DESIGNING OF CARBON NANOTUBES/COTTON FABRIC COMPOSITE FOR E-TEXTILES: EFFECT OF CARBON NANOTUBES-LENGTH ON ELECTROCONDUCTIVE PROPERTIES

Trovato V[1], Teblum E[2], Kostikov Y[2], Pedrana A[1], Re V[1], Nessim GD[2], Rosace G[1]

[1] *Department of Engineering and Applied Sciences, University of Bergamo, viale Marconi 5, 24044 Dalmine, BG, Italy*

[2] *Department of Chemistry, Bar Ilan Institute for Nanotechnology and Advanced Materials (BINA), Bar Ilan University, Ramat-Gan 52900, Israel*

E-mail: valentina.trovato@unibg.it

ABSTRACT

Nonfunctionalized carbon nanotubes featuring length over than 500 μm, were mixed with an amino-functionalized sol-gel precursor and a highly volatile solvent in order to obtain a well-dispersed solution. Finally, a thickener was added to the nanotubes dispersion thus obtaining a viscous paste, which was deposited on cotton fabrics through knife-over-roll technique thus achieving a surface coating with high electrical conductivity. The as-prepared conductive cotton fabrics were characterized by different chemical-physical techniques and showed a sheet resistance of about $9.5 \bullet 10^2$ Ω/sq. Developed conductive fabrics can find applications as conductive material or wearable sensors.

Key Words: Carbon nanotubes; sol-gel technique; Conductive polymers; Smart Textiles.

1. INTRODUCTION

Electronic Textiles arise from the demand for wearable conductive materials characterized by comfort, flexibility, stretchability and lightweight. Conductive metal oxide fibers or metals are been the building materials for the first electronic textiles, knitted or woven with conventional fibers [1]. In recent years, several technologies were assessed in order to overcome the typical disadvantages of these materials (e. g. low flexibility and comfort), among which dip coating, layer-by-layer deposition, chemical plating and so on, thus designing conductive textiles with the maintenance of flexibility and wearability of textiles. Besides, electronic textiles can be obtained by the incorporation of conductive polymers in textiles, which representative examples are: polyaniline (PANI), poly (3,4-ethylenedioxythiophene) PEDOT, polypyrrole (PPy) [2]. During the last years, a research field focused on carbon nanotubes (CNT) was grown with the aim of realizing wearable electronics for application in different fields such as sensors, antistatic materials, energy harvesting, electromagnetic shielding coating and storage [2]. The several properties of CNT, some of many consisting in ultra-lightweight, great thermal and electrical conductivity, high flexibility and aspect ratio, have made them interesting for the design of smart textiles [3]. Due to their nature, CNT are known to their tendency to agglomerate according to van der Waals attractions, and in this regard, several strategies have been investigated to overcome this feature. In this regard, an interesting approach is represented by the sol-gel technique, a synthetic route that allows realizing carbon composites ceramic-based with high electrical conductivity [4]. Moreover, the advantages coming from both the sol-gel process and CNT add up to cotton fabrics ones, by converging in the realization of smart textiles featuring interesting properties and widely studied during the last decade [5]. Textiles, as substrates, are of great importance in sensor fields thanks to the advantages they lead, among which flexibility, breathability and comfortability [6]. These features make textiles the optimum substrates for the realization of wearable devices for health monitoring, for the assessment of patient's conditions in a rapid and comfortable way.

In this work, nonfunctionalized carbon nanotubes featuring length over then 500 μm were employed for the realization of a stable and homogeneous solution for textile applications.

Carbon nanotubes were mixed with an amino-functionalized sol-gel precursor, isopropyl alcohol and a polyurethane thickener. The simultaneous use of the sol-gel precursor and a highly volatile solvent ensures the dispersion and homogeneous distribution of CNT, by acting on the π-π stacking interaction among nanotubes thus preserving their structure and electrical properties. The CNT viscous paste was deposited on cotton fabrics through knife-over-roll technique in order to obtain surface CNT-coating onto textiles with electrical conductivity. Treated cotton fabrics were characterized thoroughly by different chemical-physical technique thus confirming the efficacy of the designed procedure. Finally, the electrical properties of the CNT-textiles were tested through surface resistance measurements.

2. MATERIALS AND METHOD

(3-Aminopropyl)triethoxysilane (APTES), isopropyl alcohol and polyurethane thickener (PU) were purchased from Sigma Aldrich, and F.T.R. S.p.A, respectively. Scoured and bleached 100% cotton samples before experiments were washed with non-ionic detergent, rinsed with de-ionized water, dried and finally conditioned in a climatic chamber for 24 h, under standard conditions.
A certain amount (0.8 mg/mL) of Carbon Nanotubes (CNT), synthesized according to previous research [7-9] was mixed with 0.1 M of silica precursor (APTES) and isopropyl alcohol under vigorous stirring in ultrasonic bath for 2 h. Finally, according to Rosace et al. [10], a proper amount of PU thickener was added to the CNT solution thus obtaining a CNT viscous paste (p-CNT). The latter, was spread on cotton fabrics by knife-over-roll technique thus obtaining a thin nanotubes coating layer on the treated surface of textiles. The treated samples were cured (120 °C, 2 min) in a convection oven thus obtaining the samples coded CO_p-CNT. To test the durability of the coating, the treated fabrics were subjected to one washing cycle according to the standard EN ISO 6330:2012.
Uncoated and coated cotton fabrics were thoroughly analyzed according to different chemical-physical techniques in order to evaluate both morphology and chemical structure of samples. The morphology of textiles was investigated with a FEI Magellan 400 Extreme High-resolution scanning electron microscope (HRSEM). The presence of the coating on cotton surface and its chemical composition were investigated through Fourier Transform Infrared spectroscopy (FTIR) with a Thermo Avatar 370 equipped with an attenuated total reflection accessory (ATR) by collecting FTIR spectra in the range 4000 – 550 cm^{-1} (resolution of 4 cm^{-1} and 32 scans). Spectra of textiles samples were reported as function of Absorbance after normalization at 1200 cm^{-1}. Moreover, coated textiles were investigated as function of their electrical properties through electrical resistance measurements carried out with a Source Measurement Unit (Agilent B2961A Low Noise Power Source) by setting the sample on a plexiglass support and fixing its extremities with two metal electrodes connected to the instrumentation. The thickness of the applied coating on cotton surface allows to refer to surface resistance (Rs) thus neglecting the thickness contribution to the measured electrical resistance [11]. Rs was calculed according to the relation between measured resistance values and the width-to-length ratio of the sample, as reported in a previous work [10].

3. RESULTS AND DISCUSSION

3.1 SEM characterizations

By means of HRSEM characterizations, it was possible to investigate changes in the cotton surface morphology after the coating deposition. Uncoated cotton, as evident from the image

in Fig. 1a is characterized by fibrils and bundles and by a smooth surface. This morphology completely changes after the coating deposition (Fig. 1b). Indeed the smooth surface results characterized by several wrinkles due to the presence of carbon nanotubes. Moreover, SEM images showed the homogeneity of the coating and the formation of CNT networks responsible for the electrical conductivity of the treated textiles.

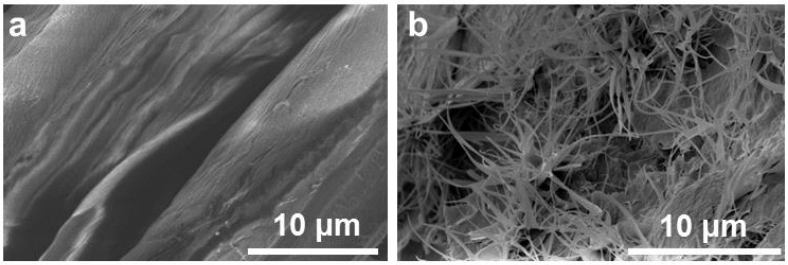

Figure 1. SEM images of uncoated cotton (a) and CO_p-CNT (b).

3.2 ATR-FTIR analysis

The presence of p-CNT coating on the surface of treated cotton fabrics, and its chemical composition, were investigated by means of ATR-FTIR spectroscopy. As evident from Fig. 1 green curve, main absorption bands of cellulose [12] (Fig. 2 on the left) results overlapped by coating IR peaks. Moreover, in the spectra of coated cotton (Fig. 2 red curve) peaks relative to C=O stretching of urethane functionalities and its interaction with N-H groups (1725 cm^{-1} and 1693 cm^{-1}, respectively), as well as the peak relative to C-N stretching and N-H bending (1537 cm^{-1}) [13], are evident and characteristic of the coating. The unique bands assigned to the sol-gel matrix is evident at 810 cm^{-1} (Si-O-Si symmetric stretching).

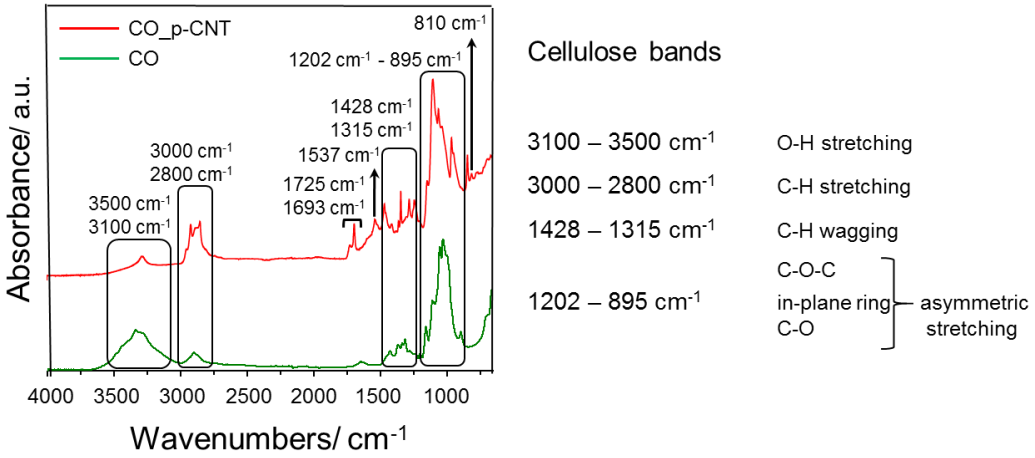

Figure 2. ATR-FTIR of uncoated cotton (CO) and coated cotton with p-CNT (CO_p-CNT). On the right, typical absorption bands of cellulose.

3.3 CNT-dispersion mechanism

According to SEM and FTIR findings, it was possible to suppose that both the APTES and the isopropyl alcohol act on the CNT dispersion. Indeed, APTES has the capability to diffuse into gaps of aggregated CNT and then, to form a self-assembled silica network on the CNT surfaces. Moreover, at alkaline pH, the charged amine groups of APTES seems to be able to generate a

Coulombic charge repulsion among CNT as a consequence of their alignment disposition opposite to CNT surfaces in accordance with some previous research [14], thus providing a uniform and well-dispersed sol. Moreover, the uniform dispersion of CNT was enhanced by the addition of isopropyl alcohol that does not interfere with CNT distances because of its complete evaporation during the curing step and as a consequence, by preserving their electrical properties. Finally, the polyurethane thickener ensured urea linkages with amine groups of the silica precursor as confirmed by FTIR spectra.

3.4 Electrical properties

For the realization of electrical conductive CNT-based coating, an important parameter to be taking into account is the percolation limit of nanotubes. It represents the minimum concentration of conductive particles useful to obtain a conductive network that broadens the whole system [15]. Several parameters influence this concentration limits, among which aspect ratio (length/diameter) and dispersion of fillers in a polymer matrix [16]. In this research study, the percolation limit of CNT was 0.16 w/w % and the surface resistance of $9.5 \cdot 10^2$ Ω/□ has been measured. As reported in literature [17], the length and dispersion of CNT influence the electrical properties of the resulting composite. In particular, high aspect ratio CNT, homogeneously dispersed, ensure lower Rs values than those of CNT with lower length (lower aspect ratio) [17]. Moreover, in order to evaluate the electrical properties of the employed CNT with high aspect ratio, their dispersion degree in the polymer matrix was evaluated. Optical image (Fig. 3) of p-CNT shows a uniform distribution of the tubes resulting in bundles highly interconnected with a low degree of aggregation and several electric contact point.

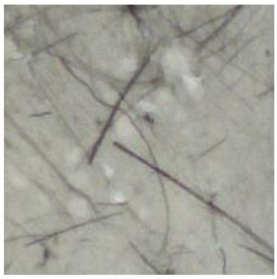

Figure 3. Optical image of p-CNT.

Compared with literature data [10, 18, 19], the obtained Rs value of the CNT coating evidenced the potentiality of high aspect ratio nanotubes and of the designed coating strategy in the realization of conductive coating for textiles applications. Furthermore, the washing fastness of the coated cotton samples was assessed in order to evaluate the CNT leaching, relevant information for human safety. Washing cycle demonstrates that p-CNT does not provide leaching from the coating thanks to the similar Rs value obtained before and after the laundering. The coating fastness could be explained according to the chemical interaction of CNT with the polymeric matrix, as previously demonstrated by FTIR analysis.

4. CONCLUSIONS

In this research study, an efficient strategy for the dispersion of long CNT, the realization of conductive coating and its application on cotton fabrics were described. Experimental findings demonstrated the homogeneity and the good dispersion of CNT in the polymeric matrix and the formation of conductive networks characterized by high surface resistance values. The designed CNT cotton fabrics benefit from the advantages of high aspect ratio CNT, the sol-gel process

and the textile fabrics by providing reliable and efficient wearable smart materials for applications in different field such as sport and healthcare.

5. REFERENCES

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