Journal of International Scientific Publications: Materials, Methods and Technologies

Volume 8, ISSN 1314-7269 (Online), Published at: http://www.scientific-publications.net

SYNTHESIS AND CHARACTERIZATION OF ELECTRICALLY CONDUCTIVE PEDOT COATINGS ON TEXTILE SUBSTRATES

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Abstract

In this article, electrically conductive coatings of poly(3, 4 – ethylenedioxythiophene) were synthetized on plain weave fabrics with the vapor phase polymerization method, to provide textile fabrics of polyester with high electrical conductivity for smart textile applications. The method used oxidant solutions of $FeCl_3 6H_2O$ and was optimized to maximize electrical conductivity. The effect of the concentration of the oxidant solution in the electrical and mechanical characteristics of the samples was investigated and correlated to their morphology, analyzed by electron microscopy imaging. The samples exhibit an important decrease of sheet resistivity with the concentration of oxidant concentration increase, with a minimum value of 25 Ohm/sq obtained for concentrations of 30 wt%. The sheet resistivity of the samples could be further decrease to 5 Ohm/sq by the application of multiple polymerization steps and was a function of the conjugated polymer content. Mechanical tenacity tests on textile samples with various degrees of electrical conductance showed tensile forces at break similar to those of pristine fabrics. The sheet resistivity values that were obtained are suitable to produce textile electrodes for physiological sensing. Washing resistance tests were carried out and showed that the electrical resistivity of the samples significantly increases in the first washing cycles.

Key words: *textile functionalization, PEDOT, electrically conductive textiles*

1. INTRODUCTION

Since the pioneer works of Shirakawa in the early 1970s and his collaborative work with Heeger and MacDiarmid (Heeger 2001, MacDiarmid 2001), conjugated polymers have become an important field of research and development. Conjugated polymers consist of a backbone structure, along which delocalized electronic states, resulting from π – orbitals overlap, provide charge mobility along the polymer backbone, consequently yielding electrical conductance (Heeger 2001). In the 1980´s, Bayer introduced the Poly(3,4-ethylenedioxythiophene) (PEDOT), a conjugated polymer that exhibits high chemical and physical stability and high electrical conductivity (500 Scm^{-1} to 1000 Scm^{-1}) (Bayer 1988). PEDOT has potential for a widefield of applications, from biomedical sensors (Rozlosnik 2009, Tsukada 2012), nerve tissue engineering (Ghasemi-Mobarakeh 2011, Abidian 2012, Valle 2007), strain sensors (Daoud 2005, Calvert 2008, Lang 2008), electrodes for organic field-effect transistors (Lee 2010), solar cells (Colladet 2007), hydrogen cathalysis (Winther-Jensen 2010) to smart textiles (Cherenack 2012, Yang 2011, Dhawan 2012).

The synthesis of PEDOT can be performed by various techniques (Bhattacharyya 2012), but concerning textile substrates, the main relevant ones are the *wet* polymerization, also referred to as liquid phase polymerization (LPP), and the vapor phase polymerization (VPP). In both methods, the oxidative polymerization is the most common, using either of the oxidants agents, Iron (III) chloride (FC) or Ferric p - toluene sulfonate (FTS). The oxidative polymerization mechanisms are well described elsewhere (Im 2007).

In the LPP method, the textile samples are immersed in homegeneous synthesis solutions constituted by the mixture of the monomer 3,4-ethylenedioxythiophene (EDOT) and the oxidant agent, at a temperature below 10 ^oC to delay the polymerization process (Knittel 2009). After a certain period of time of immersion, the samples are then submited to a drying step, at either ambient temperature or in a convection oven, during wich the polymerization of the PEDOT coating is completed. K. H. Hong et al. (Hong 2005) reported that the electrical and mechanical properties of woven fabrics coated with PEDOT by the LPP method largely depend upon the following intervenients: type of oxidant agent, the ratio of relative concentrations monomer / oxidant, the solvent, the type of fibers the textile substrate is made of. With the LPP method, fabrics with good

electromagnetic interference shielding properties, characterized by sheet resistivities as low as 10 Ohm/sq were obtained with the oxidant FTS and multiple polymerizations (Kim 2003, Jung 2007).

In the VPP method, the woven fabrics are firstly immersed in a liquid phase oxidant solution and are secondly exposed to the monomer in the vapor phase. The exposure of the samples to an atmosphere of monomer is typically performed in a reactor with controlled vacuum and temperature (Yang 2011, Bhattacharyya 2012, Bashir 2011).

The VPP method has three major advantages over the *wet* method; considerably less reagents are required; there is no need to use organic solvents due to the low solubility of EDOT in non – organic solvents (Corradi 1997); it involves lower process complexity because there is no need to keep a low temperature bath (T < 8 °C).

In this investigation, the VPP method was used to synthetyze coatings of conductive PEDOT on substrates consisting of plain weave fabrics of polyester, using two types of solvents, ethanol and water. Water solvent is considerably better choice over organic solvents, because is eco-friendly and considerably less expensive. The method was optimized to provide the coated fabrics with the highest electrical conductance with the target to attain sheet resistivities of the order or less than 10 Ohm/sq for applications in physiological sensing. Textile samples with various contents of PEDOT were prepared and electrically and mechanically tested. Washing resistance tests were also performed for product design considerations. The electrical and mechanical results were correlated with Fourier transform infrared spectroscopy and SEM analysis. The synthesis method used, proved suitable to prepare materials for smart textile applications, such as heating elements (Yang 2011) and electrodes for the sensing of physiological signals (Trindade 2010).

2. EXPERIMENTAL

2.1 Materials

The textile substrates consisted of plain weave fabrics of polyester with a thickness of 0.22 mm and a specific weight of 1.2 g/cm^2. A large piece of fabric was machine washed at 100 ºC with a mild soap and dried. Small size substrates were then cut off from the large piece to rectangular geometrical shapes, having lateral dimensions of 80 mm × 5 mm accurately obtained at a more or less one thread. The substrates were washed in methanol for 20 minutes, rinsed three times in deionized water and left to dry at 23 ºC in a room with conditioned ambient for at least 24 hours.

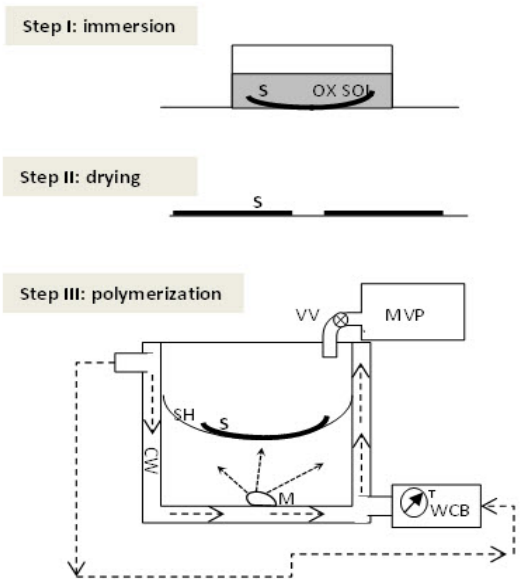


Fig. 1. Schematic representation of VPP method and reactor unit, where OX SOL = oxidant solution, S = substrate, MVP = membrane vacuum pump, VV = vacuum valve, SH = sample holder, WCB = water circulating bath, CW = circulating water, M = monomer.

For the polymerization of PEDOT, EDOT monomer (97%), Iron (III) chloride hexahydrate (97%), and methanol (99.5%) were purchased from Sigma-Aldrich and ethanol (99%) was locally purchased from Manuel Vieira & C[a].

2.2 Polymerization unit and method

Schematics of the VPP method and polymerization reactor unit are shown in Figure 1. The VPP method uses three steps; firstly, a step of immersion of the substrates in an oxidant solution of specific concentration; secondly, a drying step with conditions depending upon the solvent used; thirdly, the polymerization step, in which the samples are placed into a reactor and exposed to an atmosphere of the monomer, at certain vacuum pressure and temperature. The oxidant solutions were prepared with Iron (III) chloride hexahydrate ($FeCl_36H_2O$) dissolved in either ethanol (C_2H_5OH) or in bi-distilled water, using the aid of stirring, at ambient temperature, for at least two hours. Samples soaked in aqueous solutions of $FeCl_36H_2O$ (FC) were dried in a convection oven at 60 °C for 3 minutes, while samples soaked in organic solutions were dried in an ambient conditioned room.

The polymerization process used a droplet of 15 microliter of monomer, allowing two cycles of polymerization lasting 30 minutes each. The samples were placed on a sample holder and moved into the reactor, which was then sealed and pumped down to a vacuum pressure of 160 mTorr. Next, a vacuum valve (VV) was closed and the polymerization cycle initiated. Once the time of the polymerization cycle was completed, the reactor was vented with air, and the samples removed and immediately washed in methanol and rinsed in DI water. The samples were next put to dry in an ambient conditioned room for at least 24 hours.

2.2 Electrical characterization

The electrical characterization of the samples was performed with the two - probe method. The method is suitable for electrical measurements on homogeneous, continuous films with a relatively high electrical conductance, but could be applied to the textile samples coated with PEDOT as good degree of measurement repeatability and relative errors of less than 10% were obtained. To address the error involved, samples with a length of 120 mm were prepared and the sheet resistance of the sample was measured with the four-probe method for variable inner probes distances between 50 mm to 100 mm. The mean sheet resistance value obtained matched the two-probe typical mean value within an error of less than 10%.

In the two-probe method, two alligator clips connected the two ends of the sample to a power supply (Hameg 8040-3) and a programmable ampermeter (Hameg 8012). The data acquisition was performed via a RS232 interface and a Labview program to display and record the sample´s *I - V* curves. The mean values of electrical current, *I*, for each applied voltage, *V*, were recorded along with the sample´s geometric factor, *L/W*, where *L* = distance between the probes, and *W* = sample width. For each VPP condition, six to twelve samples were measured. For each sample, the sheet resistivity, R_{sq}, in units of Ohm/sq., was obtained by applying the Ohm´s law,

$$Rsq = V/(I \cdot L/W) \quad (1)$$

In order to graphically compare different samples, *I* - V* curves that excluded the influence of small differences in the geometric factor used in the measurements, were used, with *I** given by,

$$I^* = I \cdot L/W \quad (2)$$

The electrical tests typically used geometrical factors of sample width, *W* = 5 mm and distance between probes, *L* = 60 mm.

2.3 Tensile testing

Mechanical tenacity tests to elongation were performed with an Adamel Lhorargy dynamometer, with a 1kN loading cell. The tensile tests were performed at ambient temperature, under a crosshead speed of 20 mm/min, and a built-in program traced the tensile force as a function of percentage of sample elongation and calculated the maximum force and elongation at break.

2.4 Scanning electron microscopy

The surface morphology and longitudinal sections of pristine and polyester samples coated with PEDOT were analyzed by scanning electron microscopy (SEM) with a Hitachi S2700 microscope with an accelerating voltage of 30 kV and magnifications in the range of 35X to 250X.

2.5. Washing resistance tests

The washing resistance tests were performed with a Linitest machine, following in general the procedures of the ISO 105 of 1978. The tests consisted of cycles of machine washing in cold water, for 45 minutes with 1 g/l of a standard mild soap and completed with a standard rinsing step, followed by a drying cycle in a convection oven, at 30 °C for 40 minutes.

3. RESULTS AND DISCUSSION

3. 1 Optimization of the VPP method

Prior to the investigation of variation of the sheet resistivity of the PEDOT coatings with the oxidant concentration and solvents, the VPP process parameters, immersion time, drying time, polymerization temperature and polymerization time were tuned to obtain the process parameters providing the samples with the lowest sheet resistivity. For the optimization of the parameters soaking time and drying time, oxidant organic solutions with concentrations of 15 wt% were used. Experimental curves of sheet resistivity variation with immersion time and drying time and of sheet resistivity variation with polymerization temperature are shown in Figure 2. The parameters soaking time and polymerization temperature showed an important effect, the best process parameters corresponding to immersion and drying times of 15 minutes and a polymerization temperature of 60 °C. Similar optimization was done for samples prepared with aqueous solutions, and because significantly less volatile than the ethanol solvent, the drying procedure required a convection oven, the best results obtained at a temperature of 60 °C and a duration of 3 minutes.

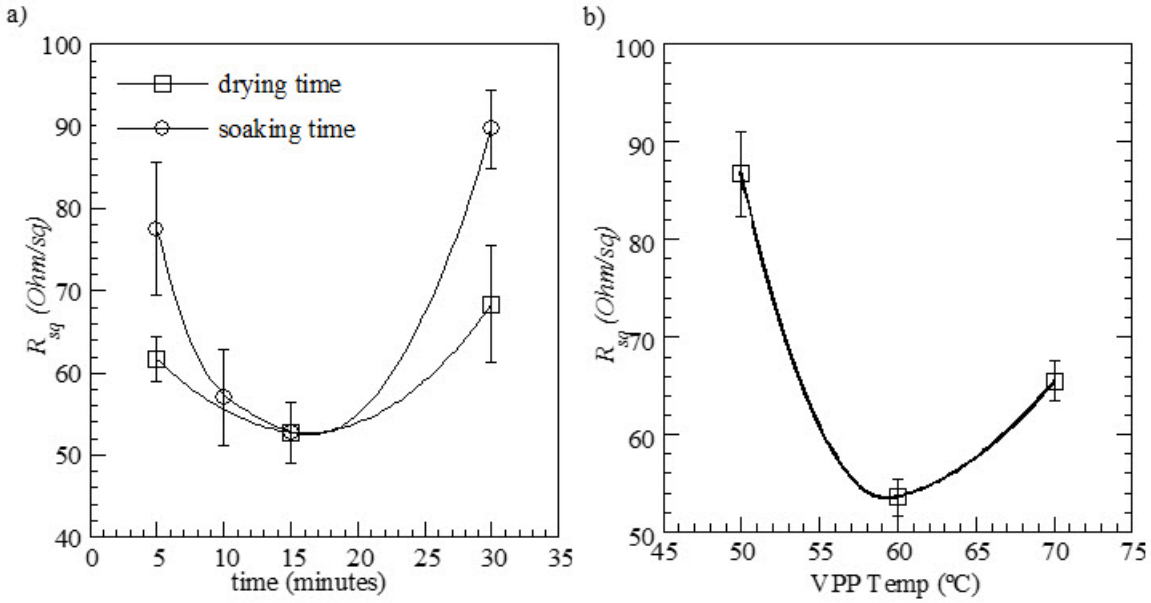


Fig. 2 Variation of sheet resistance with the VPP method parameters; a) immersion and drying time; b) polymerization temperature. Coatings prepared with oxidant solution having a concentration of 15 wt%.

The polymerization time (not shown) for duration cycles t > 15 minutes, also monitored by the visual observation of the coloration of the samples, affected little the electrical characteristics of the samples, confirming that the polymerization process was mostly completed in the first 15 minutes of the process. The polymerization time used in the following experiments was in the range of 20 to 30 minutes.

After completing the polymerization cycle, the reactor was vented with air and each pair of samples immediately washed with methanol and water.

The conditions of drying the samples after the washing procedure were investigated, by comparing the sheet resistivity of samples for the following variable drying conditions: in an ambient conditioned room (22 ºC, 50% RH) for 24 hours; in a convection oven at variable time × temperature. The samples with the lowest sheet

resistivity were those either dried in the ambient conditioned room or in the convection oven with T = 30 ºC for 50 minutes as shown by the experimental results presented in Figure 3.

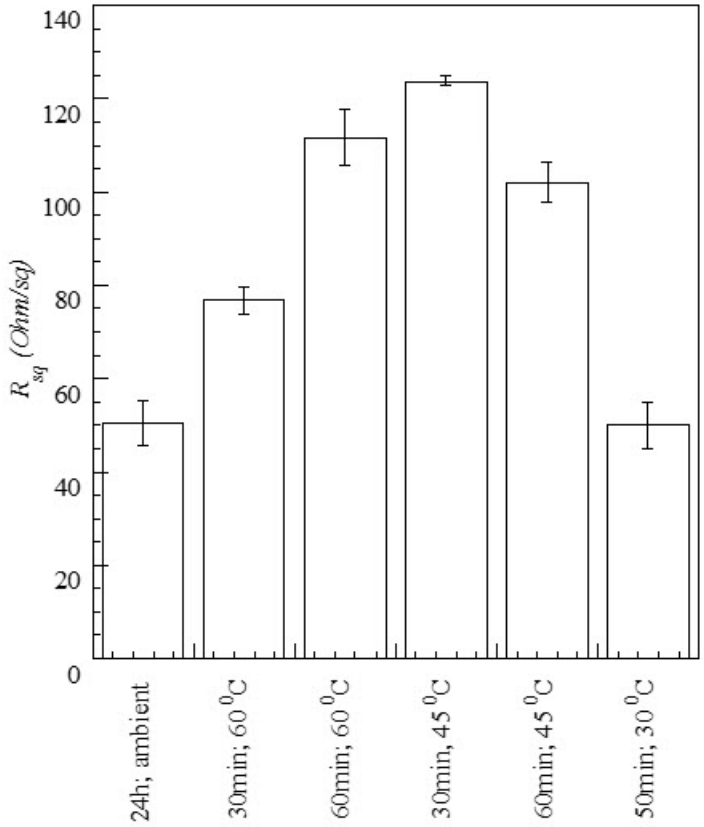


Fig. 3. Variation of sheet resistivity with final drying procedure conditions, for samples prepared with organic oxidant solutions with a concentration of 15 wt% and the VPP parameters immersion time = 15 minutes, drying time = 15 minutes, polymerization temperature = 60 ºC, polymerization time = 20 minutes. Ambient conditions correspond to T = 22 ºC and relative humidity, RH = 50 %.

3. 2 Effect of oxidant concentration

The effect of the concentration of the oxidant solution on the PEDOT coating electrical conductance was investigated. Organic oxidant solutions with concentrations of FC in ethanol of 5 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt% and 35 wt% were prepared and for each concentration, six to twelve samples were coated with PEDOT by the VPP method. For each concentration, I^* - V curves were measured and showed good linearity, increase of electrical conductance with the oxidant solution concentration increase and absence of hystheretic behavior for applied voltages in the range of 1 to 10 Volts, as shown in Figure 4. The sheet resistivity values, R_{sq}, were extracted and plotted as a function of the oxidant concentration as shown in Figure 5. An accentuated decrease of R_{sq} occurred for oxidant concentrations of 5 wt% to 10 wt%. Beyond a concentration of 15 wt%, a moderate decrease of resistance was obtained. The lowest value of $R_{sq} \cong 25$ Ohm/sq was reached at the maximum oxidant concentration of 35 wt%.

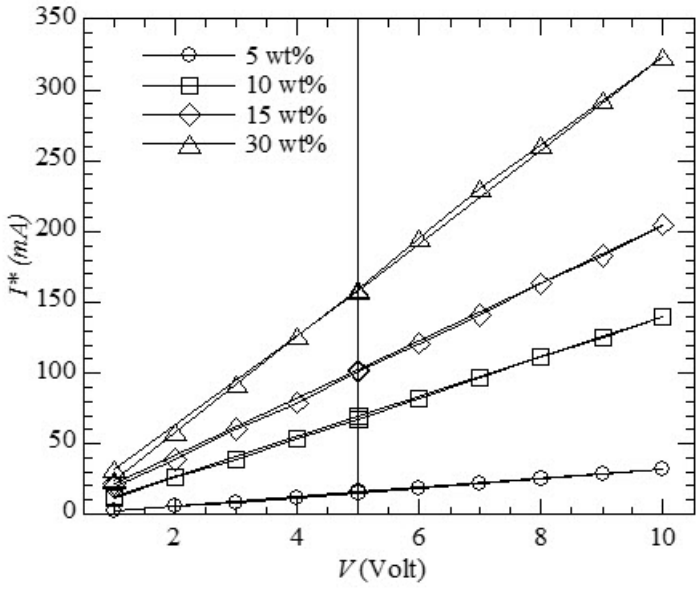


Fig. 4. Characteristic I^* - V curves obtained with organic oxidant solutions of various concentrations of FC.

Good correlation between the color of the samples and their electrical characteristics was obtained (inset of Figure 5a), indicating that the decrease in resistance was caused by an increase of PEDOT content in the coating. The darkest grey colored samples exhibit the lowest value of R_{sq} = 24 ± 1 Ohm/sq while those of light grey - bluish color exhibit the highest R_{sq} = 374 ± 23 Ohm/sq, corresponding to oxidation solutions with concentrations of 35 wt% and 5 wt%, respectively. Effectively, samples immersed in oxidation solutions of higher concentration have more oxidant available to react with the vapor of the monomer EDOT, producing coatings with higher content of PEDOT as corroborated by the SEM analysis presented next. The electrical conductivity of the samples could be further enhanced by applying several layers of polymerization, a method used by other authors to provide textile fabrics with good electromagnetic interference shielding capability (Jung 2007)]. The minimum value of R_{sq} = 5 Ohm/sq was attained after 5 cycles of polymerization as shown in Figure 5b.

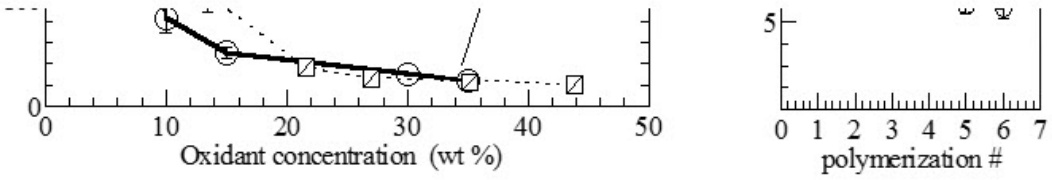


Fig. 5. a) Experimental curve of variation of sheet resistivity with organic and aqueous oxidant solutions of various concentrations of FC. Inset, photo showing color gradation of the coated samples; b) Experimental curve of sheet resistivity decrease with sucessive number of polymerization cycles applied.

3.3. Morphological Characteristics

The analysis of the morphological characteristics of samples prepared from oxidant solutions of various concentrations was performed with the SEM imaging technique. SEM images of longitudinal sections of the fibers of woven samples coated with PEDOT prepared with organic oxidant solutions with concentrations of 5 wt%, 15 wt% and 35 wt% are shown in Figure 6.

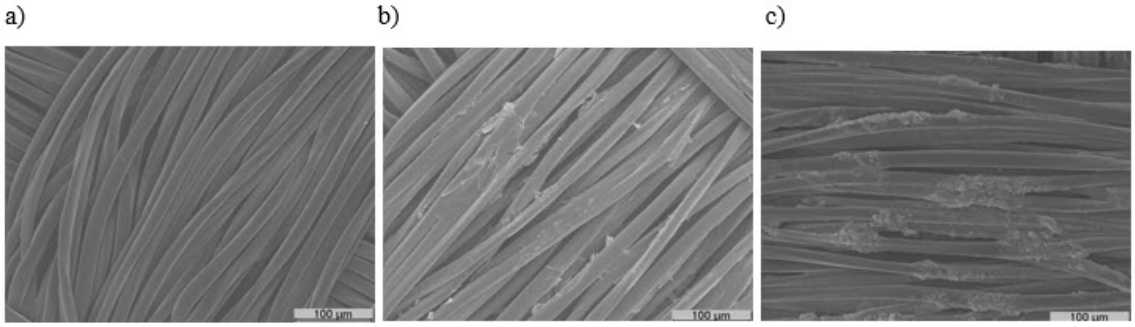


Fig. 6. SEM images of longitudinal sections of polyester woven samples functionalized with PEDOT synthetized from various concentrations of organic oxidant agent; a) 5 wt%; b) 15 wt%; c) 35 wt%.

Samples coated with PEDOT prepared with an oxidant concentration of 5 wt% exhibit very similar morphology to the pristine samples, characterized by fibers of polyester with regular cylindrical shapes and diameters in the range of 10 to 14 microns. Samples prepared with oxidant concentrations of 15 wt% exhibit fibers interconnected through PEDOT. The samples prepared with oxidant solutions with a concentration of 30 wt% exhibited considerably higher content of PEDOT, characterized by globular clusters. From high magnification imaging (not shown) it is estimated that the thickness of the polymer interconnecting the cylindrical fibers is of the order 600 nm to 1 μm. The SEM images also show no visible signs of fiber degradation. Mechanical test results presented next corroborated that no fiber degradation was present in the samples, even in those prepared at the highest concentration of oxidant (35 wt%).

3.4. Mechanical characteristics

Mechanical tests were performed with pristine woven samples and with samples coated with PEDOT prepared from oxidant solutions with concentrations of 5 wt%, 10 wt%, 15 wt% and 35 wt%. Two samples of each batch were tested and for all samples no significant variation of tensile force at break and of maximum elongation were detected. The samples were characterized by maximum tensile forces at break between 120 N and 130 N. These results corroborate the SEM analysis results that no fiber degradation was present even in samples exposed to the highest concentration of oxidant, also in agreement with the results reported by other researchers with PEDOT coatings on polyester yarns (Bashir 2011).

3.5. Washing resistance characteristics

Electrically conductive samples prepared with aqueous and organic solutions of oxidant agent with a concentration of 35 wt% were submitted to washing resistance tests in order to obtain insight concerning their maintenance and durability. Samples prepared with 3 cycles of polymerization were used in the tests. The sheet resistivity of the samples were monitored between each washing/drying step and the samples exhibited an important degradation on their electrical conductance characteristics with the washing cycles as shown by the plot presented in Figure 7. Similar results were obtained with the drying step in ambient conditions, for 24 hours, indicating that in this case, the fast ageing of the samples was mainly due to the washing. Similar trend of increase of sheet resistivity with the washing cycle was obtained for both types of samples, indicating that solvent and the thickness of the coating did not play a significant role in the ageing of the samples produced by the washing process.

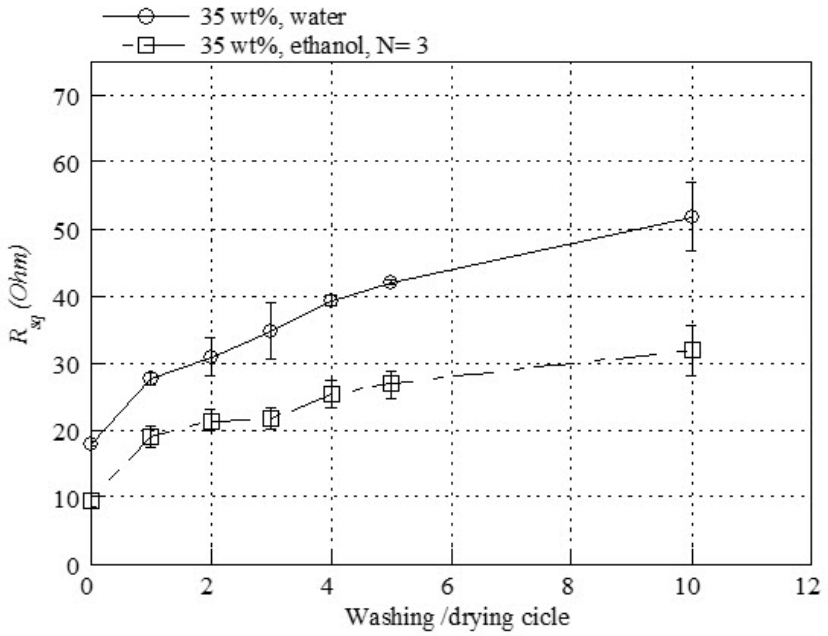


Fig. 7. Increase of sheet resistivity with the number of washing/drying cycles for electrically conductive samples prepared with aqueous and organic solutions of oxidant with concentrations of 35 wt%. N = number of polymerization cycles.

4. SUMMARY AND CONCLUSIONS

The VPP method is capable to functionalize textile fabrics of polyester with an electrical conductivity suitable to smart textile applicatios, comparable to those obtained by other researchers with the wet method, but involving considerable less process complexity and considerably less quantity of reagents. Furthermore, the experiemental results showed that no organic solvents are needed. In the VPP method the organic solvents can be completely replaced by water, which lowers considerably the cost in resosurces and is eco - friendly. The VPP method allowed to obtain woven samples with electrical conductances characterized by sheet resistivities of 50 Ω/sq and 20 Ω/sq for oxidant solutions of FC with concentrations of 15 wt% and 35 wt%, respectively. A sheet resistivity of 5 Ω/sq could be attained though the use of the highest concentration of 35 wt% in the oxidant solution and multiple polymerizations. The electrical results obtained are the best ever reported in textile substrates with the FC oxidant agent. The electrical conductance obtained is suitable to applications in smart textiles such as textile heaters (Yang 2011), electromagnetic shielding (Kim 2003, Jung 2007) and clothing integrating electrodes for physiological signal monitoring (Tsukada 2012, Trindade 2010).

The highest concentration of oxidant used, of 35wt% (1 mole) did not cause degradation of the fibers constituting the yarns the fabrics were woven with. Effectively, the tenacity strength of the samples were kept mainly unchanged upon the full range of PEDOT content investigated.

The washing resistance of the samples needs to be improved, and future work will address strategies to achieve a better washing resistance performance.

ACKNOWLEDGMENTS

This work was supported by the National Strategic Reference Frame, Operational Program Factors of Competitivity, QREN, under the grant PT 21 – Powered Textiles Séc. 21 – PPS High-tech Fashion/Fashion Fabrics and by FCT and co-financed by FEDER, through COMPETE, under the grant "Projecto Estratégico da Unidade de Materiais Têxteis e Papeleiros" and project PTDC/EEI-ELC/1838/2012 – SIVIC. J. Matos and P. Spranger would like to thank FCT and the Ministry of Economy for their scholarship funding.

REFERENCES

Abidian, M. R., Daneshvar, E. D., Egeland, B. M., Kipke, D. R., Urbanchek, M. G. 2012, ′Hybrid Conducting Polymer–Hydrogel Conduits for Axonal Growth and Neural Tissue Engineering′, *Advance in Healthcare Materials*, 1, pp. 762–767.

Bashir, T., Skrifvars, M., Persson, N. 2011, ′Production of highly conductive textile viscose yarns by chemical vapor deposition technique: a route to continuous process′, Polymer Advanced Technology, 22, 2214-2221.

Bayer, A. G. 1998, ′Polythiophenes, process for their preparation and their use′, Eur. Patent 339340.

Bhattacharyya, D., Howden, R. M., Borrelli, D. C., Gleason, K. K. 2012, ′Vapor Phase Oxidative Synthesis of Conjugated Polymers and Applications′, *Journal of Polymer Science B: Polymer Physics*, 50, pp. 1329-1351.

Calvert, P., Duggal, D., Patra, P., Agrawal, A., Sawhary, A. 2008, ′Conducting Polymer and Conducting Composite Strain Sensors on Textiles′, *Molecular Crystals and Liquid Crystals*, 484, 291, pp. [657]-302/[668].

Cherenack, K., Pieterson, L. van 2012, ′ Smart textiles: Challenges and opportunities′, *Journal of Applied Physics*, 112, pp. 091301 1-14.

Colladet, K., Fourir, S., Cleij, T., Lutsen, L., Gelan, J., Vanderzande, D. 2007, ′Low Band Gap Donor-Acceptor Conjugated Polymers toward Organic Solar Cells Applications′, *Macromolecules*, 40, pp. 65-72.

Corradi, R. and Armes, S. P. 1997, ′Chemical synthesis of poly(3,4 - ethylenedioxythiophene)′, *Synthetic Metals*, 84, pp. 453-454.

Daoud, W. A. , Xin, , J. H. , Szeto, Y. S. 2005, ′Polyethylenedioxythiophene coatings for humidity, temperature and strain sensing polyamide fibers′, *Sensors and Actuators B*, 109, pp. 329-333.

Dhawan, A., Ghosh, T. K., Muth, J. 2012, ′Formation of Textile Circuits in Textile Structures′, Ed. Mattila, H., Woodhead Publishing Limited, Cambridge, UK.

Ghasemi-Mobarakeh, L., Prabhakaran, M. P., Morshed, M., Nasr-Esfahani, M. H., Baharvand, H., Ramakrishna S. 2011, ′Application of conductive polymers, scaffolds and electrical stimulation for nerve tissue engineering′, *Journal of Tissue Engineering and Regenerative Medicine*, 5, pp. e17-e35.

Heeger, A. J. 2001, ′Nobel Lecture: Semiconducting and metallic polymers: The fourth generation of polymeric materials, *Review in Modern Physics′,* 73, pp. 681-700.

Hong, K. H., Oh, K. W., Kang, T. J. 2005, ′Preparation and Properties of Electrically Conducting Textiles by *In Situ* Polymerization of Poly(3,4 - ethylenedioxythiophene)′, *Journal of Applied Polymer Science*, 97, pp. 1326-1332.

Im, S. G., Gleason, K. K. 2007, ′Systematic Control of the Electrical Conductivity of Poly(3,4-ethylenedioxythiophene) via Oxidative Chemical Vapor Deposition′, *Macromolecules*, 40, pp. 6552 – 6556.

Jung, B. R., Kwon, Y. R., Ko, J. M., Kim, M. S., Cho, S. H., Lee, J. Y. Joo, J. 2007, ′Pet Fabric/Poly(3,4 - Ethylenedioxythiophene) Composite with High Electrical Conductivity for EMI Shielding, *Molecular Crystals and Liquid Crystals*, 464, pp. 109/[691] – 117/ [699].

Kim, H. K., Kim, M. S., Chun, S. Y., Park, Y. H., Jeon, B. S., Lee, J. Y., Hong, Y. K., Joo, J. Kim, S. H. 2003, ′Characteristics of Electrically Conducting Polymer - Coated Textiles′, *Molecular Crystals and Liquid Crystals*, 405, pp. 161-169.

Knittel, D., Schollmeyer, E. 2009, ′Electrically high-conductive textiles′, *Synthetic Metals*, 159, pp. 1433-1437.

Lang, U., Rust, P., Dual, J. 2008, ′Towards fully polymeric MEMS: Fabrication and testing of PEDOT/PSS strain gauges′, *Microelectronics Engineering*, 85, pp. 1050-1053.

Lee, M., Lee, M., Choi, J., Park, J., Song, C. 2010, ′Fine patterning of glycerol-doped PEDOT:PSS on hydrophobic PVP dielectric with ink jet for source and drain electrode of OTFTs′, *Organic Electronics*, 11, pp. 854-859.

MacDiarmid, A. G. 2001, Nobel Lecture: ′Synthetic metals": A novel role for organic polymers′, *Review in Modern Physics*, 73, pp. 701-712.

Rozlosnik, N. 2009, ′New directions in medical biosensors employing poly(3,4-ethylenedioxy thiophene) derivative-based Electrodes′, *Analytical and Bioanalytical Chemistry*, 395, pp. 637-645.

Trindade, I. G., Lucas, J., Miguel, R., Alpuim, P., Carvalho, M., Garcia, N. M. 2010, ′Lightweight Portable Sensors for Health Care′, *Proceedings of the 12th IEEE International Conference e-Health Networking Applications and Services (Healthcom)*, Lyon, pp. 175-179.

Tsukada, S. 2012, ′Conductive Polymer Combined Silk Fiber Bundle for Bioelectrical Signal Recording′, *PloS ONE (www.plosone.org)*, 7 (4), pp. e33689 1-10.

Valle, L. J., Aradilla, D., Oliver, R., Sepulcre, F., Gamez, A., Armelin, E., Alemán, C. Estrany, F. 2007, ′Cellular adhesion and proliferation on poly(3,4-ethylenedioxythiophene): Benefits in the electroactivity of the conducting polymer′, *European Polymer Journal*, 43, pp. 2342–2349.

Winther-Jensen, B., Fraser, K., Ong, C., Forsyth, M., MacFarlane, D. R. 2010, ′Conducting Polymer Composite Materials for Hydrogen Generation′, *Advanced Materials*, 22, pp. 1 - 4.

Yang, X., Shang, S., Li, L., Tao, X., Yan, F. 2011, ′Vapor phase polymerization of 3,4-ethylenedioxythiophene on flexible substrate and its application on heat generation′, *Polymer Advanced Technologies*, 22, pp. 1049-1055.