# Highly piezoresistive textiles based on a soft conducting charge transfer salt

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**The integration of *smart materials* into human wearable interfaces is a current topic of interest. This paper reports the integration into a polyester textile of a bi-layer (BL) film based on a polymeric matrix containing a top-layer of a microcrystalline network of an organic conductor. The resulting textiles, in addition to be conducting, exhibit the excellent strain sensing properties of BL films maintaining at the same time their flexibility.**

Recently, there is a great interest in developing new functional materials that can detect and react to external stimuli providing information on chemical, physical, mechanical, and/or biological changes occurring in our environment. They are known as *smart materials*. Particularly interesting is the integration of conducting smart materials in human wearable interfaces such as fabrics, since wearable electronics could offer personalized healthcare, security and comfort. The main challenge in electronic textiles (also named e-textiles) is to incorporate the material with the desired functionality into the fabrics but preserving properties of both components. Smart textiles have been mostly achieved by attaching off-the-shelf electronic components or devices such as optical fibers, piezoelectric transducers or light-emitting diodes (LEDs), directly on the clothes.[1,2,3] However, this approach often can result in deterioration of the textile mechanical properties because of the distinct nature of both components. An alternative route is the embedding or coating of the fabric with an organic conducting polymer with the added benefits that organic material can provide, like light, highly elastic, flexible, electro-conductive and easy to process, reducing thus the manufacturing costs. Several works have been reported in the last few years regarding the utilization of polymers for fabricating e-textiles for a wide variety of potential applications that range from antistatic fabrics[4] or actuators for "artificial muscles" (*i.e.* stimuli-responsive materials that react modifying their shape or dimensions),[5,6] to wound dressing products with antibacterial properties[7] or temperature, optical or strain gauge sensors. [8,9]

In the framework of smart organic materials, we recently reported on the extremely sensitive strain sensing properties of bi-layer (BL) films based on a polymeric matrix containing a conducting top-layer of a microcrystalline network of a conducting charge transfer organic salt.[10,11] These BL films exhibited a fast and fully reversible response reaching gauge factors values of 10-20, that are one order of magnitude higher than the most commonly used manganese-based electromechanical sensors. The origin of these sensing capabilities is due to the deformation of the soft crystallites which, in turn, modifies the electronic band structure of the conducting charge transfer salt. In addition, such BL films are highly stable at ambient conditions, flexible, light and inexpensive. All these encouraging results prompted us to apply these materials to produce e-textiles. Herein, we report on the integration of BL films containing the organic molecular conductors in a polyester textile, and we demonstrate that the strain sensing properties of BL films can be completely transferred on the fabric maintaining also its flexibility.

For this purpose the conducting charge transfer salt $\alpha$-(BEDT-TTF)$_2$I$_3$ [BEDT-TTF stands for bis(ethylenedithio)tetrathiafulvalene)] was chosen. The approach employed for preparing BL films on a textile was adapted from the previously reported experimental methods.[12,13,14] A solution of poly-(bisphenol-A-carbonate) (polycarbonate, PC) containing 6 % wt. of the molecularly dispersed BEDT-TTF in 1,2-dichlorobenzene was drop-cast on a polyester textile. Then the surface of the coated textile was exposed to vapors of a saturated solution of iodine in $CH_2Cl_2$. This treatment resulted in the swelling of the polycarbonate matrix and migration of neutral BEDT-TTF molecules towards the treated surface followed by a chemical redox reaction between the iodine and the BEDT-TTF molecules, which leaded to the formation of a conducting network of micro- or submicron sized crystals of $\alpha$-(BEDT-TTF)$_2$I$_3$. The resulting surface-modified textiles were fully characterized by 4-probe direct current (DC) conducting measurements, Scanning Electron Microscopy (SEM), Energy Dispersion X-ray spectroscopy (EDX), X-ray diffraction analysis and Electronic Paramagnetic Resonance (EPR).

Figure 1 shows the SEM images of the polyester textile before and after having been coated with the polymeric PC matrix containing neutral BEDT-TTF and also after having taken place the surface chemical reaction that leads to the formation of a conducting crystalline network of the BEDT-TTF salt. It can be clearly seen that the nano/microcrystals fully cover the surface fibers of the textile forming a continuous layer, which accounts for the conductivity of the material (Figure 1d), which resulted to be very similar to that measured on the BL films (see below). In addition, EDX analysis of the sulphur and iodine content proved that the stoichiometry of the salt is 2:1, that is, corresponds to (BEDT-TTF)$_2$I$_3$.

Results of X-ray analysis on the textile studied are depicted in Figure 2. Despite the complexity of the diffractogram caused by an uneven baseline coming from the polycarbonate-impregnated textile (curve b in Fig. 2), the observation of the characteristic high order reflections (curve a and insert in Fig. 2), which give a interplanar spacing of $d_{001}$ = 16.93 Å, are in agreement with the formation of the crystalline $\alpha$-(BEDT-TTF)$_2$I$_3$ phase. In addition such reflections show that the crystallites are oriented with the c*-axis mainly perpendicular to the textile surface and, consequently, the molecular conducting layers of the crystals are parallel to the surface. Thus, the data obtained are similar to that for the crystallites of the $\alpha$-(BEDT-TTF)$_2$I$_3$ phase in the BL films.[15] Moreover, the EPR spectra of the treated textiles gave a signal with a linewidth of about 80 G and *g* factor of 2.0060, which further confirmed that the crystals on the textile surface correspond to $\alpha$-(BEDT-TTF)$_2$I$_3$.[15]

As stated above, the previously described BL films, in which the PC matrix itself acts as a substrate, exhibit a high sensitivity of resistance to deformation.[10] The influence of strain on the electrical resistance of the conducting composite textiles was also investigated. For these experiments small conductive textile pieces of a typical gauge area of about 4.0 x 2.0 mm$^2$ were subjected to an electromechanical positioning system, with a computer controlled drive system, equipped with two clamps for sample mounting. The electrical resistance of the sample was measured remotely with a current/voltage source connected via GPIB to the same computer. With this setup, the change of the electrical resistance can be measured as function of the sample strain. The resistance was measured by four probe direct current clamping the sample with the conducting layer up side down and contacting it to four copper strips as shown schematically in Figure 3a. Due to the nature of the employed textiles,[16] in which two different sets of fibres (warp or chain and weft or shoot) are arranged perpendicularly to each other (*see* Figure 3b), the strain applied to the textile pieces in two well-defined directions, namely, parallel to the weft fibers (**L1**) or parallel to the warp ones (**L2**), was explored. In both cases, the strain is always applied parallel to the crystallographic *ab*-plane of the randomly conducting molecular crystals. The sheet resistance ($R_{\square}$) for both directions was found to be $R_{\square, L1}$ = 33.5 kΩ and $R_{\square, L2}$ = 32.5 kΩ for **L1** and **L2,** respectively, in the relaxed state of the sample (*i.e.* without applying strain), which demonstrates similar performance in terms of electrical conductivity for both directions.

Figure 4a (top part) shows the dependence of the electrical resistance variations upon linear multiple cycles deformation (bottom part) with a strain rate v = 0.1 μm/s for a maximum elongation of 5 μm measured along the **L1** (weft) direction. The corresponding experimental results for the **L2** (warp) direction are shown in Figure 4b. These maximal deformations correspond to relative strain values (ε) of 0.12 %, where $\varepsilon = 100\cdot(L - L_0)/L_0$,

$L_0$ and L being the lengths of the textiles samples without and under elongation, respectively. Similarly as found in BL films, these plots nicely reveal the fast response of the resistance difference $\Delta R = R - R_0$ with the deformation $\Delta L = L - L_0$, where $R_0$ and R is the sample resistance in relaxed state and under strain, respectively. Additionally, it is worth mentioning that the textile response in both directions is fully reversible. The long term stability under continuous multiple cycles deformation was also demonstrated since more than 30 cycles during about one hour were applied along **L1**(weft) and **L2**(warp) without noticing any sample degradation. Although some small variations in the absolute values of the resistances with time were observed they were attributed to small temperature changes occurring during the measurements, the on/off ratio is not affected. Therefore, it is possible to affirm that the characteristic strain sensing properties of BL films are clearly preserved when they are integrated into a textile.

The influence of the maximum applied strain on the resistance response was also investigated for these conducting textiles. Figure 5 shows the dependence of relative resistance change on the corresponding textile strain for both studied directions **L1** and **L2**. For comparison reasons the experimental data measured for BL films based on the same conducting salt[10] and the typical response of a conventional foil strain gauge based on a Cu-Ni alloy[17] are also included. At glance the plot noticeably illustrates that both composite materials (*i.e.* BL films and textiles) are much more sensitive than the commonly used Cu-Ni alloys gauge sensors. Further, noteworthy is the fact that the sensitivity (*i.e.* the slope in the graph) of the composite textile along **L1** and **L2** are almost identical to each other as well as to that reported for the corresponding BL films for the $\varepsilon$ values below 0.12 %, after which there is some slight deviation of the textile resistance response from that for the BL film. A further in-depth analysis of the data can be accomplished examining the materials gauge factors (k), which is a parameter that reflects the sensitivity of a device to deformations and is defined as the ratio between the relative resistance and strain changes [$k = (\Delta R/R_0)/(\Delta L/L_0)$]; that is, the slope in the linear regime of the curves depicted in Figure 5. The k values have been calculated at different relative strain applied to the studied textiles along **L1** and **L2** directions and compared with the analogous values for BL films. Of primary importance is to notice that for low $\varepsilon$ values (<0.12 %) k values of the conductive composite textile is practically the same for both directions as well as for the ones obtained for the corresponding BL film, which indicates that the integration of the BL film into the textile does not hamper its piezoelectrical properties and that the conducting crystalline network is completely covering all the warp and weft fibres.

In order to study the sample properties and the change of the electrical resistance under higher strain values, one has to keep in mind that the above introduced gauge factor has to be taken with caution, since then $\Delta R/R_0$ does not depend linearly on $\varepsilon$ any more indicating a physical damage of the sample. At the very first deviation from the linear regime (for strain values around 0.12 %), the resistance response upon strain is, however, fully reversible (not shown in Figure 5) and an increase of the local curve slope is observed. At further increasing strain, the resistance response is not fully reversible any more due to an irreversible damage of the sample.

The main difference between the textile and the BL film is the maximum relative strain that can be applied in the linear, fully reversible region of deformation, since for the textiles there is a more pronounced gradual transition from the elastic to the plastic deformation regimes. Indeed, the reversibility of the textile response is maintained for lower $\varepsilon$ values compared to the BL film, which responds linear and fully reversible at relative strain values of up to 1 %.[10] This suggests that the intrinsic mechanical properties of the textile composite material are the limiting factor to the maximum applied strain resulting first in a deviation from the linear regime and second ending finally in an irreversible response. This effect is illustrated by SEM images comparing the profile of a textile before and after an irreversible deformation. It was found that when an irreversible deformation is applied to the conducting composite textile, the stretching of the fibers and the conductive film located on the surface, alters the morphology of the fabric as shown in Figure 6.

In conclusion, the ultra sensitive piezoresistive properties of molecular crystals have been successfully combined with the mechanical properties of textiles obtaining a conducting composite fabric that responds extremely fast and in a reversible manner to extremely small deformations. Moreover, such flexible, light-weight, soft composite textiles can be easily prepared at low cost and are compatible with printing techniques. This work strongly contributes on the ongoing research of developing organic smart textiles, for which applications in fields such as healthcare, sports, security, fashion and military are foreseen.

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**Figure Captions**

**Figure 1.** SEM images of the virgin polyester textile (a); the textile covered with the polymeric matrix containing neutral BEDT-TTF(b); and the conductive textile covered with the network of nano/microcrystals of the α-(BEDT-TTF)$_2$I$_3$ salt (c-d).

**Figure 2.** X-ray diffraction patterns of the conducting piezoresistive textile (a) and the polymer-impregnated textile before being exposed to vapours of iodine (b); i.e., without the α-(BEDT-TTF)$_2$I$_3$ conductive crystals (see text). Inset shows the *(00l)* reflections of α-(BEDT-TTF)$_2$I$_3$ obtained after a subtraction of patterns (a) and (b).

**Figure 3.** (a) Schematic representation of the mounting of the conducting composite textile sample with the conducting layer up side down. The samples are contacted with four copper strips and fixed by clamps for the deformation transmitting. (b) SEM image of the polyester textile employed showing the two set of fibers: weft (or shoot) and warp (or chain).

**Figure 4.** Response of the resistance changes of the conducting composite textile sample upon application of multiple cycles of 5 μm deformation with a strain rate of v = 0.1 μm/s along the **L1**(weft) (a) and along the **L2**(warp) (b) directions. The curves depicted on the bottom part of the plots show the corresponding multiple cycles linear deformation (ΔL) of the sample.

**Figure 5.** Dependence of the relative resistance change of composite textiles on the relative strain applied along **L1** and **L2** directions. The corresponding data for the BL film and a commercially available Cu-Ni alloy are shown for comparison.

**Figure 6.** SEM images of a conducting textile based on $\alpha$-(BEDT-TTF)$_2$I$_3$ as prepared (a) and after irreversible deformation (b). Note that the conducting face of the textile is on the top.

## Figures

### Figure 1.

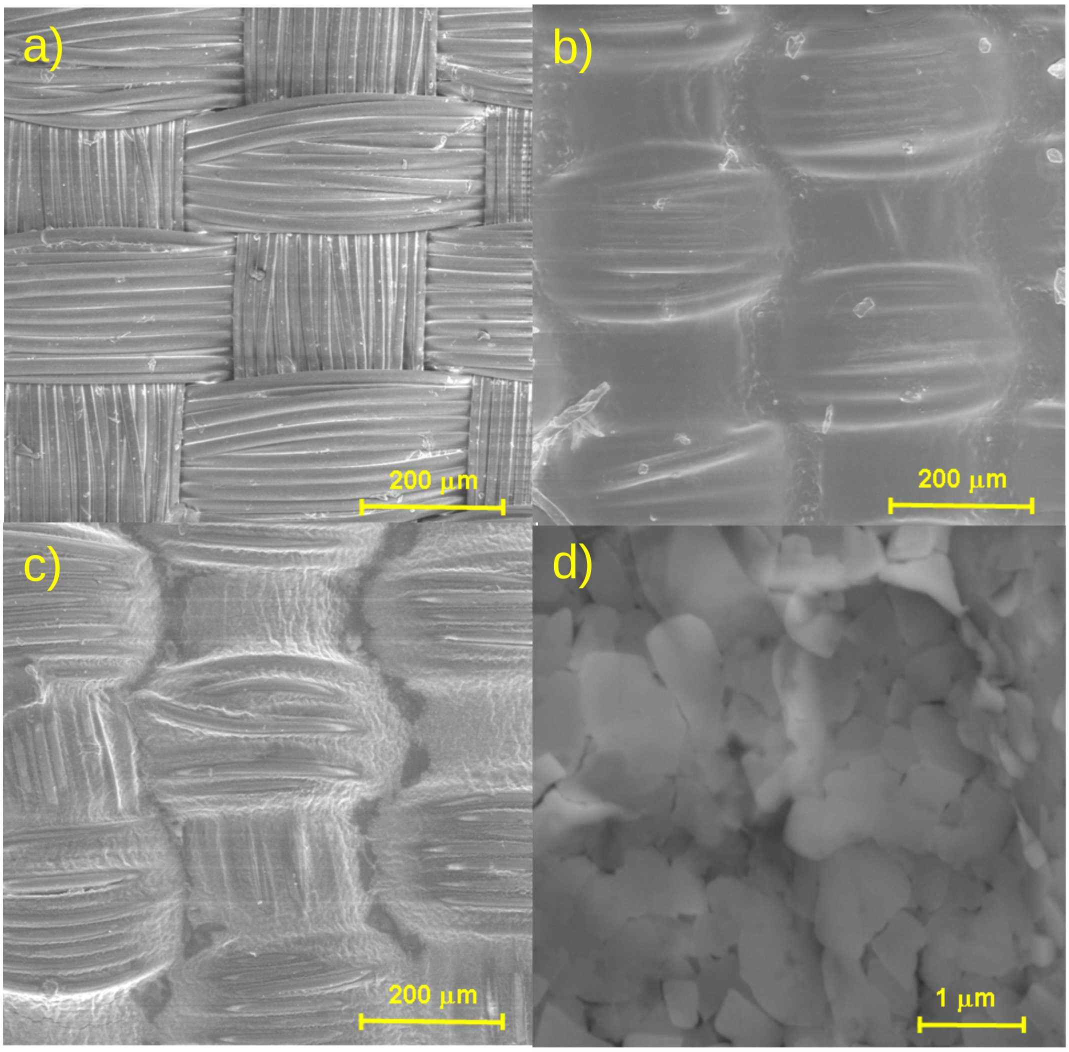


**Figure 2.**

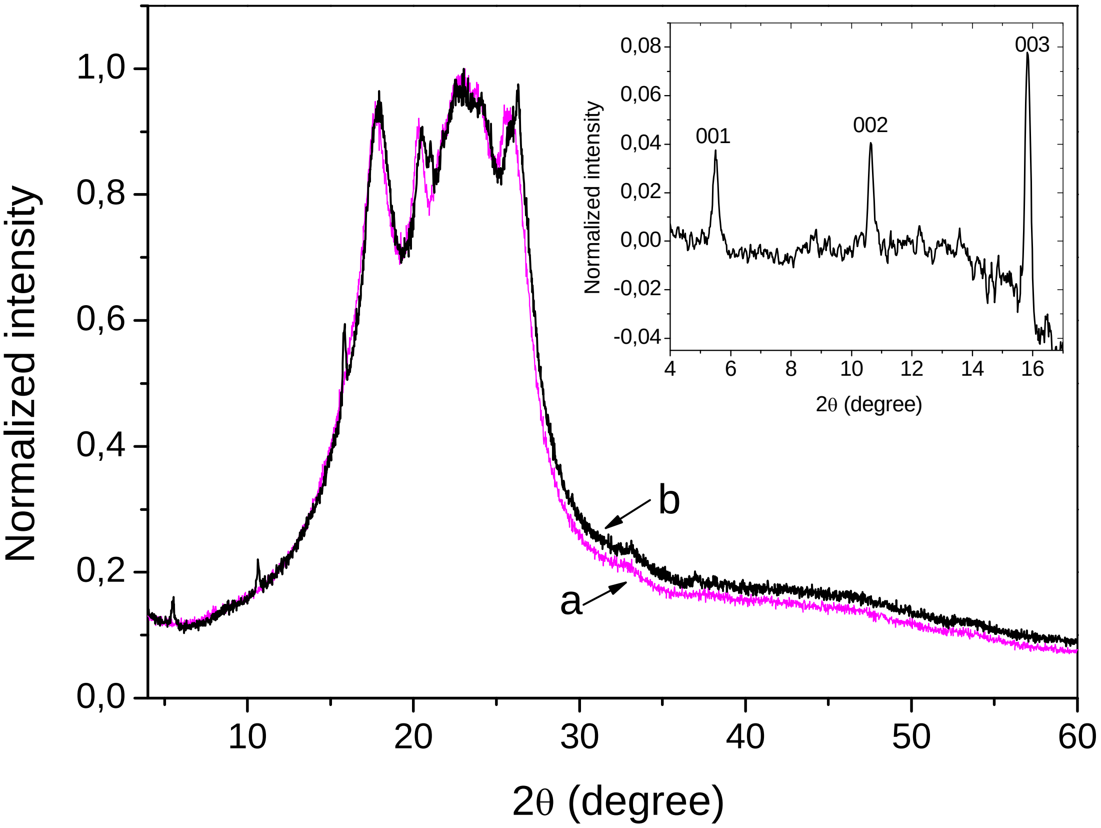


**Figure 3.**

(a)

(b)

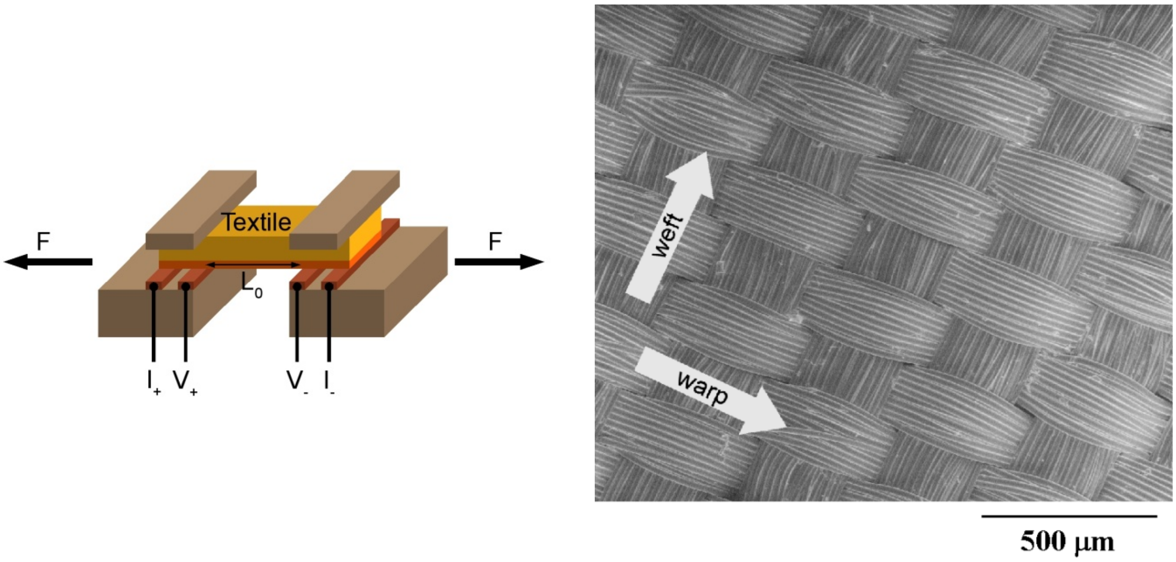
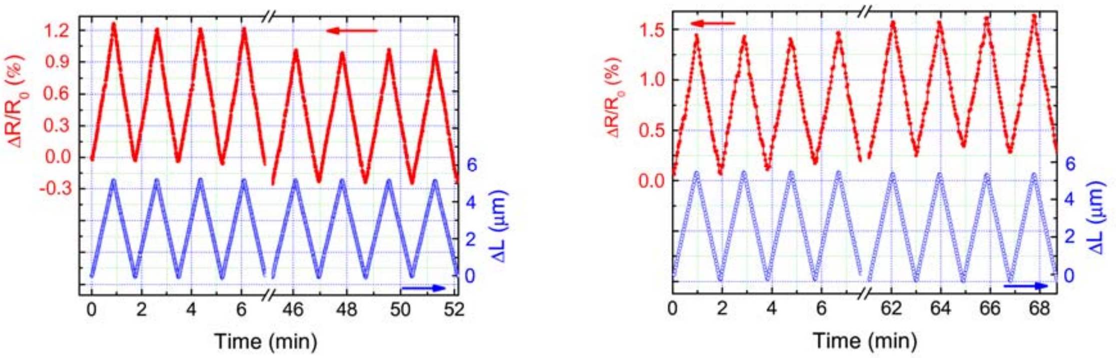


**Figure 4.**



a)

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**Figure 5.**

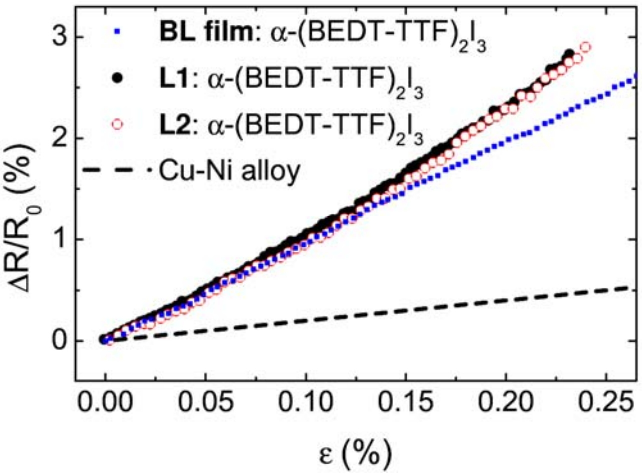
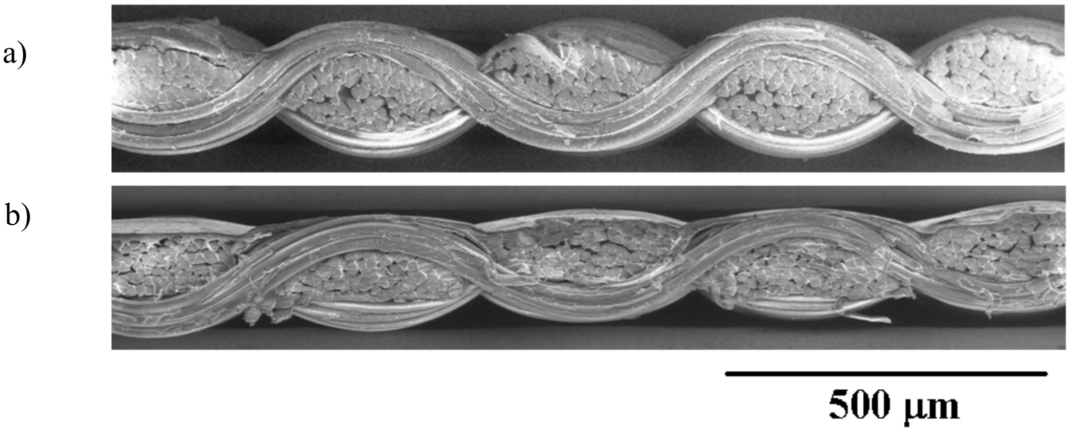


**Figure 6.**



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