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Analytical model for the prediction of the piezoresistive behavior of CNT modified polymers

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In this work a theoretical and experimental study is carried out on the piezoresistive behavior of CNT modified polymers. A novel and easy-to-be applied analytical model is developed, to predict the piezoresistive response of CNT modified polymers, where the conductive network of CNTs within the polymeric matrix is modelled accounting for the three-dimensional random orientation of the nanofiller, the CNT waviness and entangling, and the electrical properties of the material in the undeformed state.

Then, the analytical estimations are compared with the results from new experimental tests on specimens made of multi-walled CNT modified thermosetting matrix as well with data taken from the literature, showing a good agreement.

1. Introduction

In applications where high strength, stiffness and lightweight are needed, Fiber Reinforced Polymers (FRPs) represent an outstanding alternative to metallic materials such as aluminum and titanium alloys. Exploiting their exceptional properties, their employment for advanced applications has increased considerably in the last decades. Particularly, in the aeronautical, automotive and wind turbine fields, structural components made of FRPs allow the performances of the industrial products to be improved, with significant beneficial effects especially in terms of weight reduction.

Components made of fiber reinforced polymers are often subjected to fatigue and impact loads, which cause a progressive damaging of the material, in the form of matrix cracking, delamination and fiber breakage. This process does not necessarily lead to an instantaneous failure of the part, however it entails a degradation of the stiffness, and can be detrimental to the strength of the laminate and to the overall functionality of the structure. This intrinsic damage is usually barely visible, and its actual extension may be greater than that predictable by visual inspections. For these reasons a number of Nondestructive Inspection (NDI) techniques have been developed for FRPs over the recent years, with the aim to identify the degradation and damage in structural components without affecting their overall integrity. However, NDI techniques present some limitations, such as high inspection times, costs and human interactions. In contrast to NDI, Structural Health Monitoring (SHM) techniques are based on the use of multifunctional materials with the ability of sensing the damage condition, providing real-time and in-situ information on the health status of the component. Health monitoring of composite structures is a demanding task, but the associated benefits are considerable, including an increased reliability and component safety, and a significant reduction of the life cycle costs, switching from a time-based to a condition-based maintenance.

The attractive potential of this technology explains the considerable efforts devoted in the last years to the development of SHM systems for damage monitoring of composite structures, mainly through a dense network of sensors embedded or stuck on the component surface, e.g. Fiber Bragg Gratings, Acousto-Ultrasonic or Acoustic Emission sensors, or exploiting the piezoresistive behavior of carbon fibers. In this context, an innovative and promising solution for the damage monitoring of composite structures is the use of an electrically conductive CNT modified matrix. Many experimental studies proved that, thanks to their extremely high aspect ratio (length to diameter ratio), in combination with their exceptional electrical conductivity, electrical percolation in CNT based polymers can be achieved since at very low filler content [1]. In addition, due to the capacity of CNTs to penetrate and form a percolated network within the fiber bundles, a CNT modified matrix is an interesting candidate also for the nanomodification of fiber reinforced laminates. Different from conventional SHM systems, this multifunctional nanocomposite gives rise to an

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innovative solution, which does not require additional sensors, since the damage can be monitored directly measuring a bulk property of the material [2]. Indeed, the Electrical Resistance Change (ERC) of carbon nanotubes modified laminates has proven to be a reliable parameter to correlate the damage evolution (such as matrix cracks and delaminations) also in composite parts made of non-conductive fibers, e.g. glass or aramid [3–6].

Two main causes underlie the electrical resistance variation in a CNT based laminate:

1) An irreversible electrical resistance change, caused by the onset and subsequent propagation of damage;
2) a reversible electrical resistance change, due to the piezoresistive nature of the semiconductive polymer, dependent of the strain level [7].

As far as the piezoresistive behavior of CNT modified polymers is concerned, tunneling resistance is acknowledged to play a dominant role [8], and a slight variation of the thickness of the insulating matrix surrounding the junction of nanotubes may result in an abrupt increase of the tunneling resistance.

By one hand, in the frame of damage monitoring applications, it could be extremely useful being able to predict the amount of electrical resistance change due to the piezoresistive properties of the semiconductive polymer, in order to avoid an overestimation of the actual damage status. On the other hand, the piezoresistive behavior of polymers filled with conductive nanoparticles represents a key feature for manufacturing parts with strain sensing capabilities. For instance, high sensitive, stretchable strain and pressure sensors, as well as temperature sensors based on the electrical resistance change of CNT based polymers were developed and investigated [9–11]. Wichmann et al. demonstrated the potential of conductive nanocomposites to sense stress/strain via DC methods [12], and examined the influence of different CNT concentrations, showing a higher sensitivity at lower CNT contents.

Accordingly, a reliable model able to accurately predict the reversible ERC of CNT modified polymers as a function of the applied strain is highly desirable, both for SHM and self-sensing applications. To this end, several numerical models were presented in the literature in order to include the effect of the actual morphology of the nanofiller, such as the presence of agglomerates and waving [13–16].

On the contrary, despite some simplifying assumptions need necessarily to be done, the development of analytical solutions represents a powerful tool to the design of multifunctional sensing materials. Indeed, numerical methods can only provide sparse data points and no general knowledge on parameter dependency can be achieved, so that the analysis becomes a “numerical experiment” and any change of parameter values necessitates a new experiment. Therefore, approximate, closed form expressions remain highly desirable. Within this context, worth of mentioning is the work by Kuronuma et al., who proposed an analytical model to predict the ERC as a result of the mechanical deformation, based on the inter-nanotube distance variation [17]. This model requires the experimental calibration of several parameters related to the geometrical contact configuration and the initial tunneling distance, but exhibited a satisfactory agreement with experimental data on MWCNT/polycarbonate composites under tension.

In this work a comprehensive study on the piezoresistive behavior of polymers modified with CNTs is carried out. In particular, in the first part of the paper, an analytical model is presented which allows the electrical resistance change to be directly correlated to the strain level in the specimen, taking into account only the reversible part of electrical resistance change caused by the deformation. To this end, the conductive network of CNTs within the polymeric matrix is modelled considering the three-dimensional random orientation of the nanofiller, the waviness and entangling of CNTs, and the electrical properties of the material in the undeformed state.

Subsequently, the results of an extensive experimental campaign carried out on MWCNT modified thermosetting polymers are presented and discussed. Dog-bone specimens made of nanocomposites are manufactured and subjected to combined mechanical/electrical tensile tests, with the aim to investigate experimentally the strain-sensing capability for different CNT weight fractions.

Finally, the analytical predictions, as obtained by using the developed model, are compared with the new results provided in this work as well as with data from the literature, showing a satisfactory agreement.

2. Analytical model for the piezoresistive behavior of CNT modified polymers

2.1. Preliminary remarks

According to classical physics, the condition for a particle to pass over an energy barrier with a given potential is to have an energy equal to or greater than that of the barrier. Differently, quantum mechanics states that the probability for a particle to pass through a potential barrier is non-zero independently from the height of the barrier. This quantum mechanical process, known as tunneling, allows electrons to pass through thin layers of insulating materials [18]. However, since the probability that particles tunnel decreases exponentially with the thickness of the layer, only thicknesses of few nanometers can be penetrated, in practice. Considering that the diameter of carbon nanotubes is in the nanometric range, quantum tunneling has been recognized as a key mechanism to describe the electrical conduction of this typology of percolated network, overcoming the limits of classic conduction theories [8,17,19].

Accordingly, the tunneling resistance can be determined by Simmons equation [20], valid for two electrodes separated by a few nanometers thick film of electrically insulating material:

$$R_t = \frac{h^2 t}{a e^2 \sqrt{2m\phi}} \exp\left[\frac{4\pi}{h}\sqrt{2m\phi}\ t\right] \tag{1}$$

where h denotes the Planck's constant, whilst e and m represent the charge and the mass of the electron, respectively. The contact area, a, is taken to equate the square of the diameter of a nanotube, d^2, whereas t denotes the thickness of the insulating material among the electrodes, and ϕ is the height of the potential barrier of the MWCNT/polymer system under investigation.

Equation (1) has been derived after some simplifying assumptions, and does not take into account for the dielectric constant of the insulating material among the electrodes. As demonstrated by Thostenson [8] in his simulations, as far as matrices with similar values of the dielectric constant are concerned, the parameter that most influences the tunneling resistance is the thickness of the insulating layer. However, it is worth noting that, as reported by Simmons [20], the dielectric constant can significantly influence the tunnel characteristics, i.e., the lower the dielectric constant of the insulator, the lower the tunneling resistivity.

2.2. Analytical modeling

Following Ruschau [21], the conductive percolated network of randomly dispersed CNTs within the matrix can be modelled as N parallel paths of carbon nanotubes, where each path is composed