

Single wall carbon nanotubes - polymer composite materials and their biomedical applications

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received 9 February 2025

Summary. — This work aims at illustrating a new composite material (CM) useful in biomedical field. In particular, the composite obtained through the self-grafting of a Single Wall Carbon Nanotubes (SWCNT) aqueous dispersion onto the poly-dimethyl-siloxane (PDMS) film surfaces is investigated. Both electrical and mechanical properties of this CM have been analyzed, a new investigation has been carried out to confirm the stability of SWCNT grafting and the prototype of an artificial bladder has been realized. This study proves a good reliability of the CM due to about 100 μm of SWCNT penetration depth into the polymer surface and consequently its excellent electro-mechanical properties.

1. – Description

Aiming at the exploitation of the unique carbon nanotubes (CNTs) properties, recent technological research has been devoted to CNTs incorporation in polymeric CM which find applications in electronics, aerospace, sensors and medicine [1-4]. This work too is focused on achieving three-dimensional sensors based on SWCNT self-assembled on polymeric substrates. The evidence that SWCNT self-graft onto different polymeric materials [5] immediately attracted further investigation; the strongest reason is that stable self-grafting can be obtained without the introduction of reagents or chemical catalysts, but exploiting an adhesion process strongly favored by thermal cycle close to the melting temperatures of the host polymer matrices. The importance of this work lies in the use of stability, mechanical strength and extensibility properties of the adsorbed SWCNT agglomerates on polymer films; in particular, self-grafting of SWCNT bundles onto PDMS is exploited to develop a new artificial bladder prototype. The bladder is able to expand significantly to contain urine and the pressure inside it increases progressively as it fills, until it reaches the urge to urinate. The aim is therefore to reproduce this organ, in which our electrical and stretchable sensor is able to simulate the urge to urinate. Our

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approach is based on the deposition of SWCNT aqueous suspensions on the solid polymer substrate through a mask that supplies the desired geometry of the device. Upon drying of the suspensions, SWCNT self-graft on the polymer substrate; the depth of CNTs bundles penetration into the polymer gives rise to a very effective functional material. In our prior research, we realized a CM in which SWCNT self-grafted and embedded in poly-ethylene (PE) films [6]. This combination harnessed the thermoplastic properties of the polymer while leveraging the conductive and elastic attributes of CNT bundles. Such properties were used to realize arrays of submillimetre conductive tracks on PE films. These stretchable and mouldable tracks were implanted between the pia and the dura mater brain cortex of laboratory rats, allowing for successful probe of their electro-corticogram signals for several months.

2. – Materials and methods

The detailed procedure of preparation of our composite films has been described in [7], and we briefly explain here only the analytical methods used to study these CM.

SEM micrographs were obtained by a Tescan VEGA electron microscope. To properly investigate the interface between SWCNT and the PDMS, secondary electron images of the CM section were collected in high-vacuum condition and with beam energy of 2 kV and beam current of 30 pA.

To evaluate the CNT penetration depths, specimens were analysed by Confocal Raman Spectroscopy using a Horiba Xplora Plus instrument. Spectra were collected using a 50 \times objective, laser wavelength 638 nm (maximum output power 30 mW) and were extended in the spectral range from 60 cm^{-1} to 3200 cm^{-1} . The inelastic Raman scattering signal was recorded while scanning the laser focal region along the z -axis perpendicular to the sample surface: the decrease of the SWCNT Raman G band intensity allows for a qualitative evaluation of their penetration depth.

The electro-mechanical properties of the CM were investigated through load-strain, resistance-strain, and current-applied voltage cycles measurements carried out by an Elis Z20 Tensile Machine equipped with a high voltage power supply (Bertan 205 A-05R) and a digital multimeter (KDM-360CTF).

The artificial bladder prototype was fabricated using a two-component PDMS Silicone RPRO Tech33 (purchased from Reschimica) that has physical-chemical and mechanical properties very similar to the PDMS analyzed previously, even though this Silicone material is not yet certified for biomedical application. Equal volumes of base and hardener were mixed and, after 10 min of degassing, were cast on a nearly spherical inflatable support. After silicone polymerization, the support was extracted from inside the silicone model and the SWCNT strain sensing conductive track was realized across a couple of copper foil electrodes sealed into the silicone model and emerging from it, following the usual drop casting procedure. The artificial bladder thus prepared was tested by filling and emptying it with water while recording the variable electrical resistance of the conductive track.

3. – Results and discussion

SEM characterization of the CM section (obtained by soaking the CM specimens in liquid nitrogen and fracturing them) was carried out to analyse the SWCNT concentration gradient in the PDMS matrix along the direction perpendicular to the polymer film

surface. The distribution of the SWCNT bundles at the surface of the film is inhomogeneous since it arises from drop casting of a non-uniform suspension. Consequently, the concentration of SWCNT in the polymer bulk is also not uniform. Figure 1(a) shows a detail of the section fracture, where one can see that most of the CNT layer is completely soaked by the polymer.

Furthermore, volume-averaged information on the CNT diffusion into the PDMS matrix can be obtained by confocal micro Raman spectroscopy, looking at the Raman spectral fingerprints of both SWCNT and PDMS perpendicular to the film surface. By following the SWCNT contribution peak ($1580\text{--}1600\text{ cm}^{-1}$) in red and that of PDMS (CH_2 stretching mode $2900\text{--}3000\text{ cm}^{-1}$) in gray it is possible to reconstruct a 3D point-by-point Confocal Raman spectroscopy scan (fig. 1(b)), acquired to detect and localize the components of this region. From this analysis, it has been possible to evaluate the SWCNT penetration depth of about $100\text{ }\mu\text{m}$.

The investigation of the electro-mechanical properties of the CM realized is necessary in view of their use to develop elastic prosthetic devices endowed with built-in sensors and electrical connections. Figure 2(a) shows that 6 cycles of load/strain measurements performed over a strain range up to $(\delta L)/L = 40\%$ are perfectly reproducible with only minimal hysteresis. The plot shows no significant differences between the first three cycles and three subsequent cycles performed after relaxing the sample overnight with no strain. It is interesting that the corresponding resistance/strain plot, reported in red in fig. 2(b), shows a deviation of the resistance, on releasing the strain below 30 %, the final resistance remaining approximately 6% higher. The observed behaviour might be due to the decrease of the number of conductor-conductor electrical contacts and tunnelling junctions caused by the rapid filling by the polymer of the spaces between individual conductive components created by straining the composite material, Lee *et al.* [8]. Several consecutive strain/release cycles in the strain range 0–40% of the SWCNT/PDMS CM, show a repeatable behaviour with only minor resistance variations. Thus, although the electrical conduction of our composite is slightly less stable compared to its load vs. strain behaviour, it seems perfectly suitable for most application fields. Finally, the I/V plots (not shown here) for different strain values measured to check the conduction behaviour of the devices at different applied voltages show a basically linear behaviour; no qualitative deviation from a simple ohmic behaviour is however observed even on a stretched conductor.

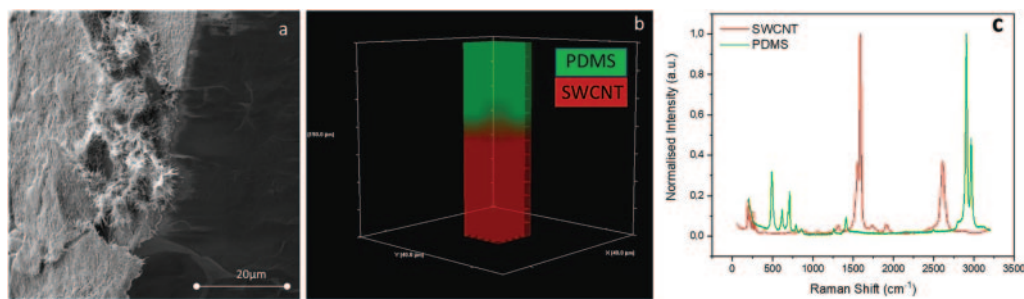


Fig. 1. – (a) SEM investigation of SWCNT/PDMS section; (b) slice-by-slice Raman 3D map, showing a qualitative picture of the distribution of CNT and PDMS within the CM film; (c) Raman spectra in which the fingerprints of SWCNT (red) and PDMS (gray) are highlighted.

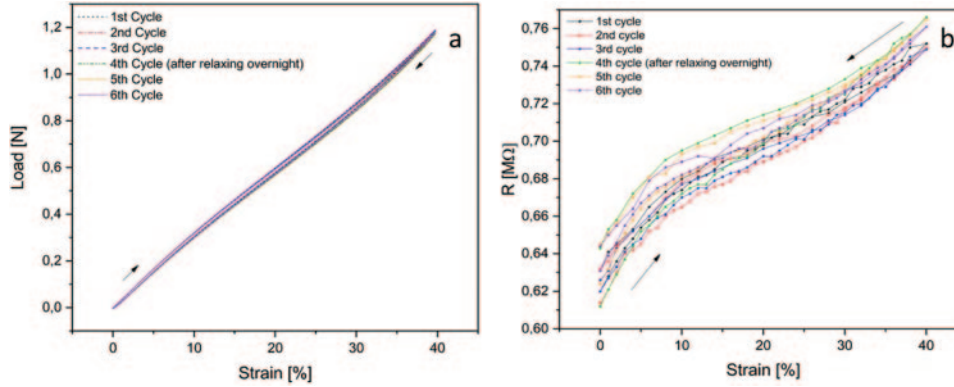


Fig. 2. – (a) Cyclic load/strain test and (b) resistance/strain test on three consecutive cycles, on a conductive track and on the same specimen after 15 hours of relaxation at the original unstretched length.

Having assessed the stability of the composite and its properties, we developed an artificial bladder prototype, endowed with a SWCNT built-in sensor of the strain due to urine filling. The strain sensor was “printed” on the model to record the complete process of filling and emptying. The resistance increases on water filling and decreases on water emptying.

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The authors acknowledge the support of the ISIS@MACH ITALIA Research Infrastructure, the hub of ISIS Neutron and Muon Source (UK) (MUR official registry U.0008642.28-05-2020, 16 April 2020), and the support of the MIMIT Project No. F/180028/01/X43, “Sistema closed-loop per la diagnosi, il monitoraggio e il trattamento di malattie neurologiche tramite Brain Machine Interface”.

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