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Processing and electrical characterization of a unidirectional CFRP composite filled with double walled carbon nanotubes

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ABSTRACT

Carbon nanotubes represent new emergent multifunctional materials that have potential applications for structural and electrically conductive composites. In the current paper we present a suitable technique for the integration of Double Walled Carbon Nanotubes (DWCNTs) in a unidirectional Carbon Fiber Reinforced Polymer (CFRP) with high volume content of carbon fiber. We showed that the electrical conductivity of the laminates versus temperature follows a non-linear variation which can be well described by the Fluctuation-Induced Tunneling Conduction (FITC) model. The parameters of this model for CFRP/DWCNTs and CFRP without DWCNTs were determined using best fit curves of the experimental data. This study has shown that DWCNTs have strong influence in the conductivity through laminate thickness. However, there are no significant effects on the electrical conductivity measured in the other two principle directions of the composite laminate. Furthermore, it was found that electron conduction mechanism of carbon fibers is dominated by the FITC.

1. Introduction

Significant progress has been made in the investigation of the multifunctionality of fiber reinforced polymers (FRPs). Beside their structural role, composite materials have the potential for deformation or temperature sensing when monitoring the electrical changes in the material. This self-sensing property is an attractive non-destructive evaluation method that undergoes intensive research. We believe that improving this sensing functionality or/and achieving new functionalities in conventional FRP can necessitate the addition of fillers in particular carbon nanotubes (CNTs). Carbon nanotubes are considered to be new emergent multifunctional materials that have potential applications for structural and electrically conductive composites [1–3]. The electrical conductivity of CFRP composites has interested many researchers for various applications such as damage and structural health monitoring of composite materials [4–7] and using carbon fibers as heating element [8]. The use of CNTs has made it possible to extend these applications to other dielectric composites such as glass fibers reinforced polymers (GFRPs). Intensive investigations are undertaken on the piezoresistivity of CNTs based-composites for damages and structural health monitoring of composite materials [9–16]. Besides, other topic dealing with processing and characterization of conventional fibers reinforced polymer matrix filled with CNTs are up-to-date [3,17].

Regarding the CFRP composites and FRP containing CNTs composites, only few papers have investigated the effect of the temperature on the electrical conductivity of these composites. In practice, during their service, CFRP structures undergo thermal variation in different situations. For instance CRFP structures can be subjected to environmental changes where an increase in temperature can occur during different mechanical loads. When the variation of the temperature is not important, one can assume a linear relation between the temperature and the resistivity [16,19]. As in the work of Kupke et al. [18] in which the authors have monitored the mechanical damage during fatigue tests by measuring the electrical resistance in the specimens. To compensate the increase of temperature in composites during experiments, they proposed a linear relation between the electrical resistance and the temperature variation. However, in case of a strong variation of the temperature inside the composite structure this assumption can lead to significant errors if an accurate model is not used. To our knowledge, no work has been yet undertaken to investigate the effect of wide range temperature variation on the electrical conductivity of CFRP structures.

In order to process fiber reinforced polymers containing CNTs, there are mainly three techniques proposed in the literature,

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depending on the nature of the polymer matrix and the reinforcement fibers structure and volume content. The first technique is the impregnation of the reinforcement fibers with a polymer matrix filled with carbon nanotubes which is the most used technique because it is easy to implement. The dispersion of CNTs in the polymer matrix can be properly controlled [20]. CNTs/Liquid Polymer mix can be transferred to the fibers reinforcement (Preform) via resin transfer molding (RTM) or vacuum assisted RTM (VARTM) process. One major constraint of this method is the fiber volume content that must be relatively low because of the permeability of conventional fibers to CNTs [3]. Another constraint of this processing technique is the increase of the matrix viscosity caused by the CNTs [21,22]. The second technique is the deposition of CNTs on reinforcement surface [23,24]. This technique can be applied either by chemical functionalization of CNTs and carbon fibers to create chemical bonds or without chemical treatment. It was found that the chemical functionalization impairs the physical properties of CNTs and carbon fibers [25,26]. The third method of manufacturing FRP/CNTs composite consists of depositing dried CNTs on the surface of the prepregs plies. A prepreg is made of one layer of long fibers (woven or unidirectional) impregnated with a polymer matrix. This method has been used by Veedu et al. [1] and García et al. [27] to place layers of vertically aligned multi-walled CNTs named "forests of CNTs". This technique increases considerably the out-of-plane mechanical properties of the composite but it has a limited influence on the electrical conductivity of the composite laminate.

In the present work we aim to manufacture CFRP composites with high carbon fiber content and filled with DWCNTs. We propose to study the frequency and temperature dependency of the electrical conductivity of the composites for a wide range of temperature; varying between −150 °C and +130 °C. The polymer subjected to this study is an epoxy-based resin (RTM6) developed for processing high performance composite materials reinforced with unidirectional carbon fibers. Attention has been given to the analysis of the microstructure and the dispersion state of DWCNTs in the composite laminate.

2. Materials and methods

2.1. Materials and Epoxy/DWCNTs suspension preparation

2.1.1. Materials

The epoxy resin (RTM6) used in this investigation is provided by Hexcel composites (Hexcel Corporation, France). It is a monocomponent resin in which the stoichiometric ratio of epoxy and amine hardener is already mixed and degassed. Carbon nanotubes used in this study are almost (80%) Double Walled Carbon Nanotubes (DWCNTs) [28] and were synthesized and purified at Paul Sabatier University (Institute Carnot-CIRIMAT) using Catalytic Chemical Vapor Deposition (CCVD) method [29]. Important characteristics of the present DWCNTs include their purity in Carbon atom (98% atomic), their average (BET) specific surface area (700 g/m^2) and the density 1.8 g/cm^3 [30]. The aspect ratio (length/diameter) of an individual DWCNT can be estimated to range between 1×10^3 and 1×10^4. Carbon fibers are unidirectional (UD) reinforcing fabrics made of Toray T700S carbon fiber-type.

2.1.2. Preparation of the Epoxy/DWCNTs mixture

To process the CFRP containing DWCNTs we first prepared an Epoxy/DWCNTs suspension. DWCNTs suspended in water were sonicated in the presence of a suitable dispersion agent called Hexadecylamine using an ultrasonic bath for 1 h at room temperature. Then a strong sonication for 15 min was performed using a 13 mm probe tip. The power source for the probe sonication was adjusted to 100 W. The weight ratio HDA:DWCNTs was taken as 1:1. This ratio was chosen based on a previous study conducted by Barrau et al. [31] on the dispersion of DWCNTs with amphiphilic molecules. The DWCNTs–HDA suspension was then mixed with the epoxy resin and stirred at 1000 rpm for 30 min at 80 °C. The mixture was subsequently degassed for 2 h and 30 min at 80 °C. Differential scanning calorimetric analysis and thermogravimetric analysis were performed on the degassed mixtures to ensure that they do not contain traceable water. Finally we used this suspension (Epoxy/DWCNTs) to impregnate UD carbon fabrics.

A preliminary study on Epoxy/DWCNTs nanocomposites showed that the electrical percolation threshold is achieved around 0.04 wt.% (0.025 vol.%) of DWCNTs. In order to achieve a high level of electrical conductivity in the material a concentration of DWCNTs in the epoxy resin equal to 0.4 wt.% (0.29 vol.%) has been used for processing the final CFRP composite.

2.2. Optical microscopy and scanning electron microscopy

The distribution and the quality of the carbon nanotubes dispersion in the composite laminates were examined using High Resolution Field Emission Scanning Electron Microscopy (HRFE-SEM). The samples were frozen in liquid nitrogen and subsequently fractured. The fractured surfaces were observed without any conductive coating using a field emission scanning electron microscope (JEOL JSM 6700-F) at a relatively low voltage of 0.7 kV.

For a qualitative and a quantitative analysis of the laminate, an optical microscope equipped with a camera was used. Five samples with dimensions of 30 mm × 30 mm × 2 mm were randomly cut out of each $[0°]_8$ laminate plate. On each sample, two perpendicular edges (one ⊥ to fibers and one // to fibers) were polished. The magnification is chosen as a function of the size of the largest void detected. Then, a large number of images (up to 100 images per kind of laminate) were analyzed using image analysis software (*imageJ*), which is a free image processing software developed by the National Institutes of Health—US. We calculated the void content in each laminate by counting the ratio of voids (dark contrast) to the remaining surface area for each image and finally we took the average. The quantitative analysis of micrographic images can provide us with an estimation of the void content in the material with a good accuracy [32,33].

2.3. Electrical conductivity—theory and experiment

Measurements were carried out by recording the impedance using a Solartron–Schlumberger frequency response analyzer together with a Novocontrol interface (broad-band dielectric converter). The alternative voltage is set to a maximum of 1 V so that self-heating of the samples can be neglected. The measurements were performed in the frequency ranged between 10^{-2} and 10^7 Hz at isothermal temperatures varying from −150 °C to +130 °C with a 10 °C step. Two samples were cut randomly from each composite plate. The dimensions samples used were 20 mm × 10 mm × 2 mm. The electrical conductivity measurements were performed on Epoxy/DWCNTs nanocomposites and Carbon fiber/Epoxy/DWCNTs composites. In order to ensure the electrical contact silver paint was applied to the surfaces. A preliminary study has been conducted in order to verify the repeatability and the accuracy of the two-point contact tests. Five samples were cut randomly from each composite plate and tested at room temperature with DC source using both two-point contact and four-point contact electrical measurements. To perform these measurements we used a DC current source (KEITHLEY Model 6221) coupled with a voltmeter (KEITHLEY 2182A). Four-point and two-point measurements gave similar values of conductivity.