fibers

MDPI

Article

Conductive Electrospun Polyaniline/Polyvinylpyrrolidone Nanofibers: Electrical and Morphological Characterization of New Yarns for Electronic Textiles

Patrícia Perdigão, Bruno Miguel Morais Faustino *, Jaime Faria, João Paulo Canejo, João Paulo Borges, Isabel Ferreira and Ana Catarina Baptista *

CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Campus de Caparica, Portugal; p.perdigao@campus.fct.unl.pt (P.P.); jm.faria@campus.fct.unl.pt (J.F.); jpgc@fct.unl.pt (J.P.C.); jpb@fct.unl.pt (J.P.B.); imf@fct.unl.pt (I.F.)

* Correspondence: bm.faustino@fct.unl.pt (B.M.M.F.); anacbaptista@fct.unl.pt (A.C.B.)

Received: 3 March 2020; Accepted: 16 April 2020; Published: 20 April 2020

Abstract: Advanced functionalities textiles embedding electronic fibers, yarns and fabrics are a demand for innovative smart cloths. Conductive electrospun membranes and yarns based on polyaniline/polyvinylpyrrolidone (PANI/PVP) were investigated using the chemical modification of PANI instead of using conventional coating processes as in-situ polymerization. PANI was synthesized from the aniline monomer and the influence of the oxidant-to-monomer ratio on electrical conductivity was studied. The optimized conductivity of pellets made with pressed PANI powders was 21 S·cm^{-1}. Yarns were then prepared from the t-Boc-PANI/PVP electrospun membranes followed by PANI protonation to enhance their electrical properties. Using this methodology, electrospun membranes and yarns were produced with electrical conductivities of 1.7×10^{-2} and 4.1×10^{-4} S·cm^{-1}.

Keywords: conductive yarn; conductive textile; polyaniline; polyvinylpyrrolidone; electrospinning

1. Introduction

Electronic textiles have attracted massive attention in the past decade due to their potential applications in wearable electronics and portable devices [1], such as healthcare detectors [2,3], portable power [4], and work and military uniforms [5,6]. Electrically conductive textiles may include conductive fabrics made of fibers or yarns characterized by displaying specific electrical conductivity [7]. Polyanilines belong to a class of intrinsically conductive polymers (ICPs) which polymeric structure consisting of alternating reduced amine and oxidized imine repeat units [8,9]. Compared to other ICPs, polyaniline (PANI) presents significant advantages such as the ease of synthesis [10,11], good environmentally stability [12], low cost of aniline monomer, high yield of the polymerization product, and applicability in a wide range of applications [13]. Its electrical conductivity allows PANI to be used in several applications such as batteries, supercapacitors, light-emitting diodes, chemical sensors and electromechanical devices, among others [13].

The preparation of pristine PANI conductive fibers or fabrics through conventional spinning methods is still a challenge. To overcome it, fabrics coating by in-situ polymerization [14,15] and fibers spinning using conventional polymers as carriers are the most common methodologies used to produce fibers with reported conductivities between 10^{-5} and 10^{-1} S·cm^{-1}.

A polymeric nanowire chemical sensor of oriented electrospun PANI nanofibers was reported by Haiqing Liu [16]. When exposed to NH_3 (0.5 ppm) individual PANI/polyethylene oxide (PEO) nanowires displayed conductivities of 0.5 S·cm^{-1}. Ying Zhu [17] reported a PANI/polystyrene (PS)

superhydrophobic composite film with a lotus-leaf-like structure prepared by electrospinning. This was the first example of a superhydrophobic surface with electrical conductivity in the range of 10^{-5}–10^{-4} S·cm^{-1} using the conductive state of PANI [17]. Kyungchan Uh [18] studied a new approach to prepare electrospun PANI nanofibers for gas sensors. The authors produced a tert-butyloxycarbonyl-protected (t-Boc) PANI followed by hydrochloric acid (HCl) treatment. The HCl-doped PANI fibers showed a conductivity of approximately 20 S·cm^{-1} and allowed gaseous ammonia (10 ppm) detection [18].

Envisaging the production of electrically conductive PANI-based yarns for smart textiles very few works have been reported so far. This work focusses on the preparation of a novel conductive yarn using electrospun PANI/PVP membranes. Instead of conventional coating processes through in-situ polymerization of electrospun fibers, we propose the electrospinning of chemically modified PANI powders with PVP. Yarns were then prepared from the electrospun membranes followed by PANI protonation to enhance their electrical properties. The electrical and morphological characterization of the produced membranes and yarns were evaluated.

2. Materials and Methods

2.1. Materials

Aniline (99.5% purity) and ammonium persulfate (98% purity) were purchased from Sigma-Aldrich (Gillingham, UK); Hydrochloric acid (HCl, 37%) and methanol (99.8% purity) were provided by Honeywell (Charlotte, NC, USA); Chloroform (for analysis-ISO-Stabilized with ethanol) and n-Hexane were purchased from Carlo Erba Reagents (Chaussée du Vexin, France); 4-(dimethylamino)pyridine was purchased from FluoroChem (Derbyshire, UK); 1-Methyl-2-pyrrolidinone (99% purity) and di-tert-butyl decarbonate (97% purity) were provided by Alfa Aesar (Heysham, UK); N,N-dimethylformamide, DMF, from Carlo Erba Reagents (Chaussée du Vexin, France); and Polyvinylpyrrolidone, Mw 1.300.000 Da, was provided by Sigma-Aldrich (Gillingham, UK).

2.2. Synthesis of PANI Powders

PANI powders were synthesized via chemical oxidative polymerization of aniline monomer, as outlined in Figure 1A. An oxidant solution of ammonium persulfate (APS) in 1 M HCl was added dropwise to an aqueous acid and organic solution of aniline (Ani) in 1 M HCl and chloroform—heterogeneous medium composed of aqueous acid and an organic phase (aq/org phase) 2:1 vol./vol., in order to prevent undesirable side reactions—protocol adapted from [18]. Five different oxidant-to-monomer ratios were studied (1:4, 1:2, 1:1, 1:0.5 and 1:0.25) to optimize the electrical conductivity of PANI powders. All reactions were carried out in an ice bath (at c.a. 0 °C) under constant mechanical stirring. After 2 h of reaction, solutions were filtered with vacuum, washed with 1M HCl solution to stop the reaction and then dried in vacuum at 90 °C.

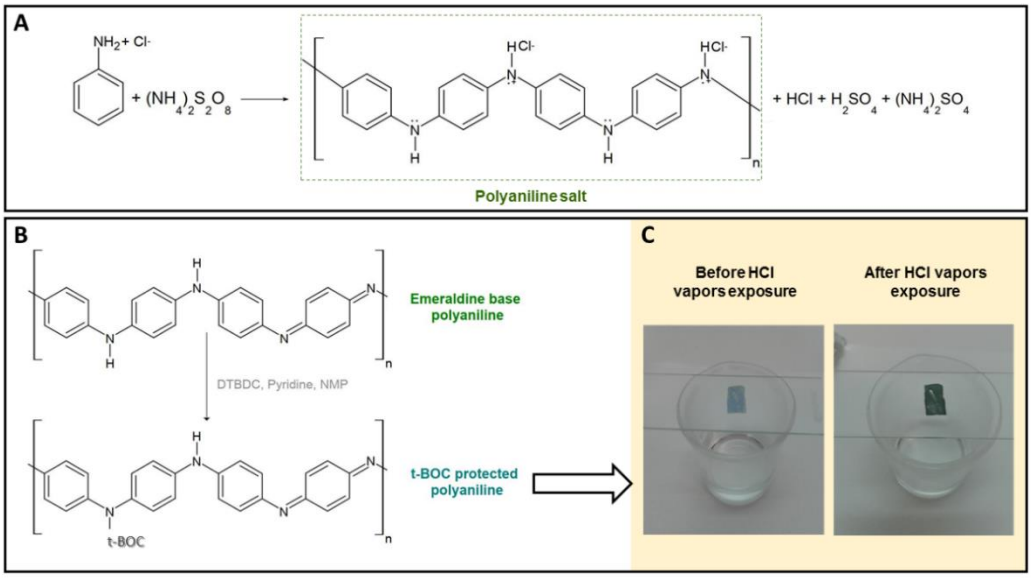

Figure 1. Resume of experimental details: (**A**) Synthesis of PANI powders by chemical oxidative process; (**B**) Chemical substitution of one of the imine groups for a t-Boc-protective group; (**C**) Illustrations of t-Boc removal process and consequent protonation of PANI membrane.

2.3. Synthesis of t-Boc Protected PANI Powders

In a three-necked round-bottom flask, the synthesized PANI powders (oxidant-to-monomer ratios of 1:2, 1.50 g) and 4-(dimethylamino)pyridine (DMAP, 5.99 g) were dissolved in 1-Methyl-2-pyrrolidinone (NMP, 30.71 mL). A solution of di-tert-butyl dicarbonate (DTBDC, 1.38 g) in NMP (15.35 mL) was added slowly to the first one. The mixture was stirred for 3 h at 80 °C under a nitrogen atmosphere. *N*-Hexane was added in large excess to precipitate the solid powder—adapted from [19]. The mixture was then washed with methanol and filtrated with vacuum. The filtrated powder was dried in vacuum at 70 °C. After grinding the t-Boc protected PANI powders, these were dissolved in *N*,*N*-dimethylformamide (DMF) and the mixture was filtered to remove any insoluble starting materials (Figure 1B).

Pellets of PANI and t-Boc protected PANI dried powders were produced by uniaxial pressing for electrical conductivity measurements. For this purpose, powders were placed into a 13 mm diameter evacuable pellet die (from Specac) and a load of 3 tons was applied for 60 s using a manual hydraulic press from Specac.

2.4. Electrospinning of t-Boc Protected PANI/PVP

A solution (15 mL) of 12 wt.% of Polyvinylpyrrolidone (PVP) in DMF with t-Boc protected PANI (0.51 g) dissolved, was prepared and left to stir overnight until homogenized. The electrospinning technique was used to produce the fibers using a high voltage power supply (Glassman), a digitally programmed syringe pump (KdScientific) and a collector. The t-Boc protected PANI/PVP in DMF (with a mass ratio of 0.3/1, respectively) solution was pumped through a 1 mL syringe with a metal needle (23-gauge) at a flow rate of 0.25 mL·h^{-1}. A high-voltage of 15.5 kV was applied to the metal needle to generate nanofibers, which were collected on a grounded aluminum foil at 15 cm distance under controlled environmental conditions (temperature of 20–25 °C and relative humidity of 30–40%). The selection of the solvent is essential for the formation of smooth and bead-free electrospun nanofibers. Since DMF is a low vapor pressure solvent, shorter collector distances (<15 cm) can result in the deposition of slightly wet fibers, with fusion of the fibers at the crossover point, resulting in an increasing of the average fiber diameter.

The average thickness of the electrospun membranes produced was measured with a digital micrometer and the obtained thickness is 243.3 ± 27.6 μm.

The crosslinking upon exposure to UV radiation is an attractive approach against the use of high-energy radiation due to the simplicity of preparation and implementation method. Since PVP has an absorption spectrum in the region of 200–280 nm, PVP-based membranes were crosslinked using a BIO-LINK® irradiation system, ultraviolet light at 254 nm, (Vilber, Collégien, France) for 45 min. The study of the optimal conditions for pristine PVP crosslinking is presented in Supplementary Materials.

After crosslinked, electrospun membranes were exposed to several HCl vapor exposure time (2, 5, 10 and 15 min) to remove the t-Boc protecting group (Figure 1C).

2.5. Electrical and Morphological Characterization

All electrical conductivity measurements of PANI pellets and PANI membranes were performed using the 4 points probes of a Hall Effect Measurement System (HMS7000 + AMP55T 0.53T, Ecopia, Gyeonggi, South Korea), applying a current of 0.5 mA for all samples. To ensure a good contact between samples and test-probes, a carbon conductive paint (Bare Conductive, London, UK) was used as electrodes.

Scanning electron microscopy (SEM) was used to evaluate the morphology of electrospun t-Boc protected PANI/PVP fibers, and PANI and t-Boc protected PANI powders. Small pieces/amounts of the samples were fixed on carbon tape, mounted on a support and sputtered with a thin layer of gold/palladium (Au/Pd), and then analysed using a Joel JSM7001F Schottky Emission Scanning Electron Microscope (Joel, Croissy-sur-Seine, France) and a Zeiss DSM962 Scanning Electron Microscope (Carl Zeiss Microscopy, Jena, Germany).

3. Results and Discussion

Conductive PANI/PVP electrospun fibers and yarns were produced from PANI powders synthetized by chemical oxidative polymerization of aniline monomer in an aqueous acid medium, using ammonium persulfate as oxidizing agent, as described in experimental details. A chemical modification of PANI powders with an acid- and thermo-labile tert-butoxycarbonil (t-Boc) group was performed, allowing its solubility in dimethylformamide (DMF) [19]. Electrical conductivity of PANI synthesized powders is dependent on: i) the nature of the reaction medium; ii) the temperature of the reaction medium; iii) the polymerization time; iv) the dopant acid concentration; v) the concentration of the oxidant; vi) the rate of addition of the oxidizing agent; and vii) the oxidant-to-monomer ratio (OM ratio). The influence of the OM ratio on the PANI powders conductivity was studied—4:1, 2:1, 1:1, 0.5:1, and 0.25:1—and the obtained yield of the chemical polymerization reaction for each OM ratio is shown in Table 1.

Table 1. Estimated yield of chemical polymerization and electrical conductivity values (as prepared and after 2 months) of PANI pellets for different OM ratios.

OM Ratio	0.25:1	0.5:1	1:1	2:1	4:1
Yield (%)	14	27	63	97	91
Conductivity (S·cm^{-1}) As prepared	13.25 ± 0.13	12.87 ± 0.10	19.24 ± 0.15	20.26 ± 0.05	0.873 ± 0.001
Conductivity (S·cm^{-1}) After 2 months	13.27 ± 0.02	12.71 ± 0.02	19.38 ± 0.03	20.64 ± 0.03	–

PANI dried powders of each OM ratio were uniaxially pressed to produce pellets for electrical characterization. To evaluate the effect of storage time under environmental conditions on electrical conductivity of PANI powders, PANI pellets as prepared and after 2 months were compared. PANI pellets were stored in the dark with uncontrolled temperature (18–25 °C) and humidity (40–70%).

As shown in Table 1, PANI powders with an OM ratio of 2:1 present the highest yield (97%) and no significant change over time on the pellets conductivity. It was clear that higher yields were

obtained for OM ratios up to 2:1. Increasing the amount of oxidant may lead to the formation of more radical cations, which increases the rate of the chemical oxidative polymerization of aniline. However, if OM ratio is too high, this can also lead to over-oxidation of the formed PANI and this can reduce the conductivity and yield of PANI.

Increasing the OM ratio from 0.25 to 2, the PANI powders conductivity is enhanced from 12.71 to 20.64 S·cm^{-1} (Figure 2A). OM ratio values over 2 can promote PANI particles aggregation and/or an excessive oxidation of aniline monomer which may cause the break of conjugated bonds in PANI structure leading to a decrease of conductivities values, as observed for 4:1 OM ratio. Raman spectroscopy technique was used to evaluate the chemical oxidation of selected PANI powders (Figure 2B). The obtained Raman spectra can be divided in three regions [20]: In region I, corresponding to C – C ring stretching vibrations, between 1650 and 1520 cm^{-1}, shows two peaks one at 1587 cm^{-1} and another at 1555 cm^{-1}, associated to the stretching modes of C = C and C – C vibrations in quinoid and semi-quinone (B) (Q) rings [21]. In region II, at which the different C – N stretching modes prevail, between 1520 and 1210 cm^{-1}, is observed: (a) a peak at 1486 cm^{-1}, attributed to C = N stretching in quinoid units (Q) and vibration of imine groups [22–24]; (b) a peak at 1411 cm^{-1}, associated to C – N bonds of tertiary amines on cyclic structures produced during the crosslinking of the polymer [22–24]; (c) a set of peaks at 1350, 1330 and 1317 cm^{-1}, corresponding to the vibrational modes of C – N$^{+\bullet}$ delocalized polaronic structures; (d) two peaks at 1255 and 1213 cm^{-1}, related to amine groups [21]. In region III, corresponding to the deformation of C – H bond, between 1210 and 1100 cm^{-1}, the Raman spectra shows a peak at 1161 cm^{-1}, attributed to emeraldine base form [25], which was also found in all OM ratios of PANI studied. Furthermore, is concluded that all the PANI powders synthesized are in the emeraldine base form as all samples present the same Raman peaks.

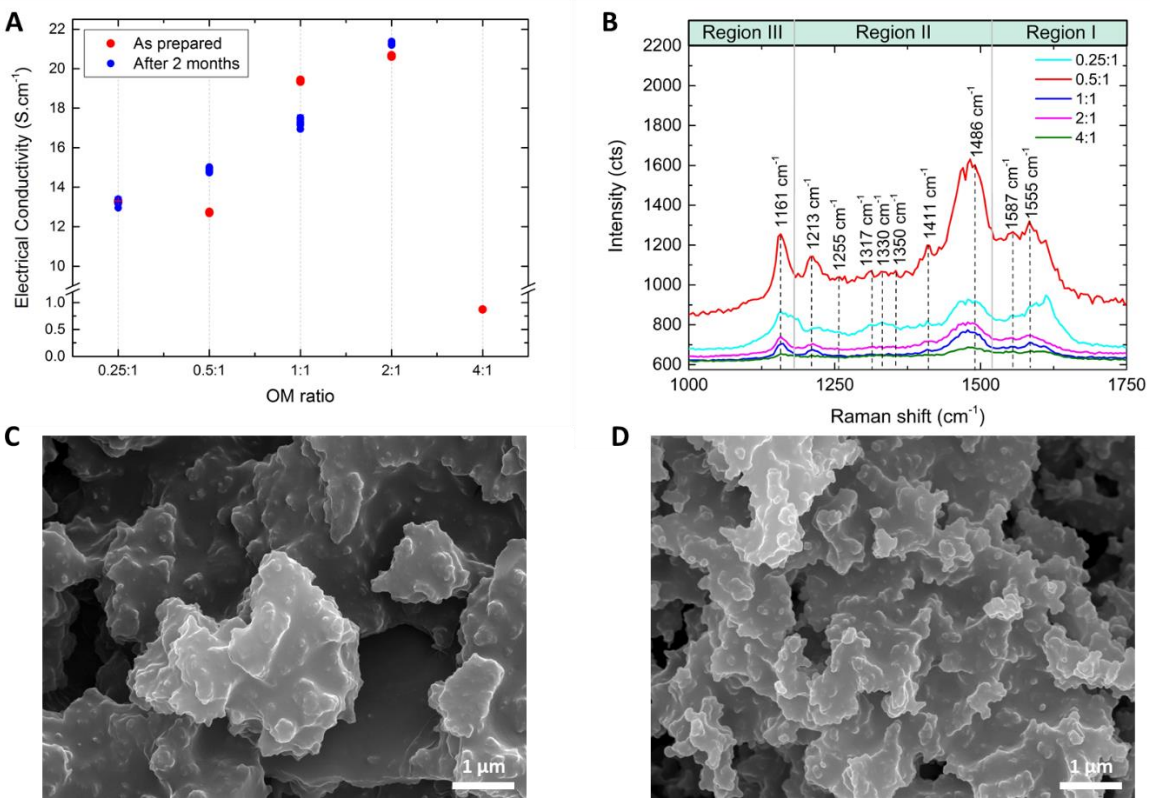

Figure 2. (**A**) Electrical conductivity of PANI pellets measured as prepared (red circles) and after 2 months (blue circles) in order to OM ratio; (**B**) Raman spectra of different PANI OM ratios synthesized; (**C**) SEM micrographs of synthesized powders of PANI 2:1 OM ration and (**D**) PANI t-Boc protected powders.

Considering the maximum yield of the chemical polymerization reaction of 97% and an electrical conductivity of 20.64 S·cm^{-1}, the 2:1 OM ratio PANI powders were selected for the chemical modification of PANI powders with t-Boc protecting group. The soluble t-Boc protected PANI was obtained by reacting PANI powders (2:1 OM ratio) with di-tert-butyl decarbonate (DTBDC) in *N*-methyl-2-pyrrolidinone (NMP) as solvent. The emeraldine base form is composed of two amine nitrogen groups followed by two imine nitrogen groups along the chain. When reacted with DTBDC, in presence of 4-(dimethylamino)pyridine (DMAP), in NMP, one of the hydrogens of the imine group is substituted by the acid-labile t-Boc group. Such chemical substitution allows t-Boc-PANI soluble in common solvents. SEM analysis of 2:1 OM ratio PANI powders (Figure 2C) and PANI (t-Boc) powders (Figure 2D) showed that chemical modification with t-Boc protecting group does not greatly modifies powder morphology.

t-Boc protected PANI membranes were obtained by electrospinning of a solution of PVP in DMF with PANI (t-Boc) dissolved. As PVP is a water-soluble polymer, it was necessary to crosslink the electrospun membranes by means of UV irradiation during 45 min to prevent fibers dissolution over time due to relative humidity. During UV exposure, pyrrolidone substituents and cyclic amines on the PVP chains generate macroradicals, whose recombination leads to intermolecular crosslinked PVP. After crosslinked, electrospun membranes were exposed to HCl vapor during different time-period to remove the t-Boc protecting group. In the presence of HCl, the complete protonation of the imine nitrogen atoms occurs which results in the formation of a delocalized polysemiquinone radical cation leading to an increase in conductivity [9].

The conductivity obtained by exposing a crosslinked non-woven mat of PANI (t-Boc) to 2, 5, 10 and 15 min of HCl vapors are displayed in Figures 2 and 3. After treatment, an increase in conductivity of electrospun membranes from 8.9×10^{-8} to 1.7×10^{-2} S·cm^{-1} is observed. These results indicate that only 2 min of HCl exposure is sufficient to turn the membrane color from blue to green (an indicative of complete protonation) displaying a conductivity of 10^{-2} S·cm^{-1}. These values are in agreement with the values found in the literature [16–18]. The SEM images of treated membranes clearly show the fusion of electrospun fibers on the surface exposed to acid vapors as the exposure time increases. A different procedure to remove t-Boc group or decrease the amount of PVP used could be explored in further studies to preserve fiber's morphology and, consequently, improve the electrical properties. The random orientation of the fibers within the PVP polymer matrix results in less contact points between PANI chains and thus reduce electrons diffusion across the membrane.

The preparation of a conductive yarn (1D structure) was obtained by manual coil of PANI (t-Boc) electrospun membrane (twists number = 5). Figures 3 and 4 shows the SEM image of a PANI yarn after HCl vapor treatment (for 2 min) to remove t-Boc protecting group. The yarn has an average diameter of 465 µm and fiber-melted surface on the outer layer. However, small fibers are still observed in the inner layers (SEM images on the right). The yarn conductivity is 4.1×10^{-4} S·cm^{-1}, lower than membrane conductivity. A possible incomplete removal of t-Boc protecting group on the core of the yarn due to the difficulty of HCl vapors penetration into the structure, may lead to a less conductive core and consequently to a decrease on conductivity when compared with the membrane. Since the conductivity is dependent on the path that the electrical charges have to make across the entire surface of the yarn structure, instead of a linear path, electrons have to travel an helicoidal pathway which contributes to the decrease of conductivity.

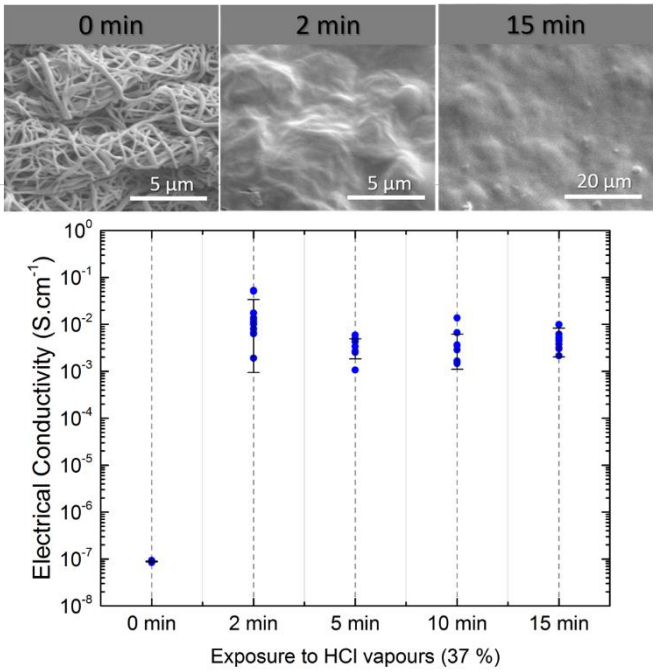

Figure 3. SEM micrographs of the membranes before and after exposure to HCl vapours (0, 2 and 15 min) and electrical conductivity measurements for every exposure time performed (0, 2, 5, 10 and 15 min).

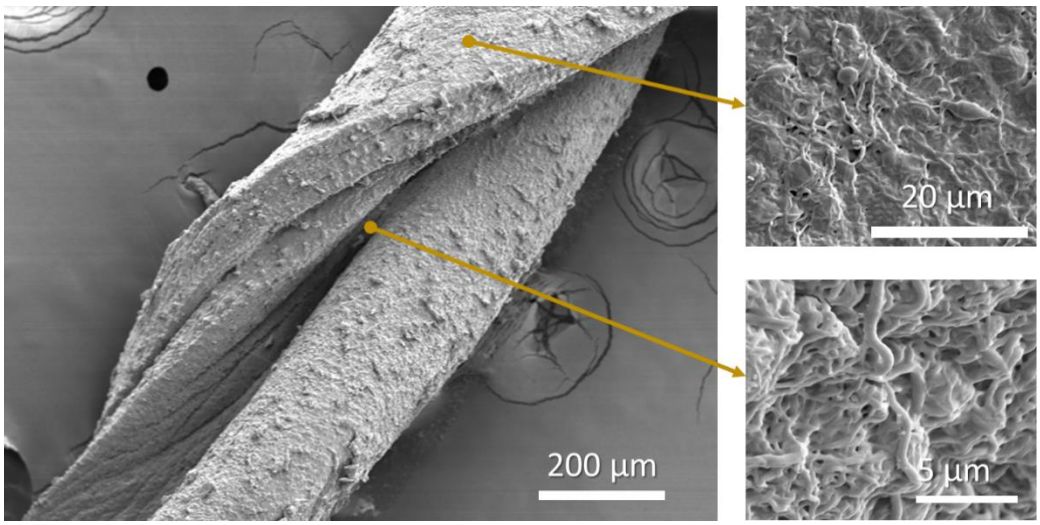

Figure 4. SEM micrographs of PANI yarn after 2 min HCl vapour treatment, with magnification of the outside layer (**top right**) and inside layer (**bottom right**).

Table 2 shows an overall comparison between the obtained conductivity for electrospun PANI fibers (membrane and yarn) with other related works found in literature. However, PANI-based yarns made from electrospun fibers still lack in literature. This preliminary attempt to produce conductive electrospun yarns based on PANI can be an interesting alternative to produce woven and knitted fabrics for electronic textiles. Further work is still required to improve electrical properties and preserve fibrous morphology of membranes and yarns. The electrospinning of multifunctional polymer-based fibers with controlled morphologies and properties is a scientific challenge and a technological accomplishment will have potential large impact on the wearable electronics market.

Table 2. Summary of several PANI-based conductive membranes using electrospinning technique found in literature and the present work.

Composition	Methodology	Structure	Conductivity [S·cm^{-1}]	Ref.
Camphoric acid doped PANI/PEO	Side-by-side ES	Membrane (2D)	3.8×10^{-4}	[26]
Camphoric acid doped PANI/PEO	Blend ES	Membrane (2D)	~10^{-5}	[26]
Sulfonated PANI/PEO	Blend ES	Membrane (2D)	~10^{-9}	[27]
Sulfonated PANI/PEO/Carbon Nanotubes	Blend ES	Membrane (2D)	~10^{-6}	[27]
Camphoric acid doped PANI/PEO and Nafion/PEO	Dual ES	Membrane (2D)	1.4×10^{-2} (after PEO removing)	[28]
Camphor sulfonic acid doped PANI/PEO	Blend ES	Fiber (1D)	8 (after PEO removing)	[29]
Camphor sulfonic acid doped PANI/PMMA	Blend ES	Fiber (1D)	2×10^{-2} (after PVDF removing)	[29]
Chemical modified PANI	ES	Fiber (1D)	20	[18]
Chemical modified PANI+PVP	Blend ES	Membrane (2D)	1.7×10^{-2}	This work
Chemical modified PANI+PVP	Blend ES	Yarn (1D)	4.1×10^{-4}	This work

4. Conclusions

This work reports for the first time a study to produce conductive yarns from electrospun PANI-based fibers envisaging their application in electronic textiles. The influence of oxidant-to-monomer ratio on the electrical conductivity of synthesized PANI powders was studied in detail. OM ratio of 2:1 led to a high chemical reaction yield of 97%, and highest electrical conductivity, 21 S·cm^{-1}. PANI (t-Boc) electrospun membrane with mean fiber diameter of 179 ± 5 nm, was produced and after 2 min of exposure to concentrated HCl the t-Boc protecting group was removed corresponding to an increase in conductivity to 1.7×10^{-2} S·cm^{-1}. Produced yarns displayed lower conductivity than previously obtained for the membranes (4.1×10^{-4} S·cm^{-1}) which can be attributed to an incomplete t-Boc protecting group substitution.

Improvements regarding electrical properties and studies on mechanical properties are still needed; however, these preliminary results show that PANI-based yarns made from electrospun fibers can be an interesting alternative to produce weaved and knitted fabrics for electronic textiles.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-6439/8/4/24/s1, Figure S1: Average weight loss percentage as a function of UV crosslinking time for PVP membranes after water immersion for 5 h.

Author Contributions: Methodology, P.P., B.M.M.F., J.F., J.P.C., J.P.B.; formal analysis, I.F. and A.C.B.; investigation, P.P., B.M.M.F., I.F. and A.C.B.; writing—original draft preparation, P.P. and A.C.B.; writing—review and editing, all authors; supervision, B.M.M.F. and A.C.B.; funding acquisition, I.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work was mainly funded by H2020-ICT-2014-1, RIA, TransFlexTeg-645241, and ERC-CoG-2014, CapTherPV, 647596, and partially funded by FEDER funds through the COMPETE 2020 Program and National Funds through FCT - Portuguese Foundation for Science and Technology under the project UID/CTM/50025/2019. The APC was funded by ERC-CoG-2014, CapTherPV, 647596.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wu, S.; Liu, P.; Zhang, Y.; Zhang, H.; Qin, X. Flexible and conductive nanofiber-structured single yarn sensor for smart wearable devices. *Sens. Actuators B Chem.* **2017**, *252*, 697–705. [CrossRef]
2. Cherenack, K.; Zysset, C.; Kinkeldei, T.; Münzenrieder, N.; Tröster, G. Woven Electronic Fibers with Sensing and Display Functions for Smart Textiles. *Adv. Mater.* **2010**, *22*, 5178–5182. [CrossRef] [PubMed]

3. Müller, C.; Hamedi, M.; Karlsson, R.; Jansson, R.; Marcilla, R.; Hedhammar, M.; Inganäs, O. Woven Electrochemical Transistors on Silk Fibers. *Adv. Mater.* **2011**, *23*, 898–901. [CrossRef] [PubMed]
4. Lee, Y.-H.; Kim, J.-S.; Noh, J.; Lee, I.; Kim, H.J.; Choi, S.; Seo, J.; Jeon, S.; Kim, T.-S.; Lee, J.-Y.; et al. Wearable Textile Battery Rechargeable by Solar Energy. *Nano Lett.* **2013**, *13*, 5753. [CrossRef]
5. Takamatsu, S.; Kobayashi, T.; Shibayama, N.; Miyake, K.; Itoh, T. Fabric pressure sensor array fabricated with die-coating and weaving techniques. *Sens Actuators A Phys.* **2012**, *184*, 57–63. [CrossRef]
6. O'Connor, B.; An, K.H.; Zhao, Y.; Pipe, K.P.; Shtein, M. Fiber Shaped Light Emitting Device. *Adv. Mater.* **2007**, *19*, 3897–3900. [CrossRef]
7. Grancarić, A.M.; Jerković, I.; Koncar, V.; Cochrane, C.; Kelly, F.M.; Soulat, D.; Legrand, X. Conductive polymers for smart textile applications. *J. Ind. Text.* **2017**, *48*, 612–642. [CrossRef]
8. Namgoong, H.; Woo, D.J.; Lee, S.-H. Micro-chemical structure of polyaniline synthesized by self-stabilized dispersion polymerization. *Macromol. Res.* **2007**, *15*, 633. [CrossRef]
9. MacDiarmid, A.G. "Synthetic metals": A novel role for organic polymers. *Curr. Appl. Phys.* **2001**, *1*, 269–279. [CrossRef]
10. Moutsatsou, P.; Coopman, K.; Smith, M.B.; Georgiadou, S. Conductive PANI fibers and determining factors for the electrospinning window. *Polymer* **2015**, *77*, 143–151. [CrossRef]
11. Boeva, Z.A.; Sergeyev, V.G. Polyaniline: Synthesis, properties, and application. *Polym. Sci. Ser. C* **2014**, *56*, 144. [CrossRef]
12. Cortés, M.T.; Sierra, E.V. Effect of synthesis parameters in polyaniline: Influence on yield and thermal behavior. *Polym. Bull.* **2006**, *56*, 37–45. [CrossRef]
13. Jelmy, E.J.; Ramakrishnan, S.; Devanathan, S.; Rangarajan, M.; Kothurkar, N.K. Optimization of the conductivity and yield of chemically synthesized polyaniline using a design of experiments. *J. Appl. Polym. Sci.* **2013**, *130*, 1047–1057. [CrossRef]
14. Baptista, A.C.; Ropio, I.; Romba, B.; Nobre, J.P.; Henriques, C.; Silva, J.C.; Martins, J.I.; Borges, J.P.; Ferreira, I. Cellulose-based electrospun fibers functionalized with polypyrrole and polyaniline for fully organic batteries. *J. Mater. Chem. A* **2018**, *6*, 256. [CrossRef]
15. Ropio, I.; Baptista, A.C.; Nobre, J.P.; Correia, J.; Belo, F.; Taborda, S.; Morais Faustino, B.M.; Borges, J.P.; Kovalenko, A.; Ferreira, I. Cellulose paper functionalised with polypyrrole and poly(3,4-ethylenedioxythiophene) for paper battery electrodes. *Org. Electron.* **2018**, *62*, 530. [CrossRef]
16. Liu, H.; Kameoka, J.; Czaplewski, D.A.; Craighead, H.G. Polymeric Nanowire Chemical Sensor. *Nano Lett.* **2004**, *4*, 671–675. [CrossRef]
17. Zhu, Y.; Zhang, J.; Zheng, Y.; Huang, Z.; Feng, L.; Jiang, L. Stable, Superhydrophobic, and Conductive Polyaniline/Polystyrene Films for Corrosive Environments. *Adv. Funct. Mater.* **2006**, *16*, 568–574. [CrossRef]
18. Uh, K.; Kim, T.; Lee, C.W.; Kim, J.-M. A Precursor Approach to Electrospun Polyaniline Nanofibers for Gas Sensors. *Macromol. Mater. Eng.* **2016**, *301*, 1320–1326. [CrossRef]
19. Lee, C.-W.; Seo, Y.-H.; Lee, S.-H. A Soluble Polyaniline Substituted with *t-BOC*: Conducting Patterns and Doping. *Macromolecules* **2004**, *37*, 4070–4074. [CrossRef]
20. Gomes, E.C.; Oliveira, M.A.S. Chemical Polymerization of Aniline in Hydrochloric Acid (HCl) and Formic Acid (HCOOH) Media. Differences Between the Two Synthesized Polyanilines. *Am. J. Polym. Sci.* **2012**, *2*, 5–13. [CrossRef]
21. Boyer, M.I.; Quillard, S.; Rebourt, E.; Louarn, G.; Buisson, J.P.; Monkman, A.; Lefrant, S. Vibrational Analysis of Polyaniline: A Model Compound Approach. *J. Phys. Chem. B* **1998**, *102*, 7382–7392. [CrossRef]
22. Kiefer, W. Recent Advances in linear and nonlinear Raman spectroscopy I. *J. Raman Spectrosc.* **2007**, *38*, 1538–1553. [CrossRef]
23. Pereira da Silva, J.E.; de Faria, D.L.A.; Córdoba de Torresi, S.I.; Temperini, M.L.A. Influence of Thermal Treatment on Doped Polyaniline Studied by Resonance Raman Spectroscopy. *Macromolecules* **2000**, *33*, 3077–3083. [CrossRef]
24. Niaura, G.; Mažeikien, R.; Malinauskas, A. Structural changes in conducting form of polyaniline upon ring sulfonation as deduced by near infrared resonance Raman spectroscopy. *Synth. Met.* **2004**, *145*, 105–112. [CrossRef]
25. Bernard, M.C.; Hugot-Le Goff, A. Quantitative characterization of polyaniline films using Raman spectroscopy: I: Polaron lattice and bipolaron. *Electrochim. Acta* **2006**, *52*, 595–603. [CrossRef]

26. Liu, W.; Zhang, J.; Liu, H. Conductive Bicomponent Fibers Containing Polyaniline Produced via Side-by-Side Electrospinning. *Polymers* **2019**, *11*, 954. [CrossRef]
27. Lin, Y.-W.; Wu, T.-M. Fabrication of water-soluble polyaniline/poly(ethylene oxide)/carbon nanotube electrospun fibers. *J. Appl. Polym. Sci.* **2012**, *126*, E123–E129. [CrossRef]
28. Simotwo, S.K.; Kalra, V. Study of Co-electrospun Nafion and Polyaniline Nanofibers as Potential Catalyst Support for Fuel Cell Electrodes. *Electrochim. Acta* **2016**, *198*, 156–164. [CrossRef]
29. Zhang, Y.; Rutledge, G.C. Electrical Conductivity of Electrospun Polyaniline and Polyaniline-Blend Fibers and Mats. *Macromolecules* **2012**, *45*, 4238–4246. [CrossRef]