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ARTICLE

Glycerol/PEDOT:PSS coated woven fabric as flexible heating element on textiles

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A polyamide 6,6 (PA66) fabric pre-treated with a double barrier dielectric (DBD) atmospheric plasma in air was coated with 1 and 5 layers of intrinsically conducting glycerol-doped PEDOT:PSS polymer (PEDOT:PSS+GLY) with the final objective of develop a cost-competitive and temperature controllable flexible-heating element to be used in clothing encapsulated between an outer and an inner separator layer in order to provide heat-reflecting property and uniform temperature distribution, respectively. FTIR, DSC, TGA, SEM, EDS, XRD and DMA analysis show significant changes in morphology, chemistry, enthalpy, crystallinity and glass transition temperature confirming that PEDOT:PSS and glycerol are not only spread over the PA66 yarn surfaces but are dispersed in the bulk facilitating relaxation and increasing structure and chain flexibility. Electrochemical and electrical resistivity (ρ) measurements confirm that the plasma treated PA66 coated with 5 layers of PEDOT:PSS+GLY presents the highest stability, resistance, capacitive behaviour and the best ability on storing the electrical energy. This configuration needs only 7.5 V to induce a temperature change up to 38 °C at a current density of 0.3 A g-1. The desired temperature is easily adjustable in function of the applied voltage and by the number of coated layers of PEDOT:PSS+GLY. Despite the need to improve the uniformity of the coating thickness on the fabric for uniform heat generation, the observed results are quite impressive since can be compared to the temperature obtained in carbon nanotube composites using similar voltages. This cost-competitive, safe, high flexible and stable thermoelectric fabric ensure its use in large area textiles as heating element in a wide range of applications such as garments, carpets, blankets and automotive seats.

Electronic Supplementary Information (ESI)

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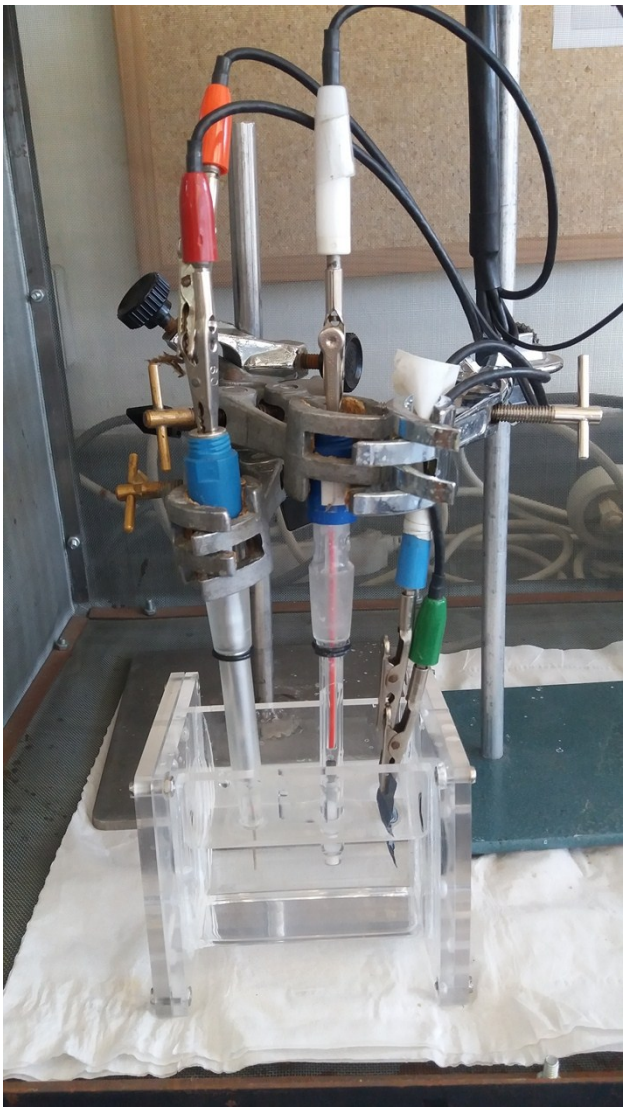

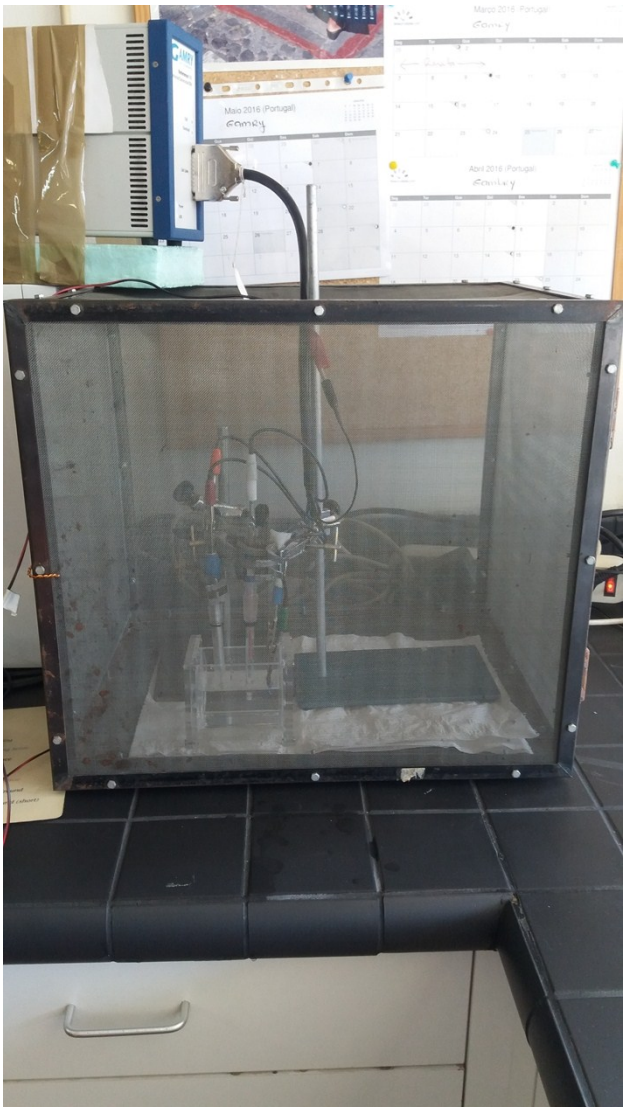

Fig. S1 Electrochemical cell set-up composed by three electrodes immersed in the electrolyte: a platinum auxiliary electrode (left), reference electrode (Center) and a working electrode with the textile sample (right). The system was isolated with a faraday cage to avoid external interferences.

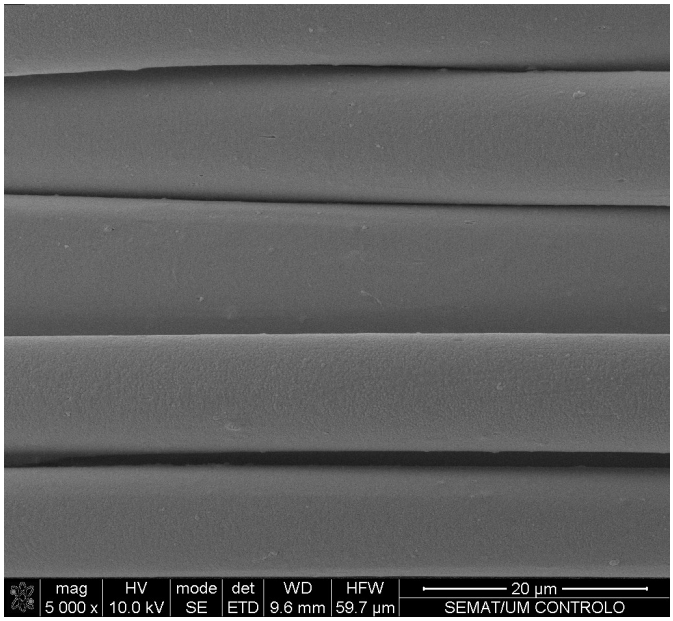

Fig. S2. SEM image of plasma treated PA66 fibers with a dosage of 2.5 kW.min.m^{-2}.

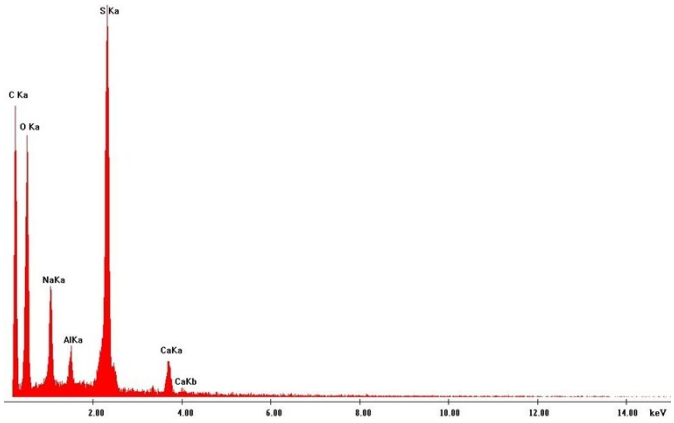

Fig. S3. EDS spectrum of DBD plasma-treated PA66 coated with 5 layers of PEDOT:PSS..

XRD and SEM analysis of the fabrics after current drops at high voltages.

The effect of the temperature in the current drops at high voltages can be observed in the XRD spectra in figure S4 and in the SEM images of the fabrics after breakdown in figure S5. The two peaks observed in the XRD spectra at approximately 20.5° and 23.5° are consistent with the diffraction of (100) and (010,110) doublet of the α phase of nylon 6,6 crystals oriented in a triclinic cell.[1] However, PEDOT:PSS that is mostly an amorphous material also show two main diffraction peak in this area at around 26º and 18.5º that arise from PEDOT thiophene ring π-π stacking and from the PSS benzene ring π-π stacking, respectively.[2] XRD shows that PA66 fibres coated with 5 layers of glycerol doped PEDOT:PSS have larger and sharper peaks when compared with the 1 layer PEDOT:PSS. The more intensive and narrow peaks in the XRD spectra in function of the polymer-coated layers indicates that PEDOT molecules in amorphous state partially change into crystalline state during the coating.[3] This can be attributed to the interaction between insoluble PEDOT:PSS and glycerol that promote the interchain coupling of PEDOT segments enhancing the conductivity.[4] The resulting reduction of the electrostatic interaction between positively charged PEDOT and negatively charged PSS in terms of the screening effect favouring the interaction between PEDOT molecules to form a crystalline structure.[5]

The same sample was also analysed after the current drop at high voltages. The current breakdown was observed in both samples (1 and and 5 layers) at the same temperature of 100 ºC despite the different voltages. The XRD spectra display a significant reduction of crystallinity peaks of the polymer, which is in good agreement with the SEM images that show the degradation of the coating integrity onto the fibres surface. Despite the previous annealing at 120 ºC has increased the degree of crystallinity and enhanced the physical properties of PEDOT/PSS, the high temperature resulting to the Joule effect significantly degraded the conductive coating.[6] The oxygen of the atmospheric air and the hygroscopic nature of the polymer are probably the most important factors that promote the irreversible structural modifications of the PEDOT:PSS chains hindering the conductivity of the coating.[7] This indicates that a suitable passivation must be provided to the PEDOT:PSS coated fabric and that high-temperature applications should be avoided.[8]

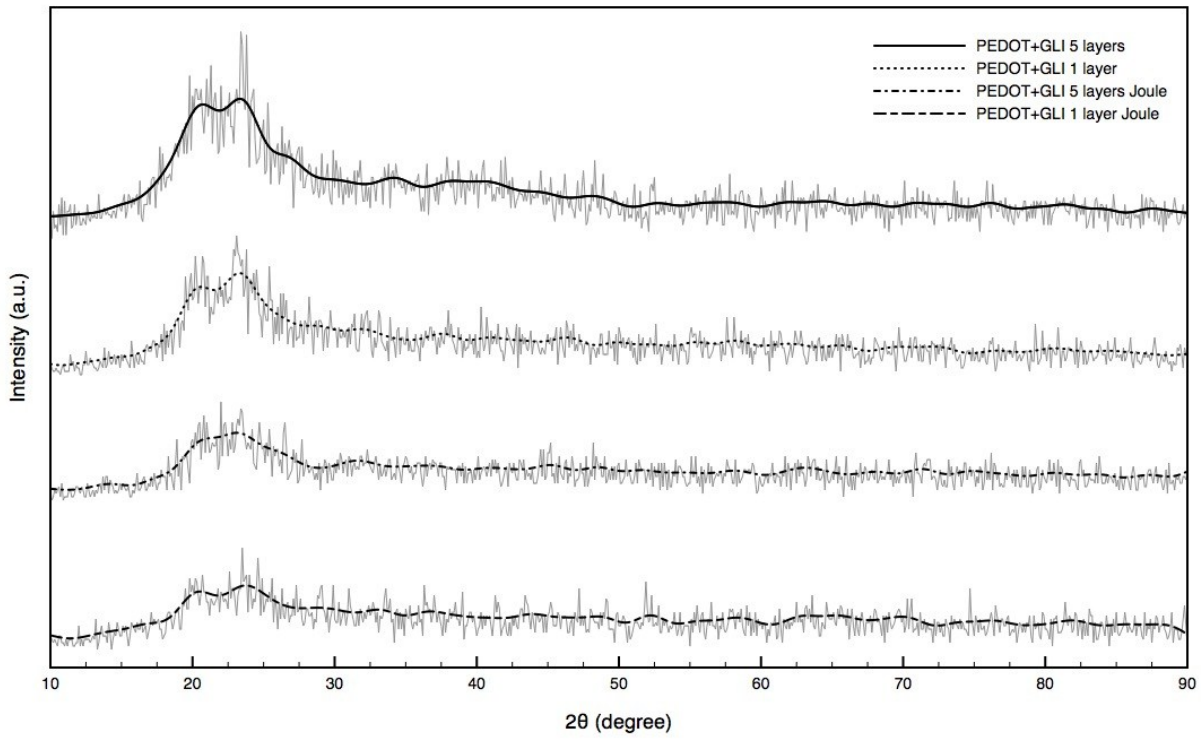

Fig. S4 X-ray diffractograms of the plasma treated PA66 fabric with 1 and 5 layers of deposited PEDOT:PSS + 5% w/w of glycerol before and after the application of the maximum voltage at which Joule effect was observed.

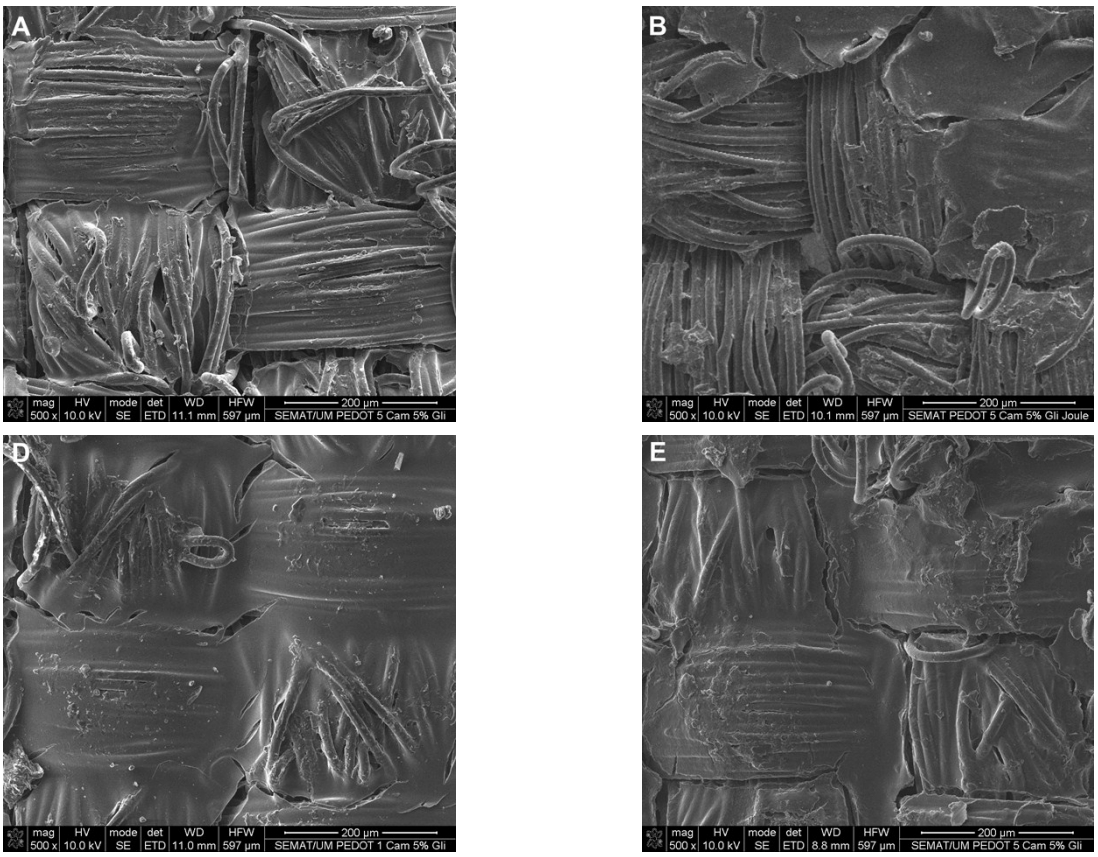

Fig. S5 SEM images of polyamide 6,6 fabric with deposited PEDOT:PSS + 5% w/w glycerol 1 layer (A) and PEDOT:PSS + 5% w/w glycerol 5 layers (B) after the application of the maximum voltage at which Joule effect was observed. The image D and E (from Fig. 7) represent the same samples before current application.

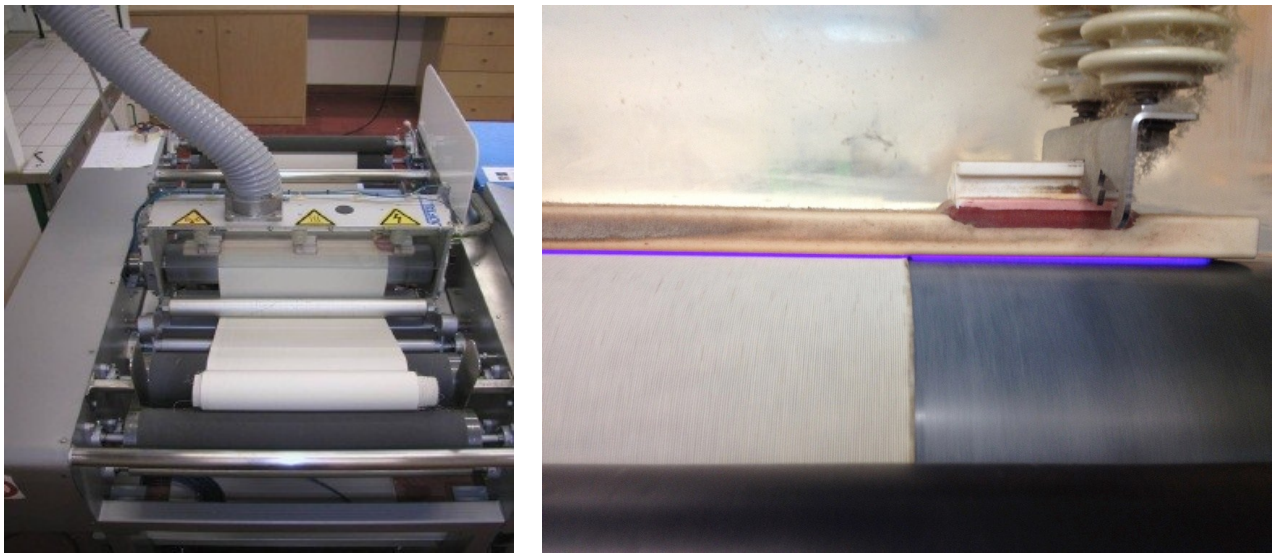

Fig. S6 Semi-industrial prototype from SOFTAL Electronics GmbH (left) and detail of the electrode system and continuous discharge (right).

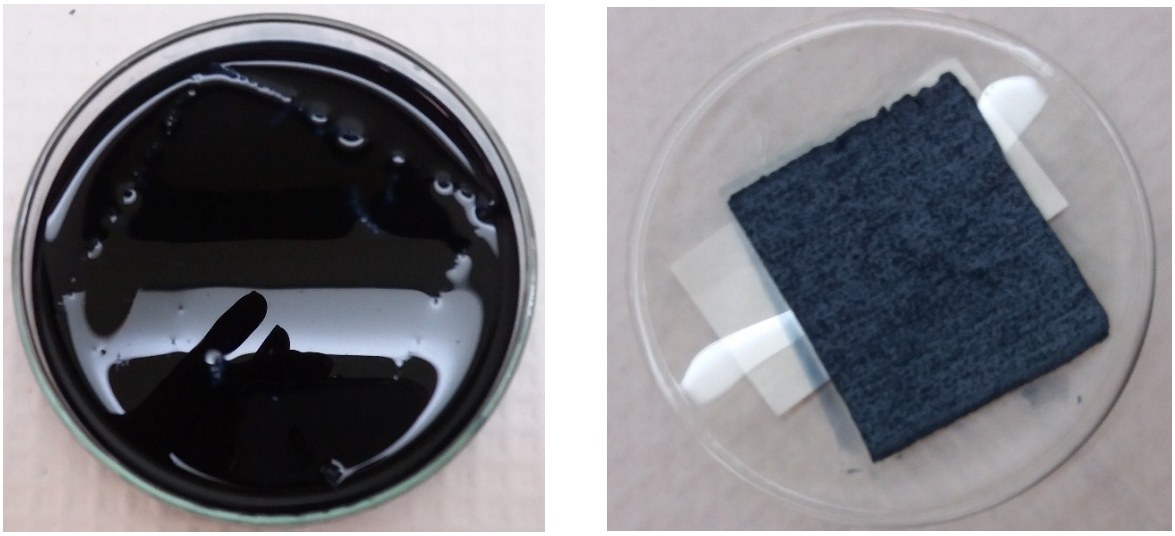

Fig. S7 Dip-coating of the fabric in the PEDOT:PSS dispersion (left) and PA66 fabric with 1 layer of deposited PEDOT:PSS (right).

Fig. S8 Joule heating experiment set-up. Left: Thermal camera (1) and fabric holder with two copper electrodes (2) configuration; Right: Thermal camera lens (1), fabric holder (2), copper anode (3), copper cathode (4) and conductive fabric (5).

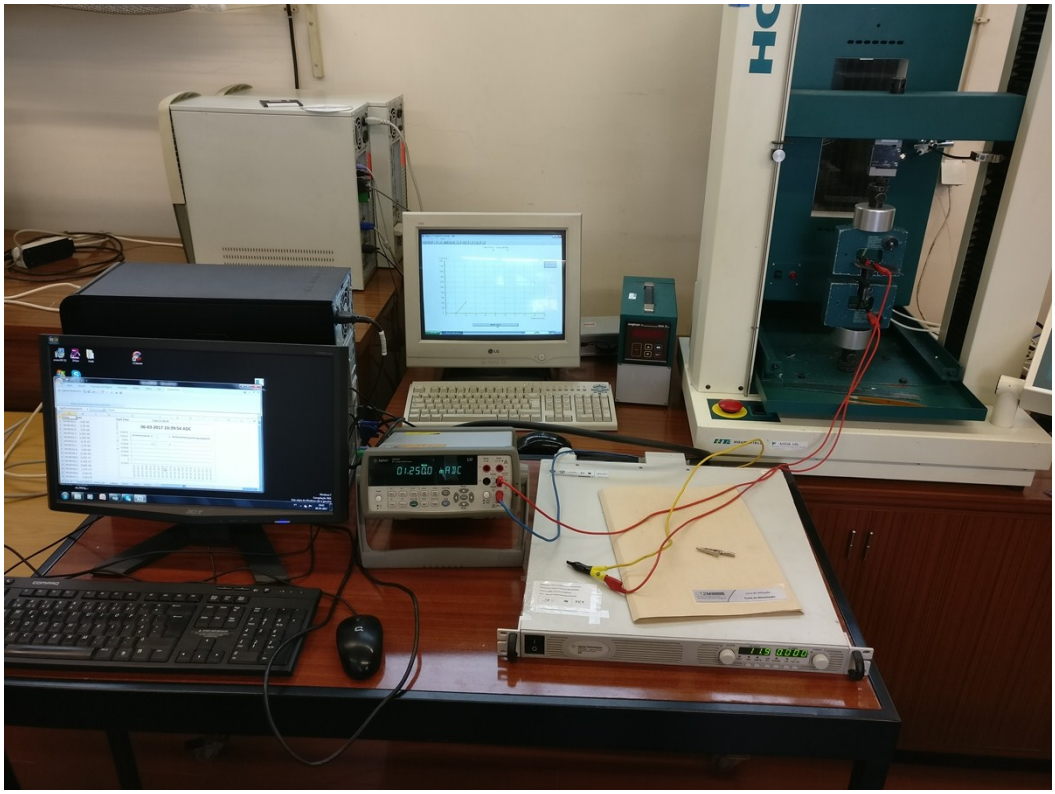

Fig. S9 Strain versus current set-up composed by an Instron Universal Testing Machine with a 2.5 kN load cell, a power generator in D.C. and a multimeter with an ammeter and a voltmeter.

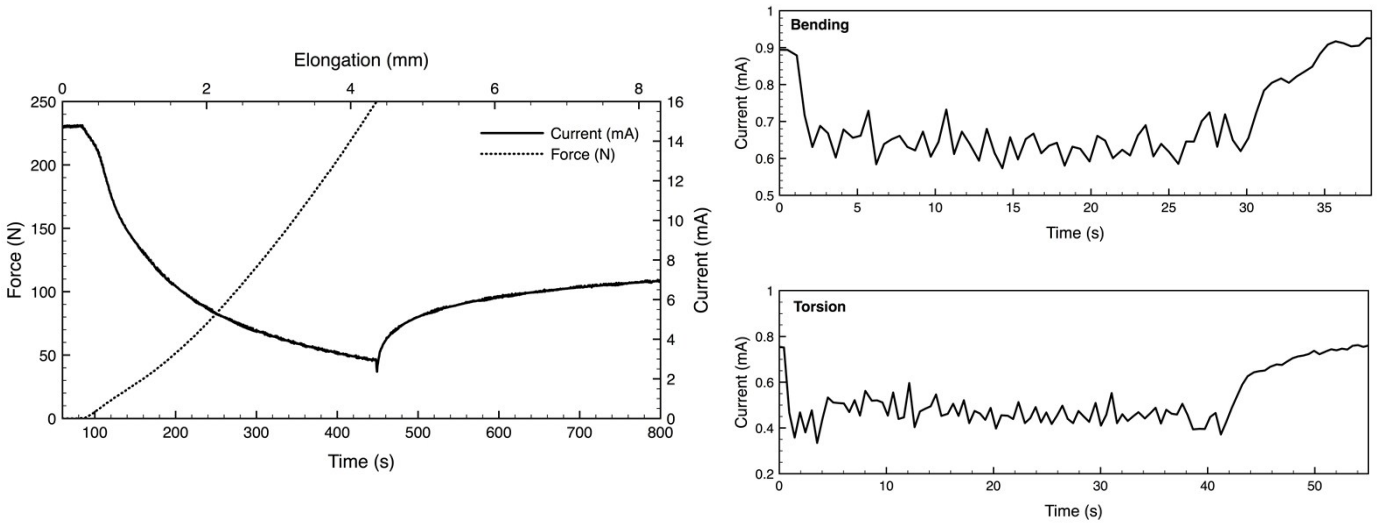

Fig. S10 Tension force and current versus time and linear deformation (main graph). Bending and torsion strain versus current (small graphs). All experiments were perfomed in a polyamide 6,6 fabric with deposited 5 layers of PEDOT:PSS + 5% w/w glycerol .

Acknowledgements

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