Structural and morphological characterizations of *MWCNT*s hybrid coating onto cotton fabric as humidity wearable sensors

Giuseppe Rosace[a,*], Valentina Trovato[b], Claudio Colleoni[a], Michele Caldara[a], Valerio Re[a], Marco Brucale[c], Elpida Piperopoulos[d], Emanuela Mastronardo[d,e], Candida Milone[d], Giovanna De Luca[f], Maria Rosaria Plutino[b,*]

[a] *Department of Engineering and Applied Sciences, University of Bergamo, Viale Marconi 5, 24044 Dalmine (Bg), Italy.*

[b] *Institute for the Study of Nanostructured Materials, ISMN – CNR, O.U. Palermo, c/o Department of ChiBioFarAm, University of Messina, Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina (Me), Italy.*

[c] *Institute for the Study of Nanostructured Materials, ISMN – CNR, O.U Montelibretti - Via Salaria Km 29,300, 00015 Monterotondo Stazione (Roma), Italy.*

[d] *Department of Engineering, University of Messina, Contrada di Dio, S. Agata, 98166 Messina (ME), Italy.*

[e] *National Interuniversity Consortium of Materials Science and Technology, INSTM, Via G. Giusti 9,50121 Florence (FI), Italy.*

[f] *Department of ChiBioFarAm, University of Messina, Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina (Me), Italy.*

*Corresponding author.

Email: giuseppe.rosace@unibg.it; rosaria.plutino@ismn.cnr.it.

Abstract

A new Multi-Walled Carbon Nanotubes (*MWCNT*s) based conducting cotton fabric was properly designed and achieved as a useful component for the development of humidity sensors. ~~With this aim in mind~~ A synthetic strategy was optimized through subsequent steps of *MWCNT*s functionalization and dispersion in a polymer matrix, by first reacting functionalized *MWCNT*s, *1*,*2*,*3*,*4*-butanetetracarboxylic acid (BTCA), polyvinyl alcohol (PVA), and then adding a polyacrylic resin. The polymeric paste thus obtained, containing a synthetic thickener, was applied by a knife-over-roll coating technique onto cotton fabric, then dried and finally cured. The polymeric coated textile samples were analyzed with different chemical-physical techniques to determine their morphological features, thermal behavior and surface resistivity. Changes in surface resistance of films were monitored as a function of relative humidity. The electrical resistance properties of the film deposited on cotton surface seem to be clearly influenced by the presence of water molecules interacting with *MWCNT*s junctions. This efficient functional fabric may be a helpful starting point to develop technical textiles, or the component of a humidity sensor, useful as sensing material for detection of environmental humidity variations.

Keywords: Carbon nanotubes; Conductive polymers; Textile coating; Technical textiles; Smart textiles; Vapor sensing.

1. Introduction

In the last years textile materials have increased their field of use beyond traditional application. In fact, compared to other materials, they show advantages such as hardness and strength but also ductility and flexibility that permit them to be easily manipulated and adapted to a wide range of end-use requirements. Thanks to the excellent combination of the above-mentioned properties, a remarkable growth in the textile industry for technical applications has been observed [1,2] [1] [2]. Particularly, many efforts have been made to develop textile materials, able to react and/or respond to external stimuli [3,4,5,6] [3] [4] [5] [6]. The resulting products are named smart textiles, also variously known as smart fabrics, electronic textiles, or e-textiles, and they are often dependent on electrical conductivity [7,8] [7] [8].

Consequently, the demand of electrically conductive textiles has increased in the fields both of “technical textiles”, to obtain materials with antistatic or electromagnetic shielding [9] [9], and "smart textiles" [10] [10], to develop sensors [11,12] [11] [12] or to improve contacts and interconnections for signal transport. They show interesting electrical properties and can be considered as an efficient replacement for classical conductive inorganic materials [13] [13]. Depending on the desired level of conductivity, durability and process demands for different applications, electrical conductivity in textile fabrics can be obtained through several methods such as metallization, electroless deposition, electrodeposition, chemical coating, carbon and metallic compound inclusion. Textile fibers can be spun with conductive particles distributed throughout the fibers or only in the cores [14,15] [14] [15]. Otherwise, metallic yarns can be inserted in woven or knitted constructions [16] [16]. Also at the level of nanofibers [17] [17] it is possible to provide textile fibers with electroconductive properties. However, probably the most interesting method is to coat fibers with conductive layers, ~~in pursuance~~ with the goal of reducing the surface resistance of the final treated textile material. Currently, there is great interest in the use of carbon nanotubes (*CNTs*), as nanoscale modifiers able to enhance the mechanical and electronic properties of conventional polymer materials [18,19] [18] [19]. The properties and applications of *CNTs* have

been a very active research fields over the last decade. In fact, they possess feature high flexibility, low mass density, and large aspect ratio (typically >1000), whereas predicted whereas theoretical analysis and some experimental data indicate extremely high tensile moduli and strengths for these materials [20,21] [20] [21]. Moreover, the introduction of oxygen functionalities onto the graphitic-like structure is a crucial step for the enhancement of the interfacial adhesion, which represents the key requirement for the improvement of mechanical and electrical properties in the final material. Considering the novel and intrinsic carbon nanotubes physical properties [22,23] [22] [23], their use in the functionalization of textile material would be of crucial importance for both fundamental research and practical applications. Because of its excellent hygroscopicity, air permeability, and electrostatic resistance, among various textile materials, cotton and other cellulose-based fibers are the most commonly used material for textiles and clothing. In the last decade, emerging research on cotton fabrics with versatile functionalities revolutionized the use of cotton fabrics as a wearable platform for tremendous interesting applications [24,25] [24] [25]. In this scenario, many research activities have been developed targeted on the modification of natural polymer fibers with carbon nanotubes [18] [26,27,28,29] [26] [27] [28] [29]. Thanks to their electrical properties, carbon nanotubes can be used for a large number of applications, among which chemical sensing. For example, variation in environmental chemical composition at room temperature can be detected by them, and this sensitivity allows their use for the realization of chemical sensors with high sensibility and versatility [30] [30]. Once the textile materials have acquired a high electrical conductivity, characterizing "organic synthetic metals" [31] [31], they become attractive for use in electronic fields, especially for the simple and low-cost preparation of electric circuits for flexible and wearable electronics.

This work has been developed with the goal of developing a cotton-based technical textile using a hybrid functional *MWCNT*s coating, able to detect environmental humidity percentage as function of electrical resistance variation. Humidity sensing is of great importance for many applications, such as food processing, air-conditioning for office buildings, greenhouse industries,

chemical plants, and storage depots [32] [32]. With this aim, a preparation procedure to obtain a hybrid coating able to introduce electric conductivity in the treated textile fabric was designed. A combination of different compounds, such as poly(vinylalcohol) (PVA), *1*,*2*,*3*,*4*-butanetetracarboxylic acid (BTCA), and polyacrilyc resin was employed with the purpose of both obtaining a stable dispersion of *MWCNT*s into the polymer matrix and still ensuring the contact between the nanotubes, necessary to allow electrical conductivity.

With the aim of fully investigating the so modified textile surface, we ~~thought worthwhile to~~ mainly focus this study on the morphological characterization and on the thermal behavior of the treated cotton fabric in comparison to the untreated one~~, as reference~~. Consequently, the cotton fabric coated with the hybrid *MWCNT*s-containing film was fully characterized by ATR FT-IR spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermo-gravimetric analysis (TGA), and atomic force microscopy (AFM). Finally, the electrical resistance of the *MWCNT*s-based cotton coating ~~were~~ was measured as a function of environmental humidity variation.

2. Experimental part

2.1. Materials and methods

Pristine *MWCNT*s (hereafter *p-MWCNTs*), used in this study were synthesized following the procedure described by Donato et al. [33] [33]. *1*,*2*,*3*,*4*-butanetetracarboxylic acid (BTCA), sodium hypophosphite monohydrate (SHP) and all chemicals were purchased from Aldrich and used as received. Poly(vinylalcohol) (PVA) and MIROX®FC (used as synthetic thickener) were kindly supplied by KemPaTex S.r.l. (Italy) and Bozzetto group S.p.A. (Italy), respectively. Scoured and bleached 100% plain-weave cotton fabric (mass per unit area of 237g/m^2), kindl~~e~~y supplied by Mascioni S.p.A. (Cuvio, Italy), was used in this research. ~~Prior of~~ Before all the experiments, the fabrics were washed in a non-ionic detergent at 40°C for 20 min at a pH of 7, rinsed several times

with de-ionized water and then dried. The cleaned samples were conditioned at 20 (±1) °C and under standard atmospheric pressure at 65 (±2) % relative humidity for at least 24 h.

p-MWCNTs were oxidized according to a reported procedure [34] [34] to introduce hydrophilic functionalities, –COOH and –OH. *p-MWCNTs* (ca. 3 g) were soaked into 300 mL of a mixture of HNO_3 (67%) and H_2SO_4 (98%), (v/v 1:1), kept at 60 °C then ultrasonicated for 6 h. The solution was cooled down to room temperature, diluted with de-ionized water, filtered under vacuum with Millipore 0.2 μm filters paper, and finally rinsed with de-ionized water to remove residual acid until pH 7 was reached. Black powder was dried to obtain functionalized multi-walled carbon nanotubes (herafter *f-MWCNTs*).

With the purpose of developing a conductive textile, *f-MWCNTs* were used in combination with an acrylic thickener by following the subsequent procedure, so that to obtain a viscous paste simple to be applied on cotton fabrics according to knife-over-roll technique.

f-MWCNTs (100 mg) were dispersed in de-ionized water (10 mL) through ultra-sonication and then heating up to 80°C. After that, PVA (50 mg), BTCA (20 mg) and SHP (catalytic amount) were slowly added, separately and subsequently, under vigorous stirring obtaining a homogeneous colloidal phase. Finally, about 130 mg of MIROX®FC were added, thus obtaining a paste (coded *f-MWCNTs* paste), that has been employed for the cotton fabric coating.

The paste was spread in a uniform manner by knife-over-roll technique [35] [35] onto the cotton fabric surface (approximately 20 cm x 30 cm), using an in-house developed coater consisting in a flat and movable knife blade under which the textile substrate is fixed. The gap between the bottom of the knife and the top of the fabric was used to control the thickness of the coating. Finally, the coated sample was cured at 120 °C for 5 minutes in a gravity convection oven. For the purpose of forming a multi-layer architecture, the fabric sample was re-coated with the same paste and then subjected to a new thermal curing.

2.2. Measurements and analyses

f-MWCNTs were fully investigated as solid residue through a wide series of chemical-physical techniques, such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), atomic force microscopy (AFM), FT-IR spectroscopy, and Thermo-Gravimetric Analysis (TGA). SEM analyses were performed by a FEI Quanta FEG 450 instrument, operating at 20 or 5 kV. TEM analyses were carried out by a JEOL JEM 2010, operating at 200 kV and equipped with a Gatan 794 MultiScan CCD camera. The morphological measurement of textile samples was performed on a Multimode 8 AFM microscope equipped with a Nanoscope V controller and a type J piezoelectric scanner (Bruker, USA) in PeakForce imaging mode, employing SNL-A probes with a nominal spring constant of 0.35 N/m (Bruker, USA). Background interpolation and surface roughness parameter calculation was performed with Gwyddion 2.45 (http://gwyddion.net/). Reported root mean squared area roughness (S_q) values are the average of at least five different regions, with the standard deviation of these measures as the uncertainty. FT-IR spectra were recorded with a Thermo Avatar 370 equipped with attenuated total reflection (ATR) accessory and using a diamond crystal as internal reflectance element. Spectra were acquired with 32 scans and in the range from 4000 to 550 cm^{-1} with a resolution of 4 cm^{-1}. TGA analyses were carried out with a NETZSCH STA 409PC instrument, using Al_2O_3 pans. The environments used were Ar and Air, using 100 mL/min and 30 mL/min for *MWCNTs* and textile samples, respectively. Thermo-Gravimetric Analysis were performed in the range RT–1000 °C, heating rate 10 °C/min.

The surface resistance was measured in a conditioned laboratory at 20°C and 65% RH, using a mechanical setup developed to investigate surface treatments on different kind of materials. Two rectangular aluminum plates (50 mm x 50 mm) separated by a settable distance are screwed on the sample, which is placed on an insulating support. The electrical resistance is then recorded by a Source-Measure Unit (Keysight Power Source B2961A). The value of surface resistivity ($R_{\square}$, also indicated as sheet resistance) was calculated by taking into account the sample width and the distance between the metallic plates, as in the following Eq. 1:

$$R_{\square} = R\,\frac{W}{L}\left[\frac{\Omega}{\square}\right] \qquad (1)$$

where R is the resistance and W/L is the width-to-length ratio of the sample. The result, in units of ohms/square (Ω/□), is used to highlight the interpretation of sheet resistance as the resistance over a fixed aspect ratio sample area [36] [36].

Due to the thickness of the coating, it was possible to approximate the resistance measurement on the surface referring to "surface resistance", neglecting the thickness contribution ~~(Ω/square)~~ [37] [37].

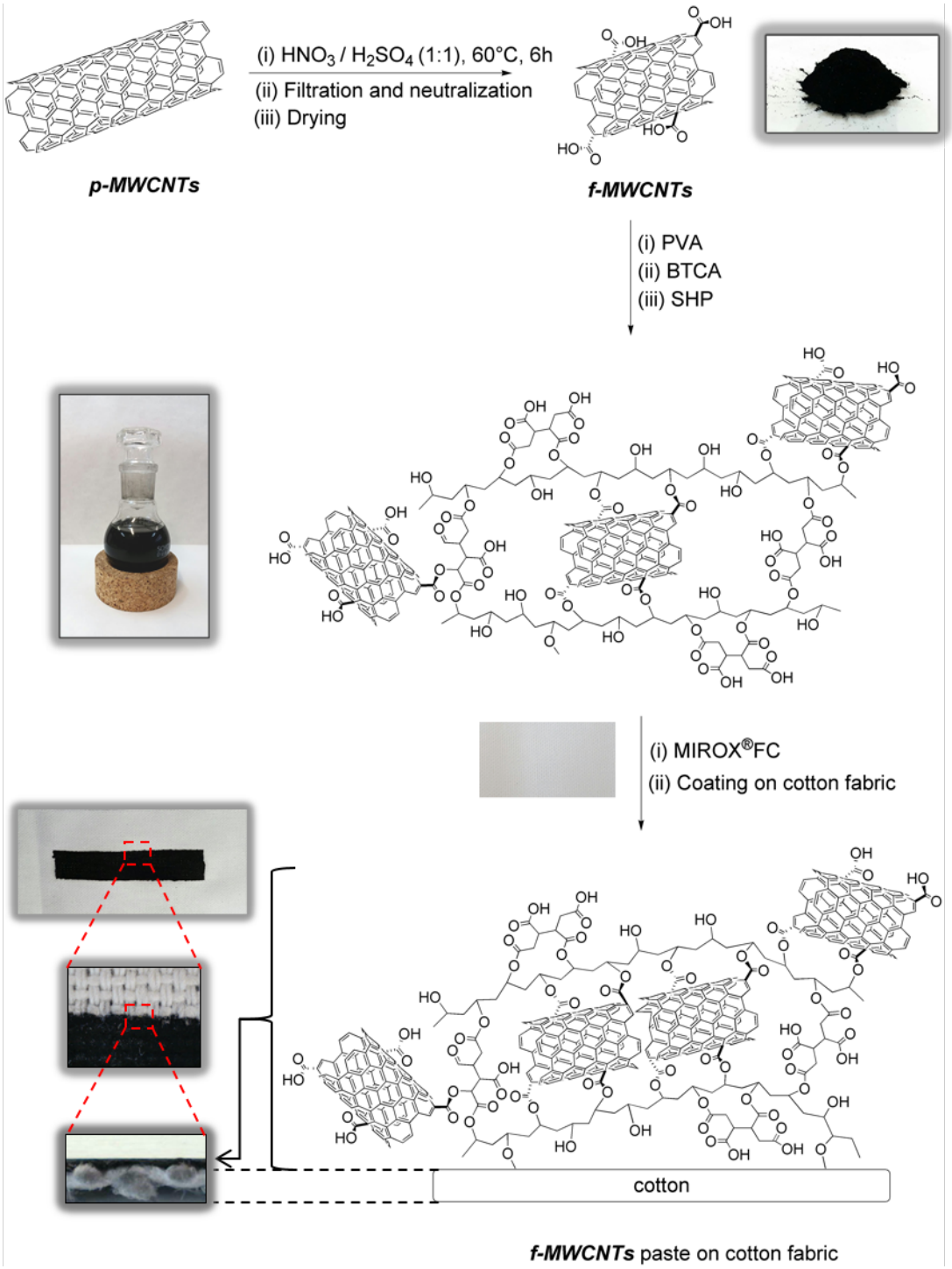
To investigate the humidity sensor performance, the electrical resistance values of both a blank and a treated cotton fabric samples were measured in the climatic chamber by connecting alligator clips to the samples extremities at a distance of 42 mm and the cable opposite end to instruments placed just outside the chamber. Considering that the tested samples have a 4 mm width, this means that we measured the total resistance of 10.5 squares. The samples resistance measurements as a function of relative humidity (% RH) and temperature were acquired at the same time for both samples using a tester (Fluke 79) and a Source-Measure Unit (Agilent Power Source B2961A). In parallel to electrical measurements, the climatic chamber relative humidity and temperature values were recorded using a high accuracy (±1.8%RH, ±0.2°C) humidity and temperature sensor (Sensirion SHT25), directly connected via an USB cable to a PC. Relative humidity values were set in the range between 56.1% and 92.0%, while temperature was varied from 4.3°C to 29.3°C.

3. Results and Discussion

3.1. MWCNTs functionalization and coating application

With the aim to obtain a conductive textile fabric, a *MWCNTs*-doped organic coating was realized and applied onto cotton samples. During a first synthetic step, carbon nanotubes were previously oxidized to improve their ~~following~~ dispersion in the mixture, by introducing polar

groups such as carboxylic and hydroxyl groups. After that, a mix of BTCA, PVA and an acrylic thickener was used, both to immobilize *f-MWCNTs* onto cotton fabric, and to maintain mutual connection of nanotubes, in order to guarantee the electrical conductivity of the film (Scheme 1).



Scheme 1. Overall synthetic scheme of subsequent steps of functionalization of *p-MWCNTs* towards the final deposition on cotton textile (*f-MWCNTs* paste on cotton fabric).

In the proposed coating, PVA is a water soluble synthetic polymer rich of hydroxyl groups with excellent emulsifying, adhesive and film forming properties [38] [38]. In the same reaction step, the acrylic thickener is used to allow the formation of a spreadable paste on fabrics, while BTCA plays a key role in the formation of coating [39] [39]. In fact, due to its four carboxylic groups, in presence of SHP catalyst, BTCA is able both to react randomly with hydroxyl groups of other chemicals (PVA, *f-MWCNTs*) and to obtain esterification reactions [40] [40] with cellulose, thus promoting the desired stable immobilization of the coating. According to previous evidences [41] [41], *f-MWCNTs* are arranged orderly in the polymeric matrix, thanks the presence of the long PVA chains, while BTCA acts as spacer and cross-linker, as proposed in the Scheme 1.

The calculated add-on% on coated samples was 3.8 % while the amount of *f-MWCNTs* in the paste was 33.0%. The so-obtained acrylic *f-MWCNTs* paste was uniformly spread on the cotton textile surface as shown in Scheme 1. We were also able to stamp directly on the fabric the shape of an Interdigitated Array (IDA) electrodes with this *f-MWCNTs* containing composite matrix (Fig. 1).

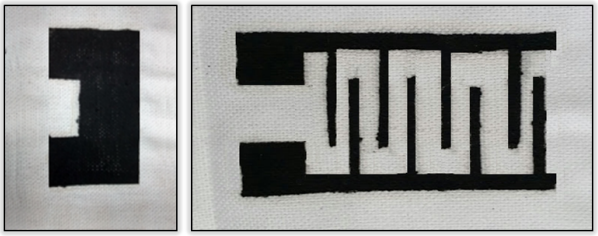


Figure 1. *MWCNT*s-based Interdigitated Electrodes of different shape obtained on cotton textile.

Similarly~~,~~ to the electrode systems investigated in this research, the obtained paste allows ~~to design~~ sensor components to be deposited on textile fabrics, providing a very effective sensing materials working at room temperatures.

3.2. Morphological characterization

3.2.1. SEM and TEM analyses.

With the objective of characterizing the morphology of the coated textile fabric, preliminary, the morphology of *p-MWCNTs* and *f-MWCNTs* was investigated by SEM and TEM analyses, in

order to highlight structural differences before and after the oxidation treatment. As reported in Fig. 2, SEM analysis shows the presence of *MWCNTs* bundles that appear as agglomerates after their functionalization (Fig. 2b).

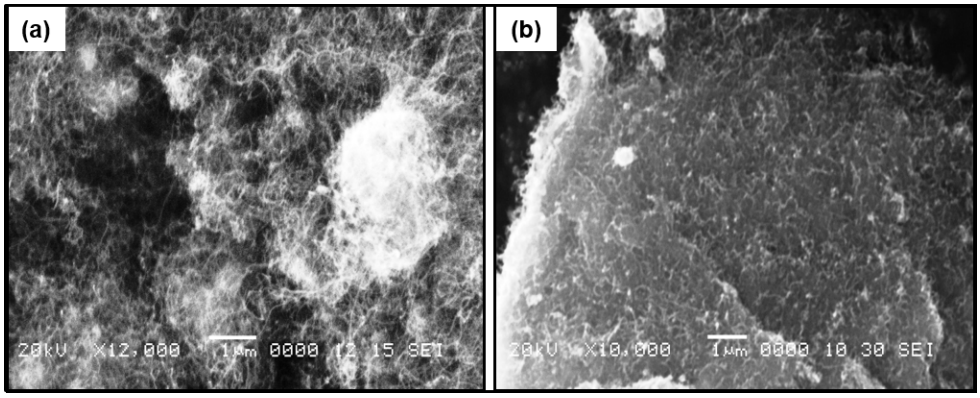


Figure 2. SEM images of (a) *p-MWCNTs* and (b) *f-MWCNTs 1:1*.

TEM analysis of pristine and functionalized *MWCNTs*, displayed in Fig. 3a-d, shows the structural modification that occurs upon oxidation.

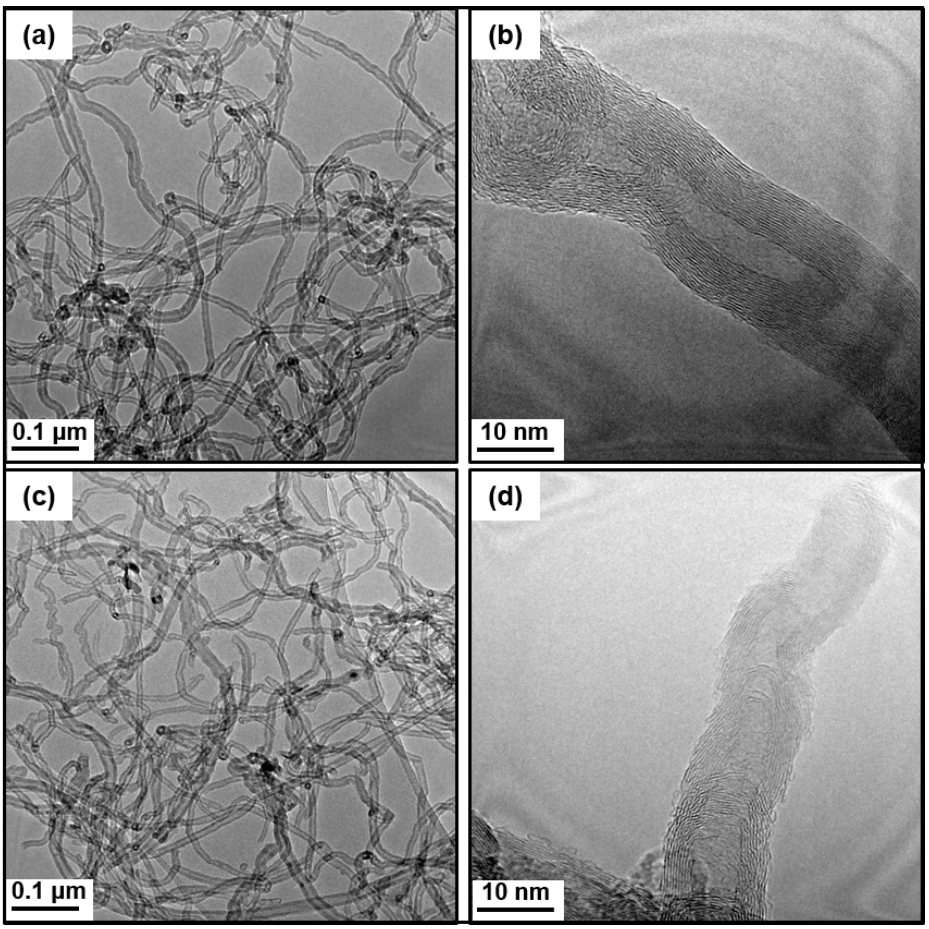


Figure 3. TEM images of (a-b) *p-MWCNTs* and (c-d) *f-MWCNTs 1:1.*

Fig. 3a shows that *p-MWCNTs* form long highly entangled carbon filaments with external diameters between 5 and 20 nm. Higher magnification images demonstrate that the *p-MWCNTs* walls mainly consist of smooth graphene layers (fig. 3b). Upon oxidation with the HNO_3:H_2SO_4 (1:1) solution, a slight reduction of the *MWCNTs* length (Fig. 3c) is accompanied by sidewalls degradation, as inferred by the presence of edges and steps at external sheet (Fig. 3d).

Fig. 4a displays the SEM images of fabric coated with the *f-MWCNTs* paste, where it is clearly shown the typical morphology of cotton fibers (*), characterized by smooth fibers, in comparison with the sample coated with two layer of *f-MWCNTs* paste (**).

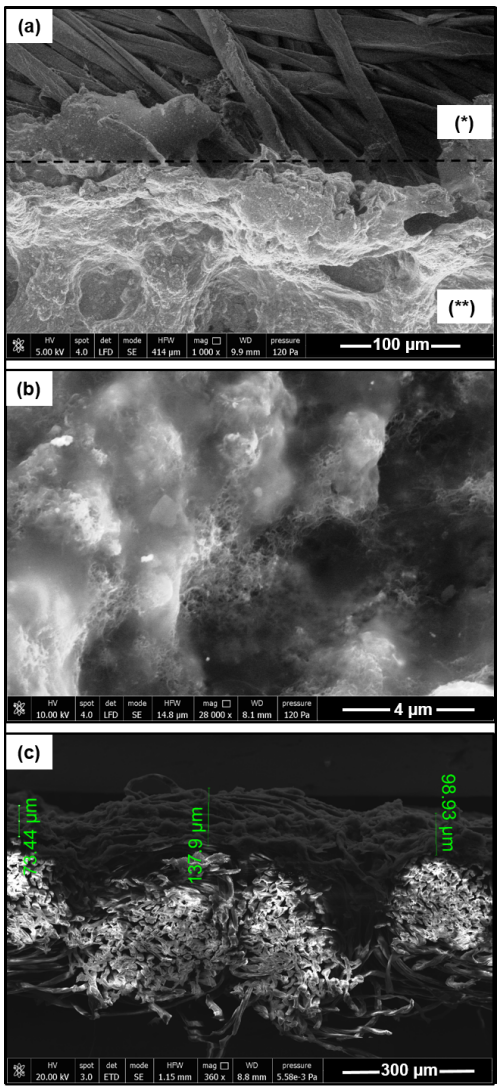


Figure 4. SEM images of : (a) the fabric covered with a polyacrilic coating based on *f-MWCNTs* paste; (b) 25 x higher magnification of a selected *f-MWCNTs* paste cotton region; (c) section of the covered cotton fabric showing the thickness value and the uniformity of the obtained coating.

The latter appears completely and homogeneously covered by the coating that exhibits a high coverage degree highly rough with a porous structure. Fig. 4b shows the presence of a carbon nanotubes network in the film coated onto cotton fabric, well exposed to the environmental humidity. Due to the porous structure, vapor molecules can reach *f-MWCNTs* influencing their electrical resistance. In fact, the presence of water affects the dielectric constant of the sensitive coating and consequently its resistance is different at diverse relative humidity levels.

The lower SEM image (Fig. 4c) was recorded on the section of the covered cotton fabric, thus showing the thickness average value, in the range between 94 and 138 μm, together with the uniformity of the resulting coating.

3.2.2. AFM analysis for surface characterization

The morphology of untreated and treated textile samples was also characterized *via* optical microscopy and PeakForce AFM imaging (Fig. 5).

As previously described elsewhere [4], AFM imaging of untreated cotton samples (Fig. 5b, left panel) shows grooves and cavities with random depths in the 10-100 nm range, corresponding to the interstitial zones in which individual fibers adjoin. Consequently, S_q values calculated on 1μm^2 randomly selected zones of the untreated cotton sample are vastly influenced by these mostly stochastic variations (S_q of untreated cotton = 42 ± 28 nm). Despite the above, the morphological alteration induced by the processing on the treated sample is so marked that it is possible to quantitatively assert its difference with regard to the untreated sample (S_q of treated cotton = 185 ± 42 nm). The untreated sample clearly shows its micrometric and nanometric constituent fibers when observed with both optical (Fig. 5a- b, left panel) and AFM microscopy. In contrast, the majority of the micrometric fibrils in the treated sample are noticeably covered with granular dark material as observed via optical microscopy (Fig. 5a, right panel); in addition, AFM microscopy (Fig. 5b, right panel) reveals how the characteristic texture formed by nanometric fibers in pristine cotton is no longer discernible after functionalization.

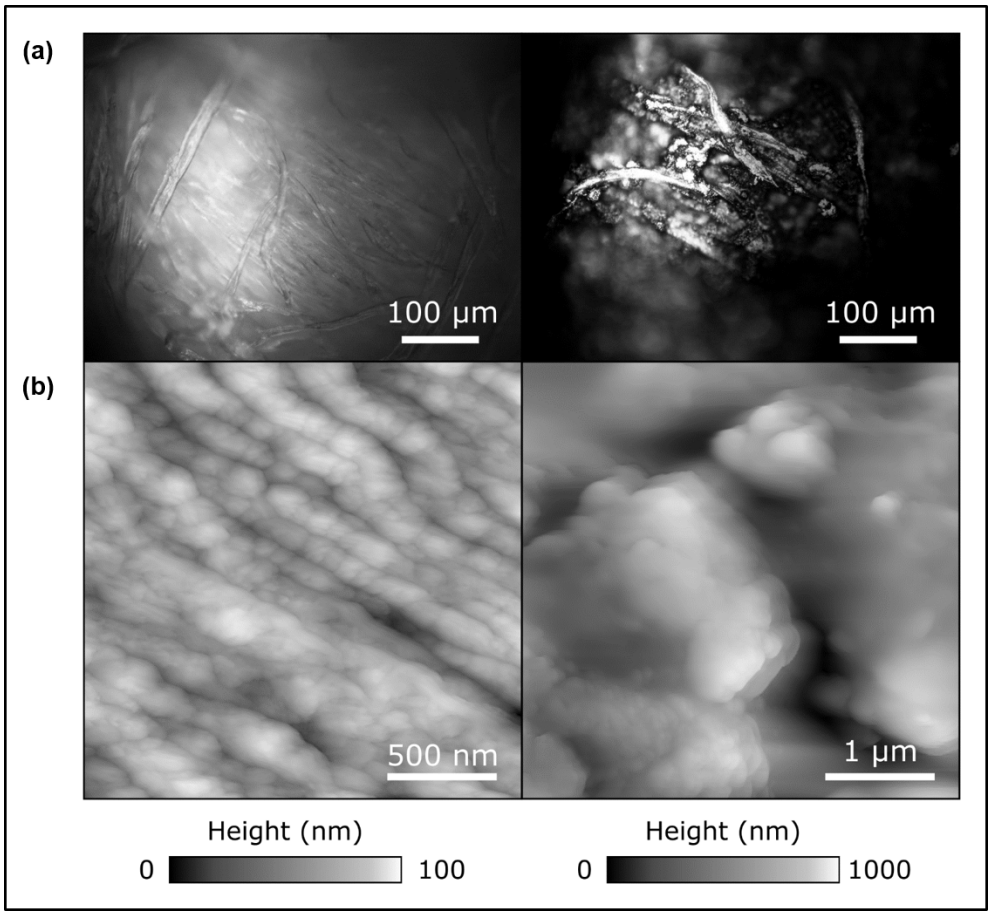


Figure 5. Representative (a) 20X optical images and (b) AFM micrographs of untreated (left column) and treated (right column) cotton samples.

3.3. FT-IR measurements

FTIR spectroscopy in ATR (Attenuated Total Reflection) mode, a surface sensitive technique with a penetration depth of only few micrometers, is a powerful tool for investigating the functional groups present on the surface of the treated cotton sample [42] [42]. Fig. 6 shows the spectra of (a) the untreated cotton, (b) the acrylic paste containing the *f-MWCNTs*, and (c) the coated fabric in the range 2000 – 800 cm^{-1}. Compared to the characteristic spectrum of the untreated cotton, the IR absorption bands of the treated fabric are deeply different due to the presence of the coating on the surface.

The coating of the *f-MWCNTs* paste onto cotton fabric is evident in the Fig. 6c by the disappearance of the characteristic bands of cellulose, such as at around 1320 cm^{-1}, 1055 cm^{-1} and

1030 cm^{-1} assigned to CH wagging, asymmetric in-plane ring stretch and C-O stretch, respectively [43] [43]. These changes are associated with the presence of the coating on the cotton fiber surface.

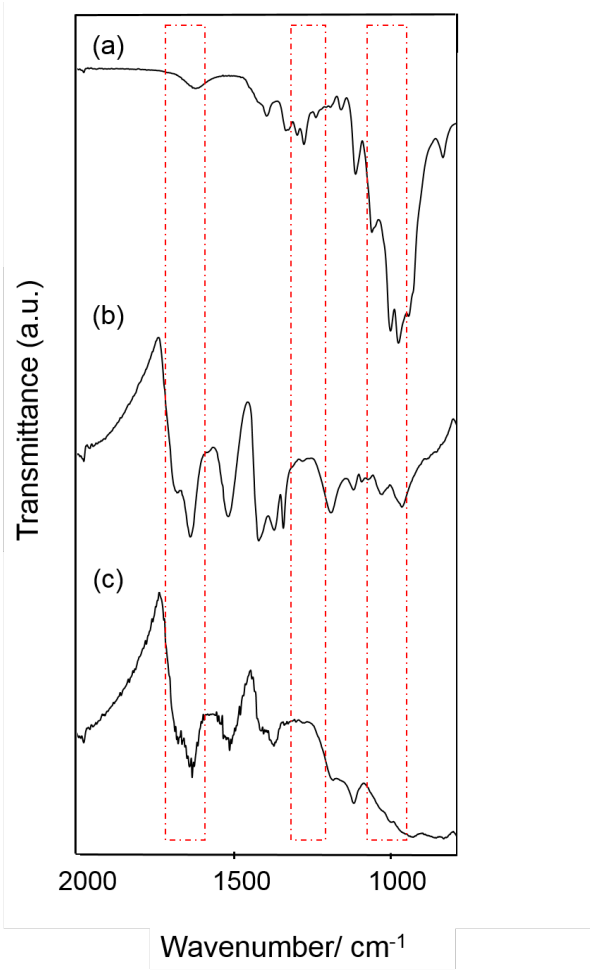


Figure 6. IR spectra of (a) the untreated cotton, (b) the *f-MWCNTs* paste, and (c) the treated cotton.

As reported previously [44] [44], three distinctive peaks can be considered to investigate the presence of *f-MWCNTs*. In fact, the absorption band at 1634 cm^{-1} is assignable to C=C stretching mode of carbon nanotubes, while bands at 1713 cm^{-1} and 1150 cm^{-1} are associated with C=O stretching and C–O stretching of COOH, respectively. Even if not completely clear because its complex chemical formulation, the spectrum of the treated cotton sample confirms the presence of *f-MWCNTs*-based coating in the applied film.

3.4. Thermo-gravimetric analyses

Following the thermal decomposition behavior of functionalized *MWCNTs* in inert atmosphere by thermogravimetric analysis, it is possible to obtain useful information on organic

functional groups [45,46] [45][46] . As reported in Fig. 7, the thermal degradation of *f-MWCNTs* occurs through a multistep process. The first step, up to a temperature of 150°C, corresponds to the evaporation of the humidity adsorbed by the sample. The second step, from 150 to 350 °C, is ascribed to the decarboxylation of the carboxylic groups present on the *MWCNTs* walls. Then, between 350°C and 600°C, the degradation of anhydrides and lactones occurs. Finally, the weight loss at temperatures above 600°C indicates the decomposition of phenols, carbonyl groups, quinones, pyrans and ethers.

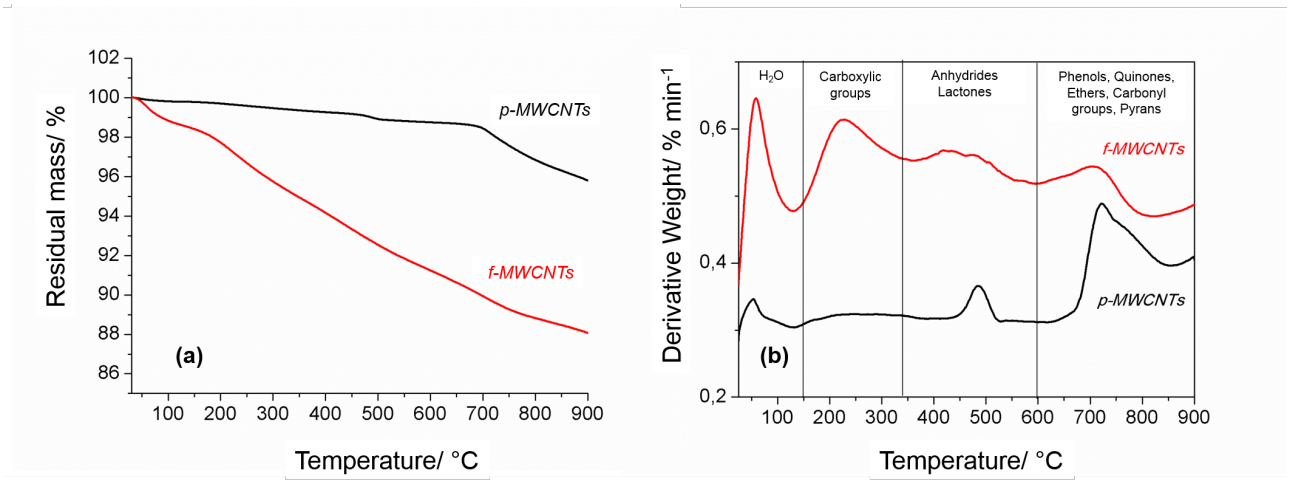


Figure 7. Plots for (a) TG analysis and (b) DTG curves on *p-MWCNTs* and *f-MWCNTs* samples.

Compared to the pristine *MWCNTs*, TG pattern of *f-MWCNTs* shows significantly difference in mass loss. This might be due to the presence of –COOH, C=O and –OH functional groups on the carbon nanotubes, which makes them more reactive and less stable. As a consequence of the above-mentioned conditions, at 900°C *p-MWCNTs* shows a weight loss of 4%, while the weight loss corresponding to *f-MWCNTs* is about 12 wt%.

The effect of *f-MWCNTs*-doped coating on the thermal stability of cotton fabric by means of TGA in air is reported in Fig. 8. For a sake of clarity the behavior of the single component is also reported. Complete oxidation of *f-MWCNTs* (black line) mainly occurs in the range of temperature 600-800 °C accordingly with literature [47] [47]; the slight weight loss observed at lower temperature agrees with decomposition of surface functional groups. Paste (red line) and *f-*

MWCNTs paste (blue line) show a multi-step decomposition in the range of temperature 200-600°C and a residual mass of 10% with respect to the initial mass assigned to the inorganic SHP. It should be noted that the addition of *f-MWCNTs* causes a reduction of the paste decomposition rate without affecting the range of stability. The untreated cotton sample curve (green line) shows two main degradation steps. The main weight loss obtained between 300 and 380°C can be due to two alternative pathways: (i) the decomposition of the glycosyl units to char and (ii) the depolymerization of such units to volatile products containing levoglucosan [48] [48]. At higher temperature (450-520 °C) complete oxidation of char occurs. Once applied onto fabric sample, the coating containing the nanotubes does not significantly modify the first decomposition step (magenta line) while a lowering of the rate of the second step is observed. The residual mass (< 1%) represents the SHP, belonging from decomposition of 3.8 wt.% paste present in the sample.

As main conclusion of TGA results, it can be suggested that the overall thermal stability of the studied textile sample, despite the presence of *f-MWCNTs* paste components, whose degradation starts at lower temperature than untreated cotton, does not present significant differences with starting material's one. This result validates the use of the final product.

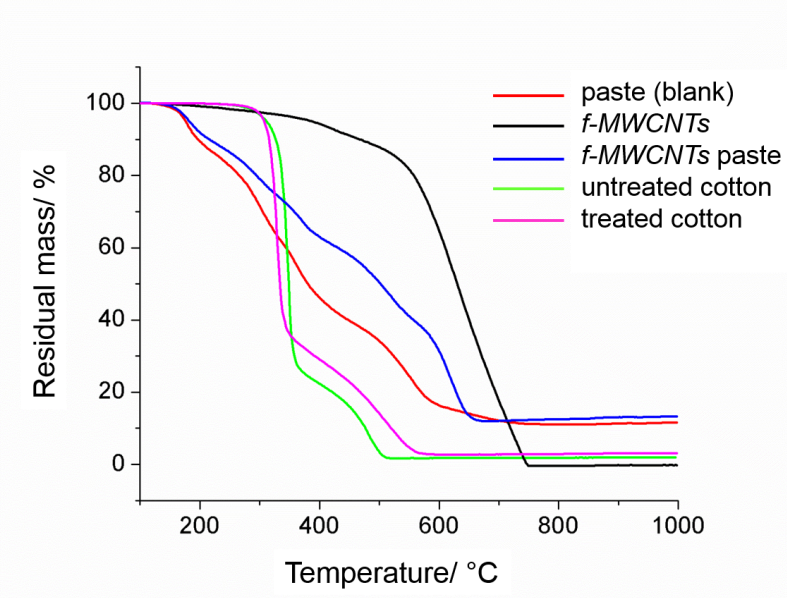


Figure 8. TGA plot relative to: paste (blank), *f-MWCNTs*, *f-MWCNTs* paste, untreated and treated cotton samples as measured under air atmosphere.

3.5. Sensing properties test

In order to study the electrical conductivity of the carbon nanotubes containing film and its possible use as humidity sensor, the film electrical resistance was measured as a function of relative humidity percentage and temperature. As previously mentioned, the blank cotton sample, without any surface treatment, did not show any dependence with % RH or temperature. In fact, due to the insulating nature of the fabric, its electrical resistance was above 10 MΩ ~~Ohm~~, exceeding the full range of the instruments. After the deposition of the *f-MWCNTs* paste, a significant decrease of the treated cotton resistance was observed, showing a value of *ca* 121.5 kΩ. Probably, *MWCNTs* are tightly electrostatically attached to PVA chains of much higher molecular weight and they are stacked in a large and crosslinked structure allowing the conductivity of the coating.

As formerly reported in literature [49] [49], electrical resistance of films doped with conductive fillers is influenced by many interactions (i.e. resistance between CNTs, resistance between CNTs and cross-linker used, resistance of water absorbed in an established region). Furthermore, several parameters like carbon nanotubes concentration, distance and reversible swelling behavior of all components can influence the above-mentioned properties. All these phenomena ~~permit~~ make it possible to use the proposed film developed with the *f-MWCNTs* paste as a humidity sensor. In fact, according ~~with~~ to previous studies [50] [50], the resistance change may depend on the interaction of water molecules with *f-MWCNTs*, mainly ~~focused o~~n because of the following reasons: the increase of the distance between the nanoparticles, reducing the tunneling effect, the swelling of the film, and the charge transfer from water to *MWCNTs*. Thanks to the high density of polar functional groups both in *f-MWCNTs* surface and in the polymeric matrix, the treated cotton fabric shows to be able to bind water molecules and to interact with environmental humidity ~~[50]~~.

The proposed sensing principle ~~explains that an~~ is based on the fact that an increase in the *MWCNTs* junction gap in the presence of humidity can trigger an important electrical resistance variation. Evidently, in presence of a gap at the *MWCNTs-MWCNTs* junction into the applied fabric

paste, being the distance between the nanotubes higher than ~~*ca* some~~ a few tens of nanometers [51] [51], the electrons, that are not characterized by a potential energy higher than the gap energy, cannot move freely around the coating. This behavior allows ~~the use of~~ the obtained functionalized fabric to be used as a humidity sensor, by measuring the electrical resistance variation under controlled conditions.

The measured sensitivity curves of treated cotton fabric in terms of electrical resistance values versus both humidity and temperature are depicted in Fig. 9a and 9b, respectively. Each electrical resistance measurement refers to a combination of relative humidity and temperature in the climatic chamber.

The resistance values of the specimen measured in the range of RH 55-75% are similar, but above 75% the sample exhibited a strong dependence with % RH, almost doubling its electrical resistance from 75% to 90%. This behavior means that the higher % RH values, the more water vapor ~~that~~ can be physically adsorbed into the coating, resulting in increased resistance. The observed increasing of resistance with increasing humidity, within the studied range, might be ascribed to the conduction decrease in the coating, where the adsorption of water molecules possibly decreases the nanoparticles density, due to the swelling of the film.

Moreover, as it is already well known [52] [52], the relative humidity is the ratio of the partial pressure of water vapor present in a gas, to its saturation vapor pressure, at a given temperature. Consequently, the variation of resistance as a function of % RH may be used also as temperature sensing. Figure 9b reports the electrical resistance values collected ~~in~~ as a function of the chamber temperature. Up to about 10°C, the resistance does not seem to be affected by the temperature variation, while at higher values the resistance increases proportionally to the relative humidity. The temperature range between 10 and 20°C of the sensor for humidity sensing can therefore be directly deduced from the resistance value of the *f-MWCNTs* based cotton coating.

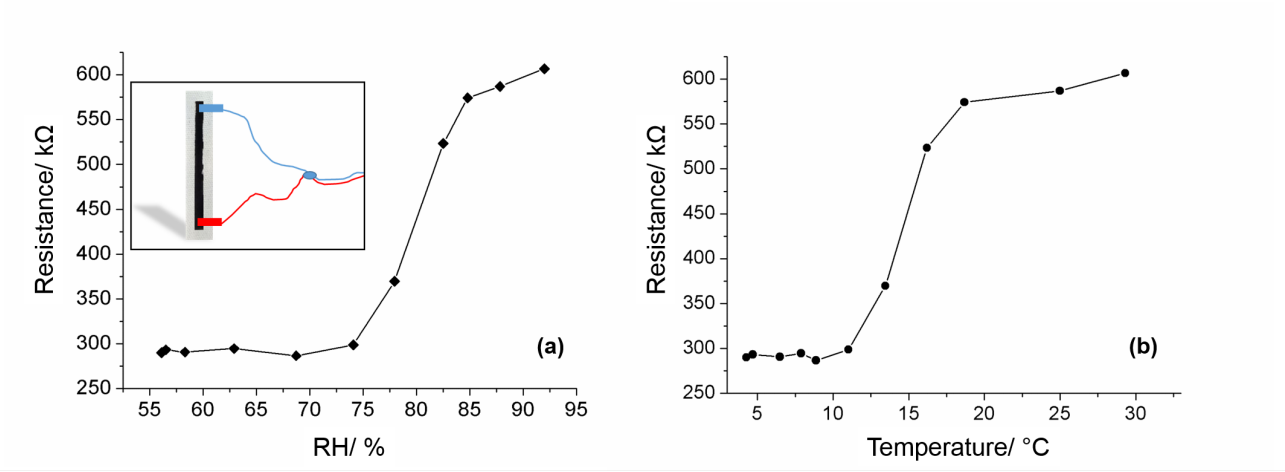


Figure 9. Plots showing the resistance dependence on (a) humidity and (b) temperature variation as measured on the *f-MWCNTs* paste treated cotton fabric.

4. Conclusions

In this study, synthetic procedures for the functionalization of Multi-Walled Carbon Nanotubes, the formation of polymer films containing *MWCNT*s, and its application on fabric have been performed. Good results were obtained with the preparation of a spreadable polymeric paste applied directly on the fabric. ~~In this regard,~~ We were able to optimize this synthetic procedure, and consequently to obtain tissue *MWCNT*s-based, which still have the characteristics of flexibility, and maintenance of the less-resistance properties. The above films have a good homogeneity and alignment of the carbon fibers, but also, in such a way~~, there is the maintenance of~~ the typical conductive properties of the *MWCNT*s are preserved. The obtained coated textile has be tested as a sensitive component of a ~~potentially new~~ prospective sensor device for humidity variation measurements. Finally, a *MWCNTs*-containing circuit mask was imprinted on cotton with quite good precisions.

Actually, this work, showing the design and the application on cotton fabric of a nanostructured coating based on *MWCNTs*, together with its successful use as sensitive system of environmental humidity, confirms the wide scale potentialities of textile fabrics, as flexible and

adaptable materials, in the realization of innovative and wearable sensors. Nevertheless, further investigations are in progress to ascertain the washing fastness of the applied coating, together with the reversibility of the sensing performances.

Acknowledgments

MURST and CNR are gratefully acknowledged for financial support. V. Trovato and M. R. Plutino wish to thank the "Nanomateriali e nanotecnologie per lo sviluppo sostenibile ed il patrimonio culturale" (CUP: G78B14000100006, 1/2012 of regione Siciliana), for V. Trovato NMA-4 grant. All authors wish to thank Lucio Maria Bonaccorsi (Department of Civil, Energy, Environmental and Materials Engineering, Mediterranea University, Reggio Calabria, Italy) for TGA analyses and Alessandro Pistone (Department of Engineering, University of Messina, Messina, Italy.) for TEM analyses

References

[1] A.R. Horrocks, S.C. Anand, eds., Handbook of technical textiles, Second ed., Woodhead Publishing, 2016.

[2] J. Hu, H. Meng, G. Li, S.I. Ibekwe, A review of stimuli-responsive polymers for smart textile applications, Smart Mater. Struct. 21 (2012) 53001. doi:10.1088/0964-1726/21/5/053001.

[3] M.R. Plutino, E. Guido, C. Colleoni, G. Rosace, Effect of GPTMS functionalization on the improvement of the pH-sensitive methyl red photostability, Sensors Actuators B. 238 (2017) 281–291. doi:10.1016/j.snb.2016.07.050.

[4] G. Rosace, E. Guido, C. Colleoni, M. Brucale, E. Piperopoulos, C. Milone, M.R. Plutino, Halochromic resorufin-GPTMS hybrid sol-gel: Chemical-physical properties and use as pH sensor fabric coating, Sensors Actuators B Chem. 241 (2017) 85–95. doi:10.1016/j.snb.2016.10.038.

[5] E. Guido, C. Colleoni, K. De Clerck, M.R. Plutino, G. Rosace, Influence of catalyst in the synthesis of a cellulose-based sensor: Kinetic study of 3-glycidoxypropyltrimethoxysilane epoxy ring opening by Lewis acid, Sensors Actuators, B Chem. 203 (2014) 213–222. doi:10.1016/j.snb.2014.06.126.

[6] M. Caldara, C. Colleoni, E. Guido, V. Re, G. Rosace, Optical monitoring of sweat pH by a textile fabric wearable sensor based on covalently bonded litmus-3-glycidoxypropyltrimethoxysilane coating, Sensors Actuators, B Chem. 222 (2016) 213–220. doi:10.1016/j.snb.2015.08.073.

[7] K. Choi, H. Park, E. Jeong, S. Peksoz, Scientometric analysis of research in smart clothing: state of the art and future direction, Hum. Centered Des. (2011) 500–508

[8] M. Stoppa, A. Chiolerio, Wearable electronics and smart textiles: A critical review, Sensors (Switzerland). 14 (2014) 11957–11992. doi:10.3390/s140711957.

[9] N.A. Aal, F. El-Tantawy, A. Al-Hajry, M. Bououdina, New antistatic charge and electromagnetic shielding effectiveness from conductive epoxy resin/plasticized carbon black composites, Polym. Compos. 29 (2008) 125–132. doi:10.1002/pc.20334.

[10] W.C. Smith, Overview of textile coating and lamination., in: W.C. Smith (Ed.), Smart Text. Coatings Laminates, Woodhead Publishing Limited, 2010: pp. 3–9.

[11] X. Tao, Smart technology for textiles and clothing - introduction and overview, in: X. Tao (Ed.), Smart Fibres, Fabr. Cloth., Woodhead Publishing Limited (2001) 1–6.

[12] Z. Li, G. Luo, F. Wei, Y. Huang, Microstructure of carbon nanotubes/PET conductive composites fibers and their properties, Compos. Sci. Technol. 66 (2006) 1022–1029. doi:10.1016/j.compscitech.2005.08.006.

[13] B. Kim, V. Koncar, E. Devaux, Electrical properties of conductive polymers: Pet - Nanocomposites' fibres, Autex Res. J. 4 (2004) 9–13.

[14] Stråât M, Rigdahl M and Hagström B. Conducting bicomponent fibers obtained by melt spinning of PA6 and polyolefins containing high amounts of carbonaceous fillers. *Journal of Applied*

Polymer Science. 2012; 123: 936-43

[15] Stråât M, Toll S, Boldizar A, Rigdahl M and Hagström B. Melt spinning of conducting polymeric composites containing carbonaceous fillers. Journal of Applied Polymer Science. 2011; 119: 3264-72.

[16] Cömert A, Honkala M, Puurtinen M and Perhonen M. The Suitability of Silver Yarn Electrodes for Mobile EKG Monitoring. In: Katashev A, Dekhtyar Y and Spigulis J, (eds.). 14th Nordic-Baltic Conference on Biomedical Engineering and Medical Physics. Springer Berlin Heidelberg, 2008, 198-201. Doi: 10.1007/978-3-540-69367-3_54

[17] Emmanuel Gasana, Philippe Westbroek, Jean Hakuzimana, Karen De Clerck, Georgios Priniotakis, Paul Kiekens, Dimitris Tseles, Electroconductive textile structures through electroless deposition of polypyrrole and copper at polyaramide surfaces, Surface & Coatings Technology 201 (2006) 3547–3551 doi:10.1016/j.surfcoat.2006.08.128

[18] Y. Liu, X. Wang, K. Qi, J.H. Xin, Functionalization of cotton with carbon nanotubes, J. Mater. Chem. 18 (2008) 3454. doi:10.1039/b801849a.

[19] Z. Spitalsky, D. Tasis, K. Papagelis, C. Galiotis, Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties, Prog. Polym. Sci. 35 (2010) 357–401. doi:10.1016/j.progpolymsci.2009.09.003.

[20] Andras Kis, Alex Zettl, Nanomechanics of carbon nanotubes, Phil. Trans. R. Soc. A, 366 (2008) 1591–1611, doi:10.1098/rsta.2007.2174.

[21] Rodney S. Ruoff, Dong Qian, Wing Kam Liu, Mechanical properties of carbon nanotubes: theoretical predictions and experimental measurements, C. R. Physique 4 (2003) 993–1008, doi:10.1016/j.crhy.2003.08.001

[22] J.-H. Pöhls, M.B. Johnson, M.A. White, R. Malik, B. Ruff, C. Jayasinghe, M.J. Schulz, V. Shanov, Physical properties of carbon nanotube sheets drawn from nanotube arrays, Carbon N. Y. 50 (2012) 4175–4183. doi:10.1016/j.carbon.2012.04.067.

[23] E.T. Thostenson, Z. Ren, T.-W. Chou, Advances in the science and technology of carbon nanotubes and their composites: a review, Compos. Sci. Technol. 61 (2001) 1899–1912. doi:10.1016/S0266-3538(01)00094-X.

[24] L. Bao, X. Li, Towards textile energy storage from cotton T-shirts, Adv. Mater. 24 (2012) 3246–3252. doi:10.1002/adma.201200246.

[25] A. Varesano, A. Aluigi, L. Florio, R. Fabris, Multifunctional cotton fabrics, Synth. Met. 159 (2009) 1082–1089. doi:10.1016/j.synthmet.2009.01.036.

[26] S. Mondal, J.L. Hu, A novel approach to excellent UV protecting cotton fabric with functionalized MWNT containing water vapor permeable PU coating, J. Appl. Polym. Sci. 103 (2007) 3370–3376. doi:10.1002/app.25437.

[27] G. Li, H. Wang, H. Zheng, R. Bai, A facile approach for the fabrication of highly stable superhydrophobic cotton fabric with multi-walled carbon nanotubes-azide polymer composites, Langmuir. 26 (2010) 7529–7534. doi:10.1021/la904337z.

[28] M.T. Byrne, Y.K. Gun'ko, Recent Advances in Research on Carbon Nanotube-Polymer Composites, Adv. Mater. 22 (2010) 1672–1688. doi:10.1002/adma.200901545.

[29] N. Nafeie, M. Montazer, N. H. Nejad, T. Harifi, Electrical conductivity of different carbon nanotubes on wool fabric: An investigation on the effects of different dispersing agents and pretreatments, Colloids and Surfaces A: Physicochem. Eng. Aspects 497 (2016) 81–89. Doi: 10.1016/j.colsurfa.2016.02.029

[30] Litao Liu, Xiongying Ye, Kang Wu, Rui Han, Zhaoying Zhou, Tianhong Cui, Humidity Sensitivity of Multi-Walled Carbon Nanotube Networks Deposited by Dielectrophoresis, Sensors 2009, 9(3), 1714-1721; doi:10.3390/s90301714

[31] H.R. Mattila, ed., Intelligent textiles and clothing, Woodhead Publishing Limited, 2006.

[32] Walid A. Daoud, John H. Xin, Yau S. Szeto, Polyethylenedioxythiophene coatings for humidity, temperature and strain sensing polyamide fibers, Sensors and Actuators B 109 (2005) 329–333

[33] M.G. Donato, S. Galvagno, M. Lanza, G. Messina, C. Milone, E. Piperopoulos, A. Pistone, S. Santangelo, Influence of carbon source and Fe-catalyst support on the growth of multi-walled carbon nanotubes, J Nanosci Nanotechnol. 9 (2009) 3815–3823. doi:10.1166/jnn.2009.NS73.

[34] C. Milone, R.S. Hameed, E. Piperopoulos, S. Santangelo, M. Lanza, S. Galvagno, Catalytic Wet Air Oxidation of p-Coumaric Acid over Carbon Nanotubes and Activated Carbon, Ind. Eng. Chem. Res. 50 (2011) 9043–9053. doi:Doi 10.1021/Ie200492g.

[35] W. Rehnby, M. Gustafsson, M. Skrifvars, Coating of textile fabrics with conductive polymers for smart textile applications, Welcome to Ambience'08. (2008) 100–103. http://bada.hb.se/bitstream/2320/3936/1/Ambience08.pdf#page=58.

[36] J. Banaszczyk, A. Schwarz, G. De Mey, L. Van Langenhove, The Van der Pauw Method for Sheet Resistance Measurements of Polypyrrole-Coated Para-aramide Woven Fabrics, Journal of Applied Polymer Science, 117 (2010) 2553–2558, doi: 10.1002/app.32186.

[37] Xiao-Yong Fang, Xiao-Xia Yu, Hong-Mei Zheng, Hai-Bo Jin, Li Wang, Mao-Sheng Cao, Temperature- and thickness-dependent electrical conductivity of few-layer graphene and graphene nanosheets, Physics Letters A, 379 (2015) 2245–2251, doi: 10.1016/j.physleta.2015.06.063

[38] R.A. Carvalho, T.M.C. Maria, I.C.F. Moraes, P.V.A. Bergo, E.S. Kamimura, A.M.Q.B. Habitante, P.J.A. Sobral, Study of some physical properties of biodegradable films based on blends of gelatin and poly(vinyl alcohol) using a response-surface methodology, Materials Science and Engineering C 29 (2009) 485–491. doi:10.1016/j.msec.2008.08.030

[39] F. Alimohammadi, M.P. Gashti, A. Shamei, A novel method for coating of carbon nanotube on cellulose fiber using 1,2,3,4-butanetetracarboxylic acid as a cross-linking agent, Prog. Org. Coatings. 74 (2012) 470–478. doi:10.1016/j.porgcoat.2012.01.012

[40] F. Alimohammadi, M. Parvinzadeh Gashti, A. Shamei, Functional cellulose fibers via polycarboxylic acid/carbon nanotube composite coating, J. Coatings Technol. Res. 10 (2013) 123–132. doi:10.1007/s11998-012-9429-3.

[41] C.F. de Lannoy, D. Jassby, D.D. Davis, M.R. Wiesner, A highly electrically conductive polymer-multiwalled carbon nanotube nanocomposite membrane, J. Memb. Sci. 415–416 (2012) 718–724. doi:10.1016/j.memsci.2012.05.061.

[42] G. Rosace, M.R. Massafra "Marking of cellulose yarn by vinyl monomer grafting" Textile Research Journal (2008) 78; 28, doi: 10.1177/0040517507082187

[43] C. Chung, M. Lee, E. K. Choe, Characterization of cotton fabric scouring by FT-IR ATR spectroscopy, Carbohydrate Polymers 58 (2004) 417–420. doi:10.1016/j.carbpol.2004.08.005

[44] A. Pistone, A. Piperno, D. Iannazzo, N. Donato, M. Latino, D. Spadaro, G. Neri, Fe_3O_4–MWCNT-PhCOOH composites for ammonia resistive sensors, Sensors and Actuators B 186 (2013) 333–342 DOI: 10.1016/j.snb.2013.06.027

[45] A. Pistone, A. Ferlazzo, M. Lanza, C. Milone, D. Iannazzo, A. Piperno, E. Piperopoulos, S. Galvagno, Morphological Modification of MWCNT Functionalized with HNO3/H2SO4 Mixtures, Journal of Nanoscience and Nanotechnology Vol. 12, (2012), 5054–5060. doi:10.1166/jnn.2012.4928

[46] A. Villa, M. Plebani, M. Schiavoni, C. Milone, E. Piperopoulos, S. Galvagno, L. Prati, Tuning hydrophilic properties of carbon nanotubes: A challenge for enhancing selectivity in Pd catalyzed alcohol oxidation. Catalysis Today 186 (2012) 76–82. doi:10.1016/j.cattod.2011.09.041

[47] S. Santangelo, G. Messina, G. Faggio, M. Lanza and C. Milone, Evaluation of crystalline perfection degree of multi-walled carbon nanotubes: correlations between thermal kinetic analyses and micro-Raman spectroscopy. J. Raman Spectrosc. 2011, 42, 593 – 602. Doi: 10.1002/jrs.2766

[48] J. Alongi, C. Colleoni, G. Rosace, G. Malucelli "Thermal and fire stability of cotton fabrics coated with hybrid phosphorus-doped silica films" J Therm Anal Calorim 110 (2012) 1207-1216

[49] K.P. Yoo, L.T. Lim, N.K. Min, M.J. Lee, C.J. Lee, C.W. Park, Novel resistive-type humidity sensor based on multiwall carbon nanotube/polyimide composite films, Sensors Actuators, B Chem. 145 (2010) 120–125. doi:10.1016/j.snb.2009.11.041.

[50] L. Liu, X. Ye, K. Wu, Z. Zhou, D. Lee, T. Cui, Humidity Sensitivity of Carbon Nanotube and Poly (Dimethyldiallylammonium Chloride) Composite Films, IEEE Sens. J. 9 (2009) 1308–1314. doi:10.1109/JSEN.2009.2030381.

[51] F. P. Zamborini, M. C. Leopold, J. F. Hicks, P. J. Kulesza, M. A. Malik, R. W. Murray, J. Am. Chem. Soc. 124 (2002) 8958-8964 doi: 10.1021/ja025965s.

[52] Zhi Chen and Chi Lu, Humidity Sensors: A Review of Materials and Mechanisms, Sensor Lett. 3, **4** (2005) 274-295, doi: 10.1166/sl.2005.045