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Stretchable conductors made of single wall carbon nanotubes self-grafted on polymer films

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Abstract. Aiming at the accomplishment of stretchable and elastic conductive devices, we report in this work electrical, mechanical and thermal characterization of a composite conductive material obtained by self-grafting of single wall carbon nanotubes bundles on different polymeric films. The dependence of resistance of micrometric composite conductors on the applied strain was measured; the current breakdown threshold was also measured together with the corresponding temperature increase. Finally, the dependence of an AC signal attenuation for a bi-layer single wall carbon nanotubes conductor sandwiching a 25 μm thick poly-ethylene film was obtained as a function of the signal frequency, and the experimental results were satisfactorily compared to a simple RLC model.

1. Introduction

In recent years the increased request for flexible and stretchable electronic devices has stimulated the study of conductive composite materials (CCM) based on carbon nanotubes (CNT) and polymer films [1]. The process of grafting CNT onto polymer film surfaces is indeed of particular importance to obtain flexible and stretchable planar devices. Such surface composites would find wide applications for sensors, electronic devices, implantable prosthetic aids, extensible displays, and even smart clothing. The particular mechanical and electrical properties of CNT [2] make both single wall (SWCNT) and multi wall (MWCNT) carbon nanotubes suitable to obtain new CCM. CNT/polymer composite materials, obtained by chemical functionalization [3] of SWCNT and MWCNT have been the object of extended studies in the last decade; less analyzed are, on the contrary, self-grafted SWCNT on polymer films, although this composite material shows significant advantages: simple realization, cheap fabrication and the combination of the mechanical properties of polymeric films [4] with the conductive properties and the strength of carbon nanotubes bundles [5]. In this study, we characterize the electrical conduction of different CCM based on SWCNT/polymer films obtained by such simple and cheap self-grafting method which does not involve chemical functionalization.

2. Experimental details

2.1. Material

Purified SWCNT, produced by the HiPCo method [6] were purchased from Carbon Nanotechnologies Inc. The diameter of the individual SWCNT is 0.7 nm, with both armchair and zig-zag species present.

SWCNT are grafted on different polymer films by the drop-casting technique. A spreading liquid was obtained by dispersion of 10 mg of SWCNT in 10 ml of a water/ethanol solution (70/30%), adding 3 mg of Sodium-dodecyl-benzene-sulfonate (SDBS), to increase the solubility of bundles. The mixture was sonicated for 10 minutes and then ball milled for two more minutes. The suspension obtained in this way was not completely uniform but finer than before ball milling, and it was possible to pass it through a 200 μm needle on suitable stencils that define the shape of the electrical conductors [7].

The polymeric film used were commercially available polymers (medium density polyethylene (MD-PE), high density polyethylene (HD-PE), poly-isoprene (natural rubber latex), polyvinyl chloride (PVC)).

2.2. Electro-mechanical characterization

The most interesting feature of this composite material is that it allows for electrical conduction through a composite wire that may be stretched in the course of its operation, even when it is of micrometric size. Therefore, we want to characterize the dependence of the wire conductance (or resistance) on the wire extension. Once this is established, the wire can be used as a reliable conducting device in strongly vibrating environments; or it can be used as a strain sensor if the resistance change is sufficiently large. To obtain the dependence on strain of the electrical resistance of a micrometric conductor (typical section of the conducting tracks is of the order of 10 μm x 500 μm), 20 mm long films of different polymers, on which tracks of SWCNT had been cast and self-grafted, were firmly clamped across the variable gap obtained on sliding a manual micrometric optical positioner from a minimum aperture of 14.7 mm to a maximum of 40 mm. An Agilent 3458A digital multimeter was connected to the copper clamping plates to measure resistance values in the DC mode while the gap was progressively extended. Details can be found in [7].

2.3. Electrical and thermal characterization

To study the limits of the electrical application of our devices, the temperature threshold of the breakdown was investigated. It can be envisaged that the random presence of thinner parts of the conductive track may give rise to hot spots, which in turn trigger the thermal breakdown of the device. Therefore, the conductor temperature was sampled by a Cr-Al low thermal capacity thermocouple (0.25 mm diameter). Spatially periodic temperature measurements were performed to know the inhomogeneity of the track thickness with a sampling density of 1 mm on the planar orthogonal directions. Fitting the thermocouple end through a drilled polycarbonate slab, which acts as a precision drive for localized temperature measurements as well as a thermal insulator of the device, more precise measurements were obtained. Finally, the current was slowly increased, and the temperature of the hottest point of the conductor was sampled, up to its breakdown limit.

2.4. Small signal characterization and modelling.

The electrical behaviour of the CCM was investigated by designing two different conductive track conformations: a single layer SWCNT conductor with a single conductive track in a range 10÷30 μm of thickness deposited on a 25 μm MD-PE substrate, and a bi-layer device with two conductive SWCNT tracks like a sandwich on both faces of the MD-PE film. The voltage attenuation as a function of frequency and the attenuation and the dephasing as a function of strain were characterized. Also, to properly characterize and compare the SWCNT device with the more complex bi-layer SWCNT device, a measurement test-bench, based on a low frequency VNA (Vector Network Analyzer), was chosen for the second device. To this purpose the bi-layer SWCNT device was mounted in series configuration on a custom 2-port coaxial test-jig), allowing accurate measurements of the expected moderately high impedance values. Measurements were performed by a Keysight ENA E5061B from 5 Hz to 10 MHz VNA on a coaxial HP 3.5 mm cal-kit and by exploiting a standard SOLT (Short Open Load and Thru) calibration technique.

3. Result and discussion

Figure 1 shows different Scanning Electron Microscope (SEM) views of a SWCNT conductive track self-grafted onto a 25 μm MD-PE film. Figure 1a is a low magnification view of the conductive track at normal e-beam incidence. Apart from the non-uniform surface structure, one can note that the grafted CNT layer, being non-uniform, induces some strains in the film, giving rise to the slight undulation of the film.

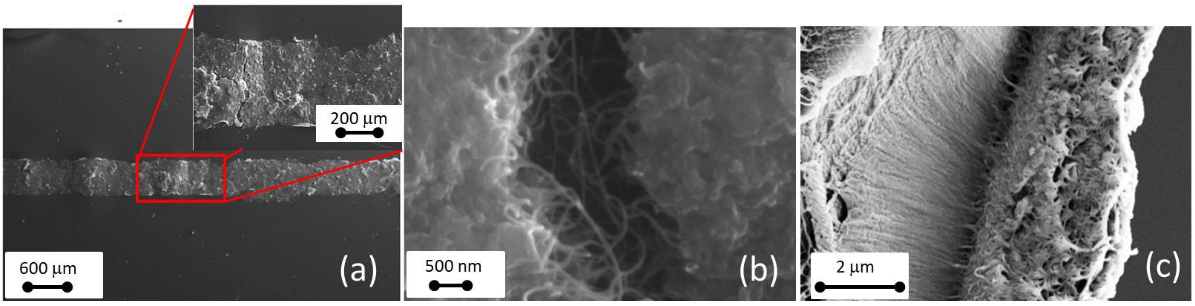

Figure 1. SEM characterization of conductive tracks: a) 0.5 mm width, 10 μm thick conductive track on a 25 μm MD-PE film, showing wrinkling of the film due to non-uniform rooting of the SWCNT into the polymer; b) a fracture in the SWCNT layer caused by straining the film, bridged by many CNT ropes; c) section of a composite conductor showing deep rooting of the CNT into the MD-PE film (Image acquired with a Cambridge S200 instrument with an incident beam energy of 20 keV).

On straining the film by more than approximately 10%, cracks begin to appear in the SWCNT upper layer, which at this stage are still well connected by CNT "ropes" which unwind from the compactly organized bundles of the track (Figure 1a - inset and Figure 1b). Electron microscopy also unveils one rather important feature of the process, which is based on different mechanisms. Figure 1c shows a section of the MD-PE film with the deposited SWCNT layer. The first SWCNT deposited on the surface tend to penetrate the soft polymeric chains structure sinking into it and, according to simulation models [8] allowing polymer macromolecules to intertwine and coil around the much more rigid carbon structure. This composite structure serves as a basis for further deposited nanotubes which hold onto them. It appears from the images that the upper layers (to which most of the conduction should probably be ascribed) are held down onto the polymer by large CNT "ropes" which appear as soaked in the polymer. On observing at larger distance from the polymer, where this soaking is probably no longer operational, CNTs are simply intertwined to more efficiently immobilized CNT layers, and the force necessary to remove the layer is only the force needed to disentangle the different SWCNT coils from each other. Thus, at least in the case of MD-PE, two different adhesion mechanisms are present: a) CNT to MD-PE for the lower deposited layers and b): CNT-CNT for the upper layers. The latter appears to be weaker than the former, given that upper layers can be progressively removed by repeated stripping of adhesive tape, but to remove the former a strong surface deterioration becomes necessary [7]. The understanding of these mechanisms accounts for the features observed in the strain-resistance experiments.

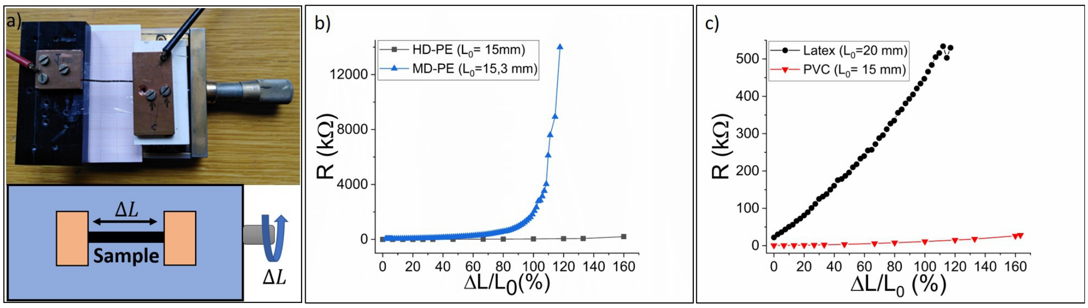

Figure 2. Resistance vs strain for devices based on different SWCNT/polymer films: a) Experimental apparatus and layout of the SWCNT/polymers device, b) HD-PE and MD-PE polymer substrates c) Latex and PVC polymer substrates.

Figure 2 reports strain-resistance plots for some of the polymer investigated.

Table 1. Strain sensitivity values for four CCM.

Polymer	Strain $\frac{\Delta L}{L_0}()$	Sensitivity $\frac{\Omega}{\mu m}$	Polymer	Strain $\frac{\Delta L}{L_0}()$	Sensitivity $\frac{\Omega}{\mu m}$
HD-PE	$0 \div 40$	0.4	**poly-isoprene (rubber latex)**	$0 \div 65$	375
	$40 \div 120$	4		$65 \div 120$	546
	$120 \div 160$	33			
MD-PE	$0 \div 50$	299	**PVC**	$0 \div 60$	0.4
	$50 \div 100$	3051		$60 \div 150$	1.2
	$100 \div 120$	71650		$150 \div 170$	4.4

It is evident how, depending on the type of application and sensitivity required in case these wires are used as strain sensors, one can use one polymer or the other, and pre-strain the composite track or not in order to adapt the sensor to the needed sensitivity or conductivity. Each polymer shows a trend with more and characteristic slopes in different regions, implying a specific sensitivity for each strain range, as reported in Table I.

Figure 3 shows the applied voltage dependence of the current in the device and its corresponding temperature, up to the thermal breakdown of the material. Note that the device breakdown does not correspond to the melting point of its polymeric substrate, but it is remarkably lower. This may imply that hot points are present in all our devices, although, due to the low resolution of our temperature sampling (1 point/mm), we could not detect them all. Note also that the behaviour of the PVC based device is noticeable different from those of the other three devices.

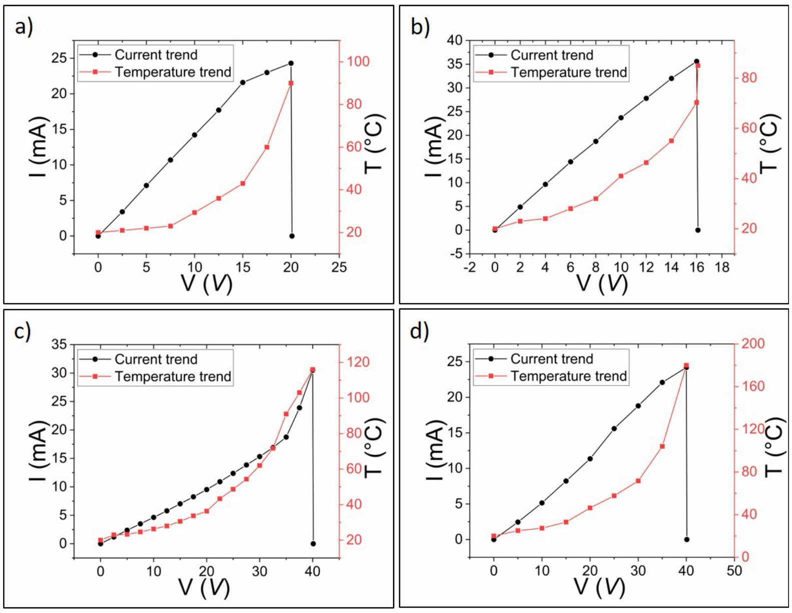

Figure 3. Current and temperature behaviour vs. applied voltage for four CCM up to their breakdown limit. a) SWCNT/MD-PE, b) SWCNT/PP, c) SWCNT/PVC, d) SWCNT/Latex.

Aiming to increase the application fields of devices, preliminary studies about frequency response have made, the measurements don't show an attenuation at a frequency lower than 100 kHz.
This range of frequencies is extended well beyond those needed for neurological applications that we tackled recently [7]. To answer requiring of high frequencies and more robust devices, the behaviour of 15 and 30 µm thick samples vs strain is analysed. The attenuation and the temporal phase shift in function of strain, at a higher frequency than the neurological typical range is studied; we show in this work a representative behaviour at 1MHz (Figure 4).
In Figure 4 it appears evident that both attenuation and dephasing increase with the device strain, thicker conductors behaving slightly better than thinner ones: the attenuation of the 15 µm sample becomes relevant at a strain of about 20%, while for the 30 µm one it increases at about 40% (Figure 4a). Some dephasing is present already with no strain, and it increases rapidly for both samples above 20% (Figure 4b). Work is in progress to assess the behaviour of SWCNT conductors on different polymers.

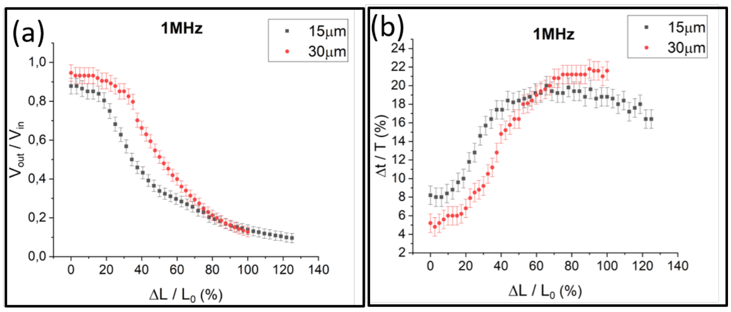

Figure 4. a) Attenuation and b) dephasing as a function of relative strain at 1MHz frequency (the bars represent the errors obtained through the propagation of the fluctuation of the signal.)

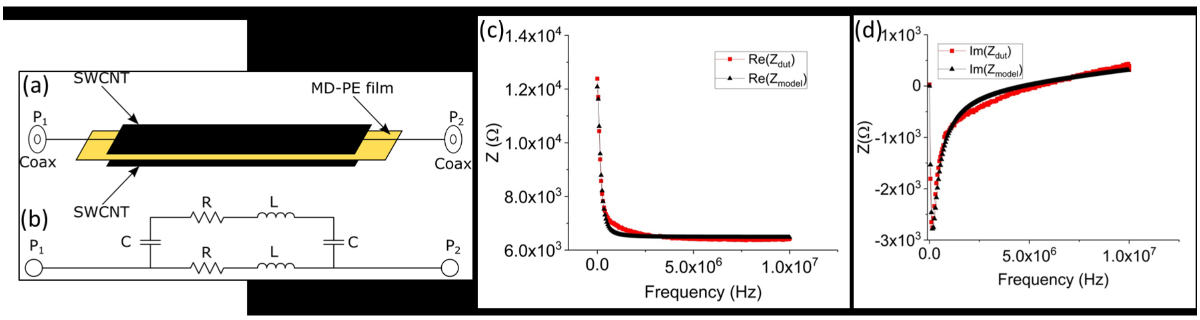

Figure 5. a) Layout of the proposed bi-layer SWCNT device; b) lumped equivalent circuit topology; c) real impedance vs frequency of a bi-layer SWCNT device: red-square scatter line measured (named Re(Z_{dut}) in the caption) and black-triangle scatter line modelled (named Re(Z_{model}) in the caption); d) imaginary impedance vs frequency of bi-layer SWCNT device: red-square scatter line (named Im(Z_{dut}) in the caption) and black-triangle scatter line modelled (named Im(Z_{model}) in the caption).

For the purpose of widening the range of application, we have also studied conductive nanotube tracks grafted on both faces of a polymer film. In Figure 5a a sketch of the bi-layer type device (made of two SWCNT layers deposited on both faces of a 25 µm thick MD- PE film) is reported together with the equivalent circuit topology (see Figure 5b) devised to represent such a physical structure. In particular, a capacitive coupling has been assumed between the layers and a simple series RL model for each layer. The good agreement between the modelled complex impedance and the measurements (Figure 5c, 5d) validates the adopted circuit topology. It is relevant to note that the capacitive coupling is strictly required to correctly predict the frequency trend. More in detail, the overall capacitive coupling was estimated in the order of 4.9 pF/µm whereas the remaining components values, i.e. the selfinductance and the series resistance of the conducting track, were estimated to be 43 pH/µm and 0.43 Ω/µm respectively. Components values were extracted by exploiting a gradient optimization algorithm to minimize the distance between measurements (see Sec. 2.4) and the modelled complex impedance.

4. Conclusions

We have fabricated and characterized stretchable and flexible conducting devices which can be used both as conductors in mechanically unstable environments and as strain sensors. SEM characterization shows deep entangling of the SWCNT in the polymer structure which supplies a much higher adsorption force between CNT and polymer with respect to the weaker adhesion of the CNT-CNT entanglement of the upper layer. Our electrical characterization shows that, depending on the application and on the sensitivity required for the strain sensor, one can choose among a selection of more or less steep behaviours of the different substrates, or can select the proper operational region of extension. We have also measured the specific conductivities of our composite conductors, obtaining values ranging approximately from 0.4 to 400 (Ω/µm) depending on the device and on the strain region. The thermal breakdown threshold is invariably lower than the polymer substrate melting point, which leads us to suspect that there may be many more hot spots than we could detect, and that our future research should focus on more uniform CNT layers, less prone to the presence of localized overheating.

Finally, the dependence on frequency of the attenuation and dephasing of an AC signal shows a stable behaviour up to almost 1 MHz. A simple RLC model accounts satisfactorily for both the real and imaginary part of the impedance. Attenuation and dephasing at 1 MHz were also measured as a function of the device strain, yielding a strong increase in both parameters above 15-20% extension.

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