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Manufacturing of conductive structural composites through spraying of CNTs/epoxy dispersions on dry carbon fiber plies

Mathieu Fogel^{a,b,*}, Patricia Parlevliet^a, Philippe Olivier^c, Éric Dantras^b

^aAirbus Group Innovations, Composite Technologies, 81663 Munich, Germany

^bUniversité de Toulouse, Physique des Polymères, Institut Carnot CIRIMAT, 31062 Toulouse Cedex 9, France

^cUniversité de Toulouse, Institut Clément Ader, 31077 Toulouse Cedex 4, France

A B S T R A C T

In this work, multiscale Carbon Fiber-Reinforced Polymers have been manufactured by inserting carbon nanotubes in the matrix of the composite material to improve and homogenize the through-thickness electrical conductivity. A first part of this work introduces a spraying technique and manufacturing process followed to produce the CNT-doped multiscale CFRP. A quality assessment of the produced material is also presented. A second part investigates the electrical conductivity, as well as a few mechanical properties of the newly manufactured material, to be able to conclude on the viability and potential of this technique. This paper presents the further development of an earlier study presenting the thermal, rheological and electrical behavior of the CNT doped epoxy matrix (Fogel et al., 2015).

Keywords:

Carbon nanotubes

Carbon fibers

Nano composites

Electrical properties

Mechanical properties

1. Introduction

Carbon-Fiber-reinforced Polymers (CFRP) have gained popularity over the years replacing traditional metallic-based structures due to the fact that they offer a much better mechanical properties/weight ratio, allowing manufacturers to reduce the weight per passenger ratio of their airplanes. Unlike their metallic counterparts, CFRPs are significantly less conductive, due to the interleaving polymeric matrix, which prohibits the electrical charges to flow through the material especially in the through-thickness direction. Inserting CNTs (Carbon Nanotubes) in the polymer matrix of CFRPs may lead to an increase in through-thickness electrical conductivity expected in order to partially fulfill electrical conductivity requirements traditionally met by metallic structures.

The introduction of CNTs into conventional fiber-reinforced polymer composites is thus assumed to significantly improve composite performance [2,3]. However, in order to manufacture such multiscale composites, three processing challenges have to be overcome: re-agglomeration [4], as well as increase in matrix viscosity and CNT filtration [5]. Two main processing routes are used in order to produce multiscale composite. The first potential approach is based on the growth or attachment of CNTs to regular

carbon fibers [6–9]. Grafting CNTs onto conventional fibers could provide higher loadings and CNTs exhibiting a radial orientation, which is expected to be the best configuration for enhancing matrix dominated mechanical properties. On the other hand, attaching CNTs on large quantities of carbon fibers requires process development in order to offer up-scalability.

A second approach for producing CNT-doped composites consists in inserting carbon nanotubes directly into the matrix of the fiber-reinforced polymer. Among the extensive research on this subject, Davis et al. [10] developed a spraying technique to deposit fluorine functionalized CNTs, which were dispersed in an ethanol solution using a high-shear mixer before being sonicated for 30 min. After the spraying process, the solvent was evaporated and deposits of CNTs at the desired percentage (up to 0.5 wt.%) remain on the fabric surface. They assumed that during the subsequent VARTM (Vacuum Assisted Resin Transfer Moulding) laminate fabrication, CNTs remained on the fabric surface but that some were dispersed in the matrix to produce what they believed to be a toughened fiber–matrix interface. Nevertheless the potential wash-out effect of the filtration effect was not investigated. In the same way, Shan et al. [11] developed a spraying technique used to deposit carboxylic acid functionalized MWCNTs on the surface of carbon fiber fabrics via a three step process. First, a solution of ethanol-dispersed CNTs was sprayed and dried on the fibers, followed in a second step by the spraying of an epoxy binder with a higher viscosity used to anchor the CNTs on the fabric. Finally,

* Corresponding author at: Airbus Group Innovations, Composite Technologies, 81663 Munich, Germany.

E-mail address: mathieufogel@gmail.com (M. Fogel).

the laminate was infused using vacuum assisted resin infusion. They reported a good CNT dispersion and that this anchoring technique was effective. The composite modified with the CNTs and binder material exhibited increased interlaminar properties (G_{Ic} increased by 24%, G_{IIc} by 11% and ILSS by 12%), while the CNT doped laminate without binder showed a decrease in these properties. While this processing methods and results are interesting, the influence of the epoxy binder alone may explain this increase in properties.

This spraying method is particularly interesting as it may overcome the issues of filtration and viscosity, and, combined with the use of the calendaring technique (as presented in [1]) can lead to the development of a process which do not require the use of a solvent and enables a nanoreinforcement targeted to the interlaminar region for a bridging effect between carbon fiber plies to seek for an increase in through-thickness electrical conductivity.

On this topic, two important works deserve to be mentioned. First the work of Bekyarova et al. [7] reported the use of electrophoresis to depose MWCNTs on woven carbon fabrics. These were subsequently infiltrated with epoxy resin using VARTM. The through-thickness conductivity was measured by four-probes testing and compared to a reference sample manufactured in the same conditions. Baseline samples exhibited a through-thickness conductivity (also known as Z-conductivity) of 6.8 S m^{-1} while the CNT treated reached 8.9 S m^{-1} (30% improvement). Furthermore, El Sawi et al. [12,13] presented a suitable technique to insert DWCNTs in a unidirectional CFRP. To do so, they developed a liquid resin infusion process in order to impregnate individual UD plies of carbon fibers by an epoxy matrix where CNTs had been previously dispersed. At room temperature, the reference CFRP reached a through-thickness conductivity of $6.6 \times 10^{-5} \text{ S cm}^{-1}$, while for the 0.4 wt.% doped CFRP it reached $5.3 \times 10^{-3} \text{ S cm}^{-1}$. Carbon nanotubes increase the electrical conductivity through the thickness by one order of magnitude, while in the two other directions the conductivity was not affected.

In this paper, we introduce an original spraying technique and manufacturing process followed to produce CNT-doped multiscale composites in order to increase the through-thickness electrical conductivity of the material. Manufacturing CNT doped CFRP with such a technique requires a good knowledge of the processing parameters involved, considering that the spray gun operates at higher processing temperatures and shear rates. That is why, it was proposed in a previous work [1] to study the thermal, rheological and electrical behavior of the CNT doped epoxy to pave the way for the CFRP manufacturing process presented in this work.

2. Materials and methods

2.1. Materials

The epoxy matrix used in this study is the commercially available MVR 444 provided by Cytec Industries Inc. This epoxy matrix is a single component resin where the epoxy prepolymer and amine hardener are already mixed together and degassed. It is typically used to manufacture aerospace composite components using vacuum assisted resin transfer molding and is usually cured at 180 °C.

The Carbon Nanotubes selected are Multi-Walled Carbon Nanotubes (MWCNT) provided by Arkema (France). A masterbatch based on Cytec's MVR 444 resin was prepared by Arkema using their Graphistrength CS1-25 MWCNTs as an additive (25 wt.%). With this method the CNT masterbatch is based on the same resin as the one used to dilute to the final CNT concentration, and by thus ensuring perfect compatibility.

Unidirectional carbon fabric from SAERTEX was used as dry reinforcement material. This non-crimp fabric is composed of TENAX J IMS60 E 13 24 K fibers in the 0° direction as well as reinforcing threads made of glass-reinforced polypropylene in the 90° and ±60° directions and stitching threads made of polyester.

2.2. Experimental methods

2.2.1. CNT dispersion

Carbon nanotubes dispersion was carried out using a three roll mill (Exakt 80E, EXAKT GmbH, Germany). The masterbatch was first diluted with uncured epoxy resin to the desired CNT concentration and then calendered. A calendaring cycle developed in a previous work was used [1]. It is composed of 9 successive cycles, with gaps between rolls decreasing progressively from 120 to 5 μm and back-roll speeds increasing progressively from 100 to 500 rpm. Mixtures were manufactured with a CNT weight content of 0.75 wt.% as it was found to be the best compromise between electrical conductivity (post-percolation electrical conductivity levels) and process-ability (limited increase in viscosity) of the CNT/epoxy dispersions.

2.2.2. Processing of CNT-modified CFRP

The spraying equipment used to deposit the CNT-epoxy dispersions on the dry carbon fiber plies was delivered by Viseco GmbH and is composed of three main parts: a spray gun as well as two control units regulating the air temperature and pressure as well as the temperature of the spray gun itself.

After being dispersed, the epoxy/CNT dispersion is poured into the gun container. By pulling the trigger a stream of material is released. In order to spray as uniformly as possible a grid spraying pattern was adopted. It turned out to be a reproducible and homogeneous method to cover the whole carbon fiber ply. Each carbon fiber layer was sprayed with the relevant amount of resin as well as the lower and upper surface of the preform. It was experimentally determined that a resin amount of $134 \pm 8 \text{ g m}^{-2}$ had to be sprayed to achieve a fiber volume fraction of 60% in the case of a 298 g m^{-2} unidirectional carbon fiber ply (a scale was used to gauge the mass deposited while spraying). The gun temperature and pressure applied were carefully chosen to avoid premature curing of the resin, achieve a viscosity as low as possible, and maintain the dispersed state of the CNT. This was done by performing linear temperature rheological sweeps for pristine and CNT-doped epoxy. A gun temperature of 60 °C and an air pressure of 2 bar were found to be optimal.

After having sprayed the CNT-doped material on the carbon fiber preform, the pre-impregnated preforms were cured with two main objectives. First, evacuate the air trapped in the preform during the spraying step to avoid the formation of porosity, and second to obtain a homogeneously and fully cured composite. In order to do so, the preform was placed in an oven and sealed in a semi-permeable membrane to enclose the pre-impregnated material in a resin-tight chamber. A layer of breather material was positioned on top to apply the vacuum homogeneously. A second chamber was then created by sealing the layout with a vacuum bag. In a first phase, the assembly is heated up to 80 °C and evacuated down to a pressure of 10^{-2} mbar continuously for 30 min. In a second step, the polymer is cured following the manufacturers recommended cycle with a first step of 1 h at 120 °C and a second step of 2 h at 180 °C.

Overall, three types of material were manufactured. A material referred as "reference infusion" was manufactured with pristine epoxy resin (without CNT) through a state-of-the-art vacuum assisted resin infusion process to serve as baseline material. A second material referred as "Spray neat", was manufactured via the help of the spraying process with pristine resin (no CNT) in order

to identify a potential influence of the spraying process. A last material referred as “sprayed CNT”, was manufactured through spraying and with a 0.75 wt.% doped epoxy matrix.

2.2.3. Characterization methods

2.2.3.1. DC conductivity measurements. Direct Current (DC) conductivity measurements were performed with the help of Keithley 2400 sourcemeter. An electrical direct current was applied to the specimen while the voltage drop between the ends of the specimen was measured. To achieve a good contact between electrodes and specimen surface a silver paint coating was deposited on the contact surfaces. The method used was a four points method, as four distinctive probes were used to measure the voltage drop and inject the current. This method is suitable for both X, Y and Z direction electrical conductivity measurements.

2.2.3.2. Dynamic dielectric spectroscopy (DDS). AC conductivity measurements were performed with a Solartron Schlumberger gain/phase analyzer SI 1260 together with a Novocontrol interface (broadband dielectric converter) in the frequency range of 10^{-1} – 10^6 Hz. The measurements were performed in a temperature range of $[-150; +150$ °C] using a controlled nitrogen thermal regulation system (Quatro Novocontrol). The CFRP samples (3 mm thick) were coated with a silver paint, and placed between two gold plated brass electrodes. Considering that only samples up to a thickness of a few millimeters can be tested with this method, it is only suitable for through thickness measurements (Z-direction). Electrical conductivity measurements were carried out by recording the complex conductivity $\sigma^*(\omega)$. The real part, $\sigma'(\omega)$ of the complex conductivity $\sigma^*(\omega)$ was investigated. The value of $\sigma'(\omega)$ at 10^{-1} Hz was considered as DC conductivity σ_{DC} . The complex conductivity obtained from the complex impedance can be written as follows Eq. (1), where σ_{DC} is the direct current conductivity, ω the pulsation and A is temperature-dependent constant [14].

$$\sigma^*(\omega) = \sigma'(\omega) + i \cdot \sigma''(\omega) \text{ with } \sigma'(\omega) = \sigma_{DC} + A \cdot \omega^s \quad (1)$$

2.2.3.3. Dynamical mechanical analysis (DMA). In order to characterize the mechanical properties of the manufactured materials, dynamical mechanical analysis measurements were performed using an ARES Rheometer from TA Instruments using a torsional beam geometry. A solid sample (width = 10 mm, length = 40 mm, thickness = 3 mm) was held in tension between the lower and upper fixtures. Axial sample deformation was applied by the lower fixture linked to the motor, while a torque sensor linked to the upper fixture measured the resulting torsional moment. The measurements were performed from room temperature to 280 °C (heating rate 5 K min⁻¹) with a frequency of 1 Hz and a strain of 0.05%.

2.2.3.4. Interlaminar fracture toughness. Laminated fiber-reinforced composite made of high strength fibers in a relatively weak matrix are susceptible to delamination. Interlaminar fracture toughness of laminated composites is normally expressed as the critical energy release, G_c . The critical energy release rate is the energy consumed to produce a unit length of crack growth through a unit area at the interlaminar interface (commonly expressed in Joules per square meters). In this work, the sample manufacture, test procedure and data processing followed the EN 6033 norm in order to determine the fracture toughness energy in mode I (opening). This test uses double cantilever beam specimens with a width of 25 mm, where a release film is inserted during CFRP manufacturing in order to introduce a pre-existing crack. On each sample, 10 opening/closing cycles were performed, with an opening speed of 2 mm min⁻¹. After each cycle the crack propagation length was measured on both sides and a mean value was calculated. The frac-

ture toughness energy in mode I was determined using Eq. (2), where A is the energy to achieve the propagated crack length, a is the length of the propagated crack and w the specimen width. The energy A is determined by the integration of the area under the load/crosshead displacement curve.

$$G_{Ic} = \frac{A}{a \cdot w} 10^6 \quad (2)$$

2.2.3.5. Interlaminar shear strength. Another interesting test procedure, which investigates the interlaminar properties of the material, is the measurement of the interlaminar shear strength (ILSS) by three-point flexure of a short beam specimen. This test provides useful information on the quality of the resin-fiber bond. The span/depth ratio of the beam is chosen so that the beam should fail by interlaminar shear rather than tensile failure. For this, a specimen of rectangular cross-section is tested in flexure on two supports. The load is applied at the center of the specimen by a loading nose midway between the supports. The ILSS determination followed the EN 2563 norm. Measurements were conducted on CFRP laminates made of 12 layers of unidirectional carbon fiber plies. A crosshead speed of 1 mm min⁻¹ was used. Furthermore, a close analysis of each fracture profile should be performed to ensure that the failures exclusively take place in interlayer planes. The apparent ILSS is calculated as presented in Eq. (3), where τ is the apparent interlaminar strength (in MPa), P_R the maximum load at the moment of first failure (in N), b the width of the specimen (mm) and h the thickness of the specimen (mm).

$$\tau = \frac{3 \cdot P_R}{4 \cdot b \cdot h} \quad (3)$$

3. Results and discussion

3.1. Quality assessment

The purpose of this section is to ensure that the materials manufactured using this non-conventional manufacturing method reach the required level of quality to produce reliable mechanical and electrical testing results.

3.1.1. Optical microscopy

Laminates made of 8 layers of UD carbon fiber plies were observed in both X (0°) and Y (90°) directions. Porosity was found to be almost nonexistent, a quantitative evaluation of the void content can be found further in this section. As seen in Fig. 1, thin dark layers can be observed at the interface between carbon fiber plies. A closer analysis of these regions showed that these are epoxy-rich layers caused by the incompressible glass-reinforced polypropylene threads stabilizing the preform at $\pm 60^\circ$. It can be assumed that these PPG threads have a negative influence on the transverse electrical conductivity of this carbon fiber semi-finished product. Finally, no influence of the spray manufacturing process and/or addition of carbon nanotubes on the consolidated ply thickness, occurrence of resin interlayers and overall laminate quality could be observed.

3.1.2. Ultrasonic inspection

Ultrasonic scans (C-Scan) were performed for three types of material manufactured. In Fig. 2, the quality level achieved through the spraying process can be observed. A laminated with sprayed neat epoxy is presented. Only a few anomalies can be observed, mostly small areas with a slight resin starvation (dark dots) and some fiber overlaps (dark lines). This overall good quality, as observed through ultrasonic inspection is a further evidence show-

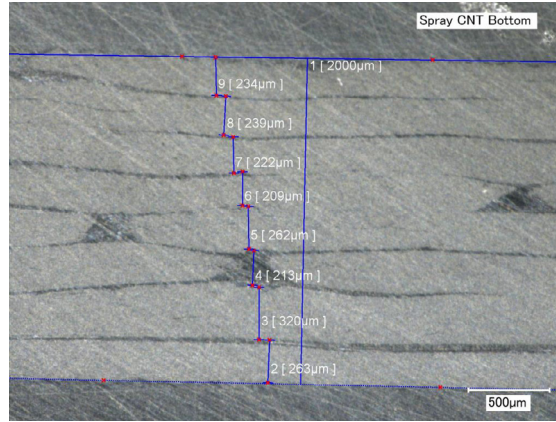
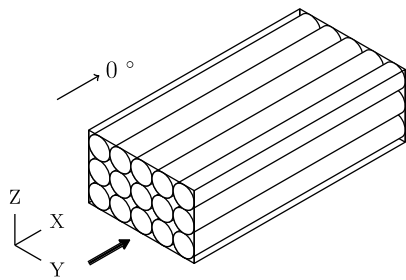


Fig. 1. Micrograph of a 0.75wt.% CNT-doped CFRP. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

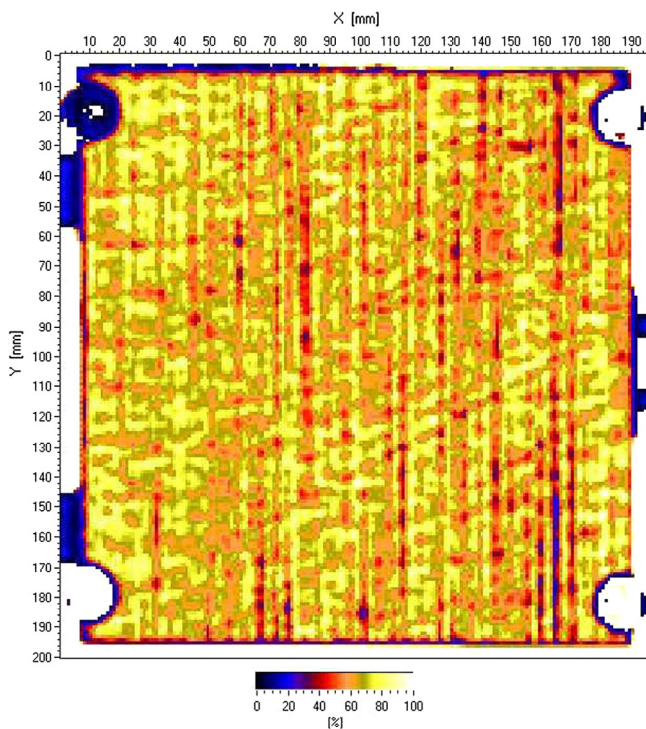


Fig. 2. C-Scan of a sample manufactured using the spraying process. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ing that the spraying process is adequate in order to produce high-quality composites.

3.1.3. Fiber volume fraction, void content and curing degree

Fiber Volume Fraction, Void Content and Curing degree are three crucial parameters to be quantified to ensure laminate quality and reliable testing results. Furthermore, the fiber volume fraction has a direct influence on the electrical conductivity of the CFRP laminate.

Fiber volume fraction and void content were determined through acid digestion (EN 2564 standard) for the three laminate types. Results obtained on multiple samples coming from different panels proved to be reproducible. No process influence or influence of the carbon nanotubes could be noticed, all fiber volume fraction values being in the range of 60 ± 1 vol.%. Furthermore, it was

noticed that the void content remained low for all three materials (≤ 1 vol.%).

As an insufficiently cured matrix could have an influence on the mechanical properties investigated, the extent of cure was determined by differential scanning calorimetry. No significant influence of the CNT or the modified manufacturing process could be noticed, all curing degrees being above 98,5%.

3.2. Electrical behavior

DC current conductivity and dynamic dielectric spectroscopy measurements were performed following the procedure described above on laminates composed of 8 layers of unidirectional fiber plies [0]_s.

3.2.1. DC conductivity measurements

Fig. 3 presents the DC electrical conductivity in the transverse direction (Z-direction) for the three types of materials manufactured, as well as the testing configuration (the hatched surface representing the location of the testing electrodes). It can first be noticed, that all results exhibit a low standard deviation, proving the reproducibility of the measurement and indicates a good homogeneity of the material. For the material used as baseline and manufactured through infusion a σ_{DC} value of $0.9 \pm 0.1 \text{ S m}^{-1}$ was measured. A noticeable decrease in DC conductivity was noticed for the sprayed reference to $0.6 \pm 0.1 \text{ S m}^{-1}$. Whereas for the CNT-doped material a significant increase to $1.6 \pm 0.2 \text{ S m}^{-1}$ was measured. These results seem to show an influence of the carbon nanotubes on the transverse conductivity of the laminate. Specifically that the CNTs increase as expected the conductivity of the CFRP material, but at a limited level.

Fig. 3 presents as well the DC electrical conductivity in the Y-direction for the three types of manufactured materials as well as the testing configuration. For the baseline infused material a σ_{DC} value of $9.3 \pm 0.3 \text{ S m}^{-1}$ was measured. A slight decrease in DC conductivity was noticed for the reference sprayed with unmodified epoxy to $8.0 \pm 0.4 \text{ S m}^{-1}$. Whereas for the CNT-doped material a noticeable increase to $13.8 \pm 0.8 \text{ S m}^{-1}$ was measured. These results seem to show again an influence of the carbon nanotubes on the Y-conductivity of the laminate. Specifically that the CNTs increase as expected the conductivity of the CFRP material. Furthermore, for the Y and Z-direction, the spraying process seems to have a negative influence on the electrical conductivity. Indeed for both direction a decrease in electrical conductivity is observed between the baseline and sprayed with neat epoxy samples. A plausible hypothesis would be the introduction of a thicker interlayer of epoxy through the spraying process, decreasing the

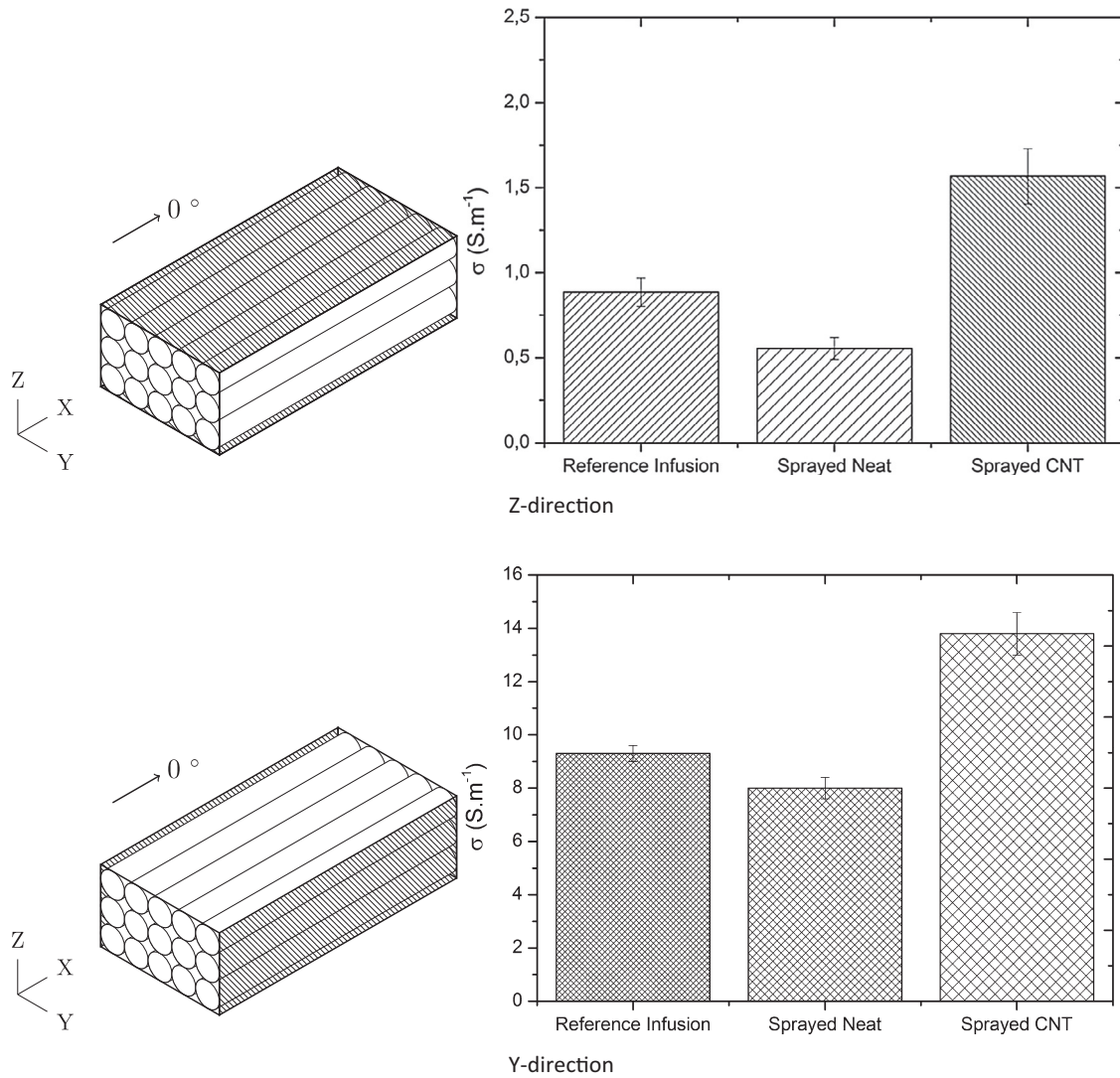


Fig. 3. DC Conductivity in the Z- and Y-direction (DC conductivity measurements).

conductivity. More investigation is required to confirm or invalidate this hypothesis.

For both Z and Y directions a modest but noticeable increase of the electrical conductivity was noticed. In these both directions, the matrix plays an important role in the conductivity behavior. Indeed, for the Z direction a thin matrix interlayer is found between the carbon fiber plies. For the Y direction, the carbon fiber bundles are fitted closer together (higher density of contacts between carbon fibers which explains a higher baseline conductivity) but a continuous carbon fiber path cannot be found. It seems that the insertion of conductive carbon nanotubes inside the matrix filling up the interstices between carbon fibers leads to a higher density of electrical contacts and thus a higher electrical conductivity. This still needs to be confirmed by the dielectric dynamic analysis as presented in the next section.

At last, measurements of the X-conductivity (along the fiber direction) were performed on the same materials. The similar electrical conductivity values were achieved for the three materials ($\sigma_{DC} \approx 10^4 \text{ S m}^{-1}$). An influence of the CNTs was not observed in that case, the conductivity being driven by the much higher conductivity of the carbon fibers, which provide a continuous conductive path along the length of the sample.

3.2.2. Dielectric spectroscopy measurements

Dielectric spectroscopy measurements have been performed in the transverse direction on the same laminates mentioned above. The dielectric behavior of the produced CFRP was studied in a frequency range from 10^{-1} to 10^6 Hz and from -150 to 150 °C. Fig. 4 presents the σ_{DC} values deduced from the value of σ' at low frequency (10^{-1} Hz) at room temperature. The σ_{DC} value for the 0.75 wt.% doped matrix is also reported for comparison [1].

The DC conductivity values (measured through DDS) obtained were respectively: $0.8 \pm 0.1 \text{ S m}^{-1}$ for the infused reference; $0.6 \pm 0.2 \text{ S m}^{-1}$ for the sprayed reference and $2.1 \pm 0.1 \text{ S m}^{-1}$ for the sprayed CNT-doped laminate. By comparing these values with those obtained through DC conductivity measurement and presented in Fig. 3, a very good agreement between those methods can be noted. From these observations obtained through two different analysis techniques, an influence of the CNTs on the transverse electrical conductivity of the CFRP can be presented. A significant increase of the volume electrical conductivity is observed: the transverse electrical conductivity of CNT doped CFRP is doubled compared to the reference material. It should moreover be noted that increasing the electrical conductivity above the percolation threshold is a substantial challenge. Furthermore, thanks

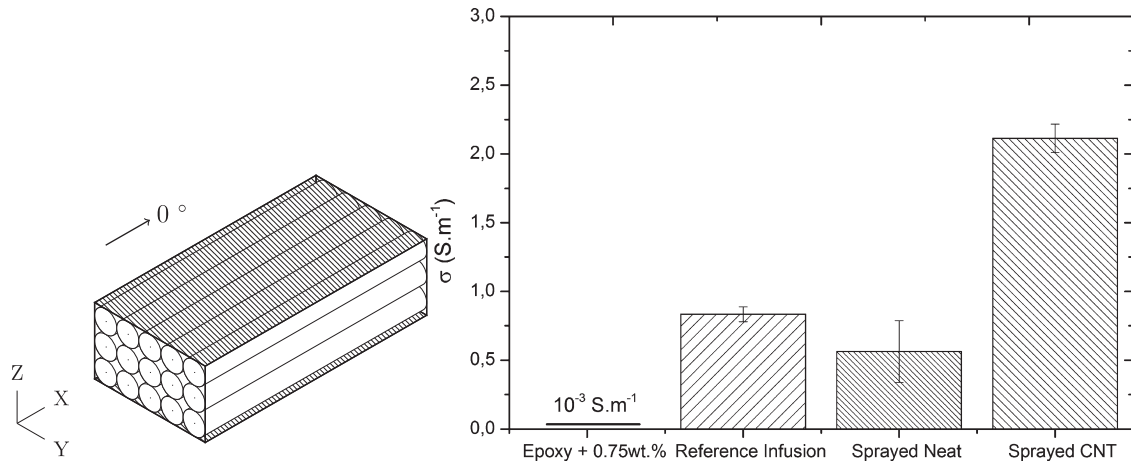


Fig. 4. DC Conductivity in the Z-direction (Dielectric spectroscopy measurements).

to the results achieved in this work, the volume conductivity of the CFRP is more homogeneous.

3.3. Mechanical behavior

3.3.1. Dynamical mechanical analysis

Fig. 5 presents the influence of the manufacturing process and the carbon nanotubes on the storage and loss moduli (left-hand side) and dissipation factor $\tan \delta$ (right-hand side). Furthermore, the first column of Table 1 presents the T_{α} values reported from the loss modulus curves. These results do not suggest an influence of the spray process or CNT on the loss modulus. The dissipation factor $\tan \delta$ highlights the mechanical relaxation phenomena inside the epoxy polymer. A principal relaxation α can be observed at high temperature and an intermediary relaxation ω observed at lower temperature. Other authors have found this peak to correlation with the heterogeneity of the network [15] or linked to the mobility of poorly cross-linked chain segments [16]. It should also be noted that a secondary relaxation β can usually also be observed for epoxy polymers at low temperature around -50°C [17] but the range of temperature investigated is too high for this relaxation to be observed. The α mechanical relaxation is associated with the anelastic manifestation of the glass transition. It matches the delocalized segment chains mobility occurring in the polymer network.

For a given polymer sample, the $\tan \delta$ main relaxation peak represents the ratio of dissipated energy to the stored energy per cycle of sample deformation. The height and width of the $\tan \delta$ peak can give a good idea of the state of the polymer network. In order to do so, the Full Width at Half Maximum (FWHM) and peak height were determined for each tested sample. The mean values of FWHM and peak height are summarized in the second and third column of Table 1. These values of FWHM and peak height do not considerably change for sprayed and/or CNT-doped materials. These results do not indicate any influence of the CNTs on the polymer network homogeneity.

3.3.2. Interlaminar shear strength

The fourth column of Table 1 presents the mean values and standard deviation of the ILSS calculated with Eq. (3). The reference samples achieved a mean interlaminar shear strength value of 72 N m^{-2} . This value is in the range of what is typically achieved for carbon fiber/epoxy composites [18]. It can also be noticed that the standard deviation for all three series tested amounts to a few Newtons per square meter, which is typical for such a test. The ILSS of laminates sprayed with neat resin stays in the same range reaching 70 N m^{-2} . It can already be stated that the spraying process seems to have no significant influence on the ILSS values, with sprayed samples performing as good as reference samples. The

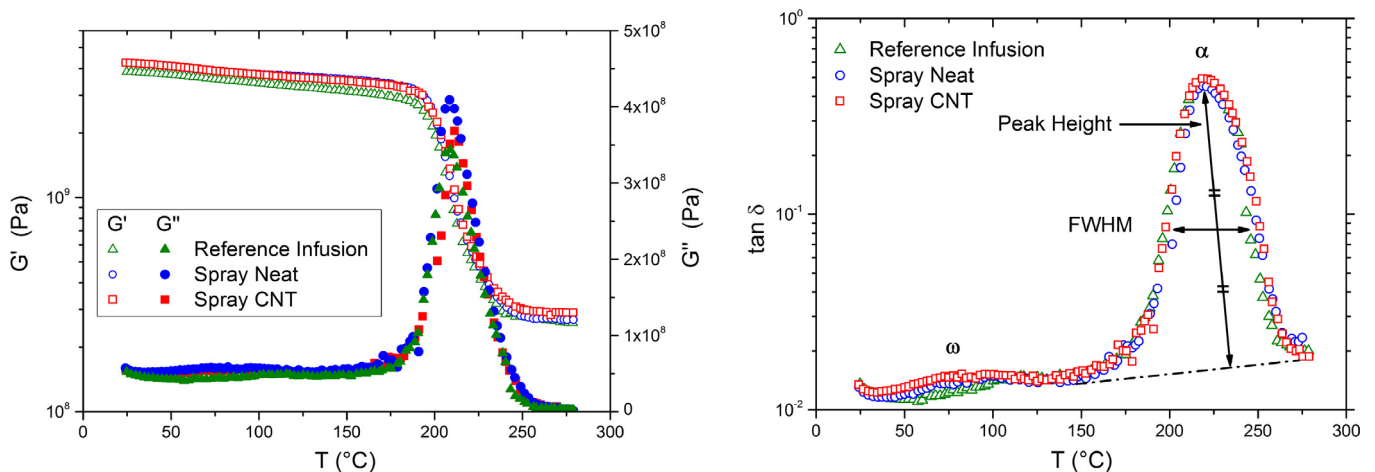


Fig. 5. Dynamical Mechanical Analysis of the three types of material produced. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Results of the DMA, ILSS and G_{Ic} testing.

	Dynamical mechanical analysis			ILSS ILSS ($N\ m^{-2}$)	G_{Ic} G_{Ic} ($J\ m^{-2}$)
	T_{α} ($^{\circ}C$)	FWHM ($^{\circ}C$)	Peak height		
Reference Infusion	209 \pm 2	33 \pm 2	0.46 \pm 0.03	73 \pm 4	423 \pm 47
Sprayed Neat Epoxy	209 \pm 1	33 \pm 1	0.47 \pm 0.04	70 \pm 3	557 \pm 61
Sprayed CNT-doped epoxy	211 \pm 1	31 \pm 1	0.44 \pm 0.01	67 \pm 4	400 \pm 32

mean value of CNT-doped materials decreases slightly to $65\ N\ m^{-2}$. This minor decrease could be explained by a less homogeneous composite laminates, which the CNTs acting as starting points for interlaminar crack initiation. Nevertheless, taking into account the variance of the results, it can be assumed that neither the spraying process nor the CNTs have a substantial influence on the interlaminar shear strength of our CFRP materials.

3.3.3. Interlaminar fracture toughness

The energy release rate in mode I was calculated using the above-mentioned method and are summarized in fifth column of Table 1. A significant increase of the G_I value was observed for the neat epoxy sprayed material and a decrease to baseline levels for the 0.75 wt.% CNT doped sprayed material. It can be assumed that the spray deposition process has a thickening effect on the matrix layer deposited at the mid-plane. A thicker matrix thickness at the fracture interface has been proved to increase G_I values [19]. Concerning the CNT doped material; we assume that the CNT may have in our case a weakening effect on the epoxy polymer, leading to lower G_I values. It was decided to perform SEM observations of the fractured surfaces in order to better understand these results.

3.3.4. SEM observation of the crack surfaces

Fig. 6 present two scanning electron microscopy (SEM) observations performed on the fracture surface of sprayed samples. The left-hand side photograph was taken on the surface of a samples manufactured with pristine epoxy, while the left-hand side photograph was taken on a 0.75 wt.% CNT-doped sample.

On the photograph presented on the left-hand side, the typical imprint left by torn-of carbon fibers can be observed, leaving an empty "bed" (semi-cylindrical pattern). The reinforcing threads made of glass- reinforced polypropylene (GFR-PP) appearing at a 60° angle can also be observed. As mentioned previously and as observed on the pictures the fibers are hardly compressible. Therefore a certain amount of resin fills up the created cavities. This is a distinctive feature common to all three materials. At last, on these neat-epoxy sprayed samples, a thicker resin layer between carbon fiber plies can be observed. These thicker resin-rich interlayers were observed on both neat and CNT-doped sprayed samples and

could be the cause of the higher G_I values obtained for the neat sprayed samples.

On the photograph presented on the right-hand side presents an enlargement of a fracture surface observation of a CNT-doped sample. A high density of CNTs can be found in these regions. The CNTs seem to be well dispersed, observing single CNTs was possible. The CNTs do not seem to adopt a preferential orientation, the nanotubes being randomly oriented. The free standing length, defined as the length that can be observed standing out of the matrix, was estimated to be approximately 280 nm.

In previous works, where an increase of the fracture toughness energy was observed (El-Sawi et al. [13] Garcia et al. [20], Wicks et al. [21,22]), overall longer CNTs were used: in the range of $10\ \mu m$ for El-Sawi, and sometimes up to $20\ \mu m$ for Wicks et al. This could lead to a higher energy involved when trying to pull out the CNTs during crack propagation. By looking at the results from the SEM observations, it seems that the nanotubes used in our study are shorter (free standing length of around 280 nm, for information the length of the CNT before processing ranges from 0.1 to $10\ \mu m$ and their outer diameter from 10 to 15 nm). Pulling this shorter CNT length out of the laminate may require less energy than for higher CNT length, and we may thus suppose that the influence of the nanotubes on the energy release rate is negligible. More investigation and experimental data with longer CNTs are required to confirm or invalidate this hypothesis.

4. Conclusions

The goal of this work was to improve and homogenize the through-thickness electrical conductivity of CFRPs. As a solution, multiscale composites manufacturing was proposed through addition of carbon nanotubes to a standard composite. Yet, the literature review reported several obstacles prohibiting the use of state-of-the-art composite manufacturing techniques to this purpose. In this work, it has been proposed to solve these issues of CNT filtering, increase of resin viscosity and upscalability through the use of an innovative spraying process. Thanks to the combined use of a calendaring and spraying process, MWCNTs were dispersed in the epoxy matrix then sprayed on the dry fiber plies and subsequently cured to produce CNT-doped CFRP.

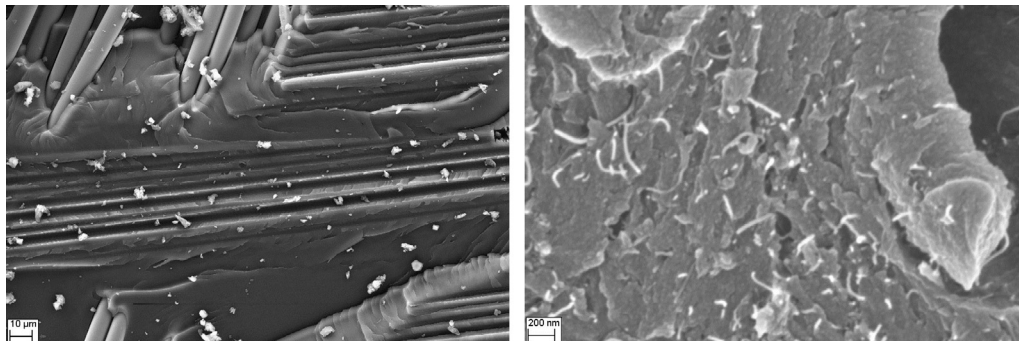


Fig. 6. SEM observation of the crack surfaces.

Little influence of the nanotubes or the spraying process on the mechanical properties (dynamical mechanical analysis, interlaminar shear strength and interlaminar fracture toughness) was noticed. The manufactured CNT-doped and/or sprayed material achieved similar mechanical properties compared to state-of-the-art CFRP materials. As reported in the literature, one of the advantages of introducing CNTs into CFRPs is to improve interfacial properties, interlaminar performance, and other matrix-controlled mechanical properties. However, no improvement of mechanical properties was obtained in the presented work. In order to do so, it might be worth using other types of CNTs or investigating further the calendaring and spraying process and optimize it to target mechanical performance improvement. On the other hand, an influence of the carbon nanotubes on the transverse (Z direction) and orthogonal (Y direction) electrical conductivity could be obtained. A slight but noticeable increase of the conductivity was achieved ($0.8\text{--}2.1\text{ S m}^{-1}$ for the Z-direction and $9.3\text{--}13.8\text{ S m}^{-1}$ for the Y-direction). More than the inherent values reached, the electrical conductivity was homogenized throughout the whole laminate. This achievement could be one step in order to solve the issue of “edge-glow” on aeronautical structures.

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