Composites Part B 145 (2018) 90–99

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Experimental and theoretical study on piezoresistive properties of a structural resin reinforced with carbon nanotubes for strain sensing and damage monitoring

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ARTICLE INFO

Keywords:
Carbon-carbon composites (CCCs)
Smart materials
Electrical properties
Mechanical testing

ABSTRACT

The development of embedded sensors based on a structural thermosetting epoxy resin reinforced with 0.3 wt% of multi-walled (MW) carbon nanotubes (CNTs) for real-time structural health monitoring is presented. The storage modulus of the composites is higher than 2000 MPa in a wide temperature range confirming their reliability as structural parts, especially for aeronautical applications. The piezoresistive properties are studied on specimens subjected to both tension and flexural stresses. The yield strength evaluated with the same approach adopted for metallic materials and alloys compares successfully with the information provided by the electrical characterization. Different levels of damages are revealed by the changes in the piezoresistive properties due to the morphological modifications in the conductive network of CNTs within the resin. The analysis of an empirical law is proposed for predicting the strain-dependence of the electrical and mechanical properties of material when the samples are subjected to stretch-release cycles. The average CNTs interparticle distances as function of bending is also estimated.

1. Introduction

New materials like polymer composites based on carbon nanoparticles (nanotubes, fibers, graphene) are increasingly being used as aircraft primary structural parts (fuselage, cockpit, tail and wings) due their superior chemical and physical properties over traditional metallic materials or alloys [1–5]. In particular, low weight, high fracture toughness against impact damages, easy processability, resistance to corrosion, flame and moisture are some of attractive properties of polymer composites for aircraft applications. However, in order to extend the usage of such materials, their reliability has to be ensured in a safe, simple and economical manner. High mechanical stresses due to vibrations in adverse weather conditions and impact damages mainly due to birds or hailstones, lightning strikes represent a critical issue for aircraft composite structures [6]. In fact, the composite may undergo to considerable degree of deformation or cracks not visually detectable compromising the structural integrity of the components [7]. Therefore, much efforts are being devoted to evaluate the influence of defects on the strength and lifetime of structural materials and quantify the critical size of damage in order to introduce reliable methods for failure detection [8]. Traditional techniques based on visual inspection, ultrasonics, radiography, thermography are often slow, labour-intensive and not sufficiently sensitive to small damages. Moreover, they require a rather long deadlock of the scanned object, which leads to fewer flights of vehicles with consequent economic losses. Therefore, aeronautic industries are keen to apply faster and smarter damage detection methods based on distributed smart sensors. In particular, as it concerns the monitoring of advanced reinforced composites employed in structural components, sensors based on electro-active polymers or piezoelectric ceramics are not suitable since they are characterized by high fragility, non-negligible weight, need of high voltage or current for their correct use. An alternative approach may be represented by the use of polymer nanocomposites. The use of small amount of nanofillers, in particular carbon nanotubes, due to their tendency to easily form electrically conductive networks when embedded within polymer resins, may confer piezo-resistive properties to the resulting materials thus leading to a multifunctional component integrating structural and sensing capabilities [9–11]. A strictly relationship between the mechanical deformations and the electrical resistance exhibited by such advanced composite materials reveal their potential for applications as strain and damage sensing [12–14]. Structural health monitoring (SHM), mainly involves a nondestructive testing (NDT) system realized

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https://doi.org/10.1016/j.compositesb.2018.03.025
Received 15 September 2017; Received in revised form 26 January 2018; Accepted 13 March 2018
Available online 15 March 2018

with integrated sensors able to continuous or periodic self-inspection for damage detection in situ. Ideally, it allows to recognize the damage type, the relative size and location thus minimizing the time and costs needed to take the structure out of service, then disassemble and inspect it [15–17]. Despite several studies aimed at investigating the strain sensing properties of composites reinforced with carbon-based nanofillers, some critical issues still remain to be clarified [18–22] in order to fully take advantage of their advantageous characteristics. In fact, the sensing performances may be different from the ones expected since it is not possible to avoid entangled aggregates due to a not uniform dispersion of the fillers within the resin which impacts on the load transfer between the two phases and affects the mechanical and the electrical response of the obtained nanocomposites. The main outcomes from several papers have been presented in a recent detailed review illustrating the physical phenomenon behind the piezoresistive properties of innovative and smart materials for strain sensors [23]. However, it is worth evidencing that most of the available works analyze the strain sensing properties of the nanocomposites by means of DC electrical characterizations, whereas only few refer to AC measurements [24–28].

In this paper an epoxy resin reinforced with 0.3 wt% of multi-walled carbon nanotubes (MWCNTs) is experimentally studied under axial and flexural stresses. In particular, after a preliminary morphological and thermomechanical analysis, aimed at confirming their suitable use in the aeronautical field as structural parts [1], the correlation between the mechanical response and the electrical properties are investigated for specimens subjected to fatigue tests. Set of cycles and different levels of intensity have been adopted for probing the long-term durability. The damage is expressed through a residual resistance strictly close to the amount of plastic strain accumulated in the matrix. Moreover, the dependence on strain of the piezoresistive properties is studied by considering numerical simulations allowing to analyze the impact of different physical parameters (i.e. interparticle separation distance, energy barrier) on the tunneling effect that governs the electrical resistance of the materials. The achieved results open the way towards the development of embedded sensors for structural health monitoring based on the same polymer composites employed for the fabrication of structural parts thus leading to multifunctional components integrating structural and sensing capabilities.

2. Materials and methods

The epoxy matrix was prepared by mixing an epoxy precursor, tetraglycidyl methylene dianiline (TGMDA) with an epoxy reactive monomer 1,4-butanediol diglycidyl ether (BDE) that acts as a reactive diluent. Instead, 4,4-diaminodiphenyl sulfone (DDS) is adopted as curing agent for this manufacturing process. All these components are provided by Sigma Aldrich. In order to obtain a uniform dispersion of the filler, the MWCNTs (3100 Grade purchased from Nanocyl S.A) were embedded into the matrix (Epoxy blend kept at 120 °C to reduce the viscosity) by using an ultrasonication for 20 min (Hielscher model UP200S-24 kHz high power ultrasonic probe). After that, DDS hardener agent was added at a stoichiometric concentration with respect to all the epoxy rings (TGMDA and BDE). The tested specimens, in agreement with geometrical specifics (Fig. 1) of ASTM standards D638 and D790 [29,30], were prepared according to a method described in Ref. [28]. Samples micrographs were performed with a field emission Scanning Electron Microscopy (SEM) apparatus (JSM-6700F, JEOL) instrument operating at 3 kV on some nanocomposites section cut from the solid samples by a sledge microtome and suitably treated as already described in Guadagno et al. [31].

FTIR spectra were obtained at a resolution of 2.0 cm^{-1} with a FTIR (BRUKER Vertex70) spectrometer equipped with deuterated triglycine sulfate detector and a KBr beam splitter, using KBr pellets. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He—Ne laser. 32 scans were signal averaged to reduce the noise. Thermogravimetric analysis (TGA) was carried out in nitrogen using a Mettler TGA/SDTA 851 thermal analyzer. The temperature range was 25–800 °C at a heating rate of 10 °C min^{-1}. Dynamic mechanical properties of the samples were performed with a dynamic mechanical thermo-analyzer (Tritec 2000 DMA-Triton Technology). Solid samples with dimensions 2 × 10 × 35 mm^3 were tested by applying a variable flexural deformation in three points bending mode. The displacement amplitude was set to 0.03 mm, whereas the measurements were performed at the frequency of 1 Hz. The range of temperature was from −60 °C to 320 °C at the scanning rate of 3 °C/min^{-1}.

Electro-mechanical tests (in axial and flexural strains according to ASTM standards D638 and D790, respectively) were performed, at room temperature, by using a Dual Column Tabletop Testing Systems (INSTRON, series 5967) set with a cross head speed of 1 mm/min for both loading and unloading. More in details, a three point-bending measurements were carried out during the flexural tests. The corresponding force was measured by the machine load cell and converted to axial stress (σ), whereas mechanical strain (ε) was calculated as the machine crosshead displacement normalized by the gage length of the test specimen. Possible slipping during the displacement were excluded by recording local deformation by means of a conventional strain gauge (RS 5 mm Wire Lead Strain, gauge factor 2.1) having a gauge resistance of 120Ω (constantly measured with a precision multimeter HP 34401A), glued to one side of the specimen. A two-probe configuration based on an electrometer Keithley 6517A (configured in the double function of voltage generator and ammeter) was used to measure the current-voltage (I—V) characteristics between the copper electrodes fixed on the sample surface using silver paint (Silver Conductive Paint, resistivity of 0.001 Ωcm) in order to ensure a good ohmic contact between the parts. Although simple, this measurement method, has successfully been applied in literature for resistance measurements in presence of tensile test [32,33]. Since the measured electrical resistance for all specimens was in the order of several kΩ, contact resistance was neglected. The same electrodes were used for the impedance spectroscopy (IS) analysis performed by using a precision LCR meter (model QuadTech 7600). The overall test setup and the geometrical features of the investigated specimens are reported in Fig. 1.

3. Results and discussion

3.1. Structural, thermal and mechanical analysis

The behavior related to the electrical properties of the nanocomposites reinforced with different filler amounts has been analyzed in depth in previous paper [28]. In the present work the sensing characteristics of the composites have been investigated for the sample loaded with of 0.3 wt% of MWCNTs. This concentration has been chosen because it is beyond the electrical percolation threshold (i.e. EPT) of the considered composite systems. Therefore, such composition is particularly suitable for achieving enhanced piezoresistive properties of the resulting material since the percolating network is more sensitive to small morphological variations due to mechanical strain [34–38]". In fact, the piezoresistive response is due to the modifications in the electrical network, e.g. loss of contact among CNTs [28,39] or change in the tunneling resistance due to the rearrangement of neighbour CNTs [40] as well as to intrinsic piezoresistivity of fillers subjected to deformations [41]. A structural analysis has been carried out in order to fully investigate the characteristics of the employed nanofillers and resulting nanocomposites. Geometrical features of the filler can be estimated from FESEM (Fig. 2 a) and TEM (Fig. 2 b) images of Fig. 2. All data are summarized in Table I reported as Fig. 2c The FTIR spectrum of MWCNTs (Fig. 2d) highlights that the walls of MWCNTs are not completely un-functionalized, as stated by the manufacturer. In particular, in the FTIR spectrum, together with expected signals (i.e. C—C stretch at 1640 cm-1 and 1543 cm-1, due to skeletal vibrations) other bands appear. In particular, the spectrum shows the presence of oxygenated