

A method to produce microelectronic devices on textile and paper substrates

I. G. Trindade*, R. Miguel*, J. Lucas*, M. Pereira* and M. Santos Silva*

*Department of Textile Science and Technology, Universidade da Beira Interior
Covilhã, Portugal, itrindade@ubi.pt

ABSTRACT

High electrical conductance coatings of poly(3, 4 – ethylenedioxythiophene) were *in situ* synthesized on textile substrates by the vapor phase polymerization method, using water as solvent. The method uses oxidant aqueous solutions with specific concentrations of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and is considerably more economically and ecologically sustainable than traditional *wet* methods. The method was optimized to maximize the electrical conductance of the coatings, and the effect of the concentration of the oxidant solutions on the electrical and mechanical characteristics of the samples was investigated and correlated to scanning electron microscopy imaging analysis. A strong decrease of electrical resistance with the increase of the concentration of the oxidant was obtained, characterized by a minimum value of sheet resistivity, R_{sq} , of 25 Ohm/sq. This value could be further decreased to 5 Ohm/sq by the application of multiple polymerization layers and was a function of the conjugated polymer content. The method is suitable to produce textile electrodes and interconnects for smart textile applications and microelectronic devices on paper and plastic substrates.

Keywords: conducting polymers, PEDOT, vapor phase polymerization, smart textiles, e-paper

1. INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a conjugated polymer with high chemical and physical stability, introduced by Bayer in the 1980's [1]. Its good stability and high conductivity made it suitable for a widefield of applications, from biomedical sensors [2], [3], nerve tissue engineering [4], [5], strain sensors [6], [7], electrodes for organic field-effect transistors [8], solar cells [9], hydrogen catalysis [10] to smart textiles [11], [12]. The best results of electrical conductivity were obtained with transparent thin film coatings of PEDOT on glass and plastic substrates, using the vapor phase polymerization (VPP) method combined with the spin coating of organic oxidant solutions. Very high electrical conductivities in excess of 1000 Scm^{-1} were obtained with thin films of PEDOT with thicknesses, t , of the order of 100nm, using an oxidant solution of Fe (III) tosylate in butanol and a base – inhibitor, pyridine [13]. A value of $\sigma = 3400 \text{ Scm}^{-1}$ with $t =$

65nm was obtained by adding to the oxidant solution a PEG-PPG-PEG block copolymer with optimized molecular weight and PEG/PPG ratio [14]. In what concerns textile substrates, the *in situ* techniques wet polymerization and VPP have been successfully applied. In both methods, oxidative polymerization is most common, using either of the oxidants agents, Iron (III) chloride (FC) or Ferric p - toluene sulfonate (FTS). In the *wet* method, liquid solutions of 3,4-ethylenedioxythiophene (EDOT) and oxidant agent, mixed together in a solvent at a temperature typically below 10°C to delay the polymerization process are used for the impregnation of the fibers [15]. After a certain period of time of immersion of the textile substrates in the solution, the samples are dried at either ambient conditions or in an oven until the polymerization is completed. K. H. Hong et al. [16] reported high dependence of the coated samples electrical properties with the type of oxidant agent and concentration ratio of monomer to oxidant, the type of organic solvents and the type of fibers constituting the yarns the fabrics are woven with. Good electromagnetic interference shielding properties, characterized by sheet resistivities as low as 10 Ohm/sq were obtained with the oxidant FTS and multiple polymerization layers [17], [18].

In the VPP method, the woven fabrics are firstly immersed in a liquid phase oxidant solution and secondly are exposed to the monomer in the vapor phase. The exposure of the substrates to an atmosphere of monomer is typically performed in a reactor with controlled vacuum and temperature [12], [19]. Research works conducted with PEDOT coatings on fabrics [12] and yarns [19], [20] showed that the electrical and mechanical characteristics may be largely affected by the concentration of the oxidant solution, the type of fibers and the VPP method parameters immersion time, drying time and polymerization temperature. The VPP method has important advantages over the *wet* method; there is no need to use organic solvents due to the low solubility of EDOT in non – organic solvents [21]; it involves lower process complexity because there is no need to keep a low temperature bath ($T < 8^\circ\text{C}$). In this investigation, the method was used to synthesize coatings of conductive PEDOT on substrates consisting of plain weave fabrics of polyester, using two types of solvents, ethanol and water. The method was optimized to provide the coated fabrics with the highest electrical conductance. Textile samples with various contents of PEDOT were prepared and electrically and mechanically

tested and the results correlated with scanning electron microscopy (SEM) analysis.

2. EXPERIMENTAL

The textile substrates consisted of plain weave fabrics of polyester, having a thickness of 0.22 mm and a specific weight of $12.0 \times 10^{-2} \text{ Kg/m}^2$, and were shaped into a rectangular geometry with lateral dimensions of 80 mm by 5 mm, accurately obtained at a more or less one thread. The substrates were washed in methanol, rinsed in distilled water and left to dry for 24 hours in a conditioned ambient room ($T = 23 \text{ }^\circ\text{C}$ and relative humidity, $\text{RH} = 50\%$).

The synthesis of PEDOT and the washing of the samples used the reagents and solvents EDOT monomer (97%), Iron (III) chloride hexahydrate (97%) and methanol (99.5%) from Sigma-Aldrich and ethanol (99%) from Manuel Vieira & C^a. Liquid oxidant solutions of various concentrations were prepared with Iron (III) chloride hexahydrate (FC) dissolved in either ethanol or in bi-distilled water with the assistance of vigorous stirring at ambient temperature. The VPP method used the following three sequential steps; firstly, the immersion of the substrates in an oxidant solution of specific concentration; secondly, a drying step, either at ambient conditions or in a convection oven; thirdly, the polymerization step, where the samples were exposed to an atmosphere of monomer in a reactor, at a vacuum pressure of 160 mTorr and stabilized reactor temperature. The polymerization process used a droplet of 15 microliter of monomer that lasted for two cycles of polymerization. After each polymerization cycle, the reactor was vented with air and the samples removed and immediately washed in methanol and rinsed in distilled water. The samples were next put to dry in an ambient conditioned room for at least 24 hours or in a convection oven at $30 \text{ }^\circ\text{C}$ for 60 minutes.

The electrical conduction of the samples was performed with the two - probe method by measurements of sheet resistivity, R_{sq} , given by

$$R_{sq} = \frac{V}{I} \cdot \frac{W}{L} \quad (1.1)$$

with V , voltage across the probes, I , electrical current, L , distance between the probes and W , width of the sample. By analogy with homogeneous thin films to which Ohm's law applies, the sheet resistivity is related to the ratio of the bulk resistivity, ρ , to the sample thickness, d , and has units of Ohm/sq,

$$R_{sq} = \frac{\rho}{d} \quad (1.2)$$

The 2-probe method is suitable for continuous film samples that are homogeneous and have relatively high electrical conductance, but may be applied to textile samples coated

with PEDOT as good degree of measurement repeatability and relative errors of less than 10% were obtained. The absolute error was addressed by comparing the 2-probe mean values with those obtained with the 4-probe method on samples with a length of 120 mm and inner probes distances in the range of 50 mm to 100 mm. The mean values of sheet resistivity obtained by the two methods were equivalent within an error of less than 10%. The electrical measurements were performed with a Hameg 8040-3 power supply, a Hameg 8012 programmable ampermeter and the data acquisition performed via a RS232 interface and a Labview program that recorded mean values of electrical current, I , for each applied voltage, V . For each VPP condition, six to twelve samples were measured.

The surface morphology and longitudinal sections of pristine and polyester samples coated with PEDOT were analyzed by SEM with a Hitachi S2700 microscope. The samples were coated with gold and the images were performed with an accelerating voltage of 20 kV and magnifications in the range of 35 - 400 X.

3. RESULTS AND DISCUSSION

The optimization of the VPP method was performed with oxidant solutions with a concentration of 0.4 mole (M) and the following parameters, maximizing the samples sheet resistivity, were applied: immersion time of the textile substrates in the oxidant solution, $t_{ox} = 15$ minutes; a drying time, $t_{dry} = 15$ minutes at ambient temperature or $t_{dry} = 3$ minutes in a convection oven at $60 \text{ }^\circ\text{C}$ if ethanol or water solvents were used, respectively; a polymerization temperature, $T_{polym} = 60 \pm 1 \text{ }^\circ\text{C}$ and polymerization time, $t_{polym} = 30$ minutes. In Fig. 1 are shown curves of sheet resistivity variation with the method parameters that mostly

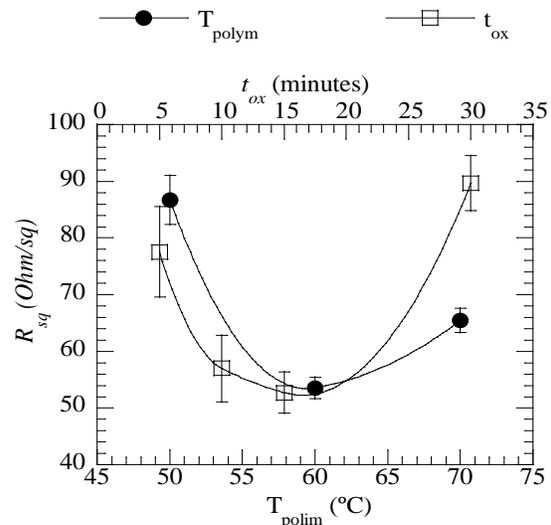


Figure 1; Experimental data of variation of R_{sq} with VPP method parameters immersion time and polymerization temperature, for samples prepared with organic solution of 0.44M. Error bars correspond to \pm standard deviation.

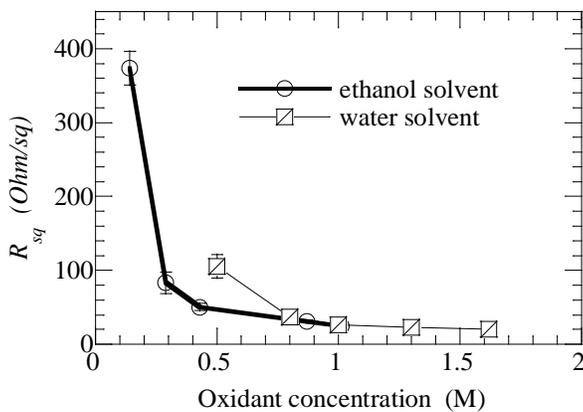


Figure 2: Experimental data of R_{sq} versus organic and aqueous oxidant solutions concentrations.

affected the samples electrical conductance, t_{ox} and T_{polym} .

The trend of sheet resistivity with the concentration of the oxidant solution was investigated. Organic and aqueous oxidant solutions of FC with concentrations in the range of 0.14 M to 1.6 M were used and for each concentration six to twelve samples were coated with PEDOT by the VPP method. The samples exhibit linear $I - V$ curves for applied voltages in the range of 1 to 10 Volts. The sheet resistivity of the samples decreased sharply with the oxidant concentration increase, in the low concentration range, leveling out for higher molar concentrations in the range of 0.8 to 1.0 M, corresponding to $R_{sq} \approx 25$ Ohm/sq. (see Fig. 2). In this range of oxidant concentration, no significant difference of R_{sq} was encountered between samples prepared with aqueous or organic solvents. The trend of R_{sq} with oxidant concentration suggests that higher concentration solutions leave in the substrates more oxidant available to react with the vapor of the monomer, producing coatings with higher content of PEDOT. The sheet resistivity could be further decreased by applying several layers of polymerization, as shown in Fig. 3, with a minimum value of $R_{sq} = 5$ Ohm/sq attained after 5 cycles of polymerization. These values are comparable to those suitable for electromagnetic shielding, obtained by means

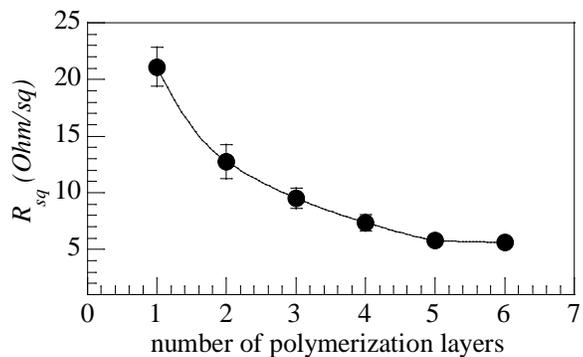


Figure 3: Variation of sheet resistivity with the number of polymerizations. Samples prepared with organic oxidant solutions with a concentration of 1 M.

of *wet* method, multiple polymerizations and using the oxidant agent FTS and a monomer solution with dimethylacetamide [18]. It is also suitable for textile electrodes to monitor physiological signals [22].

SEM images of pristine and a PEDOT coated sample prepared with an organic oxidant solution of 1 M are shown in Fig. 4. The low magnification (35X) images show the discontinuous nature of the substrates of polyester, with a plain weave structure, which was not significantly modified by the coating with high content of PEDOT. The image with a magnification of 400X (Fig 4d) show that the pristine sample has a microstructure characterized by multiple fibers of polyester of regular cylindrical shapes and diameters in the range of 10 to 14 microns, while PEDOT coated samples prepared with oxidant solutions of

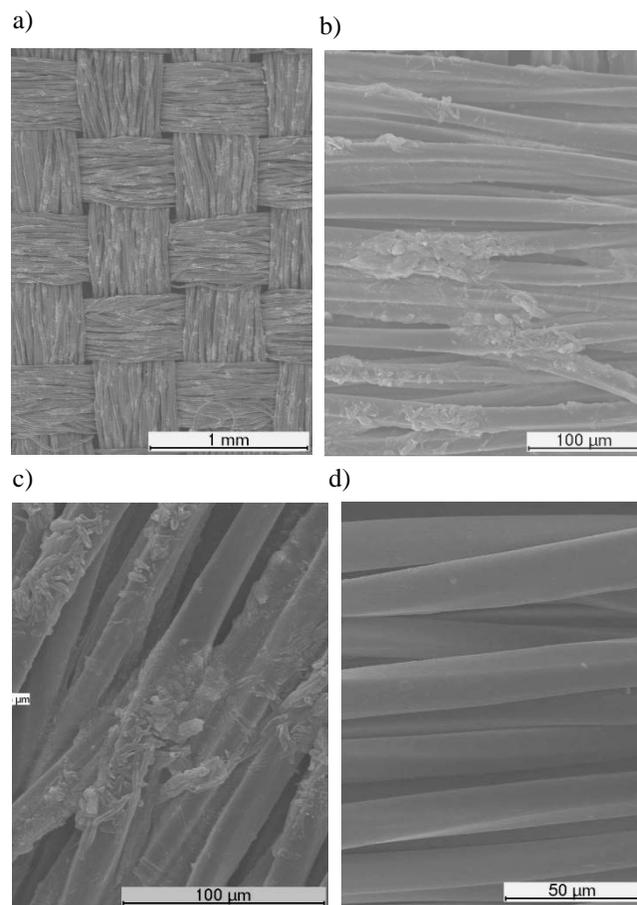


Figure 4: SEM micrographs of pristine and PEDOT coated samples with $R_{sq} = 25$ Ohm/sq (1.0 M), obtained at various magnifications, a) 35X, b) 250X, c) 400X; d) pristine sample, 400X.

high concentration have the polyester fibers interconnected through a thin coating of PEDOT and regions with globular clusters (Fig. 4b and 4c). The SEM images indicate that no fiber degradation is present, which was corroborated by mechanical tenacity tests (not presented). Unlike in thin film coatings on continuous, smooth substrates, on textile

substrates the PEDOT grows around the multiple discrete fibers, interconnecting neighbour fibers. The lowest value of resistivity extracted by applying eq. (1.2) is $\rho \cong 0.1 \Omega\text{-cm}$ ($\sigma \cong 10 \text{ Scm}^{-1}$, $R_{sq} = 5 \text{ Ohm/sq}$), but does not correspond to that of PEDOT, as a major fraction of the thickness considered, the substrate thickness, is polyester.

4. CONCLUSIONS

The synthesis of PEDOT with aqueous solutions and the VPP method is eco-friendly and unexpensive and suitable to provide textiles with high electrical conductance for smart textile applications such as electromagnetic shielding [18] and electrodes for the sensing of physiological signals [22]. It also has potential to be applied to electronic paper and organic electronics.

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¹ Universidade da Beira Interior, Rua Marquês D'Ávila e Bolama, 6201-001, Covilhã, Portugal, trindade@ubi.pt.