

## Antibacterial Efficacy of Polypyrrole in Textile Applications

Alessio Varesano\*, Claudia Vineis, Annalisa Aluigi, Fabio Rombaldoni,  
Cinzia Tonetti, and Giorgio Mazzuchetti

CNR-ISMAR, National Research Council of Italy, Institute for Macromolecular Studies, Biella, Italy

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**Abstract:** This paper describes application and evaluation of polypyrrole as an antibacterial polymer. Polypyrrole was produced embedding two doping agents: chloride and dicyclohexyl sulfosuccinate ions. Stability of the antibacterial efficacy of polypyrrole deposited on cotton fabrics was assessed before and after three different kinds of washing (namely, laundering with anionic and non-ionic detergents and dry-cleaning). Polypyrrole showed excellent antibacterial properties (100 % of bacterial reduction) against *Escherichia coli* for both doping agents. Treated fabrics were further characterised by scanning electron microscopy, energy dispersive X-ray analysis and infrared spectroscopy. The antibacterial efficacy diminished after laundings with anionic and non-ionic detergents because of two different mechanisms: the neutralisation of positive charges under alkali conditions (dedoping), and a partial removal of polypyrrole by abrasion and surfactant action. After dry-cleaning, polypyrrole embedding chloride and dicyclohexyl sulfosuccinate ions still showed excellent antibacterial efficacy. Moreover, scanning electron microscopy investigations were used to intuitively explain the bactericidal mechanism of polypyrrole on *Escherichia coli* bacteria.

**Keywords:** Antibacterial polymer, Polypyrrole, Conjugated polymer, Coating, Antibacterial textile

### Introduction

In the last few decades, antimicrobial textiles have gained interest from both academic research and industry because of their potential to provide better quality life and safety benefits to people [1]. Textile products are prone to host micro-organisms whose proliferation is responsible for diseases, unpleasant odours, colour degradation and deterioration of fabrics [2]. Antimicrobial finishes are used in many textile products, such as sportswear, outdoor apparels, undergarments, shoes, furnishings, upholstery, hospital linens, wound care wraps, towels and wipes.

Existing biocidal agents, such as triclosan, ammonium quaternary salts and silver, suffer from some critical drawbacks, for instance short active duration, high costs or leaching out from the fabrics towards the environment and to the skin of the users. Antimicrobial polymers having high molecular weight and low cost could overcome some of these problems. Antimicrobial polymers have been increasingly taken into account for the production of antimicrobial goods. This approach is particularly interesting in textile field, where antimicrobial polymers show several advantages over low-molecular weight antibacterial agents, including improved environmental stability, lack of diffusion on the wearers' skin, low skin irritation, low toxicity, good biocompatibility, low corrosion of metals and plastics, long residence time and biological activity.

An antimicrobial polymer is usually defined as a polymer having biocidal pendant groups (e.g. pyridium-type polycations) or biocidal repeat units (e.g. polybiguanides) in the polymeric chemical structure. Therefore, the simple addition of antimicrobial

molecules to a polymer matrix should not be deemed as a method for producing antimicrobial polymers. Studies on synthesis and application of antimicrobial polymers started in the 1970s [3,4].

A lot of literature has been recently produced on this topic applied to textile materials. The most used antimicrobial polymers on textiles are quaternized polymers [5,6], biguanide-based polymers [7-9] and chitosan [10-12].

In 2005, Seshadri and Bhat first reported antibacterial activity of  $\pi$ -conjugated polymers (i.e. polypyrrole (PPy) and polyaniline) [13,14]. Conjugated polymers, also called intrinsically conducting polymers (ICPs), are employed in textile field for their electrical properties [15]. ICPs can be produced by chemical oxidative polymerisation from water solutions of the monomers. Solid surfaces placed in the polymerisation bath are spontaneously coated with a film-like dense layer of ICP.

Synthesis with oxidative polymerisation produces positive charges along the backbone chain of PPy. In PPy, one positive charge is formed for each three to five repeat units. Positive charges are counter-balanced by counter-ions (also called dopant), namely anions present in the polymerisation solution that are embedded in the polymer matrix [16]. The positive charges seem to be responsible for the antibacterial activity of such kind of polymers.

Many different textile materials (such as fibres, fabrics, non-wovens, etc.) have been coated with ICPs for different purposes; scientific literature is rich of papers related to treatments with ICPs, in particular on cotton [17], viscose and lyocell [18], wool [19], silk [20], nylon [21] and polyester [22-24], but few of them deals with antibacterial textiles.

In particular, Seshadri and Bhat [14] deposited PPy on cotton fabrics by *in situ* chemical oxidative polymerisation

\*Corresponding author: a.varesano@bi.ismar.cnr.it

at cold temperature (0-5 °C). The fabrics were first impregnated with a monomer solution and then the oxidant was added. The resulting bacterial percentage reduction was 59 % against *Escherichia coli*. Some samples of PPy-coated fabrics were also treated with a solution of  $\text{CuCl}_2$  as additional antimicrobial agent that increased the antibacterial efficacy up to 98 %.

In a previous work [25], our research group coated cotton fabrics with PPy using different oxidising agents in order to assess their influence on the antibacterial properties without the use of any additional antimicrobial agent. Antibacterial properties were assessed (but not quantified) following the ISO 20645:2004 procedure (diffusion test method) using Gram negative *E. coli* (ATCC 8739). No inhibition zone was observed for all the samples. However, removing the specimen from the agar, it was observed the absence of bacteria in the contact zone under all PPy-coated fabrics. Therefore, antibacterial activity of PPy took effect just by contact because PPy was directly linked to the fabric.

In the present work, the antibacterial efficacy of PPy deposited on cotton fabrics was quantitatively evaluated under dynamic contact conditions according to ASTM E 2149-01. Moreover, bactericidal mechanism of PPy on *E. coli* bacteria was preliminarily investigated by means of scanning electron microscopy. Since the stability to washing is a critical factor for practical applications in textile field, this work also aimed to assess the durability of antibacterial properties after washing in order to find suitable washing procedures for such kind of textiles.

## Experimental

### Materials

Raw cotton knit-fabrics were kindly supplied by Yanga srl (Italy). Chemicals used for the synthesis of PPy were: pyrrole (97 %), ferric chloride hexahydrate and dicyclohexyl sulfosuccinate sodium salt (DSS) by Fluka.

The bacteria used for antibacterial test were *E. coli* (Gram negative) ATCC 11229 by Microbiologics (USA). Yeast extract agar and peptone were supplied by Liofilchem (Italy).

Other chemicals were petroleum ether and tetrachloroethylene by Riedel-de Haën (Germany), ECE detergent (according to ISO 105-C06) by EMPA Testmaterials (Switzerland) and Tween<sup>®</sup> 20 by Sigma-Aldrich (Germany).

Glutaraldehyde solution 50 wt. % in water by Sigma-Aldrich was used for fixing bacteria morphology in order to perform scanning electron microscopy investigations.

### Coating

Cotton fabrics were extracted by Soxhlet using petroleum ether for 2 h, and dried in air. PPy depositions were carried out at room temperature by plunging the fabrics (about 5 g) in stirred solution of ferric chloride (90 mM) and DSS (12 mM, when used) with a liquor ratio of 50:1 ml/g. After an impregnation of 15 minutes, pyrrole was drop-wise added to

the solution, up to the final concentration (30 mM). The solution became dark because of PPy production. The samples were pulled out from the polymerisation bath after 4 h, rinsed in cold water, squeezed and dried overnight at room temperature.

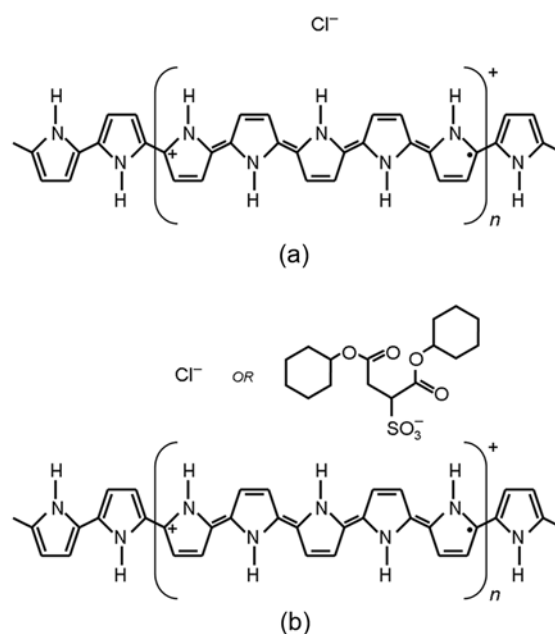
In this work, DSS had two different functions: (1) it was embedded into PPy as counter-ion (i.e. doping agent), similarly to several other chemicals with an  $-\text{SO}_3^-$  group (e.g. sodium dodecyl sulphate, naphthalene sulphonate, dodecylbenzene sulphonate) [26], otherwise, in absence of DSS, only chloride ions (deriving from ferric chloride) were embedded in PPy; (2) DSS greatly enhanced the deposition process of PPy on the fabric by lowering the surface tension (surfactant action) and increasing evenness and weight uptake. In fact, the samples treated using DSS appeared uniformly coated by a black PPy layer. The weight uptakes after PPy depositions were of 12 % without DSS and 18 % with DSS. The difference can be attributed to the higher molecular weight of DSS with respect to chloride and a more efficient deposition due to the increased wetting of fibre surface caused by the surfactant action.

Hereinafter, samples are labelled as PPy(Cl) when DSS was not used. On the contrary, when DSS was added in the polymerisation bath, both DSS and chloride ions were embedded in PPy, thus samples are labelled as PPy(DSS+Cl). The chemical structure of PPy (in polaronic form) embedding  $\text{Cl}^-$  and DSS/ $\text{Cl}^-$  are reported in Figure 1.

### Washing Conditions

Samples of the resulting PPy-coated fabrics were washed five times in a wash-wheel in three different ways:

(a) with 5 g/l standard soap (ECE) in water at 40 °C with a



**Figure 1.** Chemical structures of (a) PPy(Cl) and (b) PPy(DSS+Cl).

- liquor ratio of 50:1 ml/g in order to simulate a domestic laundering, according to ISO 105-C01 (anionic laundering);
- (b) with 1 g/l non-ionic detergent (Tween<sup>®</sup> 20) in water at 40 °C with a liquor ratio of 50:1 ml/g (non-ionic laundering);
- (c) with pure tetrachloroethylene at room temperature with a liquor ratio of 40:1 ml/g, according to ISO 105-X05 (dry-cleaning).

Each washing cycle lasted 30 minutes. For the procedures (a) and (b) after each cycle the samples were rinsed in cold water for 10 minutes, as requested by ISO 105-C01. Final drying was carried out at room temperature. For the procedure (c), the samples were squeezed and residual solvent evaporated in air in less than 1 h.

### Antibacterial Test

Antibacterial activity was evaluated following the ASTM E 2149-01 procedure, which is a quantitative method performed under dynamic contact conditions. The incubated test culture in a nutrient broth was diluted to give a concentration of  $1.5\text{-}3.0 \times 10^5$  CFU/ml (working dilution). About 1 g of fabric was transferred to flask containing 50 ml of the working dilution. All flasks were shaken for 1 h at 190 rpm at room temperature. After a series of dilutions, 1 ml of the solution was plated in nutrient agar. The inoculated plates were incubated at 37 °C for at least 24 hours and surviving cells were counted. The antibacterial activity was expressed in percentage reduction of the organisms after contact with the test specimen compared to the number of bacterial cells surviving after contact with the control.

### Preparation for Observations of Bacterial Morphology

Both PPy-treated (PPy(DSS+Cl) sample) and untreated cotton fabrics were cut in samples of 0.5 cm×0.5 cm. About 0.1 ml of nutrient broth containing *E. coli* was spread to the samples. The samples were kept in an incubator at 37 °C for 2 hours. Then, the samples were wetted with a 5 vol. % glutaraldehyde in water, stored 2 hours at 4 °C and dried at 37 °C overnight.

### Characterisations

Scanning electron microscopy (SEM) investigations were performed with a LEO (Leica Electron Optics) 435 VP SEM, at an acceleration voltage of 15 kV and a 20 mm working distance. No metallisation was carried out before SEM analysis because the samples already had good conductivities.

The fabric samples for the observations of bacterial morphology were sputter-coated with a 20 nm-thick gold layer in rarefied argon (20 Pa), using an Emitech K550 Sputter Coater, with a current of 20 mA for 180 s, in order to improve the image quality.

Energy dispersive X-ray (EDX) analysis was performed

by an Oxford Instruments Model 7060 Link ISIS interfaced to a PC using 4096 channels in the range of 10 keV.

Fourier transform infrared (FT-IR) spectra were acquired with Attenuated Total Reflection (ATR) technique in the range from 4000 to 650  $\text{cm}^{-1}$  with 100 scans and 4  $\text{cm}^{-1}$  of band resolution by means of a Thermo Nicolet Nexus spectrometer equipped with a Smart Ark<sup>™</sup> (ZnSe 45° crystal).

## Results

### Antibacterial Tests

Table 1 reports the results of the antibacterial tests. Before washing, both PPy(Cl) and PPy(DSS+Cl) fabrics showed 100 % of bacterial reduction, while untreated cotton fabric had practically no antibacterial activity. After dry-cleaning, PPy(Cl) and PPy(DSS+Cl) fabrics showed high bacterial reductions, 99 and 98 %, respectively. Antibacterial efficacy decreased after non-ionic and anionic laundrings. In particular, antibacterial activity of PPy(Cl) samples was severely degraded by anionic laundering.

### Scanning Electron Microscopy

Figure 2 shows the surfaces of PPy-coated cotton fibres before and after washing. The coating was uniform and coarse before washing, as pictures (a) and (e) show.

On the contrary, after washing the fibres generally had a quite smooth surface because of physical action due to the washing, but a PPy layer was still visible on their surface. Moreover, all the SEM images in Figure 2 were acquired without metallisation of the samples before SEM analysis because the PPy layer on the fibre surface was still electrically conductive.

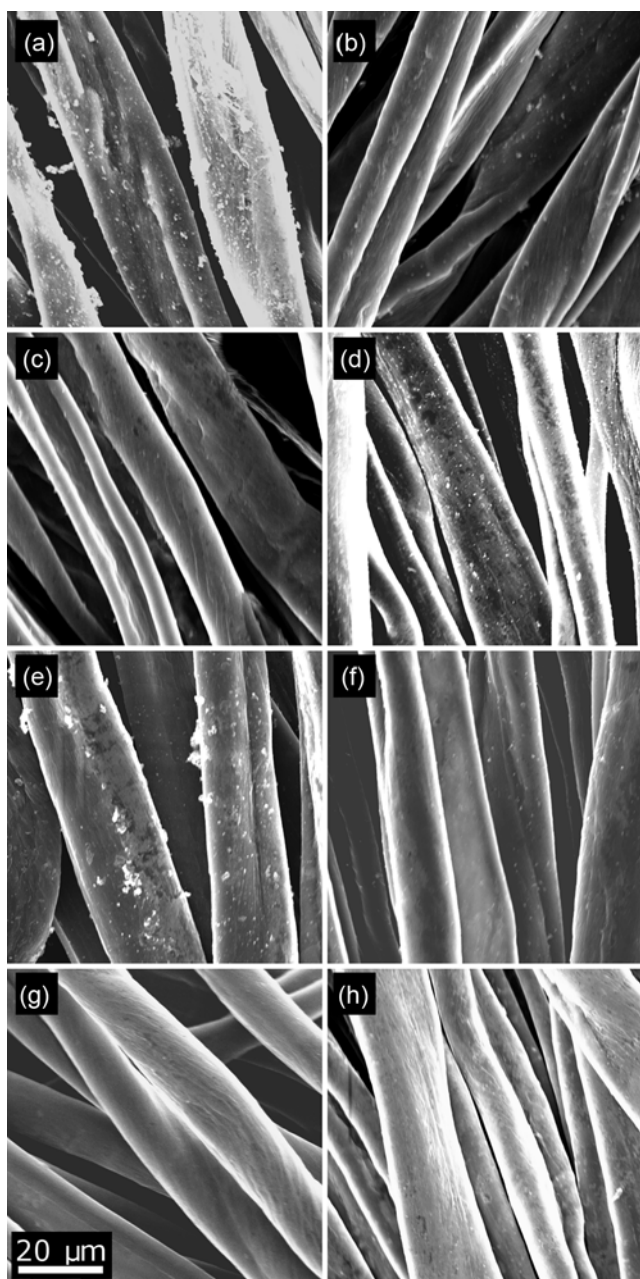
Figure 3 shows *E. coli* bacteria (indicated by arrows) on cotton fibres (a) and PPy-treated fibres (b). Bacteria on untreated cotton fibres had typical and regular bacterial shapes indicating that the *E. coli* survived on the fibre surface. On the contrary, the shape of *E. coli* cells was altered on PPy-coated fibres. In particular, bacteria appeared flattened probably due to the leakage of intracellular components from bacterial cells.

### Energy Dispersive X-ray Analysis

The EDX spectra in Figure 4 show peaks assigned to

**Table 1.** Bacterial percentage reductions of PPy-coated fabrics (before and after washing) compared with pristine cotton fabric

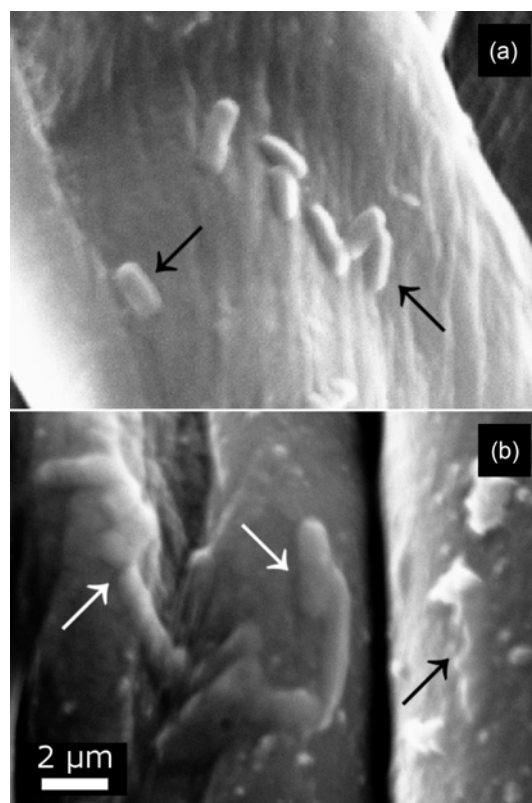
Sample	PPy(Cl)	PPy(DSS+Cl)
Before washing	100	100
After dry-cleaning	99	98
After non-ionic laundering	48	49
After anionic laundering	22	42
Untreated cotton	16	



**Figure 2.** SEM pictures of (a-d) PPy(Cl) and (e-h) PPy(DSS+Cl) samples: (a, e) before washing, (b, f) after dry-cleaning, (c, g) after non-ionic laundering, (d, h) after anionic laundering.

carbon (0.27 keV) and oxygen (0.52 keV), and a shoulder assigned to nitrogen (0.39 keV). Obviously, carbon is largely present in both cellulose, PPy and DSS (when present), oxygen can belong to cellulose or DSS, whereas nitrogen belongs to PPy.

The spectrum of PPy(Cl) fabric before washing, reported in Figure 4(i), shows a peak assigned to chloride (2.6 keV) that was embedded as counter-ions in PPy. The signal of chloride disappeared after anionic laundering and it was



**Figure 3.** SEM pictures of *E. coli* bacteria (arrows) on (a) untreated cotton fibres and (b) PPy(DSS+Cl) samples.

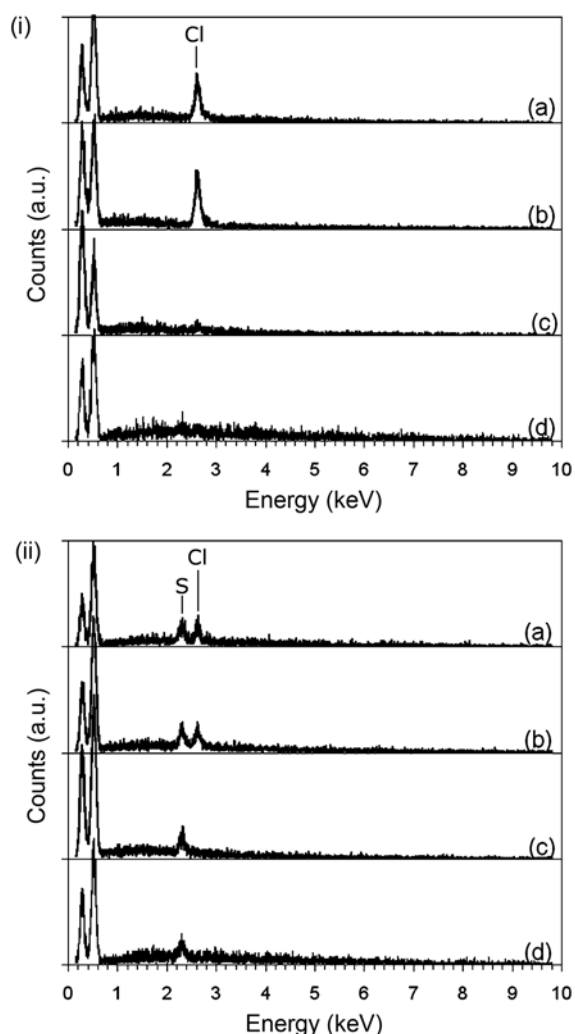
greatly reduced after non-ionic laundering. On the contrary, the peak of chloride was unaffected on the samples after dry-cleaning.

The spectrum of PPy(DSS+Cl) fabric before washing, reported in Figure 4(ii), shows signals of both chloride (2.6 keV) and sulphur (2.3 keV). The latter belongs to  $-\text{SO}_3^-$  group of DSS, therefore both  $\text{Cl}^-$  and DSS were embedded in the PPy matrix as counter-ions. Analogously to PPy(Cl) fabrics, the signal of chloride disappeared after non-ionic and anionic laundering, while it was visible after dry-cleaning. On the contrary, the sulphur peak of DSS was present after all kinds of washing.

### Infrared Spectroscopy

Figure 5 shows FT-IR spectra of uncoated and PPy-coated cotton fabrics before and after washing. The spectrum of uncoated cotton is characterized by broad bands at about  $3300$  and  $2900\text{ cm}^{-1}$  assigned to O-H and C-H stretching vibrations, and a strong absorption band at  $1030\text{ cm}^{-1}$  attributed to overlapping bands of chemical groups of cellulose, such as C-C, C-O and C-O-C.

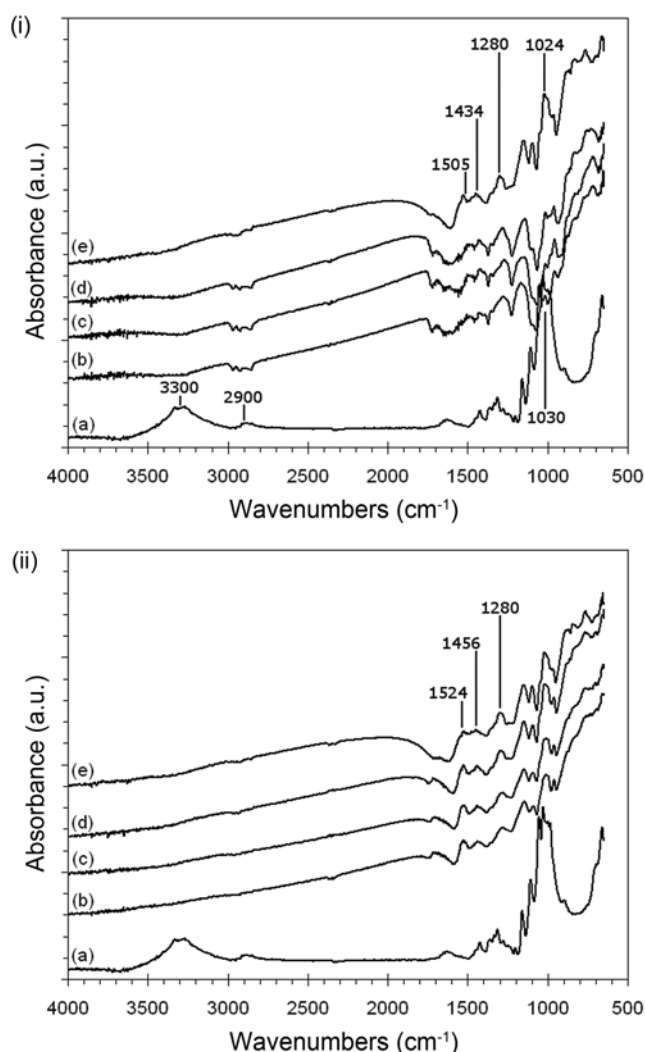
The spectral feature of the cellulose in the range from  $1250$  to  $1000\text{ cm}^{-1}$  appears greatly attenuated in the spectra of freshly PPy-coated fabrics. Since the infrared beam of the ATR technique analyses only the fibre surface with a



**Figure 4.** EDX spectra of (i) PPy(Cl) and (ii) PPy(DSS+Cl) samples: (a) before washing, (b) after dry-cleaning, (c) after non-ionic laundering, and (d) after anionic laundering.

penetration  $<1 \mu\text{m}$ , the evenness of the PPy layer on the fibres was excellent (fibre surfaces are fully covered) and PPy thickness was comparable with the infrared-ray penetration.

The spectra of PPy-coated fabrics before washing are similar. The spectra (b-e) in Figure 5(i) and (ii) show the characteristic tail of the electronic absorption of PPy in the range between  $4000\text{-}1700 \text{ cm}^{-1}$  [27]. In the PPy(Cl) samples the bands assigned to C-C and C-N stretching vibrations in the pyrrole ring [28] are centred at  $1505$  and  $1434 \text{ cm}^{-1}$ , respectively, while in the PPy(DSS+Cl) samples these bands are at higher wavenumbers ( $1524$  and  $1456 \text{ cm}^{-1}$ ). This is probably due to the steric hindrance of DSS that alters the PPy chain packing increasing C-C and C-N stretching vibration energy. The band at  $1280 \text{ cm}^{-1}$  can be attributed to C-H and C-N in-plane deformation modes. The bands in the range from  $1200$  to  $1000 \text{ cm}^{-1}$  are usually assigned to



**Figure 5.** FT-IR spectra of (i) PPy(Cl) and (ii) PPy(DSS+Cl) samples: (b) before washing, (c) after dry-cleaning, (d) after non-ionic laundering, and (e) after anionic laundering, compared with (a) uncoated cotton fabric.

breathing vibrations of pyrrole rings and in-plane deformation vibrations of C-H and N-H [28], but in PPy(DSS+Cl) samples the signals appeared more intense than in PPy(Cl) samples probably because of the absorption bands of  $-\text{SO}_3^-$  and C-O-C groups of DSS centred at  $1204$  and  $1053 \text{ cm}^{-1}$ , respectively.

## Discussion

Pristine cotton had practically no antibacterial activity, as expected. PPy(Cl) and PPy(DSS+Cl) fabric samples showed excellent antibacterial efficacy (100 % of bacterial reduction). Such results improve the findings of existing literature about bactericidal action of PPy [13,14]. The higher efficacy can be mostly attributed to a different PPy deposition method: (i)

impregnation was made with the oxidant solution for few minutes instead of monomer solution for 2 hours and (ii) deposition was carried out at room temperature instead of cooling the polymerisation bath.

After dry-cleaning, both PPy(Cl) and PPy(DSS+Cl) fabrics still showed excellent antibacterial efficacy. On the contrary, non-ionic and anionic laundering decreased the bacterial percentage reductions to about a half of the initial bacterial reduction, except for PPy(Cl) fabric after anionic laundering that dropped to about the same bacterial reduction of cotton even though the fabrics still were black, meaning that the fibres surface was still covered with a PPy layer (Figure 2).

The antibacterial efficacy decrease due to anionic and non-ionic launderings can be ascribed to two different mechanisms: (1) the neutralisation of positive charges under alkali conditions connected to a loss of doping agent from PPy (dedoping) [24] and (2) a partial removal of PPy layer on the fibre surface by abrasion and surfactant action.

The results of the antibacterial tests are consistent with both EDX and FT-IR observations taking into account the proposed decay mechanisms (i.e. dedoping and removal of PPy). It is worth noting that DSS slightly increased the stability towards anionic laundering; in fact it was observed the presence of a peak assigned to sulphur in the EDX spectra of PPy(DSS+Cl) fabrics after anionic laundering (Figure 4(ii)). On the other hand, chloride disappeared after both non-ionic and anionic laundering, but not after dry-cleaning (Figure 4). A possible explanation could be that DSS can not diffuse from PPy matrix to water so easily as chloride ions because of its greater dimension. Therefore, positive charges related to DSS are more stable against neutralising action of alkali conditions in the washing bath during anionic laundering. On the other hand, anions (such as DSS and Cl<sup>-</sup>) are insoluble in tetrachloroethylene; this is the reason why sulphur and chloride were still observed by EDX analysis on fabrics after dry-cleaning.

Considering the removal of the PPy layer, the spectral features of the PPy(Cl) samples were practically unchanged after dry-cleaning and non-ionic laundering (Figure 5(i)), while after anionic laundering, the typical adsorption bands of cellulose clearly appeared (particularly at 1024 cm<sup>-1</sup>), as a sign of removal of PPy layer. The spectra of PPy(DSS+Cl) samples after all kinds of washing were similar to the spectra of freshly PPy-coated fabric (Figure 5(ii)), although typical adsorption bands of cellulose around 1000 cm<sup>-1</sup> appeared slightly more intense on the samples after both anionic and non-ionic laundering. Finally, both the spectra of PPy(Cl) and PPy(DSS+Cl) after anionic laundering (Figure 5) showed a reduction in intensity of the tail of the electronic absorption in the range from 1900 to 1700 cm<sup>-1</sup>. This can be attributed to a loss of conjugation and it is a further symptom that dedoping of PPy took place during anionic laundering.

SEM images (Figure 3) were used to intuitively explain the bactericidal mechanism of PPy on bacteria. The shape of

bacteria on fibres coated with PPy appeared flatten and swollen due to the collapse of cytoplasmic membrane. Therefore, similarly to other antibacterial agents, it was proposed that the death of bacteria can be attributed to the leakage of cytoplasm.

## Conclusion

Excellent antibacterial efficacy against *E. coli* was obtained by coating cotton fabrics with PPy. The antibacterial action of PPy seems to be due to positive charges in the polymer chain that interact with the bacteria cell wall producing its break. Dry-cleaning was demonstrated to be a suitable washing method for PPy-coated fabrics. The use of DSS as a counter-ion of PPy slightly improved the stability to washing during anionic laundering probably because of molecule size, but the resulting stability was still not enough for market requirements. The findings will open new potential applications for conducting polymers for textiles and biomedical devices.

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