

## FT-IR Study of Dopant-wool Interactions During PPy Deposition

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(Received January 20, 2006; Revised March 8, 2006; Accepted April 7, 2006)

**Abstract:** Coating the fibre surface by *in situ* oxidative chemical polymerisation of polypyrrole (using FeCl<sub>3</sub> as oxidant) is a readily industrial applicable way to give electrical properties to wool with good ageing stability [1], although pre-treatments are required to avoid damage of the cuticle surface due to the acidic condition of the process. FT-IR and EDX analysis reveal that organic sulphonates and sulphates, used as dopants, are absorbed by wool, while chlorine ions are preferably embedded on the polypyrrole layer. The resulting electrical conductivity seems mainly due to the presence of chlorine as counter-ion of polypyrrole; nevertheless, the presence of arylsulphonate in the polymerisation bath increases the electrical conductivity of the coating layer.

**Keywords:** Polypyrrole, Conducting polymer, Dopant, Wool, Textile

### Introduction

Textile materials generally show poor electrical conductivity. Several methods have been developed to improve the electrical properties of synthetic fibres, but few of them are suitable for natural fibres, particularly for wool. Coating the fibre surface with a thin film of conducting polymers (i.e.  $\pi$ -conjugated polymers as polypyrrole and polyaniline) by *in situ* chemical oxidative polymerisation in the presence of organic dopants, is the most promising way to improve the electrical performances of natural fibre based textiles, since conducting polymers have already demonstrate good affinity to protein and cellulose fibres [1-3].

Doped  $\pi$ -conjugated polymers produced by oxidative polymerisation, contain positive charges on the backbone chain. It is supposed that the charged species are polarons (charge +e, spin 1/2) and bipolarons (+2e, 0), which are delocalized over portion of several monomer units. The mobility of charged species along the polymer chain is responsible for the electrical conduction. The charges are neutralized through the introduction in the polymer structure of negative charged counter-ions. The counter-ions (also called dopants) play an important role in the synthesis of conducting polymers, because they promote the stability of polarons and bipolarons producing complexes [4,5].

In the case of polypyrrole (PPy), positive charges are formed in the backbone chain during the chemical oxidative polymerisation. A wide range of counter-ions can be incorporated into PPy; they are generally organic sulphonates or sulphates [6-9] or inorganic ions such as ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> [9-11]. The type of counter-ion greatly influences the properties (e.g. morphology, structure, conductivity and stability) of the whole polymer [9,12-14].

On the other hand, it is well known that anionic surfactants, in particular alkylsulphates or arylsulphonates, are absorbed

by wool [15-17] and a recent work [18] has disclosed that sodium dodecylsulphate, absorbed onto wool surface, forms bilateral micelles. Moreover, it was demonstrated that anionic surfactants in acidic condition, greatly increase the acid damage of wool [15].

In a previous work [19], differences in electrical conductivity were obtained for PPy coating on different kinds of wool subjected to usual industrial treatments. In particular, the electrical conductivity was found to decrease following the series: Hercosett<sup>®</sup> wool > Basolan<sup>®</sup> wool > raw wool > Mohair fibres.

Knitted fabrics were already industrially produced from conductive wool fibres treated with PPy. The fabrics showed good properties, satisfactory performances and stability to use [1]. Moreover, it seemed that some interactions between fibres and dopant took place during the PPy deposition processes, although an exhaustive study on the interactions between the reagents (oxidant, dopant, monomer) and the substrate was not yet carried out, in spite of those influence the deposition process and the final result.

### Experimental

#### Materials

The chemicals used were Pyrrole, 97 % (Py, Fluka) as monomer; Iron (III) Chloride Hexahydrate, 98 % (FeCl<sub>3</sub>, Fluka) and Ammonium Persulfate, 98+% (APS, Aldrich) as oxidants; Naphthalenedisulfonic acid, disodium salt, 97 % (NDS, Aldrich), Naphthalenesulfonic acid, sodium salt, 90 % (NS, Aldrich), Dodecylsulfate, sodium salt, 98 % (DS, Aldrich) and Dodecylbenzenesulfonic acid, sodium salt, tech. (DBS, Aldrich) as dopants. Other chemicals were Hydrochloric Acid 0.5M (HCl, Riedel-de Haën) for pH correction and Nonylphenol-20-Ethylenglycol Ether (NPE, Ilario Ormezzano SAI) as non-ionic surfactant to facilitate the impregnation of wool.

Loose fibres were Hercosett<sup>®</sup> merino wool (18.6  $\mu$ m),

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Basolan<sup>®</sup> merino wool (21  $\mu\text{m}$ ), raw merino wool (19.5  $\mu\text{m}$ ) and Mohair fibres (30  $\mu\text{m}$ ) supplied by Filatura di Trivero S.p.A. (Gaglianico, Italy). Hercosett<sup>®</sup> and Basolan<sup>®</sup> processes are frequently used to provide felt-proofing and shrink-resistance to wool. The Hercosett<sup>®</sup> process consists of an acid chlorination step followed by the application of a polymer thin film (e.g. cationic cross-linking polyamide-epichlorhydrin polymer) on the fibre surface, in order to envelop the external scales of the cuticle cells and prevent fibres motion with differential friction in the tip-root direction, which is recognised to be responsible for shrinking and felting [16,20-23]. The chlorination results in the oxidation of cystine residues into cysteic acid residues on the surface of the wool fibres and allows the cationic polymer to spread and adhere to the wool surface [22,23]. The Basolan<sup>®</sup> process consists of a chlorination step (e.g. dichloroisocyanurate salt) followed by neutralisation and dechlorination; resistance to shrink and felt is mainly due to the oxidative corrosion of the surface scale-shaped cuticle cells [21,24]. The fibres were used as received because already scoured and no additives were present.

## Methods

A first series of samples was treated with dopants (NDS, NS, DS or DBS) and oxidants ( $\text{FeCl}_3$  or APS) or pH corrector (HCl) with the aim of evidencing the interaction between the reagents and the fibres. The concentrations of the solutions were 0.105 N of oxidant or HCl, 0.0175 M of dopant. The treatments were carried out at room temperature in the presence of the non-ionic surfactant (NPE) with water/fibres and NPE/fibres ratios 50 w/w and 0.03 w/w respectively; then the samples were rinsed twice in demineralised water.

A second series of samples was coated with PPy produced by an *in situ* chemical polymerisation in aqueous solutions. In the PPy deposition, the fibres were placed in a stirred aqueous solution containing  $\text{FeCl}_3$ , NDS and non-ionic surfactant for about 15 minutes. After the monomer was added, the solutions became black in a few minutes and the stirring was stopped. The concentrations of the polymerisation bath were 0.105 M of  $\text{FeCl}_3$ , 0.0175 M of NDS and 0.05 M of monomer (Py). The samples were pulled out from the solution after 5 h, rinsed in water and dried. PPy coated wool fibres were industrially spun and knitted, as reported elsewhere [1]. Another lot of wool was treated without the dopant in the same condition, in order to compare the electrical conductivity.

SEM investigation was performed with a LEO (Leica Electron Optics) 135 VP SEM, at an acceleration voltage of 15 kV and at 18 mm working distance. The fibres were mounted on aluminium specimen stubs with double-sided adhesive tape and sputter-coated with a gold layer in rarefied argon, using an Emitech K550 Sputter Coater, with a current of 20 mA for 180 s.

SEM-EDX analysis were performed by an Oxford Instruments Model 7060 Link ISIS interfaced to a PC using 4096 channels

in the range of 10 keV, with a preset integral of 16000 counts between 0.00 and 3.00 keV. X-ray microanalysis was performed with a dead time of about 25 %, 400 pA probe current, 15 kV accelerating voltage and 18 mm working distance.

FT-IR spectra were acquired by means of a Thermo Nicolet Nexus spectrometer, by attenuated total reflection (ATR) technique with the Smart Endurance accessory, in the range from 4000 to 550  $\text{cm}^{-1}$  with 100 scans and 4  $\text{cm}^{-1}$  of band resolution and normalized to the amide I band at 1630  $\text{cm}^{-1}$ .

Domestic and commercial washing fastness were evaluated by an Original Hanau Linitest apparatus using the ECE detergent distributed by EMPA Testmaterials, according to EN ISO 105-C06:1997 A1S. Abrasion tests were performed using a Nu-Martindale abrasion and pilling tester from James Heal & Co., with a load of 12 kN, according to EN ISO 12947-1:1998.

Electrical resistance was measured in a conditioned laboratory (20 °C, 65 % RH) by means of a digital Multimeter Escort 170 connected with the long sides of sample (8 cm  $\times$  4 cm) by 16 terminals.

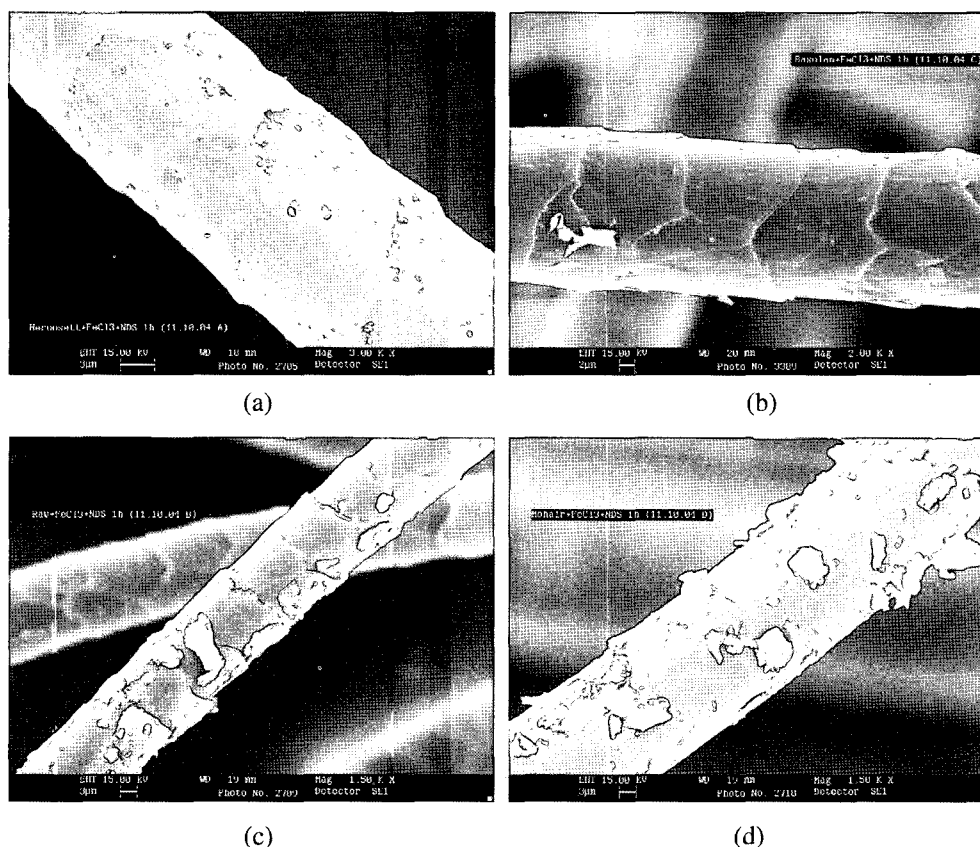
## Results and Discussion

### Analysis of Blank Treated Wool

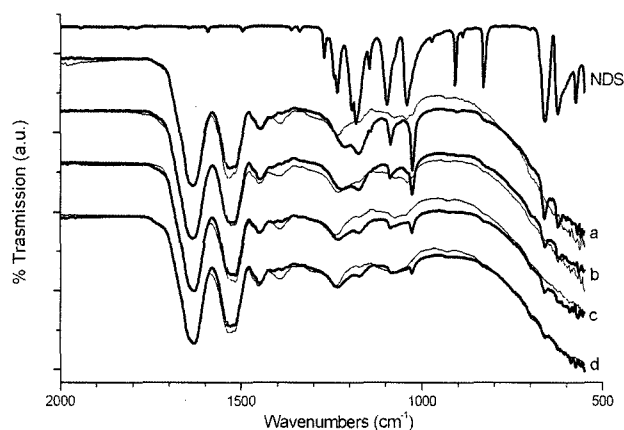
Hercosett<sup>®</sup>, Basolan<sup>®</sup>, raw wool and Mohair fibre samples, treated for 1h with  $\text{FeCl}_3$  and NDS in aqueous solution as previously described, and rinsed twice for 5 minutes in about 400 ml of stirred demineralised water to eliminate the excess of reagents, showed an intense permanent yellowing.

The SEM images of the fibres are reported in Figure 1. The surface of wool fibres consists of cuticle cells overlapping to form a structure like tiles on a roof. In Mohair fibres, this typical scaled structure is less emphasized and the surface is smoother because the cuticle cells are thinner. As can be noted, Hercosett<sup>®</sup> wool (a) and Basolan<sup>®</sup> wool (b) show no damage of the cuticle cells, on the contrary of raw wool (c) and Mohair fibres (d). The explanation may be that the acidic chlorine-based oxidation step in Hercosett<sup>®</sup> and Basolan<sup>®</sup> processes essentially modify the cuticle cells [20-23]: raw wool (c) and Mohair fibres (d), which were not previously treated, show the detachment of some cuticle cells, in accordance with literature which asserts that surfactants can have a significant influence on the reactions of wool to acids [15].

Figure 2 shows the FT-IR spectra of NDS dopant powder,  $\text{FeCl}_3$ /NDS treated samples (thick lines) and untreated wool (thin lines) for comparison. NDS spectrum shows the typical absorption of aromatic sulphonates. The bands in the range 1250-1000  $\text{cm}^{-1}$  can be attributed mainly to  $-\text{SO}_3^-$  groups and in particular to the asymmetric and symmetric S=O stretching vibrations, whereas the bands at 830, 660 and 620  $\text{cm}^{-1}$  can be assigned to the aromatic C-H bending vibration absorptions. The spectra of the untreated samples (thin lines) show the typical featuring of keratins. Peptide group ( $-\text{CONH}-$ ) give spectral bands at 1630, 1520 and 1235  $\text{cm}^{-1}$  assigned to I, II



**Figure 1.** SEM images of  $\text{FeCl}_3/\text{NDS}$  treated (a) Hercosett wool ( $\times 3000$ ), (b) Basolan wool ( $\times 2000$ ), (c) raw wool ( $\times 1500$ ), (d) Mohair fibres ( $\times 1500$ ).

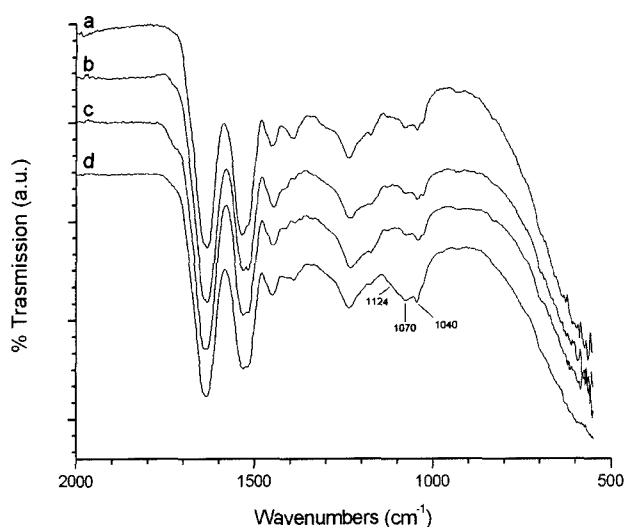


**Figure 2.** FT-IR spectra of NDS powder, untreated (thin line) and  $\text{FeCl}_3/\text{NDS}$  treated (thick line) wool: (a) Hercosett wool, (b) Basolan wool, (c) raw wool, (d) Mohair.

and III amides, respectively. Finally, the spectra of  $\text{FeCl}_3/\text{NDS}$  treated samples show some modification in the range of  $1250\text{--}1000\text{ cm}^{-1}$  and below  $700\text{ cm}^{-1}$ . The positions of these new sharp peaks are in good agreement with the bands of the NDS. Moreover, the peak intensity of the sharp peak at  $1030\text{ cm}^{-1}$  decreases in the order: Hercosett<sup>®</sup> wool > Basolan<sup>®</sup>

wool > raw wool > Mohair fibres. Thus, it seems that the NDS was absorbed onto the fibres, and in particular on Hercosett<sup>®</sup> and Basolan<sup>®</sup> treated wools. The band at  $1390\text{ cm}^{-1}$  attributed to  $-\text{CH}_3$  bending [25] strongly decreases in intensity in the spectra of the treated samples. Wool contains a large amount of amino acids with methyl-terminal side chain: Alanine (5.2%), Isoleucine (3.1%), Leucine (7.0%), Threonine (6.6%), Valine (5.5%) and Methionine (0.4%). The disappearance of that band is probably due to conformational rearrangements induced by acidic condition, which hind the  $-\text{CH}_3$  symmetric bending mode.

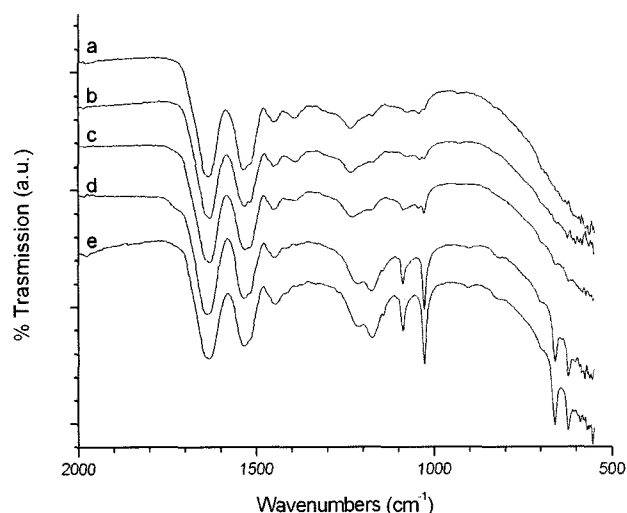
Samples of Hercosett<sup>®</sup> wool were treated for 5 h in aqueous solution, as previously described, with  $\text{FeCl}_3$  or HCl or APS only, and rinsed twice for 5 minutes in about 400 ml of stirred demineralised water. Only the fibres treated with  $\text{FeCl}_3$  became yellow-brown. FT-IR analysis of these samples is reported in Figure 3. No significant modifications were noted in the spectra of  $\text{FeCl}_3$  (b) and HCl treated (c) Hercosett<sup>®</sup> wools with respect to untreated (a) Hercosett<sup>®</sup> wool. The spectrum of APS treated (d) Hercosett<sup>®</sup> wool shows an absorption increase in the range  $1140\text{--}1100\text{ cm}^{-1}$  due to S-O stretching of the oxidized species of cystine S-S bonds (Cys-S-S-Cys). In particular, the absorption bands at 1040, 1070 and  $1124\text{ cm}^{-1}$  are assigned respectively to cysteic acid (Cys-



**Figure 3.** FT-IR spectra of (a) untreated wool, (b)  $\text{FeCl}_3$  treated wool, (c) HCl treated wool, (d) APS treated wool.

$\text{SO}_3\text{H}$ ), cystine-S-monoxide (Cys-SO-S-Cys) and cystine-S-dioxide (Cys-SO<sub>2</sub>-S-Cys) [1,26-28] produced by the treatment with APS, not evidenced after the previous described treatment with  $\text{FeCl}_3$ . On the other hand, the absorption band of inorganic sulphate is centred near  $1100\text{ cm}^{-1}$  [26]; therefore, it is possible that some residues of APS contribute to the absorption increase. The bands of cysteine-S-sulphonate (or Bunte salt, Cys-S-SO<sub>3</sub>H) at  $1024$  and  $1190\text{ cm}^{-1}$  [1,26-28] remain the same, as expected.

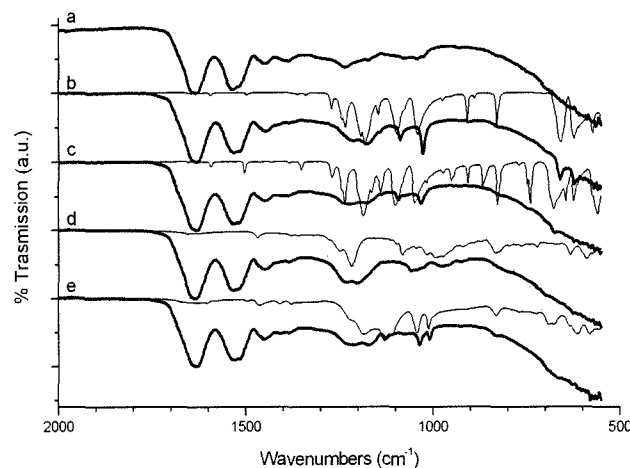
Figure 4 shows FT-IR spectra of Hercosett® wool after different NDS treatments lasting 5 h in aqueous solution, after being rinsed twice for 5 minutes in about 400 ml of stirred demineralised water. The FT-IR spectrum (b) of the sample treated with NDS does not show the NDS absorption



**Figure 4.** FT-IR spectra of (a) untreated wool, (b) NDS treated wool, (c) APS/NDS treated wool, (d) HCl/NDS treated wool, (e)  $\text{FeCl}_3$ /NDS treated wool.

bands, indicating that the dopant is not absorbed by the wool and it is removed in consequence of the rinses. On the other hand, the spectrum (c) of APS/NDS treated Hercosett® wool shows weak absorptions in the range  $1100\text{--}1000\text{ cm}^{-1}$  related to the cystine oxidation (as previously reported), whereas the spectra (d) of HCl/NDS treated wool and (e) of  $\text{FeCl}_3$ /NDS treated wool show sharp peaks at  $1085$ ,  $1025$ ,  $660$  and  $620\text{ cm}^{-1}$  and a broad band at  $1175\text{ cm}^{-1}$ , already attributed to NDS (see Figure 2). Thus, the presence of NDS onto the Hercosett® wool seems to be promoted by an acidic pH.

Samples of Hercosett® wool were treated for 1 h with a solution of  $\text{FeCl}_3$  and dopant, and rinsed twice for 5 minutes in about 400 ml of stirred demineralised water. It should be highlighted that NS and DBS slowly react with ferric ions and form a gelatinous precipitate in about 3 h. On the contrary, DS rapidly precipitate with  $\text{FeCl}_3$ , hence the suspension was filtered and the clarified solution was used to treat the fibre samples. Figure 5 shows FT-IR spectra of the dopant powder (thin line) and treated Hercosett® wool (thick line). The main changes in the spectra of treated wool with respect to the untreated one (a) are reported in Table 1 and compared with peaks of the dopant powder. In the  $\text{FeCl}_3$ /NDS and  $\text{FeCl}_3$ /NS treated wool samples, it is interesting to note a shift at lower wavenumbers of the symmetric S-O stretching vibrations, suggesting interactions between dopants and wool. In the acidic condition ( $\text{pH} < 4$ ), the amino and carboxyl groups and the side-chains of wool keratins are in the cationic form ( $\text{H}_3\text{N}^+\text{-wool-COOH}$ ), therefore this could promote electrostatic interactions between keratin chains and anionic groups ( $-\text{SO}_3^{2-}$ ) of dopants. All the dopants tested in our experiments were absorbed or fixed onto wool, but solely the NDS is suitable for the doped PPy deposition, due to its stability in solution with  $\text{FeCl}_3$ .



**Figure 5.** FT-IR spectra (a) untreated wool, (b) NDS powder (thin line) and  $\text{FeCl}_3$ /NDS treated wool (thick line), (c) NS powder (thin line) and  $\text{FeCl}_3$ /NS treated wool (thick line), (d) DS powder (thin line) and  $\text{FeCl}_3$ /DS treated wool (thick line), (e) DBS powder (thin line) and  $\text{FeCl}_3$ /DBS treated wool (thick line).

**Table 1.** New absorption bands in the FT-IR spectra of FeCl<sub>3</sub>/dopant treated wool related to some dopant peaks (see Figure 5)

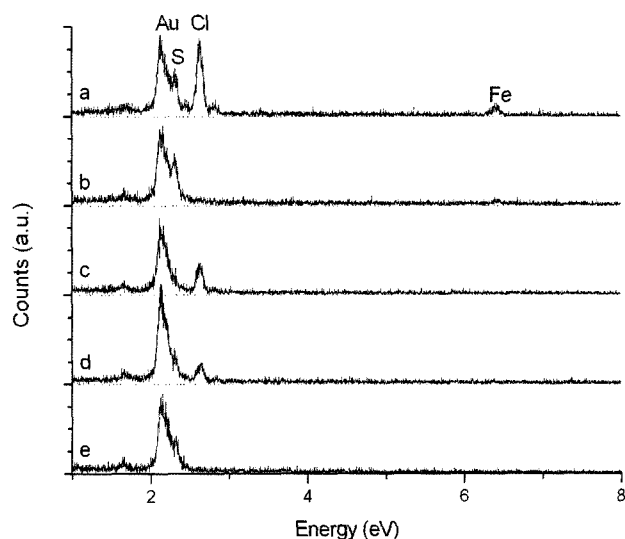
Dopant	New peaks (cm <sup>-1</sup> )	Dopant peaks (cm <sup>-1</sup> )
NDS	1175	1180
	1085	1100
	1025	1045
	660	660
	620	620
NS	1160	1180
	1085	1100
	1025	1045
DS	1200	1215
	1000~900	1000~900
DBS	1170	1185
	1130	1125
	1040	1045
	1010	1010

**Analysis of PPy Coated Wool**

PPy coated Hercosett® wool fibres, obtained as previously described, were industrially intersected, spun and knitted producing electrically conducting fabrics with a cover factor of 1.27 mm tex (according to Woolmark Test Method 169), good handle and a deep and even black colour.

The fabric obtained from PPy coated Hercosett® wool with NDS was tested for domestic and commercial washing and abrasion resistance. Fabric samples were examined with EDX microanalysis, FT-IR and SEM.

EDX spectra are reported in Figure 6. In every sample,

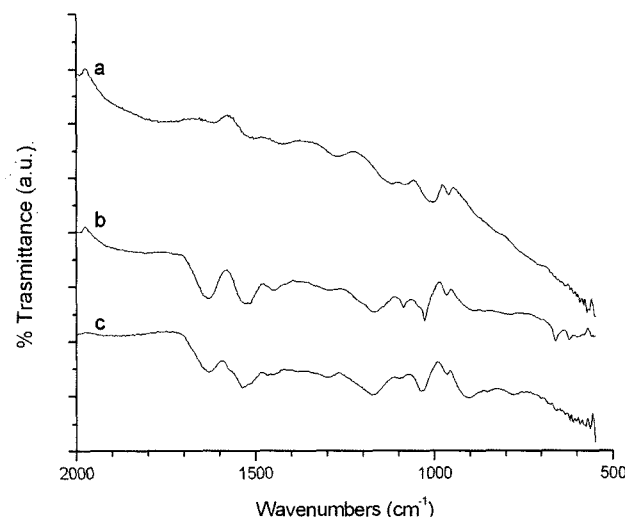


**Figure 6.** EDX spectra (a) FeCl<sub>3</sub> treated wool, (b) FeCl<sub>3</sub>/NDS treated wool, (c) freshly PPy coated wool, (d) knitted fabric from PPy coated wool, (e) knitted fabric from PPy coated wool after washing test.

gold is present due to sample preparation (sputter coating) and sulphur is naturally widely present in wool keratin. The spectra (a) and (b) are related to FeCl<sub>3</sub> and FeCl<sub>3</sub>/NDS treated wool respectively. The spectrum (a) shows a huge presence of chlorine and iron; instead, the spectrum (b) shows some presence of chlorine and iron in traces. In addition, NS and DBS showed the same behaviour, but the spectra are not reported here for sake of brevity. The spectrum (c) of freshly PPy coated Hercosett® wool shows the peak of chlorine. Thus, it seems that NDS was absorbed by wool preferably with respect to chlorine; whereas chlorine was embedded onto PPy, leading to an improvement of the PPy properties that could be attributed to structural changes [29]. Moreover, the absence of sulphur in the spectra (c) could demonstrate that the size of the sample-beam interaction volume does not exceed the PPy thickness and the PPy only was detected. Chlorine is still present in the spectrum (d) referring to newly knitted fabric, whereas the chlorine peak completely disappears after three washing cycles, as shown by spectrum (e). Table 2 reports the electrical resistance of the washed samples and the coefficient of variation (CV%) of the measurements. A decrease in conductivity is observed. On the other hand, the degree of the colour degradation after the washing cycles was evaluated to be 4/5 (when 5 is excellent stability and 1 is poor). Thus, the loss in conductivity seems slightly related to the leak of PPy, but rather due to the lowering of chlorine partially compensated by ions OH<sup>-</sup> [30,31].

**Table 2.** Surface resistivity after domestic washing cycles

Number of washing cycles	0	1	2	3
Resistivity (kΩ/square)	0.94	4.64	17.3	42.5
CV (%)	8.7	2.3	8.6	12.2

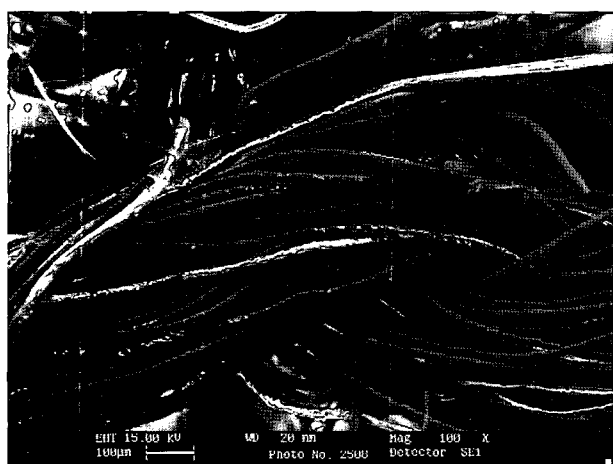


**Figure 7.** FT-IR spectra (a) freshly PPy coated wool, (b) knitted fabric from PPy coated wool after abrasion test (40000 run), (c) knitted fabric from PPy coated wool after three washing cycles.

Figure 7 reports the FT-IR spectra of freshly coated fibres (a), knitted fabric from PPy coated Hercosett® wool after the abrasion test (b) and after three washing cycles (c). The spectrum (a) shows some weak bands in the region 1700-1200  $\text{cm}^{-1}$  probably due to the overlapping of spectral features of PPy and wool [1]. In the literature, Davidson and Turner [8] assigned the band at 960  $\text{cm}^{-1}$  to fraction of PPy free from the influence of the dopant. Spectral features of wool are mainly shown in the region 1700-1200  $\text{cm}^{-1}$  of the spectra (b) and (c), but the increase in intensity of the amide II at 1520  $\text{cm}^{-1}$  (with respect to the amide I at 1630  $\text{cm}^{-1}$ ) is probably due to contributions of C=C/C-C stretching of PPy [8]. The sharp bands at 1085, 1025, 660 and 620  $\text{cm}^{-1}$  in the spectrum (b) are the signal of the presence of NDS, as previously said. Whereas, in the spectrum (c) the absorption bands at 1170, 1030 and 910  $\text{cm}^{-1}$  are quite similar to the feature of the spectrum (a), and may be attributed to PPy ring breathing, C-H in-plane bending and C-H bending [8] respectively. The band at 960  $\text{cm}^{-1}$  is still present and its position is stable even after washing, is in good agreement with the conclusions of Davidson and Turner [8].

SEM image in Figure 8 shows the PPy coated Hercosett® wool fabric after the abrasion tests. As the sample was not sputter-coated with gold in this case, the zones where the PPy coating was mechanically removed by abrasion appear white, due to the lack of conductivity that causes electrical charge accumulation from the primary electron beam of the microscope. The appearance of NDS absorption bands after the abrasion test is related to the huge de-coating. It was pointed out that, although the fabric was seriously damaged, its electrical conductivity remains satisfactory [1].

For comparison, the electrical resistivity was also measured on the fabrics produced from both coated Hercosett® wool with NDS and coated Hercosett® wool without NDS, obtaining average surface resistivities of 940 and 1400  $\Omega/\text{square}$ , respectively. This result shows that the presence of NDS in the polymerisation bath enhances the electrical conductivity.



**Figure 8.** SEM image of the fabric after abrasion test.

## Conclusion

In this study, loose wool fibres were coated with PPy by *in situ* chemical oxidative polymerisation, with the aim of producing electrical conductive wool textiles for apparel and technical uses. Untreated fibres (i.e. raw wool and Mohair) showed the damage of the cuticle layer after treatments with  $\text{FeCl}_3$  and dopants, while shrink resistant fibres (i.e. Hercosett® and Basolan® treated wool) were particularly suitable for the PPy deposition process. Wool shows an interaction with organic dopants during polymerisation. The interaction plays an important role on the resulting properties. FT-IR and EDX analysis show that the organic dopant is preferably absorbed by wool, whilst chlorine is preferably embedded onto the conductive PPy coating as counter-ion. On the other hand, loss of chlorine from the PPy/wool composite was observed after washing, leading to an increase of the surface resistivity of the fabrics; nevertheless, the presence of NDS in the polymerisation bath enhances the final electrical conductivity.

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