NANOCOMPOSITE LAYERS FOR SPACECRAFT PROTECTION: FROM MULTISCALE NUMERICAL MODEL TO EXPERIMENTAL DATA

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Abstract

In space environment, the surfaces of a spacecraft interact with the surrounding charged particles. Depending on the orbit, this interaction can induce a significant absolute charge on the structures and/or a differential charge collected among components. These phenomena generate electrostatic discharges with catastrophic consequences for the satellites. In this work, we investigate the volumetric electrical properties of nanocomposites made of aerospace-grade epoxy resin (RTM6) with single wall carbon nanotubes (SWCNT) as fillers to mitigate the electrostatic discharge phenomenon. In particular, we developed a highly conductive nanocomposite layer satisfying the NASA requirements for geostationary orbit. The study is divided into two parts, an experimental and a numerical one. In the first part, we fabricated nanocomposite samples and characterized their electrical properties at various frequencies. The electrical experimental results were compared with the numerical ones, which were calculated using a multiscale approach.

1. Introduction

Carbon-based nanoparticles are investigated as possible solution for a large number of technological challenges that range from multifunctional structures to electromagnetic shield and sensing [1-2]. This opportunity is particularly relevant in the aerospace field, where the multifunctional characteristics of such materials can further satisfy the lightweight requirement by replacing complex and heavier subsystems of a spacecraft [3-5]. For these reasons, carbon nanoparticles are often investigated as reinforcements for epoxy matrix, which is the predominant polymer used for structural applications in spacecraft and aircraft vehicles. The interaction of the spacecraft with the space environment induces an absolute charge in the structures (which are typically covered with dielectric materials to satisfy the thermo-optic specific purpose) and a differential charge collected between its components [6]. This phenomenon can generate electrostatic discharges with catastrophic consequences for the satellites.

In this work, we investigate the volumetric electrical properties of nanocomposite materials made of aerospace-grade epoxy resin and single wall carbon nanotubes (SWCNT) to mitigate the electrostatic discharge phenomenon. In particular, we developed a highly conductive nanocomposite layer satisfying the NASA requirements for geostationary orbit [7]. At the same time, we determined numerically the conductivity of the matrix mofidied with SWCNTs and that of carbon fiber-reinforced composites with the modified resin. The numerical analysis was performed based on the multiscale approach using the software Digimat. The electrical experimental results were compared with the numerical ones.

2. Experimental Part

2.1 Materials and Nanocomposite Processing

In this study, we used pristine single-walled carbon nanotubes (SWCNT) by Tuball. The selected resin was the aerospace-grade mono-component RTM6 manufactured by Hexcel, formulated for resin transfer molding process (RTM). The rheological behavior of RTM6 resin is strongly dependent on the sample temperature. The dispersion procedure was tuned taking into account the temperature dependent viscosity versus the low heat transfer to the resin, in order to allow both nanofiller mobility into the mixture and to preserve the resin pot life. In this procedure, the resin was initially pre-heated up to 90 °C with a constant rate of 2 °C/min. When the resin was homogenously heated, the desired amount of the nanofiller was blended for about 90 min in an ultrasonic bath at 90 °C. In this last step, the mixture was also degassed in order to eliminate air bubbles. The specimens were realized by pouring the mixture in a silicon mold and curing at 180 °C for 2 h.

2.2 Electrical Measurements

The characterization of the electrical properties of the nanocomposite samples was carried out at various frequencies in electrical impedance spectroscopy (EIS) experiments using an Agilent E4980A Precision LCR Meter. The samples were contacted by means of flat copper plates, which were pressed and kept parallel to each other. Impedance measurements were performed under the parallel circuit model. Specifically, the results reported here are based on the equivalent parallel resistance (R_P), as provided by the instrument.

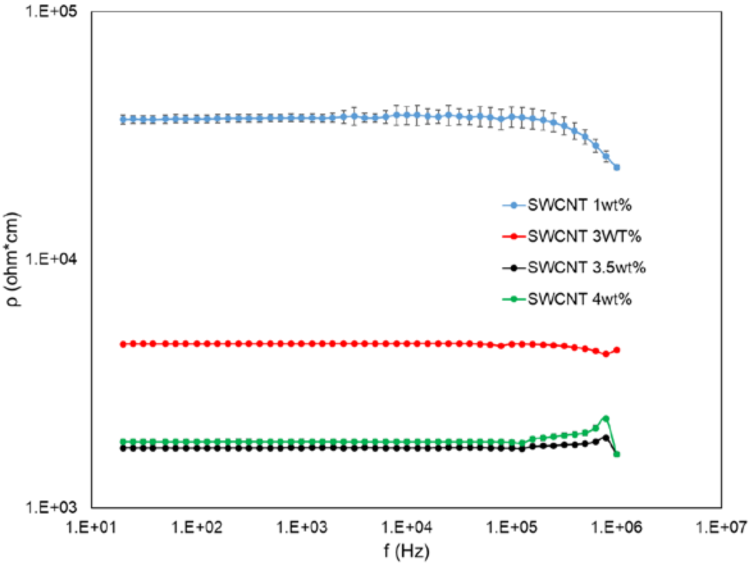

Figure 1. Volumetric electrical resistivity of RTM6/SWCNT epoxy nanocomposites with different loadings (% by weight) of SWCNT as a function of testing frequency.

Fig. 1 shows the trend of the volumetric electrical resistivity of the SWCNT-based nanocomposites. For all concentrations, the resistivity is constant with the testing frequency and decreases with the increasing of SWCNT concentration. In particular, the resistivity decreases of one order of magnitude passing from 1 wt% to 3 wt% of SWCNTs. The resistivity continues to decrease up to 3.5 wt% of SWCNTs, after that the nanocomposite material reaches a conductivity saturation and no remarkable differences can be detected. On the other hand, it is not convenient to adopt a higher weight percentage of SWCNTs because the viscosity of the nanocomposite mixture increases significantly with the concentration of the nanofillers. This aspect compromises the success of the fabrication process.

According to the NASA guidelines, in order to prevent charging effects the volume resistivity of materials to be used in space (geostationary orbit) must be smaller than 10^9 Ohm·cm. Therefore, the nanocomposite materials fabricated in this work satisfy such requirement and can be adopted to produce carbon fiber-reinforced laminates. After converting the resistivity to conductivity, the volumetric electrical conductivity of the nanocomposites at 1 wt% and 4wt% is $2.6 \cdot 10^{-3}$ S/m and $5.4 \cdot 10^{-2}$ S/m, respectively.

3. Multiscale Analysis

The electrical properties of a nanocomposite made of single wall carbon nanotubes (SWCNTs) and RTM6 epoxy resin have been evaluated using the software Digimat. In particular, the analysis were carried out using the tool Digimat-MF, a mean-field homogenization based software which aims at predicting the behavior of multi-phase materials.

In general, the electrical properties of nanocomposite materials strongly depend on the inclusions volume fraction, shape, aspect ratio (the ratio between the length and the outer diameter of the carbon nanotube) and level of clusterization. In fact, an important phenomenon which might or not occur when conductive inclusions are used as reinforcement in composite materials, is the percolation phenomenon. In particular, the electrical conductivity of the composite depends strongly on the inclusions volume fraction; for low volume fractions, the electrical conductivity is basically that of the matrix, typically a dielectric material. Then, when the volume fraction of the inclusions reaches a certain threshold value, the nanocomposite conductivity increases by several orders of magnitude. This threshold is called percolation threshold and depends on the type of inclusions. Percolation occurs when inclusions are in electrical contact with each other (electrons can jump from one inclusion to another), spanning from one side to the other of the representative volume element (RVE). Therefore, when the percolation threshold is reached, the network of conductive inclusions that has formed rapidly increases the electrical conductivity of the nanocomposite.

In Digimat-MF, the following percolation law is implemented, where two parameters, the critical exponent t and the percolation treshold φ_c , are introduced:

$$\sigma_c = \sigma_{in} \left(\frac{\varphi - \varphi_c}{1 - \varphi_c} \right)^t \tag{1}$$

Eq. 1 is the standard percolation law, which can be applied to different phenomena other than electrical conductivity. It states that when the inclusions volume fraction φ is greater than the percolation threshold φ_c the electrical conductivity of the composite σ_c evolves according to this law.
As already explained, the aspect ratio of the inclusions and the level of clusterization have an important effect on the percolation phenomenon. To take these factors into account, Li et al. [8] studies on carbon nanotubes percolation threshold have been considered. These authors have studied the effect of clusterization and aspect ratio on the percolation threshold, obtaining the following expression:

$$\varphi_c = \frac{\varepsilon\xi\pi}{6} + \frac{(1-\xi)27\pi d^2}{4l^2} \tag{2}$$

where ε is the localized volume fraction of CNTs in clusters and ξ is the volume fraction of agglomerated CNTs in the nanocomposite. The highest value of ε is 1, which corrresponds to the situation in which the CNTs are closely packed, where CNTs are tightly entangled in clusters. As concerns ξ, a high value of this parameter means that there is a high number of CNTs entangled in clusters. On the other hand, in the ideal situation of perfectly dispersed nanotubes in the polymer matrix, the value of ξ is equal to zero. This is the condition that was assumed for the electrical analysis carried out using Digimat-MF. With the value of ξ equal to zero, Eq. 2 becomes:

$$\varphi_c = \frac{27\pi d^2}{4l^2} \tag{3}$$

In this expression (Eq. 3), only the dependance on the aspect ratio survives, and it can be seen that the higher is the aspect ratio the lower is the percolation threshold. The aspect ratio considered in our analysis is AR = 55, where the length is 110 nm and the diameter is 2 nm. If the ideal condition of perfectly dispersed SWCNTs is assumed, then the value of $\varphi_c = 7.01 * 10^{-3}$ is obtained.

As concerns the critical exponent t, a value from current literature has been considered. The critical exponent mostly depends on the dimensionality of the system and in three dimensions it assumes a value of $t = 1.94$ [9]. In fact this parameter, for a three-dimensions problem, is typically around 2 when carbon nanotubes are considered [10].

After the evaluation of the electrical properties of RTM6/SWCNT nanocomposite, the properties of a 12k single-ply plain weave carbon fiber composite were evaluated at mesoscale level through the analysis of adequate RVEs. The carbon fibers considered are the Toray T300 produced by the Toray company. In particular, two cases are compared: the case in which the matrix phase is the neat RTM6 epoxy resin and the case in which the matrix phase is the RTM6/SWCNT 1 wt% nanocomposite, which allows the realization of lightweight nanocomposites with high electrical conductivity. The properties evaluated in the previous paragraph were considered for the analysis.

In Fig. 2 the geometry of the RVE analyzed is represented. As concerns the RVE size (a transversely isotropic behavior of the RVE is expected when a certain RVE size is reached), convergence of the analysis was reached with an RVE size of 8×8×0.77 mm^3 and 250,000 finite elements. The carbon fibers volume fraction of the analyzed RVE is about 60%.

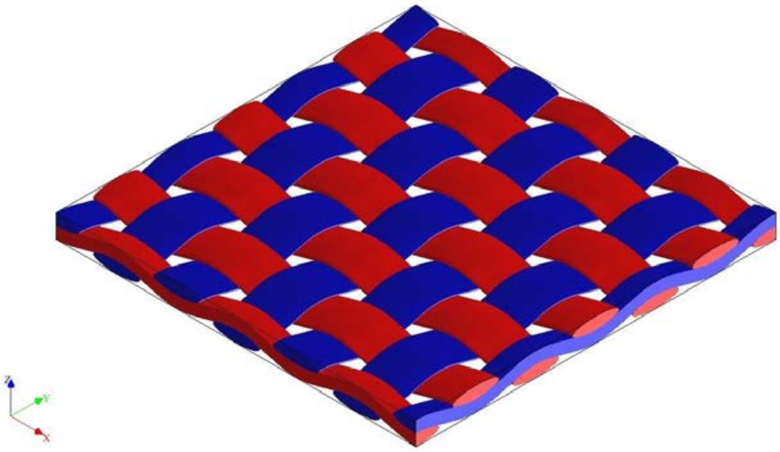

Figure 2. Geometry of the single-ply plain weave carbon fiber composite (RVE).

4. Results

To investigate the effect of the percolation phenomenon on the nanocomposite electrical properties, different SWCNT concentrations have been considered: 0.5 wt%, 1 wt% and 2 wt%. On the microscopic scales, both Digimat-MF and Digimat-FE tools can be used to evaluate the electrical properties of nanocomposite materials. However, the electrical analysis have been performed using Digimat-MF for two main reasons. First of all, Digimat-MF requires lower CPU times than Digimat-FE; secondly, in Digimat-FE the standard percolation law (Eq. 1) is not implemented and the percolation phenomenon is expected to occur when a certain distance between the inclusions is reached. Therefore, the classical percolation model developed in Digimat-MF was used, obtaining the results listed in Table 1:

Table 1. Electrical conductivity by classical percolation model for RTM6/SWCNT composites with different SWCNT concentrations using Digimat-MF.

	Neat RTM6	RTM6/SWCNT 0.5 wt%	RTM6/SWCNT 1 wt%	RTM6/SWCNT 2 wt%
σ_c (S/m)	10^{-10}	$2.2 \cdot 10^{-9}$	10.8	204.2

When the concentration of SWCNTs is 0.5 wt%, the value of the electrical conductivity is low and basically equal to that of the matrix. In fact, since we are below the percolation threshold, the increase in electrical conductivity is very low and the nanocomposite is still an insulating material. By increasing the SWCNTs concentation to 1 wt%, being over the percolation threshold, the electrical conductivity of the nanocomposite increases by several orders of magnitude reaching the high value of 10.8 S/m. The electrical conductivity still increases following the percolation law, reaching the value of 204.2 S/m when the concentration of SWCNTs is brought to 2 wt%.

Regarding the results found for the RTM6/SWCNT 1 wt% system, they are reasonable in the hypothesis of perfect dispersion of the inclusions [10]. Even if such analysis was made with the hypothesis of perfect SWCNTs dispersion, the results found with Digimat-MF are in good agreement with some experimental results reported in the literature. When the SWCNTs concentration is increased to 2 wt% and the hypothesis of perfectly dispersed SWCNTs is maintained, a very high value of electrical conductivity is obtained. This value is much higher than the corresponding experimental results that we obtained and those in the literature [11]. This discrepancy is explained by the fact that, for high concentrations of carbon nanotubes, the assumption of ideal conditions, which neglect the formation of clusters, becomes unrealistic. In addition, these results are obtained in the case of perfect SWCNTs dispersion and for SWCNT aspect ratio AR = 55. Different results are expected when considering different dispersion states or aspect ratio values.

Regarding the electrical conductivity of the single-ply plain weave carbon fiber composite, the results found for the two cases analyzed are shown in Table 2, where σ_i is the electrical conductivity along the i direction. A significant increase of the electrical conductivity in the z-direction (out of plane direction) is observed when the matrix phase is the RTM6/SWCNT 1 wt% nanocomposite. Therefore, by adding 1 wt% of SWCNTs to the matrix phase it is possible to obtain composite materials with high electrical properties.

Table 2. Electrical conductivity of the single-ply plain weave carbon fiber composite

	σ_x/ σ_y (S/m)	σ_z (S/m)
Neat RTM6	$1.9{\cdot}10^4$	$5.3{\cdot}10^{-6}$
RTM6/SWCNT 1 wt%	$2.7 \cdot 10^4$	57.1

5. Conclusions

This work aimed to reduce the volumetric electrical resistivity of the aerospace-grade monocomponent resin RTM6 in order to meet the NASA requirements for spacecraft materials, when the material is exposed to space environment in geostationary orbit. To reach this target, we doped the epoxy matrix with differente weight percentage of SWCNTs, measuring the variation of the volumetric resistivity as a function of the testing frequencies. The experimental results show that the increasing of concentration of carbon nanofiller in the epoxy matrix produces a reduction of the volumetric electrical resistivity of the nanocomposite material. In particular, the nanocomposite material made of 1 wt% of SWCNTs dispersed in RTM6 epoxy resin already satisfies the NASA requirements, because the volumetric resistivity undergoes a severe reduction, passing from the value of 10^{13} Ohm·cm for the neat resin to that of 10^4 Ohm·cm for the nanocomposite. This result is particularly relevant for the manufacturing process, because the viscosity of the nanocomposite mixture increases significantly with the concentration of the nanofillers, compromising the success of the process. In addition, the nanocomposites show a purely resistive behaviour in the range of frequensies between 10 Hz- 10^6 Hz.

The multiscale analysis was performed to investigate the electrical properties of the nanocomposites made of carbon fiber fabric and SWCNT/epoxy, in view of replacing the onerous experimental part. The comparison between numerical and experimental results, related to the SWCNT/epoxy, highlights that, under the hypothesis of perfectly dispersed SWCNTs, a higher value for the electrical conductivity is obtained by numerical analysis with respect to that measured on the experimental samples. The numerical value is much higher than our experimental values and those that can be found in the literature. This discrepancy can be explained by the fact that, when dealing with high mass/volume fractions, considering ideal conditions, meaning ignoring the formation of clusters, is a strong assumption. On the other hand, modelling the lamina with the electrical properties of SWCNT/epoxy at 1wt%, a significant increase of the electrical conductivity in the z-direction (out of plane direction) was observed with respect to the in-plane conductivities.

Acknowledgments

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