Electrical Conduction in vertically Aligned Carbon Nanotubes Polymer Nano-composites with High Packing Density

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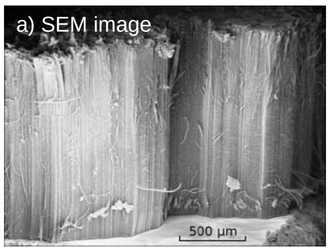
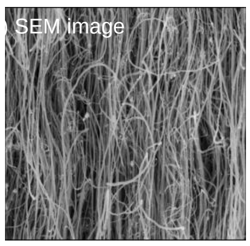
Abstract and introduction

Carbon nanotube reinforced polymer composites may provide a unique option for the aviation industry due to their potential high strength-to-weight ratio and multifunctionality. Specifically their electrical conductivity and consequent shielding effectiveness can be strongly enhanced by featuring vertically aligned nanotube arrays in the polymer composites. We report here a detailed study of the electrical transport mechanism within aligned carbon nanotube reinforced polymer composites. The experimental part of our investigation relies on extensive use of both macroscopic and high spatial resolution experimental techniques by which we shed light on the factors dominating the electrical transport, namely the contact resistance which depends on the wetting properties of CNT-metal interface, and the resistance at point-junctions which scale with the size of interconnecting tubes. Our modeling effort describes well our experimental observations and reveal the keys to enhance further the nanocomposite intrinsic electrical conductivity and to reduce its interfacial contact resistance in order to achieve improved device performance.

Vertically Aligned CNTs





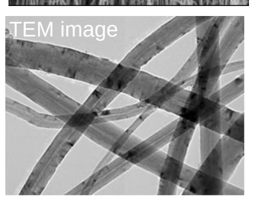
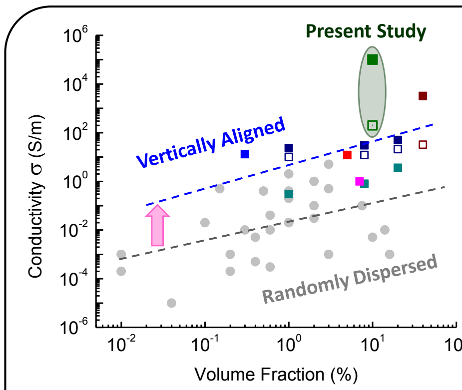


Figure X0: a) SEM images of vertically aligned carbon nanotubes grown on quartz substrate by catalytic chemical vapor deposition. b) high magnification SEM images reveal that the multiwall CNTs array presents a high degree of alignment ± 7° over a length exceeding a millimeter. c) high magnification TEM images show that MWCNTs have improved structural and crystalline properties. The image analysis reveal broad distribution of CNTs diameter between 10 to 110 nm.

Macroscopic Electrical Conductivity



		Material Description	Reference
●		Randomly dispersed CNT, Matrix: Epoxy	Bauhofer *et al*. Compos. Sci Technol (2009)
■	□	Aligned MWCNTs, Matrix: Epoxy	Cebeci *et al*. Compos. Sci Technol (2009)
■		Aligned MWCNTs, Matrix: PMMA	Peng *et al*. Chem Phys Lett (2009)
■	□	Aligned MWCNTs, Matrix: Epoxy	Hinds *et al*. Science (2004)
■		Aligned MWCNTs, Matrix: PEDOT/Epoxy	Vaddiraju *et al*. Appl Mat Interfaces (2009)
■		Aligned MWCNTs, Matrix: VRM34	Megalini *et al*. Nano Syst Technol (2009)
■	□	Aligned MWCNTs, Matrix: Si Elastomer	Yao *et al*. Nanotechnology (2006)
■	□	Aligned MWCNTs, Matrix: Epoxy	Souier et al. [1,2]

● Volume conductivity ■ Cross-plane conductivity □ In-plane conductivity

Figure X1: Review of prior data for the electrical conductivity of CNT-Polymer composites. The electrical conductivity seems to increase with the CNT filler density following a power law as predict by the percolation theory. A significant enhancement of the electrical conductivity is obtained by featuring mechanically densified and vertically aligned multiwall CNT composites, making them material of choice for electrical shielding applications.

We present a vertically aligned epoxy composite with the **highest electrical conductivity** reported in the field with **10^5 S/m** in the cross-plane and **200 S/m** in the in-plane directions. In this study, we aim, by using conductive AFM and appropriating modeling effort, to shed light on factors dominating electrical transport in order to explain the unique electrical properties of our material. We aim further to discuss the factors limiting the measurements of the intrinsic composite conductivities by macroscopic techniques.

High resolution nanoscale measurements
1. Cross-plane conductivity

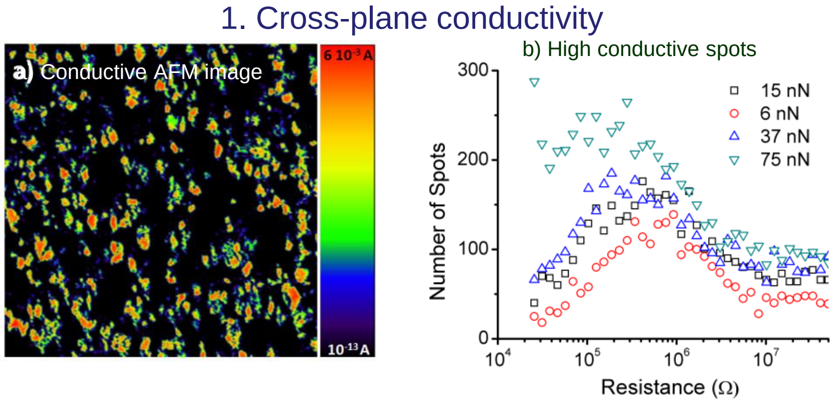


Figure X2: a) High magnification conductive atomic force microscopy image and the corresponding histogram of resistance obtained at various tip-sample loads (*F*). The conductive spots are attributed to protruding CNTs. Their average CNTs diameter is 50 nm which corroborates the TEM analysis. In the line with SEM imaging, the packing density of the composite is 5×10^{13} CNT/m2 which correspond to a volume fraction of 10%.

The resistance values vary between 10 kΩ to 10 MΩ correspond to two contribution : 1) the intrinsic resistance of the tube R_{CNT} (independent of the load) and 2) the contact resistance between the tube (load dependent) which is estimated using Sharvin formulas. This equation was used to fit he experimental data. The local cross-plan conductivity of the composite is evaluated at 10^5 S/m, the value that matches perfectly the macroscopic 4 probes measurements.

C-AFM resistance model :

$$R_{C-AFM} = R_{CNT} + \frac{2e^2}{h} + \frac{4\rho l}{3\pi\left(\frac{3R_{tip}F}{4E^*}\right)^{2/3}}$$

High resolution nanoscale measurements
2.In-plane conductivity

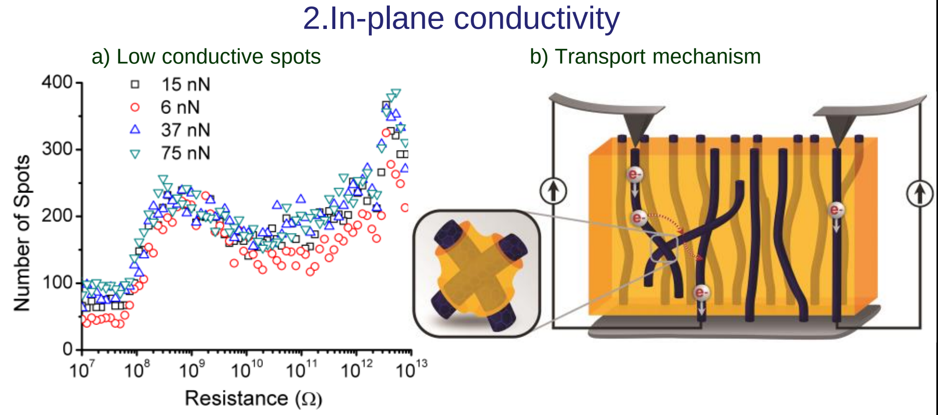


Figure X3: a) The histogram of low conductive spots extracted from C-AFM image and b) the schematic of the electron transport within the composite, during C-AFM measurements. Surprisingly, the C-AFM resistances values do not spread in a continuous fashion, but exhibit two well-defined log-normal distributions. The second distribution of resistance is independent of tip-sample interaction and was attributed to tunneling trough interconnecting CNTs junctions. This scenario is possible when the considered CNT has a poor contact with the back-electrode (here silver paint). In this particular situation , the electrical transport is dominated by the in-plan conductivity. A model based on electron tunneling at CNT-polymer-CNT junction is proposed to fit the experimental C-AFM data.

Tunneling resistance model :

$$R_{tunnel} = \frac{V}{6.2\times10^{10}A_c(\Delta s)^{-2}\left[\varphi\exp\left(-1.025\Delta s\varphi^{1/2}\right)-(\varphi+V)\exp\left(-1.025\Delta s(\varphi+V)^{1/2}\right)\right]}$$

Conclusion

Structural and electrical characterization of the vertically aligned multi-wall CNT arrays embedded in epoxy resin have been performed by means of scanning and transmission electron microscopes coupled to conductive atomic force microscopy C-AFM. The composite exhibits a **highest reported electrical conductivity** measured with Macroscopic and Nanoscopic techniques. We point out the theoretical and experimental method used to extract the intrinsic electrical conductivity of CNTs by varying tip-sample contact force. Moreover, a tunneling model is used to describe the electron transport trough interconnecting MWCNTs junctions which dominate the in-plane electrical conductivity. Our modeling effort describes well our experimental observations and reveal the keys to enhance further the nanocomposite intrinsic electrical conductivity and to reduce its interfacial contact resistance in order to achieve improved device performance.

1. Tewfik. Souier, Marco Stefancich, Matteo Chiesa. Characterization of multi-walled carbon nanotube-polymer nanocomposites by scanning spreading resistance microscopy. Nanotechnology 23 405704 (2012).

2. Tewfik Souier, Sergio Santos, Amal Al-Ghaferi, Marco Stefancich and Matteo Chiesa. Enhanced electrical properties of vertically aligned carbon nanotube-epoxy nano-composites with high packing density.

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