

A systematic study on the effects of doping agents on polypyrrole coating of fabrics

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ABSTRACT: Polypyrrole is widely used as coating to produce electrically conductive textiles. Counter-ions (i.e. doping agents) were embedded in polypyrrole to improve electrical conductivity. Good electrical performances are required for several applications, such as microwave attenuation/electro-magnetic interference shielding, heat generation, electro-static discharge protection, sensing, and energy storage. In this work, a systematic study was carried out on the effects of doping agents in coating cotton fabrics with a thin polypyrrole layer. A total of 11 compounds were selected and compared as counter-ions. The electrical performances of the coated fabrics were assessed with measures of electrical conductivity. Moreover, evenness and morphology of the resulting polypyrrole layer were discussed. As the final result, the best performances in terms of electrical conductivity (i.e. low surface resistivity) were measured using on dicyclohexyl sulfosuccinate, 2,6-naphthalenedisulfonate or 1,5-naphthalenedisulfonate as doping agents. The weight increases after polypyrrole deposition on the fabrics were greater than 15% and polypyrrole deposited on the fibers as a uniform film. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42831.

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INTRODUCTION

Fabrics and textile materials with electrical properties can be easily produced by coating fiber surfaces with thin layers of inherently conducting polymers (ICPs). Applications of the resulting materials vary from microwave attenuation/electro-magnetic interference (EMI) shielding,^{1–5} resistive heating and electro-static discharge (ESD) protection,^{6,7} sensors^{8–11} and energy storage.¹² Among the ICPs, polypyrrole (PPy) is one of the most promising candidates for producing electrically conductive fabrics with a huge range of surface resistivity, from tens to millions Ω /square. Moreover, PPy-coated fabrics exhibited other properties related to the chemical structure of the polymer, such as flame resistance,¹³ antibacterial activity,^{14–17} hydrophobicity.¹⁸

PPy-coated fabrics are usually produced by *in situ* polymerization of pyrrole. During synthesis with oxidative polymerization, positive charges are introduced along the backbone chain of PPy. These charges are counter-balanced by counter-ions (also called dopants or doping agents), namely anions present in the polymerization solution that are embedded in the polymer matrix.

Many different textile materials (such as fiber, fabric, nonwoven, etc.) have been coated with ICPs for different purposes. Literature is rich of papers related to treatments of textile materials with ICPs and many different fibers (cotton,^{19–23} viscose and lyocell,^{24,25} wool,^{26–28} silk,^{29–31} polyamides,^{32–35} polyacrylonitrile,³⁶ and polyester,^{26,37–40} for instance) were coated with PPy. Moreover, many different doping agents were used to improve electrical performances of PPy. The most common dopants are organic sulphates^{41,42} because of their better stability in comparison with inorganic counter-ions. To the best of our knowledge, extensive and systematic studies to assess the best doping agents able to produce the most electrically conductive fabrics have not been carried out yet. In addition, a comparison of the effects of different doping agents embedded into PPy during its deposition on fabrics is missing in literature. In textile application, a good dopant must produce not only a highly conductive polymer, but also an even polymer layer on fibers, therefore it must not hinder synthesis and deposition of the conducting polymer on the fiber surface. Moreover, the textile substrate on which PPy is deposited can have a great influence on the electrical performances. Consequently, the comparison between results was carried out using

Table I. List of the Doping Agents

#	CAS No.	Counter-ions name	Abbreviation	Purity (%)	Molecular weight of the ion (g mol ⁻¹)
1	n.a.	Sulphate from the oxidant (without additional dopant) ^a	-	n.a.	96.1
2	23386-52-9	Dicyclohexyl sulfosuccinate	DCSS	98	361.4
3	6192-52-5	<i>p</i> -Toluenesulfate	pTS	98	171.2
4	1655-45-4	2,6-Naphthalenedisulfonate	2,6NDS	97	286.3
5	207569-02-6	1,5-Naphthalenedisulfonate	1,5NDS	97	286.3
6	831-59-4	1,3- Benzenedisulfonate	BDS	80	236.2
7	25704-18-1	Polystyrene sulfate, Mw 70,000	PSS	n.a.	206.2 ^b
8	25155-30-0	Dodecylbenzenesulfate	DBS	90	325.5
9	81-11-8	4,4'-Diamino-2,2'-stilbenedisulfonate	DASDS	85	368.4
10	3734-67-6	Azophloxine, Acid Red 1	AAR	90	
11	25956-17-6	Allura Red AC	ALR	98	450.45
12	81-16-3	2-Amino-1-naphthalenesulfonate	ANS	98	222.3

^aSince the polymer was synthesized using ferric sulphate as oxidant, it is assumed that PPy had embedded sulphate as counter ion.

^bMolecular weight of the monomer unit.

exactly the same kind of standard material, because the evaluations of the results on different materials could lead to misjudgements.

The aim of the work is to compare 11 compounds as doping agents of PPy layer on cotton fabrics. The selected compounds represent different categories characterized by a different number in sulfate groups (monovalent, divalent), and the presence of different chemical groups: nitrogen groups (primary amine, secondary amine, azo, amide), oxygen groups (alcohol, succinate), and hydrophobic groups, including aromatic or cyclic groups (benzene, naphthalene, cyclohexane). The electrical performances of the coated fabrics were evaluated. Moreover, evenness and morphology of the resulting PPy deposition were discussed.

In this work, a cotton fabric was chosen as the textile substrate to carry out the study, because of its excellent chemical affinity towards PPy;¹⁴ in addition, it is the second most used textile fiber after polyester, and covers more than 30% of the textile fiber consumption in the world.⁴³

EXPERIMENTAL

Materials

The fabric was a plain cotton cloth (Bleached Desized Cotton Print Cloth, Style 400) with a weight of 0.102 kg m⁻², supplied by Ausiliari Tessili (Italy). The fabric has 34.0 warp ends per cm (yarn count 18.0 tex) and 31.5 filling picks per cm (yarn count 14.0 tex). All reagents were supplied from Sigma-Aldrich and used as received without further purification. Pyrrole was 97% and ferric sulphate was ~80% (moisture 20%, Fe 21–23%) supplied by Sigma-Aldrich, doping agents are listed in Table I with their purities. All dopants were purchased from Sigma-Aldrich. Figure 1 reports the chemical structures of the doping agent anions used in this work.

Methods

The fabric was stored in a conditioned laboratory at 20°C and 65% RH at least 24 h before the use. The fabric was cut in samples with dimensions 5 cm × 8 cm (about 0.4 g) in both weft and warp directions. PPy depositions were carried out at room temperature following the procedure reported in literature.^{44–47} Briefly, the samples were dip in a stirred solution 0.045M of ferric sulphate and a doping agent (when used) at the concentration of 0.012M. For PSS (being a polymer), the molecular weight of the monomer unit was used to calculate the concentration. Liquor ratio was 50:1, i.e. the ratio between the volume of solution (in mL) and the weight of the fabric (in g). After an impregnation of 15 minutes, pyrrole was added to the solution at the concentration of 0.03M. The solution became dark in a few minutes because of PPy production and the doping agent was embedded into PPy as counter-ion during synthesis. The samples were pulled out from the polymerization bath after 4 h, rinsed in cold water, gently squeezed, and dried overnight at room temperature. Then, the samples were stored in a conditioned laboratory at 20°C and 65% RH at least 24 h before tests. Hereinafter, the samples are labelled as “PPy(x)”, where x is the dopant abbreviation reported in Table I. The PPy depositions were carried out in triplicate for each dopant and for each fabric direction (weft and warp).

The coated samples were weighted and photographed at the same conditions. The amount of PPy added to the fabrics is expressed as percentage of weight increase calculated by the following equation:

$$\% \text{ weight increase} = (m_A - m) / m \times 100 \quad (\text{Eq. 1})$$

where m is the initial weight of the conditioned fabrics, and m_A is the weight after PPy deposition, rinsing, drying, and conditioning.

In order to evaluate the amount of water contained in the PPy-coated fabrics the moisture regain of the fabrics was measured, according to ASTM D2495. Briefly, samples of coated fabrics

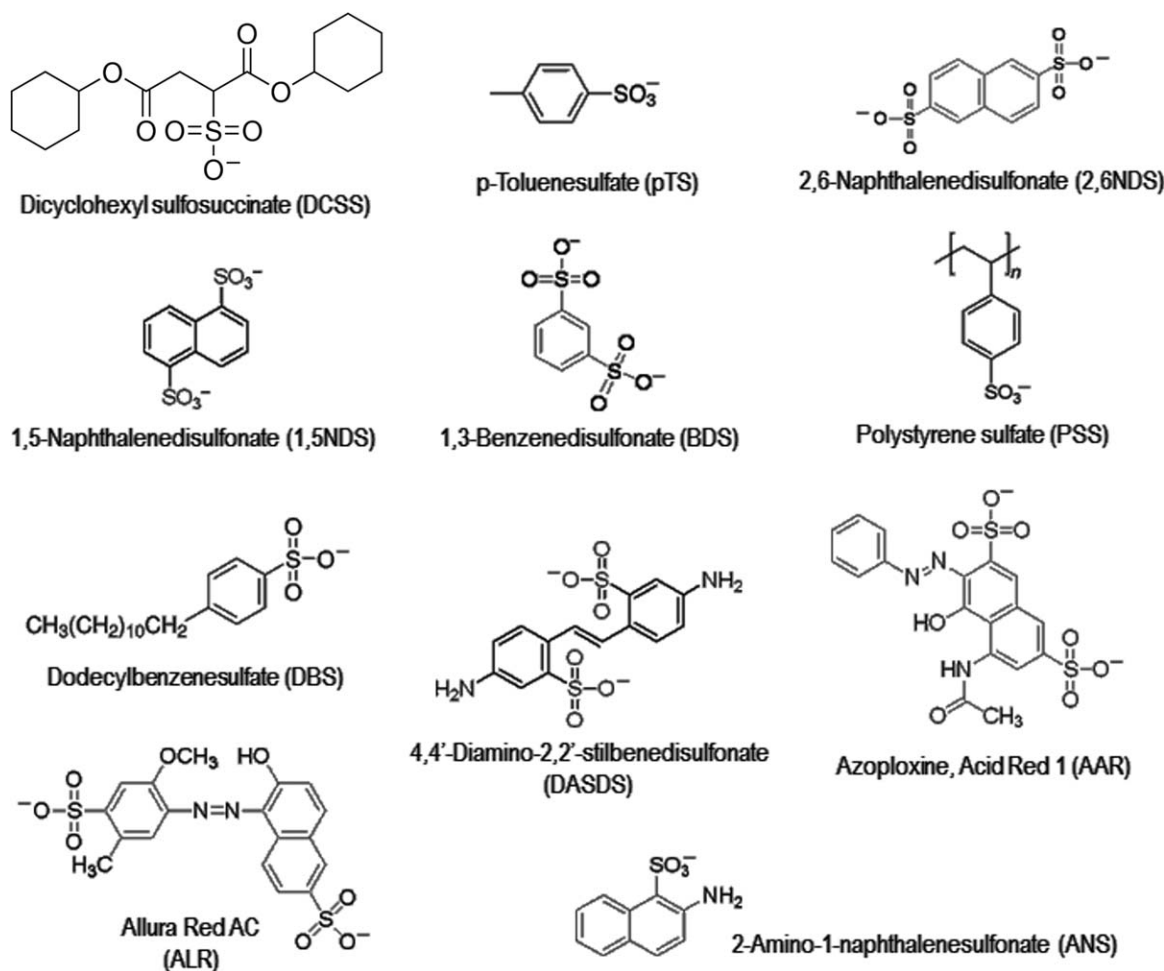


Figure 1. Chemical structures of the doping agents.

were maintained in an oven at 105°C until a constant weight (dry weight). Then they were exposed to standard at 20°C and 65% RH until a constant weight (wet weight). The moisture regain was evaluated using the following equation:

$$\% \text{ moisture regain} = (w-d)/d \times 100 \quad (\text{Eq. 2})$$

where w and d are the wet weight and the dry weight (in g), respectively.

Surface resistivity of PPy-coated fabrics was measured in electrical direct current at 20°C and 65% RH using an Amersham EPS2A200 generator by General Electric Company (USA) connected to the shortest side of the sample by means of 16 alligator clips (eight for the positive pole and eight for the negative pole). The generator measures voltage and current values. The surface resistivity (ρ) was calculated by the following equation derived by Ohm's law:

$$\rho = (V/I)(W/D) \quad (\text{Eq. 3})$$

where V is the voltage (expressed in V), I is the current (in mA), W is the width of the sample (i.e. the length of the sides electrically connected to the generator), and D is the length of the sample (i.e. the distance between the electrified sides of the sample). Therefore, W is 5 cm and D is 8 cm. The surface resistivity is expressed in k Ω /sq.

When an electrical current flows through a conductive material, it produces heat that is connected to the applied electrical power. Since the temperature influences the resistivity of the conductive material itself, the generator was set for applying a total electrical power of 1 W during the tests. In this way, all the samples reached the same temperature by heating Joule effect and the surface resistivities can be properly compared. The generator cannot run as the connected resistor (i.e. the sample) has a resistance higher than 102 k Ω (open circuit). Therefore, surface resistivities above 64 k Ω /sq. (102 k Ω \times 5 cm/8 cm) were not measured.

Scanning electron microscopy (SEM) observations were carried out with a LEO (Leica Electron Optics) 435 VP SEM. SEM parameters were 15 kV acceleration voltage and 30 mm working distance. Specimens were sputter-coated with gold before SEM observation in an Emitech K550 Sputter Coater with a current of 20 mA for 5 minutes in rarefied argon at 20 Pa.

The surface morphology of the samples was examined by an Atomic Force Microscopy (AFM) Nano-R2TM Pacific Nanotechnology (USA), equipped with a Si cantilever. Analyses were performed in close-contact (noncontact) mode; the attractive forces acting between the tip and the specimen were measured and topographic images were constructed by scanning the tip

Table II. Average Surface Resistivities (on Weft and Warp Directions), Weight Increases, and Moisture Content of the PPy-Coated Fabrics

#	Sample	Surface resistivity (k Ω /sq)		Weight increase (%)	Moisture content ^a	Note
		Weft	Warp			
1	PPy(-) ^b	>64	>64	7.7 \pm 0.5	0.68	Uniform film-like layer
2	PPy(DCSS)	1.27 \pm 0.18	0.73 \pm 0.16	17.1 \pm 5.8	0.74	Uniform film-like layer
3	PPy(pTS)	21.5 \pm 10.2	11.4 \pm 5.1	11.9 \pm 3.0	0.47	Uniform film-like layer
4	PPy(2,6NDS)	2.57 \pm 0.57	1.92 \pm 0.72	15.0 \pm 5.7	0.84	Uniform film-like layer
5	PPy(1,5NDS)	2.63 \pm 0.86	1.83 \pm 0.45	16.1 \pm 5.5	0.79	Uniform film-like layer
6	PPy(BDS)	7.2 \pm 1.2	3.85 \pm 0.61	11.7 \pm 2.9	0.66	Uniform film-like layer and aggregates
7	PPy(PSS)	>64	27.6 \pm 9.4	19.9 \pm 8.7	0.64	Aggregates
8	PPy(DBS)	11.5 \pm 1.9	7.4 \pm 1.0	13.8 \pm 1.4	0.67	Uneven film-like layer
9	PPy(DASDS)	>64	44 \pm 11	12.9 \pm 4.5	0.42	Partial deposition, scale-like structures
10	PPy(AAR)	>64	>64	4.2 \pm 0.4	-	Partial deposition
11	PPy(ALR)	>64	>64	2.7 \pm 0.9	-	Partial deposition
12	PPy(ANS)	>64	>64	3.2 \pm 1.4	-	Partial deposition

^aas weight ratio against cotton (moisture regain of uncoated cotton fabric is 5.0%).

^bWithout additional doping agent.

above the surface at a distance of 50–150 Å. Scanned images were processed with NanoRuleTM software by Pacific Nanotechnology. Roughness values were obtained as average on at least three different points of samples.

Fourier transform infrared (FT-IR) spectra were acquired using the Attenuated Total Reflection (ATR) technique in the range from 4000 to 650 cm⁻¹ with 100 scans and 4 cm⁻¹ of band resolution by means of a Thermo Nicolet Nexus spectrometer equipped with a Smart ArkTM (ZnSe 45° crystal).

RESULTS

Electrical and Weight Measurements

The surface resistivity of the samples differs from weft to warp because of differences in the structure of the fabric. In weaving, the highly tensioned warp threads result in a straight conformation, while the weft threads revolve around the warp threads theoretically resulting in $\pi/2$ times yarn length per fabric length unit. Therefore, different values of surface resistivity have usually measured in weft and warp directions after coating with PPy. For this reason, the surface resistivities of the coated fabrics was measured on both weft and warp directions. The average values reported in Table II are the results of electrical resistivity measurements on three different samples for each dopant and direction. It is worth to note that the resistivities in weft direction are about 1.6 (\pm 0.2) times greater than in warp direction, a value close to the theoretical value of 1.57.

The increases in weight because of the PPy deposition were also evaluated. Table II reports the average values of the weight increase percentages obtained by averaging six measures (three measures for each direction), in fact no significant differences in PPy uptake were observed on weft and warp samples, as expected. Furthermore, the weight increases more when a dop-

ing agent is used than PPy without any addition. In fact, PPy(-) showed a weight increase of 7.7%, while the other samples had higher weight increases (>10%). Nevertheless, the only exceptions are AAR, ALR, and ANS that probably hinder synthesis and deposition of PPy. As a result, the weight gain using a dopant can be attributed to the higher molecular weight of the doping agents compared to sulphate ions. However, it is even possible that the doping agents enhance the PPy deposition.

The data in Table II show that there does not exist a direct, obvious correlation between weight increase and surface resistivity. It means that the surface resistivity depends on different factors: (1) the intrinsic conductivity of the PPy, (2) the amount of PPy on the coated fabric, and (3) the structure and morphology of the PPy. Additional compounds added to the polymerization bath can affect these three factors. For instance, PPy(PSS) showed the highest weight increase (close to 20%), but poor electrical properties (i.e. high surface resistivity). Therefore, PSS is not a good dopant for PPy. As well as, PPy(pTS), PPy(BDS), PPy(DBS), and PPy(DASDS) have quite high weight increases, but also quite high surface resistivities. However, the presence of pTS, BDS, DBS, or DASDS produced an improvement in the electrical properties compared to the samples without doping agent. On the other hand, the best results in terms of electrical performance (low surface resistivity) were reached only when the weight increase is greater than 15%. From this point of view, the best doping agents resulted to be DCSS, 2,6NDS, and 1,5NDS.

The presence of water can affect the weight increases and electrical properties of PPy-coated fabrics. In order to investigate and quantify the amount of water absorbed as moisture in the coating, moisture regains were measured. Pristine cotton fabric showed a moisture regain of 5.0%. In particular, Table II shows

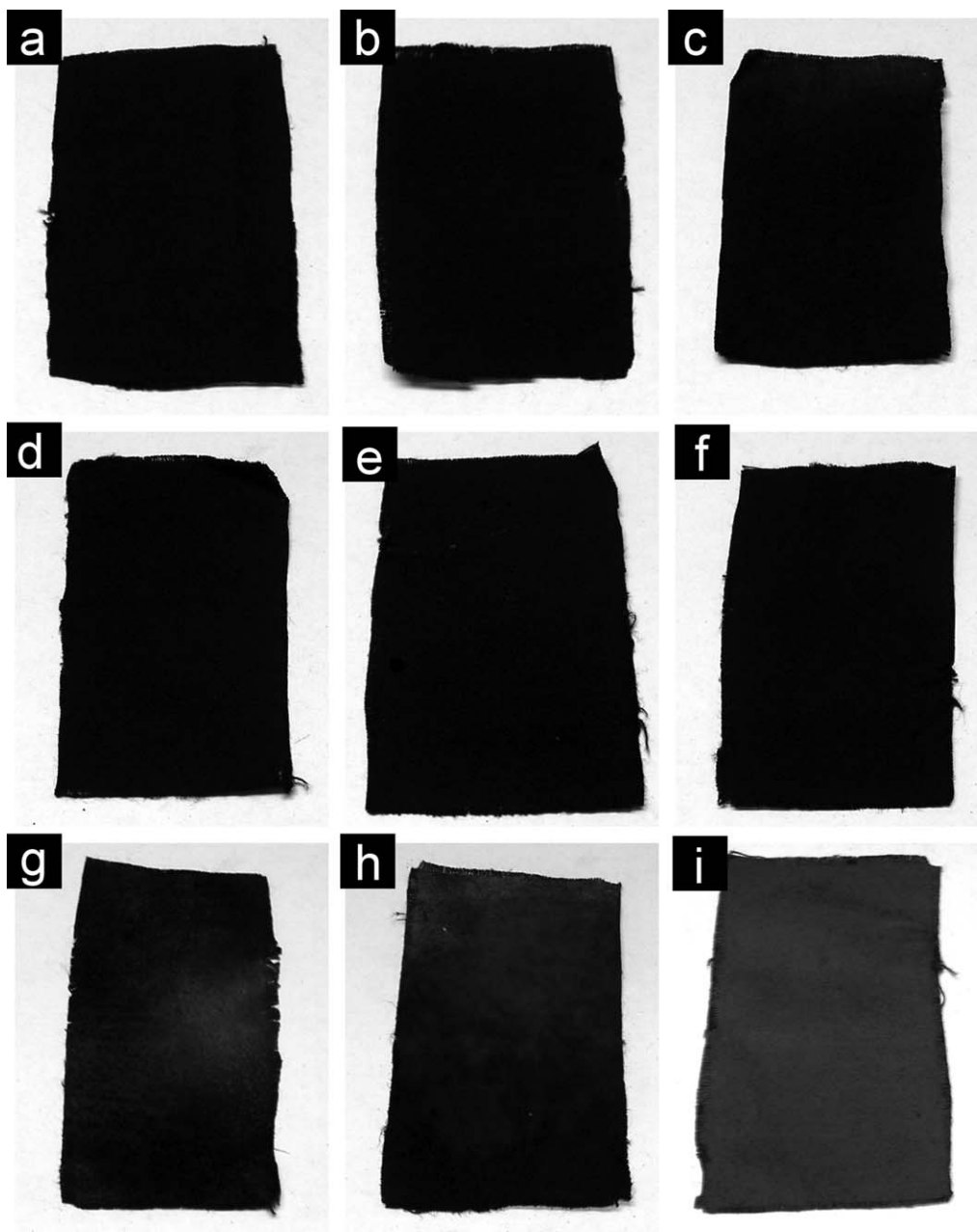


Figure 2. Pictures of the PPy-coated fabrics (warp direction): (a) PPy(-), (b) PPy(DCSS), (c) PPy(pTS), (d) PPy(2,6NDS), (e) PPy(1,5NDS), (f) PPy(BDS), (g) PPy(PSS), (h) PPy(DBS), and (i) PPy(DASDS).

the ratio between the moisture content of the PPy-coated fabrics and pristine (uncoated) cotton fabrics used as reference. All the values are below 1 meaning that the PPy coating has a water content lower than those of cotton. In particular, PPy(-) has a moisture regain ratio of 0.68, close to the values of PPy(BDS), PPy(PSS) and PPy(DBS), but the conductivity of the latter samples was slightly improved. A slightly higher moisture regain (in the range 0.74–0.84) was observed in the samples that showed the best electrical properties, i.e. PPy(DCSS), PPy(2,6NDS), and PPy(1,5NDS). Finally, the lowest moisture regains were measured on the sample PPy(pTS) and PPy(DASDS) that showed poor electrical properties.

Pictures of the coated fabrics are reported in Figure 2. The samples PPy(-) coated without the use of additional dopants (picture a) showed an even black color, therefore the high surface resistivity of PPy(-) is because of poor intrinsic conductivity of this PPy. Uniform coatings were obtained also using DCSS, pTS, 2,6NDS, 1,5NDS, and BDS (pictures b–f). Again, a uniform coating does not mean that the coated fabric surely has a good electrical property, but a uniform coating is mandatory to have good electrical property. In fact, PPy(pTS) and PPy(BDS) samples (pictures c and f, respectively) show a uniform black color, but poor electrical properties. On the other hand, PPy(DCSS), PPy(2,6NDS), and PPy(1,5NDS)

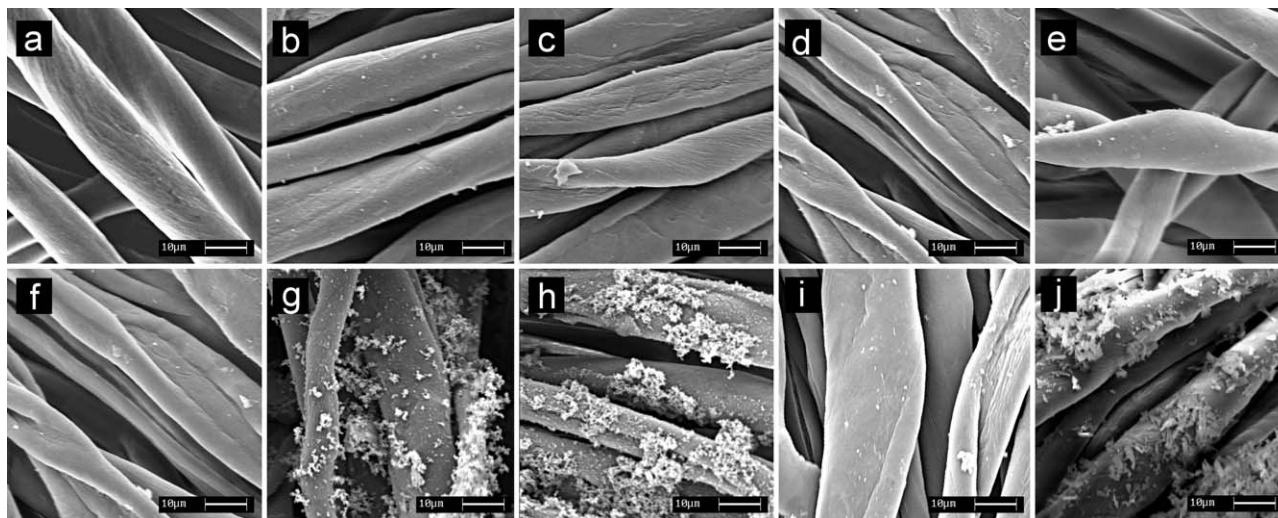


Figure 3. SEM pictures of (a) uncoated cotton fibers and PPy-coated fibers: (b) PPy(-), (c) PPy(DCSS), (d) PPy(pTS), (e) PPy(1,5NDS), (f) PPy(2,6NDS), (g) PPy(BDS), (h) PPy(PSS), (i) PPy(DBS), and (j) PPy(DASDS).

samples (pictures b, d, and e, respectively) have both uniform black color and excellent electrical properties. On the contrary, PPy(PSS) and PPy(DBS) samples (pictures g and h) show uneven depositions, that resulted in poor conductivities. While, DASDS hinders the deposition of the PPy, resulting in grey fabrics (picture i). The worst results were obtained with AAR, ALR, and ANS that probably interfere with synthesis and deposition of the PPy resulting in negligible weight increases.

Microscopy Observations

SEM and AFM observations can help to understand the relation between electrical properties of the fabrics and morphologies of PPy. Figure 3 shows SEM pictures of several samples. Cotton fibers have irregular or flatten cross-sections; at high magnification wrinkles are visible on the fiber surface (picture a). After PPy-coating, the fibers show a very uniform film-like dense layer, however the typical wrinkledness of the cotton is still visible. In addition, the coating shows some small particles of PPy deposited on the surface that increase the overall roughness of the fibers (pictures b–f). PPy(-), PPy(DCSS), PPy(pTS), PPy(1,5NDS), and PPy(2,6NDS) samples show this kind of coating, that is the best structure to assure a continuous electrical pathway. On the contrary, PPy(BDS) and PPy(PSS) samples (pictures g and h) have an uneven deposition of big aggregates of PPy particles on the fibers. In this case, the poor electrical property of the fabric is probably because of the discontinuous electrical pathway, i.e. electrical charges have to jump from an aggregate to another and the overall resistance increases. PPy(DBS) (picture i) shows an uneven PPy deposition, i.e. some fibers were coated with a thin layer of PPy and other fibers were not coated at all. A unusual morphology was observed on the PPy(DASDS) sample (picture j) that shows a scale-like structure on the fibers and the electrical pathway resulted interrupted.

On the other hand, in order to obtain finer image resolution than SEM analyses and to determine a quantitative measurement of roughness, AFM characterization was performed on the

sample that showed the highest conductivity in order to characterize the layer surface. Roughness of the PPy layer was compared with the pristine cotton fiber surface.

In Figure 4, 3D morphology of untreated and PPy(DCSS), PPy(1,5NDS), and PPy(2,6NDS)-treated cotton samples are compared. The former shows a smooth surface, whereas the other samples appear rougher; quantitative measurements of average roughness on $4.0 \mu\text{m}^2$ areas, reported a value of 10 nm for the untreated sample, 24, 98, and 188 nm for the samples treated with PPy(DCSS), PPy(1,5NDS), and PPy(2,6NDS) coating, respectively. AFM evidences that the fiber surface changes at the submicron scale after PPy deposition compared to the cotton fiber surface. Moreover, the resulting layer surface is composed of small particles (with a size of 200–400 nm) merged each other. Additionally, PPy(1,5NDS) and PPy(2,6NDS) coatings show at nanometer scale some discontinuities in the layer surface, not detectable with SEM analysis. It seems that dopants with structure α and β naphthalene disulfonate produce crystal structure that lead to a rougher surface than PPy(DCSS). Therefore, the continuous contact of the particles and their interpenetration without discontinuities on PPy(DCSS) coating can explain its higher electrical conductivity in comparison to PPy(1,5NDS) and PPy(2,6NDS); in the case of the last two dopants' different structures (α and β) seem to have a considerable effect in the roughness without a significant difference in the electrical conductivity.

Infrared Spectroscopy

Figure 5 shows ATR-FTIR spectra of uncoated and PPy-coated cotton fabrics. The spectrum of cotton is characterized by bands from 3000 to 2800 cm^{-1} assigned to O–H and C–H stretching vibrations, a band at 1595 cm^{-1} assigned to stretching of O–C–O groups, and a strong absorption band centered at about 1070 cm^{-1} related to overlapping bands of several chemical groups of cellulose (i.e. C–C, C–O and C–O–C).⁴⁸ The strong peak at $\sim 900 \text{ cm}^{-1}$ is attributed to the cellulose ring out-of-phase asymmetric stretching.⁴⁸

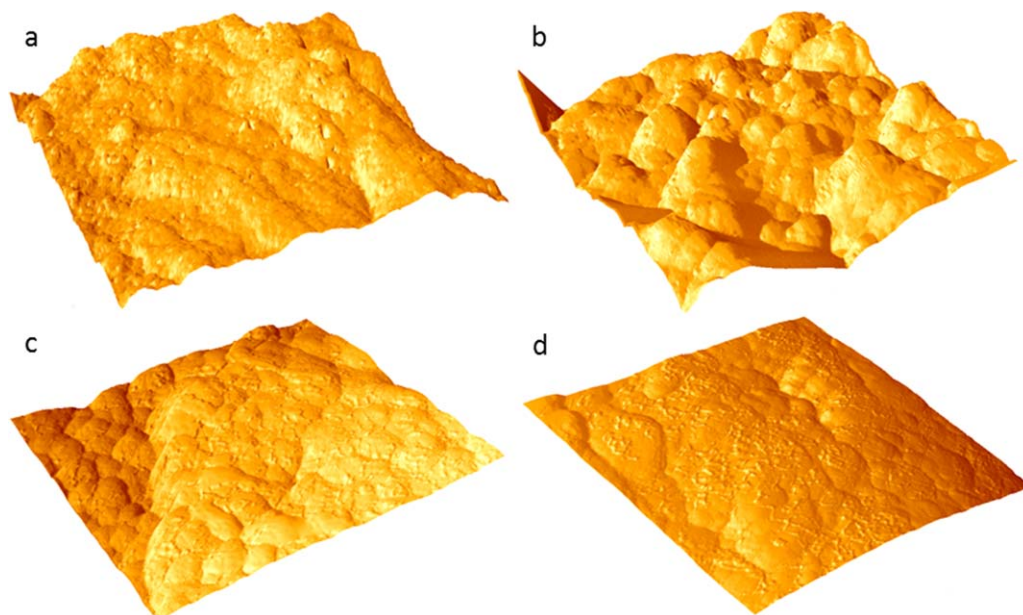


Figure 4. AFM pictures of (a) uncoated cotton fibers, (b) PPy(DCSS)-coated fibers, (c) PPy(1,5NDS)-coated fibers, and (d) PPy(2,6NDS)-coated fibers ($2 \mu\text{m} \times 2 \mu\text{m}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The spectral feature of the cellulose in the range from 1250 to 900 cm^{-1} appears attenuated in the spectra of PPy-coated fabrics (spectra a–h), since the infrared beam of the ATR technique analyzes the fiber surface with a penetration of about $1 \mu\text{m}$ (greater than the PPy layer). The characteristic absorption bands of PPy are also visible. In particular, the bands at about 1630 , 1520 , and 1450 cm^{-1} are assigned to N–H in-plane scissoring, C–C and C–N stretching vibrations, respectively.⁴⁹ In particular, the latter band overlap the weak band at 1430 cm^{-1} of –OH in-plane bending of cellulose. Moreover, benzene ring (pTS, BDS, PSS, and DBS) and naphthalene (2,6NDS and 1,5NDS) have strong and narrow peaks between 1660 and 1500 cm^{-1} (assigned to aromatic C=C stretching). These peaks were not clearly observed in the spectra because of overlapping with the bands of PPy and cellulose.

In the range from 1200 to 1000 cm^{-1} there are bands assigned to breathing vibrations of pyrrole rings and in-plane deformation vibrations of C–H and N–H of PPy, but the strong bands of cellulose in this region partially hide the signals of PPy. Moreover, some small spectral differences from 1200 to 1000 cm^{-1} can be attributed also to the doping agents embedded in PPy. In particular, the absorption band of $-\text{SO}_3^-$ groups of the doping agents embedded in PPy(–), including inorganic sulphate ions, are from 1200 to 1050 cm^{-1} .^{50,51} This seems to be band particularly intense in PPy(PSS) (spectra g) probably because of the large number of $-\text{SO}_3^-$ groups of PSS.

DISCUSSION

Electrical conductivity of a PPy-coated fabric mainly depends on the intrinsic conductivity of PPy, on the amount of the PPy embedded in the fabric structure, and on the shape of the PPy (e.g. film, particles, and aggregates). How a doping agent affects these factors is not a trivial matter. The attempt to correlate some doping agent characteristics (related to molecular weight,

steric hindrance, and ionic strength) and the results on the fabrics were not conclusive probably because of the complexity of the whole system that includes interactions at molecular level between the forming PPy, the counter-ion molecules, and the oxidant in both water solution and on the fiber surface.

The best results in terms of electrical conductivity (i.e. low surface resistivity) were measured on PPy(DCSS), PPy(2,6NDS), and PPy(1,5NDS) samples probably because of their counterion size and chemical structure. Furthermore, the conductivity as well as the complete and uniform deposition of PPy are better when the size of the counter ions decreases. PPy deposited on the fibers as a film leads to a weight increase greater than 15% of the samples. In addition, it is necessary to say that these

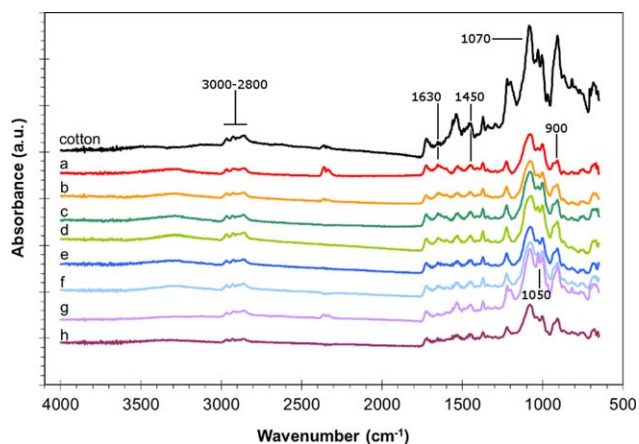


Figure 5. FT-IR spectra of uncoated cotton and PPy-coated fabrics: (a) PPy(–), (b) PPy(DCSS), (c) PPy(pTS), (d) PPy(2,6NDS), (e) PPy(1,5NDS), (f) PPy(BDS), (g) PPy(PSS), and (h) PPy(DBS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

counter ions have the ability to accept almost the same hydrogen bond number: seven for PPy(DCSS) and six for PPy(2,6NDS) and PPy(1,5NDS). This could be an explanation for the different surface resistivity between samples: is reached with PPy(DCSS) reaches the lowest value because of its highest hydrogen bond number to accept towards other counter ions. Furthermore, α and β naphthalenesulfonates present the same surface resistivity and have the same capacity to accept hydrogen bond. This permits to state that there is no difference between them in the deposition process of PPy on cotton, but the difference appears in the aspect of roughness.

On the opposite, the highest weight increase (about 20%) was measured on PPy(PSS), but a high surface resistivity was measured, too. The result depends on the morphology of PPy on the fibers that showed aggregates instead of an even layer. Furthermore, conductivity also depends on the length of chain in counter ions and in this case the PPy(PSS) has the largest chain of all dopants. As a result, it has a lower conductivity.

PPy(pTS), PPy(BDS), and PPy(DBS) showed an improvement in the electrical properties compared to the samples without doping agent, but not as good as the best compounds. The reasons may be different: pTS produced an even, film-like deposition; therefore, the intrinsic conductivity of PPy doped with pTS is probably low; BDS produced a coating with aggregates; therefore, the shape of PPy is unsuitable to be a good conductor even if BDS could be a good dopant; DBS produced an uneven film-like coating. In addition, it seems that *p*-benzenesulfate (pTS and DBS) improves conductivity but in the case of DBS, the length of chain reduces the process of deposition on cotton. In addition, it is necessary to say that between these three counter ions, BDS (divalent counter ion) presents the lowest surface resistivity, and has the largest capacity to accept hydrogen bond. This aspect confirms the previous statement, but unfortunately, *m*-benzene disulfonate (divalent counter ion) produces not uniform layer film in the cotton. On the other hand, compounds with amine functional groups (i.e. DASDS, AAR, ALR, and ANS) have negative effects on the process; they do not produce a coating, hinder the deposition or interfere with the PPy synthesis.

The nature of the dopant affects the moisture content in the sample, but it is lower than the moisture in uncoated cotton fibers. It is possible that hygroscopicity of cotton fibers has been lightly reduced and the raise of weight in PPy-coated fabrics is mainly because of the presence of PPy. Moisture content seems not to fully justify the enhancement in electrical properties since PPy(-) has a moisture regain close to PPy(BDS), PPy(PSS), and PPy(DBS). However, the best electrical properties were measured on PPy(DCSS), PPy(2,6NDS), and PPy(1,5NDS) that showed a slightly higher moisture regain.

In conclusion, all dopants (except PSS and compounds with amine groups) improve conductivity. Divalent counter-ions, in general, have better conductivity than monovalent one. DCSS, 2,6NDS, and 1,5NDS are the best doping agents to be used for the chemical synthesis of PPy on cotton in order to obtain highly electro-conductive fabrics. The use of one of these three chemical compounds resulted in good weight increase, evenness,

and morphology of the PPy layer, and low electrical resistance of the coated fabrics. Consequently, dopants with the highest capacity to accept hydrogen bond (in this case from oxygen) improve the conductivity on cotton. It produces different molecular structure of layer on cotton and a different morphology (confirmed by AFM analysis). The observations reported in this work lead us to the following final considerations:

1. A doping agent must show a good chemical affinity with both PPy (e.g. chemical structure without nitrogen groups) and fibers (e.g. fast wetting of the fabric);
2. It should have a surfactant action on PPy particles, thus the particles should be able to glue together and deposit on the fiber surfaces;
3. It must be chemically stable, i.e. the dopant must not interfere with PPy synthesis and it must react neither with the oxidant nor with the fibers.
4. It should have a small dimension.
5. It ought to be able to accept a large number of hydrogen bond (in this case from oxygen).

CONCLUSION

Eleven compounds were selected and compared as counter-ions of PPy. The selected compounds represent different categories characterized by a different number in sulfate groups (monovalent, divalent), and the presence of different chemical groups including primary amine, secondary amine, azo, amide, alcohol, succinate, and hydrophobic groups, such as benzene, naphthalene, and cyclohexane. The electrical performances of the coated fabrics were measured and compared. Evenness and fine morphology of the resulting PPy layers were observed and discussed.

The best performance in terms of electrical conductivity (i.e. low surface resistivity) was obtained using dicyclohexyl sulfosuccinate, 2,6-naphthalenedisulfonate or 1,5-naphthalenedisulfonate as doping agents of PPy coating on cotton fabrics.

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