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Piezoresistive response of spray-printed carbon nanotube/poly(vinylidene fluoride) composites

Armando Ferreira [a], S. Lanceros-Mendez [a, b, *]

[a] Center/Department of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[b] BCMaterials, Parque Científico y Tecnológico de Bizkaia, 48160 Derio, Spain

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ABSTRACT

The performance of piezoresistive materials based on carbon nanotube/poly(vinylidene fluoride), CNT/PVDF, composites prepared by spray printing is reported. It is shown that for a CNT concentration close to the percolation threshold, where the piezoresistive response is the largest, the electromechanical response, characterized by the gauge factor, reach values up to 4.4, similar to the values obtained for hot-pressing prepared materials. Further, it is demonstrated that tunnelling is the main mechanism responsible for the electrical response, independently of the preparation method of the material or the microstructural features. The large value of the gauge factor and the easy processing method demonstrates the suitability of these materials for cost effective and large-scale sensor applications.

1. Introduction

Surface coatings are important in science and technology with applications that span domains as diverse as biomaterials, optical coatings, photovoltaic cells or corrosion protection. Intense efforts are being directed toward the development of solution-based methods such as ink-jet printing, screen-printing, doctor blading, and spray coating that can meet the manufacturing requirements for cost-effective and large area processing [1,2].

Many methods are also specific for a given application and only a few are applicable to a wide range of materials and surfaces. An effective and simple solution-based method for the preparation of composite nanoscale films on surfaces is spray-coating. The main advantages of this technology are being cost-effective, allowing high production speed, efficient use of materials, good reproducibility and compatibility with different substrates [3–5].

Increasingly attractive for the development of smart coatings, are functional materials with sensor and/or actuator capabilities such as piezoelectric, pyroelectric, electrostrictive, magnetostrictive or piezoresistive materials, among others, though their use is still very limited for large area applications [6–8].

In this scope, force, pressure and deformation measurements have particularly large significance for practical applications. Different piezoresistive materials whose response is based on different physical mechanisms have been developed: metals typically show gauge factors around 2.0 to 3.2 [9]. In the case of silicon, the gauge factors can reach values up to 120 and silicon based devices have been fabricated with gauge factors as high as 843 [10]. However, these materials are mechanically fragile, show very limited flexibility and are difficult to shape, requiring also complex manufacturing processes and being limited to small area applications.

These facts led to the development of piezoresistive polymer based sensors than can be overcome the aforementioned limitations. Polymer based piezoresistive sensors are typically based either in conductive polymers [11] or in polymer composites with conductive fillers [12].

Conductive fillers include carbon black [13,14], metal powder [15], carbon nonofibers (CNF) [16] and carbon nanotubes (CNT) [17–19], In particular, composites based on CNT and CNF have been developed with gauge factors up to ~4.6 leading to suitable polymer-based strain sensors [20,21].

Poly(vinylidene fluoride) – PVDF – has been used as a polymer matrix for the development of composites mainly due to its piezoelectric properties, when the material is in its β-phase [22]. Sensor and actuator devices have been thus developed based on this polymer and their composites [8,23–27]. On the other hand, PVDF in the nonpolar α-phase is also an interesting material for the development of polymer composites due to its large dielectric constant, chemical inertness, thermal stability and suitable

* Corresponding author. Center/Department of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal.
E-mail address: lanceros@fisica.uminho.pt (S. Lanceros-Mendez).

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mechanical properties [28,26,29]. Further, the development of CNT filled PVDF composites will add suitable electrical characteristics to the material that, at specific filler contents, will induce electro-mechanical responses appropriate for strain sensor applications [30,31].

Taking all of the above into account, the present work reports on the piezoresistive response of CNT/PVDF composites prepared by spray printing in order to provide easy fabrication of large area and patterned –through suitable masks-force and deformation sensors. Further, the sprayed materials are analysed in comparison to similar composites prepared by solvent casting and hot pressing in order to study the origin of the conduction mechanism of the composites.

2. Experimental

2.1. Sample preparation

Single-walled carbon nanotubes (SWCNT, AP-SWNT grade) were purchased from Carbon Solutions Inc., Riverside, California. This SWCNT powder material is synthesized by the electric arc reactor method using Ni/Y catalyst and contains ~30 wt.% metal residue. The average diameter and length of the SWCNT is 1.89 nm and 509 nm, according to atomic force microscopy measurements [32]. Poly(vinilydene fluoride), PVDF, was purchased from Aldrich (M_w ~ 534,000, as obtained by gas phase chromatography).

The composite with thicknesses between 15 and 20 μm were produced by mixing different amounts of CNT (0–5 wt.%) with 20 ml of N,N-dimethylformamide (DMF, Merck 99.5%). The solutions were placed in an ultrasound bath for 6 h in order to optimize CNT dispersion. After this step, 2 g of PVDF were added to the initial solution and placed in a magnetic stirrer for complete dissolution of the polymer and to avoid CNT aggregates. Flexible films were obtained by spray-printing, using a commercial airbrush (Airbrush Kit - Ventus), at a distance of 10 cm using an airbrush pressure of 3 psi. Solvent evaporation and consequent crystallization was performed inside an oven at controlled temperature of 30 °C.

2.2. Sample morphology and CNT dispersion

The morphology of the sample and the dispersion of the CNT were observed by Scanning Electron Microscopy (Leica Cambrigde apparatus, room temperature) after coating the samples with gold by magnetron sputtering (Polaron Coater SC502).

2.3. Electrical conductivity measurements

The room temperature direct-current (DC) sheet electrical resistivity of the samples was calculated from the characteristic I–V curves measured with a Keithley 487 picoammeter/voltage source. Two parallel rectangular gold electrodes were first deposited by magnetron sputtering (Polaron Coater SC502) on one side of the samples. The sheet resistivity $\rho(\Omega.sq)$ was calculated by:

$$\rho = R\frac{D}{L}, \tag{1}$$

where R is the surface resistance, D is the length of the electrode (6 mm) and L is the distance between the electrodes (1 mm). The electrical conductivity is given as $1/\rho$.

2.4. Electro-mechanical characterization

Electro-mechanical tests were performed, as reported in Ref. [31], by measuring the surface resistance change ($\Delta R/R$) with an with an Agilent 34401A multimeter during the mechanical deformation of the sample, applied with an universal testing machine from Shimadzu (model AG-IS, with a load cell of 500 N). Previously, gold electrodes were deposited by sputtering (Polaron Coater SC502) onto one of the sides the samples. The experiment consisted of 4 loading and unloading cycles at a velocity of deformation of 2 mm min^{-1} and 1 mm in z-displacement (Fig. 1).

The sensitivity to strain was quantitatively evaluated by the gauge factor (*GF*): [33].

$$GF = \frac{dR/R}{dl/l}, \tag{2}$$

where R is the steady-state electrical resistance of the material before deformation and dR is the resistance change caused by the variation, dl, in length, l [33]. In terms of geometrical and intrinsic contributions and for the surface mode measurements (Fig. 1) the GF can be expressed as: [33].

$$GF = \frac{dR/R}{\varepsilon_l} = (1+\upsilon) + \frac{d\rho/\rho}{\varepsilon_l} \tag{3}$$

where, $\varepsilon_l = dl/l$, υ is the Poisson ratio and ρ is the electrical resistivity.

The strain on the sample, for the experimental conditions used for the measurement of the GF (a = 15 mm and $l = 3a$), was calculated by: [34].

$$\varepsilon = \frac{3dz}{5a^2}. \tag{4}$$

where d is the material thickness, z is the displacement of the loading bar, a the distance between first and second points of the 4-point bending system, and l is the distance between the lower supports (taken as the length of the sample).

Electro-mechanical tests were performed in samples with concentrations around the percolation threshold, as it was demonstrated that the *GF* is larger for these concentration [31,35]. Each test consisted in up/down cycles of z-displacement. The *GF* was calculated for each cycle using Eq. (2) by taking the best fit by linear regression and given as the average of four different measurements for each sample.

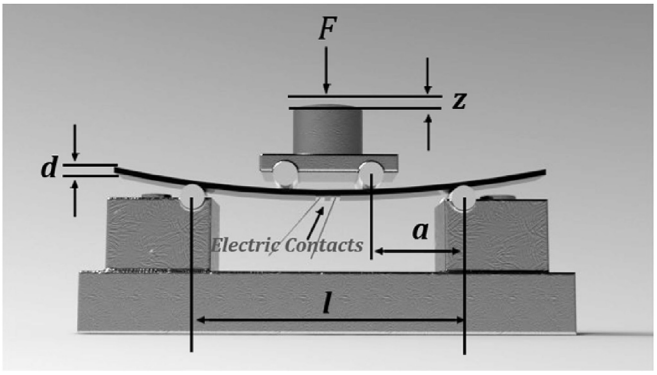

Fig. 1. Schematic representation of the 4-point bending tests: z is the vertical displacement, d is the thickness of the sample (~1 mm), a is the distance between the first and the second bending points (15 mm) and l the distance between the lower supports (45 mm).