Smart coatings of epoxy based CNTs designed to meet practical expectations in aeronautics

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Abstract

A smart coating exhibiting self-diagnostic capability is designed to meet industrial requirements in aeronautics. The coating made of epoxy-based carbon nanotubes (CNTs) has been applied on industrial Carbon Fiber Reinforced Plastics (CFRPs) currently employed in aeronautics. The correlations between mechanical strain and electrical properties of coated CFRPs highlights the feasibility in manufacturing CFRPs having integrated high sensitivity in providing an effective real-time structural health monitoring. The reliability of the developed CFRPs, in the normal operational temperature range of aircrafts, opens new perspectives in the field of self-responsive structures in aeronautics. Self-responsive panels can simultaneously act as sensor and structural element.

Keywords:

A. Carbon-carbon composites (CCCs)

B. Smart materials

B. Electrical properties

D. Mechanical testing

1. Introduction

Among the family of ultra-light structural materials, polymer-based composite materials have been introduced massively in the recent years in aeronautical applications and other fields like civil, automotive, aeolian engineering, etc. Recently, the two world leaders in the manufacture of aircraft, i.e. Boeing and Airbus, have placed on the market the 787 and A350 airbuses respectively, where the presence of composite material exceeds 50% of the airframe. An objective in technological innovations is the maintenance of highly reliable and safe transportation systems. Since the complexity of components and systems increases and the vulnerability of non-metallic materials to environmental hazards such as rain, storms, turbulence, icing, lightning, fog, volcanic ash, wind speed, wind direction, wind variation, or the like, needs of frequent time-consuming controls, the development of new advanced methodologies for real-time structural health monitoring is one of the hottest topics in the field of aircraft design. The development of innovative Non-Destructive Testing (NDT) techniques consisting in the appropriate design of self-responsive resin (and/or in coatings for airframe components) for the investigation of crack initiation, fatigue discontinuities, different types of defects etc.. can provide a substantial breakthrough to the problem. A such self-responsive resin can simultaneously act as structural element and sensor.
Recent developments in sensing technology have attractive potential for resolving numerous issues related to aircraft diagnostics in order to extend the life of structures with an overall safety improvement. The goals of any structural damage monitoring and assessment system are to ensure reliability and safety and to minimize life-cycle cost of the structures. Damage assessment has applications in the majority of engineering structures and mechanical systems ranging from aerospace systems to equipment manufacturing. As a result, a multitude of different approaches appears in the literature to address the problem of damage issues. Non-Destructive Testing (NDT) have been developed mainly for enhanced safety in the aeronautical industry for the detection, location and characterization of damage in composite materials. The state-of-the-art NDT techniques for composite materials can be found in [1, 2] and the main ones are as follows: visual inspection, optical methods, eddy-current ultrasonic inspection, acoustic emission; vibration analysis, radiography and thermography. The design of a Structural Health Monitoring (SHM) systems implies the implementation of a damage detection strategy around a structure, i.e. a strategy whose main goal is to detect any changes in the geometrical or material properties of a structure or its boundary conditions. A new possible approach in order to have a SHM system consists in the development of polymeric materials filled with conductive nanofillers such as carbon nanotubes

(CNTs) or other carbon nanostructured forms or magnetic nanoparticles characterized by interesting properties suitable in the field of sensing devices. Electrical techniques are non-invasive way to monitor damage in carbon-fiber-reinforced composites under static or dynamic loading conditions [3-6]. This approach is not applicable to composites where fibers are non-conducting (such as glass or aramid fibers). This problem has been overcome with the use of multi-walled nanotubes dispersed in the epoxy phase to design a distributed sensors able to evaluate the onset and evolution of damage in advanced fibrous composites [7]. The damage detection in composite parts by matrix conductivity measurements offers several advantages compared to traditional optical fibre sensors. For instance, due to their elevated cost it is not possible to apply a dense network of optical glass fibres to large composite components. Another reason is that if a crack is propagating without crossing one of the sensors, the damage would not be detected. Finally, in some cases, the optical fibres may also be a source of damage initiation when inserted in composite parts [8, 9]. Thanks to their low density and their good adhesive and mechanical properties, epoxy resins are the most diffuse matrices for structural composites. In this work, starting from the optimized carbon-nanotubes-epoxy nanocomposite already developed by our group [10], the piezoresistive behaviour of an epoxy–CNT nanocomposite has been studied on its application as a strain sensor in a carbon fiber reinforced composite subjected to tensile loads. For this reason, the epoxy components mixture has been used as a conductive coating that can be easily poured and cured onto the surface of the composite for strain and damage sensing purposes. Subsequently, the electrical resistance change, due to the piezoresistive nature of the film coating, as a function of composite deformation has been studied.

2. Experimental

2.1 Materials

The epoxy resins diglycidyl ether of bisphenol A (DGEBA), the hardener 4,4 diaminodiphenylsulfone (DDS) were supplied by Aldrich Chemicals. Multi-walled carbon nanotubes, 3100 Grade, (MWCNTs) are been obtained from Nanocyl S.A. The morphological characterization of the MWCNTs has been carried out by high resolution transmission electron microscopy (HR-TEM). Most of MWCNTs show an outer diameter from 10 to 30 nm, but also an outer diameter lower than 10 nm or larger than 80 nm has been observed. Nanotubes length is from hundreds of nm to few mm. Number of walls, varies from 4 to 20 in most nanotubes [10]. The weight ratio between epoxy precursor and DDS was 10/2.85; they have been mixed at 120 °C and the MWCNTs filler (0.1% by weight) was added and dispersed with high power ultrasonic probe (Hielscher model UP200S-24 kHz) for 20 min.

2.2. Sample preparation and testing

The specimens analysed in this work have been obtained following a well-defined procedure described in previous papers [11, 12]. Fiber-reinforced composite parts have been cut into flat coupons 20 cm x 35 cm with a nominal thickness of 1.15 mm. A diamond tip water-cooled saw blade has been used. The surface of Carbon Fiber Reinforced Plastics (CFRP) parts has been treated by sandblasting in order to increase the roughness of the surface for a greater adhesion of the conductive coating to the laminate. Subsequently they have been cleaned and dried prior to coat them.

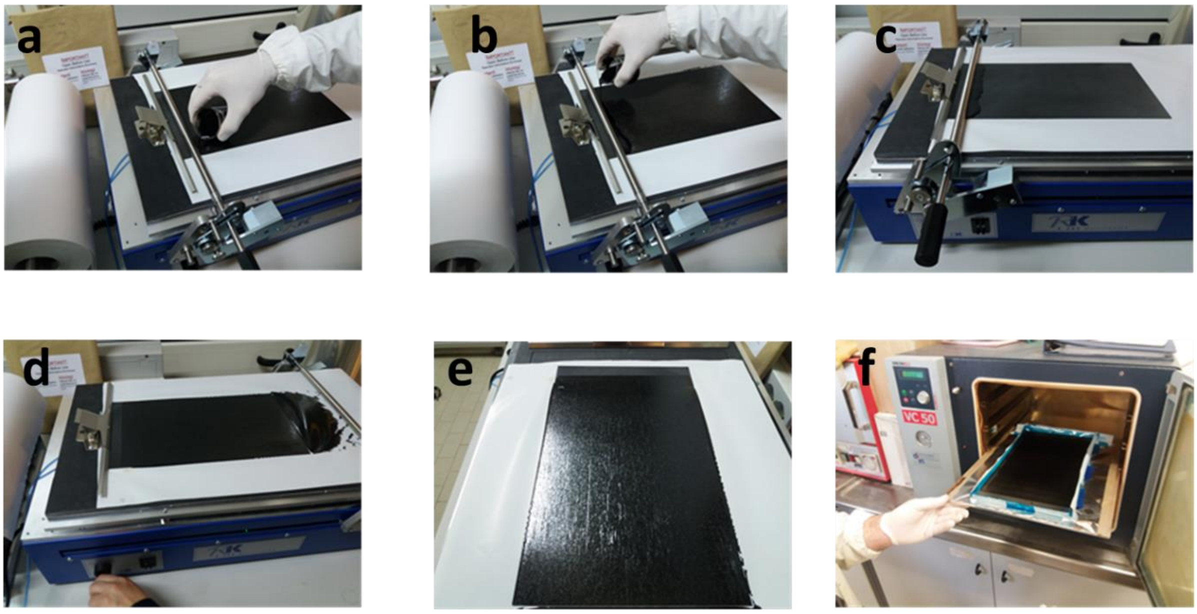

Fig. 1. Illustration of the fabrication process of coated CFRP specimen.

In order to obtain a uniform conductive resin coating on the panels produced, a "K303 MULTICOATER" of the RK Printcoat Instrument has been used, i.e. a surface coating applicator. The panel has been deposited on the multicoater and clamped by means of a vice (see figure1a) in order to avoid movements during the covering. After the clamping, the appropriate head has been applied. Subsequently the mixture loaded with the carbon nanotubes has been deposited along the head and finally the movement of the head at programmed speed (1mm/min) has been activated (see figure 1 b,c,d,e). Finally, the laminate, with the conductive coating, has undergone a curing cycle of 1h at 150 °C and 3 hours at 220 °C (see figure 1f).

The carried-out process step allowed to have a coating thickness of about 150 μm. Different from conventional SHM systems, these multifunctional composites can be applied with successful on various surface giving rise to an innovative solution for monitoring structural deformation and damage directly measuring electrical resistance change, due to the piezoresistive properties of the developed coating, without require further additional sensors. For this purpose, suitable electrical contacts have been deposited on the panel by using silver paint (RS 186-3600 with volume resistivity 0.001 Ω·cm, when fully hardened). As a matter of fact, to prevent that bulk currents (i.e. those passing through the material given the high electrical conductivity of the CFRP) provide a contribution to the measured surface current, the electrical measurement configuration has been opportunely studied. In particular a guard ring "collects" such currents which can be drained downstream of the measuring instrument, toward the mass of the system. The experimental results confirm the correctness of this ploy since an electrical resistance of 30 Ω and of the order of kΩ. is measured adopting a configuration equipped with and without the guard ring, respectively. In fact, the first value is not plausible being too much low for proposed conductive coating, whereas the second one is comparable to that observed only on the resin loaded with 0.1% by weight of carbon nanotubes [10]. The electrode-sample system is shown schematically in Fig. 2. The two-probe method, performed with a Multimeter Keithley 6517A configured as voltage generator and HP 3458A Digital Multimeter employed as ammeter, has successfully been applied in literature, although simple, for resistance measurements in presence of tensile test [13, 14]. Moreover, as evident from Fig.2, in order to exclude possible slipping during the displacement, the local deformation was detected by means of a conventional strain gauge (RS 5 mm Wire Lead Strain, gauge factor 2.1 and gauge resistance of 120 Ω) bonded to one side of the specimen, whose electrical resistance change has been constantly measured with a precision multimeter HP 34401A.

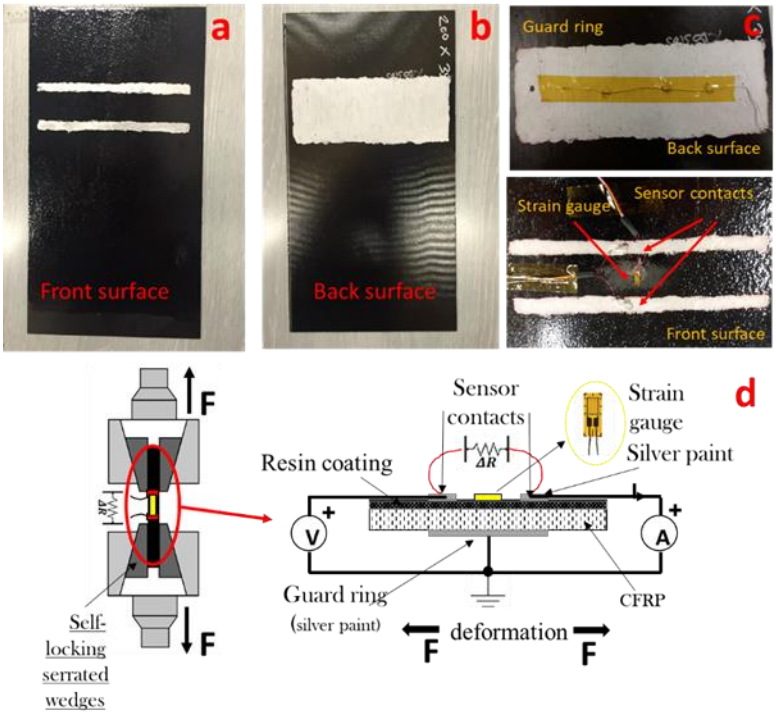

Fig. 2. Front and back surfaces of the panel and schematic of electrodes configuration adopted for the electrical measurements

Tensile tests have been carried out by using an MTS 370.50 Universal Testing System at 1 mm/min crosshead speed and equipped with 500 KN load cell and hydraulic grips. In order to evaluate the glass transition temperature of the nanocomposite system, Dynamic Mechanical Properties have been carried out in air by 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 30°C to 300°C at the scanning rate of 3°C*min^{-1}.

3. Results and discussion

3.1 Mechanical and electrical analysis

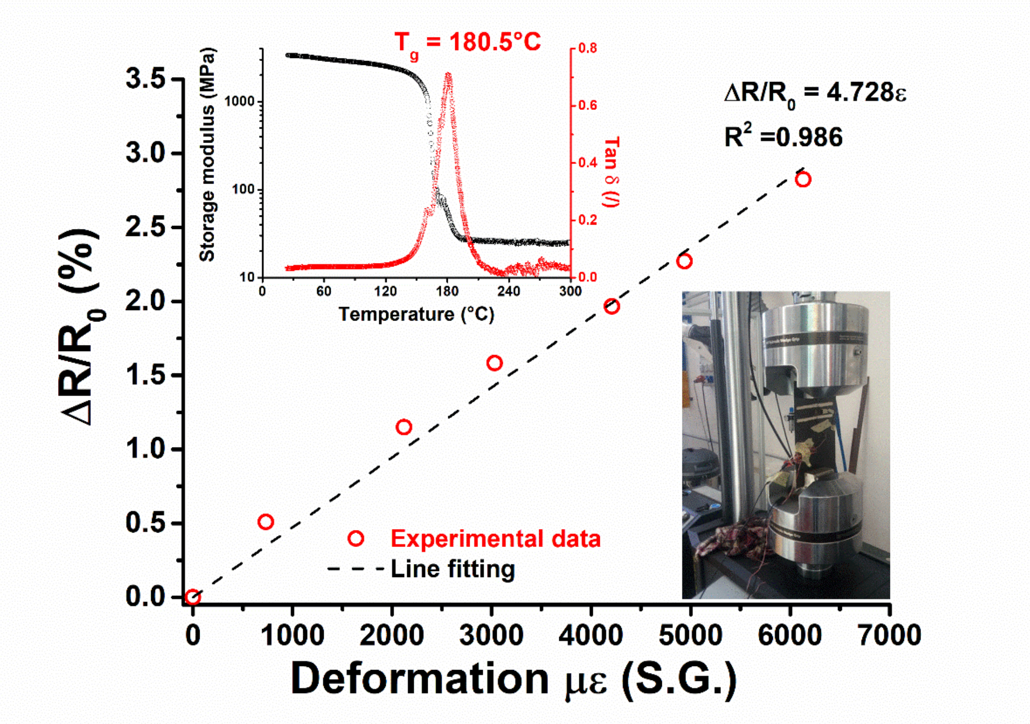

Fig. 3. Piezoresistive characterization in tensile tests of coated CFRP specimen.

Fig. 3 shows the mechanical and piezoresistive performance of the coated conductive epoxy-laminate. In particular, the results concern the normalized change of electrical resistance $\Delta R/R_0$, where R_0 is the steady-state electrical resistance of the material without applying any strain (i.e. ε =0) and $\Delta R = R - R_0$ is the change in R, plotted against the axial strain (ε) detected by strain gauge. In the all analyzed range of strains, a linear behaviour is observed with normalized change of electrical resistance. The increase of the resistance of the applied coating with increasing tensile strain agrees with the assumption that in a conductor-filled polymer the main electrical conduction mechanism occurs via "tunneling effect" which requires that the filler particles must be sufficiently close (at the so-called "tunneling distance") to each other to allow the electron flow [15, 16]. Consequently, the tunneling resistance changes between neighboring CNT due to the enlargement of inter-tube distance and/or a decreasing of the electrical contact areas. Both phenomena lead to an increase of the resistance exhibited by the conductive material. The interpolating line of $\Delta R/R_0$ curve of experimental data allows to evaluate the Gage Factor (G.F. = $\Delta R/\varepsilon R_0$) of the conductive coating, that in this case is about 4.7. The sensitivity factor or otherwise called gauge factor is a very important feature of the strain sensor for which it is necessary to give some clarifications. Processing conditions and material properties play a notable role in determining the sensor sensitivity. In particular, to improve the sensitivity of the sensor system, the following condition are needed:1) lower content of CNTs close to the percolation threshold, 2) lower curing temperature, 3) higher stirring or mixing rate, 4) higher height of barrier of matrix and 5) higher electrical conductivity of filler. In other words, in order to obtain a high value of G.F. it is necessary to maximize the tunneling resistance (see condition 1,3,5) and to use soft materials such as thermoplastic or thermosetting polymers with a low glass transition temperature (see condition 2,4) [17]. In previous works, high values of sensitivity factor are been obtained, using thermoplastic matrices such as polysulfone (G.F. = 6.2) [14] or Poly(methyl methacrylate) (G.F. = < 6) [18] not applicable in the field of aeronautical materials where most of the materials are based on epoxy resins. In other papers, the sensitivity factor has been evaluated in a non-linear strain range [19] that is when most likely the polymer has permanently deformed, with the consequent non-applicability of the sensor in dynamic stress cycles. In other cases, epoxy resins have been used to reach G.F. up to 8.54 [20], but with the drawback related to the too low glass transition temperature (71 °C) to be used for structural components in the aeronautical field. In our case, a high G.F. has been achieved bearing in mind that the components of a resin normally used in the field of structural materials for aeronautical applications [21, 22]. In particular, this epoxy coating has high modulus and a high glass transition temperature (see inset figure 3), confirming high reliability if employed as structural aeronautical parts working in the normal operational temperature range of aircrafts. Moreover, the found linearity in figure 3 ($\Delta R/R_0$ vs ε) allows us to affirm that the coating applied to the CFRP will allow dynamic strain cycles to be applied in the range of strain considered. It is worth noting that, unlike thermoplastic nanocomposites, the developed self-diagnostic coating is expected to be not subject to plastic deformations during its operational conditions, hence providing considerably reliability also after a huge number of operating cycles. These last-mentioned experiments have been performed on same formulation here used as functional coating. The results, published in a previous paper, highlighted that microscale damages resulted directly related to the resistance changes and hence easily detectable in a non-destructive way by means of electrical measurements [10]. A very relevant result of the present paper is the applicability of the thermosetting filled formulation (with suitable CNT concentration) as coating to confer self-diagnostic function to structural aeronautical panels. From prelaminar tests carried out on structural panels and on automotive components, this strategy seems to be easy to implement and can constitute the first step of industrialization processes.

Studies are ongoing about the electro-mechanical behaviour with dynamic strain cycles applaiyng the developed functional coating on structural panels reinforced with different fibers (Carbon Fiber and Glass Fiber).

4. Conclusions

An uniform conductive coating made of epoxy based MWCNTs has been stratified on aeronautical CFRPs. Measurements of electrical resistance as a function of applied strain have been performed on panels. The Gage Factor of the coated CFRPs has been found of 4.7 which is the higher value achieved until now for thermosetting resins. This value is not a trivial result, considering the chemical nature of the functional coating here described, which is based on thermosetting matrix characterized by mechanical performance able to meet the industrial requirements of primary structures. Furthermore, it is worth noting that for thermosetting matrices, the range of elastic deformation, where the sensor properties can be employed is narrow with respect to that of a thermoplastic matrix; but a slight lower value of the G.F. with respect to thermoplastic nanocomposites is widely balanced by the absence of plastic deformations due to many repeated stress-strain cycles. The appropriate choice both of the components of the epoxy resin and the carbon nanotube concentration, allows to prepare a conductive coating with high sensitivity factor and a high glass transition temperature, conditions for which the developed strain sensor result reliable in the normal operational temperature range of the aircraft.

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