Preparation and properties of electro-conductive fabrics based on polypyrrole: covalent vs. non-covalent attachment

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Abstract. Electro-conductive fabrics were prepared via in situ oxidative polymerization of pyrrole (Py) in the presence of unmodified and chemically modified cotton fabrics. Chemical modification of cotton fabric was achieved by covalent attachment of a bifunctional linker molecule to the surface of the fabric, followed by incorporation of a monomer unit onto the linker. The fabrics were characterized using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electron spectroscopy, and thermal analysis. Furthermore, the effect of Py concentration on the degree of polypyrrole (PPy) grafting, surface morphology, electrical resistivity, and laundering durability were studied for both types of cotton fabrics. Reductions of several orders of magnitude in surface and volume electrical resistivities were observed for both non-covalently and covalently linked cotton-PPy systems, whereas the effect of covalent pre-treatment of the fabric was stronger at low Py concentration. On the other hand, at higher monomer concentration, the electrical properties and laundering durability of the fabrics were comparable for both unmodified and chemically pre-treated cotton fabrics, indicating that only a small fraction of PPy chains were chemically grafted onto the fabric surface with the majority of the polymer being connected to the fabric through hydrogen bonds.

1. Introduction
Over the past few decades, intrinsically conductive polymers (ICPs) have been in the center of extensive research due to their unique properties, which include electrical conductivity, light weight, and solution processability [1–3]. Consequently, ICPs have found numerous applications in a range of flexible and low-cost organic electronic devices such as organic photovoltaics (OPVs), light emitting diodes (LEDs), field effect transistors (FETs), sensors, actuators and more [4–10]. Due to their mechanical flexibility, electro-conductive polymers have been applied as thin layers on a variety of rigid and flexible substrates such as glass, silicon wafers, polyesters, and fabrics [11–13]. Combining fabric with ICPs opens possibilities for production of smart textiles with advanced properties such as electrical conductivity, dissipation of static charges and microwave energy, shielding of electromagnetic radiation, heat generation, and sensing. Consequently, the potential applications of electro-conductive fabrics based on organic polymers span over a wide range of areas such as military, sportswear, protective clothing, and medical garments [14–23]. The properties of the ICP-fabric
systems depend on the type of polymer, type of fabric, the yarn density of the fabric, and the processing method used.

Among different types of ICPs that have been applied to textiles, polyaniline (PANI), polythiophene (PT) and polypyrrole (PPy) show the most promising results in terms of high electrical conductivity and simple processing. The two main methods for incorporation of ICPs into fabrics include direct coating with the solution of ICP or in situ polymerization of the precursor monomers in the presence of fabric. It was previously shown that direct coating can be achieved by spray painting and hand brushing [24] or dip coating techniques [25], whereas in situ polymerization is generally performed either in solution using oxidative coupling polymerization [15–19,22,23,26,27] or by the exposure of the fabric to the monomer in vapor phase [28,29]. It is important to establish a uniform polymer coating that allows an efficient charge transport without significantly affecting the mechanical properties of the fabric. In most studied systems, these methods result in a formation of physical bonding between the fabric and the conductive polymer coating; a very limited number of studies have described chemical grafting of ICPs to the fabric [30,31].

Herein, we report a simple method for the preparation of PPy-based electro-conductive cotton fabrics obtained by covalent grafting of conjugated monomers to the surface of the fabric, followed by in situ polymerization of pyrrole (Py). To establish a covalent bonding between the monomers and the fabric, the fabric was first grafted with a bifunctional linker molecule, 10-undecenoyl chloride, which contains acyl chloride and alkene groups. The acyl chloride group of the linker reacted with the hydroxyl present on the surface of cotton, forming an ester bond, and the remaining alkene moiety was used for covalent binding to the conjugated monomer using thiol-ene click reaction conditions [32,33]. In situ oxidative polymerization of Py was done using ferric chloride as an oxidant and water as a solvent. One of the main goals of the study was to examine the effect of chemical pretreatment of the fabric on the electrical resistivity and laundering durability of the electro-conductive coating. This was done in comparison with the PPy-cotton system having only physical bonding between PPy and cotton. In addition, the effect of the amount of Py monomer used for the polymerization on the degree of PPy grafting, electrical resistivity, and final morphology of the polymer on the surface of the fabric was also studied. The fabrics were characterized using Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and elemental and thermal analyses.

2. Experimental

2.1 Materials
Cotton woven fabric (100% cotton, weight: 147 g m⁻²) was used as a substrate textile and washed twice in a washing machine at 90 °C before use. The fabric was dried in a vacuum oven at 65 °C for 12 hours prior to use. Py and triethylamine were purchased from Merck. Chloroform, dichloromethane, and hexane were purchased from Bio-Lab Ltd. 10-Undecenoyl chloride, 2-thiophenethiol, 2,2-dimethoxy-2-phenyl-acetophenone (DMPA), 3-hexylthiophene (3HT), ferric chloride, acetonitrile, and chlorobenzene were purchased from Sigma-Aldrich and used as received.

2.2. Characterization
The degree of PPy grafting was estimated according to the following equation:

\[ W \% = \frac{W_f - W_i}{W_i} \times 100 \]  

(1)

where Wt% is weight percent, and W₀ and W_i are the initial and final weights, respectively. The measurements were carried out on three specimens for each sample and the average Wt% is reported.

FTIR spectra were measured using a Bruker Alpha-P FTIR spectrometer with an attenuated total reflectance (ATR) crystal. Spectra were recorded in a range between 400–4000 cm⁻¹ at a resolution of 2 cm⁻¹ with 24 scans.
XPS signals were recorded with Kratos Axis Ultra spectrometer using an Al Kα monochromatic radiation X-ray source (1486.7 eV). Data were collected and analyzed by using a Casa XPS (Casa Software Ltd.) and the Vision data processing program (Kratos Analytical Ltd.). High-resolution XPS spectra were collected with a takeoff angle of 90° (normal to analyzer); vacuum condition in the chamber was 1.9 x 10⁻⁶ Torr, for the C 1s, O 1s, N 1s, Cl 2p, and S 2p levels with pass energy of 20 and 0.1 eV step size. The binding energies were calibrated using C 1s peak energy as 285.0 eV.

Elemental analysis for N, C, H, O, and S were performed in triplicate for each studied PPy-cotton system. The samples were weighed using a Sartorius microbalance to the nearest 1 μg and analyzed with a Thermo Flash EA-1112 Elemental analyzer. The instrument was calibrated with special standards for elemental analysis.

Contact angles were measured with a Dataphysics-OCA20 system at the standard atmosphere conditions (25 °C and 60% relative humidity) using 5 μL deionized water droplets. All reported values of the contact angles were determined by averaging values measured at least on 5 different points for each sample surface.

Surface morphologies of the original and modified cotton fabrics were studied using extra high-resolution scanning electron microscopy (HRSEM) with a MagellanTM 400L Instrument. Prior to the analysis, the samples were coated with a thin layer of gold (5 nm) by sputtering under rarefied argon atmosphere.

Thermal gravimetric analysis (TGA) was used to estimate thermal stability of the pristine and modified cotton fabrics using a TGA Q50 (TA Instruments). During the measurement the temperature was increased from 25 to 600 °C at a heating rate of 10 °C min⁻¹. All the measurements were carried out under oxygen atmosphere. Thermal decomposition temperature was taken as the onset of significant weight loss of the heated sample.

Differential scanning calorimetry (DSC) measurements were performed in a TA Q200 instrument (TA Instruments-Waters LLC) using a heating rate of 10 °C min⁻¹. Samples were analyzed in heat-cool-heat cycles between -20 and 400 °C.

Electrical resistivity measurements were performed using a resistivity chamber (Keithley Model 8009). Voltage (range between 1-100 V) and current (range between 20 mA - 200 μA) were applied using an electrometer (Keithley Model 6517B), and the surface and volume resistivity were recorded. This procedure was adapted from the ASTM D-257 standard method. The fabrics were prepared at the same size (7 cm diameter) and positioned between two pressed electric contacts. The measurements were performed at the standard atmosphere conditions (25 °C and 60% relative humidity).

Washing durability tests were performed according to BS-EN ISO 105 C-06, test method A1S, using a standard wash fastness Launder-Ometer machine (Roaches Washtec Instrument). The fabrics were washed in a rotating closed can containing 150 mL aqueous solution of an ISO standard European colour fastness establishment (ECE) detergent at 40 °C, pH 8.5 and 40 rpm for 30 minutes in the presence of 10 stainless steel balls. One washing cycle is equivalent to about three home machine launderings according to the ISO test method. After each cycle, the fabrics were first rinsed with water to remove the residual detergent, followed by air-drying and vacuum oven drying at 65 °C overnight. Electrical resistivity measurements were performed before and after each of the six washing cycles. Washed fabrics were labelled with a prefix “w”.

2.3. Experimental Details

2.3.1. Chemical grafting of PPy onto cotton fabric. The synthetic route for covalent modification of cotton fabric, followed by graft polymerization of Py is shown in Figure 1. In the first step, a bifunctional linker molecule, containing an acyl chloride and a double bond, was attached to the surface of cotton fabric via an esterification reaction. This step resulted in incorporation of alkene groups into the fabric, which are suitable for further chemical reaction. Next, 2-thiophenethiol was applied onto the fabric utilizing thiol-ene click reaction conditions, leading to the covalent attachment of thiophene molecules to the surface of cotton fabric. It is important to note that a commercially
available 2-thiophenethiol was employed as a monomer for chemical binding to the fabric, since the corresponding Py analogue is unknown. Finally, in situ oxidative polymerization of Py was carried out using ferric chloride as an oxidant and water as a solvent.

**Figure 1.** Synthetic pathway for chemical grafting of PPy onto cotton fabric.

**Preparation of MC-1**
Cotton fabric (0.5 g, 3.1 mmol) was dried overnight in a vacuum oven at 65 °C prior the reaction and then placed in an Erlenmeyer flask. Chloroform (100 mL), 10-undecenoyl chloride (23.8 g, 117.4 mmol), and triethylamine (13.1 g, 129.7 mmol) were then added to the flask, and the reaction mixture was stirred for 6 hours at room temperature. After the reaction was completed, the fabric was purified by Soxhlet extraction for 24 hours using chloroform as a solvent, followed by drying in a vacuum oven at 65 °C.

**Preparation of MC-2**
To a solution of chloroform (60 mL), 2-thiophenethiol (3.9 g, 33.6 mmol), and DMPA (5 wt%), the MC-1 fabric (0.5 g, 3.1 mmol) was added. The flask was purged with argon for 2 minutes and irradiated with a UV lamp (Spectroline Model SB-100PC/F, 230 V) for 30 minutes. After the reaction was completed, the fabric was taken out and purified by Soxhlet extraction using chloroform (24 hours), followed by drying in a vacuum oven at 65 °C.

**Preparation of MC-PPy**
Polymerization of Py was performed using various monomer amounts of 3, 5, 10, and 25 wt% based on the weight of the cotton fabric taken for the polymerization. Monomer concentration in the polymerization solution ranged from 1 to 2.3 mg ml⁻¹. The molar ratio between the monomer and the oxidant was 1:2.2 and was kept constant for all polymerization reactions. MC-PPy fabrics were first soaked in an aqueous solution containing Py monomer for 30 minutes, followed by the addition of an aqueous solution of ferric chloride, and reaction mixture was stirred at room temperature for 6 hr.
After polymerization was completed, the fabrics were washed several times with water, and purified using Soxhlet extraction with dichloromethane for 24 hours. Finally, fabric was dried in a vacuum oven at 65 °C overnight prior to further analysis.

Due to the fact that PPy is insoluble in most known organic solvents and in order to provide a support for its covalent grafting onto the cotton fabric, a model reaction using poly(3-hexylthiophene) (P3HT) was done (experimental procedure is provided in the Supporting Information). Since P3HT has good solubility in the chlorinated solvents such as chloroform, it was possible to completely remove a non-covalently attached polymer from the fabric after the polymerization and perform surface analysis of the fabric. Thus, unmodified cotton and MC-2 fabric were polymerized with 3HT under the similar polymerization conditions described above. These samples are referred to as NC-P3HT and MC-2-P3HT, respectively.

2.3.2. Non-covalent incorporation of PPy into cotton fabrics. In order to compare fabrics with covalent and non-covalent attachment of PPy, oxidative polymerization of Py was performed in the presence of unmodified cotton fabrics under the polymerization conditions described above. The physical incorporation of PPy into the cotton fabric takes place due to presence of hydroxyl groups (OH) in the molecular structure of cellulose as well as microporous nature of the cotton fabrics, which both lead to the formation of extensive hydrogen bonding between the fabric and PPy (Figure 2) [34].

![Figure 2](image-url)

**Figure 2.** Schematic representation of hydrogen bonds formed through physical incorporation of PPy into the cotton fabric, achieved by oxidative polymerization of Py in the presence of unmodified cotton fabric.

3. Results and Discussions

3.1. Degree of PPy grafting

Figure 3 shows PPy weight percent in the MC-PPy fabrics prepared with different Py percentages. The results show a good correlation between the amount of Py used for the polymerization and the final degree of polymer grafting in the fabric, which indicates the high efficiency of the developed chemical multi-step polymer grafting methodology. For example, using 10% Py in the polymerization solution afforded 8.5 wt% PPy in the functionalized fabric, whereas 25% Py led to ~23 wt% PPy. These values are considerably higher than the ones previously reported in the literature for PPy-functionalized textiles [31].
Figure 3. PPy weight percent in MC-PPy fabrics prepared with different Py percentages.

3.2. Characterization of the chemically grafted cotton fabrics

Figure 4 shows ATR-FTIR spectra of the chemically grafted cotton fabrics obtained from each treatment step. MC-1 and MC-2 fabrics show a broad signal at around 3300 cm\(^{-1}\) for O-H stretch, a peak at 2885 cm\(^{-1}\) for C-H stretch in alkanes, and a peak at 1026 cm\(^{-1}\) for C-O stretch; these signals are typical of the pristine cotton fabric. A new signal at 1732 cm\(^{-1}\) in the spectrum of MC-1 fabric was assigned to C=O stretching vibration, which was attributed to the newly formed ester linkage. This demonstrates that the functional linker molecule was successfully covalently attached onto the cotton fabric. The formation of C=C bonds in the MC-1 fabric could not be detected in the ATR spectra since the bands of the adsorbed water in cotton appear at 1642 cm\(^{-1}\) and are superimposed on those of C=C stretching vibrations [35,36]. In addition, the peak at 747 cm\(^{-1}\), which appears for MC-2 fabric, was assigned to C-S groups; the presence of this peak indicates that the thiophene ring was successfully covalently attached through the linker molecule. Furthermore, ATR-FTIR spectra for the model reaction with P3HT (Supporting Information) supports the fact that P3HT was chemically grafted onto the cotton fabric: The unmodified and NC-P3HT fabrics displayed only signals typical of the pristine cotton fabric. In contrast, the MC-2-P3HT fabric displayed also typical signals of P3HT (C-H stretch of aromatic and aliphatic bonds located in 1450–1600 cm\(^{-1}\) region). The ATR-FTIR spectrum for pristine P3HT is presented in the Supporting Information.
Further evidence for chemical modification of the cotton fabric surface by each of the treatment steps was obtained by analysis of surface composition by XPS. As shown in Table 1, the carbon content for MC-1 fabric was higher than that of unmodified fabric due to the increase in carbon-carbon and hydrocarbon (C-C/C-H) concentration, whereas the oxygen content was lower as expected. Figure 5 presents high-resolution C1s spectra for MC-1 fabric and the unmodified fabric. The results for MC-1 fabric showed that the intensity of C-C/C-H peak around 285 eV was increased relative to unmodified fabric, whereas the intensity of the C-O peak around 287 eV was reduced due to the increase in the amount of hydrocarbons and the consumption of hydroxyl groups during esterification reaction, respectively. In addition, the appearance of the O-C=O peak around 289 eV in the MC-1 fabric confirmed that the functional linker molecule was successfully chemically grafted onto the cotton fabric via the esterification reaction. Moreover, no evidence for the presence of sulfur was detected in analysis of the unmodified fabric, but the S2p content after the thiol-ene click reaction was 0.38, indicating higher abundance of sulfur on the surface of MC-2 fabric than unmodified fabric.

Table 1. Apparent surface chemical compositions (in atomic concentration %) of tested fabrics as determined by XPS.

| Sample           | O 1s | N 1s | C 1s | S 2p | O/C ratio | N/C ratio |
|------------------|------|------|------|------|-----------|-----------|
| Unmodified cotton| 34.12| 1.46 | 64.42| 0.00 | 0.53      | 0.02      |
| MC-1             | 27.82| 1.17 | 69.95| 0.00 | 0.40      | -         |
| MC-2             | 28.95| 1.11 | 68.38| 0.38 | 0.42      | -         |
| MC-PPy-3%        | 22.01| 5.65 | 71.23| 0.34 | 0.31      | 0.08      |
| MC-PPy-5%        | 21.11| 6.03 | 71.51| 0.52 | 0.30      | 0.08      |
| MC-PPy-10%       | 15.35| 9.90 | 72.84| 0.66 | 0.21      | 0.14      |
| MC-PPy-25%       | 11.71| 11.55| 75.77| 0.25 | 0.15      | 0.15      |
| NC-P3HT          | 30.06| 1.26 | 67.25| 0.72 | 0.45      | -         |
| MC-2-P3HT        | 5.29 | 0.22 | 86.21| 6.06 | 0.06      | -         |
Chemical grafting of PPy on the surface of MC-PPy fabrics was confirmed by the presence of a relatively intense N1s peak (∼400 eV) as shown in Figure 6a (and Figure S4 in the Supporting Information). In addition, XPS survey scans for MC-PPy fabrics prepared with various Py amounts (Table 1) show that the carbon and the nitrogen contents increased with increasing Py percentage, whereas the oxygen content decreased. This resulted in an increase in N/C ratio with increasing Py percent, indicating higher abundance of nitrogen-containing Py units on the surface of cotton. Furthermore, high-resolution N1s spectra of MC-PPy fabrics prepared with different Py percentages (Figure 6b) showed that the intensity of C-N-C peak around 400 eV was increased with increasing Py percentage as expected. XPS results for the model reaction with P3HT described in the Supporting Information indicates that P3HT was chemically grafted onto the cotton fabric.
3.3. Surface Properties

Next, changes in the surface properties of the chemically modified cotton fabrics were investigated for each treatment step using contact angle analysis; results are shown in Figure 7. As a result of the hydrophilic nature of cotton fabric a droplet of water was quickly absorbed into the unmodified cotton fabric (Figure 7a). After chemical grafting of cotton fabric with the functional linker molecule, the
water contact angle was about 138° (Figure 7b), which indicates good hydrophobicity. Furthermore, MC-2 fabric showed a slight increase in the water contact angle, to about 144° (Figure 7c) owing to the addition of C and S atoms. We also found that for chemical graft polymerization with 10% Py and above, MC-PPy fabrics were hydrophilic (Figure 7d). This is presumably due to the formation of hydrogen bonds between the hydroxyl groups present on the fabric and the amine hydrogen atom of Py rings. For the cotton fabrics modified with 5% Py monomer, a water contact angle of about 138° was observed, indicating that chemical graft polymerization in this case resulted in the formation of lower amount of PPy on the surface of the fabric.

![Figure 7](image)

**Figure 7.** Representative photographs of (a) unmodified cotton, (b) MC-1, (c) MC-2 and (d) MC-PPy-10% fabrics used to determine water contact angles.

3.4. **Thermal Analysis**

Thermal properties of MC-PPy fabrics prepared with different Py percentages were evaluated using TGA and DSC measurements. PPy decomposed in the temperature range between 200-600 °C, and decomposition of cotton occurred between 320 to 500 °C as evident in TGA curves shown in Figure 8a. MC-PPy fabrics decomposed in the temperature range between 215-350 °C, and thus showed slightly lower thermal stability in comparison with the unmodified cotton. The initial weight loss of 7%-14% around 265 °C was consistent with the level of modification of the fabric with PPy, with the highest weight loss percentage observed for MC-PPy-25%. For comparison, the unmodified cotton fabric exhibit 5% weight loss at this temperature range. An additional weight loss for the MC-PPy fabrics was observed between 300 and 350 °C, corresponding to initial breakdown of cotton. Similar behavior of the reduction in thermal stability after incorporation of PPy was also reported for PPy/nylon/lycra composite [23]. DSC thermograms for the unmodified and PPy-modified cotton fabrics are shown in Figure 8b. A thermogram for the unmodified fabric displayed a strong endothermic peak at 360 °C, which was attributed previously to the thermal degradation of cotton [37,38]. A progressive shift of the decomposition peak toward lower temperatures, from 360 to 330 °C, was observed when Py percentage increased in the MC-PPy fabrics, which was attributed to the degradation of PPy. A similar trend of the thermal degradation temperature with increasing Py concentration was previously reported for cellulose-PPy textiles [27].
Figure 8. (a) TGA curves for unmodified cotton, MC-PPy-3%, MC-PPy-5%, MC-PPy-10%, and MC-PPy-25% fabrics and (b) DSC second heating cycle for the unmodified cotton, MC-PPy-3%, MC-PPy-5%, and MC-PPy-10% fabrics.

3.5. Surface Morphology
Surface morphologies of MC-PPy fabrics prepared with increasing Py percentages were analyzed using HRSEM. The results showed that the unmodified cotton has fibers with a relatively smooth surface morphology (Figure 9a). On the other hand, the images obtained for PPY-modified cotton showed that cotton fibers were completely coated with PPY for all Py percentages. In addition, PPY aggregates were also formed (Figure 9b-e) due to the previously described supramolecular assembly of the PPY macromolecules on the surfaces of cotton fibers [30]. These aggregates had irregular...
intervals and a feature size between 80-160 nm (Supporting Information). The analysis indicated that as the Py percentage in the polymerization solution increased, the cotton fibrils became more massively covered with PPy, resulting in a thicker PPy layer and an increased density of aggregates deposited on the fibers. HRSEM micrographs for NC-PPy fabrics prepared with increasing Py percentages (Supporting Information) showed similar surface morphologies to MC-PPy fabrics.

Figure 9. HRSEM images of: (a) unmodified cotton, (b) MC-PPy-3%, (c) MC-PPy-5%, (d) MC-PPy-10%, and (e) MC-PPy-25% fabrics.
3.6. Electrical Resistivity

One of the advantages of incorporation of ICP into cotton fabric having porous structure, is the possibility to obtain both surface and volume electrical conductivities [25]. Electrical resistivity measurements of MC-PPy fabrics prepared with different monomer amounts revealed that both surface and volume resistivities were several orders of magnitude lower than resistivities of the unmodified fabric (Figure 10). In fact, surface resistivity of the fabric prepared using 3% Py was three orders of magnitude lower (3.1×10^6 Ω square^-1) relative to the unmodified fabric (1.2×10^8 Ω square^-1). The surface resistivities were even lower for the fabrics prepared with 5 and 10% Py, showing average values of 3.6×10^5 Ω square^-1 and 5.6×10^4 Ω square^-1 respectively.

Volume resistivity measurements showed a reduction of five orders of magnitude for the fabrics prepared with initial concentration of Py of only 3% (5.4×10^5 Ω cm^-1) relative to the unmodified fabric (2.5×10^10 Ω cm^-1). These results indicate that Py penetrated into the cotton fibers and a continuous polymer network was formed throughout the fabric. The results also revealed that there was no further decrease in surface and volume resistivity of MC-PPy fabrics beyond 10% and 3% pyrrole, respectively, suggesting that the effect of PPy layer thickness on the electrical resistivity becomes negligible when the amount of the conducting polymer exceeds a certain amount. A similar effect was also reported for polyaniline chemically grafted cotton fabric: Above 10 wt% degree of polymer grafting no increase in conductivity was observed [30].

Our data showed that PPy had stronger effect on volume than on surface resistivity of the fabric, indicating that a larger fraction of the PPy was incorporated into the fabric rather than onto its surface, which was also previously observed by us for P3HT-cotton fabrics [25]. In addition, a comparison between electrical resistivity of MC-PPy and NC-PPy fabrics showed that surface resistivity at the lowest Py percentage of MC-PPy fabric (MC-PPy-3%) was one order of magnitude lower than the one obtained for the cotton fabric treated only with PPy (NC-PPy-3%), as reflected in resistivity values of 3.1×10^6 Ω square^-1 and 1.1×10^7 Ω square^-1, respectively (Supporting Information). This improvement in surface electrical resistivity is attributed to the covalent binding of PPy to the surface of cotton fabric. A similar trend of the reduction in surface conductivity was previously reported for polypropylene fabrics covalently functionalized with PPy [31]. When the initial concentration of Py was higher than 3%, comparable values of surface and volume resistivities were obtained for both MC-PPy and NC-PPy fabrics.

The degree of substitution of the cotton fabric with the bifunctional linker molecule was estimated from the elemental analysis of the fabrics (see Supporting Information for calculation details). These analyses revealed that only 2.8% of the fabric was covalently modified. This value indicates that chemical modification occurred predominantly on the surface of the fabric. The relatively low degree of substitution of MC-1 fabrics could explain why volume resistivity was not influenced by the covalent pretreatment of the fabric and why the improvement in surface resistivity was observed only for 3% initial concentration of pyrrole. At higher Py concentration, the electrical properties were most influenced by the hydrogen bonding between PPy and cotton, whereas at lower Py percentage the covalent bonding was the determining factor.
Figure 10. Surface (a) and volume (b) resistivity of unmodified cotton, MC-PPy-3%, MC-PPy-5%, MC-PPy-10%, and MC-PPy-25% fabrics. The resistivities were collected for 1 volt and a range of 20 mA.

3.7. Washing Durability
In order to evaluate washing durability of PPy coating, the fabrics were subjected to six Launder-Ometer cycles, which are equivalent to about twenty home machine launderings. Surface and volume resistivity measurements revealed an increase in surface resistivity of approximately four orders of magnitude. Volume resistivity was less affected by the washings with an increase of only two orders of magnitude (Figures 11a; Figure 9 in the Supporting Information). The increase in the surface
resistivity was attributed to the destructive washing test, which lead to the partial delamination of the PPy from the surface of the fabric. Support for this hypothesis is found in SEM micrographs (Figure 11b), which showed that after six Launder-Ometer cycles the amount of PPy aggregates on the surface of w-MC-PPy-10% fabric was significantly reduced. The electrical resistivity properties of NC-PPy fabrics before and after washing were similar to those of the MC-PPy fabrics. The PPy covalently bonded fabrics were not noticeably more durable (Supporting Information). This is probably due to the low degree of substitution of the MC-1 fabric.

**Figure 11.** (a) Surface and volume resistivities of MC-PPy-10% fabrics obtained before and after six Launder-Ometer cycles. The resistivities were collected for 1 volt and a range of 20 mA. (b) HRSEM images of MC-PPy-10% (left) and w-MC-PPy-10% (right) fabrics before and after six Launder-Ometer cycles.
4. Conclusions

Electro conductive fabrics with a continuous PPy network were successfully prepared by chemical and physical grafting of PPy onto cotton fabrics. SEM and electrical resistivity analyses showed that the fibers were completely covered with a PPy layer and exhibited both surface and volume electrical resistivities in the range of semiconductors. Based on the relatively low degree of substitution, it only a small fraction of PPy chains were chemically grafted onto the fabric surface, while most were physically grafted onto the fabric through hydrogen bonds. Thus, covalent bonding had a stronger effect at lower Py amount used for the polymerization, whereas at a higher percentage of the monomer, the electrical properties were more influenced by the physical bonding. Washing durability studies showed some mechanical destruction of the fabric surface, which mainly affected surface resistivity of the fabrics. In addition, durability was not noticeably higher for the chemically grafted fabrics as a result of the low degree of substitution. Our future attempts will be directed toward further modifications of PPy chemically grafted fabrics using hydrophobic fabrics such as polyester and polypropylene, as well as using functional linker molecules with higher functionality. These modifications are expected to increase the efficiency of covalent fabrication over physical fabrication of ICPs onto fabrics.

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