectrum of yellow dye and pre-treatment agent from Sample 16 ..................................................................................76
Figure 4.29 UV-Vis spectrum of purple dye from Sample 16....................77
Figure 4.30 UV-Vis spectrum of purple dye and pre-treatment agent from Sample 16 ..................................................................................77
Figure 4.31 UV-Vis spectrum of red dye from Sample 16.........................78
Figure 4.32 UV-Vis spectrum of red dye and pre-treatment agent from Sample 16 ..................................................................................78
Figure 4.33 UV-Vis spectrum of dark blue from Sample 16.....................79
Figure 4.34 UV-Vis spectrum of dark blue dye and pre-treatment agent from Sample 16 ..................................................................................79
Figure 4.35 Mass spectrum of light blue dye extracted from Sample 16.......80
Figure 4.36 Mass spectrum of yellow dye extracted from Sample 16.........81
Figure 4.37 Mass spectrum of dark blue dye extracted from Sample 16.......82
Figure 4.38 Mass spectrum of red dye extracted from Sample 16.........................82
Figure 4.39 Mass spectrum of purple dye extracted from Sample 16.....................83
Figure 4.40 DAD chromatograph of Sample 16 at 254 nm.................................84
Figure 4.41 DAD chromatograph of Sample 16 at 410 nm ............................84
Figure 4.42 DAD chromatograph of Sample 16 at 540 nm ............................85
Figure 4.43 DAD chromatograph of Sample 16 at 660 nm ............................85
Figure 4.44 Mass spectrum of peak with retention time at 2.558 minutes.........85
Figure 4.45 Mass spectrum of peak with retention time at 3.248 minutes...........86
Figure 4.46 Mass spectrum of peak with retention time at 3.58 minutes..........87
Figure 4.47 Mass spectrum of peak with retention time at 4.061 minutes.........87
Figure 4.48 Mass spectrum of peak with retention time at 5.601 minutes.........88
Figure 4.49 DAD chromatographs of yellow dye at 254, 410, 540 and 660 nm...89
Figure 4.50 DAD chromatographs of dark blue dye at 254, 410, 540 and 660 nm..90
Figure 4.51 DAD chromatographs of purple dye at 254, 410, 540 and 660 nm....91
Figure 4.52 DAD chromatographs of light blue dye at 254, 410, 540 and 660 nm...91
Figure 4.53 DAD chromatographs of red dye at 254, 410, 540 and 660 nm........92
Figure 4.54 Mass spectrum of yellow dye at 2.294 minutes..........................93
Figure 4.55 Mass spectrum of dark blue dye at 5.735 minutes.......................94
Figure 4.56 Mass spectrum of purple dye at 3.741 minutes............................94
Figure 4.57 Mass spectrum of light blue dye at 3.648 minutes.......................95
Figure 4.58 Mass spectrum of red dye at 0.322 minutes...............................96
Figure 4.59 UV-Vis spectrum of acetone and pre-treatment agent...............98
Figure 4.60 UV-Vis spectrum of Disperse Blue 56 in acetone.......................98
Figure 4.61 UV-Vis spectrum of Disperse Blue 56 in acetone and pre-treatment agent.................................................................99
Figure 4.62 UV-Vis spectrum of ethyl acetate and pre-treatment agent............100
Figure 4.63 UV-Vis spectrum of Disperse Blue 56 in ethyl acetate...............100
Figure 4.64 UV-Vis spectrum of Disperse Blue 56 in ethyl acetate and pre-treatment agent...............................................................101
Figure 4.65 UV-Vis spectrum of acetonitrile (ACN) and pre-treatment agent……102
Figure 4.66 UV-Vis spectrum of Disperse Blue 56 with ACN……………………..102
Figure 4.67 UV-Vis spectrum of Disperse Blue 56 with ACN and pre-treatment agent..............................................................................................................103
Figure 4.68 UV-Vis spectrum of chlorobenzene and pre-treatment agent...........104
Figure 4.69 UV-Vis spectrum of Disperse Blue 56 with chlorobenzene.............104
Figure 4.70 UV-Vis spectrum of Disperse Blue 56 with chlorobenzene and pre-treatment agent..............................................................................................................105
Figure 4.71 SEM images of (a) Sample 10 and (b) Sample 10+ at 1000 times magnification..............................................................................................................106
Figure 4.72 SEM images of (a) Sample 16 and (b) Sample 16+ at 1000 times magnification..............................................................................................................106
1. Introduction

With the development of inkjet printing and the increasing demand of outdoor polyester fabrics, the requirements for PET fabrics are increased. To improve the color saturation, color yield and color fastness, pretreatment methods are applied. Because disperse dyes are easy to be printed on PET fabrics, and penetrate into hydrophobic fibers, they are widely applied in the printing of PET.

An advanced pretreatment process has been developed by Company A. However, following the pretreatment process, a detectable color shift occurs between the non-pretreated and pretreated PET fabrics.

The following literature review covers the basic concepts and categories of disperse dyes, the properties of polyester fibers and fabrics and the classification of pretreatment methods. The overview of the printing process together with the mechanism, type of dyes and modification methods are also discussed.

The physical factors, such as the coating of the fibers, and chemical factors, including the reaction between disperse dyes and pretreatment agent, are possible reasons of the color shift. Scanning electron microscope (SEM) was used to examine fiber surface. Ultraviolet-visible spectroscopy (UV-vis), mass spectroscopy and high-performance liquid chromatography (HPLC) were also used to identify the extracted and isolated disperse dyes.
2. Literature review

2.1 Disperse Dyes

Disperse dyes are one of the most popular classes of dyes in the world market, and are used for the coloration of synthetic fibers, such as polyester, acetate, triacetate and nylon\textsuperscript{1}. In 2006, there were more than 1 million tons of disperse dyes produced worldwide \textsuperscript{2}.

Disperse dyes were first developed in the 1920’s, to meet the new requirements of dyeing cellulose acetate, which was the first hydrophobic fiber developed on a commercial scale \textsuperscript{2, 3}. In 1923, Ellis developed sulphoricinoleic acid (SRA), as an agent to improve the solubility of water-insoluble azo dyes in aqueous alkali to improve the dyeing process \textsuperscript{3}. Disperse dyes are classified according to their special colorant class and given a definition by the Society of Dyers and Colorists \textsuperscript{1, 3}.

Disperse dyes are colored organic compounds, which are nonionic, planar and usually used to dye hydrophobic fibers in weakly acidic medium \textsuperscript{2, 4, 5}. The water solubility of disperse dyes is very low at room temperature, thus, they are usually mixed with water in the form of a dispersion \textsuperscript{6, 7}. Disperse dyes have a relatively small molecular weight and small particle size, which is usually less than 1 \(\mu\text{m}\) \textsuperscript{2}. Disperse dyes dissolve in the dyebath in mono molecular form, and then diffuse into the fiber and are dissolved within the fibers \textsuperscript{8}. Basically, the solubility of dyes in aqueous medium relates to the molecular structure of disperse dyes. The amino,
azo, hydroxyethylamino and other functional groups in disperse dyes have nitrogen, oxygen or sulfur atoms, which are electronegative. The atoms interact with water molecules, and disperse dyes dissolve in aqueous solution. However, only a small percentage of disperse dyes dissolve in water and the dissolved dyes diffuse into hydrophobic fibers.

To improve dye-uptake of hydrophobic fibers, the solubility of disperse dyes in aqueous medium is increased. There are four parameters which can influence the dye solubility, including temperature, the existence of dispersing agents (hold dyes in dispersion), the particle size of dye and the presence of surface active agents (lower the surface tension of dyes in dispersion), which are usually anionic surfactants.

Because of their small size, disperse dye molecules can disperse fairly easily into fibers. They interact with fibers in many ways, such as hydrogen bonds, van der Waals forces, and via forming strong π–π interactions. The polar functional groups in disperse dyes, including –NO\textsubscript{2}, -OH and –CN, contribute to the forming of hydrogen bonds. In the process of dyeing, dye molecules diffuse into hydrophobic fibers and form molecular bonds with them. However, dyeing process of disperse dyes is reversible. The wash fastness has a positive correlation with the dyeability of disperse dyes to fibers. Polyester fibers dyed with disperse dyes usually exhibit good washing fastness if dyed under high pressure or with dye carriers.
More than 50% of disperse dyes are monoazo dyes, with small molecular weights, and 25% of disperse dyes are anthraquinonoid (AQ) dyes. A quarter of disperse dyes are composed of other classes, such as naphthalimide, benzodifuran, coumarin, methyne and nitrodiphenylamine dyes. 

2.1.1 Azo dyes

Azo dyes can be made of an amine or phenol which is coupled with a diazotized amine, to produce one or more azo bonds (-N=N-) . Benzenic or naphthalenic rings, with –OH groups, can be a part of the structure of azo dyes. Disperse azo dyes are applied in many fields, including textiles, leather, food, ink, paper, plastic and biological-medical applications. Azo dyes cover the whole gamut of colors, from yellow to greenish blue, with the help of a wide range of donor-acceptor systems.

2.1.1.1 Monoazo dyes

The general structure of disperse monoazo is shown in Fig. 2.1. Most of monoazo dyes are based on aminoazobenzene dyes, which have typical donor-acceptor chromogens. The characteristics of monoazo dyes in commerce, including cost, ease of manufacture, color and fastness are influenced by the groups in positions R1-R7. Some monoazo dyes are hydroxyazobenzene, which have better lightfastness when dyeing synthetic fibers. For example, C.I. Disperse Orange 30,
C.I. Disperse Blue 79 and C.I. Disperse Red 1 are disperse monoazo dyes, as shown in Fig. 2.2.

![Figure 2.1 The general structure of aminozobenzene disperse dyes.](image)

Figure 2.1 The general structure of aminozobenzene disperse dyes.

![C.I. Disperse Orange 30](image) ![C.I. Disperse Blue 79](image) ![C.I. Disperse Red 1](image)

Figure 2.2 Some commercial disperse dye structures based on aminoazobenzene disperse dyes.

2.1.1.2 Disazo dyes

Disazo dyes are synthetized by two diazotizations and couplings, and have two azo (-N=N-) bonds in their molecular structure. For example, C.I. Disperse
Orange 29 and C.I. Disperse Yellow 23 are disazo dyes, which are shown in Fig. 2.3.

![C.I. Disperse Orange 29](image) ![C.I. Disperse Yellow 23](image)

Figure 2.3 Examples of disazo disperse dyes.

2.1.1.3 Heterocyclic azo dyes

Heterocyclic azo dyes are derived from heterocyclic diazo components and coupling components, such as aminobenzene couplers, with the formation of azo (\(\text{N} = \text{N}\)) bonds. At first, heterocyclic amines were developed and used to produce red and blue azo disperse dyes. Heterocyclic azo dyes have good tinctorial strength and excellent brightness, especially bright blue-green colors, compared with the disperse dyes synthetized by aniline-based components. Most heterocyclic azo dyes have five-membered rings, with one to two nitrogen atoms and one sulphur atom in the ring structure. C.I. Disperse Blue 15, C.I. Disperse Red 58 and C.I. Disperse Red 177 are heterocyclic diazo dyes, which are shown in Fig. 2.4.

Because of the high electronegativity of amino-substituted thiazone, thiophene and benzothiazole compounds, a bathochromic shift occurs in corresponding dyes,
compared with the dyes derived from amino-substituted benzoid and nitroaniline
compounds.\textsuperscript{22, 24}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{c1}
\caption{Examples of heterocyclic azo disperse dyes.}
\end{figure}

\subsection{2.1.2 Anthraquinone dyes}

Anthraquinone disperse dyes have the general structure with 8 carbon atoms
and their attached hydrogen atoms, which could be replaced by substituents at \(\alpha\)-
position (1\textsuperscript{th} and 4\textsuperscript{th} position), such as nitro, amino, hydroxyl group.\textsuperscript{11} Most of
anthraquinone dyes have the color range from bright red to blue. C.I. Disperse Red
15 and C.I. Disperse Red 60 are anthraquinone dyes.\textsuperscript{4} The chemical structure of C.I.
Disperse Red 15 and C.I. Disperse Red 60 are shown in Fig. 2.5.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{c2}
\caption{Examples of anthraquinone disperse dyes.}
\end{figure}
2.1.3 Disperse dyes with other chromophores

The disperse dyes derived from other chromophores, including benzodifuranones, coumarins, methines, naphthalimides, nitrodiphenylamines and quinophthalones have been developed and applied to obtain higher brightness with lower cost. C.I. Disperse Yellow 42, which has the structure of nitrodiphenylamine, has high lightfastness on polyester. C.I. Disperse Yellow 54 has the structure of quinophthalone, which is widely used in many applications. Some brilliant yellow dyes, such as C.I. Disperse Yellow 82, are disperse dyes with the coumarin structure. There are some disperse dyes with other chromophores as shown in Fig. 2.6.

Figure 2.6 Examples of disperse dyes with other chromophores.
2.1.4 The relationship between structure and color of azo dyes

Azo dyes cover the visible color spectrum, and the color relates to the molecular structure of dyes. The functional groups of dyes play an important role in electron-donating and electron-attracting and influence the properties of the conjugated system. In azo dyes, the monoazo dyes with two benzene rings, or one benzene ring and one pyrazolone ring, have yellow or orange colors. The dyes with one benzene ring and one naphthalene ring have orange or red colors. The dyes with two naphthalene rings have red, violet or blue colors. The dyes with multiple naphthalene and benzene rings, have black color. Besides, the electronegativity of functional groups affects the conjugated system, and influences the color of dyes.25

The azo dyes including the azo disperse dyes have these features. For example, C.I. Disperse Orange 3 has nitro and amino groups, which are stronger electron-donating or electron-attracting groups than those on C.I. Disperse Yellow 3. Thus, C.I. Disperse Orange 3 absorbs light at a longer wavelength than C.I. Disperse Yellow 3.25 The chemical structures of these two disperse dyes are shown below (Fig. 2.7).

![Chemical structures of C.I. Disperse Orange 3 and C.I. Disperse Yellow 3](image)

Figure 2.7 Examples of disperse dyes.
2.1.5 Mechanism of dyeing polyester fabric with disperse dyes

Because polyester fibers are hydrophobic, with high molecular weight and low moisture absorbance, it is hard for natural dyes to dissolve into them\(^6\). Disperse dyes could be used to dye polyester fibers in a process, as the form of solid solution, by diffusing into the amorphous regions of polyester fibers\(^9\). However, because of the low solubility of disperse dyes, the rate of dyeing and dye up-take are limited, at room temperature\(^9\).

The rate of dyeing is affected by several factors, including fiber morphology, degree of hydrophobicity of the fiber and dyeing assistants\(^9\). The large size of amorphous regions, and high degree of hydrophobicity of the fiber, creates more open spaces in fibers, which helps more disperse dyes diffuse into fibers\(^9\). Dye carriers and swelling agents are useful to decrease the temperature of the dyeing system\(^9\).

Temperature and pressure are two important elements in dyeing with disperse dyes in aqueous solution. For example, in rapid dyeing, which is a traditional method, it is common to set the temperature to 120-130°C in a closed high-pressure equipment\(^1\). The movements of molecules, including molecules of fibers and dyes, are all improved under high temperature. The movements create open spaces (voids) in the amorphous phase of fibers as well, and improve the swelling of disperse dyes\(^9\). Besides, high temperature increases the solubility of disperse dyes and improves their diffusion into the fiber in dyeing process\(^9\).
pressure also helps disperse dye diffuse more readily into polyester by increasing the movements of molecules \(^6\).

Dye carriers, which were found in the 1950’s, were commonly used in the dyeing of polyester with disperse dyes, to decrease the temperature of dyeing process to less than 100°C while making similar if not better products \(^1\,^6\). Carriers are mostly hydrophobic aromatic organic compounds, such as diphenyl, methyl-naphthalene, aromatic esters and halogenated aromatics \(^1\,^9\). Dye carriers are used to accelerate the movement of polyester molecules, to penetrate and open the amorphous regions of polyester fibers, create holes in fibers and help disperse dyes go through solution-fiber interface and stay inside \(^1\). Because carriers are smaller than disperse dyes, and they are hydrophobic, they can diffuse into the gap of polyester fibers and separate them \(^9\). Carriers can also partially solubilize disperse dyes and promote the swelling, resulting in improvements in color strike and intensity. The sorted list of carriers based on their enhancement of color yield is: orthophenyl phenol, methyl naphthalene, trichlorobenzene, biphenyl and butyl benzoate \(^6\). The effect of carriers might be the combination of the two factors \(^6\).

However, it is essential to remove dye carriers after the dyeing process. Dye carriers are usually toxic with bad smells, and they may result in skin irritation \(^9\). They should be removed after dyeing process by scouring \(^1\,^6\). Because of the environmental and health concerns associated with the use of carrier, their use in the developed world is currently very restricted. Some examples of dye carriers are shown in Fig 2.8.
2.1.6 Applications to polyester

Because disperse dyes are capable to dissolve in hydrophobic fibers, such as polyester and acetate, they are widely used in the coloration of textiles, such as garments, sportswear and automotive fabrics.

Garments and sportswear are washed frequently and must have good wash fastness. Phthalimide-based azo disperse dyes and benzodifuranone dyes have high wash fastness and produce bright shades on the fabrics. Phthalimide-based azo disperse dyes are easy to be removed in an alkaline medium, which is less harmful to the environment compared with reductive clearing.

Some automotive fabrics, including seat covers, are made from polyester. Cars are exposed to sunlight, and thus the temperature of the interior of the car, especially in summer could be high. Automotive fabrics should have good light fastness. Some disperse dyes are widely used in automotive fabrics, such as C.I. Disperse Yellow 42, C.I. Disperse Red 60, C.I. Disperse Yellow 86 and C.I. Disperse Red 167:1, which are shown in Fig 2.9. In dyebaths, the disperse dyes
can be mixed with ultraviolet (UV) absorbers, such as benzophenone and benzotriazole derivatives, to improve the lightfastness of polyester fabrics.  

![Chemical structures of disperse dyes]

C.I. Disperse Yellow 42  
C.I. Disperse Red 60  
C.I. Disperse Yellow 86  
C.I. Disperse Red 167:1

Figure 2.9 Some examples of disperse dyes applied to automotive fabrics.

There are several dyeing methods applied in dyeing polyester, including carrier dyeing, high temperature dyeing and dyeing by the Thermosol™ process. These are briefly described in the following sections.

**a. Carrier dyeing**

In carrier dyeing, the dyebath contains dilute dispersing agent, dye carrier and disperse dyes. The materials are run in the bath at 60°C. Then the temperature is raised to the boil gradually. The carrier dyeing is conducted at the boil for 60 min. After dyeing, the dye carriers are removed by hot-air drying at 150-180°C.
b. High temperature dyeing

High temperature dyeing is the most widely used dyeing method for polyester and involves the use of pressurized equipment. In this method inter-chain connections are decreased while the movements of dye molecules and the rate of dyeing are promoted. High temperature dyeing process can be divided into three phases, which are adsorption phase, diffusion phase and clearing phase. The adsorption phase is a key step to the levelness of dyeing. The adsorption rate of dye, which is influenced by heating rate, needs to be carefully controlled in the adsorption phase. The dye adsorption is influenced from dye concentration, temperature gradient, also the type of fiber and auxiliary. In the heating process, dyeing rate reaches the maximum at a specific temperature, which is known as the critical dyeing temperature (CDT). The temperature in the rapid-dyeing method should be set just below the CDT, when the disperse dyes are added into the dyebath. After that, the temperature is raised gradually to around CDT. In the two steps, the exhaustion rate is controlled to process proper level dyeing. Then, the temperature is raised to the top dyeing temperature at the highest rate.

The diffusion phase is the process in which dyes diffuse into polyester fibers, at a relatively higher but a low speed. The total time required in diffusion phase is influenced by the properties of dyes and dyeing depth. To produce fabrics with pale shades, medium shades and deep shades, the standard time for dyeing are 10-20 min, 20-30 min to 30-35 min respectively.
The clearing phase is a process after the completion of dyeing to remove the dyes, carriers and surfactants remaining on the surface of polyester, which may reduce the brightness of products. The contamination could be removed with some treatment methods, such as reductive treatment, oxidative treatment and using detergents. The reduction clearing, which is a strong clearing, employs sodium dithionite and caustic soda for 20 min at 70-80°C. Oxidative treatment is suitable to remove anthraquinone dyes.

c. Thermosol process

Thermosol process™ is a useful method for dyeing polyester or polyester/cellulose fibers with disperse dyes. The process is usually applied to woven and knitted materials.

At the beginning of the Thermosol process, dye dispersion covers the surface of the polyester fabric. The dispersion is then dried in a hot flue air dryer and heated cylinders. The fabric is then heated in air or by hot metal surfaces to 190-220°C for 1-2 min during which the dye is sublimated. The gaseous dye penetrates the fiber and is dissolved within the fiber matrix. The substrate is then cooled down which reduces the pore sizes and improves the fastness properties of the dyed substrate.
2.2 Polyester and woven polyester fabric

2.2.1 Overview of polyester

Polyester is one of the most popular commercial synthetic fibers in the world, which was first synthetized by Carothers in 1930s. The yield of polyester in 2002 was 21 million tons, which is 58% of total yield of synthetic fibers worldwide. Polyester consists of polyethylene terephthalate (PET), poly(ethylene naphthalate) (PEN), poly(butylene terephthalate) (PBT), poly(propylene terephthalate) (PPT), poly(lactic acid) (PLA) and thermotropic polyester (LCP).

As a synthetic fiber, polyesters have high strength and stiffness, good dimensional stability and heat resistance, high chemical resistance and good wash-wear properties. Polyesters have many applications, including textiles, films, tires, composite materials, biomedical components, packaging, bottles and sporting equipment. Polycondensation reactions are good ways to synthetize polyester. There are several typical ways to produce polyester fibers or composites, such as monofilament extrusion, spinning, blow molding and injection molding.

To produce polyester fibers, the cost and processability are the main requirements of industry. For example, the melting point is under the limitation of commercial heating fluids. And the glass transition temperature of polyester is not high that the fiber orientation, stabilization and fiber morphology in process is easy to be controlled. The processing temperature of polyester is 260-300°C. Furthermore, the control of fiber morphology in the process enables the production
of polyester fibers with good thermal stability, dimensional stability, mechanical and chemical properties, which satisfy the requirements of various material \(^{30}\). Polyesters are hydrophobic materials, with high molecular weight and crystallinity, and these features lead to low dyeability \(^6,^{10}\). Unlike traditional dyeing processes, polyesters usually require high temperature and pressure to promote the penetration and swelling of fiber and improve shades \(^6\).

Polyethylene terephthalate (PET) was developed by a polycondensation process, with dimethyl terephthalate (DMT) or terephthalic acid (PTA), and ethylene glycol (EG) \(^{29,32,33}\). PET is hydrophobic with a high molecular weight, high crystallinity and compact structure, when made by heating under vacuum \(^6,^{10}\). PET can be synthetized with transesterification, direct esterification and polycondensation \(^{29}\). PET with high molecular weight can be used to make films, which are applied in food packaging and decoration \(^{29}\). PET can also be used in injection molding, to make rigid materials under high temperature and pressure \(^{29}\). The chemical structure of PET is shown in Fig 2.10.

\[
\begin{array}{c}
\text{O} \\
\text{C} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{O} \\
\end{array}
\]

Figure 2.10 Chemical structure of polyethylene terephthalate (PET).
Poly(butylene terephthalate) (PBT) is synthetized using dimethyl terephthalate (DMT) or terephthalic acid, and butanediol\(^{29}\). Compared with PET, PBT has a higher number of methylene groups in its repeating unit, leading to higher flexibility and lower melting point and glass transition temperature\(^{29}\). PBT has good dimensional stability and insulating properties. Thus, PBT is applied in the automotive industry and for making electrical components, such as plug connectors. PBT can also be used to make sportswear, especially swimwear\(^{29}\). The chemical structure of PBT is shown in Fig 2.11.

![Chemical structure of poly(butylene terephthalate) (PBT).](image)

Poly(dihydroxymethylcyclohexyl terephthalate) (PDT) was developed in 1958, as a new hydrophobic polyester fiber\(^{29}\). PDT is made using a polycondensation reaction of dimethyl terephthalate. In its repeating unit PDT contains heterocyclic rings which improve the melting strength and decrease molding shrinkage\(^{29}\). As a result, PDT can be used in blow molding and injection molding to make polymer products or composites. The chemical structure of PDT is shown in Fig 2.12.
Besides PET, PBT and PDT, there are some unsaturated polyesters, which are usually applied in construction and automotive industries. Unsaturated polyesters have low molecular weight, and are synthesized using unsaturated dicarboxylic acid and saturated carboxylic acid \(^{29}\). With the help of peroxide initiators, unsaturated polyesters can be used to synthesize polymers with a high degree of cross-linking. They can be reinforced by glass fibers \(^{34}\). Unsaturated polyesters have some applications, including molding compositions \(^{29}\).

### 2.2.2 Synthesis of polyester

To synthesize polyester fiber, dimethyl terephthalate (DMT) and pure terephthalic acid (TA) are good starting materials with low cost. Ethylene glycol can also be used to react with TA or DMT in the manufacturing of polyester \(^{30,35}\). In the production of polyester fibers, ester interchange occurs between the two monomers \(^{30}\).

The formation of bishydroxyethylterephthalate (BHET) is the first step of polyester polymerization. In the reaction, temperature and pH are important factors. This reaction is shown below \(^{30,32}\):
\[
CH_3OCO-C_6H_4-COOCH_3 + 2HOCH_2CH_2OH \\
\rightarrow HOCH_2CH_2OCO-C_6H_4-COOCH_2CH_2OH + 2CH_3OH↑
\] (1.1)

BHET is isolated from the mixture after the reaction. After that, two molecules of BHET react with each other and produce one glycol molecule, which is an ester interchange reaction. In the reaction, antimony trioxide (Sb$_2$O$_3$) can be selected as a catalyst\textsuperscript{30, 32}. The melt polymerization operates under high temperature (higher than 285°C) and high pressure, with the viscosity on the order of around 3000 poise. During the polymerization, the system needs uniform stirring and a constant shear history. Then, the polymers are forced through spinnerets and made into strands and chips\textsuperscript{30, 32, 35}.

Solid phase polymerization is the method to improve the molecular weight of polyester from the chips produced in the last stage\textsuperscript{32, 36}. The polyester chips are fed into spinning machine for melt spinning and transformed into fiber. In the process, polyester chips are heated at around 160-170°C for crystallization\textsuperscript{30, 32}. The melt polymerization needs to balance the speed of chain-forming and chain-breaking in the process, to prevent forming connections between molecular chains\textsuperscript{32}. Then, the temperature in the machine is increased and approaches the melting point, with high vacuum and without water vapor. Under these conditions, the material has high inherent viscosity (IV). For textiles, the IV requirement in spinning process is around
The fluid is converted into fibers with high semicrystalline morphology and high orientation. In the spinning process, some troublesome byproducts are produced in the structure, such as diethyleneglycol (DEG) units. DEG units can decrease the crystallinity, thermal stability and other properties of polyester. The removal of the byproducts in the spinning process is an important issue.

The drawing process is necessary after the spinning process, which is able to improve the crystallinity, orientation, tenacity and elongation of the fiber. After the drawing process, the fibers have higher modulus. In the process, the fibers are drawn by rolls, with nearly maximum draw ratio under relatively low temperature. The filament is wound onto a bobbin at the end of the process.

Besides, heat-setting process is conducted to prevent heat shrinkage. Fibers can be heated by hot air, hot rollers and steam. After heat-setting, the fibers obtain good dimensional stability and crease resistance, even good resistance to being out of shape after fabrication.

Yarn bulking process is carried out to meet the requirements of fabric appearance. Partially oriented yarn (POY) can be produced at high-speed spinning. POY can be textured, and the bulk is increased to improve comfort and warmth retention. False-twist bulking is one of bulking methods used to create good 3-D structures of fibers. The false-twist bulking process operates during drawing by twisting, and the fibers are heated above the glass transition temperature. The process creates spiral crimp on the surface of the filament at high speed. After
heat-setting process and bulking process, the fabrics fabricated by bulking yarns exhibit good dimensional stability and appearance \(^{30, 35}\).

### 2.2.3 Physical properties of polyester fibers

Polyester is a semicrystalline polymer with a high degree of orientation and is widely used in textiles and for other applications. The tensile strength and modulus of the polymer depends on the type of polyester. Polyester fibers have good recovery with low elongation \(^{37}\), good resilience and good abrasion resistance \(^{35}\). The physical properties of polyester fibers are listed in Table 2.1 \(^{30, 31, 35}\).

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 20°C</td>
<td>g·cm(^{-3})</td>
<td>1.3-1.4</td>
</tr>
<tr>
<td>Color</td>
<td>-</td>
<td>White to gray</td>
</tr>
<tr>
<td>Refractive index, 20°C</td>
<td>-</td>
<td>Calc.=1.5392-1.5557; exp =1.5750</td>
</tr>
<tr>
<td>Contact angle of water, 20°C</td>
<td>degree</td>
<td>72.0-75.0</td>
</tr>
<tr>
<td>Melting temperature, DSC</td>
<td>°C</td>
<td>245-265</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>°C</td>
<td>Calc.=76-88; exp.=60-85</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>GPa</td>
<td>3.2 (p-Aramid); 3.5 (PBO)</td>
</tr>
</tbody>
</table>
### Physical Properties

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile modulus</td>
<td>GPa</td>
<td>70-130 (p-Aramid); 240 (PBO)</td>
</tr>
<tr>
<td>Shear modulus</td>
<td>GPa</td>
<td>1.8 (p-Aramid); 1.3 (Thermotropic copolymer)</td>
</tr>
<tr>
<td>Elongation</td>
<td>%</td>
<td>100-250</td>
</tr>
<tr>
<td>Tensile yield strain</td>
<td>%</td>
<td>4</td>
</tr>
<tr>
<td>Tenacity (yarn) (standard atmosphere)</td>
<td>cN tex$^{-1}$</td>
<td>25-95</td>
</tr>
<tr>
<td>Moisture regain</td>
<td>%</td>
<td>0.4</td>
</tr>
</tbody>
</table>

#### 2.2.4 Chemical properties of polyester fibers

Polyester fibers have low moisture regain and high chemical resistance to acids and bleaching, but they are harmed by strong alkalis $^{35}$. The characteristics of chemical resistance $^{31,35}$ of polyester fibers are listed in Table 2.2.

<table>
<thead>
<tr>
<th>Chemical Agent</th>
<th>Chemical Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dilute/concentrated</td>
<td>Good/Fair</td>
</tr>
<tr>
<td>Alkalis</td>
<td>Poor</td>
</tr>
<tr>
<td>Alcohols</td>
<td>Good/Fair</td>
</tr>
<tr>
<td>Chemical Agent</td>
<td>Chemical Resistance</td>
</tr>
<tr>
<td>-------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Esters</td>
<td>Fair-Poor</td>
</tr>
<tr>
<td>Aromatic hydrocarbons</td>
<td>Good</td>
</tr>
<tr>
<td>Aliphatic hydrocarbons</td>
<td>Good</td>
</tr>
<tr>
<td>Halogenated hydrocarbons</td>
<td>Poor</td>
</tr>
<tr>
<td>Greases and oils</td>
<td>Good</td>
</tr>
<tr>
<td>Good solvent</td>
<td>Phenol, DMSO (hot), nitrobenzene</td>
</tr>
</tbody>
</table>

2.2.5 Properties of woven polyester fabric

Fibers can be woven into fabrics by interlacing filling yarns and warp yarns. Many different fabric constructions can be created by different ways of interlacing, such as plain weave, twill weave and satin weave\(^{35}\).

Plain weave is the most common and basic fabric construction within woven fabrics\(^{35}\). The structure of plain weave is shown in Figure 2.13. Plain weave is classified into balanced weave and unbalanced weave, depending on whether the type and diameter of yarns are the same. Fabrics with balanced-weave have higher durability because the external force on the fabrics would be uniformly distributed\(^{35}\).
Figure 2.13 The structure of plain weave.

Twill weave is one of traditional fabric constructions with less intersection points between filling yarns and warp yarns. With less intersection and smaller gap between yarns in the same direction, twill weave structure helps the yarns hold tight and improve the tensile strength and durability of fabrics. Twill-weave fabrics have higher resistance to abrasion.\(^3^5\)

Satin weave is a structure which is widely used in decoration, with less intersections and longer floats, but the tensile strength of satin-weave fabrics is lower. The surface of satin-weave fabrics is smooth.\(^3^5\)

There are some important factors contributing to the properties of woven fabrics, including the type of yarns, yarn count, fabric count (the number of yarns in a unit length) and fabric construction. Tensile strength of yarns has a positive correlation with the breaking strength of fabrics. Fabrics woven by strong yarns have
high breaking strength. Because the tensile stress can be transferred and shared by yarns through intersections, the breaking strength and shear strength of plain woven fabrics are higher than those in twill woven and satin woven fabrics. Fabrics with higher fabric count have higher breaking strength, because there are more yarns which could share the stress.35

In woven fabrics, shear deformation or shrink after swelling occurs easily in loose constructions or those with a low dimensional stability.36

2.2.6 Applications of woven polyester fabrics in textiles

Woven polyester fabrics are widely used in apparel and home furnishing in textiles. Polyester fabrics and polyester/cotton blend fabrics are popular in the worldwide market as the materials of fashion apparel. Because polyester yarns made from trilobal polyester fibers have similar appearance with silk, they can be used to fabricate suits and jackets with high quality.35 Polyester fabrics woven from microfibers are utilized in sportswear.32

Home furnishings include carpets, curtains, draperies and sheets.35 Home furnishings from woven polyester fabrics need to be hydrophobic with good flame resistance, good heat resistance and offer adequate comfort and hand.35,38 The melting point of polyester is around 245-265°C, with an auto-ignition temperature of 450-500°C. The structural unit of polyesters only contains carbon, oxygen and hydrogen, which means its byproducts of complete combustion are less toxic.34
a result, polyester is suitable for home furnishing applications. Polyester yarns used in carpet are partially oriented yarns (POY), which are made from staple fibers and textured 39.

It has also been shown that, woven polyester fabrics are treated with plasma to produce conductive fabrics, its surface energy and surface roughness are increased. Negative charges exist on the surface of polyester fabric, and it promotes the adhesion of reduced graphene oxide (RGO), which has good electrical conductivity, to produce conductive fabrics 40.

Woven polyester fabrics are used in biomedical textiles, especially for use in the cardiovascular system, such as vascular prostheses and artificial heart valves. Polyester has good biocompatibility and dimensional stability and low biodegradation property with low cost 32, 41.

2.3 Pretreatment methods of polyester for use in textiles

2.3.1 Coating

To enhance the properties of polyester fabrics, they are treated with several coating agents for different purposes. The improved or created properties of polyester fabrics include optical properties, UV stability, bacterial, thermal, and fire resistance as well as electrical properties 42, 43.

Polyester fabrics can be treated with titanium dioxide (TiO2) nanoparticles in an ultrasonic bath. After the pretreatment, the fabrics have better properties of self-
cleaning, hydrophilicity and UV protection. The self-cleaning of polyester fabrics is improved by the coating of TiO₂ nanoparticles, with the pad-dry-cure process, anodization, chemical vapor deposition or thermal oxidation. After the modification, the photocatalytic discoloration of organic pollutants, such as red wine and red beet, is accelerated with the help of TiO₂ photo-catalysis.

Polyester fabrics may also be treated with SiO₂ nanoparticles together with a binder (acrylate-based copolymer). Before SiO₂ pretreatment, alkaline pretreatment is carried out to increase the adhesion of SiO₂. With the help of SiO₂ nanoparticles, color strength and color yield of polyester after dyeing or printing are improved. The temperature of dyeing and steaming after printing are decreased with the presence of a binder. The fixation rate is accelerated by the binder, which promotes disperse dye attachment onto polyester fabrics.

To improve the bactericide properties of fabrics, sol-gel method and nanotechnologies are applied in textiles field. N-halamines, silver and quaternary ammonium salts are effective biocides, which can deactivate microorganisms, and are applied for coating onto polyester fabrics. TiO₂ nanoparticles are also good antibacterial agents for textiles, and may be applied with the help of a crosslinking agent on fabrics such as wool/polyester.

The UV-shielding property of PET textiles is significantly improved by coating the surface of PET textiles with zinc oxide (ZnO) nanorods, using the hydrothermal method at around 90°C. Silica shell is then covered on ZnO nanorods, in a reactive layer-by-layer deposition process, and the coating is then finished.
Because ZnO is bio-safe, it is harmless to the skin. It has also been shown that coating with ZnO microparticle powder improves the UV-protection property and hydrophobicity of the fiber by reducing the charge on the surface. This modification helps the development of outdoor PET fabrics. TiO₂ nanoparticles are also used as a coating on polyester fabric to improve its UV-protective property.

Polyester fabrics can be coated by electrically conductive materials, including polyaniline (Pani), polypyrrole (PPy), metal nanoparticles, graphene and its derivatives. Chemical metallization and vapor deposition processes are applied to coat polyester fabrics with conductive materials. Because of its good electrical properties, reduced graphene oxide (RGO) is suitable for forming sheets, which are attached on the surface of polyester fabrics.

### 2.3.2 Chemical pretreatments

Before the printing or dyeing, some chemicals are applied to pretreat PET fabrics. The chemicals includes organic solvents and catalysts mixed with caustic soda (NaOH). The surface properties and dyeability are improved after the chemical pretreatments, including the color saturation, color strength.
2.3.2.1 Solvent pretreatment

The properties of PET fabrics, including crystallinity, shrinkage, weight loss and absorption of water, can be changed by solvent pretreatment \(^56\). The solvents include phenol, dimethyl formamide (DMF) and nitrobenzene, which need to be mixed with water before pretreatment. After the solvent pretreatment, the dyeability of disperse dyes onto microdenier polyester fabrics and the color strength after dyeing are both improved. The breaking strength of microdenier polyester fabrics is improved by treatment with phenol, however, fabric shrinkage and weight loss occurs \(^57\).

2.3.2.2 Caustic soda pretreatment

Caustic soda (NaOH) can be mixed with catalysts, such as hexamethylene diamine (HMDA) and cetyl-trimethyl ammonium bromide (CTAB), and made into aqueous pretreatment solution for polyester substrates. This treatment results in improving the surface color depth of microdenier polyester fabrics \(^57\).

2.3.3 Plasma treatment

Plasma treatment is a surface modification technology, which is becoming increasingly popular for applications in textiles. The plasma treatment oxidizes the surface of polyester fabrics \(^58\). Compared with traditional pretreatment methods, plasma treatment is clean, ecologically friendly with low cost and is less time
The parameters in plasma treatment, including discharge power, system pressure, system temperature, treatment duration, plasma dosage and type of gas (or vacuum), influence the results of treatment. \(^59, 60\)

The plasma treatment can enhance the coating adhesion, surface cleaning, antibacterial, electrical and physical properties, and improve color fastness, dyeing and printing properties of textiles. \(^61, 62\) In atmospheric plasma treatment, hydroxyl and carboxylic groups are generated. The surface of polyester fabrics is oxidized, etched and ablated by these groups. \(^58\)

The adhesion of polypyrrole (PPy) to woven polyester fabrics can be improved by low-pressure oxygen plasma treatments. The additional C-O and O-C=O groups are formed in the decomposition of molecular chains and the oxidation of polyester. The surface energy and roughness are improved by the treatment. \(^62\)

It has also been shown that while plasma treatment of polyester improves the surface energy and surface roughness, it generates negative charges, which prevent the adhesion of reduced graphene oxide (RGO). With the help of protein bovine serum albumin (BSA), which is an intermediate coating agent, the adhesion of RGO was however, improved. \(^40\)

Plasma treatment can induce chemical interactions at C-H radical groups of the benzene ring of polyester. The coating adhesion of a nonionic lubricating agent is increased, to improve the smoothness of the surface after coating. \(^63\)

Low temperature oxygen plasma treatment can be employed to improve the anti-static properties of polyester fabrics. \(^60\)
2.4 Inkjet printing

2.4.1 Overview of inkjet printing

Inkjet printing is an advanced and popular printing technology for textiles, which belongs to digital printing. The technology is convenient and eco-friendly. Compared with conventional textile printing, inkjet printing helps shorten the whole process of printing, especially the design sampling and proofing. The inkjet printing process requires less water and energy. Furthermore, the good control of printing helps the printing performance with so many creative designs, which is better than screen printing in this aspect. Because inkjet printing is a non-contact process, it can prevent mechanical damages. In inkjet printing the colorants, including dyes and pigments, are ejected from printheads to the surface of fabrics, and the path is controlled by the computer software. There are three most important factors in inkjet printing system, which are printhead, ink and medium (substrate). Medium is the material which receives ink, such as fabrics and paper. The viscosity, surface tension and density of inks are also important factors influencing the outcome of the printing process.

The inkjet machines are classified into two types, continuous ink jet (CIJ), and drop-on-demand (DOD). In continuous ink jet, the dyes or pigments are incorporated into small drops in the ejecting process, spread onto fabric and form different designs. In the DOD mode, the single drop ejects with a tail. The DOD mode utilizes different printheads, including thermal, piezoelectric and electrostatic...
The resolution of inkjet printing can reach up to 720 dpi (dots per inch).

Inkjet printing is widely applied in several fields. It is used in bio-printing, such as drug screening, printing cells, and printing precursors as colloidal suspensions. Inkjet printing is also applied in electronic devices, including sensors, solar cells, transistors, light-emitting diodes (LEDs) and memory devices.

2.4.2 Mechanism and process of inkjet printing

The inkjet printing system has some essential components, including printhead, machine, ink, substrate and software. Sometimes a pretreatment is also needed. In inkjet printing process, the ink is ejected from the printhead onto the substrate, and forms images on the surface with the help of specialized software.

There are two major DOD types: thermal and piezoelectric. In DOD printing process, the ink is ejected from a nozzle. In piezoelectric printheads, printing is operated under the control of electric signals created by the change of voltage. The electrical pulse leads to the deformation of ink chamber, and squeezes the ink out. At the same time, a shockwave is generated to break up the ink into small liquid drops before the ejection. The piezo heads are easier to be controlled than thermal or electrostatic printheads, because the volume of ink does not change. Also piezo heads can reach higher productivity.
In CIJ inkjet printing, a continuous flow of droplets with small diameter is ejected and controlled by electrical fields and high frequency vibrations by the change of piezoelectric action. Binary and multi-deflection are two major types of CIJ mode. The diameter of charged droplets can reach 10-15 microns, to print images with high quality and high resolution.

In the process of ejection, small drops fall down with the combined influence of gravity and air friction, which can also change the direction of ink drops. When the drops attach onto the surface of the fabric, the ink spreads and penetrates into yarns. Then, the liquid evaporates and the colorants stay on the surface and form patterns or designs with different shades and color strength.

The viscosity of inks influences the flow properties in ejection and the spreading on the fabrics. The viscosity of inks relates to the compression and shear stress in nozzles and the difficulty of spreading. Among these parameters, the three essential components are the printhead, substrate and ink.

The printhead needs to be reliable, which means it should not interact with the ink, have small diameter and does not clog. Besides, if the viscosity of ink is relatively high, or some solid materials exist, the evaporation of liquid needs to be considered. The nozzle geometry designs influence the concentration gradients of ink, and the quality of images on media.

The physical and mechanical properties of ink, such as hydrophobicity, viscosity, surface tension, and the drop size, velocity and frequency, play an important role on printing behavior. The inks are applied in two ways, one is process
colors and the other is spot colors. Process colors imply mixing different ejected
droplets at the same point on fabric, to get a desired color. Spot colors denote every
point on fabric is printed by a single droplet ejected from the nozzle \(^{66}\).

Because of the low viscosity of inks, substrates especially textiles, are usually
pretreated before inkjet printing to improve the absorption of colorants, while
preventing wicking and bleeding \(^{73}\).

Furthermore, to decrease the evaporation and the possibility of clogging
during printing, humectants are used as additives to the ink formulation. Some
auxiliary chemicals are also used to enhance light fastness and color intensity \(^{73, 75}\).

### 2.4.3 Dyes and colorants in inkjet printing

Inks applied to inkjet printing have several components, such as colorants,
carriers and auxiliary additives. The colorants can be categorized by their molecular
structure and functional groups. The carriers of inks include water, organic solvent
and some fluids. In inkjet printing, most inks are water-based \(^{73}\). Inks can be divided
into dye-based inks and pigment-based inks, according to the properties of colorants.
Disperse dyes, reactive dyes, acid dyes and pigments are widely used as colorants
in inkjet printing.

Inks are required to have good flow properties to have good formulation of
droplets, for printing at high speed with high resolution. The performance of inks
mainly depends on pH, surface tension and viscosity \(^{67}\). Inks must have high color
yield and good fastness properties\textsuperscript{76, 77}. Compared with dye-based inks, the printing process with pigment-based inks is more convenient, because steaming and washing are not needed after printing\textsuperscript{73, 78}. However, pigment-based inks must have higher UV-resistance and show good resistance to washing, because pigments remain on the surface of the fabric\textsuperscript{66}.

Polyester is a good substrate for textile inkjet printing, and disperse dyes and pigments can be applied for printing polyester. Disperse dyes contain functional groups including -NO\textsubscript{2} and –CN and are hard to dissolve in water. In inkjet printing, with disperse dyes the dye-based ink is spread onto fabrics, which then penetrates into fibers, and forms solid-solid solutions with the substrate\textsuperscript{73}.

Reactive dyes are water soluble dyes which are primarily used for the coloration of cellulosic substrates. In printing, reactive dyes with functional groups as chlorotriazine and dichlorotriazine, react with hydroxyl groups of cellulose fibers and form covalent bonds between them. Because the reaction with the leaving group will happen under alkaline conditions, reactive dyes need to be printed onto alkali-padded substrates\textsuperscript{73}.

Acid dyes are water-soluble dyes and are used for the coloration of nylon and protein substrates. Acid dyes with sulfonate groups react with amino groups in protein or nylon fibers, and form ionic bonds between them. Van der Waals bonds and hydrogen bonds help the fixation of acid dyes on these fibers\textsuperscript{73}.

The colorants in pigment inks are solid and insoluble in carriers, but the molecules are gathered by cross-linking of resins to form tiny groups\textsuperscript{66, 73}. The
groups separate in the ink, and have a size of less than 0.1 micron. After inkjet printing, bonds are formed between the resin and fiber, and thus pigments are ‘fixed’ onto the fibers. Although resin is important in fixation of pigments, it increases the viscosity of pigments, which can potentially result in the blockage of print heads.

2.4.4 Surface modification of polyester fabrics for inkjet printing

Polyester is a potential material for inkjet printing, because it has high strength and resilience with low cost. However, because polyester fabrics are hydrophobic, inks are hard to spread onto and penetrate into them. Polyester fabrics have low dyeability and limited color saturation, color yield and outline sharpness.

To improve the surface properties of polyester fabrics, and the quality of printing, a pretreatment process is needed before inkjet printing. After the pretreatment, ink can be only printed onto the pretreatment agent coating, which covers the surface of the substrate. Because the ink does not fully penetrate into the fibers, it leads to stronger or brilliant colors and higher color saturation. The pretreatment helps improve the add-on value of textile products. The pretreatment methods and formulas depend on different inks and substrates.

Post-treatments, by steaming the fabrics after printing for about 10 minutes at 100°C, are also used to improve the dyeability of fibers inside the yarns, as well as color fastness.
Polyester fabrics can be treated by scouring and bio-treatment. Sodium alginate, water and Brewer's yeast filtrate or enzyme are mixed together to get an uncolored printing paste. After the coating of polyester fabrics, they are printed by pigment-based inks and fixed by heat-setting. With the bio-treatment, the color fastness and color strength are improved.

To modify polyester fabrics, three types of lipases, including penicillium roqueforti, porcine pancreas and porcine pancreas/candida cylindracea are applied to enzymatically catalyze the hydrolysis of ester bonds in polyester molecules. After the enzymatic treatment, the surface wettability and absorbency of polyester fabrics are improved.

Chitosan (CH), the mixture of glycine (Gly), and N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (HTACC) and the mixture of β-cyclodextrin and citric acid, can be used as pre-treatment reagents to modify polyester fabrics before inkjet printing. The color gamut, color saturation, outline sharpness and appearance, are all improved after the pre-treatments. The washing fastness of HTACC pretreated fabrics is improved.

It has been found that treatments of polyester substrate involving changing its surface morphology, and attaching certain polar groups to it, increase the ink holding ability and improve surface energy, anti-bleeding performance, water capillarity, water wettability and resin adhesion of the fabrics in ink-jet printing.
2.4.5 Applications of inkjet printing

2.4.5.1 Applications in textiles

Inkjet printing is widely used for the coloration of textiles, such as apparel, home textiles, carpets, flags and banners. In 1970s, inkjet printing was applied to produce carpets. With the development of digital printers, the production rate and the quality of products keep improving. However, because the cost of high speed production units is relatively high, inkjet printing has been more widely used for sampling and proofing, although this trend is recently changing.

Inkjet printing is applied in the coloration of apparel, because it is able to print images at a high resolution, up to 720 dpi, and the process is controlled precisely by computer signals. With the precise control, the technology can print fine and creative designs or effects for designers and consumers. With the development of three-dimensional designs, inkjet printing is more widely used in custom designs. Inkjet printing can be applied to produce fitted, precise and creative garments.

A portion of sheets, pillows, curtains and other home textiles are produced by inkjet printing. Inkjet printing is a relatively ideal technology for designers, to achieve their complicated and creative designs. The products must have good wash fastness and color resolution, however. Curtains should also have good flame resistance which can be obtained with the help of suitable pretreatments.

Millitron technology™ is a good method applied in digital carpet printing. With the help of technology, delivery pressure is controlled according to the thickness and
pile types of carpets, to achieve different ink penetration and color appearance. In the printing of carpets high speed printing is required. Millitron technology™ enables printing carpets at a speed of about 20 meters per minute. However, both high printing speed and high resolution are needed to satisfy production and consumer requirements.

Inkjet printing is applied in the production of flags and banners, which are known as soft signage. Because of the end use of flags and banners, ink must penetrate through the fabric to obtain double-sided colorful products. Besides, flags and banners need good light fastness and wash fastness. Thus, the inks must have good flow and fastness properties.

2.4.5.2 Applications in other fields

Inkjet printing is not only a technology applied for the coloration of textiles, but also used in several other fields, such as electronics, bio-medicals and coating of films. There are several materials used in inkjet printing, including metals, polymers, ceramics and even biological materials and cells. The viscosity of materials and the temperature in machine depends on the design of printheads, the mechanism of printing and the properties of materials, to get better products.

Inkjet printing is used to fabricate polymer light-emitting diodes (PLEDs) and polymer light-emitting electrochemical cells (PLCs), solar cells, transistors, memory devices and billboards, because of the precise deposition of the material in the
process, including the control of area and thickness, and the reduced wastage of materials. Inkjet printing is used to fabricate different scale of electronics, including micro-electronics and nano-electronics. For example, the semiconducting polymer nanospheres or aqueous dispersions are ejected by inkjet printing and conjugated on several substrates, such as poly(styrenesulfonate)/polystyrene (PSS/PS) substrate, to fabricate polymer light-emitting diodes (PLEDs), which are down to 20 $\mu$m. Besides, organic semiconductors, such as poly(ethylenedioxythiophene) (PEDOT) aqueous dispersion, are printed onto the surface of substrates to form conjugated systems. After inkjet patterning deposition, such as photolithography and etching, polymer thin film transistors (TFTs) are deposited.

Inkjet printing is also employed in bioengineering. Biomolecules, cells or bacteria can be deposited by modified thermal inkjet printers, onto substrates, such as organs and tissue. DNA chips, proteins and cell arrangements can also be deposited. For example, Chinese Hamster Ovary (CHO) and motor neuron cells are printed onto gel-based bio-papers for tissue engineering, by thermal inkjet printer with little damage. Bacterial cells and antibiotics can also be deposited on bio-paper with multiple-layer inkjet printing, to form high-density cell arrays via thermal inkjet printing which can be used to evaluate the drug delivery or toxicity.
2.5 Research plan

With the improvement of inkjet printing and interest in its use for polyester fabrics, development of new pretreatment methods is more and more important in the coloration of textiles, to improve the color saturation, color gamut and color fastness. To print polyester fabrics, disperse dyes and pigments are mostly used. Coating, solvent pretreatment, caustic soda pretreatment and plasma pretreatment are usually applied in the pretreatment process for polyester fabrics \(^{42, 43, 57}\).

Interestingly, it has been found that the application of the pretreatment to dyed PET fabrics can lead to a shift in color in the treated areas. The pretreated fabrics exhibit different L*a*b* values compared with the untreated fabrics. The possible factors for the observed color shift include physical factors and chemical factors.

To determine the factors which lead to shifting color, the following experiments were conducted:

(1) Measurement of the L*a*b* values of untreated and pretreated polyester fabric samples using a spectrophotometer, and analysis of the differences in color;

(2) Scanning electron microscopy (SEM) studies, to observe the superficial difference of samples to assess possible physical factors;

(3) Extraction and isolation of the disperse dyes from polyester fabric samples;

(4) Ultraviolet-visible spectroscopy (UV-vis), high-performance liquid chromatography (HPLC) and mass spectrum for structural identifications of disperse dyes to pin down the possible chemical factors.
A description of the fabrics used in this study is given in Table 2.3.

Table 2.3 The list of polyester fabric samples.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Sample ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1+</td>
<td>All We Do White</td>
</tr>
<tr>
<td>2,2+</td>
<td>All We Do Green</td>
</tr>
<tr>
<td>3,3+</td>
<td>All We Do Black</td>
</tr>
<tr>
<td>4,4+</td>
<td>All We Do White</td>
</tr>
<tr>
<td>5,5+</td>
<td>All We Do Blue</td>
</tr>
<tr>
<td>6,6+</td>
<td>All We Do Yellow</td>
</tr>
<tr>
<td>7,7+</td>
<td>Fruit of the Loom White</td>
</tr>
<tr>
<td>8,8+</td>
<td>Fruit of the Loom Green</td>
</tr>
<tr>
<td>9,9+</td>
<td>Fruit of the Loom Black</td>
</tr>
<tr>
<td>10,10+</td>
<td>Gildan Performance White</td>
</tr>
<tr>
<td>11,11+</td>
<td>Gildan Performance Blue</td>
</tr>
<tr>
<td>13,13+</td>
<td>Gildan Performance Yellow/Green</td>
</tr>
<tr>
<td>14,14+</td>
<td>Gildan Performance Dark Blue</td>
</tr>
<tr>
<td>15,15+</td>
<td>Gildan Performance Red</td>
</tr>
<tr>
<td>16,16+</td>
<td>Gildan Performance Black</td>
</tr>
<tr>
<td>17,17+</td>
<td>Gildan Soft Style 65% Grey</td>
</tr>
<tr>
<td>18,18+</td>
<td>Hanes Cool Dry Yellow</td>
</tr>
<tr>
<td>19,19+</td>
<td>Hanes Cool Dry Light Blue</td>
</tr>
<tr>
<td>20,20+</td>
<td>Hanes Cool Dry Red</td>
</tr>
<tr>
<td>21,21+</td>
<td>Hanes Cool Dry Dark Blue</td>
</tr>
<tr>
<td>22,22+</td>
<td>Hanes Cool Dry Black</td>
</tr>
<tr>
<td>23,23+</td>
<td>Augusta Sportswear Lt Blue</td>
</tr>
<tr>
<td>25,25+</td>
<td>Augusta Sportswear Gold</td>
</tr>
<tr>
<td>26,26+</td>
<td>Augusta Sportswear Dark Blue</td>
</tr>
<tr>
<td>Sample Number</td>
<td>Sample ID</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>27,27+</td>
<td>Augusta Sportswear Red</td>
</tr>
<tr>
<td>28,28+</td>
<td>Augusta Sportswear Black</td>
</tr>
<tr>
<td>29,29+</td>
<td>Alo Red</td>
</tr>
<tr>
<td>30,30+</td>
<td>Alo Dark Blue</td>
</tr>
<tr>
<td>31,31+</td>
<td>Alo Black</td>
</tr>
<tr>
<td>32,32+</td>
<td>Gildan Dry Blend Gold Yellow</td>
</tr>
<tr>
<td>33,33+</td>
<td>Gildan Dry Blend Lt Blue</td>
</tr>
<tr>
<td>34,34+</td>
<td>Gildan Dry Blend Red</td>
</tr>
<tr>
<td>35,35+</td>
<td>Gildan Dry Blend Dark Blue</td>
</tr>
<tr>
<td>36,36+</td>
<td>Gildan Dry Blend Black</td>
</tr>
<tr>
<td>37,37+</td>
<td>Anvil Yellow/Green</td>
</tr>
<tr>
<td>38,38+</td>
<td>Anvil Dark Blue</td>
</tr>
<tr>
<td>39,39+</td>
<td>Anvil Gray</td>
</tr>
<tr>
<td>40,40+</td>
<td>American Apparel Yellow</td>
</tr>
<tr>
<td>41,41+</td>
<td>American Apparel Med Blue</td>
</tr>
<tr>
<td>42,42+</td>
<td>American Apparel Red</td>
</tr>
<tr>
<td>43,43+</td>
<td>American Apparel Green</td>
</tr>
<tr>
<td>44,44+</td>
<td>American Apparel Black</td>
</tr>
</tbody>
</table>
3. Experimental

3.1 Materials

The un-pretreated and pretreated fabrics used in the research are polyester fabrics, which were provided by Company A. The pretreatment method applied in the research was developed by Company A. The pretreatment reagent is aqueous and is provided as an emulsion including water and inorganic salts.

Ethyl acetate and hexane were used for dye extraction, dye isolation and thin layer chromatography (TLC). Acetone, ethyl acetate, acetonitrile (ACN) and chlorobenzene were used in UV-Visible absorption spectroscopy (UV-Vis).

HPLC grade acetonitrile was applied in the dye identification with the help of HPLC method and mass spectrometry. And the ACS grade acetonitrile was prepared for UV-Vis, to discover the influence of pretreatment agent.

The chemicals used in the research are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Certified ACS Grade Solvent</td>
<td>VWR International, LLC</td>
</tr>
<tr>
<td>Hexane</td>
<td>Certified ACS Grade Solvent</td>
<td>VWR International, LLC</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>Certified ACS Grade Solvent</td>
<td>VWR International, LLC</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>Laboratory Grade</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>HPLC Grade</td>
<td>EMD Millipore Corporation</td>
</tr>
</tbody>
</table>

3.2 Instruments
In order to measure color strength, an X-Rite Color i7 bench-top spectrophotometer coupled with Color iMatch Professional software was used. The average L*a*b* values and color difference (Delta-E2000) at $\lambda_{\text{max}}$ between non-pretreated and pretreated polyester fabrics were determined.

The Thomas Wiley Mini-mill was used to grind the sample fabrics, for better dye extraction of samples. Rotavapor® R-300, a type of rotary evaporation equipment, was used for solvent evaporation after dye extraction.

The scanning electron microscope (SEM) was produced by FEI Company, Hillsboro, Oregon. The SEM was used to observe the surface morphology of PET fabrics and compare the difference between two sets of samples. Quorum Technologies SC7620 Mini Sputter Coater made by Quorum Technologies, Kent, UK, was applied to coat an ultrathin layer of electrically conducting material onto the samples in an order to facilitate the scanning process.

Ultraviolet-Visible absorption spectroscopy (UV-Vis) was done using an Agilent Technologies Cary 300 UV-VIS Spectrophotometer, with the help of Cary Win UV software.

The Agilent Technologies 6520 Accurate-Mass Quadrupole-Time-of-Flight (Q-TOF) mass spectrometry and Agilent Technologies 1200 series HPLC liquid chromatography system equipped with an electrospray ionization (ESI) source and a photodiode array detector (DAD), to record mass spectra, with the help of Agilent MassHunter Acquisition and Agilent MassHunter Qualitative Analysis B.06.00 (computer software).
3.3 Thin Layer Chromatography (TLC) of dyes

Thin layer chromatography (TLC) is a visual detection method to determine the number of components in the dye mixture, based on differences in their \( R_f \) values. \( R_f \) value is defined as the distance the components travel from the starting point divided by the distance of the solvent travels on the plate. TLC plates, produced by EMD Millipore, were aluminum plates coated with silica gel. In the TLC process, the dye was first extracted from PET fabrics, and then dissolved in ethyl acetate. The microcapillar was dipped into the dye solution and the solution applied to the TLC plate. After drying, the TLC plate was placed into a chamber containing a small quantity of hexane/ethyl acetate 2:1 solution. Upon developing of TLC plate, spots for the different components, because of having different \( R_f \) values, were revealed.

3.4 Dye extraction and isolation

The Thomas Wiley Mini-mill was used to mill the sample fabrics. The steel cutting knives and the high rotation speed of the cutting knives helped the grinding of polyester fabrics.

After the grinding, the mixture of dyes was extracted by a soxhlet extractor system. The soxhlet extractor system was consisted of 250 mL round bottom flask, a bulb condenser and a soxhlet extractor. Ethyl acetate was the solvent for extracting the dyes from the polyester powder. Before assembling the soxhlet extractor system,
the fabric powder was placed in a cellulose extraction thimble, and the extraction thimble was placed in a soxhlet extractor.

The 250 mL round bottom flask containing 125 mL ethyl acetate was heated at 80 °C for 4 hours. Ethyl acetate was evaporated and condensed by the bulb condenser, then dripped into the cellulose extraction thimble. Dyes were dissolved in ethyl acetate, and flowed into the 250 mL round bottom flask.

After the dye extraction, dye solution was evaporated using a Rotavapor R-300 at 45°C. Before complete evaporation the solution was transferred to small glass bottle. The mixture of dyes in a powder form, after solvent evaporation, was stored at room temperature.

Flash column chromatography was selected as an effective way to purify the mixture of disperse dyes, because disperse dyes in the admixture had different Rf values when running downward in the column in the organic solvent.

To prepare the flash column chromatography system, sand, silica gel and sand were poured into the column and compacted step by step. The volume ratio of three components was 1:30:1. The edge of sand and silica gel should be flat. After the column was fixed, the dye mixture was added into it. The eluent was prepared and applied to the top of the column. When running flash column chromatography, compressed air was applied to speed up the process. The band of each dye was collected using 200 mL beakers one by one and evaporated by Rotavapor R-300 at 45°C.
Before the flash column chromatography, thin layer chromatography (TLC) was employed to find out the best solvents and ratio of solvents. According to TLC results, hexane/ethyl acetate 2:1 was selected as the eluent for dye isolation in flash column chromatography. After dye isolation, the purity of disperse dye was examined by TLC.

To further purify the isolated dyes, glass silica gel, preparative layer plates provided by Analtech were used to isolate the dyes. In the preparative layer process, the eluent was hexane/ethyl acetate 2:1. After the process, the silica gel for each dye component was collected, extracted by ethyl acetate, evaporated and stored in a small glass vial. Different dyes were collected separately.

3.5 Surface morphology

A scanning electron microscope (SEM), manufactured by FEI Company, Hillsboro, Oregon was used to study surface morphology of the treated and untreated fibers and to compare the difference between two sets of samples. Before performing SEM experiments, the PET fabric samples were prepared by cutting into small pieces, to fit the size of specimen stub. The samples were attached onto the specimen stubs separately, and placed into an SC7620 Mini Sputter Coater manufactured by Quorum Technologies. Sputter coater coated the samples with an ultrathin layer of electrically conducting material. After that, the samples were placed into the SEM, and the detection was carried out with the help of the associated software.
3.6 UV-Visible absorption spectroscopy

Ultraviolet-Visible absorption spectroscopy (UV-Vis) manufactured by Agilent Technologies Cary 300 UV-VIS Spectrophotometer, with Cary Win UV software was employed to aid with the analysis of samples. In the preparation of UV-Vis, dye powders or commercial dye powders were dissolved in different organic solvents, such as acetone, ethyl acetate, acetonitrile and chlorobenzene. Dye solution was filled into a cuvette, which was placed in the sample slot of the spectrophotometer. At the same time, another cuvette was filled with the pure organic solvent and placed in the reference slot. The UV-Vis spectra were obtained over the range of 250 nm to 800 nm.

3.7 Mass spectroscopy

Mass spectroscopy, manufactured by Agilent Technologies 6520 Accurate-Mass Quadrupole-Time-of-Flight (Q-TOF) mass spectrometry was used for the analysis of components. In the sample preparation, the dye samples were dissolved in methanol at a concentration ratio of 1:1. A 1:10000 dilution was then prepared to obtain 1 ppm of the dye solution in a glass vial.

3.8 High-performance liquid chromatography (HPLC) spectroscopy
An Agilent Technologies 1200 series HPLC liquid chromatography system with an electrospray ionization (ESI) source was used to run the samples for further analysis. In the sample preparation, the dye samples were dissolved in acetonitrile.
4. Results and Discussion

4.1 Color measurements

Color is seen and distinguished, and color differences are observed by human. However, color visions of persons are different. To characterize the color, standards of color specification were developed. Based on Munsell circle (in Figure 4.1), in 1976, the International Commission on Illumination (CIE) created a three coordinate system, which is CIELAB, to locate a color in an opposite-color space. One of these color spaces is CIE L*a*b*. The L* represents lightness (black or white), ranging from 0-100. The a* represents redness (represented by a*) or greenness (represented by -a*), ranging from 70 to -40. The b* represents yellowness (represented by b*) or blueness (represented by -b*), ranging from 100 to -60. The L*a*b* color space is shown in Fig. 4.2.

![Figure 4.1 The Munsell circle](image)

Figure 4.1 The Munsell circle.
The CIELAB coordinates are calculated by equations which relate to CIE XYZ tristimulus values. The X, Y, Z values in CIE XYZ system represent the amount of a red primary, a green primary and a blue primary individually\(^91\). The equations for \(L^*a^*b^*\), hue (\(h\)) and chroma (\(C^*\)) are listed in Equations 4.1 to 4.6\(^93\),\(^95\).

\[
L^* = 116f \left( \frac{Y}{Y_n} \right) - 16 \tag{4.1}
\]

\[
a^* = 500[f \left( \frac{X}{X_n} \right) - f \left( \frac{Y}{Y_n} \right)] \tag{4.2}
\]

\[
b^* = 200[f \left( \frac{Y}{Y_n} \right) - f \left( \frac{Z}{Z_n} \right)] \tag{4.3}
\]

\[
\Delta C_{ab}^* = [(a^*)^2 + (b^*)^2]^{1/2} \tag{4.4}
\]

\[
\Delta h_{ab}^* = \tan^{-1} \left( \frac{b^*}{a^*} \right) \tag{4.5}
\]

\[
f(\omega) = \begin{cases} 
(\omega)^{1/3} & \omega > 0.008856 \\
7.787(\omega) + \frac{16}{116} & \omega \leq 0.008856 
\end{cases} \tag{4.6}
\]
In the Munsell color system, the colors are specified using three attributes, including hue, value (lightness), and chroma (saturation). Color difference is also described by the three attributes. In Figure 4.3, different value and chroma are shown at different hues.

![Figure 4.3 The colors for Munsell planes with different hues.](image)

To evaluate the color difference between standard (S) and batch (B), the CIELAB color difference formula is used. The total color difference is calculated by Equation 4.5 to 4.10.

\[
\Delta E_{ab}^* = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2} 
\]

\[
\Delta L^* = L_B^* - L_S^* 
\]

\[
\Delta a^* = a_B^* - a_S^* 
\]

\[
\Delta b^* = b_B^* - b_S^* 
\]
According to the color measurement data, the DEcmc (2:1) and CIEDE2000 were calculated. The DEcmc (2:1) values are calculated by the CMC color difference formula, with the Equation 4.11 to 4.14.

\[
\Delta E_{\text{CMC}} = \left[ (\Delta L^*/2S_L)^2 + (\Delta C_{ab}*/S_C)^2 + (\Delta h_{ab}*/S_H)^2 \right]^{1/2} \tag{4.11}
\]

\[
S_L = \begin{cases} 
0.040975 L_S^* / 1 + 0.01765 L_S^*, & L_S^* \geq 16 \\
0.511, & L_S^* < 16
\end{cases} \tag{4.12}
\]

\[
S_C = 0.638 + \frac{0.0638 C_{ab,s}^*}{1 + 0.0131 C_{ab,s}^*} \tag{4.13}
\]

\[
S_H = S_C (Tf + 1 - f) \tag{4.14}
\]

where

\[
f = \frac{\left( C_{ab,s}^* \right)^4}{\left( C_{ab,s}^* \right)^4 + 1900} \tag{4.15}
\]

\[
T = \begin{cases} 
0.36 + \left| 0.4 \cos(h_{ab,s} + 35^\circ) \right|, & h_{ab,s} \leq 164^\circ \text{ or } h_{ab,s} \geq 345^\circ \\
0.56 + \left| 0.2 \cos(h_{ab,s} + 168^\circ) \right|, & 164^\circ < h_{ab,s} < 345^\circ
\end{cases} \tag{4.16}
\]

Because CMC (2:1) is not accurate when analyzing colors in grey and blue regions, the CIEDE2000 was developed as an improved color difference formula. CIEDE2000 values of PET fabric samples can be calculated by the formula shown in Equation 4.15 to 4.19. According to CIE94, \( k_L = 2 \) and \( k_C, k_H \) are both 1 in textiles.

\[
\Delta E_{\text{2000}} = \left[ \left( \frac{\Delta L'}{k_L S_L} \right)^2 + \left( \frac{\Delta C'}{k_C S_C} \right)^2 + \left( \frac{\Delta H'}{k_H S_H} \right)^2 + R_T \left( \frac{\Delta C'}{k_C S_C} \right) \left( \frac{\Delta H'}{k_H S_H} \right) \right]^{1/2} \tag{4.15}
\]

\[
S_L = 1 + \frac{0.015(U - 50)^2}{\left[ 20 + (U - 50)^2 \right]^2} \tag{4.16}
\]
\[ S_C = 1 + 0.045C' \] (4.17)
\[ S_H = 1 + 0.015C'T \] (4.18)
\[ R_T = -\sin(2\Delta\theta) R_C \] (4.19)

where

\[ T = 1 - 0.17 \cos(\bar{h'} - 30^\circ) + 0.24 \cos(2\bar{h'}) + 0.32 \cos(3\bar{h'} + 6^\circ) \]
\[ - 0.20 \cos(4\bar{h'} - 63^\circ) \]

\[ \Delta\theta = 30 \exp \left[ - \left( \frac{\bar{h'} - 275^\circ}{25} \right)^2 \right] \]

\[ R_C = 2 \left[ \frac{(C')^7}{(C')^7 + 25^7} \right]^{\frac{1}{2}} \]

\[ L' = L^* \]
\[ a' = (1 + G)a^* \]
\[ b' = b^* \]
\[ C' = [(a')^2 + (b')^2]^{\frac{1}{2}} \]
\[ h' = \tan^{-1} \left( \frac{b'}{a'} \right) \]
\[ G = 0.5 \left\{ 1 - \left[ \frac{(C')^7}{(C')^7 + 25^7} \right]^{\frac{1}{2}} \right\} \]
In the research, the untreated polyester fabrics and pretreated polyester fabrics were divided into a control group and experimental (pre-treated) group. The samples in the control group were labeled Number 1 to Number 44, and the samples in the pretreated group were labeled Number 1+ to Number 44+. In the color measurement, the untreated PET fabrics were selected as standards and the pretreated PET fabrics were batchs, by each pair separately.

The untreated and pretreated PET fabrics were observed using the CIE 2001 standard colorimetric observer. In the color measurement, UV component of the source was included, and the specular component was included, with an aperture size of 30mm. The CIE illuminant D65 is the light source. Each sample was measured 3 times on the front side, and the measurement data was the average of 3 readings. Each time the sample measured, the samples were selected to be at different positions and angles in each reading. The intra-instrument variability was computed following CIEDE2000 (2:1:1) and DE\textsubscript{CMC} (2:1). With the help of an X-Rite Color i7 bench-top spectrophotometer, the average L*a*b* values of samples, as well as their color difference (Delta-E2000) at $\lambda_{\text{max}}$ between non-pretreated and pretreated polyester fabrics were determined, the results of which are shown in Table 4.1. DL*, Da*, Db*, DE\textsubscript{CMC} and DE2000 means the difference in L*a*b* color values between a batch against a standard and the total color difference calculated with two different tolerancing methods. The 2-D graphs, in Figures 4.4-4.9, show the relationships among L*, a* and b* of samples.
Table 4.1 The color attributes of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color</th>
<th>DL*</th>
<th>Da*</th>
<th>Db*</th>
<th>DE_{CMC}</th>
<th>DE2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1+</td>
<td>White</td>
<td>-0.01D</td>
<td>-0.23 G</td>
<td>0.27 Y</td>
<td>0.29</td>
<td>0.27</td>
</tr>
<tr>
<td>2,2+</td>
<td>Green</td>
<td>-2.28 D</td>
<td>1.94 R</td>
<td>2.23 Y</td>
<td>1.65</td>
<td>1.65</td>
</tr>
<tr>
<td>3,3+</td>
<td>Black</td>
<td>-0.81 D</td>
<td>-0.03 G</td>
<td>0.21 Y</td>
<td>0.78</td>
<td>0.35</td>
</tr>
<tr>
<td>4,4+</td>
<td>White</td>
<td>0.21 L</td>
<td>-0.22 G</td>
<td>0.20 Y</td>
<td>0.28</td>
<td>0.26</td>
</tr>
<tr>
<td>5,5+</td>
<td>Blue</td>
<td>-2.69 D</td>
<td>1.50 R</td>
<td>-1.13 B</td>
<td>1.71</td>
<td>1.68</td>
</tr>
<tr>
<td>6,6+</td>
<td>Yellow</td>
<td>-0.54 D</td>
<td>0.18 R</td>
<td>-1.31 B</td>
<td>0.49</td>
<td>0.38</td>
</tr>
<tr>
<td>7,7+</td>
<td>White</td>
<td>-0.79 D</td>
<td>0.29 R</td>
<td>0.50 Y</td>
<td>0.73</td>
<td>0.65</td>
</tr>
<tr>
<td>8,8+</td>
<td>Green</td>
<td>-1.06 D</td>
<td>-1.06 G</td>
<td>-1.88 B</td>
<td>1.06</td>
<td>1.02</td>
</tr>
<tr>
<td>9,9+</td>
<td>Black</td>
<td>0.77 L</td>
<td>-0.31 G</td>
<td>0.50 Y</td>
<td>1.09</td>
<td>0.69</td>
</tr>
<tr>
<td>10,10+</td>
<td>White</td>
<td>-0.47 D</td>
<td>0.43 R</td>
<td>-0.06 B</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>11,11+</td>
<td>Blue</td>
<td>-0.80 L</td>
<td>-0.42 G</td>
<td>-0.87 B</td>
<td>0.60</td>
<td>0.68</td>
</tr>
<tr>
<td>13,13+</td>
<td>Yellow/Green</td>
<td>-0.67 D</td>
<td>4.70 R</td>
<td>2.43 Y</td>
<td>2.28</td>
<td>2.31</td>
</tr>
<tr>
<td>14,14+</td>
<td>Dark Blue</td>
<td>1.37 L</td>
<td>0.23 R</td>
<td>2.03 Y</td>
<td>1.20</td>
<td>1.22</td>
</tr>
<tr>
<td>15,15+</td>
<td>Red</td>
<td>-0.07 D</td>
<td>-1.75 G</td>
<td>-1.40 B</td>
<td>0.84</td>
<td>0.65</td>
</tr>
<tr>
<td>16,16+</td>
<td>Black</td>
<td>4.44 L</td>
<td>0.05 R</td>
<td>0.44 Y</td>
<td>4.38</td>
<td>1.56</td>
</tr>
<tr>
<td>17,17+</td>
<td>Grey</td>
<td>-0.60 D</td>
<td>0.12 R</td>
<td>0.61 Y</td>
<td>0.65</td>
<td>0.52</td>
</tr>
<tr>
<td>18,18+</td>
<td>Yellow</td>
<td>-1.55 D</td>
<td>1.19 R</td>
<td>1.96 Y</td>
<td>1.03</td>
<td>0.93</td>
</tr>
<tr>
<td>19,19+</td>
<td>Blue</td>
<td>-0.57 D</td>
<td>-0.41 G</td>
<td>-0.51 B</td>
<td>0.46</td>
<td>0.45</td>
</tr>
<tr>
<td>20,20+</td>
<td>Red</td>
<td>-1.53 D</td>
<td>-2.58 G</td>
<td>-0.13 B</td>
<td>1.30</td>
<td>1.03</td>
</tr>
<tr>
<td>21,21+</td>
<td>Dark Blue</td>
<td>-1.68 D</td>
<td>0.65 R</td>
<td>2.45 Y</td>
<td>1.67</td>
<td>1.82</td>
</tr>
<tr>
<td>22,22+</td>
<td>Black</td>
<td>2.38 L</td>
<td>-0.21 G</td>
<td>0.07 Y</td>
<td>2.25</td>
<td>0.87</td>
</tr>
<tr>
<td>23,23+</td>
<td>Blue</td>
<td>-1.73 D</td>
<td>0.47 R</td>
<td>-2.96 B</td>
<td>1.82</td>
<td>1.29</td>
</tr>
<tr>
<td>25,25+</td>
<td>Gold</td>
<td>-1.75 D</td>
<td>2.42 R</td>
<td>-2.91 B</td>
<td>2.39</td>
<td>2.07</td>
</tr>
<tr>
<td>26,26+</td>
<td>Blue</td>
<td>-1.33 D</td>
<td>0.85 R</td>
<td>3.62 Y</td>
<td>2.02</td>
<td>2.33</td>
</tr>
<tr>
<td>27,27+</td>
<td>Red</td>
<td>-1.01 D</td>
<td>-4.32 G</td>
<td>-2.85 B</td>
<td>2.07</td>
<td>1.65</td>
</tr>
<tr>
<td>28,28+</td>
<td>Black</td>
<td>0.37 L</td>
<td>-0.28 G</td>
<td>0.30 Y</td>
<td>0.67</td>
<td>0.51</td>
</tr>
<tr>
<td>29,29+</td>
<td>Red</td>
<td>-0.12 D</td>
<td>-3.42 G</td>
<td>-1.89 B</td>
<td>1.51</td>
<td>1.22</td>
</tr>
<tr>
<td>Sample</td>
<td>Color</td>
<td>DL*</td>
<td>Da*</td>
<td>Db*</td>
<td>DE$_{CMC}$</td>
<td>DE2000</td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------------</td>
<td>--------</td>
</tr>
<tr>
<td>30,30+</td>
<td>Dark Blue</td>
<td>-0.25 D</td>
<td>0.25 R</td>
<td>2.09 Y</td>
<td>1.56</td>
<td>1.40</td>
</tr>
<tr>
<td>31,31+</td>
<td>Black</td>
<td>1.88 L</td>
<td>-0.22 G</td>
<td>0.38 Y</td>
<td>1.89</td>
<td>0.80</td>
</tr>
<tr>
<td>32,32+</td>
<td>Gold Yellow</td>
<td>2.02 L</td>
<td>0.59 R</td>
<td>2.60 Y</td>
<td>1.20</td>
<td>0.98</td>
</tr>
<tr>
<td>33,33+</td>
<td>Blue</td>
<td>0.89 L</td>
<td>-0.52 G</td>
<td>0.36 Y</td>
<td>0.58</td>
<td>0.49</td>
</tr>
<tr>
<td>34,34+</td>
<td>Red</td>
<td>-0.67 D</td>
<td>-2.80 G</td>
<td>-1.59 B</td>
<td>1.21</td>
<td>0.93</td>
</tr>
<tr>
<td>35,35+</td>
<td>Blue</td>
<td>0.66 L</td>
<td>-0.21 G</td>
<td>0.19 Y</td>
<td>0.41</td>
<td>0.29</td>
</tr>
<tr>
<td>36,36+</td>
<td>Black</td>
<td>2.21 L</td>
<td>-0.10 G</td>
<td>0.01 Y</td>
<td>2.17</td>
<td>0.75</td>
</tr>
<tr>
<td>37,37+</td>
<td>Yellow/Green</td>
<td>-0.28 D</td>
<td>1.54 R</td>
<td>-0.41 B</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td>38,38+</td>
<td>Blue</td>
<td>1.96 L</td>
<td>1.31 R</td>
<td>0.18 Y</td>
<td>1.38</td>
<td>1.26</td>
</tr>
<tr>
<td>39,39+</td>
<td>Grey</td>
<td>0.06 L</td>
<td>-0.64 G</td>
<td>0.14 Y</td>
<td>0.86</td>
<td>0.93</td>
</tr>
<tr>
<td>40,40+</td>
<td>Yellow</td>
<td>-0.07 D</td>
<td>1.60 G</td>
<td>-0.08 B</td>
<td>1.02</td>
<td>1.06</td>
</tr>
<tr>
<td>41,41+</td>
<td>Blue</td>
<td>2.10 L</td>
<td>-0.74 G</td>
<td>2.32 Y</td>
<td>1.6</td>
<td>1.22</td>
</tr>
<tr>
<td>42,42+</td>
<td>Red</td>
<td>3.81 L</td>
<td>-6.93 G</td>
<td>-6.34 B</td>
<td>4.31</td>
<td>3.53</td>
</tr>
<tr>
<td>43,43+</td>
<td>Green</td>
<td>3.28 L</td>
<td>3.55 R</td>
<td>-0.40 B</td>
<td>2.29</td>
<td>2.11</td>
</tr>
<tr>
<td>44,44+</td>
<td>Black</td>
<td>8.05 L</td>
<td>-0.20 G</td>
<td>0.16 Y</td>
<td>7.89</td>
<td>2.77</td>
</tr>
</tbody>
</table>

The analysis of color difference was based on the combination of DE$_{CMC}$ and DE2000. According to the color measurement data, there are several pairs of samples which have large color difference, such as Sample 2, 5, 8, 13, 14, 16, 20, 21, 23, 25, 26, 27, 29, 30, 38, 40, 41, 42, 43 and 44. The DE$_{CMC}$ values or DE2000 values of them are higher than 1.0. Color differences (expressed in DE2000) greater than 1.0 are shown in Bold in Table 4.1, and represent unacceptable visual variations between samples. In Table 4.1, The D in DL$^*$ value means turned darker, L means lighter, G means greener, R means redder, Y means yellower and B means bluer.
In the analysis of color measurement data, the 2-D graphs among L*, a* and b* shown the color difference between pretreated and untreated samples. For example, in Figure 4.4, L* value of Sample 2 decreased from 67.06 to 64.78, which means pretreated sample (Sample 2+) is darker. The a* value increased from -34.81 to -32.86, which means pretreated sample turned redder. In Figure 4.5, the b* value increased from 54.67 to 56.90, which means pretreated sample turned yellower.

According to the DL* values of samples, a majority of dark colored pretreated PET fabrics turned darker, but most of black samples, 5 of 9 blue samples and a grey, a red and a green sample turned lighter. Based on the Da* values of samples, a majority of dark colored pretreated PET fabrics turned greener, but most of yellow samples turned redder. There is no significant feature found in Db* values.

Figure 4.4 2-D graph of a*L* values for Samples 1-22 and Samples 1+ to 22+. 
Figure 4.5 2-D graph of b*L* values of Samples 1-22 and Samples 1+ to 22+.

Figure 4.6 2-D graph of a*b* values of Samples 1-22 and Samples 1+ to 22+.
Figure 4.7 2-D graph of $a^*L^*$ values of Samples 22-44 and Samples 22+ to 44+.

Figure 4.8 2-D graph of $b^*L^*$ values of Samples 22-44 and Samples 22+ to 44+. 
DECMC (2:1) and DE2000 (2:1:1) results show that several pairs exhibit relatively large color differences, including Samples 13, 16, 25, 26, 42, 43 and 44. Several sample pairs, not printed by disperse dyes including Samples 1, 4, 7 and 10, were also measured. Results are shown in Table 4.1, which do not exhibit significant differences between samples.

The differences between samples, expressed in DE2000, spread from 0.20 to 3.530 units. Majority of samples exhibit differences of less than 2.00 units however. Compared with non-pretreated samples, L* values of black samples are increased but that for other printed samples are decreased. Thus the black PET fabrics became lighter but PET fabrics with other colors became darker as a result of the treatment.
4.2 Dye extraction and isolation

The powder fabric samples were placed in a soxhlet extractor system for 4 hours together with solvents to extract dyes. The solvents from extracts were evaporated and then dye powders were collected.

Flash column chromatography was used to isolate individual dyes from dye mixture. After the flash column chromatography, fractions were collected separately and evaporated. The isolated dyes were transferred to glass thick-layer chromatography plates for further purification, using 2:1 hexane/ethyl acetate as eluent. Pictures of the items used in dye extraction and isolation, and the samples, are shown in Figures 4.10-4.13. The weights of dye extracts are shown in Table 4.2.

Figure 4.10 The mini-mill used to powder fabric samples.
Figure 4.11 A powdered fabric sample for dye extraction.

Figure 4.12 The soxhlet extractor system for dye extraction.
Figure 4.13 Examples of dye extracts.

Table 4.2 The weights of dye extracts of Samples 2-22 and Samples 2+ to 22+.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Weight of Dye Extract for untreated sample (g)</th>
<th>Weight of Dye Extract for Pretreated sample (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2+</td>
<td>0.007</td>
<td>0.222</td>
</tr>
<tr>
<td>3,3+</td>
<td>0.042</td>
<td>0.155</td>
</tr>
<tr>
<td>5,5+</td>
<td>0.034</td>
<td>0.226</td>
</tr>
<tr>
<td>6,6+</td>
<td>0.017</td>
<td>0.162</td>
</tr>
<tr>
<td>8,8+</td>
<td>0.030</td>
<td>0.188</td>
</tr>
<tr>
<td>9,9+</td>
<td>0.027</td>
<td>0.271</td>
</tr>
<tr>
<td>11,11+</td>
<td>0.027</td>
<td>0.183</td>
</tr>
<tr>
<td>13,13+</td>
<td>0.030</td>
<td>0.157</td>
</tr>
<tr>
<td>14,14+</td>
<td>0.031</td>
<td>0.104</td>
</tr>
<tr>
<td>15,15+</td>
<td>0.061</td>
<td>0.159</td>
</tr>
<tr>
<td>16,16+</td>
<td>0.069</td>
<td>0.242</td>
</tr>
<tr>
<td>Sample Number</td>
<td>Weight of Dye Extract for untreated sample (g)</td>
<td>Weight of Dye Extract for Pretreated sample (g)</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>17,17+</td>
<td>0.016</td>
<td>0.238</td>
</tr>
<tr>
<td>18,18+</td>
<td>0.009</td>
<td>0.222</td>
</tr>
<tr>
<td>19,19+</td>
<td>0.018</td>
<td>0.259</td>
</tr>
<tr>
<td>20,20+</td>
<td>0.028</td>
<td>0.165</td>
</tr>
<tr>
<td>21,21+</td>
<td>0.022</td>
<td>0.264</td>
</tr>
<tr>
<td>22,22+</td>
<td>0.018</td>
<td>0.230</td>
</tr>
</tbody>
</table>

### 4.3 Thin Layer Chromatography (TLC) of dye extracts

To further analyze color differences, components in dye mixtures were separated and analyzed individually. Disperse dyes on Samples 1-22 and Samples 1+ to 22+ were extracted and analyzed, and white and dark colored samples were included. Solutions of fabric extracts were applied to TLC plates and developed with 2:1 hexane/ethyl acetate. According to Figures 4.14 and 4.15, there is no significant difference between dyes before and after the pretreatment, including color and location of spots.
Figure 4.14 TLC plate of Samples 2-14 and Samples 2+ to 14+.

Figure 4.15 TLC plate of Samples 15-22 and Samples 15+ to 22+.
4.4 Characterization of extracts from Samples 5, 5+, 6, 6+, 8, 8+, and 13, 13+

According to TLC results, Sample pairs 2, 5, 6 and 13 had two dyes in their extracts. Because of the low number of components for our initial characterization studies, these samples were selected.

4.4.1 UV-Vis spectra

According to Figures 4.16-4.19, the UV-Vis spectra of Samples 5 and 5+ are similar and the UV-Vis spectra of Samples 13 and 13+ are also similar, including the $\lambda_{\text{max}}$ (wavelength absorbed) and the trend of curves. To prepare the solution of Samples 5, 5+ and 13, 13+, ethyl acetate was selected as the solvent. Based on the UV-Vis spectra, there was no impact of the pretreatment on the dyes present.

![Figure 4.16 UV-Vis spectrum of Sample 5.](image)

![Figure 4.17 UV-Vis spectrum of Sample 5+.](image)
Figure 4.18 UV-Vis spectrum of Sample 13.

Figure 4.19 UV-Vis spectrum of Sample 13+.

4.4.2 Mass spectra

The disperse dyes extracted from Samples 5, 5+, 6, 6+, 8, and 8+ were analyzed by mass spectrometry in negative or positive electrospray ionization (ESI) mode. The mass spectra of Samples 5 and 5+ are shown in Figures 4.20-4.23. According to the TLC results of the samples, each of them had two disperse dyes. However, the spectra of dye mixtures did not show two clear peaks. Also, mass spectra for the dye mixtures did not help the identification and the determination of basis for color shifting.
Figure 4.20 Mass spectrum of Sample 5 in negative ESI.

Figure 4.21 Mass spectrum of Sample 5+ in negative ESI.
Figure 4.22 Mass spectrum of Sample 5 in positive ESI.

Figure 4.23 Mass spectrum of Sample 5+ in positive ESI.
4.5 Characterization of Sample 16 extract

4.5.1 Dye separations

Sample 16, a black PET fabric, was selected as the prototype since it gave a large color shift after pre-treatment. Figure 4.24 shows the resulting thick-layer plate for Sample 16 extract. There were 5 dyes collected, including light blue, yellow, dark blue, purple and red dye.

Figure 4.24 TLC plate from Sample 16 extract.
Table 4.3 The weights of isolated dyes from Sample 16 extract.

<table>
<thead>
<tr>
<th>Color</th>
<th>Weight (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light blue</td>
<td>0.5</td>
</tr>
<tr>
<td>Yellow</td>
<td>1.2</td>
</tr>
<tr>
<td>Dark blue</td>
<td>1.5</td>
</tr>
<tr>
<td>Purple</td>
<td>0.8</td>
</tr>
<tr>
<td>Red</td>
<td>1.9</td>
</tr>
</tbody>
</table>

4.5.2 The UV-Vis spectra

After dye isolation from the Sample 16 mixture, UV-Vis analyses were conducted. Ethyl acetate was used as the solvent. Dye solutions were divided into two test tubes with the same volume, 5 mL, and 10 drops of pretreatment agent was added into one of the test tubes and mixed well. Then, the tubes were sealed. Relatively clear dye solutions were collected after stratification. The dye solutions with and without pretreatment agent were analyzed.

Figures 4.25-4.34 show the wavelength of maximum absorption ($\lambda_{\text{max}}$) and the trend of absorption curve. The $\lambda_{\text{max}}$ of light blue, yellow, red, purple and dark blue dyes in visible band were 667, 422, 510, 535 and 603 nm respectively. According to the comparison between UV-Vis spectra of disperse dyes and that of disperse dyes
and pretreatment agent, there were no significant differences before and after pretreatment.

Figure 4.25 UV-Vis spectrum of light blue dye from Sample 16.

Figure 4.26 UV-Vis spectrum of light blue dye and pre-treatment agent from Sample 16.
Figure 4.27 UV-Vis spectrum of yellow dye from Sample 16.

Figure 4.28 UV-Vis spectrum of yellow dye and pre-treatment agent from Sample 16.
Figure 4.29 UV-Vis spectrum of purple dye from Sample 16.

Figure 4.30 UV-Vis spectrum of purple dye and pre-treatment agent from Sample 16.
Figure 4.31 UV-Vis spectrum of red dye from Sample 16.

Figure 4.32 UV-Vis spectrum of red dye and pre-treatment agent from Sample 16.
Figure 4.33 UV-Vis spectrum of dark blue from Sample 16.

Figure 4.34 UV-Vis spectrum of dark blue dye and pre-treatment agent from Sample 16.
4.5.3 Mass spectra

After obtaining the UV-Vis spectrum of Sample 16, which was used to identify the specific disperse dyes and assess possible changes in molecular structure of dyes, the mass spectra of isolated dyes from Sample 16 were recorded. Ethyl acetate is present in the mass spectra background. The direct injection mass spectra of isolated dyes from Sample 16 were recorded to determine the molecular weight and calculate the possible formula of the specific dye.

In Figure 4.35, peak 447.2930 comes from the light blue dye. The light blue dye has a possible formula of $\text{C}_{20}\text{H}_{45}\text{N}_3\text{NaO}_2\text{S}_2$ with a likelihood match of 88.79%.

Figure 4.35 Mass spectrum of light blue dye extracted from Sample 16.
In Figure 4.36, peak 301.1415 corresponded to the yellow dye, which had 4 possible formulas: $\text{C}_{16}\text{H}_{21}\text{NaO}_4$ with 98.23% match, $\text{C}_{16}\text{H}_{22}\text{O}_4$ with 98.23% match, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{O}_3$ with 97.89% match and $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2$ with a 97.75% match.

![Mass spectrum of yellow dye extracted from Sample 16.](image)

Figure 4.36 Mass spectrum of yellow dye extracted from Sample 16.

In Figure 4.37, the peak 399.2734 is significant in mass spectra, and was obtained from the dark blue dye in Sample 16.
In Figure 4.38, peak 357.2618 corresponded to the red dye, which had 3 possible formulas: $C_{18}H_{37}NaO_5$ with a 96.67% match, $C_{18}H_{38}O_5$ with a 96.97% match and $C_{18}H_{34}N_3O_4$ with a 95.81% match. Peak 399.3086 had 2 possible formulas, which were $C_{12}H_{38}N_{12}OS$ with a 90.11% match and $C_{21}H_{43}NaO_5$ with a 88.55% match.

Figure 4.37 Mass spectrum of dark blue dye extracted from Sample 16.

Figure 4.38 Mass spectrum of red dye extracted from Sample 16.
In Figure 4.39, peak 313.2349 had 4 possible formulas: $\text{C}_{16}\text{H}_{33}\text{NaO}_4$ with a 95.9% match, $\text{C}_{16}\text{H}_{34}\text{O}_4$ with a 95.9% match, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{O}_3$ with a 95.43% match and $\text{C}_{16}\text{H}_{21}\text{NaO}_4$ with a 95.29% match. Peak 691.4192 had one possible formula, $\text{C}_{38}\text{H}_{63}\text{NNaO}_5\text{S}$, with a 88.04% match.

![Mass spectrum of purple dye extracted from Sample 16.](image)

**Figure 4.39** Mass spectrum of purple dye extracted from Sample 16.

### 4.5.4 High-performance liquid chromatography (HPLC) spectra

High-performance liquid chromatography (HPLC) is a useful method to separate dye mixture into individual dyes by their different flow rates in a column, which contains a solid adsorbent material. Each component could be separated and quantified by different flow rates at different velocities in the instrument.
4.5.4.1 HPLC purification and mass spectra of dye mixture

In HPLC purification, the most significant peak (response unit) at special acquisition times could be determined from DAD chromatographs at 254, 410, 540 and 660 nm. According to Figures 4.40-43, there were 5 significant peaks at 2.558, 3.248, 3.58, 4.061 and 5.601 minutes, although TLC analysis of Sample 16 showed that there were 7 dyes on the fabric. It is possible that the concentration of 2 components in the mixture was too low to be detected in the solution applied to the column.

Figure 4.40 DAD chromatograph of Sample 16 at 254 nm.

Figure 4.41 DAD chromatograph of Sample 16 at 410 nm.
After HPLC purification, mass spectra of Sample 16 were extracted at 5 retention times, including 2.558, 3.248, 3.580, 4.061 and 5.601 minutes, which are shown in Figures 4.44-48.
According to mass spectrum at 2.558 minutes (Figure 4.44), the m/z peak at 425 and 447 corresponded to the protonated molecule (M+1) and sodiated molecule (M+Na). The m/z peak at 871 corresponded to the sodiated dimer molecule (2M+Na). So, the molecular weight of this dye was 424, and this component had a λ<sub>max</sub> at 425 nm.

Figure 4.45 Mass spectrum of peak with retention time at 3.248 minutes.

According to mass spectrum at 3.248 minutes (Figure 4.45), the m/z peak at 424 and 446 corresponded to the protonated molecule (M+1) and sodiated molecule (M+Na). The m/z peak at 869 corresponded to the sodiated dimer molecule (2M+Na). So, the molecular weight of this dye was 423, and this component had a λ<sub>max</sub> at 450 nm.
According to mass spectrum at 3.58 minutes (Figure 4.46), the m/z peak at 493 and 515 corresponded to the protonated molecule (M+1) and sodiated molecule (M+Na). The m/z peak at 1007 corresponded to the sodiated dimer molecule (2M+Na). So, the molecular weight of this dye was 492 and this component had a \( \lambda_{\text{max}} \) of 500 nm.

Figure 4.46 Mass spectrum of peak with retention time at 3.58 minutes.

According to mass spectrum at 3.58 minutes (Figure 4.46), the m/z peak at 493 and 515 corresponded to the protonated molecule (M+1) and sodiated molecule (M+Na). The m/z peak at 1007 corresponded to the sodiated dimer molecule (2M+Na). So, the molecular weight of this dye was 492 and this component had a \( \lambda_{\text{max}} \) of 500 nm.

Figure 4.47 Mass spectrum of peak with retention time at 4.061 minutes.
According to mass spectrum at 4.061 minutes (Figure 4.47), the m/z peak at 506 and 528 nm corresponded to the protonated molecule (M+1) and sodiated molecule (M+23). So, the molecular weight of this dye was 505, and this component had a $\lambda_{\text{max}}$ at 500 nm.

![Figure 4.47 Mass spectrum of peak with retention time at 4.061 minutes.](image1)

According to mass spectrum at 5.601 minutes (Figure 4.48), the m/z peak at 486 and 508 corresponded to the protonated molecule (M+1) and sodiated molecule (M+Na). The m/z peak at 993 corresponded to the sodiated dimer molecule (2M+Na). So, the molecular weight of this dye was 485, and this component had a $\lambda_{\text{max}}$ at 600 nm.

![Figure 4.48 Mass spectrum of peak with retention time at 5.601 minutes.](image2)

4.5.4.2 HPLC purification and mass spectra of isolated dyes from Sample 16

After dye extraction and TLC isolation, 5 dyes were collected. HPLC was run to separate the components in the sample. With the help of mass spectrometer after HPLC purification, fragmentation patterns were given to identify mass-to-charge ratio...
and molecular weight of dyes. In the experiments, the mass spectra of yellow, dark blue, purple, light blue and red dyes were analyzed.

**a. HPLC purification of 5 isolated dyes from Sample 16**

![DAD chromatographs of yellow dye at 254, 410, 540 and 660 nm.](image)

Figure 4.49 DAD chromatographs of yellow dye at 254, 410, 540 and 660 nm.

According to DAD chromatographs of yellow dye at the wavelength of 254 and 410 nm in Figure 4.49, there was 1 significant peak at 2.294 minutes.
Figure 4.50 DAD chromatographs of dark blue dye at 254, 410, 540 and 660 nm.

According to DAD chromatographs of dark blue dye at the wavelength of 254 and 540 nm in Figure 4.50, there was 1 peak which was relatively significant.
Figure 4.51 DAD chromatographs of purple dye at 254, 410, 540 and 660 nm.

According to DAD chromatographs of purple dye at the wavelength of 254 and 540 nm in Figure 4.51, there was 1 peak which is relatively significant.

Figure 4.52 DAD chromatographs of light blue dye at 254, 410, 540 and 660 nm.
According to DAD chromatographs of light blue dye at the wavelength of 254 and 660 nm in Figure 4.52, there was 1 peak which was relatively significant.

Figure 4.53 DAD chromatographs of red dye at 254, 410, 540 and 660 nm.

According to DAD chromatographs of red dye at the wavelength of 254 and 660 nm in Figure 4.53, there was 1 peak which was relatively significant.
b. Mass spectra of isolated dyes from Sample 16 after HPLC purification

According to mass spectra of yellow dye with the retention time at 2.294 minutes (Figure 4.54), the m/z peak at 425 and 447 corresponded to the protonated molecule (M+1) and sodiated molecule (M+Na). The m/z peak at 871 corresponded to the sodiated dimer molecule (2M+Na). So, the molecular weight of this dye was 424. Combined with the HPLC of dye mixture of Sample 16, yellow dye was the component which was first detected in dye mixture of Sample 16 shown in Figure 4.44. Furthermore, combined with possible formula and properties, the yellow dye was C.I. Disperse Yellow 114. 
According to mass spectra of dark blue dye with the retention time at 5.735 minutes (Figure 4.55), the m/z peak at 486 corresponded to the protonated molecule (M+1). The m/z peak at 993 corresponded to the sodiated dimer molecule (2M+Na). So, the molecular weight of this dye was 485. Dark blue dye was the fifth component detected in the dye mixture of Sample 16 shown in Figure 4.48.

Figure 4.56 Mass spectrum of purple dye at 3.741 minutes.
According to mass spectra of purple dye with the retention time at 3.741 minutes (Figure 4.56), the m/z peak at 493 and 515 corresponded to the protonated molecule (M+1) and sodiated molecule (M+Na). The m/z peak at 1007 corresponded to the sodiated dimer molecule (2M+Na). So, the molecular weight of this dye was 492. Purple dye was the third component detected in the dye mixture of Sample 16 shown in Figure 4.46.

![Mass spectrum of light blue dye at 3.648 minutes.](image)

Figure 4.57 Mass spectrum of light blue dye at 3.648 minutes.

According to mass spectra of light blue dye with the retention time at 3.648 minutes (Figure 4.57), the m/z peak at 380 corresponded to the protonated molecule (M+1). The m/z peak at 781 corresponded to the sodiated dimer molecule (2M+Na). So, the molecular weight of light blue dye was 379.
Figure 4.58 Mass spectrum of red dye at 0.322 minutes.

According to mass spectrum of red dye with the retention time at 3.648 minutes (Figure 4.58), the m/z peak at 506 corresponded to the protonated molecule (M+1). The m/z peak at 528 corresponded to the sodiated molecule (M+Na). So, the molecular weight of this dye was 505. Red dye was the fourth component detected in the dye mixture of Sample 16, shown in Figure 4.47. Furthermore, combined with possible formula and properties, the yellow dye was C.I. Disperse Red 167:1.

Compared with direct-injection mass spectra, HPLC purification and mass spectra were very useful. The molecular weights of isolated dyes were determined successfully, but this method did not result in the analysis of all 7 samples from the dye mixture of Sample 16, and therefore has limitations.

4.6 Analysis of commercial disperse dyes with pretreatment agent

In this component of the study, some commercial disperse dyes from different families were selected to substitute the disperse dyes on the samples. Four anthraquinone dyes (Disperse Blue 60, Blue 56, Red 60 and Red 91), three azo
Disperse dyes (Disperse Orange 30, Red 167:1 and Blue 79) and two other disperse
dyes (Disperse Yellow 42 and Disperse Yellow 54) were used. Acetone, ethyl
acetate, acetonitrile and chlorobenzene were used as solvents to dissolve the nine
disperse dyes.

Dye solutions were divided between two test tubes with the same volume, 5
mL, and 10 drops of pretreatment agent was added into one of two test tubes and
mixed well. Then, the tubes were sealed. Relatively clear dye solutions were
collected after stratification.

The dye solutions with and without pretreatment agent were analyzed using a
Cary 300 UV-VIS Spectrophotometer. In Figures 4.59-61, the UV-Vis spectra of the
mixture of acetone and pretreatment agent, dye solution and dye solution with
pretreatment agent are shown. According to Figure 4.59, the mixture of acetone and
pretreatment agent had $\lambda_{\text{max}}$ at 344 nm. While the spectrum had noise it showed
quite low absorption at 250-310 nm. The spectral curve increased rapidly at 310-344
nm, and decreased slowly in 344-800 nm. The UV-Vis spectra of dye solution with or
without pretreatment agent were analyzed. The spectra had peaks at 585 and 626
nm, but the UV-Vis of dye solution with pretreatment had higher intensity at 310-338
nm.
Figure 4.59 UV-Vis spectrum of acetone and pre-treatment agent.

Figure 4.60 UV-Vis spectrum of Disperse Blue 56 in acetone.
In Figures 4.62-64, the UV-Vis spectra of the mixture of ethyl acetate and pretreatment agent, dye solution and dye solution with pretreatment agent are shown. According to Figure 4.59, the mixture of ethyl acetate and pretreatment agent had $\lambda_{\text{max}}$ at 279 nm. The absorption peak intensity was low, but it was without the noise seen when using acetone as solvent. The UV-Vis spectra of dye solution with or without pretreatment agent had peaks at 584 and 626 nm, but the UV-Vis of dye solution with pretreatment also had a relatively high absorption in 250-350 nm. This was attributed to a solvent pretreatment interaction.
Figure 4.62 UV-Vis spectrum of ethyl acetate and pre-treatment agent.

Figure 4.63 UV-Vis spectrum of Disperse Blue 56 in ethyl acetate.
Figure 4.64 UV-Vis spectrum of Disperse Blue 56 in ethyl acetate and pre-treatment agent.

In Figures 4.65-67, the UV-Vis spectra of the mixture of acetonitrile (ACN) and pretreatment agent, dye solution and dye solution with pretreatment agent are shown. According to Figure 4.65, the mixture of ACN and pretreatment agent had $\lambda_{\text{max}}$ at 272 nm. The curve decreased with increasing wavelength. The UV-Vis spectra of dye solution with and without pretreatment agent had peaks at 580 and 620 nm, but the UV-Vis spectrum of dye solution with pretreatment agent had a relatively high absorption at 250-300 nm range, and the curve was similar to the mixture of solvent and pretreatment agent.
Figure 4.65 UV-Vis spectrum of acetonitrile (ACN) and pre-treatment agent.

Figure 4.66 UV-Vis spectrum of Disperse Blue 56 with ACN.
In Figures 4.68-70, the UV-Vis of the mixture of chlorobenzene and pretreatment agent, dye solution and dye solution with pretreatment agent are shown. According to Figure 4.68, the mixture of ACN and pretreatment agent had \( \lambda_{\text{max}} \) at 288 nm and had significant noise. The curve slowly increased with increasing wavelength in the 288-800 nm range. The UV-Vis spectra of dye solution with and without pretreatment agent had peaks at 580 and 624 nm, and did not show a significant difference.
Figure 4.68 UV-Vis spectrum of chlorobenzene and pre-treatment agent.

Figure 4.69 UV-Vis spectrum of Disperse Blue 56 with chlorobenzene.
Figure 4.70 UV-Vis spectrum of Disperse Blue 56 with chlorobenzene and pretreatment agent.

According to the UV-Vis spectra of commercial dyes in several families, the pretreatment agent had no significant influence on these dyes.

4.7 SEM analysis

The surface properties of untreated and pretreated PET fabric samples were analyzed using scanning electron microscopy (SEM). Samples 10, 10+, which are white samples, and Samples 16, 16+, which are black samples, were taken as representative examples. According to Figure 4.71 and Figure 4.72, the fibers of untreated PET fabrics had a relatively smooth surface, but that of the pretreated PET fabrics had many undulations on the surface and showed a heavy coating. The
comparison of SEM images between Samples 10 and 16 showed that the presence of dye did not change the nature of the fiber-pretreatment interaction. This would influence the light absorption and contribute to a shift in color.

![SEM images of (a) Sample 10 and (b) Sample 10+ at 1000 times magnification.](image)

**Figure 4.71** SEM images of (a) Sample 10 and (b) Sample 10+ at 1000 times magnification.

![SEM images of (a) Sample 16 and (b) Sample 16+ at 1000 times magnification.](image)

**Figure 4.72** SEM images of (a) Sample 16 and (b) Sample 16+ at 1000 times magnification.
5. Conclusions

The results of this study indicate that a standard color measurement tool can be used to establish color differences between PET fabrics before and after pretreatment for ink-jet printing. Further, thin layer chromatography (TLC) and UV-Vis spectroscopy of dye extracts from the same fabric pairs can be used to determine whether the color differences are due to chemical interactions.

The results of this study indicated that black, dark blue, and certain red fabrics were more susceptible to color shifts following the pretreatment. Interestingly, while such fabrics often contained multiple dye components, none proved more sensitive than another to the pretreatment agent. In a separate set of experiments, it was also shown that no specific dye chromophore (azo, anthraquinone, nitrodiphenylamine, etc.) within the disperse dye family stood out as the cause of the observed color changes. These results suggest that the lack of the pretreatment agent to disperse dyes that are locked inside the fibers was not the reason for the TLC results from extracts obtained before and after fabric pretreatments.

It was also found that a combination of chromatography and high resolution mass spectrometry can be used to establish the identity of the components in a complex mixture, as demonstrated by the isolation and characterization of the 5 dyes in a black fabric, two of which were identified as C.I. Disperse Red 167:1 and C.I. Disperse Yellow 114.

SEM analysis showed differences between the surface properties of untreated and pretreated PET fabrics. The results suggest that the surface of
pretreated PET fibers had a heavy white coating that influenced light absorption and reflection, leading to the color shift.
References


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APPENDIX

Appendix A

L*a*b* values of 44 pairs of PET samples.

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Continued.

| 44+ | 22.76 | 0.28 | -1.34 |
Appendix B

Mass spectrum of Sample 5, 5+, 6 and 6+.

Figure 1. Mass spectrum of Sample 6 in positive ESI.

Figure 2. Mass spectrum of Sample 6+ in positive ESI.
Figure 3. Mass spectrum of Sample 6 in negative ESI.

Figure 4. Mass spectrum of Sample 6+ in negative ESI.
Figure 5. Mass spectrum of Sample 8 in positive ESI.

Figure 6. Mass spectrum of Sample 8+ in positive ESI.
Figure 7. Mass spectrum of Sample 8 in negative ESI.

Figure 8. Mass spectrum of Sample 8+ in negative ESI.
Appendix C

UV-Vis spectra of all selected commercial disperse dyes and organic solvents

1. Disperse Red 167:1

Figure 1. UV-Vis of Disperse Red 167:1 with ethyl acetate.

Figure 2. UV-Vis of Disperse Red 167:1 with ethyl acetate and pre-treatment agent.
2. Disperse Red 91
Figure 5. UV-Vis of Disperse Red 91 with ethyl acetate.

Figure 6. UV-Vis of Disperse Red 91 with ethyl acetate and pre-treatment agent.
Figure 7. UV-Vis of Disperse Red 91 with acetonitrile.

Figure 8. UV-Vis of Disperse Red 91 with acetonitrile and pre-treatment agent.
3. Disperse Red 60

Figure 9. UV-Vis of Disperse Red 60 with ethyl acetate.

Figure 10. UV-Vis of Disperse Red 60 with ethyl acetate and pre-treatment agent.
4. Disperse Blue 60

![Figure 11. UV-Vis of Disperse Blue 60 with ethyl acetate.](image1)

![Figure 12. UV-Vis of Disperse Blue 60 with ethyl acetate and pre-treatment agent.](image2)
Figure 13. UV-Vis of Disperse Blue 60 with ACN.

Figure 14. UV-Vis of Disperse Blue 60 with ACN and pre-treatment agent.
5. Disperse Blue 79

Figure 15. UV-Vis of Disperse Blue 79 with ethyl acetate.

Figure 16. UV-Vis of Disperse Blue 79 with ethyl acetate and pre-treatment agent.
Figure 17. UV-Vis of Disperse Blue 79 with ACN.

Figure 18. UV-Vis of Disperse Blue 79 with ACN and pre-treatment agent.
6. Disperse Yellow 42

Figure 19. UV-Vis of Disperse Yellow 42 with ethyl acetate.

Figure 20. UV-Vis of Disperse Yellow 42 with ethyl acetate and pre-treatment agent.
Figure 21. UV-Vis of Disperse Yellow 42 with ACN.

Figure 22. UV-Vis of Disperse Yellow 42 with ACN and pre-treatment agent.
7. Disperse Yellow 54

Figure 23. UV-Vis of Disperse Yellow 54 with ethyl acetate.

Figure 24. UV-Vis of Disperse Yellow 54 with ethyl acetate and pre-treatment agent.
Figure 25. UV-Vis of Disperse Yellow 54 with ACN.

Figure 26. UV-Vis of Disperse Yellow 54 with ACN and pre-treatment agent.
8. Disperse Yellow 86

Figure 27. UV-Vis of Disperse Yellow 86 with ethyl acetate.

Figure 28. UV-Vis of Disperse Yellow 86 with ethyl acetate and pre-treatment agent.
9. Disperse Orange 30

Figure 29. UV-Vis of Disperse Orange 30 with acetone.

Figure 30. UV-Vis of Disperse Orange 30 with acetone and pre-treatment agent.
Figure 31. UV-Vis of Disperse Orange 30 with ethyl acetate.

Figure 32. UV-Vis of Disperse Orange 30 with ethyl acetate and pre-treatment agent.
Figure 33. UV-Vis of Disperse Orange 30 with ACN.

Figure 34. UV-Vis of Disperse Orange 30 with ACN and pre-treatment agent.