Plasma-based surface modifications of polyester fabrics and their interaction with cationic polyelectrolytes and anionic dyes

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Abstract

Salem, Tarek

“Plasma-based surface modifications of polyester fabrics and their interaction with cationic polyelectrolytes and anionic dyes”

Plasma-based surface modifications offer many interesting possibilities for the production of high value-added polymeric materials. In this work, different plasma-based synthetic concepts were employed to endow poly(ethylene terephthalate) (PET) fabrics with accessible amine functionalities. These concepts were compared to find out the appropriate engineering methods, which can be further accepted by textile industries to overcome the limited reactivity of PET fabric surfaces, while the bulk characteristics are kept unaffected.

Amine functionalities were introduced onto the surface of PET fabrics using either low-pressure ammonia plasma treatment or coating oxygen plasma-treated PET fabric with cationic polyelectrolytes. Two different cationic polyelectrolytes were used in this study namely poly(diallyldimethylammonium chloride) as an example of strong polyelectrolytes and poly(vinyl amine-co-vinyl amide) as an example of weak polyelectrolytes. The modified surfaces were characterized by a combination of various surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS), electrokinetic measurements and time-dependent contact angle measurements. Furthermore, the amine functionalities introduced by different surface modifications were used for the subsequent immobilization of various classes of anionic dyes to evaluate the efficiency of different surface modifications. Color strength (K/S) and fastness measurements of colored fabrics were also explored. Their results can be taken as a measure of the extent of the interaction between different modified surfaces and anionic dyes.

Finally, it was demonstrated that anchoring poly(vinyl amine-co-vinyl amide) layer onto PET fabric surfaces modified with low-pressure oxygen plasma is an efficient approach to improve coloration behavior and to overcome different problems related to PET fabrics coloration, such as coloration of PET/wool blend fabric with a single class of dyes. This is a crucial step towards the substrate independent surface coloration, which becomes dependent on the properties of the top layer rather than chemical structure of the fibers.

Keywords

Plasma treatment, poly(ethylene terephthalate) (PET), adhesion, polyelectrolytes, poly(vinyl amine-co-vinyl amide) (PVAm), XPS, zeta-potential, metachromacy and anionic dyes.
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# Table of Contents

1 Introduction

1.1 Overview and motivation

1.2 Objective and synthetic concepts

2 Theoretical Background

2.1 Textile fibers

2.2 PET fibers: production and applications

2.2.1 PET/wool blend fabrics

2.2.2 Coloration of PET fabrics

2.3 Anionic dyes

2.3.1 Acid dyes

2.3.2 Reactive dyes

2.3.3 Direct dyes

2.3.4 Printing textile fabrics with anionic dyes

2.4 Plasma surface modification of textiles

2.4.1 Nature of plasma

2.4.2 Plasma-based modification methods of textiles

2.4.2.1 Simple plasma treatment of textile surfaces

2.4.2.2 Adsorption of polyelectrolytes on plasma treated textile surfaces

2.5 Use of polyelectrolytes in textile applications

2.5.1 Polyelectrolyte classifications

2.5.2 Poly(diallyldimethylammonium chloride) (PDADMAC)

2.5.3 Poly(vinyl amine-co-vinyl amide) (PVAm)

2.5.4 Polyelectrolyte/dye interactions

3 Experimental Part

3.1 Materials

3.1.1 PET fabric

3.1.2 PET/wool blend fabric

3.1.3 PET film

3.1.4 Plasma gases
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1.5</td>
<td>Polyelectrolytes</td>
<td>28</td>
</tr>
<tr>
<td>3.1.6</td>
<td>Dyestuffs and auxiliaries of printing pastes</td>
<td>29</td>
</tr>
<tr>
<td>3.1.7</td>
<td>Solvent and other chemicals</td>
<td>30</td>
</tr>
<tr>
<td>3.2</td>
<td><strong>Surface modification methods of PET fabrics</strong></td>
<td>30</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Ammonia plasma treatment</td>
<td>30</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Oxygen plasma treatment</td>
<td>31</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Coating of oxygen plasma-treated PET fabrics with cationic polyelectrolytes</td>
<td>31</td>
</tr>
<tr>
<td>3.3</td>
<td><strong>Characterization methods</strong></td>
<td>31</td>
</tr>
<tr>
<td>3.3.1</td>
<td>X-ray photoelectron spectroscopy (XPS)</td>
<td>31</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Electrokinetic measurements</td>
<td>33</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Kinetics measurements of wetting</td>
<td>35</td>
</tr>
<tr>
<td>3.3.4</td>
<td>ATR- FTIR spectroscopy</td>
<td>35</td>
</tr>
<tr>
<td>3.3.5</td>
<td>Differential scanning calorimetry measurements (DSC)</td>
<td>36</td>
</tr>
<tr>
<td>3.3.6</td>
<td>Atomic force microscopy (AFM)</td>
<td>37</td>
</tr>
<tr>
<td>3.3.7</td>
<td>Scanning electron microscopy (SEM)</td>
<td>38</td>
</tr>
<tr>
<td>3.4</td>
<td><strong>Coloration of PET fabrics by printing</strong></td>
<td>38</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Preparation of printing pastes</td>
<td>38</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Printing and post-treatment methods</td>
<td>39</td>
</tr>
<tr>
<td>3.5</td>
<td><strong>Characterization methods of printed PET fabrics</strong></td>
<td>39</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Color strength measurements of printed fabrics</td>
<td>39</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Color fastness of printed fabrics</td>
<td>40</td>
</tr>
<tr>
<td>3.5.2.1</td>
<td>Color fastness to washing</td>
<td>40</td>
</tr>
<tr>
<td>3.5.2.2</td>
<td>Color fastness to rubbing</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td><strong>Results and Discussion</strong></td>
<td>41</td>
</tr>
<tr>
<td>4.1</td>
<td><strong>Low-pressure ammonia plasma treatment</strong></td>
<td>41</td>
</tr>
<tr>
<td>4.1.1</td>
<td>XPS characterization</td>
<td>42</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Electrokinetic measurements</td>
<td>47</td>
</tr>
<tr>
<td>4.1.3</td>
<td>Surface morphology</td>
<td>49</td>
</tr>
<tr>
<td>4.1.4</td>
<td>Kinetics measurements of wetting</td>
<td>49</td>
</tr>
<tr>
<td>4.1.5</td>
<td>Stability of the ammonia plasma-treated PET fabric</td>
<td>52</td>
</tr>
<tr>
<td>4.1.6</td>
<td>Determination of the degree of crystallinity by DSC</td>
<td>54</td>
</tr>
<tr>
<td>4.2</td>
<td><strong>Surface functionalization of PET fabric with cationic polyelectrolytes</strong></td>
<td>55</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Low-pressure oxygen plasma treatment</td>
<td>55</td>
</tr>
<tr>
<td>4.2.1.1</td>
<td>XPS characterization</td>
<td>57</td>
</tr>
<tr>
<td>4.2.1.2</td>
<td>Electrokinetic measurements</td>
<td>58</td>
</tr>
<tr>
<td>4.2.1.3</td>
<td>Surface morphology</td>
<td>60</td>
</tr>
</tbody>
</table>
Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.1.4 Kinetics measurements of wetting</td>
<td>60</td>
</tr>
<tr>
<td>4.2.1.5 Stability of the oxygen plasma-treated PET fabric</td>
<td>62</td>
</tr>
<tr>
<td>4.2.1.6 Determination of the degree of the crystallinity by DSC</td>
<td>64</td>
</tr>
<tr>
<td>4.2.2 Coating of oxygen plasma-treated PET fabric with cationic polyelectrolytes</td>
<td>65</td>
</tr>
<tr>
<td>4.2.2.1 XPS characterization</td>
<td>66</td>
</tr>
<tr>
<td>4.2.2.2 ATR-FTIR spectroscopy</td>
<td>71</td>
</tr>
<tr>
<td>4.2.2.3 Electrokinetic measurements</td>
<td>72</td>
</tr>
<tr>
<td>4.2.2.4 Surface morphology</td>
<td>75</td>
</tr>
<tr>
<td>4.2.2.5 Kinetics measurements of wetting</td>
<td>76</td>
</tr>
<tr>
<td>4.3 Surface activity of modified PET fabrics towards anionic dyes</td>
<td>79</td>
</tr>
<tr>
<td>4.3.1 Anionic acid dyes</td>
<td>79</td>
</tr>
<tr>
<td>4.3.2 Anionic reactive dyes</td>
<td>82</td>
</tr>
<tr>
<td>4.3.3 Fastness properties of colored PET fabrics</td>
<td>87</td>
</tr>
<tr>
<td>4.4 Surface functionalization of PET/wool blend fabric with PVAm</td>
<td>90</td>
</tr>
<tr>
<td>4.4.1 XPS characterization</td>
<td>90</td>
</tr>
<tr>
<td>4.4.2 Electrokinetic measurements</td>
<td>92</td>
</tr>
<tr>
<td>4.4.3 Kinetics measurements of wetting</td>
<td>93</td>
</tr>
<tr>
<td>4.4.4 Surface morphology</td>
<td>94</td>
</tr>
<tr>
<td>4.4.5 Evaluation of PVAm coating stability</td>
<td>96</td>
</tr>
<tr>
<td>4.4.6 Printing properties of PET/wool blend fabric</td>
<td>97</td>
</tr>
<tr>
<td>4.4.7 Fastness properties of colored PET/wool blend fabric.</td>
<td>98</td>
</tr>
<tr>
<td>5 Summary and Outlook</td>
<td>100</td>
</tr>
<tr>
<td>6 References</td>
<td>104</td>
</tr>
<tr>
<td>7 Selbändigkeitserklärung</td>
<td>116</td>
</tr>
<tr>
<td>8 Curriculum Vitae</td>
<td>117</td>
</tr>
<tr>
<td>Publications from this work</td>
<td>118</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1.1 Global apparel fiber market trends from 1980 to 2010 ........................................ 2
Figure 1.2 Step-wise mechanism of the aminolysis reaction of PET..................................... 3
Figure 1.3 Schematic representation of the different synthetic routes investigated in the present work for introduction amine-containing groups onto PET fabric surfaces... 5
Figure 2.1 Classification of textile fibers according to their origin........................................ 6
Figure 2.2 End uses of PET fibers......................................................................................... 7
Figure 2.3 PET fiber production output.................................................................................. 8
Figure 2.4 Textile dye classes global market share............................................................... 11
Figure 2.5 The chemical structure of C.I. Acid yellow 69.................................................... 12
Figure 2.6 Schematic representation of acid dye fixation on fibers by ionic bond................. 12
Figure 2.7 The reaction mechanism of cellulose anion with MCT type reactive dye.... .... 13
Figure 2.8 The reaction mechanism of cellulose anion with VS type reactive dye............. 13
Figure 2.9 The chemical structure of C.I. Direct Yellow 4.................................................... 14
Figure 2.10 Schematic representation of different synthetic approaches used for surface functionalization of textiles based on low-pressure plasma treatment............ 18
Figure 2.11 Schematic representation of plasma effects on a polymer surface.................... 19
Figure 2.12 Classification scheme of polyelectrolytes......................................................... 21
Figure 2.13 Cyclopolymerization of DADMAC and structures of resulting polymers. ...... 22
Figure 2.14 Protonation/deprotonation equilibrium of PVAm............................................ 23
Figure 2.15 Enamine-Imine tautomerism in vinyl amine...................................................... 24
Figure 2.16 Synthesis of PVAm from hydrolysis of PVFA................................................... 24
Figure 2.17 Chemical structure of poly(vinyl amine-co-vinyl amide) copolymer................. 25
Figure 2.18 An amino and formamide groups formed an amidine group.......................... 25
Figure 2.19 Molecular arrangements in J- (a) and H-aggregates (b)................................... 26
Figure 3.1 Chemical structures of the polyelectrolytes used to modify PET fabric surface.................................................................................................................. 28
Figure 3.2 Schematic representation of chemical labeling of primary amino group by TFBA ............................................................................................................................................. 33
Figure 3.3 Schematic representation of the electrochemical double layer at the interface according to the Gouy-Chapman-Stern-Grahame (GCSG) model............................ 34
Figure 3.4 Schematic representation of streaming measuring cell for fabrics.................. 34
Figure 4.1 Possible surface functionalization reactions on PET fabric using ammonia plasma........................................................................................................................................ 42
Figure 4.2 Wide-scan XPS spectra of the unmodified PET fabric (a) and ammonia plasma-treated (600 s) PET fabric (b). The peaks are assigned to the corresponding chemical elements................................................................. 43
Figure 4.3 High-resolution C 1s XPS spectra of the unmodified PET fabric (a) and ammonia plasma-treated (600 s) PET fabric (b).............................................................................. 45
Figure 4.4 Atomic percent of the total nitrogen and fraction of –NH₂ groups that able to react with TFBA after ammonia plasma treatments as determined by XPS and TFBA labeling. ...................................................................................... 46
Figure 4.5 High-resolution N 1s XPS spectrum of ammonia plasma-treated (600 s) PET fabric. ........................................... ................................................... ............................. 47

Figure 4.6 $\zeta$-pH dependence for the unmodified PET fabric and ammonia plasma-treated PET fabric at different treatment time. ................................................... 48

Figure 4.7 Three-dimensional AFM images of PET fibers showing surface roughness of the unmodified PET fiber (a) and the ammonia plasma-treated (600 s) PET fiber (b). ........................................... ................................................... ............................. 49

Figure 4.8 Contact angles of water droplets in dependence on resting time on the unmodified PET fabric and ammonia plasma-treated PET fabric at different treatment time. The error of each measurement is $\pm 2^\circ$. ................................................... ............................. 50

Figure 4.9 Image sequences of water droplet applying to the unmodified PET fabric surface (a) and the ammonia plasma-treated PET fabric surface (b). .......... 51

Figure 4.10 The [N]:[C] atomic ratio of ammonia plasma-treated (600 s) PET fabric as a function of the ageing time in the air under ambient conditions. ......................... 52

Figure 4.11 Effect of ageing time on the contact angles of water droplets in dependence on resting time on the ammonia plasma-treated (600 s) PET fabric. The error of each measurement is $\pm 2^\circ$. ................................................... ............................. 53

Figure 4.12 DSC thermograms of the unmodified and ammonia plasma-treated PET fabrics 2nd heating run (a), and the effect of plasma treatment time on percent of crystallinity for different PET fabrics (b). ................................. 54

Figure 4.13 Possible surface functionalization reactions on PET fabric using oxygen plasma. ........................................... ................................................... ............................. 56

Figure 4.14 High-resolution C 1s XPS spectra of (a) unmodified PET fabric and (b) oxygen plasma-treated (600 W, 15 s) PET fabric................................................... 58

Figure 4.15 $\zeta$-pH dependence for the unmodified PET fabric and oxygen plasma-treated PET fabric at different treatment power for 15 s (a) and $\leq 30$ s (b). ........ 59

Figure 4.16 Three-dimensional AFM images of single PET fiber showing surface roughness of unmodified PET (a) and oxygen plasma-treated (600 W, 15 s) PET fabric (b). ........................................................................................................ 60

Figure 4.17 Contact angles of water droplets in dependence on resting time on the unmodified PET fabric and the oxygen plasma-treated PET fabric at different treatment power for 15 s (a) and $\leq 30$ s (b). The error of each measurement is $\pm 2^\circ$. ........................................................................................................ 61

Figure 4.18 High-speed image sequences at different resting time for water droplet applying to oxygen plasma-treated (600 W, 15 s) PET fabric................................................... 62

Figure 4.19 The [O]:[C] atomic ratio for oxygen plasma-treated (600 W for 15 s) PET fabric as function of the ageing time in air under ambient conditions. ......................... 62

Figure 4.20 Effect of ageing times on the contact angles of water droplets in dependence on resting time on oxygen plasma-treated (600 W, 15 s) PET fabric surface. The error of each measurement is $\pm 2^\circ$. ........................................................................................................ 64

Figure 4.21 DSC thermograms of the unmodified and oxygen plasma-treated PET fabrics 2nd heating run (a), and the effect of plasma treatment conditions on percent of crystallinity for different PET fabrics (b). ................................. 65
Figure 4.22 Wide-scan XPS spectra of the unmodified PET fabric (a), oxygen plasma-treated (600 W, 15 s) (b), PDADMAC-treated PET obtained with $C_{PDADMAC} = 3$ wt. % (c) and PVAm-treated PET obtained with $C_{PVAm} = 3$ wt. % (d). The intensity of all spectra were related to the O 1s peak. ........................................ 67

Figure 4.23 Schematic representation of counterion effect on the adsorption of PDADMAC at the oxygen plasma-treated PET fabric................................. 69

Figure 4.24 Schematic representation of heat-induced cross-linking reaction............. 69

Figure 4.25 High-resolution C 1s XPS spectra of the unmodified PET fabric (a), the oxygen plasma-treated (600 W, 15 s) PET fabric (b), PDADMAC-treated PET fabric obtained with $C_{PDADMAC} = 3$ wt. % (c), and PVAm-treated PET fabric obtained with $C_{PVAm} = 3$ wt. %......................................................... 70

Figure 4.26 High-resolution N 1s XPS spectrum of PDADMAC-treated PET fabric obtained with $C_{PDADMAC} = 3$ wt. % (a), and PVAm-treated PET fabric obtained with $C_{PVAm} = 3$ wt. % (b). .......................................................... 71

Figure 4.27 ATR-FTIR spectra of the unmodified PET fabric (a), the oxygen plasma-treated (600 W and 15 s) PET fabric (b), PVAm-treated PET before (c) and after heat treatment at 120 °C (d). The spectra have been shifted vertically for clarity. . 72

Figure 4.28 $\zeta$-pH dependence for the unmodified PET fabric, the oxygen plasma-modified (600 W, 15 s) PET fabric and PDADMAC-treated PET fabrics obtained with different concentrations of PDADMAC.............................. 73

Figure 4.29 $\zeta$-pH dependence for the unmodified PET fabric, the oxygen plasma-treated (600 W, 15 s) PET fabric and PVAm-treated PET fabrics obtained with different concentrations of PVAm........................................ 74

Figure 4.30 SEM images of the unmodified PET fabric (a), oxygen plasma-treated (600 W, 15 s) PET fabric (b), PDADMAC-treated PET fabric obtained with a $C_{PDADMAC} = 3$ wt. % after rinsing (c) and PVAm-treated PET obtained with a $C_{PVAm} = 3$ wt. % after rinsing (d).................................................................................. 76

Figure 4.31 Contact angles of water droplets in dependence on resting time on the unmodified PET fabric, oxygen plasma-treated (600 W, 15 s) PET and plasma modified-PET coated with PDADMAC and PVAm obtained with 3 wt. % of polyelectrolyte. The error of each measurement is ± 2°................................. 77

Figure 4.32 Chemical structures of the anionic acid dyes used in this work as an example for PET fabrics coloration......................................................... 79

Figure 4.33 K/S absorption spectra of different PET fabrics printed with C.I. Acid Red 18 after ammonia plasma treatment (a), PDADMAC coating (c), PVAm coating (e), and printed with C.I. Acid Blue 80 after ammonia plasma treatment (b), PDADMA coating (d) PVAm coating (f).................................................................................. 80

Figure 4.34 The binding mechanism of acid dye with modified PET fabric surface........ 81

Figure 4.35 Chemical structures of anionic reactive dyes used in this work to color ammonia plasma-treated and polyelectrolyte-modified PET fabrics. Dyes C.I. Reactive Violet 2 and C.I. Reactive Blue 5 are typical MCT dyes, while C.I. Reactive Violet 5 and C.I. Reactive Black 5 are VS dyes. .................................................. 83
Figure 4.36 K/S absorption spectra of ammonia plasma modified PET printed with C.I. Reactive Blue 5 (a) and with C.I. Reactive Violet 2 (b). K/S absorption spectra of PVAm-treated PET printed with C.I. Reactive Blue 5 (c), C.I. Reactive Violet 2 (d), C.I. Reactive Violet 5 (e) and C.I. Reactive Black 5 (f). ........................................ 84

Figure 4.37 Schematic representation of the binding mechanism of (a) MCT dyes and (b) VS dyes with modified PET fabric surfaces containing –NH₂ groups. .............. 85

Figure 4.38 ζ-pH dependence for the unmodified PET/wool fabric, oxygen plasma-modified (600 W, 15s) PET/wool fabric and PVAm-treated PET/wool fabric obtained with CₚᵥAm = 3 wt. %. .................................................................................. 93

Figure 4.39 Contact angles of water droplets in dependence on resting time on the unmodified PET/wool fabric and oxygen plasma-treated (600 W, 15 s) PET/wool fabric. The error of each measurement is ± 2°. ........................................ 94

Figure 4.40 SEM images of PET/wool fabrics: (a) the unmodified (1000X), (b) the unmodified (5000X), (C) unmodified PET component (50000X), (d) unmodified wool component (50000X), (e) oxygen plasma-treated (600 W, 15 s) PET component, (f) oxygen plasma-treated (600 W, 15 s) wool component, (g) PVAm-treated PET component, and (h) PVAm-treated wool component......... 95

Figure 4.40 (Continued.) ........................................................................................................ 96

Figure 4.41 K/S absorption spectra of the unmodified PET/wool fabric and PVAm-treated PET/wool obtained with CₚᵥAm = 3 wt. % printed with C.I. Acid Red 18 (a) and C.I. Acid Blue 80 (b) ........................................................... 97

Figure 4.42 Digital photos of the unmodified PET/wool blend fabric and PVAm-treated PET/wool blend fabric printed with C.I. Acid Red 18 (a), C.I. Acid Blue 80 (b)... 98
List of Tables

Table 2.1 Plasma gases and their applications .......................................................... 18
Table 3.1 Polyelectrolytes used to modify PET fabric surfaces ................................ 28
Table 3.2 Dyestuffs used in this study ....................................................................... 29
Table 3.3 Auxiliaries used in print pastes in this study .............................................. 29
Table 3.4 Other chemicals used in this study ............................................................ 30
Table 4.1 The elemental surface composition and atomic ratios determined by XPS for the unmodified and ammonia plasma-treated PET fabrics for the indicated treatment time ................................................................. 43
Table 4.2 The elemental surface composition and elemental ratio determined by the XPS for the unmodified and oxygen plasma-treated PET fabrics under different operating conditions. The unmodified PET indicated by plasma power = 0 and modification time = 0 ........................................................................................................ 57
Table 4.3 The elemental surface composition and elemental ratios determined by XPS for the unmodified, oxygen plasma-, PDADMAC- and PVAm- treated PET fabrics ................................................................. 68
Table 4.4 UV/Vis absorption maxima $\lambda_{\text{max}}$ of anionic dyes in aqueous solution and on modified PET fabrics with different cationic polyelectrolytes .......................................................... 86
Table 4.5 Color fastness properties of different modified PET fabrics printed with C.I. Acid Red 18 and C.I. Acid Blue 80 ................................................................. 87
Table 4.6 The effect of rinsing on [N]:[C] atomic ratio determined by XPS. The unmodified and different modified PET fabric surfaces with PDADMAC or PVAm rinsed at 40 °C, pH 10 for 30 min ........................................................................... 88
Table 4.7 Color fastness properties of PVAm-treated PET fabrics printed with different reactive dyes .......................................................................................................................... 89
Table 4.8 The surface elemental composition and elemental ratios determined by XPS for the unmodified PET/wool fabric, oxygen plasma-treated (600 W, 15 s) PET/wool, fabric and PVAm-treated PET/wool fabric obtained with $C_{\text{PVAm}}$ = 3 wt. % ......................................................................................................................... 91
Table 4.9 The effect of washing on the [N]:[C] elemental ratio determined by XPS. ..... 96
Table 4.10 Color fastness properties of PVAm-treated PET/wool blend fabric printed with C.I. Acid Red 18 and C.I. Acid Blue 80 .................................................................................. 99
List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
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<td>Allyldimethylamine</td>
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<td>Atomic force microscopy</td>
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<tr>
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</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
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<tr>
<td>BHET</td>
<td>Bis(2-hydroxyethyl)terephthalate</td>
</tr>
<tr>
<td>C.I.</td>
<td>Color index</td>
</tr>
<tr>
<td>Co.</td>
<td>Company</td>
</tr>
<tr>
<td>Con.</td>
<td>Concentration</td>
</tr>
<tr>
<td>$C_{PDADMAC}$</td>
<td>PDADMAC concentration</td>
</tr>
<tr>
<td>$C_{PVAm}$</td>
<td>PVAm concentration</td>
</tr>
<tr>
<td>DADMAC</td>
<td>Diallyldimethylammonium chloride</td>
</tr>
<tr>
<td>DAMA</td>
<td>Diallylmethylamine</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DMT</td>
<td>Dimethyl terephthalate</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry measurements</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
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<td>ESCA</td>
<td>Electron spectroscopy for chemical analysis</td>
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<tr>
<td>FDA</td>
<td>Food and drug administration</td>
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<td>eV</td>
<td>Electron volt</td>
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<tr>
<td>GCSG</td>
<td>Gouy–Chapman–Stern–Grahame model</td>
</tr>
<tr>
<td>GHz</td>
<td>Gigahertz</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
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<td>High-technology</td>
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<td>Hz</td>
<td>Hertz</td>
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<tr>
<td>IEP</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>IFAM</td>
<td>Institut für Fertigungstechnik und Angewandte Materialforschung</td>
</tr>
<tr>
<td>IHP</td>
<td>Inner helmholtz plane</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>IRE</td>
<td>Internal reflection element</td>
</tr>
<tr>
<td>ISO</td>
<td>International organization for standardization</td>
</tr>
<tr>
<td>kHz</td>
<td>Kilohertz</td>
</tr>
<tr>
<td>MCT</td>
<td>Monochlorotriazinyl</td>
</tr>
<tr>
<td>18-MEA</td>
<td>18-methyl eicosanoic acid</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>MTAAC</td>
<td>Methyltriallylammomium chloride</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>MW</td>
<td>Microwave</td>
</tr>
<tr>
<td>OHP</td>
<td>Outer helmholtz plane</td>
</tr>
<tr>
<td>PDADMAC</td>
<td>Poly(diallyldimethylammonium chloride)</td>
</tr>
<tr>
<td>PELs</td>
<td>Polyelectrolytes</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>pH</td>
<td>Hydrogen ion concentration</td>
</tr>
<tr>
<td>PVAm</td>
<td>Poly(vinyl amine-co-vinyl amide)</td>
</tr>
<tr>
<td>RF</td>
<td>Radiofrequency</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard cubic centimeters per minute</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>TFBA</td>
<td>4-Trifluoromethylbenzaldehyde</td>
</tr>
<tr>
<td>TPA</td>
<td>Terephthalic acid</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>Ultraviolet/visible</td>
</tr>
<tr>
<td>VS</td>
<td>Vinyl sulphone</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>wt. %</td>
<td>Weight percent</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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1 Introduction

1.1 Overview and motivation

A shift toward highly functional and added value textiles is now recognized as being essential to the sustainable growth of the textile industry (1). To achieve this purpose, textiles have undergone several surface modifications to alter their surface characteristics such as wetting and adhesion. Most of these modifications are carried out by wet chemical methods (2; 3). Such modifications are successful on natural fibers as they have naturally-occurring graft-sites on their surfaces such as the hydroxyl groups on cellulose fibers, which offer a platform for surface modifications. However, many other textile materials lack such reactive functional groups or sites on their polymer chains, e.g., polyester.

Poly(ethylene terephthalate) (PET), the main member of polyester polymers, is the most widely used fabric in the textile industries. Over the years, polyester has become synonymous with PET. PET fabrics exhibit desirable properties, including high-tensile strength, dimensional stability, resistance to many chemicals and environmental conditions (4). These remarkable attributes make it an excellent candidate for a variety of potential applications including, but not limited to, technical textiles, domestic textiles, the automotive industry and medical textiles (5). Statistics show that sharing of PET in the total textile production (about 42%) still dynamically grows and has begun to grab market share from cotton (Figure 1.1) (6). This is due to the above-mentioned advantages combined with the material’s cheapness and availability of the raw materials with the possibility to recycle PET fibers. For example, PET bottles and other PET products have recently attracted attention as new recyclable resources for the production of fibers. Moreover, PET is stronger than the most natural fibers. Therefore, it is used with those fibers to produce more resilient and wrinkle free blend fabrics (i.e. PET/wool and PET/cotton) (7).

Unfortunately, like the most synthetic polymers, PET does not possess good adhesion and wetting properties, due to its inherently low surface free energy. As mentioned previously, PET does not exhibit reactive functionalities, such as –NH₂, – COOH, and/or -OH groups wanted for different interactions, which makes the molecule of PET has limited reactivity and innately hydrophobic. The low surface free energy and the resulting poor adhesion to other materials have created numerous technical challenges, such as less wearing comfort,
limitation in coloration properties, build-up of electrostatic charges, insufficient soil release, and difficulties in finishing and poor washability (8). In addition, PET has limited reactivity toward antimicrobial agents that are used to suppress bacteria, molds, algae, and microorganisms that cause some health-concerned problems. These limitations in functional properties of PET fabrics have constrained their further application in garments and other industries. As a result, significant efforts have been expended to overcome the PET limitations and to facilitate a broad spectrum of uses.

![Global apparel fiber market trends from 1980 to 2010](image)

**Figure 1.1** Global apparel fiber market trends from 1980 to 2010 (6).

Accordingly, the surface design and development of highly functional PET fabrics have become increasingly important in various industrial fields such as adhesives, food packaging, printing and biomedical technologies. To improve PET’s performance and obtain new applications, it is often necessary to introduce specific functional groups onto its surface. In particular, nitrogen-containing PET fabrics can be considered as a potential substrate for the versatile applications. Implanted amino groups, with their associated polarity and reactivity, can be useful in the coupling and immobilization of a variety of functional molecules, which typically contain functional groups able to interact with amino groups.

For this purpose, various approaches have been developed for modifying PET fibers properties. The introduction of nitrogen-containing functionalities by conventional wet chemical reactions is one possible means for altering the physical and chemical nature of the PET fabric to adapt its surface for different applications. The feasibility of
incorporating amino groups into the surface of PET fibers by reaction with monofunctional, bi-functional or multifunctional amines was investigated (8-11). For instance, aminolysis of PET fibers with diamines. In this reaction, ester bonds along PET react with amines to give amides. The aminolysis reaction mechanism (Figure 1.2) involves the nucleophilic attack of the amine at the electron-deficient carbonyl carbon to form a tetrahedral intermediate, under basic conditions; the tetrahedral intermediate is deprotonated, followed by expulsion of the alcohol leaving group from the tetrahedral intermediate, which leads to the formation of an amide and an alcohol (12).

![Figure 1.2 Step-wise mechanism of the aminolysis reaction of PET.](image)

Other surface engineering methods were also employed to obtain PET fabric surface decorated with nitrogen-containing groups. The use of chitosan to modify the PET fabric surface was reported as one probable approach to introduce amino groups. However, because of the limited reactivity of the PET fabric surface, it is essential for PET fabric to undergo pretreatment prior modification to improve the adhesion with chitosan (13; 14). In connection with this pretreatment, alkaline hydrolysis with sodium hydroxide is well known to make PET fabrics more wettable. The alkaline hydrolysis of PET fibers starts
from the outer shell of the fiber by breaking polymer chains, and creating additional hydroxyl and carboxylic groups (9; 15; 16).

In spite of these surface modifications of PET fibers have been somewhat shown to be an effective method to achieve surface modification for many years. However, alkaline hydrolysis and aminolysis inadvertently involve polymer degradation and the surface of the PET fibers is removed layer by layer, leads to a loss in the strength of the fabric and may adversely affect the overall product performance (8). These effects reduce the range of its applications, especially in the technical area. In addition, these conventional methods have a greater environmental impact because the generation of corrosive and hazardous chemical waste (17; 18). At the same time, the environmental restrictions concerning the wastewater produced by conventional textile finishing techniques are getting more and more severe. This poses a challenge that has led to search for alternative surface engineering methods that need less energy consumption and cause less environmental contamination in the textile finishing processes (19).

In this context, physicochemical approaches stand out as the most promising alternative to reduce environmental problems associated with the textile industry. Physicochemical approaches include ultraviolet (UV), γ-ray, electron beam, and plasma treatments. Among these techniques, plasma treatment is becoming an attractive alternative method for surface modification of textile substrates (20-23). Surface modification by plasma treatment is simple, time efficient process, environmentally friendly process and the modification is limited to the outermost layers of several hundred angstroms while the bulk properties can be kept unchanged as well as the touch of the textiles (24; 25). It provides a reactive medium at the ambient temperature that can introduce functional groups onto the surface of a treated substrate depending on plasma parameters such as power, gas used, duration of treatment and pressure (26).

1.2 Objective and synthetic concepts

As described above, an interest in the present work is to find out appropriate engineering methods, which can be further accepted by textile industries for surface functionalization of PET fabrics to overcome its limited reactivity and to keep the bulk characteristics unaffected. Toward this goal, two typical plasma-based synthetic concepts were thoroughly employed and compared to endow PET fabrics with accessible amine functionalities to provide more flexibility in their uses. In this work, coloration with anionic dyes was used
to evaluate the effectiveness of different plasma-based surface modifications of PET fabrics.

Plasma-based modified PET fabrics that contain amine functionalities have been achieved by use directly low-pressure ammonia plasma treatment to produce –NH₂ groups. The second approach was the adsorption of cationic polyelectrolytes from aqueous solution to plasma-treated PET fabric in which negatively charged groups were introduced by low-pressure oxygen plasma. Oxygen plasma was applied in order to promote adhesion to PET fabric surface through the introduction of carboxylic groups that interact with the subsequent coating layer (Figure 1.3). Cationic polyelectrolytes used in this study were poly(diallyldimethylammonium chloride) (PDADMAC) as a strong polyelectrolyte and poly(vinyl amine-co-vinyl amide) (PVAm) as a weak polyelectrolyte. Afterwards, an appropriate annealing procedure was developed to stabilize the polymer layer on PET surface.

![Diagram](image)

**Figure 1.3** Schematic representation of the different synthetic routes investigated in the present work for introduction amine-containing groups onto PET fabric surfaces.
2 Theoretical Background

2.1 Textile fibers
Textile fibers have been used for thousands of years, and their importance in the world today is greater than ever before (27). The use of fibers has been expanding from modern apparel, home furnishings, and medicine to high-performance applications. The textile industry uses substantial quantities of fibers in the construction of fabrics that undergo several mechanical and chemical treatments before reaching their end user. Textile fibers may be either of natural or man-made origin (Figure 2.1). Natural fibers can be mainly divided into plant fibers of cellulosic origin (cotton), protein fibers of animal origin (wool, silk), and mineral fibers (asbestos). Man-made fibers regenerated from natural sources are called regenerated fibers that can be obtained by mechanical and/or chemical processes of vegetable or animal origin fibers, while the fibers from synthetic organic or inorganic origins are often called synthetic fibers (6).

![Textile Fibers Classification Diagram](image)

**Figure 2.1** Classification of textile fibers according to their origin (6).
2.2 PET fibers: production and applications

Polyesters are a category of polymers, which contain at least one ester-linking group per repeating unit in their main chain (28). They are one of the most important classes of polymers in use today. In their simplest form, polyesters are produced by the polycondensation reaction of a glycol (diol) with a dicarboxylic acid (diacid) or its diester. Hundreds of polyesters exist due to the myriad of combinations of diols and diacids. The earliest work on polyesters was done by W. H. Carothers at DuPont in the early 1930s (29). The workhorse of polyesters is PET, which is used for packaging, bottles and for the production of fiber for textile products. Fiber applications include not only wearing apparel, curtain, upholstery, thread, tire cord, and fabrics for industrial filtration but also for a wide variety of industrial applications (Figure 2.2) (30). The PET fibers were firstly discovered in UK laboratories of the Calico Printers Association in 1941.

![Figure 2.2 End uses of PET fibers (30).](image)

Industrially the PET is produced by step-growth polycondensation from ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). Two processes are used for the synthesis of PET. The first stage is an ester interchange to produce bis(2-hydroxyethyl)terephthalate (BHET) along with small amounts of larger-sized oligomers (31). The reactants DMT and EG are heated at temperatures increasing from 150 to 210 °C, and the methanol is continuously distilled off.

\[
\begin{align*}
\text{H}_3\text{C}-\text{O}-\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O}-\text{CH}_3 \\
+ \quad \text{2 HO}-\text{CH}_2-\text{CH}_2-\text{OH} \\
\downarrow \\
\text{HO}-\text{CH}_2-\text{CH}_2-\text{O} & \quad \text{C} \\
\text{C} & \quad \text{O}-\text{CH}_2-\text{CH}_2-\text{OH} \\
\text{+} \quad \text{2 CH}_3\text{OH}
\end{align*}
\]

Catalysts: Zinc, Calcium or Manganese acetate
In the second-stage, the temperature is raised to 270–280 °C and polymerization proceeds with the removal of ethylene glycol being facilitated by using a partial vacuum of 0.5–1 torr (32-34).

\[
\text{n HO-CH}_2\text{-CH}_2\text{-O-} \quad \text{O} \quad \text{O}
\quad \text{C} \quad \text{C-CH}_2\text{-CH}_2\text{-OH}
\]

270-280 °C
Catalyst: Antimony(III) oxide

\[
\left[ \text{C-} \text{O-CH}_2\text{-CH}_2\text{-O} \right]_n + \text{n HO-CH}_2\text{-CH}_2\text{-OH}
\]

The production of PET accelerated in the early 1960s when processes to produce pure TPA were improved (35; 36). The linear homopolymer PET constitutes the majority of the polyester fibers produced and consumed globally. PET for industrial fibers has a higher degree of polymerization, higher molecular weight and higher viscosity. The normal molecular weight range lies between 15000 and 20000, with the normal extrusion temperature 280-290 °C. The PET fiber was commercialized through the 1950s as Dacron® in the United States and as Terylene® in the United Kingdom. The global PET fiber production has demonstrated an upward trend in recent years (Figure 2.3) (37). PET fiber production was reaching about 35 million tons in 2010; this figure is especially impressive when we note that, PET was not introduced as a commercial product until 1953 (37).

![Figure 2.3 PET fiber production output (37).](image-url)
Besides excellent properties, the growth of PET fiber production may be assigned to the combination of many factors: low production costs, ability to be blend with natural fibers such as cotton to give a better feel, has outstanding crease resistance and can be treated with cross-linking resins to impart-press (wash-and-wear) properties. This increase forever changed the world map of fibers production.

2.2.1 PET/wool blend fabrics

Textile fabrics containing more than one kind of fibers are termed as blend, union or a mixture (38). The reasons for developing such fabric unions may be offered the most valuable options for economic reasons on raw material cost (if one of the component fibers is relatively expensive), or to develop a material with enhanced or unique properties, which cannot be achieved easily with fabrics made from a single fibers type. Due to the wide range of fibers properties and characteristics, there are almost limitless opportunities for the creation of blends of different type, composition and fabric structure. Therefore, blends are a way to enable the production of fabrics with a unique and novel diverse range of properties using existing fibers types (39; 40).

Wool is an elastic and biodegradable protein fiber. However, wool suffers from a number of intrinsic properties that severely limit its use as textile fibers for many applications. The most common one is the propensity of wool fabrics to undergo felting shrinkage when agitated in aqueous solutions. Another problem experienced by pure wool fabrics is the maintenance of creases. These problems may be overcome by chemical methods or the application of polymers to the surface of the fibers. Another route is to blend wool with polyester.

Chemically, the principal component of the wool fiber is the protein keratin (41). The protein molecules consist of a long polypeptide chain constructed from the eighteen commonly encountered amino acids that are found in most naturally-occurring proteins (42; 43). At intervals, the polypeptide chains are linked together by disulfide (—S—S—) bridges derived from the amino acid cystine. These bonds can easily be broken and reformed, causing the wool to have significant problems with shrinkage and wrinkling. There are also ionic links between the protonated amino (—NH₃⁺) groups and carboxylate (—COO⁻), which are located on the amino acid side-groups and at the end of the polypeptide chains (42; 44; 45). Many of the functional groups on the wool fiber play some part of the forces of attraction involved when dyes are applied to the fibers.
From a morphological point of view, the wool fiber is a nanocomposite of high complexity with a clear hierarchy. The fiber is surrounded by cuticle cells, which consist of at least of four layers, the epicuticle, the A-layer and the B-layer of the exocuticle cells and the endocuticle.

The epicuticle has been considered to consist of lipids (including 18-methyleicosanoic acid (18-MEA)), proteins, and/or carbohydrates, and, due to its chemical inertness, has been called a resistant membrane. It is highly resistant to attack from alkalis, oxidizing agents, and proteolytic enzymes. It is about 2.5 nm thick and amounts to approximately 0.1 % of the weight of the fiber (42).

Blends of polyester with wool represent an attempt to achieve the combination of desirable properties of both fibers. They allow the production of fabrics having good wear properties, dimensional stability, mechanical strength, abrasion resistance and attractive handle. Because wool/polyester blend fabrics can show the complementary properties over fabrics composed only of one of these two fibers wool/polyester blend fabrics have gained a considerable share in woven suiting. The most common blend ratios are 55:45 and 70:30 PET/wool (46).

2.2.2 Coloration of PET fabrics

The value of the textile materials destined for the domestic market is increased by coloration, which is achieved either by dying or by printing. The objectives of coloration are imparting the desired color to textile materials and, in the case of using functional dyes, introducing additional functional properties (i.e. anti-microbial, UV protection, optical sensor for pH). This could result in combination of interesting functionality and unique characteristics of textile materials by coloration (47-50).

As shown in Figure 2.4, different classes of dyes are used in coloration of textile materials. These dyes are water-soluble, sparingly water-soluble dyes, alternatively water-insoluble pigments (47). The choice of the dyes molecules is dependent on the functional groups in the fiber structure, dye molecules and the potential interaction between these groups (51; 52). Dyes bond to textile materials with Van der Waals forces, ionic and covalent bonding (53). In the textile coloration, a single class of dyes predominates on the substrate concerned, for example, acid dyes on polyamides and wool, basic dyes on acrylic, disperse dyes on polyesters and cellulose acetate.
When PET fibers first appeared, they presented many problems for traditional dyers. PET fibers do not have dye sites, neither basic nor acidic groups. For this reason, it is colored mainly with non-ionic disperse dyes. This class of dyes possesses no specific chemical reactivity toward the fibers and does not require the formation of specific interactions with functional partner groups. Thereby coloration of PET relies on Van der Waals forces to hold the dye on the fiber. On the other hand, natural fibers like wool, cotton, silk, and then later man-made ones like rayon and polyamides were well known and had been good dye affinities because the fibers had pendant groups such as –NH₂, –COOH, and/or –OH. These dyes were developed to interact with such groups. All classic cationic and anionic dyes for wool, silk and cotton had water-solubilizing ionic groups like –NR₃⁺ and –SO₃⁻, such dyes had no affinity for PET (55).

In fabric blends, because different fibers have a different chemical structure blends suffer from inherent disadvantages. In these blends, usually coloration requires two classes of dyes during the two-stage process to produce solid shades; disperse dyes for the PET component and acid dyes for the wool (56; 57). This greatly hinders the simultaneous process of coloration.

As the PET fibers market grew, it has been recognized that dyes other than disperse dyes would be valuable, which facilitate a broad spectrum of PET uses. In this context, anionic dyes would play a much larger industrial role if they successfully applied to PET fabrics. Consequently, it is possible to widen the scope of coloration of PET fabric as well as use a single set of dyes for blend fabrics such as PET/wool fabrics, thereby reducing complexity in coloration technology and effluent treatment (58). In addition, it is possible to apply some dyes specifically designed for high-technology (Hi-tech) applications such as
biomedical and pH sensitive dyes. The following discussion will focus on anionic dyes namely reactive, acid and direct dyes.

2.3 Anionic dyes

2.3.1 Acid dyes

Acid dyes can be used to color fibers within the cationic groups such as wool, silk and polyamide. Sodium sulfonate groups incorporated into the structure of acid dyes work both to impart water solubility to the acid dye molecule as well as to serve as binding sites for the coloration process. In the case of wool, amino groups are protonated in an acidic medium to form cationic centers. Acid dye molecules were fixed through ionic bond. Figure 2.5 shows an example of acid dyes namely C.I. Acid Yellow 69.

![Figure 2.5 The chemical structure of C.I. Acid yellow 69.](image)

One drawback of coloration by acid dyes is limited wash fastness. Since the bond holding the dye molecules to the substrate is an ionic bond (Figure 2.6), an ion-exchange reaction can readily take place in the presence of water or steam, effectively removing the dye from the substrate. Dye removal can occur with every washing or steaming, causing the overall color of the material to fade.

![Figure 2.6 Schematic representation of acid dye fixation on fibers by ionic bond.](image)
2.3.2 Reactive dyes

Reactive dyes are water-soluble dyes and widely used for coloration cellulosic fibers as well as their blends under alkaline conditions. They contain a group capable of forming a covalent bond with the hydroxyl groups in the cellulosic polymer during the coloration process. The two main reactive groups are the monochlorotriazinyl (MCT) group and the beta-sulphatoethylsulphone (masked vinyl sulphone (VS)). The alkali added to the dyebath initiates the desired dye/fiber reaction. At higher pH, a larger percentage of the cellulose hydroxyl groups are dissociated and, thus, forming cellulosate anions. These react with the dye by either nucleophilic substitution or nucleophilic addition reactions (47). MCT reactive dyes contain a triazinyl ring with halide substituent, which are easily attacked in a nucleophilic substitution reaction by a cellulosate anion, forming a permanent ether linkage between the substrate and the triazinyl ring. Reactions involving MCT type reactive dye are shown in Figure 2.7.

![Figure 2.7](image)

**Figure 2.7** The reaction mechanism of cellulosate anion with MCT type reactive dye.

VS reactive dyes form a covalent bond between the dye molecule and the fiber via a nucleophilic addition reaction. Reactions involving a VS reactive dye are shown in Figure 2.8.

![Figure 2.8](image)

**Figure 2.8** The reaction mechanism of cellulosate anion with VS type reactive dye.
The major advantage of using reactive dyes to color cellulosics fibers is excellent fastness properties. The dye molecules are permanently attached to the fiber because a covalent bond is formed. Thus, little to no dye is removed during subsequent washings. Therefore, fabrics colored with reactive dyes should pose no problems for the end-user of the product.

2.3.3 Direct dyes

Direct dyes are defined as anionic dyes with substantivity for cellulosic fibers. The molecules of direct dyes are similar in structure to those of acid dyes but they are larger. There is, however, no clear demarcation between acid and direct dyes. They are available in a full range of hues but are not noted for their color brilliance. The major drawback is their moderate fastness to washing (59; 60).

![Chemical structure of C.I. Direct Yellow 4.](image)

C.I. Direct yellow 4 (Figure 2.9) exhibits color changing from yellow to orange with pH variation in the pH range 6.5-8 (61). This halochromic change makes it useful as a pH-indicator. Halochromic textiles can be used as sensors that give an indication of the environment’s pH by an easy visual color observation and can be applied in a broad range of applications. For example, investigation the skin pH variations of burn patients, the skin pH changes during the healing process. By using a halochromic wound bandage, it would be possible, without having to remove the gauze so without damaging the wound, to follow this recovery process by following the color change of the bandage (61).

2.3.4 Printing textile fabrics with anionic dyes

Textile printing or patterned dyeing is the most versatile method used for applying color in a localized design to textile fabrics (62). This is usually achieved by applying thickened
pastes. The printing paste on the fabric may be regarded as a miniature localized dye bath, highly concentrated thickened solutions, containing the dye and all the additives necessary for the coloration process. In particular, the viscosity of a print paste determines the volume of paste transferred to the fabric and the degree to which it spreads on and into the surface fabrics.

Various methods have been developed for producing printed textile fabrics, such as rotary screen-printing, flat-bed screen-printing, transfer and roller printing (63). Except for transfer and roller printing, all of these techniques require a screen for color application to the fabrics (64). Printing process is consisting of sequences of operations; the sequence of operations is printing the fabric with a thickened paste containing the dyes, followed by drying and steaming or thermofixation. During steaming, the dyes re-dissolve in the water condensed on the paste films and diffuse into the fibers. A final washing removes the thickener, unfixed dyes and other chemicals from the fabric (60).

Thickening agents play a paramount role in the formulation of printing pastes, ensuring through the modulation of the rheological properties, a homogeneous distribution of the printing paste on the screen and its uniform flow through the screen openings. The selection of the thickening agent is determined by the print paste stability for storage and compatibility of thickening agents with the added dyes as well as chemicals in the print paste. Depending on their chemical structure, dyes may interact with thickening agents, to form complexes or to give a chemical reaction, so causing a variation of the rheological properties of the printing pastes and, hence, of their application characteristics (65-67). Thus, anionic polymers are rarely compatible with cationic dyes. The hydroxyl groups in most carbohydrate gums react with reactive dyes and therefore, they are excluded.

Sodium alginates have become very important for printing paste thickening because of their ready solubility. They are especially important for pastes of reactive dyes for several reasons: the extent of interaction is very small, the absence of hydroxyl groups and the repulsion of dye anions by the ionized carboxyl groups of the polymer under alkaline conditions (68). The repulsion promotes migration of the dye from the thickener into the fabric during steaming, which results in better color yields. The alginate film after drying and dye fixation is washed out easily (62). On the other hand, the preferred thickening agents for printing with acid dyes are of the galactomannan type. These are stable in the acidic conditions, which are required at the fixation stage of dyes.
2.4 Plasma surface modification of textiles

Many properties of textiles are more related to the outer surface rather than to the bulk. Accordingly, the surfaces of textiles offer a platform for functional modifications to meet specific requirements for a variety of applications. In this context, plasma treatment is investigated as an attractive alternative to conventional wet chemical treatment and pretreatment processes. For example, shrink resistance, water repellent finishing or improvement of coloration properties, which tend to alter the mechanical properties of the fabric and are environmentally hazardous. Plasma processing can be applied to both individual yarns and fabrics, which add a lot of flexibility and broaden the field of application. Moreover, it brings a competitive solution to the environmental and economical problems related to water; reduction of processing times, energy usage and it decreases the effluents to be disposed.

2.4.1 Nature of plasma

Plasma is defined as an ionized gas composed of highly excited atomic, molecular, ionic and radical species, as well as photons and electrons (69; 70). Chemically reactive species of plasma, resulting from ionization, fragmentation and relaxation after an excitation process, are energetic enough to dissociate a wide variety of chemical bonds, resulting in a significant number of simultaneous recombination mechanisms (4; 71). From a macroscopic point of view, plasma is considered neutral with the density of electrons and negative ions being equal to the density of the positively charged ions, known as plasma quasi-neutrality. In order to form and sustain plasma, an energy source must be used. The electric field required for plasma generation may be produced by using either direct current (DC) or alternating current (AC) power supplies. Several types of power supply are used: low frequency (50-450 KHz), radio frequency (RF) (13.56 or 27.12 MHz) and microwave (MW) (2.45 GHz) (4; 72).

A first broad classification of plasmas may be done in terms of their thermodynamic properties: thermal (or hot) plasmas and non-thermal (or cold) plasmas regarded as plasmas in thermodynamic equilibrium and non-equilibrium, respectively. In the first class, all the species composing the plasma are in thermodynamic equilibrium. The temperature of all active species (electron, ion and neutral) is the same, of the order 1000 K. Therefore, thermal plasmas are clearly unsuitable for treating textiles. It is typically used where heat is required, such as for cutting, welding or spraying. Cold plasmas, on the other hand, are maintained at around room temperature or slightly above it. The temperature of neutral and
positively charged species is low, while the electrons are relatively in much higher temperature. Therefore, equilibrium between all the species is far from established. Consequently, cold plasma is well suited for the treatment or surface modification of temperature-sensitive materials such as textile materials (73; 74).

The non-thermal plasmas can be classified into two accepted types based on the gas pressure at which they are generated: low-pressure and atmospheric pressure plasmas. Typical low-pressure plasmas operate in the range between 0 and 1 mbar, a vacuum chamber and the necessary vacuum pumps are required. The atmospheric pressure plasmas are operated at one atmosphere (74).

2.4.2 Plasma-based modification methods of textiles

Plasma is a very reactive environment in which several different interactions between plasma species and a surface are possible. Over the past several years, the number of possible plasma-based modifications has increased dramatically to tailor specific surface properties of textiles. Despite the increasing use of plasmas in the surface tailoring of polymers, not yet all aspects about how plasma processing can lead to a wide variety of different functionalities or interaction mechanisms between plasma species are fully explored or well understood (75). In many applications, the functional groups can be introduced onto the surface in situ by plasma treatment and/or on subsequent exposure to the atmosphere, which can serve as anchoring sites for paints, adhesives and for bioactive molecules. There are several synthetic approaches have been used to modify the surface of textiles as shown in Figure 2.10. The following discussion will be limited to simple plasma treatment and adsorption of polyelectrolytes on plasma-treated surfaces approaches used in the present study.

2.4.2.1 Simple plasma treatment of textile surfaces

For many applications, a short exposure of the polymer surface to a low-pressure plasma is sufficient to obtain, e.g., a better wettability or an improved adhesion. Plasmas (NH₃, H₂O, and O₂) offer a versatile and viable tool to alter the surface properties of textile materials without affecting the bulk properties. Plasma treatments are used to introduce the radicals or functional group onto a polymeric surface in a controlled and reproducible manner as well as the creation of charged surfaces (Table 2.1). In these systems, no additional molecular layer is deposited. One of the major limitations of plasma technologies is the diversity of functional groups produced by the multitude of chemical reactions that occurs in the plasma (76).
Figure 2.10  Schematic representation of different synthetic approaches used for surface functionalization of textiles based on low-pressure plasma treatment.

Table 2.1 Plasma gases and their applications.

<table>
<thead>
<tr>
<th>Plasma gas</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidizing gases (O(_2), air, H(_2)O, N(_2)O)</td>
<td>Removal of organics by oxidation and to leave oxygen species in the polymer surface.</td>
</tr>
<tr>
<td>Nobel gases (Ar, He)</td>
<td>To generate free radicals in surfaces, to cause cross-linking or to generate functional groups for further reactions.</td>
</tr>
<tr>
<td>Active gases (NH(_3))</td>
<td>To generate amino groups.</td>
</tr>
<tr>
<td>Fluorinated gases (CF(_4), SF(_6))</td>
<td>Fluorinated surface groups such as –CF(_2) and –CF(_3) are introduced into the surface, which make it inert and hydrophobic.</td>
</tr>
</tbody>
</table>

Plasma treatment can modify the surface of a polymer substrate by physical and chemical changes. The plasma capable of exerting four major effects (77), that is, surface ablation or etching, surface functionalization, surface cross-linking, and deposition (Figure 2.11) with concomitant effects on wetting, coloration, surface adhesion, electrical conductivity and
other characteristics of interest in the textile industry. Depending on the plasma parameters, one of these changes can predominate on the others. The nature of the modification of a textile surface by plasma treatments is governed by a variety of factors: the type of the used gas, the power and duration of the treatment (78). It was observed that, the results from different workers contradict one another; the discrepancy is often attributable to differences in treatment conditions (6; 79; 80).

![Schematic representation of plasma effects on a polymer surface.](Image)

The application of simple plasma treatments for improved wettability has been done on all possible fiber materials, with varying success. The treatment aims at the introduction of water compatible functional groups such as –COOH, –OH and –NH₂. The wettability of textile surfaces is usually monitored by indirect methods such as absorption time, because their porous structure immediately absorbs the liquid drop (81; 82). The PET fabric was treated by plasma initiated in various gases (N₂, O₂, air, CO₂ and NH₃) by Wróbel et al. (83). The best results were obtained after treatment with oxygen, nitrogen and air plasma. Costa et al. (84) also studied the effects of gas composition on the wettability of PET fabrics. Molina et al. (45) reported on an improved wettability of keratin fibers with water vapor plasma. Although plasma exposure can dramatically alter wettability, an ageing effect is observed. The popular consensus is that the polar groups undergo migration into the bulk of the modified materials in order to reduce the interfacial tension (85). The impact of a nitrogen plasma treatment on the dyeing properties of wool fabric was also studied (86). The nitrogen plasma introduced new -NH₂ groups onto the wool surface, thereby enhancing the extent of dye exhaustion. Recently, Raffaele-Addamo et al. (87) applied RF
plasma in air or argon to PET fibers and showed an increased color depth upon dying with disperse dyes. Additionally, simple plasma treatment can be considered as a key technique in various multistep strategies, including the immobilization of predeposited molecules as well as the surface functionalization for subsequent grafting or adsorption procedures (Figure 2.10).

2.4.2.2 Adsorption of polyelectrolytes on plasma modified textile surfaces

Another route to durable surface modifications is the use of low-pressure plasma treatments combined with the subsequent adsorption of appropriate polyelectrolytes for the construction of surface reactive textile materials (88; 89). The adsorption of polyelectrolytes onto surfaces is strongly favored when the polyelectrolyte and the surface carry opposite charges. In such systems, small amounts of adsorbed polyelectrolyte become very effective. Hence, surface properties can be controlled by the chemical structure of the polyelectrolytes used. The definition of “coating” in the following paragraphs is a polymeric layer deposited on top of a textile structure. The usefulness of combined treatment strategies to modulate various surface properties is given by the following examples. Shan-hui Hsu et al. (90) studied various air plasma treatments followed by application of chitosan to achieve the antibacterial effects to nylon fabrics. Bratskaya et al. (91) also studied the application of chitosan on oxygen plasma treated polypropylene surfaces to improve their wettability, dying behavior and antimicrobial properties.

2.5 Use of polyelectrolytes in textile applications

Polyelectrolytes (PELs) are a special class of polymers whose repeating units contain charged or chargeable groups along or pendent to the polymer backbone and are primarily water-soluble (92-94). An important property of polyelectrolytes is their tendency to adsorb on substrate surfaces. This is used to modify solid surfaces and interfaces by polyelectrolyte based coatings (95-97). The adsorption of PELs onto textiles has been subject of numerous investigations because of the simple procedure for application (98; 99).

The ability to modify the chemistry of textile surfaces by polyelectrolyte-based coatings provides a straightforward mechanism for controlling surface chemistry and therefore the properties of the modified surface (100; 101). Besides the entropic effects, the polyelectrolyte adsorption is mainly controlled by electrostatic interactions between the oppositely charged surface of some natural fibers and the polyelectrolyte. Cotton, for instance, has a multitude of naturally occurring hydroxyl and carboxylic acid groups along
the cellulose chain, which can serve as anchor sites for the adsorption process. However, many other textile materials, particularly polypropylene and PET, lack such reactive groups or sites on their polymer chains. In this case, it is important to produce a surface containing active groups that could react electrostatically with a polyelectrolyte. The adsorption of polyelectrolytes depends heavily on the surface charge density, the polymer charge density, the ionic strength of the solution and the molecular properties like conformation or molar mass (92).

2.5.1 Polyelectrolyte classifications
As shown in Figure 2.12, polyelectrolytes can be categorized according to their origin into natural (e.g., polynucleic acids and polypeptides), modified natural (e.g., chitosan and cellulose), and synthetic (e.g., poly(4-styrene-sulfonic) or PDADMAC). In terms of the nature of the ionic groups, they can be classified as polyacids/polyanions, polybases/polycations, that depending on whether the ionizable groups are all anionic or all cationic. A special class of polyelectrolytes is called “polyampholytes”, macromolecules that carry both anionic and cationic groups covalently bound to the polymer chain. Based on composition they are homopolymers and copolymers.

![Figure 2.12 Classification scheme of polyelectrolytes.](image-url)
Polyelectrolytes can be subdivided into strong or weak based on the charge density of the macromolecule. Strong polyelectrolytes that remain fully charged over the entire pH range, in other words charge density is fixed over the entire pH range (102; 103). For example, in the PDADMAC nitrogen is quaternized and no change in the degree of charging is possible due to the absence of an acidic hydrogen atom. On the other hand, weak polyelectrolytes whose charge density can be tuned by solution pH-value, such as PVAm (104).

In the last few years, water-soluble cationic polyelectrolytes have attracted particular interest for their applications in the surface modification and finishing of textile materials to improve their quality and properties (104-106). Because the most of naturally-occurring textile surfaces are negatively charged. They are used as finishing agents for color fastness, light fastness, preparation of polymeric water-soluble dyes (98) as well as the removal of dyestuffs and detergents from wastewater via a coagulation process before it is discharged (100; 101; 107-109). In this work, we will report on the surface modification of PET fabrics using the water-soluble polymer PDADMAC and PVAm (Lupamine®9095).

### 2.5.2 Poly(diallyldimethylammonium chloride) (PDADMAC)

PDADMAC is one of the most important commercial polymer of the allyl monomers. It is a cationic functional polymer that has outstanding utility in many applications as a flocculent (110; 111), fixing agent (112; 113), antistatic agent (96), and antibacterial agent (114; 115) in textile industry. It should be mentioned that it was the first polymer to be approved by the U.S. Food and Drug Administration (FDA) for the use in potable water treatment (116).

Free-radical polymerization of diallyldimethylammonium chloride (DADMAC) results in a water-soluble linear polymer containing five-membered pyrrolidinium units (Figure 2.13) (96; 117; 118). Depending on the purity of the raw materials and the reaction conditions the technical monomer solutions can contain small amounts of, for example, allyldimethylamine (ADMA), diallylmethyamine (DAMA), or methyltriallylammonium chloride (MTAAC) (119).

![Figure 2.13 Cyclopolymerization of DADMAC and structures of resulting polymers.](image-url)
Although the PDADMAC was first prepared in the 1950s (120), research interest in PDADMAC has not diminished. This is based on its unique chemical structure, PDADMAC molecules possess a backbone of cyclic units and a charged quaternary ammonium group found in each monomer unit provides the polymer with high water solubility and solution properties corresponding to those of strong polyelectrolytes.

2.5.3 Poly(vinyl amine-co-vinyl amide) (PVAm)

PVAm is a weak PEL containing a controllable number of reactive and accessible primary amino groups on the polymer backbone. It is an interesting candidate for solid surface functionalization in aqueous solutions (121; 122), because it has a high chemical potential for subsequent derivatization reactions with electrophilic agents.

The charge degree of PVAm depends on the protonation/deprotonation equilibrium of the amino groups (Figure 2.14). The protonation/deprotonation equilibrium can be easily influenced by the pH value of a surrounding aqueous medium. The stability of the adsorbed polyelectrolyte layer can be also affected by the environmental conditions. For practical applications and subsequent functionalization reactions, it is recommended that the PVAm layer to be stabilize by cross-linking reactions (123). Various procedures such as heat-induced cross-linking reactions involving two or more functional groups, amino groups can react with aldehyde, anhydrides, and carboxylic acids, proved to be an interesting route in the formation of covalent bonds in the electrostatically or H-bonding stabilized polymer complexes (124-126) and polyelectrolyte multilayers (127; 128).

\[
\begin{align*}
\text{NH}_2^n & \quad \text{H}^+ \quad \text{OH}^- \\
\text{NH}_3^n & \quad \text{OH}^- 
\end{align*}
\]

**Figure 2.14** Protonation/deprotonation equilibrium of PVAm.

PVAm cannot be synthesized directly from the vinyl amine monomer because according to the enamine-imine tautomerization vinyl amine is fully converted to its corresponding imine (Figure 2.15). Therefore in industry, PVAm can be synthesized only via indirect routes by modifications of other polymers that are readily available. Attempts have been
made to synthesize PVAm via the hydrolysis of poly(N-vinylimide)s (129), poly(N-vinylcarbamate)s (130) and poly(vinylacetamide) (98).

![Enamine-Imine tautomerism in vinyl amine.](image)

**Figure 2.15** Enamine-Imine tautomerism in vinyl amine.

Poly(N-vinyl formamide) (PVFA) was used for simple and economical production of PVAm (131; 132). PVFA can be easily converted into PVAm by hydrolysis in either acidic or basic aqueous solution (Figure 2.16) (132; 133).

![Synthesis of PVAm from hydrolysis of PVFA.](image)

**Figure 2.16** Synthesis of PVAm from hydrolysis of PVFA.

The hydrolyzation reaction does not fully cleave the formamide group, as consequence copolymers with different formamide/amino group ratios are produced (Figure 2.17). Hence, the degree of hydrolysis of the formamide groups is an excellent tool to control the desired charge density of the polyelectrolyte (131). It is known that an aqueous solution of PVAm with the degree of hydrolysis larger than 90 % (Lupamine®9095) can be used to form an ultrathin film on hydrophilic surfaces (134).
Moreover, the coexistence of amino and formamide groups along the polymer backbone may form amidine groups (Figure 2.18). The amidine formation can take place when polymers with a degree of hydrolysis in the order of 20–80% are used. Furthermore, acidic surface groups can also induce the amidinium ion formation (135).

Non-protonated primary amino groups in the PVAm molecules have a high synthetic potential, which can be used for versatile subsequent derivatization reactions (121; 136). The nucleophilic character in combination with the free-electron pair distinguishes the primary amino group. Therefore, it can react with a variety of electrophilic compounds such as carbonyl, acid anhydrides, isocyanates, oxiranes and carboxylic acid derivatives (132; 137).

2.5.4 Polyelectrolyte/dye interactions

The interactions of different water-soluble cationic polyelectrolytes with anionic azo dyes have been reported. This interaction is often accompanied by marked changes in the absorption spectrum of the dye. This effect is known as metachromacy (138).

As a global definition, metachromacy is the phenomenon whereby the ionic dyes change their color in aqueous solution as a result of their interaction with oppositely charged macroions, or charged surfaces (128). This is a consequence of the interactions of the dye
orbitals with each other or with the orbitals of polyanion, when the dye molecules in close proximity on the macroion chain or on the surface \(138\). The substrates inducing such spectral changes of the dye are called chromotropes. Spectral changes as bathochromic (\(\lambda_{\text{max}}\) shift to a longer wavelength, red) or hypsochromic (\(\lambda_{\text{max}}\) shift to a lower wavelength, blue) shifts were reported for several anionic dye/cationic polyelectrolyte systems \(139; 140\). These changes in the absorption spectrum have often used as the basis of quantitative determination of the small amounts of cationic polyelectrolytes in natural and industrial water \(141\).

In addition, the aggregation of dye molecules in an ordered structure on the external surface or embedded in the polyelectrolyte layer (with corresponding dipoles) results in spectral changes. Shifts in the absorption spectra are depending on the mutual orientation of the interacting dipole moments \(142\). The arrangement changes the energy difference between ground and excited state of the dye molecule \(143\). When the dipole moments are in-line, the arrangement is termed J-aggregates (Figure 2.19a), which decrease the difference between ground and excited states of dye molecule leading to a bathochromic (red) shift. In the case of, the dipole moments are parallel; the arrangement is termed H-aggregates (Figure 2.19b), which increase the difference between ground and excited states of dye molecule, then the spectra exhibit a hypsochromic (blue) shift \(142; 143\).

Numerous synthetic polycations with cationic centers were studied include poly(ethyleneimine) \(144\) and poly(vinylpyridin) \(145\) have been used as chromotropes for the metachromacy of anionic dyes. Chitosan as a natural polycation with amino groups has been also used as a chromotrope for anionic dyes \(140\). Particularly, in textile industries, cationic polyelectrolytes were used for selective adsorption of anionic dyes from wastewater \(96\).
3 Experimental Part

3.1 Materials

3.1.1 PET fabric
Commercial PET 100% weave fabric of (165 g/m²) used as the substrate for modification throughout this study was supplied by private sector Co., Egypt. The PET fabric was washed before use with an aqueous solution containing 0.5 g/L non-ionic detergent Tissocyl CSB (Zschimmer & Schwarz, Burgstädt, Germany) and 1 g/L sodium carbonate. The liquor-to-fabric ratio of the aqueous solution was kept at 50:1 for 60 min at 70 °C. After washing the fabric was thoroughly rinsed with deionized water, dried at room temperature until constant weight and kept in desiccators before use in the experiments. It was observed that, although PET fabric was carefully cleaned before any further modification, surface contaminants are not completely removed. The samples used for the modification procedures were 4x4 cm² in size and 0.3 mm in thickness.

3.1.2 PET/wool blend fabric
Commercial PET/wool weave blend fabric of (150 g/m²); with a blend composition of 70 % PET and 30 % wool was supplied by El-Mehala El-Kobra Co., Egypt. The fabric was washed by treatment in a bath containing 0.5 g/L non-ionic detergent Tissocyl CSB and sodium carbonate 1g/L at the liquor-to-fabric ratio of 50:1 for 30 min at 50 °C followed by rinsing with deionized water, dried at room temperature until constant weight and kept in desiccators before use in the experiments. The samples used for the modification procedures were 4x4 cm² in size and 0.3 mm in thickness.

3.1.3 PET film
PET films were used as model substrates for Attenuated total reflectance-fourier transform infrared (ATR-FTIR) studies. The PET films, having a smooth surface, are quite amenable to make a good contact with the surface of the internal reflection element (IRE) to be studied by ATR-FTIR. The PET films were kindly supplied from Fraunhofer Institut für Fertigungstechnik und Angewandte Materialforschung (IFAM), Bremen, Germany. PET film with a thickness of 16 µm was cut to a dimension of 4 x4 cm² samples. Prior to the surface modification experiment, the PET films were washed for 10 min in an ultrasonic
bath successively in acetone and water to remove surface contaminants, dried in the air at the room temperature and kept in desiccators before use in the experiments.

### 3.1.4 Plasma gases

Ammonia (99.99 %) and oxygen (99.95 %) were used as process gases for plasma treatments of PET fabric samples. Process gases were purchased from Messer Griesheim, Germany.

### 3.1.5 Polyelectrolytes

The cationic polyelectrolytes used in the study to build different molecular architectures on PET surfaces were the strong polyelectrolyte PDADMAC obtained as a 20 wt.-% aqueous solution and the weak polyelectrolyte PVAm (Lupamine® 9095) obtained as a 22 wt.-% with a hydrolysis degree > 90 %. The polyelectrolytes were used without further purification. The molecular masses, charge densities and supplier of cationic polyelectrolytes are summarized in Table 3.1. The molecular structures of the polyelectrolytes are presented in Figure 3.1.

#### Table 3.1 Polyelectrolytes used to modify PET fabric surfaces.

<table>
<thead>
<tr>
<th>Polyelectrolyte</th>
<th>Molar mass (g/mol)</th>
<th>Charge density (meq/g)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(diallyldimethylammonium chloride) (PDADMAC)</td>
<td>200000-350000</td>
<td>6.27</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
<tr>
<td>Poly(vinylformamide-co-vinylamine) (PVAm) (Lupamine® 9095)</td>
<td>340000</td>
<td>5.47</td>
<td>BTC Specialty Chemical Distribution GmbH</td>
</tr>
</tbody>
</table>

(a) The values were determined by polyelectrolyte titrations (146).
(b) The molar mass given here is the molar mass of pre-polymer PVFA, which was used for hydrolyzation reaction

\[
\text{PDADMAC} \quad \text{PVAm (Lupamine® 9095)}
\]

**Figure 3.1** Chemical structures of the polyelectrolytes used to modify PET fabric surface.
3.1.6 Dyestuffs and auxiliaries of printing pastes

The commercial six anionic dyes in this study are listed in Table 3.2. The chemical structures of these dyes will be presented in section 4.3. Other auxiliaries used in the formulation of print pastes are listed in Table 3.3.

Table 3.2 Dyestuffs used in this study.

<table>
<thead>
<tr>
<th>Dye</th>
<th>C.I. generic name</th>
<th>Class</th>
<th>$\lambda_{\text{max}}$ (nm)$^{(a)}$</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C.I. Acid Red 18</td>
<td>Acid dye</td>
<td>507</td>
<td>Bruno Ludewig GmbH</td>
</tr>
<tr>
<td>2</td>
<td>C.I. Acid Blue 80</td>
<td>Acid dye</td>
<td>581,625</td>
<td>Bruno Ludewig GmbH</td>
</tr>
<tr>
<td>3</td>
<td>C.I. Reactive violet 2</td>
<td>Reactive dye</td>
<td>551</td>
<td>Bruno Ludewig GmbH</td>
</tr>
<tr>
<td>4</td>
<td>C.I. Reactive Blue 5</td>
<td>Reactive dye</td>
<td>600</td>
<td>Bruno Ludewig GmbH</td>
</tr>
<tr>
<td>5</td>
<td>C.I. Reactive Violet 5</td>
<td>Reactive dye</td>
<td>560</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
<tr>
<td>6</td>
<td>C.I. Reactive Black 5</td>
<td>Reactive dye</td>
<td>597</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
</tbody>
</table>

(a) UV/Vis spectra were recorded on a Lambda 800 spectrophotometer (Perkin–Elmer, Germany).

Table 3.3 Auxiliaries used in print pastes in this study.

<table>
<thead>
<tr>
<th>Auxiliaries</th>
<th>Used as</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum guar</td>
<td>Thickener for acid dyes print pastes</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
<tr>
<td>Sodium alginate</td>
<td>Thickener for reactive dyes print pastes</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
<tr>
<td>Urea</td>
<td>A very common constituent of print pastes as it acts as both dye solvent and hygroscopic agent (147)</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
<tr>
<td>Ludigol</td>
<td>A mild oxidizing agent (147)</td>
<td>BTC Specialty Chemical Distribution GmbH</td>
</tr>
<tr>
<td>Contripon AT</td>
<td>Defoamer</td>
<td>Zschimmer &amp; Schwarz GmbH &amp; Co KG</td>
</tr>
</tbody>
</table>
3.1.7 Solvent and other chemicals
Water purified and deionized (reverse osmosis followed by ion exchange and filtration) by Milli-RO 5 Plus and Milli-Q Plus systems (Millipore GmbH, Germany) was used in all experiments as solvent. Its conductivity was < 1 µS cm\(^{-1}\). The other chemicals used in this study are given in Table 3.4.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate anhydrous</td>
<td>Fluka</td>
</tr>
<tr>
<td>Citric acid</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
<tr>
<td>4-Trifluoromethylbenzaldehyde (TFBA)</td>
<td>Merck</td>
</tr>
</tbody>
</table>

3.2 Surface modification methods of PET fabrics
3.2.1 Ammonia plasma treatment
Ammonia plasma treatment was carried out in a computer-controlled MicroSys apparatus by Roth&Rau, Wüstenbrand, Germany. The cylindrical vacuum chamber, made of stainless steel, had a diameter of 350 mm and a height of 350 mm. The base pressure obtained with a turbomolecular pump was < 10\(^{-7}\) mbar. On the top of the chamber, a 2.46 GHz electron cyclotron resonance plasma source RR160 by Roth&Rau with a diameter of 160 mm and a maximum power of 800 W was mounted. The plasma source can be operated in a pulsed mode. The process gas was introduced into the active volume of the plasma source via a gas flow control system. When the plasma source was on, the pressure was measured by a capacitive vacuum gauge. Samples were introduced by a load-lock-system and placed on a grounded aluminum holder near the center of the chamber. The distance between the sample and the excitation volume of the plasma source was about 200 mm. For the experiments of this work, the following parameters were used: power 400 W, pulse frequency 1000 Hz, duty cycle 10 % (i.e. effective power 40 W); ammonia gas flow 15 standard cubic centimeters per minute (sccm), pressure 7x10\(^{-3}\) mbar (148).
3.2.2 Oxygen plasma treatment

Oxygen plasma treatment of PET fabric surfaces was carried out in a plasma processor 440 (Technics Plasma, Kirchheim, Germany). The apparatus was equipped with a 2.4 GHz microwave source (maximum output power 600 W), which was connected with a quartz window to a vacuum chamber with dimensions of 350 x 350 x 350 mm$^3$ (base pressure 0.02 mbar). The process gas was introduced into the chamber via a gas-flow control system. After switching on the microwave source, homogenous plasma was formed in the chamber volume. The PET fabric samples were treated in dependence on input discharge power and treatment time using the following parameters: input discharge power (100 W, 300 W, and 600 W) and treatment time (15 s, and 30 s); oxygen gas flow 10 sccm; pressure, 0.14 mbar (149).

3.2.3 Coating of oxygen plasma-treated PET fabrics with cationic polyelectrolytes

Immediately following the oxygen plasma exposure, the fabric samples were immersed in 0.1, 0.5, 1, or 3 wt. % aqueous cationic polyelectrolyte solution for 3 h at the pH corresponding to the solution of each cationic polyelectrolyte with no adjustment, i.e., pH 6 for PDADMAC, and pH 8 for PVAm. During the adsorption, the solution was gently shaken at 25 °C. After adsorption, PET fabric samples were annealed in a convection oven for 1 h at 120 °C (91; 150). In order to remove weakly adsorbed polymer, the fabric samples were extensively rinsed with deionized water until constant water conductivity was < 1 µS/cm measured with SevenMulti (Mettler-Toledo GmbH, Schwerzenbach, Switzerland), then dried for 30 min at the same temperature. Finally, they conditioned on air and stored in desiccators before use in characterization and coloration methods.

3.3 Characterization methods

3.3.1 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a surface sensitive method allowing to identify and to quantify the chemical elements in the surface region of a solid and provides quantitative information on the chemical structure, atomic composition, and chemical bonding state. The spectral information appears from a depth of approximately 8–10 nm in maximum (151). The technique is based upon the determination of the kinetic energy of photoelectrons expelled from the core levels of sample surface atoms by absorption of monochromatic soft X-ray photons in the so-called photoelectric effect (152). Core level
Experimental Part

binding energies measured by XPS are specific to the emitting elements in a reliable way and shift due to changes in their chemical bonding environments. Photoelectrons whose binding energies can be calculated according to the following equation (153):

\[ E_B = h\nu - E_{\text{kin}} - \phi \]

where \( h\nu \) is the energy of the incident X-ray photons, \( E_B \) is the binding energy of the photoelectrons, \( E_{\text{kin}} \) is the kinetic energy of the photoelectrons, and \( \phi \) is the work function that is the energy which is necessary to transfer an electron from the Fermi level to the vacuum level (151). The energy conservation law of the photoelectric effect allows determining the core level \( E_B \) from the measurement of the \( E_{\text{kin}} \) of the corresponding photoelectrons.

XPS measurements were carried out by means of an Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK). The spectrometer was equipped with a monochromatic Al KR (\( h\nu = 1486.6 \) eV) X-ray source of 300 W at 15 kV. The kinetic energy of the photoelectrons was determined with a hemispherical analyzer set to pass energy of 160 eV for wide-scan spectra and 20 eV for the high-resolution element spectra. During all measurements, electrostatic charging of the sample was avoided by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same amount that was necessary to set the C 1s peak to 284.76 eV for the carbon of the phenyl ring (154). Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. Spectrum background was subtracted according to Shirley (155). The high-resolution spectra were deconvoluted by means the spectra deconvolution software. Free parameters of component peaks were their \( E_B \), height, full width at half-maximum, and Gaussian-Lorentzian ratio.

Selective chemical labeling reactions of primary amino groups (-NH\(_2\)) were carried out using the method by Favia et al (156). The PET fabric samples were exposed to vapor of 4-trifluoromethyl benzaldehyde (TFBA) for 60 min at room temperature before XPS analysis by placing the PET fabric in a closed glass vessel together with TFBA (1 ml) (Figure 3.2).
The aldehyde group of TFBA (II) selectively reacts with –NH\(_2\) (I) functional groups on the PET fabric surface, giving rise to the Schiff base (III) containing a trifluoromethyl group, and subsequently analyzed the surface with XPS. The F1s peaks were used for quantifying the number of –NH\(_2\) groups among all other nitrogen functionalities (157-159). According to the stoichiometric ratio of (III) the determined amount of fluorine must be three times the amount of amino groups.

### 3.3.2 Electrokinetic measurements

Determination of the electrokinetic or zeta-potential for textile fabrics are interesting to investigate distinct surface charges result from different modification steps or finishing processes such as purification and coatings used in textile industries (160-163). It is well established that the charge distribution differs remarkably between the bulk phase of a liquid and the phase boundary between a solid and a liquid. At this phase boundary, charges resulting from the dissociation of ionogenic groups at the solid surface as well as from the adsorption of ions in the bulk, will then be accumulated, i.e., the formation of what is known as an electrochemical double layer or Stern layer (164; 165). Based on this conception, the electrokinetic behavior of surfaces can be demonstrated. Using the values obtained by measuring the streaming potential between two electrodes, the zeta-potential (\(\zeta\)) can then be calculated.

Figure 3.3 shows a schematic of the electrochemical double layer based on the Gouy-Chapman-Stern-Grahame model (GCSG-model) (160; 166). According to this model, the electrochemical double layer is divided into the inner Helmholtz plane (IHP), the plane of the centers of strongly adsorbed ions; the potential at this plane is \(\Psi^{\text{IHP}}\) and the outer Helmholtz plane (OHP) that is the plane of the centers of oppositely charged ions; the potential at this plane is \(\Psi^{\text{OHP}}\). The remaining excess of charges is compensated by ions in
the so-called diffuse or mobile layer. In the electrokinetic experiment, an external force field is applied to the solid/liquid system and generates a relative movement between the fixed part and the diffuse part. The plane between the immobile and mobile planes is called “surface of shear” or “slipping plane” and the potential at this surface is called the electrokinetic or $\zeta$ potential. It depends on the surface charge density and the double-layer thickness (167).

**Figure 3.3** Schematic representation of the electrochemical double layer at the interface according to the Gouy-Chapman-Stern-Grahame (GCSG) model after (160).

In the present work, electrokinetic measurements were carried out to determine the zeta-potential of the PET surface as a function of the pH values of the electrolyte solution using the streaming potential method. Streaming potential is generated when a liquid is forced to flow directly through a parallel-plate channel formed between two sample surfaces separated by a narrow slit (Figure 3.4).

**Figure 3.4** Schematic representation of streaming measuring cell for fabrics.
The streaming potential was determined using EKA electrokinetic analyzer from Anton Paar (Graz, Austria). The pH values were adjusted with 0.1 mol·L⁻¹ HCl or 0.1 mol·L⁻¹ KOH. To prevent a significant change in the ionic strength by adding HCl and KOH, all measurements were carried out in 10⁻³ mol·L⁻¹ KCl. The apparently ζ-potential values were calculated from the measured streaming potential values by the use of the Smoluchowski equation (168).

$$\zeta = -\frac{dU}{dp} \frac{\eta \kappa}{\varepsilon_r \varepsilon_0}$$

Where U is the streaming potential, p the pressure, εᵣ and ε₀ the dielectric constant and the vacuum permittivity of the liquid phase, η the viscosity of the liquid phase and κ is the conductivity of the measuring fluid. Surface conductivity of the fabric samples was not taken into account. Furthermore, a lot of information can be gained from electrokinetic measurements, for example polyelectrolyte adsorption.

3.3.3 Kinetics measurements of wetting

The wetting properties of the PET fabric surfaces before and after plasma treatment were estimated by means of dynamic wetting measurements, which were carried out with a FibroDAT 1122HS dynamic contact angle tester (Fibro System, Sweden) equipped with a high speed video camera according to the sessile drop method. A microliter syringe was used to place a deionized water droplet (Millipore water having a surface tension of γᵥ = 72.8 mN/m at 23 °C) of a 10 µl volume on the fabric surface under investigation by a short stroke from an electromagnet (169). The strength of stroke was minimized to avoid oscillation effects. The data were collected after the water droplet stabilized on the surface. The instrument was located in a temperature-controlled laboratory maintained at 23 ± 1°C. Relative humidity of 50 ± 3 % was kept constant. The initial contact angle of water and the absorption time (i.e. time recorded after the drop had completely penetrated into the PET fabric surface) were used to evaluate the wettability of PET fabrics before and after plasma treatment. The contact angle and the absorption time of water droplets shown for each sample are averages of five single measurements (169).

3.3.4 ATR- FTIR Spectroscopy

Infrared spectroscopy can be used to identify functional groups present in polymer layers. When an infrared (IR) beam irradiates a sample, chemical bonds periodically stretch, contract, and bend (among other vibration modes) and IR radiation is absorbed at defined
wavenumbers (ν). In the ATR-FTIR sampling technique the examined film is placed on the surface of IRE and the IR beam is directed into a crystal of the relatively higher refractive index under a certain angle θ exceeding the critical angle. The beam of radiation enters from an optically dense (ATR crystal) into a less optical dense medium (sample with lower refractive index). The IR beam reflects from the internal surface of the crystal and at the reflection point an evanescent wave is created, which penetrates into the sample being in intimate contact with the ATR crystal. Some of the energy of the evanescent wave is absorbed by the sample and the reflected radiation returns to the detector. Rationing and logarithming the wavenumber v dependent intensities reordered from the coated sample IRE (I_s (ν)) and the bare reference IRE (I_R (ν)) gives the absorbance spectrum A(ν) according to

\[ A(ν) = - \log \left( \frac{I_s (ν)}{I_R (ν)} \right) \]

Practically, in this work, samples of the unmodified and different modified PET films were analyzed by ATR-FTIR spectroscopy using a commercial ATR-FTIR attachment (OPTISPEC, Zürich, Switzerland). The ATR-FTIR attachment was installed on the IFS 55 Equinox FTIR spectrometer (BRUKER Optics GmbH, Ettlingen) equipped with globar source and MCT detector. Samples (2 x 4 cm²) of the unmodified and different modified PET films were pressed against trapezoidal ZnSe internal reflection elements (IRE) (50 x 20 x 2 mm³). The IRE and film were clamped together onto a home built in-situ-ATR-FTIR cell. Spectra were recorded at 2 cm⁻¹ resolution between 4000 cm⁻¹ and 400 cm⁻¹. The examination was limited to the region 1150-1880 cm⁻¹ where the effects of annealing process can be seen.

### 3.3.5 Differential scanning calorimetry measurements (DSC)

Thermal analysis by DSC can give some insight into the structure and properties of the polymer by determination of the glass transition temperature (T_g), the melting temperature (T_m) and the degree of crystallinity (X_DSC). The T_g represents an approximate measure of conformational rigidity and the transition from a frozen state to an amorphous state whereby there is sufficient thermal energy for bond torsion to occur and for the polymer to exhibit elastomeric properties (170).

The degree of crystallinity of polyester fiber is determined by integrating the peak area of a differential scanning calorimetry curve. This method is based on a thermodynamic definition of order and it requires the absolute value of the heat of fusion of the ideal polymer crystal. The heat of fusion obtained from this is directly proportional to the crystallinity.
The measurements were conducted under nitrogen as inert atmosphere using a differential scanning calorimeter (DSC Q 1000, TA Instruments, USA). The DSC analyses have been carried out to determine the influence of plasma treatments on $T_m$, $T_g$ and $X_{DSC}$ of the unmodified and different plasma-treated PET fabrics. The samples were subjected to a heating-cooling-heating cycle between -80 to 300 ºC at a scan rate of 10 ºC/min. The results of the second heating run were generally reported. The crystallinity $X_{DSC}$ was determined, according the commonly known relationship:

$$X_{DSC} (\%) = \frac{\Delta H_m}{\Delta H^o} \times 100$$

where $\Delta H_m$ is the heat of fusion for the fiber-forming PET polymer, calculated from the area under the peak of the DSC heating curve and $\Delta H^o$ is the heat of fusion for an 100% PET polymer. The reported $\Delta H^o$ for PET is 140 J/g was used for crystallinity percent calculation (170).

### 3.3.6 Atomic force microscopy (AFM)

Surface roughness of PET fibers were characterized by AFM (NanoScope V Dimension 3100, Veeco, USA) using silicon-SPM-sensors (Budget Sensors, Bulgaria) with a tip radius lower than 10 nm and a resonance frequency of about 300 kHz. Two or three PET fibers were fastened to a steel sample mount. A tapping mode was used to scan the fiber surface. Each AFM image was analyzed in terms of arithmetic mean roughness (Ra) of 0.6 µm x 0.6 µm area on the surface of the samples. Ra of PET fibers was calculated from the following equation by the instrument software (171):

$$Ra = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} (z_{ij} - z_{cp})^2$$

Ra is the arithmetic mean roughness, N is the number of data points in the image, $i$ and $j$ are the pixel locations on the AFM image, $z_{ij}$ is the height value at $i$ and $j$ locations, $z_{av}$ is the average height value within the given area and $z_{cp}$ is the height value of the center plane.

The basic principle of AFM is the sample interacts with a sharp tip attached to the free end of the cantilever. Tips are typically made from Si$_3$N$_4$ or Si. The changes of the interactions due to surface features leads to a bending of the cantilever in contact mode or a change in amplitude (A) of the oscillating cantilever in tapping mode. The motion of the cantilever is
detected in a photodetector as a shift of the laser reflecting from the back of the cantilever. The scanner corrects the changes in the bending of the cantilever or the change in the amplitude, in order to keep the cantilever state constant. It also moves the sample during scanning. This produces a topographical image from the sample (height image) recorded from the scanner movement. Tapping mode is often useful for soft samples because it reduces the tip-sample contact time.

### 3.3.7 Scanning electron microscopy (SEM)

Surface morphologies of unmodified and different modified PET fabric surfaces were evaluated by SEM Ultra 55 equipped with field emission gun (Carl Zeiss NTS GmbH, Oberkochen, Germany) operating at electron energy of 2 keV. Prior to the analysis, the samples were sputter-coated with a thin layer 3 nm of platinum under vacuum in an argon atmosphere using a sputter coater (Bal-Tec SCD 500, USA) to avoid or minimize sample charging under the electron beam.

### 3.4 Coloration of PET fabrics by printing

#### 3.4.1 Preparation of printing pastes

The printing pastes with the anionic dyes C.I. Acid Red 18 and C.I. Acid Blue 80 were formulated according to the following recipe:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>By weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye</td>
<td>1</td>
</tr>
<tr>
<td>Guar gum</td>
<td>1.5</td>
</tr>
<tr>
<td>Urea</td>
<td>10</td>
</tr>
<tr>
<td>Ludigol</td>
<td>0.5</td>
</tr>
<tr>
<td>Citric acid*</td>
<td>0.5</td>
</tr>
<tr>
<td>Contripon AT</td>
<td>0.2</td>
</tr>
<tr>
<td>Water</td>
<td>86.3</td>
</tr>
</tbody>
</table>

* Only in the case of PET fabric surface modified with ammonia plasma or PVAm

The printing pastes with the anionic dyes C.I. Reactive Violet 2, C.I. Reactive Violet 5, C.I. Reactive Blue 5 and C.I. Reactive Black 5 were prepared according to the following recipe:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>By weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye</td>
<td>1</td>
</tr>
<tr>
<td>Sodium alginate</td>
<td>5</td>
</tr>
<tr>
<td>Urea</td>
<td>10</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>3</td>
</tr>
<tr>
<td>Contripon AT</td>
<td>0.2</td>
</tr>
<tr>
<td>Water</td>
<td>80.8</td>
</tr>
</tbody>
</table>
3.4.2 Printing and post-treatment methods

The aforementioned formulated printing pastes of the anionic dyes were applied to the unmodified and different modified PET fabrics by using a conventional flat screen-printing method (63). After printing, the printed fabric samples were dried in the air followed by steaming at 100 °C for 20 min for C.I. Acid Red 18 and C.I. Acid Blue 80. However, C.I. Reactive Violet 2, C.I. Reactive Violet 5, C.I. Reactive Blue 5 and C.I. Reactive Black 5 were fixed by thermofixation in a thermostatic oven (Memmert, Switzerland) at 180 °C for 3 min. Then, the printed fabric samples were washed with cold water and soaped using 3 g/L of non-ionic detergent (Tissocyl CSB) at 60 °C for 15 min at a liquor-to-fabric ratio of 50:1. Afterward, the samples are rinsed in cold water to remove unfixed dyes and finally air-dried.

3.5 Characterization methods of printed PET fabrics

3.5.1 Color strength measurements of printed fabrics

The PET fabrics printed under different conditions of treatments were individually tested for their color strength (K/S). The K/S values are a function of the spectral reflectance at a given wavelength and are defined as the ratio between light absorption (K) and scattering (S) characteristics of the sample. The color strength K/S values of the printed fabrics were instrumentally determined from reflectance measurements with the following Kubelka-Munk equation (172; 173):

$$\frac{K}{S} = \frac{(1-\beta)^2}{2\beta}$$

where (\(\beta\)) is the degree of remission = R/100. Reflectance (R) obtained from a software calculation is expressed as a percent value. (S) is the scattering coefficient and (K) is the absorption coefficient of the printed fabrics. The K/S\(_{\text{max}}\) value corresponded to the largest value of K/S over the scanned wavelength is commonly used to describe the color strength of a dye-substrate system (174). Therefore, the increase of the K/S\(_{\text{max}}\) value can be used as a characteristic for different surface modification approaches applied to PET.

The colorimetric measurement by reflectance was carried out in ACS imaging system CS-5 Chroma Sensor colorimeter (standard illuminant D65; 10° standard observer). The reflectance of the printed fabrics was measured over the wavelength range of 400–700 nm. In the process, the unprinted fabrics were used as a reference. Each fabric sample was
folded twice, and three scans were performed at different places on the fabric surface. The average value was recorded.

3.5.2 Color fastness of printed fabrics
Textiles are subjected to frequent washing and rubbing during their usage. Hence, color fastness of printed modified fabrics has been assessed to determine the degree of wash down. The samples were visually assessed using gray scales (175; 176). The gray scale ranges from 5, for no shade change (or no stain on the adjacent fabric), to 1, for a severe shade change (or staining), with half points (between 4 and 5, 3 and 4, 2 and 3, 1 and 2) in between.

3.5.2.1 Color fastness to washing
The color fastness to washing was determined according to the ISO standard method 105-C02 (1989). The printed samples (4x4 cm$^2$) were sewed between two pieces of cotton and wool fabrics. The composite sample was immersed in an aqueous solution containing (5 g/l soap and 2 g/l sodium carbonate) at the liquor ratio of 50:1. The bath was thermostatically adjusted to 40 °C. The test was run for 30 minutes. The samples were then removed, rinsed twice with occasional hand squeezing, then dried. Evaluation of the wash fastness was established using the gray scale reference for color change.

3.5.2.2 Color fastness to rubbing
The color fastness to rubbing was determined according to the ISO standard method 105-X12 (1987). This test is designated for determining the degree of color, which may be transferred from the surface of the colored fabric to another surface by rubbing. A colored test sample fastened to the base of a crockometer was rubbed with white crock test fabric under controlled conditions.

Dry rubbing test
The test sample was placed flat on the base of the crockometer. A white testing fabric was mounted. The covered finger was lowered onto the test sample and caused to slide back and forth 20 times by making ten complete turns at a rate of one turn/s. The white test sample was then removed for evaluation using the gray scale.

Dry rubbing test
The white test sample was thoroughly wetted out in deionized water to a 65 % pick up. The procedure was run as before. The white test samples were then air-dried before evaluation.
4 Results and Discussion

4.1 Low-pressure ammonia plasma treatment

Among nitrogen-containing plasmas, ammonia plasma is widely used to modify the surface of polymeric materials to improve their wettability, printability, and biocompatibility (177). The ammonia plasma treatment gives rise to nitrogen functionalities, such as amino (–NH$_2$), imino (–CH=NH), on polymer surfaces. The amino group seems to be one of the most attractive ones, due to the versatile applications provided by the rich amine chemistry (178).

In the work reported herein, the PET fabric was modified with ammonia plasma to control its surface reactivity and polarity. Consequently, the coupling and immobilization of different anionic molecules, particularly anionic dye molecules, can be regulated. The ammonia plasma treatments were carried out at 10, 30, 60, 120 and 600 s. Moreover, their effects on the surface properties of PET fabric were investigated.

The introduction of nitrogen-containing functional groups onto the PET fabric surface may be explained through different expected reaction mechanisms resulted from interaction between ammonia plasma reactive species and PET fabric surface (Figure 4.1) (179). It is assumed that UV, electrons and ions in ammonia plasma probably attack ester groups along the PET chain by two different routes. As a result, oxygen (route 1) or carbon (route 2) radicals will be formed at the ends of the PET polymer chains making the surface more reactive. This may lead to elimination reactions of ester groups, i.e. decarboxylation as shown in the first route. Ammonia plasma contains H radicals and N radicals like NH radicals and NH$_2$ radicals. These radicals might be involved in ester group scission and can react with carbon or oxygen radicals that were generated after ester group scission. Hence, numerous different nitrogen-containing functional groups are introduced by these reaction mechanisms as shown in the expected two routes (179; 180). In addition, the oxygen (route 1) radicals may combine with hydrogen radicals generated from ammonia plasma, which results in the formation of the oxygen-containing polar groups, such as carboxylic groups on the fabric surface.
**Route (1)**

\[
\begin{align*}
\text{Repeating unit of PET polymer} \\
\text{Ammonia plasma} \\
\text{Decarboxylation - CO}_2 \\
\text{NH}_2 \text{ radicals}
\end{align*}
\]

**Route (2)**

\[
\begin{align*}
\text{Repeating unit of PET polymer} \\
\text{Ammonia plasma} \\
\text{NH} \text{ radicals}
\end{align*}
\]

*Figure 4.1* Possible surface functionalization reactions on PET fabric using ammonia plasma.

### 4.1.1 XPS characterization

Figure 4.2 shows wide-scan XPS spectra of the unmodified PET and ammonia plasma-treated PET fabrics. A typical XPS wide-scan spectrum of the PET fabric surface (Figure 4.2a) depicts two peaks characteristic of carbon (C 1s) and oxygen (O 1s). However, after ammonia plasma treatment (Figure 4.2b), one additional peak appeared for nitrogen (N 1s). The N 1s peak indicates that the nitrogen-containing functional groups were introduced onto the surface of the PET fabric by ammonia plasma treatment.
The elemental surface compositions of surface region and the corresponding atomic ratios of the unmodified and different ammonia plasma-treated PET fabrics are summarized in Table 4.1. Surface chemical composition induced by ammonia plasma treatments was determined by XPS analysis during 30 min after modification. The stoichiometry value of the unmodified PET fabric surface calculated from the repeating unit of the PET polymer chains was found to be \([\text{O}]:[\text{C}]_{\text{stoi, PET}} = 4:10\) with \(\text{C}\) (at. %) value of 71.4 and \(\text{O}\) (at. %) value of 28.6 (181).

Table 4.1 The elemental surface composition and atomic ratios determined by XPS for the unmodified and ammonia plasma-treated PET fabrics for the indicated treatment time.\(^{(a)}\)

<table>
<thead>
<tr>
<th>Treatment time (s)</th>
<th>C (at. %)</th>
<th>O (at. %)</th>
<th>N (at. %)</th>
<th>[N]:[C]</th>
<th>[O]:[C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(^{(b)})</td>
<td>72.1</td>
<td>25.6</td>
<td>0</td>
<td>0</td>
<td>0.35</td>
</tr>
<tr>
<td>10</td>
<td>72.6</td>
<td>23.0</td>
<td>1.5</td>
<td>0.02</td>
<td>0.32</td>
</tr>
<tr>
<td>30</td>
<td>72.4</td>
<td>22.1</td>
<td>3.0</td>
<td>0.04</td>
<td>0.31</td>
</tr>
<tr>
<td>60</td>
<td>70.2</td>
<td>22.9</td>
<td>4.4</td>
<td>0.06</td>
<td>0.33</td>
</tr>
<tr>
<td>120</td>
<td>68.2</td>
<td>22.1</td>
<td>7.1</td>
<td>0.1</td>
<td>0.32</td>
</tr>
<tr>
<td>600</td>
<td>63.6</td>
<td>20.8</td>
<td>12.2</td>
<td>0.19</td>
<td>0.33</td>
</tr>
</tbody>
</table>

\(^{(a)}\) It should be noted that Si as surface contaminant is not completely removed and effect of plasma on the variation of Si at. % not involved in discussion.

\(^{(b)}\) Unmodified PET fabric
Table 4.1 demonstrates that the unmodified PET fabric surface displayed significantly lower value of [O]:[C] atomic ratio than the stoichiometrical PET. This is probably due to the adsorption of a small amount of an adventitious hydrocarbon layer onto the PET fabric surface or the residual processing agents that might deposit on the fabric surface during the manufacturing processes of the PET fabric.

On the other hand, the results obtained after the ammonia plasma treatment indicated that as the treatment time increases from 10 to 600 s, the nitrogen content increases while the carbon content decreases in the surface region. As a result, the [N]:[C] atomic ratio increases proportional to the treatment time. For instance, after the ammonia plasma treatment of PET fabric for 10 s the [N]:[C] atomic ratio increases from 0 to 0.02, while after 600 s the [N]:[C] atomic ratio value increases significantly to 0.19 indicating the incorporation of nitrogen-containing functional groups onto the PET surface. The increase in nitrogen content may be attributed to the increase in the number of reactive species, in the plasma environment increases, involved in the functionalization process (182).

Additional insight into the surface chemistry can be obtained through deconvolution of the XPS spectra to investigate what were chemical functional groups introduced onto the surface of the PET fabric after ammonia plasma treatment. The high-resolution C 1s spectra of the unmodified and ammonia plasma-treated PET fabric surface for 600 s are presented in Figures 4.3a-b. The C 1s spectrum of the unmodified PET fabric surface (Figure 4.3a) mainly contains three distinct component peaks indicated by italic letter. The component peak $A$ corresponds to unsaturated hydrocarbon –C–C–/C–H, carbon atoms in phenyl ring (284.7 eV). Component peak $C$ corresponds to C–O, methylene carbon atoms singly bonded to oxygen (286.1 eV). Component peak $E$ corresponds to O=C–O, ester carbon atoms (288.6 eV). In addition, there are shake-up peaks (291.1 eV) results from $\pi \rightarrow \pi^*$ electron transitions between the occupied and unoccupied $\pi$-orbitals of the phenyl rings. Their appearance is very typical for intact conjugated $\pi$-systems in arenes. The binding energies of these component peaks are consistent with those reported by Beamson and Briggs for clean PET films (154).

Additional component peaks were necessary to fit the measured spectrum. Component peak $D$ at (286.7 eV) represents also O–C groups. Its binding energy most likely corresponds to alcoholic groups, but considering the [C]:[O] ratio (determined from the C1s spectrum and its comparison with the ratio determined from the wide-scan spectrum) the component peak must appear from ether groups. The second additional component
peak Si shows C–Si, carbon atoms singly bonded to Si of residual processing agents. Although PET fabrics were carefully cleaned before any further modification, surface contaminants are not completely removed as shown in the presence of Si.

After ammonia plasma treatment, the C 1s spectrum of the ammonia plasma-modified PET fabric is shown in Figure 4.3b. With respect to the unmodified PET fabric (Figure 4.3a); the plasma-treated PET sample shows origin of the component peak B (285.9 eV) and component peak F (287.6) in addition to main component peaks of the unmodified PET fabric surface. Concluding from the binding energy of component peak B formation the C–N bond that may be attributed to introduction of new nitrogen-containing functional groups at the surface such as amino group (183), and the binding energy of component peak F assigned to number of functionalities, such as N=C=O and C=O groups (154).

**Determination of the –NH₂ groups by TFBA**

Direct identification and quantification of amino groups by XPS are not possible when the amino groups coexist with other nitrogen containing species with similar chemical shifts (184; 185). The basic principle of determination of the primary amino groups is to have a specific reaction between the –NH₂ functional groups and a special marker molecule. The marker molecule must have at least one element that does not exist in the original sample. Therefore, in the case of the successful reaction, the target functionality can be detected unambiguously by the new element exists in the XPS spectra. TFBA has been found to satisfy the above-mentioned criteria and was used in our study to prove the presence of –NH₂ groups (158). The aldehyde group of TFBA reacts selectively with surface-near –NH₂ groups forming a Schiff’s base containing a trifluoromethyl groups (as shown in Figure 3.3.
in experimental part). This covalently linked TFBA via imine bonds, whereby $[-\text{NH}_2]$ concentration could readily be deduced from the fluorine concentration [$F$], at the surface determined by XPS.

The labeling results in Figure 4.4 illustrate the concentration of $\text{–NH}_2$ groups for the different plasma treatment times. It can be seen that the concentration of nitrogen introduced on the surface rises to the maximum and the amount of $\text{–NH}_2$ groups is significantly lower than the amount of total nitrogen determined from wide-scan spectra. That behavior was expected, because other nitrogen-containing functional groups were produced simultaneously, such as amide groups. Furthermore, the TFBA molecule has a high steric demand. The large TFBA molecules may not be able to react with all of the amino groups on the PET fabric surface.

This labeling reaction indicates that the incorporation of primary amino groups onto the surface varies between 0.3 and 1% by the ammonia plasma. This suggests that by plasma treatment it is difficult to obtain a $\text{–NH}_2$ surface functionalization with high selectivity since other nitrogen functionalities are formed simultaneously (186). This is generally referred to as “unspecific functionalization” (187; 188). Reaction mechanisms in plasma are quite different from reactions in solutions or gas phase. Many of reactions occurring in plasma are not controlled. Hence, numerous different nitrogen-containing functional groups are expected.

![Figure 4.4](image-url)

**Figure 4.4** Atomic percent of the total nitrogen and fraction of $\text{–NH}_2$ groups that able to react with TFBA after ammonia plasma treatments as determined by XPS and TFBA labeling.
From the previous studies (158; 189), the application of IR spectroscopic in the determination of other nitrogen functionalities present at the polymer surfaces is limited. The reason behind that is the IR sampling depth higher than the outer layer onto which new functionalities are introduced. Whereas, XPS is a powerful tool in surface analysis, therefore the high-resolution N 1s XPS was taken into consideration (Figure 4.5).

![Figure 4.5 High-resolution N 1s XPS spectrum of ammonia plasma-treated (600 s) PET fabric.](image)

The high-resolution N 1s spectrum (Figure 4.5) confirmed the addition of different nitrogen functionalities to the PET surface during plasma treatment. The high-resolution N 1s spectrum was decomposed into two main component peaks (component peaks $F$ and $G$) showing the presence of the two chemical states of nitrogen. Nitrogen species with a BE around 398.9 eV attached to the phenyl ring contribute to component peak $F$. Component peak $G$ at higher BE 400.1 eV appears from nitrogen species attached on saturated carbon atoms, such as methylene groups (154; 190).

### 4.1.2 Electrokinetic measurements

The introduction of the Brønsted-basic amino groups can be additionally proved by streaming potential measurements that are very sensitive to analyze charge formation processes on solid surfaces. Figure 4.6 shows the determined zeta-potential values ($\zeta$) for the unmodified and different ammonia plasma-treated PET fabrics as a function of the pH values of an aqueous KCl with a concentration of $10^{-3}$ mol·L$^{-1}$ solution. The linear shape of the function $\zeta=\zeta$(pH) of the unmodified PET fabric sample over investigated pH range is typical for non-polar solid surfaces without dissociating surface groups. Thus, the adsorption of the potential-determining ions $\text{H}^+$ and $\text{OH}^-$ control the charge formation of the unmodified PET fabric surface.
Results and Discussion

Figure 4.6 $\zeta$-pH dependence for the unmodified PET fabric and ammonia plasma-treated PET fabric at different treatment time.

At pH < 4, the zeta-potential of the unmodified PET fabric is positive because the adsorption of $\text{H}_3\text{O}^+$ ions from the electrolyte solution onto the fabric surface. With increasing the pH value, zeta-potential decreases. At pH = 4 there is neither an excess of negative nor positive charges in the shear plane, and the corresponding zeta-potential is zero. The pH value where zeta-potential equals to 0 is called the isoelectric point (IEP = pH|$_{\zeta=0}$). At pH > IEP, negative zeta-potential values are observed due to a preferential adsorption of $\text{OH}^-$ from electrolyte solution.

The change of the interfacial charge at the PET fabric surfaces was observed after ammonia plasma treatment, which causes a remarkable shift of the IEP to a higher pH value compared to the unmodified PET fabric. The shifts of IEP toward a higher pH reflect changes of chemical structure of PET fabric surface. It was assumed that these changes caused by an additional contribution of Brønsted basic groups into the surface region of PET fabric. Even with the shortest modification time of 10 s, the IEP value is shifted towards pH 4.25 (IEP for the unmodified PET around pH 4). With longer modification time, the shift increases giving IEP for 30 s modified sample at pH 5. By extrapolating the curve of the zeta-potential for 60 s, the IEP was approximately observed at pH 6.1. If PET fabric surface is modified with ammonia plasma for 120 s the IEP is slightly shifted to about pH 6.2 and reaches approximately pH 6.5 after 600 s. According to Stern theory
Results and Discussion

(166), IEP corresponds to the number of the Brønsted basic groups on the ammonia plasma-treated PET fabric surface. In the case of all the amino groups are protonated, these ammonium species can be gradually deprotonated by increasing pH-value and, consequently, the zeta-potential value decreases, at IEP all ammonium species are deprotonated. This qualitatively corresponds to XPS results where [N]:[C] ratio dependent on the treatment time.

4.1.3 Surface morphology

In order to investigate the impact of the ammonia plasma treatment on the surface morphology of PET fabric surface AFM was carried out. Figure 4.7 shows AFM images corresponding to the unmodified and ammonia plasma-treated (600 s) PET single fibers. Indeed, no major difference can be observed between the unmodified and modified fibers. The mean roughness value (Ra) was calculated, it was 6.1 nm for the unmodified and 6 nm for the ammonia plasma-treated. Therefore, it was concluded that surface functionalization processes prevailing over etching under investigated operating conditions (191).

\[
\text{Ra} = 6.1 \text{ nm} \quad \text{Ra} = 6 \text{ nm}
\]

**Figure 4.7** Three-dimensional AFM images of PET fibers showing surface roughness of the unmodified PET fiber (a) and the ammonia plasma-treated (600 s) PET fiber (b).

4.1.4 Kinetics measurements of wetting

The wettability of materials can be characterized by wetting experiments, which is routinely evaluated based on the static contact angle, to quantify the wettability (192). However, the static contact angle cannot be used to evaluate the wetting behavior of heterogeneous structures such as textile fabrics, because water is able to penetrate the pores of fabrics by capillary forces (193). Therefore, the effectiveness of plasma treatment with
regard to wettability was investigated by the time-dependent contact angle measurements. Figure 4.8 shows time-dependent changes in the contact angle of 10 µl water droplet placed on the surface of the PET fabric before and after ammonia plasma at different treatment time.

![Image](image.png)

**Figure 4.8** Contact angles of water droplets in dependence on resting time on the unmodified PET fabric and ammonia plasma-treated PET fabric at different treatment time. The error of each measurement is ± 2°.

It was obvious that the measurements of contact angle in the first few seconds are not stable due to the oscillation effects of water droplet applied to the surface. Time-dependent contact angles of water, shown in Figure 4.8, reveal a clear difference between the unmodified and different plasma-treated PET fabric surfaces with ammonia plasma. For the unmodified PET, the contact angle of the water droplet after its stabilization is about 112° and the droplet spreading is hindered. This means that the PET fabric surface is hydrophobic; the observed hydrophobicity explains the preferential adsorption of OH⁻ ion, which was observed in the electrokinetic experiments. Besides the chemical structure of the PET fiber lacks of polar groups, the woven structure and hydrophobic processing agents that are used during the fabric production contribute in the high measured contact angle value.

On the other hand, the ammonia plasma treatment of PET fabric resulted in the production of more hydrophilic surface with increasing plasma treatment time from 10 to 600 s. At
low modification time of 10 s, the contact angle remained unchanged (Figure 4.8). As explained by the XPS results, the formed hydrophilic groups are insufficient to control the wetting behavior. Most of the surface area seems to be unmodified. As the plasma treatment time is increased to 30 s the contact angle shows an initial decrease in comparison to the unmodified PET fabric and 10 s treatment time. As the treatment time is increased to 120 s, the contact angle decreased rapidly from 112° to about 88°. Further increase in treatment time to 600 s, initial contact angles significantly decreased and water absorptivity is greatly enhanced by ammonia plasma treatment. The observed differences in the time-dependent wetting behavior can be explained by the different chemistry of the PET fabric surfaces.

Figure 4.9 illustrates the image-sequence of water droplets applied to the surface of the unmodified and ammonia plasma-treated (600 s) PET fabrics, respectively. Figure 4.9a shows that the water droplet does not spread on the unmodified PET fabric surface during the first 1.8 s and the shape of the water droplet is nearly spherical. Figure 4.9b points out that the water droplet fully spreads on the plasma-treated PET fabric surface within 1.8 s. This change in the wetting behavior can be attributed to the polar groups introduced onto the surface, which improve the wettability of the PET fabric.

![Image](image.png)

**Figure 4.9** Image sequences of water droplets applying to the unmodified PET fabric surface (a) and the ammonia plasma-treated (600 s) PET fabric surface (b).
4.1.5 Stability of the ammonia plasma-treated PET fabric

The functional groups introduced onto the PET fabric surface can be unstable and lose reactivity over time. Changes in contact angle and surface atomic composition have been used to quantify the kinetics of surface restructuring (177; 194). In this regard, the ammonia plasma treatment of PET fabrics was examined along time by a combination of XPS results (Figure 4.10) and time-dependent contact angle measurements (Figure 4.11) as surface-sensitive techniques. To examine the stability of ammonia plasma-treated PET fabric, the fabric modified for 600 s presenting high [N]:[C] atomic ratio was chosen. The modified fabric was stored in the air under normal conditions of temperature and humidity for different storage times (1, 7 and 14 days) after plasma treatment. In Figure 4.10, the ageing behavior was studied by XPS. The first-time measurements were made 1 day after modification, the [N]:[C] atomic ratio at the surface is slightly less than [N]:[C] ratio recorded immediately after plasma treatment, gradually decreased from 0.19 to 0.17 after 1 day. After 7 days of storage in air, the [N]:[C] ratio of plasma modified-PET surface was reached a value of 0.15. Afterwards, the surface composition remains nearly unchanged during the following week. Based on the results obtained from the XPS measurements during ageing, the PET fabric surface lost about 21 % of its overall nitrogen containing groups induced by plasma treatment after 14 days.

![Figure 4.10](image)

**Figure 4.10** The [N]:[C] atomic ratio of ammonia plasma-treated (600 s) PET fabric as a function of the ageing time in the air under ambient conditions.

Changes in wettability induced by the introduction of the polar functional groups can be time-dependent. Many researchers report this effect, often called ageing or hydrophobic recovery, on plasma-treated surfaces (183; 195). The ageing was evaluated by determination
of water-absorption time, which is required by the water droplet to be completely absorbed into the fabric (Figure 4.11). It was observed that the water-absorption time gradually increased in the first week of storage. Afterwards, no significant differences in water-absorption time were found after storage in the air between 7 and 14 days. This is consistent with the results of XPS analysis (Figure 4.10). It is also important to note that not all the hydrophilic nature achieved by the plasma treatment is lost during the ageing process. Several factors have been reported to influence the stability of the modified surfaces, including contamination, the chemical structure of the original polymer and the storage environment, all may contribute to the overall decay phenomena (196; 197).

The most plausible explanation of ageing phenomenon based on a process of thermodynamic relaxation. After plasma treatment, the polymer can be considered as a non-homogeneous material regarding its surface and bulk properties. From the thermodynamic point of view, the surface always has a tendency to rearrange continuously in order to minimize its surface free energy (198). Hence, allowing chain migration into the bulk of the material and reorientation of the surface polar groups away from the surface during storage. Surface rearrangement can therefore affect results from surface analyses and explain the gradual deterioration of the surface properties and the effect of wettability reversal.

![Figure 4.11](image.png)

**Figure 4.11** Effect of ageing time on the contact angles of water droplets in dependence on resting time on the ammonia plasma-treated (600 s) PET fabric. The error of each measurement is ± 2°.
4.1.6 Determination of the degree of crystallinity by DSC

In an attempt to show the effect of the ammonia plasma treatments on the bulk properties of PET fabric, DSC studies were performed on PET fabrics before and after the ammonia plasma treatment, in which the heat flow is measured as a function of temperature. The main objective of performing DSC was to investigate the effect of the ammonia plasma treatment on the \( T_m \), \( T_g \) (Figure 4.12a) and the degree of crystallinity (Figure 4.12b) of the unmodified and different ammonia plasma-treated PET fabrics.

![DSC thermograms](image)

**Figure 4.12** DSC thermograms of the unmodified and ammonia plasma-treated PET fabrics from 2\(^{nd}\) heating run (a), and the effect of plasma treatment time on percent of crystallinity for different PET fabrics (b).

It was found that DSC thermograms (Figure 4.12a) of ammonia plasma-treated PET fabrics exhibit no significant changes regarding the melting point in comparison with the unmodified PET fabric. It can be seen that the DSC thermograms of PET fabrics showed an endothermic peak with the maximum at 250 °C, which due to the \( T_m \). In addition, the thermograms do not reveal any significant features that are attributable to the surface modifications. Figure 4.12b shows the values of the degree of crystallinity for the unmodified and ammonia plasma-treated PET fabrics. It is also observed that no considerable changes are observed in the degree of crystallinity of PET fabric after the ammonia plasma treatments compared to the unmodified PET fabric. This may be due to the limited penetration depth of the plasma to the outermost surface, but the crystallinity is a bulk internal property of the polymer. Accordingly, the DSC is not sensitive enough to
Results and Discussion

detect those changes caused by plasma (at the surface). Thus, the results obtained by DSC analysis confirm that plasma treatments do not interfere with bulk properties of fabrics.

In conclusion, the ammonia plasma increases the amount of nitrogen-containing groups on the surface of PET fabric, without significant damage of the bulk material. It was also observed that ammonia plasma treatment like the most of simple plasma treatments results in diversity of functional groups produced by the multitudes of chemical reactions that take place on the PET fabric surface. To overcome this, a new tool for selective surface modification of PET fabric with amine functionalities was investigated.

Functionalized surfaces with the highest degree of retained amine functionalities seem very important for the development of functional materials (91). For that purpose, in the next part of this study, the functionalization of a hydrophobic PET fabric surface with cationic polyelectrolytes was performed. However, in order to anchor cationically charged polyelectrolytes it was necessary to produce functional surface groups having the ability to be negatively charged in aqueous environment. Therefore, the oxygen plasma treatment was used as a preliminary stage to enhance surface polarity, reactivity of PET fabric and to keep the mechanical and the physical properties of the bulk PET without serious impairment. Afterwards, cationic polyelectrolytes were immobilized on the plasma-treated surface from their aqueous solution.

4.2 Surface functionalization of PET fabric with cationic polyelectrolytes

In term of industrial applications, PDADMAC and PVAm were selected according to their applications and commercial availability. The main goal of the application of cationic polyelectrolytes is to modify the PET fabric to provide a high surface charge density required for a better interaction with anionic molecules.

4.2.1 Low-pressure oxygen plasma treatment

The reproducible functionalization of the PET fabric surface with oxygen plasma requires optimization of the operating plasma parameters. In this study, the aim of the optimization was to minimize the process of material ablation and equip the PET fabric surface with a sufficient density of carboxylic acid groups, which can dissociated in an aqueous medium and provides anchoring sites for the polyelectrolyte molecules. The chosen plasma discharge powers for this study were 100, 300 and 600 W; and for each power, a treatment time of 15 and 30 s were performed.
Indeed, when the PET fabric surface contacts with oxygen plasma, the following expected reactions (Figure 4.13) occurred at the surface of the PET fabrics. Oxygen plasma treatment generates polymer chain scissions of the ester bonds of PET by high-energy electrons and photons (UV-radiation). These chain scissions create a large amount of very reactive chain-ends, such as free radicals, which then react easily with the reactive species present in the oxygen plasma such as OH radicals, excited molecular oxygen O₂ and H radicals. At the chain-ends, these reactions create some oxidized groups like carbonyl, carboxyl and hydroxyl groups (199; 200).

**Route (1): the formation of hydroxyl groups**

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{CH}_2\text{CH}_2\text{O} & \quad \text{Oxygen plasma} \\
\rightarrow & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\cdot & \quad + \quad \text{O} \\
\text{H} & \quad \text{CH}_2\text{CH}_2\text{O} \\
\end{align*}
\]

Repeating unit of PET polymer

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\cdot & \quad + \quad \text{H}^+ \\
& \quad \rightarrow \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{OH} & \quad \text{Decarboxylation} \\
\rightarrow & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\cdot & \quad + \quad \text{OH} \\
& \quad \rightarrow \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{OH} \\
\end{align*}
\]

**Route (2): the formation of carbonyl and carboxyl groups**

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{CH}_2\text{CH}_2\text{O} & \quad \text{Oxygen plasma} \\
\rightarrow & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\cdot & \quad + \quad \text{O} \\
\text{CH}_2\text{CH}_2\text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\cdot & \quad + \quad \text{H} \\
& \quad \rightarrow \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\cdot & \quad + \quad \text{O}_2 \\
& \quad \rightarrow \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\cdot & \quad + \quad \text{H} \\
& \quad \rightarrow \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\cdot & \quad + \quad \text{OH} \\
& \quad \rightarrow \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\cdot & \quad + \quad \text{H} \\
& \quad \rightarrow \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{OH} \\
\end{align*}
\]

**Figure 4.13** Possible surface functionalization reactions on PET fabric using oxygen plasma.
To confirm chemical and morphological alteration of the PET fabric after oxygen plasma treatment at different treatment conditions, XPS, electrokinetic measurements, AFM, kinetics measurements of wetting and DSC were performed. Then the results were compared to those obtained for the unmodified PET fabric.

### 4.2.1.1 XPS characterization

The elemental surface compositions and the corresponding atomic ratio [O]:[C] of the unmodified and different oxygen plasma-treated PET fabrics determined by XPS are summarized in Table 4.2. Changes in the surface composition were noticeable for all plasma modified-PET fabrics. After oxygen plasma treatment, the [O]:[C] atomic ratio is significantly increased. The [O]:[C] atomic ratio can be further increased by a higher plasma power and a longer treatment time. The oxygen content and [O]:[C] atomic ratios do not change anymore when the plasma treatment time is increased from 15 s to 30 s at 600 W. This shows that there is a saturation of the plasma effect on the PET fabric. These obtained results suggest that oxygen plasma treatment enabled the introduction of oxygen functional groups onto the hydrophobic PET surfaces.

<table>
<thead>
<tr>
<th>Plasma Power (W)</th>
<th>Modification time (s)</th>
<th>C (at. %)</th>
<th>O (at. %)</th>
<th>[O]:[C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>72.1</td>
<td>25.6</td>
<td>0.35</td>
</tr>
<tr>
<td>100</td>
<td>15</td>
<td>62.2</td>
<td>35.5</td>
<td>0.57</td>
</tr>
<tr>
<td>300</td>
<td>15</td>
<td>61.9</td>
<td>36.0</td>
<td>0.58</td>
</tr>
<tr>
<td>600</td>
<td>15</td>
<td>56.6</td>
<td>39.9</td>
<td>0.7</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>57.6</td>
<td>38.9</td>
<td>0.67</td>
</tr>
<tr>
<td>300</td>
<td>30</td>
<td>57.1</td>
<td>39.3</td>
<td>0.68</td>
</tr>
<tr>
<td>600</td>
<td>30</td>
<td>56.5</td>
<td>39.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

In order to investigate the oxygen functional groups introduced onto the PET fabric surfaces by oxygen plasma treatment, high-resolution XPS analysis of C 1s peaks was performed. In comparison with the unmodified PET fabric (Figure 4.14a), the XPS C 1s spectrum of the oxygen plasma-treated (600 W, 15 s) PET fabric shows a high amount of
introduced oxygen-containing functional groups (Figure 4.14b). The shape of the high-resolution C 1s spectrum of the oxygen plasma-treated PET fabric is qualitatively similar to the C1s spectrum of the unmodified PET fabric in addition to two new component peaks. The first component peak B corresponding to introduced keto groups C=O (287.5 eV) which indicates a partly oxidized, but intact polymer chain. The second new component peak F at 289.6 eV indicates the presence of carboxyl groups O=C–OH. If the carbon atoms of the phenyl rings are directly involved in the oxidation reaction forming carboxylic groups, the phenyl rings must be destroyed. However, the presence of the shake-up satellite peaks in Figure 4.14b clearly shows the presence of delocalized π-electron systems of intact phenyl rings. Obviously, the oxidation reaction is largely selective to cleave the ester bond and oxidize the residual methylene group of the ethylene unit. It seems also possible to form carboxylated phenyl ring (Figure 4.13). The π-electron delocalization can include the carboxylate group, hence wider shake-up peaks are observed. These results show that the oxygen plasma treatment introduced different polar groups.

Figure 4.14 High-resolution C 1s XPS spectra of (a) unmodified PET fabric and (b) oxygen plasma-treated (600 W, 15 s) PET fabric.

4.2.1.2 Electrokinetic measurements

The XPS findings indicate that the oxygen plasma treatment introduce carboxylic acid groups, which are weak Brønsted acids. The presence of weak acidic groups should influence the electrokinetic properties. Hence, streaming potential measurements can be applied to prove the existence of Brønsted acids groups on the PET fabric surface. Figure 4.15 shows the determined zeta-potential values for the unmodified and different oxygen plasma-treated PET fabrics as a function of the pH values of an aqueous KCl with a
concentration of $10^{-3}$ mol·L$^{-1}$ solution. An alteration of the charge state was observed after the oxygen plasma treatment.

The gradual shift of IEP to a lower pH values (Figure 4.15a) indicates the contribution of Brønsted acidic groups to the interfacial charge introduced by the plasma treatment. Combined with the results obtained by high-resolution C1s spectrum (Figure 4.15b) it can concluded that the plasma treatment forms oxygen-containing groups that are acidic carboxylic acid groups (O=C–OH). Hence, the strong IEP shift is mainly caused by formation of carboxylate groups (O=C–O$^-\$) which are negatively charged and contribute to the net surface charge. Figure 4.15a shows that the higher the discharge power of the oxygen plasma treatment, the higher the shift of the IEP from about pH 4 for the unmodified PET to lower pH of about 2.6 for oxygen plasma-treated (600 W, 15 s) PET fabric indicating the increase in the number of surface acidic groups. The function $\zeta = \zeta$(pH) in the pH range before the appearance of the plateau is reached, show the stepwise dissociation of carboxylic acid groups, which is driven by OH$^-$ ions with increase pH-values. With longer modification time 30 s (Figure 4.15b) the shifts increase, giving IEP for 100 W modified PET fabric at pH value of 3.25 and for 300 W modified PET fabric at pH 2.9. If PET fabric is modified with oxygen plasma at 600 W for 30 s the shift in IEP not exceed beyond pH 2.6, and this might be due to the formation of acidic groups at the surface was saturated at 600 W for 15 s. The dissociated carboxylic acid groups
introduced by oxygen plasma can be used as anchoring sites for subsequent functionalization with cationic polyelectrolytes. High-resolution XPS spectra and streaming potential measurements confirm that the PET fabric surface was oxidized by the oxygen plasma treatment.

4.2.1.3 Surface morphology

Plasma-induced morphological changes of PET single fibers were investigated by AFM. AFM images of the unmodified and oxygen plasma-treated (600 W, 15 s) PET fibers (Figure 4.16) show no significant surface morphological changes on the PET fiber after the oxygen plasma treatment. It was found that the Ra of oxygen plasma-treated PET was nearly kept unchanged 6.3 nm after plasma compared with the Ra= 6.1 of the unmodified PET fabric. Therefore, it is concluded that surface functionalization processes prevailing over etching under investigated operating conditions (191).

![AFM images of single PET fiber showing surface roughness of unmodified PET (a) and oxygen plasma-treated (600 W, 15 s) PET fabric (b).](image)

**Figure 4.16** Three-dimensional AFM images of single PET fiber showing surface roughness of unmodified PET (a) and oxygen plasma-treated (600 W, 15 s) PET fabric (b).

4.2.1.4 Kinetics measurements of wetting

The effects of the functional surface groups introduced by the oxygen plasma treatment on the wetting behavior of PET fabrics can be observed from the time-dependent contact angle measurements. It is noticed that all of the oxygen plasma-treated PET fabrics exhibited a marked increase of wettability. It was not possible to measure the advancing or
receding contact angles of the oxygen plasma-treated PET fabric. Therefore, the wettability was evaluated by measuring water-absorption time that obtained from the time-dependent contact angle measurements. This proved a much better diagnostic tool for a systematic investigation of the wettability imparted to PET fabrics by operating under different plasma conditions. Note that for the unmodified PET fabric the water droplet was not absorbed at all but remained on the surface.

Figure 4.17a shows the variations of water-absorption time of water droplets (10 µl) on the surface of PET fabrics with respect to the discharge power at treatment time of 15 s. It was found that the water-absorption time decreased as the discharge power increased from 100 to 600 W. The water-absorption time measured immediately after the modification was always lower than 0.1 s compared with more than 100 s for the unmodified PET fabric. This suggested that the wetting behavior of the PET fabric was enhanced remarkably after plasma treatment even with short treatment time 15 s and short discharge power 100 W. It indicated the effectiveness of oxygen plasma to switch wetting behavior of PET fabric surface from hydrophobic to hydrophilic. On the other hand, increasing the exposure time from 15 to 30 s within the discharge plasma power range 100-600 W (Figure 4.17b), exhibits comparable results regarding water-absorption time. The decrease of water-absorption time can be attributed to the introduction of oxygen-containing polar groups such as carboxylic acid groups. The existence of such group was shown in the high-resolution C1s XPS spectrum (Figure 4.14b).

**Figure 4.17** Contact angles of water droplets in dependence on resting time on the unmodified PET fabric and the oxygen plasma-treated PET fabric at different treatment power for 15 s (a) and ≤ 30 s (b). The error of each measurement is ± 2°.
Figure 4.18 illustrates the image sequence of a water droplet applied to the surface of oxygen plasma-treated fabrics at 600 W for 15 s. As can be seen the droplet fully spreads on the plasma-treated PET fabric surface within 0.025 s after being dropped on it compared with the unmodified PET fabric.

![Figure 4.18](image)

**Figure 4.18** High-speed image sequences at different resting time for water droplet applying to oxygen plasma-treated (600 W, 15 s) PET fabric.

4.2.1.5 Stability of the oxygen plasma-treated PET fabric

The plasma modified fabric at 600 W, 15 s presenting a high [O]:[C] atomic ratio value of 0.7 was chosen for the stability study. It was stored in the air under normal conditions of temperature and humidity for different storage periods (1, 7 and 14 days). The stability of the modified surfaces was tested with respect to XPS and the time-dependent contact angle.

![Figure 4.19](image)

**Figure 4.19** The [O]:[C] atomic ratio for oxygen plasma-treated (600 W for 15 s) PET fabric as function of the ageing time in air under ambient conditions.
In general, long storage time of the oxygen plasma-treated PET fabrics results in a weak loss of oxygen-containing groups (Figure 4.19). Within 1 day after plasma treatment, the [O]:[C] atomic ratio increases slightly from 0.7 to 0.75. Then, it decreases as a function of storage time. The PET surface lost about 22% of its overall oxygen functionalities after 1 week and the surface composition remains unchanged during the following week. The modified PET fabric stored for 14 days keeps about 74% more oxygen than the unmodified PET fabric.

The observed increase in [O]:[C] atomic ratio from 0.7 to 0.75 after 1 day of ageing could be explained as follow. During the plasma process, the PET fabric surface is continuously bombarded by a number of particles, such as electrons, photons, and ions, which may lead to the formation of free radicals (Figure 4.13). These free radicals were trapped at and below the PET fabric surface during plasma treatments. After the samples were removed from the plasma chamber and stored in the air, these long-live free radicals become available to interact with atmospheric oxygen from the air. The existence of long-live trapped free radicals was documented in the case of the plasma-treated polymers (201). Trapped free radicals are considered one of special features in the plasma-polymerized films, for instance, styrene plasma-polymerized films (202). Yasuda et al (203) have reported on some stable radicals remain in the glass substrate as living radicals caused by UV radiation from plasma treatments. Wakida et al (204) concluded that the free-radicals intensity of the plasma-treated fibers, such as wool, silk and PET depend considerably on the plasma characteristics and their chemical constitutions.

After a storage time of 1 week in the air, the [O]:[C] atomic ratio of the outermost surface slightly decreased from value of 0.75 to 0.61. The minimization of the interfacial energy and entropic effects are assumed the driving forces of the restructuring process.

The stability of the modified surface regarding wettability of PET fabric along time has been investigated (Figure 4.20). It is evident that the initial contact angles were increased at the beginning of the measurement accompanied with a slight increase of water-absorption time. As mentioned above, the wetting results can be explained by the findings of the XPS studies.
Figure 4.20 Effect of ageing times on the contact angles of water droplets in dependence on resting time on oxygen plasma-treated (600 W, 15 s) PET fabric surface. The error of each measurement is ± 2°.

4.2.1.6 Determination of the degree of the crystallinity by DSC

DSC technique was used to investigate the effect of low-pressure oxygen plasma on the $T_m$, $T_g$ (Figure 4.21a) and the degree of crystallinity (Figure 4.22b) of the unmodified PET and different plasma-treated PET fabrics. Figure 4.21a shows the DSC thermograms of the unmodified and different oxygen plasma-treated PET fabrics. It can be seen that the $T_m$ for different oxygen plasma-treated PET fabrics were nearly similar (250 °C) to the unmodified PET fabric. The thermograms do not reveal any significant features that are attributable to the surface modifications. Additionally, experiments reveal no reduction in the glass transition temperature ($T_g \approx 80$ °C) of the unmodified and different plasma-treated PET fabrics. It is also found that, the oxygen plasma treatment with a treatment time up to 30 s at discharge power 600 W has no significant effect on the degree of bulk crystallinity (Figure 4.21b). Thus, the obtained results confirm that oxygen plasma treatments do not affect the bulk properties of the fibers.
Results and Discussion

To summarize the results of oxygen plasma treatments, it can be clearly seen that the XPS spectroscopic and electrokinetic findings prove the presence of Brønsted acidic surface groups. Such groups may play a significant role in adhesion promotion by increasing the wettability of the PET fabric surface and providing the necessary functionalities for interacting with subsequent coating layers of cationic polyelectrolytes. The optimum conditions were achieved for the plasma power of 600 W and 15 s treatment time at which no damage and saturation occurred. Subsequently, these parameters were used for the further investigations.

4.2.2 Coating of oxygen plasma-treated PET fabric with cationic polyelectrolytes

In the next step, the cationic PELs such as PDADMAC or PVAm were coupled to oxygen functionalities, which were introduced by oxygen plasma (600 W, 15 s) in the preliminary step. The concentration of the aqueous polyelectrolyte solution during adsorption varies between 0.01, 0.5, 1 and 3 wt. %.

PDADMAC contains a large number of quaternary ammonium groups. Nevertheless, PDADMAC bears quaternized ammonium groups which are considered as inert and not suitable for further chemical derivatization reactions. However, in some technical applications quaternary ammonium groups are suited to improve strongly adhesion
properties of modified surfaces to anionic molecules such as anionic dyes (205) or used as flocculant in water treatment plants (111).

In comparison with PDADMAC, PVAm is a potential polyelectrolyte candidate for many applications. Depending on the pH of the aqueous solution, the primary amino groups of PVAm can be partly protonated (−NH$_3^+$) or they can be present as charge-neutral amines (−NH$_2$). In this context, PVAm can be considered as a weak cationic polyelectrolyte. After loading PVAm on PET, a large number of the reactive primary amino groups remain available for many subsequent chemical functionalization reactions (131; 132). Besides the positive contribution of the entropy, the electrostatic interactions between the negatively charged of oxygen plasma-treated PET fabric surface and the positively charged polyelectrolytes support the adhesion between the PET and the cationic polyelectrolytes.

4.2.2.1 XPS characterization

The changes in the chemical structure of the different modified PET fabric surfaces were investigated using the XPS. Figure 4.22 compares XPS wide-scan spectra of the unmodified PET (a), oxygen plasma-treated PET (b) and PDADMAC-treated PET (c) or PVAm-treated PET (d) fabrics.

From comparing of the XPS wide-scan spectra, the adsorbed polyelectrolyte can be easily identified by the N 1s peak appeared on the PET fabric modified with PDADMAC and PVAm showing the existence of nitrogen on the PET fabric surface. In the case of PDADMAC the nitrogen originates from the quaternary ammonium groups of PDADMAC. While, N 1s peak originates from the amino and residual formamide groups of PVAm. On the other hand, the spectrum of the unmodified (Figure 4.22a) and oxygen plasma-treated PET fabrics (Figure 4.22b) showed no traces of nitrogen. This can be considered as an indication of a successful formation of a PDADMAC or PVAm layer covering the PET fabric surface.
Table 4.3 shows the elemental surface composition and the corresponding atomic ratios of different modified PET fabric surfaces determined by the XPS. After the deposition of PDADMAC or PVAm onto the oxygen plasma-treated PET fabric surface, regardless the polyelectrolytes concentration, the carbon content as well as nitrogen content increases. Meanwhile the relative oxygen content decreases in the surface region. The $\frac{[N]}{[C]}$ atomic ratio is considered as an accurate measure of the amount of deposited polyelectrolyte. In the case of PDADMAC, it was found that the $\frac{[N]}{[C]}$ atomic ratio increases from 0.03 obtained with 0.1 wt. % to 0.05 obtained with 3 wt. % of PDADMAC solution. Likewise, for the PVAm the $\frac{[N]}{[C]}$ atomic ratio increases from 0.06 obtained with 0.1 wt. % to 0.1 obtained with 3 wt. % of PVAm solution.

Figure 4.22 Wide-scan XPS spectra of the unmodified PET fabric (a), oxygen plasma-treated (600 W, 15 s) (b), PDADMAC-treated PET obtained with $C_{PDADMAC} = 3$ wt. % (c) and PVAm-treated PET obtained with $C_{PVAm} = 3$ wt. % (d). The intensity of all spectra were related to the O 1s peak.
On the other hand, the [O]:[C] atomic ratio decreased from 0.7 to 0.31 when the oxygen plasma-treated PET fabric was treated by 3 wt. % of the PDADMAC solution. Similarly, treating the oxygen plasma-treated PET fabric surface with 3 wt. % PVAm solution decreases the [O]:[C] atomic ratio from 0.7 to 0.27. This indicates that, carboxylic acid groups or their dissociated forms are widely covered by the applied polymers. Therefore, they play a significant role in the adhesion promotion of PDADMAC and PVAm onto the PET fabric surface.

The N 1s peak appears only from the polyelectrolyte layer. Therefore, the [N]:[C] atomic ratio is considered an accurate measure of the adsorbed polyelectrolytes amount. According to Table 4.3, the PET fabric modified by the PVAm revealed significantly higher [N]:[C] atomic ratio values in comparison to the PET fabric modified by PDADMAC. This is associated with a strong electrostatic repulsion between positively charged quaternary ammonium groups in PDADMAC chains. The electrostatic repulsion makes PDADMAC chains stiff and stretched, and consequently, hampering the adsorption of PDADMAC onto the PET fabric surface. Moreover, Cl\(^-\) counterion may shield the interaction between the PDADMAC chains and carboxylate groups on the oxygen plasma-treated PET fabric (Figure 4.23). In addition, it contributes to decrease the

<table>
<thead>
<tr>
<th>Modification conditions</th>
<th>C (at. %)</th>
<th>O (at. %)</th>
<th>N (at. %)</th>
<th>[N]:[C]</th>
<th>[O]:[C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified PET fabric</td>
<td>72.1</td>
<td>25.6</td>
<td>0</td>
<td>0</td>
<td>0.35</td>
</tr>
<tr>
<td>Oxygen plasma-treated PET</td>
<td>56.6</td>
<td>39.9</td>
<td>0</td>
<td>0</td>
<td>0.7</td>
</tr>
<tr>
<td>0.1 wt. % PDADMAC</td>
<td>65.4</td>
<td>29.6</td>
<td>2.0</td>
<td>0.03</td>
<td>0.45</td>
</tr>
<tr>
<td>0.5 wt. % PDADMAC</td>
<td>66.1</td>
<td>28.3</td>
<td>2.3</td>
<td>0.035</td>
<td>0.43</td>
</tr>
<tr>
<td>1 wt. % PDADMAC</td>
<td>67.7</td>
<td>26.0</td>
<td>3.1</td>
<td>0.046</td>
<td>0.38</td>
</tr>
<tr>
<td>3wt. % PDADMAC</td>
<td>69.9</td>
<td>21.6</td>
<td>3.7</td>
<td>0.053</td>
<td>0.31</td>
</tr>
<tr>
<td>0.1 wt. % PVAm</td>
<td>71.5</td>
<td>22.6</td>
<td>4.6</td>
<td>0.06</td>
<td>0.32</td>
</tr>
<tr>
<td>0.5 wt. % PVAm</td>
<td>72.9</td>
<td>20.8</td>
<td>5.5</td>
<td>0.07</td>
<td>0.28</td>
</tr>
<tr>
<td>1 wt. % PVAm</td>
<td>72.2</td>
<td>20.2</td>
<td>6.7</td>
<td>0.09</td>
<td>0.28</td>
</tr>
<tr>
<td>3wt. % PVAm</td>
<td>72.3</td>
<td>19.4</td>
<td>7.4</td>
<td>0.1</td>
<td>0.27</td>
</tr>
</tbody>
</table>
adsorbed amount of PDADMAC (206; 207). As a result, during washing of PDADMAC/PET fabric, all weakly bounded macromolecules were removed from the PET fabric surface, while the strong-deposited PDADMAC remained onto the surface.

\[
\text{NH}_3\text{H}N\text{H}_2\text{O}O\text{O}N\text{Cl}\text{Cl}^\ominus
\]

**Figure 4.23** Schematic representation of counter-ion effect on the adsorption of PDADMAC at the oxygen plasma-treated PET fabric.

In contrast to the PDADMAC, the PVAm copolymer with a degree of hydrolysis higher than 90 % contains, in excess, non-protonated amino groups at working pH 8. Hence, the PVAm macromolecules seem to be more flexible and, therefore, a higher amount of PVAm was adsorbed onto the PET fabric surface.

Besides the electrostatic interaction between PVAm layer and the oxygen plasma-treated PET fabric surface, the electron pair transfer from the n-electrons of the amino groups to the conjugated π-electron in phenyl ring in the PET also contributes to the stability of the adsorbed PVAm layer. Moreover, the PVAm layer has been stabilized by a subsequent thermal treatment. Where the amide groups have been formed between the primary amino groups of the PVAm, and the carboxylic groups introduced onto the PET fabric surface by oxygen plasma (Figure 4.24). The formation of the amide groups is supported by ATR-FTIR analysis, which will be discussed later.

\[
\text{NH}_3\text{H}N\text{H}_2\text{O}O\text{O}N\text{Cl}\text{Cl}^\ominus + \text{HO}_2\text{C}_2\text{O} \rightarrow \text{HO}_2\text{C}_2\text{O} + \text{NH}_3\text{H}N\text{H}_2\text{O}O\text{O}N\text{Cl}\text{Cl}^\ominus
\]

**Figure 4.24** Schematic representation of heat-induced cross-linking reaction.
In comparison with the oxygen plasma-treated PET fabric surface (Figure 4.25b), the high-resolution C 1s XPS spectra of PDADMAC-treated PET (Figure 4.25c) and PVAm-treated PET fabrics (Figure 4.25d) contain an additional component peak \( G \) at 286.3 eV. It arises from C–N\(^+\) and C-N bonds showing the presence of PDADMAC and PVAm, respectively.

**Figure 4.25** High-resolution C 1s XPS spectra of the unmodified PET fabric (a), the oxygen plasma-treated (600 W, 15 s) PET fabric (b), PDADMAC-treated PET fabric obtained with \( C_{PDADMAC} = 3 \) wt. % (c), and PVAm-treated PET fabric obtained with \( C_{PVAm} = 3 \) wt. %.

Generally, in high-resolution N 1s XPS spectra, nitrogen bound to carbon in primary, secondary or tertiary amines or amides typically occurs at BE values of 399–400 eV. Whereas, cationic quaternary ammonium and protonated amino groups nitrogen species are significantly shifted to a higher BE values of 401.5–402.5 eV. The high-resolution N 1s XPS spectrum of the PDADMAC-treated PET fabric (Figure 4.26a) was decomposed into two component peaks. This indicates the presence of both “uncharged” N–C (component peak \( L \)) and “charged” quaternary nitrogen C–N\(^+\) (component peak \( M \)) species. It is known that PDADMAC has fully quaternized nitrogen atoms, and does not contain uncharged primary, secondary or tertiary amines. The existence of this uncharged nitrogen in the
commercial product may be attributed to the small impurities or possibly due to the undesired free-radical side-reactions occurring during the cyclopolymerisation. These uncharged nitrogen species may be part of the polymer backbone or distinct uncharged moieties (208).

![Figure 4.26](image)

**Figure 4.26** High-resolution N 1s XPS spectrum of PDADMAC-treated PET fabric obtained with $C_{PDADMAC} = 3$ wt. % (a), and PVAm-treated PET fabric obtained with $C_{PVAm} = 3$ wt.% (b).

The high-resolution N 1s spectrum of the PVAm-treated PET (Figure 4.26b) was decomposed also into two component peaks ($M$ and $L$). The amino groups of the PVAm polymer can be protonated by hydronium ions. Figure 4.26b shows such protonated amino groups (component peak $M$), clearly separated from the non-protonated amino groups (component peak $L$). Nitrogen involved in the amide groups contributes to component peak $L$. The ratio of the two component peak areas $[M]:[L]$ can be considered as the protonation-deprotonation equilibrium of the amine-functionalized surface (131; 132).

### 4.2.2.2 ATR-FTIR spectroscopy

The ATR-FTIR spectra of the PVAm-treated PET fabric before and after the thermal treatment at 120 °C were compared. As well as the unmodified and the oxygen plasma-treated PET fabrics were obtained to follow the changes in the functional groups after each modification step (Figure 4.27).

It was found that, the IR spectrum of the plasma-treated PET did not show remarkable changes when compared to the unmodified PET fabric. Although, the XPS and streaming potential measurements revealed the introduction of new oxygen functionalities onto PET fabric surface by oxygen plasma treatment.
Results and Discussion

Figure 4.27 ATR-FTIR spectra of the unmodified PET fabric (a), the oxygen plasma-treated (600 W and 15 s) PET fabric (b), PVAm-treated PET before (c) and after heat treatment at 120 °C (d). The spectra have been shifted vertically for clarity.

This can be ascribed to the surface chemical changes resulting from plasma treatment are confined to a very thin surface layer. Hence, the local concentration of the formed oxygen functionalities in this surface layer is not high enough to be sensed by ATR-FTIR spectroscopy. In Figure 4.27, ATR-FTIR spectra of the PET samples modified with 3 wt. % of PVAm before (Figure 4.27c) and after (Figure 4.27d) thermal treatment on the PET fabric surface are given. Before thermal treatment, the formed layer is confirmed by the complete disappearance of the characteristic absorption bands at 1715 cm\(^{-1}\) (\(\nu(C=O)\)) and 1245 cm\(^{-1}\) (stretching \(\nu(C-O)\)) of the ester groups of PET, since the PET fabric is covered by PVAm. Therefore, new characteristic absorption bands at 1670 cm\(^{-1}\) (amide I, mainly \(\nu(C=O)\) stretching) and 1580 cm\(^{-1}\) (amide II, mainly \(\nu(NH)\) bending) were formed indicating the formation of amide groups onto the PET fabric surface. After thermal treatment (Figure 4.27d), it is obvious that the intensity of both absorption bands at 1670 and 1580 cm\(^{-1}\) have increased in comparison to sample before thermal treatment.

4.2.2.3 Electrokinetic measurements

Streaming potential measurements are very sensitive to analyze charge formation processes on solid surfaces. With increasing the pH value of an ambient aqueous solution, the
carboxylic groups existing on the solid surface progressively undergo dissociation reactions. The formed carboxylate groups (O=C–O⁻) are negatively charged and contribute to the net surface charge. The adsorption of polyelectrolytes at the charged surface is used frequently for charge reversal \( (209; 210) \). The changes induced by coating of the PET fabric surface with PDADMAC or PVAm can be characterized by electrokinetic measurements. The coating of plasma modified-PET fabric with different concentrations (0.1, 0.5, 1 and 3 wt. %) of PDADMAC aqueous solution was investigated (Figure 4.28).

![Figure 4.28](image)

**Figure 4.28** ζ-pH dependence for the unmodified PET fabric, the oxygen plasma-modified (600 W, 15s) PET fabric and PDADMAC-treated PET fabrics obtained with different concentrations of PDADMAC.

The effects of oxygen plasma treatments of PET fabric on the IEP values have already been discussed. After coating plasma-treated PET fabric surface with PDADMAC, a positively charged surface was observed over the pH-range changed in dependence of the concentration of the PDADMAC solutions. As a result, the IEP values display a significant shift towards higher pH values as the concentration of PDADMAC increases. For example, the adsorption from a lower concentrated PDADMAC solution \( (C_{PDADMAC} = 0.1 \text{ wt. %}) \) is characterized by IEP value that was significantly shifted from about 2.6 in the case of oxygen plasma-treated PET to about 7.5 in the case of PDADMAC-treated PET fabric. With increasing concentration of PDADMAC, the IEP values gradually shift to higher
values up to pH 10.8 ($C_{PDADMAC} = 3$ wt. %), approximately. The curve shapes clearly show the presence of plateau origins from the positive charged quaternary ammonium groups at high concentration of the PDADMAC. The shift of IEP values can be considered as the formation of more closed and dense PDADMAC layer on the fabric surface, shielding charges of the oxygen plasma modified-PET fabric surface.

Similarly, after adsorption of PVAm from different aqueous solution (0.1, 0.5, 1 and 3 wt. %.) lead to different IEP values (Figure 4.29). The adsorption from a lower concentrated PVAm solution ($C_{PVAm} = 0.1$ wt. %) is characterized by IEP value which is significantly shifted from about 2.6 in the case of oxygen plasma-treated PET to about 8 in the case of PVAm-treated PET. The adsorption from higher concentrated PVAm solution ($C_{PVAm} = 0.5$ wt. %) increases the shift of the IEP value to the pH 8.5. With increasing concentration of PVAm solution the IEP gradually shifts towards higher value pH 9.3 ($C_{PVAm} = 3$ wt. %).

This behavior is resulted from the existence of potential amine groups on the outermost surface of the modified PET after the adsorption of PVAm. In the pH range < IEP, all amino groups that able to be positively charged are protonated. With increasing OH⁻
Results and Discussion

concentration, the protonated amines were gradually deprotonated in the aqueous solution, consequently, the zeta-potential values decreased. This confirmed that only hydronium and hydroxyl ions determine the surface potential, and indicate that the PVAm is covering the PET fabric.

Moreover, the streaming potential measurements demonstrated that the formed PVAm or PDADMAC layers onto the oxygen plasma-treated PET fabric surface were able to resist the strong shear forces during the measurement. In the electrokinetic experiment, the streaming liquid with a pressure of 250 mbar, in a maximum, causes a considerable mechanical shear stress on the coated solid surface. Accordingly, if the formed polyelectrolyte layers are removed during measurements, then either the IEP will be shifted to a lower pH value, or the $\zeta = \zeta(pH)$ functions seem to be discontinuous. Indeed, these two assumptions have not occurred. This is an excellent proof for the mechanical stability of the polyelectrolyte layers built-up on the plasma-treated surfaces.

The results obtained by electrokinetic investigation were in a good agreement with the XPS. The increase of PDADMAC or PVAm concentration leads to a significant increase of the measured [N]:[C] atomic ratio (Table 4.3) as well as shifts the IEP values of polyelectrolyte modified PET fabric to higher pH values. It is worth mentioning that, the results of PVAm adsorption show chemically defined PET fabric surface decorated with amino groups in comparison with ammonia plasma treatment.

4.2.2.4 Surface morphology

The SEM images of different modified PET fabric surfaces were given in Figure 4.30, to follow the morphological changes after each modification step. The SEM images of the surfaces were measured at a magnification of 30000X. Figures 4.30a and b illustrate the surface of the unmodified PET fabric and the plasma-treated PET, respectively. The surfaces are relatively smooth with some contaminants especially in Figure 4.30b. Moreover, these SEM images do not reveal significant differences between them, indicating that there was no etching occurred to the fabric surface after oxygen plasma treatment.
Results and Discussion

Figure 4.30 SEM images of the unmodified PET fabric (a), oxygen plasma-treated (600 W, 15s) PET fabric (b), PDADMAC-treated PET fabric obtained with a $C_{\text{PDADMAC}} = 3$ wt. % after rinsing (c), and PVAm-treated PET obtained with a $C_{\text{PVAm}} = 3$ wt. % after rinsing (d).

After coating the oxygen plasma-treated PET fabric surface with different cationic polyelectrolytes, it can be seen that polyelectrolytes adhered to PET fabric surface. In the case of PDADMAC, the surface is not fully covered by a layer but by separated islands (Figure 4.30c). The SEM image in Figure 4.30d shows a uniform coating of PVAm layer on the surface of the PET fabric.

4.2.2.5 Kinetics measurements of wetting

It was found that a water droplet placed on the polyelectrolyte modified PET fabric surface was absorbed within a few seconds, and it was not possible to measure the contact angle of the coated PET. The degree of wettability was evaluated by measuring the water-absorption time. As already explained for the unmodified PET fabric, the water droplet was not absorbed at all but remained on the surface within the investigated time range. In the case of the polyelectrolyte-treated PET fabric surface, there are excess of polar groups on the outermost PET fabric surface, which are still not interacted with the
opposite charges on the oxygen plasma-treated PET fabric. This excess of polar groups improves the wettability of polyelectrolyte-treated surfaces (Figure 4.31). Moreover, Figure 4.31 compares the water-absorption time of the unmodified PET and different modified PET fabrics.

It was found that, the water-absorption time decreases in the order: unmodified PET > PDADMAC-treated PET > PVAm-treated PET > oxygen plasma-treated PET fabrics. This suggests that the adsorption of the polyelectrolytes has a slight effect and decreases the surface wettability of the plasma modified-PET fabric surface.

\[\text{Figure 4.31} \quad \text{Contact angles of water droplets in dependence on resting time on the unmodified PET fabric, oxygen plasma-treated (600 W, 15 s) PET and plasma modified-PET coated with PDADMAC and PVAm obtained with 3 wt. % of polyelectrolyte. The error of each measurement is } \pm 2^\circ.\]

The decrease in the water-absorption time after polyelectrolyte adsorption on the plasma modified-PET fabric surface might be explained by the fact that, the absorption of water by a textile is largely determined mainly by two parameters. The first one is the surface free energy of the fiber material, and the second one is the capillary effects of the yarn and the fabric (193). A coating covering the PET fabric surface can influence the absorption in several ways. The coating can act as a barrier, preventing a direct contact of the liquid with the fibers, stopping or at least decelerating the absorption by the fiber material. The coating
can also influence the capillary forces by blocking pores; therefore, it changes the wettability of the fabric.

In conclusion, the surface modification of PET fabric by the attachment of cationic polyelectrolytes onto PET fabric surface provides a simple means to modify PET fabric and makes it wettable. The anchoring polyelectrolyte layer can also serve as binding sites for desirable attachment of other functional molecules, which are able to strongly complex with the introduced amine functionalities. In particular, Section 4.3 demonstrates the interaction of different modified PET fabrics towards various classes of the anionic dyes, in order to evaluate the effectiveness of different surface modifications.
4.3 Surface activity of modified PET fabrics towards anionic dyes

Coloration of PET fabrics with anionic dyes, namely acid and reactive dyes, is generally impossible. This is attributed to, the fact that, the unmodified PET does not contain amine groups in their structure needed for the dye/fiber reaction mechanism. Therefore, the efficiency of different surface modifications have been compared in terms of K/S absorption spectra and fastness test obtained from the printing experiments with different classes of anionic dyes.

4.3.1 Anionic acid dyes

In order to evaluate the activity of different modified PET fabrics towards anionic acid dyes, four different sets of PET fabrics: unmodified PET, ammonia plasma-treated PET, PDADMAC-treated PET and PVAm-treated PET were independently printed with two different acid dyes. Which are C.I. Acid Red 18 and C.I. Acid Blue 80 dyes the structure of the two dyes are shown in Figure 4.32.

![Chemical structures of the anionic acid dyes](image)

**Figure 4.32** Chemical structures of the anionic acid dyes used in this work as an example for PET fabrics coloration.

Figure 4.33 shows several K/S absorption spectrum in the visible region of C.I. Acid Red 18 or C.I. Acid Blue 80 dyes after application on different modified PET fabric. The K/S absorption spectra of different modified PET fabrics were compared to the unmodified PET fabric. The results displayed that the ammonia plasma treatments, (Figures 4.33a-b), had no positive effect on the fixation of neither of C.I. Acid Red 18 nor C.I. Acid Blue 80 molecules, regardless of the ammonia plasma treatment time.
Figure 4.33 K/S absorption spectra of different PET fabrics printed with C.I. Acid Red 18 after ammonia plasma treatment (a), PDADMAC coating (c), PVAm coating (e), and printed with C.I. Acid Blue 80 after ammonia plasma treatment (b), PDADMAC coating (d) PVAm coating (f).
Since the negatively charged dye anions exhibit electrostatic attraction towards the positively charged groups, such as protonated amine (Figure 4.34). Therefore, it may be postulated that the surface functional groups introduced by ammonia plasma treatment are insufficient and not effective in fixing dye molecules on the PET fabric surface. The most plausible explanation based on the XPS results (Figure 4.4). The ammonia plasma treatment introduces a great variety of different nitrogen-containing functional groups rather than amine groups, which are needed as anchoring sites for the binding between the PET fabric surface and anionic dyes.

In contrast to the ammonia plasma-treated PET fabric, it was found that the printed PDADMAC-treated PET (Figures 4.33c-d) and PVAm-treated PET fabrics (Figure 4.33e-f) exhibited K/S\(_{\text{max}}\) values remarkably higher than the unmodified PET fabric. The results indicated that K/S\(_{\text{max}}\) values depend on the amount of accessible functional groups within the surface, which can chemically bind acid dye molecules. Therefore, The K/S\(_{\text{max}}\) values increases gradually with increasing the concentration of polyelectrolyte solution from 0.1 to 3 wt. %. Moreover, when the polyelectrolyte-anchoring layer on the PET fabric is in contact with water of anionic dye printing pastes, it swells and dye molecules become embedded in this layer. As a result, good fixation of the dye molecules is achieved. This explanation is supported by the dependence of K/S\(_{\text{max}}\) values on the adsorbed amount of polyelectrolyte as shown in the Figure 4.33. The modified PET fabric surfaces with 3 wt. % polyelectrolyte solution has the highest K/S\(_{\text{max}}\) among all fabric samples. The extent of improvement in K/S\(_{\text{max}}\) values reflects the positive impacts of these modification approaches.

i) Protonation and cation formation

\[
\text{PET} - \text{NH}_2 \quad \quad \rightarrow \quad \text{PET} - \text{NH}_3^+ 
\]

ii) Dissociation of dye molecules

\[
\text{Dye} - \text{SO}_3\text{Na} \quad \quad \rightarrow \quad \text{Dye} - \text{SO}_3^- + \text{Na}^+ 
\]

iii) Fiber/Dye bonding

\[
\text{PET} - \text{NH}_3^+ + \text{Dye} - \text{SO}_3^- \quad \quad \rightarrow \quad \text{PET} - \text{NH}_3^+ \text{O}_3\text{S} - \text{Dye} 
\]

**Figure 4.34** The binding mechanism of acid dye with modified PET fabric surface.
It is clearly seen from Figure 4.33 that, the PVAm-treated PET fabric exhibited $K/S_{max}$ values significantly higher than the PDADMAC-treated PET fabric for C.I. Acid Red 18 (Figure 4.33c,e) and C.I. Acid Blue 80 (Figure 4.33d,f). For instance, the $K/S_{max}$ value was 1.8 for PVAm-treated PET printed with C.I. Acid Red 18 compared to 0.9 in the case of PDADMAC-treated PET fabric obtained with 3 wt. % polyelectrolyte concentration. In other words, the PDADMAC-treated PET fabric may have a lower accessibility of acid dyes compared with PVAm-treated PET fabric. The variation between PDADMAC and PVAm comes from the strong interactions of PDADMAC toward its Cl$^{-}$ counter ions and consequently forms weaker complexes with anionic sulphonic acid groups in dye structure. This can be also attributed to, as discussed before, the adsorbed amount of PVAm is higher than the adsorbed amount of PDADMAC. Then, PVAm layer provides more anchoring sites for anionic dye molecules.

It is important to note that the coloration of PET fabric becomes dependent on the properties of the top layer rather than its chemical structure. Accordingly, it can be concluded that creating a tailor-made surface with PVAm or PDADMAC layer improve the coloration of PET fabric toward anionic acid dyes without changes in the bulk properties.

### 4.3.2 Anionic reactive dyes

As a part, of continuing interest in exploring the viability of the plasma-based modified PET fabric surface toward anionic dyes. The amino groups are studied to immobilize anionic reactive dyes onto ammonia plasma-treated PET or PVAm-treated PET fabrics via covalent bonds. This class of dyes is commonly used for cellulosic substrates coloration.

Figure 4.36 shows the K/S absorption spectrum of three sets of PET fabrics: the unmodified PET, ammonia plasma-treated PET and PVAm-treated PET fabrics printed with two types of anionic reactive dyes. C.I. Reactive violet 2 and C.I. Reactive Blue 5 are typical MCT dyes as well as C.I. Reactive Violet 5 and C.I. Reactive Black 5 dyes are typical VS dye (Figure 4.35).
The results obtained with anionic reactive dyes reveal a behavior similar to anionic acid dyes (Figure 4.33). As shown in Figure 4.36, irrespective of the used dye structure, $K/S_{\text{max}}$ values are always noticed higher for prints obtained using PVAm-treated PET fabrics as compared to unmodified and ammonia plasma-treated PET fabric.
Figure 4.36 K/S absorption spectra of ammonia plasma-treated PET fabric printed with C.I. Reactive Blue 5 (a) and with C.I. Reactive Violet 2 (b). K/S absorption spectra of PVAm-treated PET printed with C.I. Reactive Blue 5 (c), C.I. Reactive Violet 2 (d), C.I. Reactive Violet 5 (e) and C.I. Reactive Black 5 (f).
Additionally, it is clearly seen in Figure 4.36 that the K/S\textsubscript{max} values of the printed fabrics increase with increasing concentration of PVAm solution from 0.1 to 3 wt. %. For instance, the K/S\textsubscript{max} value of about 2 was obtained by 3 wt. % compared to about 0.6 for 0.1 wt. % PVAm-treated PET printed with C.I. Reactive Violet 5. This could be attributed to the relatively higher primary amino groups, which in turn brings a significant increase in the dye binding sites.

Different binding mechanisms govern the fixation of different anionic reactive dye systems according to the scheme shown in (Figure 4.37).

![Diagram of binding mechanisms](image)

**Figure 4.37** Schematic representation of the binding mechanism of (a) MCT dyes and (b) VS dyes with modified PET fabric surfaces containing –NH\textsubscript{2} groups.

Coloration with reactive dyes differs from all other applications of water-soluble dyes insofar as the final goal is to achieve a dye/fiber covalent bond. The covalent bonds are usually formed as depicted in Figure 4.37, where amino groups representing the fiber nucleophiles are involved in nucleophilic substitution (Figure 4.37a) or addition reactions (Figure 4.37b). In nucleophilic substitution reactions a leaving group in the reactive dye systems basing on halogenated nitrogen heterocyclic, is displaced as a result of an interaction with a nucleophilic group such as,–NH\textsubscript{2}, on the modified PET fabric surface under alkaline conditions.

The second pivotal dye/fiber reaction includes nucleophilic addition reaction involving an activated double bond. The sulphatoethylsulphone group of C.I. Reactive Violet 5 and C.I. Reactive black 5 is readily β-eliminated under alkaline conditions to produce an activated
Results and Discussion

VS group. The schematic representation of the reaction of VS group with the amino groups present on the modified PET fabric surfaces shown in Figure 4.37b.

Table 4.4 gives the $\lambda_{\text{max}}$ values of the investigated dyes in aqueous solution and for the dye/polycation pairs on PET fabric surface. It was observed that the $\lambda_{\text{max}}$ values of the dyes on polyelectrolyte-modified PET fabric shift to longer wavelengths. In the published literature (211), the previously reported results explained the new absorption spectra of the anionic acid dye/cationic polyelectrolyte pairs by the intermolecular interaction of the cationic sites on polyelectrolytes with the anionic sulfonate groups ($-\text{SO}_3^-$) of anionic dye molecules. In addition, there have been many other reports concerning bathochromic spectral shifts, which depend on the aggregation and adsorption state of dyes on the external surface or embedded in a polyelectrolyte layer (212-214). Besides the aggregations, the red shift of anionic acid dye/PVAm pairs can be explained in terms of a large number of primary amino groups involved in electron pair donor-acceptor interaction with $\pi$-system (215) in C.I. Acid Red 18 and C.I. Acid Blue 80.

The observed red shift of reactive dyes on PVAm-treated PET fabric is invoked as evidence for the intermolecular interaction between the reactive dyes and primary amino groups on PVAm-treated PET fabric surface. That interaction resulted in an increase in the electron density on the dye chromophore.

<table>
<thead>
<tr>
<th>Dye used</th>
<th>$\lambda_{\text{max}}$ in H$_2$O [nm]</th>
<th>$\lambda_{\text{max}}$ of the dye/PDADMAC pairs on PET fabric [nm]</th>
<th>$\lambda_{\text{max}}$ of the dye/PVAm pairs on PET fabric [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.I. Acid Red 18</td>
<td>507</td>
<td>512</td>
<td>511</td>
</tr>
<tr>
<td>C.I. Acid Blue 80</td>
<td>581, 625</td>
<td>587, 640</td>
<td>587, 640</td>
</tr>
<tr>
<td>C.I. Reactive violet 2</td>
<td>551</td>
<td>Not applied</td>
<td>580</td>
</tr>
<tr>
<td>C.I. Reactive Blue 5</td>
<td>600</td>
<td>Not applied</td>
<td>630</td>
</tr>
<tr>
<td>C.I. Reactive violet 5</td>
<td>560</td>
<td>Not applied</td>
<td>580</td>
</tr>
<tr>
<td>C.I. Reactive Black 5</td>
<td>597</td>
<td>Not applied</td>
<td>610</td>
</tr>
</tbody>
</table>
4.3.3 Fastness properties of colored PET fabrics

The permanency of the bond between the dye molecules and the surface of different modified PET fabrics can be investigated by the fastness tests of printed PET fabrics. Table 4.5 depicts the color fastness results to washing and rubbing of printed polyelectrolyte-modified PET fabrics using C.I. Acid Red 18 and C.I. Acid Blue 80. The fastness properties were visually assessed using standard gray scale \( (175; 176) \). The color fastness ratings for the unmodified and ammonia plasma-treated PET fabrics are not given since there is no affinity between the used dyes and PET surfaces. The gray scale ranges from 5, for no shade change, to 1, for a severe shade change with half points (between 4 and 5, 3 and 4, 2 and 3, 1 and 2) in between.

<table>
<thead>
<tr>
<th>Polyelectrolyte Polyelectrolyte con. (wt. %)</th>
<th>C.I. Acid Red 18</th>
<th>C.I. Acid Blue 80</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Washing fastness</td>
<td>Rubbing fastness</td>
</tr>
<tr>
<td></td>
<td>Alteration</td>
<td>Dry</td>
</tr>
<tr>
<td>PDADMAC</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2-3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2-3</td>
</tr>
<tr>
<td>PVAm</td>
<td>0.1</td>
<td>2-3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

It was observed that, the color fastness to washing of printed polyelectrolyte-modified PET fabrics in terms of shade change (alteration) is comparable for two dyes. Gray scale ratings of alteration vary in the range between moderate (2) to good (3). The lower ratings in washing fastness can be explained by the positively charged sites introduced onto PET fabric by cationic PELs can be occupied by OH\(^{-}\) at the pH 10 of fastness test, and a large amount of dye desorbs into the soap solution, which makes alteration rating lower than expected from previous reported results \( (216) \).
Another property of the printed polyelectrolyte-modified PET fabrics that deserves assessment is fastness to rubbing. Rubbing fastness of the samples is assessed in terms of dry and wet rubbing. Table 4.5 indicates that polyelectrolyte-modified PET fabrics printed using C.I. Acid Red 18 and C.I. Acid Blue 80 show comparable rubbing fastness properties. In all cases, the rubbing fastness results range between moderate (2) and good (3). The lower ratings in rubbing fastness can be explained as the positively charged sites, which are introduced either by PDADMAC or by PVAm, are concentrated on the surface of the PET fabric. Consequently, much acid dyes are attracted at the modified PET fabric surface. This is the reason for the reduction in rubbing fastness. When the printed samples were rubbed by a test-fabric, a large amount of dye was transferred to the test-fabric.

Rating of the obtained fastness properties reflects that, the polyelectrolyte layer coating the PET fabric surface plays a significant role in fastness properties. The wash fastness properties of the printed PET fabrics modified with PVAm are better than those modified with PDADMAC. These results again suggest that the stability of PVAm layer improves the fastness properties to washing.

The stability of the polyelectrolyte coating layer was ascertained by XPS measurements. The [N]:[C] atomic ratios (Table 4.6) for different polyelectrolyte-modified PET fabrics were compared before and after washing under similar conditions of color fastness to washing test (pH10, 40 °C for 30 min).

<table>
<thead>
<tr>
<th>Table 4.6</th>
<th>The effect of rinsing on [N]:[C] atomic ratio determined by XPS. The unmodified and different modified PET fabric surfaces with PDADMAC or PVAm rinsed at 40 °C, pH 10 for 30 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unmodified PET</td>
</tr>
<tr>
<td>Before washing</td>
<td>After washing</td>
</tr>
<tr>
<td>[N]:[C]</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> Polyelectrolyte-treated PET fabric obtained with 3 wt. % PDADMAC or PVAm after oxygen plasma (600 W, 15 s).

In the case of PDADMAC-treated PET fabric, it was found that the [N]:[C] atomic ratio is significantly decreased from 0.05 to 0.03. However, in the case of PVAm-treated PET fabric there is a marginal loss in [N]:[C] atomic ratio from 0.1 to 0.09. It should be noted that, even the [N]:[C] atomic ratio decreased to 0.09, it is still higher than 0.03 in the case...
of PDADMAC-treated PET fabric. This result indicates that PDADMAC coated layer was not stable enough when submitted to washing in an alkaline environment. As the OH¯ can solvate the electrostatic interaction between quaternary ammonium groups and negatively charged groups on the plasma modified PET fabric surface. However, the covalent amide bond enhances the stability of the PVAm coating layer on the PET fabric. This calls for the potential value of PVAm-treated PET fabric.

Table 4.7 summarizes color fastness to washing and rubbing of PVAm-treated PET fabric printed with different four reactive dyes. In terms of the gray scale assessment, the color change of the printed samples is comparable for all dyes and range between good (3) and very good (4).

<table>
<thead>
<tr>
<th>Dye</th>
<th>PVAm con. (wt. %)</th>
<th>Washing fastness</th>
<th>Rubbing fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Alteration</td>
<td>Dry</td>
</tr>
<tr>
<td>C.I. Reactive Blue 5</td>
<td>0.1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>C.I. Reactive Violet 2</td>
<td>0.1</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>C.I. Reactive Violet 5</td>
<td>0.1</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>C.I. Reactive Black 5</td>
<td>0.1</td>
<td>3-4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

The higher fastness obtained for the PET fabric modified with PVAm using reactive dyes may be due to the formation of strong covalent bonds between the reactive dyes and PVAm modified PET fabric. In addition, the formation of ionic bonds between the protonated amino groups on PET surface and the anionic sites on the reactive dyes. On the other hand, the rubbing fastness ratings for printed PVAm-treated PET are slightly lower than of wash fastness. As suggested previously, the decrease in rubbing fastness can be
attributed to the higher dye concentration and coloration on the surface of the PVAm-treated PET.

From these findings, it was demonstrated that the anchoring PVAm layer onto PET fabric surface modified with low-pressure oxygen plasma is an efficient approach for improving the interactions of PET fabrics with different anionic dyes. PET fabric modified with this synthetic route present the highest concentration of primary amino groups as determined by XPS measurements. This provides an efficient way to improve the surface interactions with anionic dyes as determined by K/S measurements and good stability. Modified PET fabric surface with PVAm may find numerous applications to overcome other problems related to PET coloration. Therefore, in this next section, an attempt was also made to solve another limitation of PET fabrics coloration.

4.4 Surface functionalization of PET/wool blend fabric with PVAm

PET/wool blends have gained considerable share textile industries because they possess a number of undeniable advantages over fabrics composed only of one of these two fibers. However, one of the major problems that restrict the application of PET/wool textiles is that two classes of dyes are required for coloration to produce solid shades because of the vastly different physicochemical nature of the two components (217). PET/wool blend fabrics are most frequently colored using disperse dyes for the PET component and acid dyes for the wool, this greatly hinders simultaneous process of coloration.

In the present work, it is interesting to explore on the viability of using PVAm to modify PET/wool blend fabric and to attain solid shades on PET/wool blend fabric using one class of dyestuffs, i.e. acid dyes. Applying 3 wt. % PVAm onto the oxygen plasma-treated PET fabrics (600 W, 15 s) was selected for the further experiments.

4.4.1 XPS characterization

The oxygen plasma treatment of the PET/wool surface fabric followed by immobilizing of the positively charged polyelectrolyte PVAm was ascertained via XPS analysis. The elemental surface compositions and the corresponding atomic ratios are reported for the unmodified PET/wool, oxygen plasma-treated PET/wool and the PVAm-treated PET/wool blend fabrics (Table 4.8). The detected sulfur in PET/wool blend fabrics originates from thio-ester bonds between fatty acids and protein matrix of the epicuticle and from disulfide bonds in the protein layer of the epicuticle (218). Nitrogen in the unmodified blend fabric arises from epicuticle protein material, positioned under fatty acid layer (41).
Table 4.8 The surface elemental composition and elemental ratios determined by XPS for the unmodified PET/wool fabric, oxygen plasma-treated (600 W, 15 s)\(^{(a)}\) PET/wool, fabric and PVAm-treated PET/wool fabric obtained with \(C_{\text{PVAm}} = 3\) wt. %.

<table>
<thead>
<tr>
<th>Fabric sample</th>
<th>C (at %)</th>
<th>O (at %)</th>
<th>N (at %)</th>
<th>S (at %)</th>
<th>[N]:[C]</th>
<th>[O]:[C]</th>
<th>[S]:[C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified PET/wool</td>
<td>73.9</td>
<td>18.5</td>
<td>5.2</td>
<td>1.6</td>
<td>0.07</td>
<td>0.25</td>
<td>0.02</td>
</tr>
<tr>
<td>Oxygen plasma-treated PET/wool</td>
<td>59.8</td>
<td>30.1</td>
<td>7.7</td>
<td>1.8</td>
<td>0.13</td>
<td>0.5</td>
<td>0.03</td>
</tr>
<tr>
<td>PVAm-treated PET/wool</td>
<td>70.9</td>
<td>15.9</td>
<td>11.1</td>
<td>1.4</td>
<td>0.17</td>
<td>0.22</td>
<td>0.02</td>
</tr>
</tbody>
</table>

\(^{(a)}\) These modification conditions were selected as optimal based on a previous investigation on PET.

It is apparent that the changes in elemental surface compositions and the corresponding atomic ratios are very pronounced after oxygen plasma treatment. The quantitative data confirm that, while oxygen and nitrogen content increase, the carbon content decreases. Meanwhile, the relative amount of sulfur remains practically unmodified. The reduction in carbon content was probably due to either etching effect of the plasma treatment on the wool fiber resulting in the removal of fiber surface material or the oxidation of the wool fiber surface may reduce the carbon element content by bringing about oxygen introduction. The [O]:[C] atomic ratio has significantly increased from 0.25 to 0.5 indicates an increase of oxygen functional groups because of intensive oxidation of PET/wool fabric surface, in addition to the oxidation of hydrocarbon chains of fatty layer of wool. At the same time, the atomic ratio [N]:[C] has considerably increased from 0.07 to 0.13. The nitrogen in the chemical composition of the PET/wool is associated with the amide chemical groups existing in the wool fibers. Therefore, the increasing in the [N]:[C] atomic ratio tentatively attributed to the partial removal of the hydrophobic outermost fatty acid chains. Thus, making accessible the protein epicuticle layer under the fatty layer, whereas epicuticle has a thickness of 2.5–7 nm (218).

After the application of PVAm onto the oxygen plasma-treated PET/wool blend fabric, it was found that the [N]:[C] atomic ratio has increased from 0.13 to 0.17 and the [O]:[C] atomic ratio has notably decreased from 0.5 to 0.22. This finding indicates that oxygen functional groups introduced by oxygen plasma treatment are involved in the adsorption process. At the same time, the [S]:[C] atomic ratio has slightly decreased from 0.03 to
0.02. This indicates that sulfur in cysteic acid residues, which produced by oxidation of the cystine residues, may be also involved in the adsorption process (45).

On the basis of the above results, a number of conclusions about the structural changes in PET/wool blend fabric surface following oxygen plasma treatment can be drawn. Besides modification of wool fibers in the blend sample using oxygen plasma would result in partial removal of the hydrophobic fatty layer, the newly oxygen functional groups were formed. These structural changes can be confirmed by the results of the electrokinetic measurements (Figure 4.38) and kinetics measurements of wetting (Figure 4.39).

### 4.4.2 Electrokinetic measurements

It is reported that streaming potential measurements are used to monitor the surface charge during different surface modification steps of PET fabric. In the same way, the presence of a PVAm layer on the PET/wool blend fabric was ascertained by the streaming-potential measurements. In which, the IEP values were determined by measuring the zeta-potential as a function of pH. The \( \zeta \)-pH plot of the blend fabric samples modified with oxygen plasma and followed by loading of PVAm from its aqueous solution (3 wt. %) is shown in Figure 4.38.

The electrokinetic investigation of PET/wool blend fabric after oxygen plasma treatment shows that the IEP value shifts in the direction of more acidic pH (from about 4 for the unmodified PET/wool blend fabric to 3 for PET/wool fabric after oxygen plasma treatment). This can be attributed to the existence of negatively charged groups, such as \( -\text{SO}_3^- \) and \( -\text{COO}^- \) after oxygen plasma treatment. The formation of \( -\text{SO}_3^- \) groups may result from oxidation of disulphide bonds in wool fibers to form strongly acidic sulphonic acid groups (219). These results indicate that PET/wool blend fabric seems to be negatively charged and can electrostatically interact with the positively charged PVAm macromolecules.

The application of the PVAm has the expected effect of displacing the function \( \zeta = \zeta(pH) \) towards a higher pH value. Actually, the IEP is shifted to a much higher value of pH 9. The changes of the electrokinetic surface properties clearly showed that a significant amount of PVAm bound to the surface. This implies that the number of free amino groups of the PVAm dominates the outermost surface lead to charge reversal of negatively charged plasma-treated PET/wool blend fabric.
4.4.3 Kinetics measurements of wetting

Figure 4.39 reveals a clear difference between the unmodified PET/wool and oxygen plasma-treated blend fabrics. The unmodified PET/wool blend fabric is highly hydrophobic, showing no wetting at all. This can be attributed to the combined effect of hydrophobic nature of PET and wool fiber surfaces. The hydrophobic nature of wool fibers is owing to the specific properties of its exocuticles and epicuticles. The exocuticle is hydrophobic because it contains a high degree (about 35%) of disulphite cross-linking in the A-layer. The epicuticle surrounds each cuticle cell of the wool fiber, and it consists of fatty acid (about 25% by mass), the main component of which is 18-methyleicosanoic acid. Fatty acid chains of 18-methyleicosanoic acid are covalently bound to the wool fiber as a thio-ester to cysteine and are oriented away from the fiber to produce a “polyethylene like” layer at the fiber surface, thus making the epicuticle hydrophobic. On the contrary, the oxygen plasma-treated PET/wool fabric is hydrophilic, with wetting time of < 0.1 s at conditions were studied for 100 % PET (600 W, 15s), resulting in relatively quick water absorption, thus the capability to transport liquids through pore system, this being a prerequisite for effective PVAm adsorption.
4.4.4 Surface morphology

Figure 4.40 shows the morphologies of the unmodified and different modified PET/wool blend fabric surface. Figures 4.40a and b show SEM images of the unmodified PET/wool fabric at magnification of 1000X, 5000X respectively. The SEM images at magnification of 1000X and 5000X show the arrangement of PET and wool fibers within a woven fabric structure. The fibers are relatively parallel.

In the case of the PET component of blend fabric, SEM images do not reveal significant differences between unmodified (Figure 4.40c) and oxygen plasma-treated surfaces (600 W, 15 s) (Figure 4.40d). On the other hand, the oxygen plasma treatment leads to a rougher surface in the case of the wool component of blend fabric (Figures 4.40f-g), by introducing groove along the fiber because of the etching effect of plasma, which cause the partial removal of the cuticle surface. The grooving effect induced by the oxygen plasma may increase the nitrogen content, as expected from the XPS findings.

After oxygen plasma treatment and subsequent PVAm loading, SEM images show the uniform coatings onto the PET component (Figure 4.40e) and wool component (Figure 4.40h). This implies that PVAm forms adhered layer on PET/wool blend fabric. The
Results and Discussion

The presence of this layer on the surface of both fibers would render the dye molecules attached to it.

Figure 4.40 SEM images of PET/wool fabrics: (a) the unmodified (1000X), (b) the unmodified (5000X), (C) unmodified PET component (50000X), (d) the unmodified wool component (50000X), (e) oxygen plasma-treated (600 W, 15 s) PET component, (f) oxygen plasma-treated (600 W, 15 s) wool component, (g) PVAm-treated PET component, and (h) PVAm-treated wool component.
Results and Discussion

4.4.5 Evaluation of PVAm coating stability

The stability of the obtained PVAm layer under the similar conditions of standard wash fastness tests was evaluated (pH 10 at 40 °C for 30 min). As shown in Table 4.9, the XPS results revealed no significant changes in [N]:[C] before and after washing. From this result, it can be concluded that the PVAm layer is stable.

Table 4.9 The effect of washing on the [N]:[C] elemental ratio determined by XPS.\(^{(a)}\)

<table>
<thead>
<tr>
<th></th>
<th>Unmodified PET/wool blend</th>
<th>PVAm (3 wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before washing</td>
<td>After washing</td>
</tr>
<tr>
<td>[N]:[C]</td>
<td>0.07</td>
<td>0.07</td>
</tr>
</tbody>
</table>

(a) The unmodified and PVAm-treated PET/wool fabrics washed at 40°C, pH 10 for 30 min.
4.4.6 Printing properties of PET/wool blend fabric

Figure 4.41 depicts the effect of an applied surface modification method on the K/S absorption spectra of PET/wool blend fabric printed with C.I. Acid Red 18 (Figure 4.41a) and C.I. Acid Blue 80 (Figure 4.41b). It is clear that the two acid dyes showed a higher K/S\textsubscript{max} on the PVAm-treated PET/wool blend fabric as compared to the unmodified PET/wool blend fabric. For instance, K/S\textsubscript{max} values increase with C.I. Acid Red 18 from 5 for the unmodified to 7.1 for modified PET/wool blend fabrics. It is worthy to mention that, the higher K/S\textsubscript{max} values of the unmodified PET/wool with both C.I. Acid Red 18 and C.I. Acid Blue 80 compared with unmodified PET fabric (Figure 4.41) reflect the positive impact of the contribution of wool component in blend samples along with its high affinity for anionic acid dyes.

These significant increases in K/S\textsubscript{max} values are a direct consequence of modifying PET/wool blend fabric surface by loading PVAm layer. The most probable mechanism of the interaction between PVAm layer and dye is likely to be ionic interaction of the anionic sulfonate groups (−SO\textsubscript{3}−) of anionic dye molecules with protonated amino groups of PVAm layer on the modified fabrics in acid medium. Therefore, the loading PVAm enables additional quantity of acid dyes to be bound to the fabric. This result confirms the positive effect of coating PET/wool blend fabric surface with PVAm layer on coloration properties.

![Figure 4.41 K/S absorption spectra of the unmodified PET/wool fabric and PVAm-treated PET/wool obtained with C\textsubscript{PVAm} = 3 wt. % printed with C.I. Acid Red 18 (a) and C.I. Acid Blue 80 (b).](image)
Additionally, from the Figure 4.42, it can be observed that the color of the unmodified PET/wool blend fabric is light and non-uniform. On the other hand, the color of the PVAm-treated PET/wool blend fabric is heavy, solid and uniform. This gives an intuitionist proof that loading PVAm can improve coloration of PET/wool blend fabric. Moreover, the obtained findings show that after PVAm treatment it is possible to color PET/wool blend fabric with only one acid dye, which shows substantivity only to wool fibers. Thus, the coloration becomes independent of the chemical structure of PET or wool fibers because only the PVAm coating layer is colored without changes in the bulk properties of blend fabric.

Figure 4.42 Digital photos of the unmodified PET/wool blend fabric and PVAm-treated PET/wool blend fabric printed with C.I. Acid Red 18 (a), C.I. Acid Blue 80 (b).

4.4.7 Fastness properties of colored PET/wool blend fabric.

The color fastness to washing and rubbing of the unmodified PET/wool and PVAm-treated PET/wool blend fabrics printed with C.I. Acid Red 18 and C.I. Acid Blue 80 were tested (Table 4.10). The fastness properties were visually assessed using a standard gray scale (175; 176).
Table 4.10 Color fastness properties of PVAm-treated PET/wool blend fabric printed with C.I. Acid Red 18 and C.I. Acid Blue 80.

<table>
<thead>
<tr>
<th>PET/wool fabric</th>
<th>C.I. Acid Red 18</th>
<th></th>
<th>C.I. Acid Blue 80</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Washing</td>
<td>Rubbing</td>
<td>Washing</td>
<td>Rubbing</td>
</tr>
<tr>
<td></td>
<td>fastness</td>
<td>fastness</td>
<td>fastness</td>
<td>fastness</td>
</tr>
<tr>
<td>Unmodified</td>
<td>3-4</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>PVAm-treated PET/wool (a)</td>
<td>3-4</td>
<td>3</td>
<td>2-3</td>
<td>3</td>
</tr>
</tbody>
</table>

(a) PVAm-treated PET/wool fabric obtained by coating oxygen plasma-treated PET/wool fabric with PVAm from 3 wt.% aqueous solution.

It was observed that the washing and rubbing fastness ratings for the two dyes obtained with PVAm-treated PET fabrics were the same as the ratings of the unmodified blend fabric. This implies that the dye-substrate bonding mechanism, in principle, remains the same. For the PVAm-treated PET/wool blend fabric, the rubbing fastness results range between moderate (2) and good (3). The lower ratings in rubbing fastness can be explained by the high dye concentration (dye accumulation) on the fabric surface of the printed modified blend fabric.
5 Summary and Outlook

The surface chemistry plays a very important role in the performance of polymeric materials during their applications. Among all polymers, poly(ethylene terephthalate) (PET) is the main synthetic polymer in fiber industries and the production of fabrics. It is also used in other industries including packaging, construction and automotive. Unfortunately, PET materials exhibit poor wetting with polar liquids and show low adhesion in composites and joins. These limitations in functional properties of PET fabrics cannot be compensated by a direct modification to adjust the fiber surface to requested and specific applications because PET surfaces are not endowed surface groups necessary for surface reactions. However, it is essential for PET fabric to undergo pretreatment prior modification reactions. The largely surface inertness of PET fibers and fabrics created numerous scientific and technical challenges to overcome problems in the PET’s disadvantageous properties such as less wearing comfort, limitation in coloration properties, build-up of electrostatic charges, insufficient soil release and poor washability. Nevertheless, the PET surface inertness has constrained uses of PET fabrics for the further application in garments and other industries. Actually, the effective and efficient modification of PET is a challenge to overcome its limited reactivity and provide more flexibility in their uses. Surface modifications seem to be attractive tools with this objective because they are guaranteeing to maintenance the key bulk properties.

The current work aimed at the endowing PET fabrics surface with accessible amine functionalities. For the introduction of amine functionalities, two plasma-based approaches have been successfully achieved. In the first approach, the PET fabric surface is directly exposed to the low-pressure ammonia plasma treatment, leading to surfaces preferably containing primary amino groups and some other nitrogen-containing groups. In the second approach, the PET fabric surface was modified by low-pressure oxygen plasma in order to introduce oxygen-containing functional groups such as carboxylic groups. These carboxylic groups can act as an anchor for the adsorption of cationic polyelectrolytes from aqueous solution to PET fabric surface. Afterwards, an appropriate annealing procedure was used at 120 °C for 1 h to stabilize the polymer layer on PET fabric surface.

Cationic polyelectrolytes used in this study were poly(diallyldimethylammonium chloride) (PDADMAC) with a molar mass of 200000-350000 g/mol as an example of strong
polyelectrolytes and poly(vinyl formamide-co-vinyl amine) (PVAm) with 340000 g/mol as an example of weak polyelectrolytes.

In addition to surface modification of PET fabric, attention was directed towards the characterization of the different modified PET fabrics surface by a combination of various surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS), electrokinetic measurements and time-dependent contact angle studies. Finally, the amine functionalities introduced by different surface modifications were used for the subsequent immobilization of anionic dye molecules such as acid and reactive dyes to evaluate the efficiency of different surface modifications. The reaction of the modified PET fabric surfaces with anionic dyestuffs can be considered as a model reaction allowing to evaluate the surface reactivity and to show the possibility for the large molecules to get access to the reactive surface centers.

The main results of different surface modifications can be summarized as follows:

1. The surface chemical compositions of ammonia plasma and polyelectrolyte-modified PET fabrics were evaluated by XPS and were compared to the unmodified PET fabric. In the wide-scan XPS spectra of different modified PET fabrics surface, one additional peak was appeared for N 1s adjacent to the characteristic main two peaks of carbon (C 1s) and oxygen (O 1s) of unmodified PET. The N 1s peak indicates that the nitrogen-containing functional groups were introduced onto the surface of PET fabric.

2. The PET fabric surface modified by oxygen plasma has been characterized by XPS. It was determined that oxygen plasma induced the formation of additional polar groups, such as carboxylic acid groups. In comparison with the unmodified PET fabric, the [O]:[C] atomic ratio was increased by two-fold at 600 W for 15 s.

3. In comparison with the unmodified PET fabric surface, the elemental surface compositions of surface region and the corresponding atomic ratios of ammonia plasma and polyelectrolyte-modified PET fabrics displayed that the [N]:[C] atomic ratio is reached to 0.19 after ammonia plasma treatment for 600 s. In the case of coating with cationic polyelectrolytes, the [N]:[C] atomic ratio is reached to 0.05 and 0.1 after modification with 3 wt. % PDADMAC and 3 wt. % PVAm, respectively. Therefore, it could be an indication of a successful formation of the PDADMAC or PVAm layer covering the PET fabric surface.
4. Additionally, the incorporation of the Brønsted acidic or basic groups were analyzed by streaming potential measurements that are very sensitive to analyze charge formation processes on solid surfaces. The change of the interfacial charge at the PET fabric surfaces was studied after different surface modifications, which causes remarkable shifts of the isoelectric points (IEP) compared to the unmodified PET fabric. It was found that the IEP value for the unmodified PET was around pH 4. The IEP value for ammonia plasma-treated PET fabric surfaces shifted to about pH 6.5 after 600 s plasma treatment time. After coating oxygen plasma-treated PET fabric surfaces with cationic polyelectrolytes, the IEP value is significantly shifted from 2.6 for the oxygen plasma-treated PET fabric surface to 10.8 of PDADMAC-treated PET fabric surface obtained with $C_{PDADMAC} = 3$ wt.%. In the case of PVAm adsorption on plasma-treated PET, the IEP value shifted to 9.3 obtained after modification of surface with $C_{PVAm} = 3$ wt. %.

5. The shift of the IEP can be considered as the formation of more closed and dense polyelectrolyte layer on the fabric’s surface shielding charges of the oxygen plasma-treated PET fabric surface. These findings were supported by SEM investigations.

6. The plasma-treated surfaces were found to be relatively stable over 14 days of storage in air.

7. The effectiveness of different modified PET fabrics with regard to wettability was investigated by the time-dependent contact angle measurements. It was found that, different surface modifications induced conversion of PET fabric from hydrophobic to hydrophilic substrate and keeping intact its bulk properties.

8. Contrary to ammonia plasma treatment, polyelectrolyte-modified PET fabric surface leads to a more defined surface chemistry.

The main results of surface activity of modified PET fabrics towards anionic dyes can be summarized as follows:

1. The ability of amine functionalities created by different surface modifications to interact with different classes of anionic dyes was compared. It was shown that ammonia plasma treatments had no positive effect on the fixation of both neither acidic dyes nor reactive dye molecules regardless of the ammonia plasma treatment time. In contrast to ammonia plasma-treated PET, it was found that color strength ($K/S_{max}$) values obtained
from K/S absorption spectra of PET fabrics coated with either PDADMAC or PVAm was remarkably increased compared to that of the unmodified PET fabric surface.

2. It was found that the type of polyelectrolyte played a role in color strength results. The results show that regardless of the concentration of polyelectrolyte solution, the color strength values were much higher for the PVAm-treated PET fabrics printed with C.I. Acid Red 18 or C.I. Acid Blue 80 as compared to those of the PDADMAC-treated PET fabrics.

3. The permanency of the bond between the dye molecules and the surface of different modified PET fabrics can be investigated by the fastness tests of printed PET fabrics to washing and rubbing. A high coloration fastness indicated a strong dye molecule bonding, which in turn, is an indication of permanency of the amine functionalities. The color fastness values to the washing of the PVAm-treated PET fabrics printed with anionic reactive dyes were in the range between good to very good as compared to moderate to good in the case of anionic acid dyes.

Finally, it was demonstrated that anchoring PVAm layer onto PET fabric surface modified with low-pressure oxygen plasma is an efficient approach to improve coloration behavior and to overcome different problems related to PET fabrics coloration, such as coloration of PET/wool blend fabric with a single class of dyes.

For future studies, it is proposed that the anchoring PVAm layer onto PET fabric surface may allow another potential application of modified PET fabric bearing primary amino groups. These anchoring groups could be offered new possibilities for creation of smart textiles based on PET fabrics with multifunctional properties such as chameleon textiles. This group of smart textiles changes their color when external stimuli such as pH (halochromism) or temperature (thermochromism) are applied. In addition, due to their good chemical reactivity, primary amino groups are widely used in biochemistry for covalent coupling of biological active molecules.
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7 Selbständigkeitserklärung

Hiermit erkläre ich des Eides statt, die vorliegende Arbeit selbstständig und ohne unerlaubte Hilfsmittel durchgeführt zu haben.

Chemnitz, den 01.11.2011                                                                                      Tarek Salem
8 Curriculum Vitae

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1993-1997 B.Sc. [Chemistry] with degree (very good with honors), Chemistry department, faculty of Science, Cairo University, Egypt.

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Thesis is entitled “Studies on heat transfer printing of some natural and synthetic fabrics”.

3/2009-2011 Doctoral candidate in Chemistry department, faculty of Science, Chemnitz University, Germany.

Research Experiences

2002-2004 Assistant researcher, Textile research division, dyeing, printing and auxiliaries dept., NRC. Cairo, Egypt.

2004-2007 Researcher assistant, Textile research division, dyeing, printing and auxiliaries dept., NRC. Cairo, Egypt.

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Publications from this work

List of publications


Contributions to workshops/conferences

Talk

1. Tarek Salem, Steffi Uhlmann, Mirko Nitschke, Alfredo Calvimontes, Rolf-Dieter Hund, and Frank Simon.” Modification of plasma pre-treated PET fabrics with poly-DADMAC and its surface activity towards acid dyes” the XXX FATIPEC congress, November 9 - 11, 2010, Genoa, Italy.


Poster

1. Tarek Salem, Steffi Uhlmann, Mirko Nitschke, Alfredo Calvimontes, Rolf-Dieter Hund, and Frank Simon.” Surface modification of PET to improve their printing behavior” 16th Neues Dresdner Vakuumtechnisches Kolloquium, October 16 - 17, 2008, Dresden, Germany.

Poster-talk
