ABSTRACT

During the last years, intensive research is undertaken to develop electronic textiles (so-called e-textiles). There is a clear trend from fabrics or garments hosting electronic components embedded in the textile substrate to e-textiles made from yarns or fibres already possessing electronic properties. The development of passive devices, such as textile electrodes that measure body parameters is already well proceeded. However, there is a great need in developing textiles possessing active functions.

We investigated the possibility to develop a textile monofilament with integrated switching and amplification functions, by depositing an organic thin film transistor (OTFT) on the monofilament with a cylindrical form.

In this presentation preliminary results are shown related to this development. A discussion is given on the methods used to deposit and characterise an OTFT.

In a first step, a conductor layer (copper) has been chemically plated on a cylindrical polyester monofilament. Subsequently, an insulating layer has been deposited on the monofilament by a dip coating method using polymers with low conductivity like polyimides and polyethylenes. In the same way, the filament was coated with a third layer made up by a semiconductor (polythiophenes or TIPS pentacene). Being of organic origin, the semiconductor constituent offers electronic properties of a semiconductor and physical properties of organic molecules which are very flexible and physically compatible with a textile structure.
1. INTRODUCTION

The last year’s intensive research is being done in the field of the so called “Intelligent textiles” [1-5]. In the beginning it was a matter of introducing some electronics in fabrics and clothing. More recently researchers are focusing their efforts on providing textiles with electronic properties. In this way many passive devices are already present on textiles [5, 6]. It could be interesting to provide active functions on the textile towards a new class of textiles with electronic properties. Among others switching and amplification properties would lead to new functionalities on the textile. The aim of this work is to develop a monofilament with transistor properties starting with a polyamide 6 (Nylon) monofilament and a polyester (PET) monofilament. Fig 1 shows a schematic representation of the structure of a thin film transistor (in our case an organic one) that should be achieved on top of a fiber (the gate).

![Thin Film Transistor Diagram](image)

**Figure 1** - Schematic representation of thin film transistor

As one can see in Fig.1, the gate (the fiber in our case) should clearly be electroconductive. Therefore the first stage towards the transistor fiber was to make the starting material electroconductive. In this paper, the metallization of both, the polyamide 6 and polyester monofilament is described. Initially, an electroless deposition process of polypyrrole is performed, followed by a second coating with metallic Copper. Polypyrrole is of particular interest because it shows a relatively high electrical conductivity and high stability and suitable for Copper coating as demonstrated in [7].

2. EXPERIMENTAL PROCEDURES

Pure polyamide 6 and polyester filaments with a diameter of 50 and 80 µm respectively were used in this research. First a polypyrrole coating was performed on the fiber by an oxidative polymerization of pyrrole. Subsequently a copper coating was deposited in an electroless way.

The characterization of the obtained fiber was done by energy dispersive x-ray (EDX), scanning electron microscopy (SEM) and profilometry. The fiber was characterized electrically by resistance measurements.
2.1 Test Materials

2.1.1 Oxydative polymerization of pyrrole onto the fiber.

Prior to the pyrrole polymerization, the fibers were subject to a washing in a 2M NaOH aqueous solution. The fibers were immerged in the solution for 30min and afterwards intensively rinsed in water.

The fibers were then immersed in solutions, containing different concentrations of the pyrrole monomer, for about 1 hour. The different pyrrole monomer concentrations investigated are given in Table 1.

**Table 1: Concentration values of the different compounds used in the deposition of pyrrole at polyaramide**

<table>
<thead>
<tr>
<th>Compound</th>
<th>c (mol L⁻¹)</th>
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<tbody>
<tr>
<td>Pyrrole</td>
<td>0.020</td>
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<tr>
<td></td>
<td>0.040</td>
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<tr>
<td></td>
<td>0.070</td>
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<td></td>
<td>0.10</td>
</tr>
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<td></td>
<td>0.15</td>
</tr>
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In the next step a stock solution containing 0.0932 mol L⁻¹ FeCl₃ and 0.0132 mol L⁻¹ benzene sulphonic acid was added to the pyrrol solution in order to initiate the polymerization reaction to generate polypyrrole at the surface of the fiber. The volume of the added stock is always identical to the initial volume of the pyrrole solution. This means that the actual optimized concentration of FeCl₃ and benzene sulphonic acid during sensitization is 0.0466 and 0.0066 mol L⁻¹. The optimal deposition time was about 60 minutes. Shorter deposition times resulted in inhomogeneously coated fibers with a decreased surface coverage. On the other hand, longer deposition times did not really improve the layer properties as obtained after 60 minutes. Therefore an optimized deposition time of 60 minutes is respected. Figure 2 shows the mechanism of the oxidative polymerisation of pyrrole.

![Figure 2: Mechanism of the oxydadive polymerization of pyrrole.](image)
2.1.2 Electroless deposition of Cu(II) at PPy modified fibers

Prior to depositing copper onto the polypyrrole coated fiber, it is necessary to activate and sensitize the surface by tin and palladium compounds (tin and palladium chloride are possible examples). Tin centers create a “seed” layer which initiates subsequently the chemical adsorption of palladium centers. The “seed” layer created by palladium is then used to electrolessly deposit copper onto the polypyrrole coated fiber.

The polypyrrole coated fibers were immersed in the sensitization/activation solution for about 10 minutes to allow the formation of the palladium active centers, followed by dipping the structures in a 5% HCl solution for about 60 s. This was done to remove Sn(II) centers that are not replaced by palladium during the previous activation step. The concentration of PdCl₂ and SnCl₂ were set as 5.9x10⁻³ and 9.8x10⁻² mol L⁻¹, values that were based on available literature. Finally the structures were rinsed thoroughly with deionised water in order to prevent the copper solution (used in the next step) from contamination.

The deposition of copper was performed in a solution containing Cu(II), formaldehyde for the reduction of Cu(II) to metallic copper (reaction 1), sodium hydroxide to activate formaldehyde and Rochelle salt to avoid precipitation of Cu(II) as copper hydroxide.

\[
Cu(II) + 2 \text{HCHO} + 4 \text{OH}^- \rightleftharpoons Cu + \text{H}_2 + 2 \text{H}_2\text{O} + 2 \text{HCOO}^- \quad (1)
\]

It was not possible to deposit directly copper onto the sensitized/activated fiber. A possible explanation can be the fact that nitrogen centers in the pyrrole structure act as an acceptor for growing the copper layer onto it.

Post treatment of the surface was done by immersing the textile samples in a citric acid and sodium hypophosphite solution. Finally the structures were washed with water and dried in a furnace. Figure 3 shows the structure of the cross-section of the copper coated fiber.

Figure 3: Schematic representation of a Polypyrrole-Copper coated fiber (cross-section).
2.2 The fiber characterization
The layer thickness was measured with profilometry equipment from Rank Taylor Hobson, type TALYSURF.

The fiber morphology was investigated using scanning electron microscopy. The surface chemical composition was done by EDX measurements.

Conductivity measurements of the treated samples are based on the fundamentals of a division measurement over a known resistor and an unknown one, being the sample. A resistor of 1000 ohm was used in series with the unknown sample resistance. The applied potential was varied from 1 to 20V over both resistors from DC to AC and with a change in frequencies for the AC behavior. The resulting unknown resistance is calculated with the following formula (Eq. 1).

\[
R_{\text{unknown}} = \frac{(V_{\text{tot}} - V_{\text{known}})}{V_{\text{known}}} \times R_{\text{known}}
\]

3. RESULTS AND DISCUSSION

To produce copper coated fibers for characterization a plating solution was made up of copper sulfate with a concentration of 0.04 mol L\(^{-1}\); formaldehyde 5.0 g L\(^{-1}\) (from a stock solution of 37 %); Rochelle salt 0.18 mol L\(^{-1}\); Sodium hydroxide concentration 0.25 mol L\(^{-1}\) and deposition time = 480 s. These conditions were found to be ideal for the optimal electrical conductivity of the copper coated fiber taking into account the best obtained surface coverage (paragraph 3.2 and 3.3). The presented results concern polyester fibers. Compared to those of polyamide 6 no significant difference was found.

3.1 Profilometry
Profilometry allows determination of the thickness of the copper layer, which is about 0.2±0.1 µm.

3.2 Scanning electron microscopy
Figure 4 shows a copper coated PET monofilament. From this figure it is clear that the copper layer was regular and very smooth and visually very good coated.
The EDX analysis of the surface of the modified fiber showed a chemical composition of the top layer made up of more than 97% of Copper.

### 3.3 Conductivity measurements

The copper coated fibers showed a resistivity of $1.9 \times 10^{-6} \, \Omega m$ which is comparable to the resistivity of pure copper ($1.7 \times 10^{-8} \, \Omega m$).

### 4. CONCLUSION AND FUTURE WORK

In this work copper has been successfully deposited onto polyester and polyamide 6 fibers. The developed copper coated fibers showed a homogenous and smooth coating with a good electrical conductivity. The obtained fibers constitute a good substrate to be used as a gate for the transistor fiber development. Toward the transistor fiber, this copper coated fiber is now being investigated. Different techniques to put an insulating layer onto the copper layer are being tested: self assembled monolayer formation, dip coating and fluid bed coating. On top of the insulating layer the organic semiconductor will be coated before we put a drain and source (both made of metallic Copper) on the top layer.

### 5. REFERENCES


3. Schwarz, A., Van Langenhove, L., Report on State-of-the-art on intelligent textiles,
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