

Correlation between electrical conductivity and manufacturing processes of nanofilled Carbon Fiber Reinforced Composites¹

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ABSTRACT

This paper describes the difference on the electrical performance of carbon fiber reinforced composites (CFRCs) when two different *Resin Film Infusion* (RFI) manufacturing techniques are used. The nano-filled resin was infused into a carbon fiber dry preform using either a traditional approach or an unconventional bulk infusion technique. The nanofilled resin consisted of an epoxy matrix prepared by mixing a tetrafunctional epoxy precursor with a reactive diluent to reduce the viscosity of the epoxy precursor, in which 0.5 % wt multiwall carbon nanotubes (MWCNTs) were dispersed. The measured in plane and out of plane electrical conductivities of the panel manufactured using the bulk infusion, were $2.0 \times 10^4 \text{S/m}$ and 3.9 S/m respectively. The in plane and out of plane electrical conductivities of the panel prepared using the traditional resin film infusion were $1.1 \times 10^4 \text{S/m}$ and 1.7 S/m respectively. Morphological investigations on the sections of etched panels have highlighted that this difference in the electrical conductivity was strictly related to the different distribution of CNTs between the carbon fibres (CFs) of the plies. In the case of the traditional processing technique, the network of carbon nanotubes was found to be preferentially arranged between the plies of CFs in direction approximately parallel to the plane of the panel, whereas CNTs were found more profusely arranged through the section of the panel in the direction perpendicular to the plane for samples manufactured with the bulk infusion approach.

Keywords: Carbon-carbon composites (CCCs); Thermosetting resin; Electrical properties; Resin film infiltration (RFI)

INTRODUCTION

Carbon fiber reinforced composites (CFRCs) are expected to contribute more than 50% of the structural mass of future aircrafts. Carbon fiber composites can be classified on the basis of the length (short or continuous) of the employed fibers. Continuous carbon fibers, aligned unidirectionally or forming a woven fabric have stronger effect on the mechanical, electrical, and thermal properties and give rise to composites characterized by higher anisotropy than that of found with short fibers [1]. In particular, CFRCs based on epoxy resins exhibit some rather inherent unsatisfactory characteristics, such as poor electrical conductivity. Epoxy resins are known, in fact, for their good or excellent properties covering an extensive range of applications [2-4], but at same time for their undesired electrical insulating behavior which limits their applicability as aeronautical materials. This drawback has raised concern over the performance of the composite structure during a lightning strike event due to the remarkable risk that a puncture of the structural part would cause a catastrophic failure of the aircraft.

In a traditional aircraft structure, the aluminium skin of the aircraft provides a highly conductive path for the lightning to flow around the structure without causing damage. Without a conductive path on the skin of a composite aircraft the lightning may pass through the airframe which could vaporize metal control cables, weld hinges on control surfaces and explode fuel vapours within fuel tanks. These *direct effects* also typically include vaporization of resin in the immediate strike area, with possible burn-through of the laminate. *Indirect effects* occur due to electromagnetic phenomena: high and steep-fronted transient over-voltages can damage and even destroy on board electronics or ignite potentially dangerous sparks. In addition electromagnetic interference may affect the proper functioning of the different on board electrical and electronic systems.

Airplanes get struck by lightning frequently; obviously and fortunately, they are built to withstand such stresses.

Modern composites are reinforced with conductive metal fibres or metal screen in order to dissipate lightning currents. But many of these solutions add additional weight and partially reduce the advantage of the composite applications.

However, in the last decade, the availability of different nanofiller or nanostructured conductive materials has sensibly contributed to the continuous improvement of the engineering properties or abilities of the composites for aeronautic or automotive industries.

By choosing the appropriate control of the material structure, as well as the appropriate fillers this critical point may be suitably overcome.

In particular, one strategy to increase the application range of epoxy resin impregnating layers of CFs is to incorporate nanoscale conductive fillers, such as carbon nanotubes (CNTs) [5-13], that are intrinsically characterized by high electrical conductivity. However, the incorporation of CNTs inside of epoxy matrices to manufacture CFRCs is not a trivial issue. In fact, even though CNTs hold much promise to impart tailored electrical conductivity to the composite panels, there are still several unresolved questions related to their distribution in the matrix and to the processability of the CNTs filled systems [14-15]. The existing liquid moulding processes, such as resin transfer moulding (RTM) and vacuum assisted resin transfer moulding (VARTM) may be adapted to manufacture CFRCs impregnated with CNTs nanofilled resins. Unfortunately, loading percentages of CNTs larger than 0.3-0.5% by weight may lead to unacceptable high resin viscosities. In addition to the viscosity issues related to the high CNTs contents, filtration of the nanofillers by the fibrous medium may also lead to inadequate final component quality.

Traditional liquid infusion process for CNTs nanofilled resin may lead to undesired filtration effects mainly due to “deep bed filtration” mechanisms causing a gradual reduction of the available flow channel dimensions. Clogging of the fibrous porous media and slowing down the resin flow front progression resulting in longer infusion cycles cause CNTs concentration gradients [16].

In this paper, in order to obtain high electrical conductivity, multi-wall carbon nanotubes (MWCNTs) were embedded inside an epoxy resin based on a mixture of tetraglycidylmethylenedianiline (TGMDA) and 1,4-butandiol diglycidylether (BDE). This particular epoxy formulation has proven to be very effective for improving nanofiller dispersion due to a decrease in the viscosity [17-20] and, in addition, it has been found to reduce the moisture content which is a very critical characteristic for aeronautic materials [17,21]. Furthermore, in order to minimize the filtration effects [22-23], the traditional liquid infusion process has been modified as described in the sequel.

The amount of MWCNTs inside the epoxy mixture used to impregnate plies of carbon fiber cloths was chosen by studying the electrical behavior of the nanofilled resin alone (without carbon fibers - CF). The electrical percolation threshold (EPT), i.e. the value of filler content ensuring the transition from insulating to conducting behaviour of the composite, was found to be in the range [0.1 - 0.32 % wt]. Also the ac measurements confirmed that the EPT ranges between 0.1 - 0.32% wt. An amount of 0.5% wt, beyond the EPT has been, then, adopted to prepare the nanofilled epoxy mixture used to manufacture the carbon-fiber reinforced panels through two different techniques: a traditional infusion approach and an unconventional process using inspired by Resin Film Infusion technique allowing to minimize the filtration effects via a better compaction and reduced resin flow paths. In this last case, a thick wet film of resin has been placed under the carbon preform (400mm x 400mm) made laminating 7 plies of carbon fiber cloths, in a vacuum bag, without any tube connection with external reservoirs, so that the resin

is forced through the shortest possible path for infiltration, reducing at the minimum the necessary time and filtering problem. Using this last approach, the temperature can be better controlled during the infiltration, without any gradient along the resin path. Moreover, during the final phase of infiltration and during the curing it is possible to add autoclave pressure to better compact the preform, squeezing out the excess of resin, once the preform is full impregnated under vacuum. It is found that the reduced flow path strongly affect the nanotubes dispersion between the CF plies.

EXPERIMENTAL

Materials

Nanofilled resin

The epoxy matrix was prepared by mixing the epoxy precursor, tetraglycidylmethylenedianiline (TGMDA) (epoxy equivalent weight 117–133 g/eq), with an epoxy reactive monomer 1-4 butanedioldiglycidyl ether (BDE) that acts as a reactive diluent. The curing agent used for this study is 4,4-diaminodiphenyl sulfone (DDS). The epoxy mixture was obtained by mixing TGMDA with BDE monomer at a concentration of 80%:20% (by wt) epoxide to flexibilizer. The curing agent was added at a stoichiometric concentration with respect to all the epoxy rings (TGMDA and BDE), this mixture will be named hereunder T20BD formulation.

The MWCNTs (3100 Grade) were purchased from Nanocyl S.A. Transmission electron microscopy (TEM) investigation has shown for MWCNTs an outer diameter ranging from 10 to 30 nm. The length of MWCNTs is from hundreds of nanometers to some micrometer. The number of walls varies from 4 to 20 in most nanotubes. The specific surface area of MWCNTs determined with the Brunauer–Emmett–Teller (BET) method is around 250-300 m²/g; the carbon purity is > 95% with a metal oxide impurity <5% as it results by thermogravimetric analysis. Epoxy blend and DDS were mixed at 120°C and

the MWCNTs were added and incorporated into the matrix *via* ultrasonication for 20 min. An ultrasonic device, Hielscher model UP200S (200 W, 24 kHz) was used. The epoxy mixture T20BD was filled with MWCNTs at 0.5% concentration by wt. This nanofilled sample will be named hereunder T20BDCNTs formulations. This concentration was chosen because the curve of dc volume conductivity vs. MWCNTs concentration (the percolation curve shown in Fig. 1) highlighted that the electrical percolation threshold (EPT) is lower than 0.32 %, therefore for this amount of MWCNTs the nanofilled formulation is beyond the EPT [21-24]. The value of the dc conductivity corresponding to the selected 0.5%wt concentration is 0.03 S/m.

The formulation T20BDCNTs is also characterized by good dynamic mechanical properties. In fact, it is found that the incorporation of a small concentration of MWCNTs(0.32%) in the temperature range of $-60 \div 180$ °C causes an increase in the elastic modulus value with respect to the modulus of the unfilled epoxy matrix. Values between $3600 \div 1800$ MPa are found in the temperature range of $-60 \div 180$ °C. The nanofilled formulation is characterized by values of glass transition temperature (T_g) higher than 180 °C [21, 25].

CFRCs –Manufacturing Process

INFUSION –PANEL MANUFACTURED USING TRADITIONAL APPROACH

In the classical scheme of infusion the resin is heated in a reservoir connected to the vacuum bag by a small diameter nylon tube (8 mm) (see Fig. 2). Under the vacuum bag, on the preform, a distribution medium is used to facilitate the flow of the resin on the surface on the panel. In this way the resin has no difficulties to reach every point on the surface, while the vacuum in the preform pores attracts the resin along the shortest normal path (few mm).

The usual values of viscosity accepted in the typical infusion process is approximately 300 mPas, and the injection temperature does not exceed 80°C.

Rheometric analysis of the nanofilled formulation T20BDCNTs shows that an acceptable value of viscosity is reached at quite high temperature (100 °C), which is unusual, but still feasible with disposable materials normally used for infusion.

This classical liquid infusion approach was followed using a sequence of different steps. First, a water based PTFE release agent (Release All Safelease 30 Airtech) was poured on a mold plate. (Release All Safelease 30 Airtech). The mold was covered by layers of release film (Release Ease 234 TFP-HP Airtech). As release film, PTFE coated fibreglass was used to increase the porosity to allow excess resin, volatiles and trapped air to escape into the breather during injection and curing. 7 plies were layered on the mold. The laminate was covered by a release film and by a double layer of distribution medium (Resinflow 90 HT Tmax 177°C) for the $\frac{3}{4}$ of the major length. The distribution medium was a mesh to flow easy the resin on the surface of the laminate. At the end of the mesh the resistance of flowing resins increases so it can impregnate the preform. A breather cloth was placed in the opposite edge. A double bag strategy, which generally increases the reliability of the process and distributes better the squeezing effect of vacuum during the curing phase was applied.

The panel on the mold and the nanofilled resin reservoir were thermostated at 120°C in a autoclave/oven. Once the injection was completed, the cure cycle started.

The panel was cured increasing the temperature with a ramp of 3°C/min up to 190°C. That temperature was maintained for 3 hours, then was cooled slowing with a rate of 2°C/min. The obtained panel will be named hereunder P1T sample.

INFUSION –PANEL MANUFACTURED USING THE UNCONVENTIONAL APPROACH

A thin layer of liquid epoxy mixture containing MWCNTs (0.5% by wt) was spread on a release films (*Release Ease 234 TFP-HP Airtech*); then a dry preform (400mm x 400mm) made laminating 7 plies of carbon fiber cloths (SIGMATEX (UK) LDT 193GSM (*grams square meter*) /PW (*plain wave*) /HTA40 E13 3K(*3000 fibers each tow*)) was placed on mixture forcing it to flow through the thickness of the preform using an external supplementary pressure inside an autoclave. This procedure has allowed that the length of the impregnation path was considerably reduced with respect to the traditional approach, and the process can be forced by means of the pressure application. A further advantage of this technology is associated to the smaller length of the infiltration path which reduces the effects of infiltration through the preform, ensuring a more uniform distribution of the nanofiller through the panel thickness. In fact, the edges of the preform were sealed to force the resin to flow only through the thickness. Then, the laminate was covered by a porous release film and a distribution media to allow the resin to escape from the upper side and a breather media to receive the excesses of the resin.

This impregnation process was performed at the same temperature set up for the injection in the traditional approach ($T=120^{\circ}$). Finally, it was placed in a vacuum bag and transferred into the autoclave for the curing. The obtained panel will be named hereunder P2B sample.

Methods

Morphological Investigation

The morphology of CFRCs was investigated before and after etching procedure to remove a fraction of the resin around the nanofiller and better evidence the morphological feature.

Micrographs were obtained by using a Field Emission Scanning Electron Microscope (FESEM, mod. LEO 1525, Carl Zeiss SMT AG, Oberkochen, Germany).

Strips of CFRCs were cut out from the panels and analyzed in direction parallel (i.e. in plane) and perpendicular (i.e. out of plane) to the panel plane. Some of the samples were etched before the observation by FESEM microscopy. The etching reagent was prepared by stirring 1.0 g potassium permanganate in a solution mixture of 95 ml sulphuric acid (95-97%) and 48 ml orthophosphoric acid (85%). The filled resins were immersed into the fresh etching reagent at room temperature and held under agitation for 36 hours. Subsequent washings were done using a cold mixture of 2 parts by volume of concentrated sulphuric acid and 7 parts of water. Afterwards the samples were washed again with 30% aqueous hydrogen peroxide to remove any manganese dioxide. The samples were finally washed with distilled water and kept under vacuum for 5 days. The samples were placed on a carbon tab previously stuck to an aluminum stub (Agar Scientific, Stansted, UK). The samples were covered with a 250-Å-thick gold film using a sputter coater (Agarmod. 108 A).

Electrical Measurements

An electrical characterization of samples obtained with the two techniques has been carried out in order to investigate the DC volumetric conductivity along the fiber direction, i.e. the in plane value indicated as $\sigma_{v//}$, and that characteristic of the direction perpendicular to the fibers, i.e. the out of plane value, named $\sigma_{v\perp}$.

The measurement of $\sigma_{v//}$ has been performed by using strip samples of about $1.7 \times 4.0 \times 0.17$ cm³ whereas $\sigma_{v\perp}$ is carried out on specimens shaped as square tiles of about $6 \times 6 \times 0.17$ cm³.

Before performing the electrical measurements, the samples have been cleaned with acetone and thermally pretreated at 80°C for 24h. In order to ensure good ohmic contacts

between the electrode measurement and the sample surface, a silver paint (Alpha Silver Coated Copper Compound Screening, with a thickness of about 50 μ m and a resistivity of 0.7 Ω -square) is deposited.

Electrical measurements have been performed at room temperature with a four (Fig. 3) or three (Fig. 4) electrode arrangement for $\sigma_{v//}$ and $\sigma_{v\perp}$, respectively, by using two multimeters HP 34401A (for current I_1), HP 3408A (for the current I_t) and the electrometer Keithley 6514A (for the voltage V_m).

In Fig. 3, a and b are the length and width of the volumetric contact, respectively and s is the thickness of the CFRC samples.

In Fig. 4 D_1 and D_2 are the diameter of the inner and outer electrode of the top side, respectively, D_3 is the electrode diameter of the bottom side and s is the sample thickness. Geometrical dimensions, with their relative uncertainty in the form $x\pm\Delta x$, of the electrode configuration for the strip sample are reported in Table 1.

In this case, the volumetric conductivity is calculated using the following expression:

$$\sigma_{v//} = \frac{1}{R_c} * \frac{a}{b * s} \quad (1)$$

where $R_c=V_m/I_1$ is the sample resistance and a , b and s the geometric quantities of Fig. 3.

Instead, the Table 2 summarizes the geometrical dimensions of the electrode configuration for the square sample.

By setting g and K_v equal to:

$$g = \frac{D_2 - D_1}{2} \quad (2)$$

$$K_v = \left(\frac{D_1}{2} + 0.5 * \frac{g}{2} \right)^2 \quad (3)$$

the out of plane conductivity is evaluated according to equation :

$$\sigma_{\perp} = \frac{1}{R_c} * \frac{s}{\pi * K_v} \quad (4)$$

where $R_c = V_m/I_l$ is the measured resistance of the sample. In order to improve the statistical validity of the results limiting the effects of possible material non uniformity associated to the manufacturing process, each data point is obtained as the average of five measurements.

RESULTS AND DISCUSSION

Carbon fiber reinforced panels: morphological investigation

Fig. 5 shows the FESEM images of some cross sectional areas of the non-etched panels P1T (a) and P2B (b). The figure clearly shows the number of plies in the two panels. Unlike sample P2B, sample P1T does not retain perfect parallelism between the layers. Strips of these panels were cut out from the panels and analysed in direction parallel to the panel plane. As described in the experimental section, these samples were treated with a strong etching reagent before observing them by means of FESEM. It is worth noting that the adopted etching procedure has proven to be very effective to remove part of the resin surrounding the nanotubes, leaving their network in the resin clearly visible.

Figs. 6 and 7 show the FESEM images of samples obtained from different regions of the etched panel P1T. The same morphological arrangement of CNT network is detected in all regions. Moreover, the network of CNTs tends to be preferentially arranged between the plies of CFs in direction approximately parallel to the plane of the panel.

Fig. 8 shows the FESEM images of the etched panel P2B manufactured using the unconventional process.

In this case, a significant contribution of carbon nanotubes arranged preferentially through the section of the panel in the direction perpendicular to the plane was found in many regions. Also in this case, regions on different strips of the panel P2B show the same morphological organization of the CNT network as shown in Fig. 9 where it is

possible to observe the CNT network entering between the carbon fibers along the transverse direction perpendicular to the panel plane.

In conclusion the morphological organization of the nanofiller network inside the panels is strongly influenced by the method used to manufacture the panels.

Electrical and rheological properties

The performance of the adopted impregnating epoxy system and the effectiveness of the implemented manufacturing processes can be evaluated in terms of electrical properties of the fabricated panels.

The voltage–current characteristics (i.e. V-I) measured with a four and three electrode geometry for the composites P1T and P2B are shown in Figs 10 (a-b), respectively.

The slope of the I-V characteristics, i.e. resistance R_c in (3) and (4) of the panel manufactured using the traditional technique is larger than that of the sample made with the new bulk infusion technique both for the in plane and for the out of plane components.

In particular, the obtained $\sigma_{v//}$ is 11.3 kS/m for the systems P1T, whereas a value of 19.5 kS/m is found for the system P2B manufactured with the unconventional technique. Also for the out of plane conductivity $\sigma_{v\perp}$ the system P2B shows higher values. In fact, a value of 3.9 S/m is achieved for this type of system, whereas a value of 1.7 S/m is detected for the system P1T.

It has to be considered that, in order to reliably dissipate lightning currents without embedding weight-adding, conductive wires or screens inside the composites employed in aircraft structural parts (e.g. fuselage or wings), a sufficiently high equivalent bulk conductivity of the composite, typically in the order of 10 S/m, has to be achieved [13, 19]. Both values of $\sigma_{v\perp}$ obtained with our formulations, and particularly that for the P2B system are, to the best of the authors knowledge, rather close to such target values and

among the highest ones presently achieved. For example, for a 8 plies CFR system impregnated with an epoxy composite filled with Double Wall CNTs at a weight fraction of 0.4%wt, a value of the transverse conductivity of 0.123 S/m has been obtained [26]. A more ample analysis of the literature data concerning the performances achieved with different CNT-based impregnation systems and fabrication approaches will be presented in a separate forthcoming paper. In any case, it is worth noting that, as indicated by the numerous and notable efforts performed by different research academic and industrial groups, an increment of a factor of two, as that allowed by the novel infusion approach, may be a significant step toward the achievement of the target performance.

By comparing the results in Table 3, it can be noticed that rather large improvements, equal respectively to about 72% for the in plane conductivity and 120% for the out of plane conductivity, are achieved by the innovative bulk infusion process. As a matter of fact, for the overall performances of the composite the most important effect is the increase in the out of plane conductivity, since the in plane conductivity reaches high values with both processes. Such significant increment of the $\sigma_{v\perp}$ values achieved for the P2B system may be explained by considering the adopted approach, since, at least before the infusion phase, the impregnating nanofilled resin has identical characteristics.

In fact, during the bulk infusion process, the mixture is forced to flow through the thickness; consequently the impregnation paths are significantly reduced with respect to those related to the traditional approach where the resin travel mainly along the fiber direction in the plane. Consequently, for the former approach the formation of voids is less probable and, most of all, the distribution of CNTs through the panel thickness can be facilitated. In fact, as evidenced also by the morphological investigations, CNTs embedded in the resin are forced, between the different plies, to align themselves preferably in the direction normal to the panel (see images of Figs 8-9), thus contributing to form conducting bridges between the carbon fiber layers. In this way, the $\sigma_{v\perp}$ may

increase by the formation of an increased number of parallel paths. These paths positively affect also the in plane conductivity of the P2B system. Such a mechanism may be less effective within panels manufactured with the traditional approach (see Figs. 6-7) where a higher probability of random distribution is generated by the longer path along the panel plane.

Rheological measurements made in steady shear flow at 120°C, corresponding to the injection/impregnation temperature, provide a further experimental evidence to support the hypothesis that flow condition strongly affects the geometrical arrangements of the CNTs inside the matrix.

The incorporation of CNTs in the formulated epoxy resin mixture significantly modify the rheological behavior. In fact in Fig. 11 a shear thinning behavior, with η values much higher at lower shear rate, is observed.

It is well-known that shearing flow tends to align the fibers in the shear direction [27]. Thus suspension with aligned fibers exhibits lower viscosity than that with randomly orientated fibers as these last experience lower resistance. This phenomenon could be extended to the nanoscale in CNT/polymer suspensions.

It is generally recognized that during composite processing, such as injection or compression molding, CNT suspension undergoes to a modest amount of shear which orients the CNTs in the direction of the shear or stretching [28]. The observed shear thinning behavior of the epoxy mixture is hence a further evidence of the alignment of CNTs in the main direction of the flow under both traditional and unconventional processes.

The same conclusions have been gathered at lower temperatures by Nobile et al. [29]. They analyzed the rheological behavior of the same formulations used in this paper at two different temperature (50 and 75°C), and compared the obtained results on both CNT filled and unfilled systems. Small amplitude oscillatory shear measurements at 1% strain,

within the linear viscoelasticity region, were performed in the frequency range between 0.01 and 100 rad/s. Measurement of the complex viscosity show that the unfilled resin exhibits essentially a Newtonian behavior while for the CNTs filled resins a shear thinning behavior is observed. The trend of the storage (G') and the (G'') loss modulus with the frequencies indicates the formation of a percolation network.

The above interpretation, which is indeed supported by the SEM morphological analysis, would benefit from a confirmation based on theoretical study concerning the effects on the percolation properties (EPT, achievable conductivity values) imposed by the diverse characteristics (distance end to end, direction of propagation, velocity) of the resin flow inside the panel associated to the two infusion approaches. However, such a very interesting topic, requiring an extensive and time consuming numerical modeling activity is beyond the scope of the present communication and will be considered in future papers. In the current literature, the effect of the filler alignment on the percolation characteristics has been dealt with both theoretically and experimentally with rather heterogeneous results. For example in a numerical simulation study [30] the highest conductivity is achieved when CNTs are partially aligned rather than for perfectly or randomly (i.e. isotropically) aligned structures. For low CNTs concentration the highest conductivity is achieved for very weak orientation i.e. when the isotropic case is approached.

On the other side, in the experimental study by Wang et al. [31] it has been shown that for composites where a preferential CNT alignment is obtained by repeatedly stretching the material, the electrical percolation threshold along the stretching direction is lower than the value perpendicular to the CNTs orientation. Moreover, the electrical conductivity along the stretched direction is higher than perpendicularly to it. In [26] the increment of the transversal conductivity of carbon fiber aeronautical composites impregnated with CNT-filled epoxy is associated to a bridging effect due to the CNTs in the interlaminar region between plies. Similar results are also reported for glass fiber

composites impregnated, respectively with a CNTs filled matrix [32] or with carbon nanofibers [33].

CONCLUSIONS

In this paper we have shown the results obtained using two different *Resin Film Infusion* (RFI) manufacturing techniques to obtain panels with CFs impregnated using resin with 0.5 wt % CNT loading. In addition to a traditional approach, an unconventional bulk infusion technique has been used to infuse the nano-filled resin into a carbon fiber dry preform. For the panel manufactured using the bulk infusion the obtained in-plane electrical conductivity is $2.0 \times 10^4 \text{S/m}$ (in-plane electrical conductivity) and 3.9 S/m (out of plane value), whereas lower values, respectively $1.1 \times 10^4 \text{S/m}$ and 1.7 S/m for the in-plane and out of plane conductivity, are achieved with the traditional technique.

Significant improvements, equal respectively to about 72% for the in plane and 120% for the out plane conductivity are achieved by the bulk infusion process with respect to the traditional approach. Such remarkable increments can be associated to the mechanisms governing the infusion process. Most likely, the voids formation inside the impregnating resin is less pronounced with the bulk infusion due to the shortest (i.e. top-down through the thickness) path that the resin has to complete the infusion process.

Morphological investigations on the sections of etched panels highlighted that the difference in the electrical conductivity is closely correlated to the different distribution of CNTs between the carbon fibers (CFs) plies. In particular, it was found that, in the case of traditional processing technique, the network of carbon nanotubes tends to be preferentially arranged between the plies of CFs in directions approximately parallel to the plane of the panel, whereas CNTs are more profusely arranged through the section of

the panel in the direction perpendicular to the plane for samples manufactured with the bulk infusion approach.

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LIST OF TABLE CAPTIONS

TABLE 1. Geometrical dimension of the electrode configuration for the strip sample.

TABLE 2. Geometrical dimension of the square sample electrode configuration.

TABLE 3. Values of $\sigma_{v//}$ and $\sigma_{v\perp}$ for the P1T and P2B systems.

LIST OF FIGURE CAPTIONS

Fig. 1. Percolation curve for the considered T20BDCNTs system.

FIG. 2. Infusion - classical scheme.

FIG. 3. Arrangement for the measurement of the volumetric in plane DC conductivity: electric circuit (on the left); geometric structure for four point method (on the right).

FIG. 4. Arrangement for the measurement of the out of plane volumetric DC conductivity: electric circuit (a); geometric structure of the top and down electrodes (b).

FIG. 5. FESEM images of the cross sectional areas of the not etched panels P1T (a) and P2B (b).

FIG. 6. FESEM images of the etched panel P1T: the strips have been observed in direction parallel to the panel plane.

FIG. 7. FESEM images of the etched panel P1T: the strips have been observed in direction parallel to the panel plane.

FIG. 8. FESEM images of the etched panel P2B: the strips have been observed in direction parallel to the panel plane.

FIG. 9. FESEM images of the etched panel P2B: the strips have been observed in the section perpendicular to the panel plane.

FIG. 10. I-V characteristic: a) along the fiber direction; b) perpendicular the fiber direction.

FIG. 11. Viscosity curve for the CNT filled epoxy matrix at 120°C.