IMPACT OF CARBON NANOTUBES ON ELECTRICAL CONDUCTIVITY OF CARBON FIBER MULTISCALE COMPOSITES

M. Arguin[1], F. Sirois[2], D. Therriault[1*]
[1] Laboratory for Multiscale Mechanics, Center for applied research on polymers (CREPEC), École Polytechnique de Montréal, Montreal (QC), Canada,
[2]Laboratory in Electrical Energy, École Polytechnique de Montréal, Montreal (QC), Canada
* Corresponding author (daniel.therriault@polymtl.ca)

Keywords: *multiscale composites, electrical conductivity, nanocomposites*

Carbon fiber/epoxy composites have poor electrical conductivity in the through-the-thickness direction generating a very inefficient current diffusion between each ply. In this contribution, multi-walled carbon nanotubes have been added to the epoxy matrix to enhance the conductivity through the thickness of a composite panel. Two processes, vacuum assisted resin transfer molding (VARTM) and hand lay-up, were compared in order to investigate the impact of adding conductive nanotubes in the epoxy matrix on the electrical conductivity of the composite. Two different nanotube loadings were studied (i.e., 0.5 wt.% and 1 wt.%). In both cases, the best through the thickness conductivity was obtained with 1wt.% loading of carbon nanotubes, with an increase of 33% and 53% for the VARTM and hand lay-up processes respectively. However, more samples with higher MWCNT loadings should be considered where filtration would be more important.

1. Background and motivation

For more than fifty years, composite materials have been used for various applications such as sports goods, road structures, cars, boats and aircrafts. These materials are light and feature mechanical properties generally equal or superior to those of metallic structures. However, their electrical conductivity is much lower than their metallic counterparts.

Carbon fibers have a relatively high electrical conductivity of 1000 S/m. Hence, carbon fibers reinforced polymer composites represent a combination of excellent mechanical properties and reasonable electrical conductivity, making them a strategic choice for multifunctional applications (e.g., where specific mechanical and electrical properties are required). In the case of aircrafts, metallic structures are generally used where high electrical conductivities are required, such as for lightning strike protection or current return networks. Therefore, carbon fiber composites with the appropriate electrical conductivity could potentially replace those structures.

Although carbon fibers are conductive, each tow inside the composite is isolated by an insulating matrix, which considerably limits the diffusion of the current between the plies. Thus, if an electrical current is injected at the surface of a composite panel, the current will mostly flow in the first few plies, creating heat and fast degradation of the material. Increasing the electrical conductivity of the resin provides lower resistance between the plies, which helps in avoiding hot spot problems and results in better electrical performance and longer service lifetime.

Various nanoparticles featuring different geometries and inherent electrical conductivities, such as carbon nanotubes (CNTs) [1], graphene sheets [2] and silver nanowires [3] can be added to the polymer to increase its conductivity by creating a percolation network within the host material. Based on the percolation theory, polymer conductivity can be considerably enhanced by adding less than 1 wt.% of conductive nanoparticles [4]. However, this enhancement depends of many parameters such as the type and the aspect ratio of the nanoparticles. The addition of multi-walled carbon nanotubes (MWCNTs) in order to create multiscale composites (i.e. fiber reinforced polymers with nanofillers inside the matrix) has already showed a great efficiency at improving their mechanical and electrical properties [5, 6]. Different industrial processes can be adapted to manufacture multiscale composites, such as resin transfer molding (RTM) [7] and vacuum assisted resin transfer molding (VARTM) [8]. For those two processes, an increase in mechanical and electrical properties has been reported when adding up to 0.5 wt.% of carbon nanotubes (CNTs). For higher concentrations, filtration of the CNTs has been observed during the resin injection and creation of MWCNT-rich zone near the resin inlet. Two kinds of filtration may happen during the process: cake filtration and retention [9]. Another process often used in the industry is hand lay-up. To the best of our knowledge, this process has not been investigated well for multiscale composites from an electrical point of view. For hand lay-up, the resin is first manually deposited between each ply before applying the pressure. Unlike with the RTM and VARTM processes, MWCNTs should be uniformly dispersed into the composite panels and filtration might not play an important role during the process. Fig. 1 illustrates VARTM and hand lay-up processes studied in this contribution.

Here, we investigated if the addition of multi-wall carbon nanotubes (MWCNTs) to the matrix of a carbon/epoxy composite could reasonably improve its electrical conductivity, especially through its thickness. The idea here is to create a percolation network between each ply of the composite in order to increase the distribution of the injected current through the thickness.

2. Methodology

2.1 Materials

Each composite panel were made with carbon fibers and an epoxy matrix. Injectex GF420-E01-100 carbon fabric was used as fibers because it is a well-balanced fabric having the same conductivity in the warp and the weft direction. The epoxy matrix was a 2-part Diglycidyl Ether of Bisphenol F Epon 862 (Miller Stephenson) and an Epikure curing agent 3274 (Miller Stephenson). This resin is able to cure at room temperature and has been selected for its low viscosity. As conductive nanoparticles, 0553CA MWCNTs (Skyspring Nanomaterials Inc.) and they have an average diameter of 15nm and an average length of 15µm.

2.2 Nanocomposite formulation

MWCNTs were first dispersed into acetone using an ultrasonication bath (Cole Parmer 8891) for 30 min. Then, the epoxy monomer was added into the nanoparticles dispersion and stirred for one more hour. The acetone was evaporated using a vacuum oven (Cole Parmer 282A) at 50°C for 24 h. Three passes on three-roll mixer were applied on the nanocomposite at a gap of 15 µm and a roll speed of 250 rpm. Two different loadings of MWCNTs were considered, i.e., 0.5wt.% and 1wt.%. Finally, curing agent was added to the epoxy monomer and the nanocomposite mixture was degased in a vacuum oven at room temperature for one hour.

2.3 Multiscale composite fabrication

Two different processes were used to manufacture carbon fiber/epoxy composite: VARTM and hand lay-up. One composite panel composed of 8 plies was manufactured at each loading and four samples were obtained from each panel.

In the VARTM process, dry fabrics were first cut at the size of the desired composite panel. Then, the fabric was placed on a plane mould and a peel ply and a vacuum bag were deposited on the fabric. A vacuum pressure of 0.1bar was applied on the fabric and the reinforced resin was injected.

For composite panel made by hand lay-up, the carbon fabric was cut the same way as in VARTM. The resin was then deposited on each ply with a paint brush and the plies were stack on a flat mold. Then, a peel ply and a breather/bleeder fabric were put on the panel before putting the mould inside a vacuum bag. A vacuum pressure of 0.1bar was applied on the composite until the resin is cured.

Four samples were cut in the middle of each composite using an isomet precision saw (Buehler). Each sample was 75 mm length and 12.5 mm width. The density and the fiber fraction of each sample were experimentally measured based on ASTM D792-08 and ASTM D3171-11 respectively.

2.4 Microscopy

The quality of MWCNTs was verified with TEM observations (Jeol JEM-2100F). Optical images of nanocomposite dispersion were obtained using a BX61 optical microscope (Olympus) to verify the quality of the dispersion. Finally, a cross-section of each sample were cut with isomet precision saw (Buehler). Before the inspection, each cross-section was polished using a metagrid polisher (Buehler). During the polishing, a grid 420 paper (Buehler) and 9µm and 3µm diamond suspension (Buehler) were used. A mirror finish was obtained using a 0.05µm alumina suspension (Masterprep, Buehler). Cross-section observation of each sample was done with the BX61 microscope (Olympus) to verify the fraction of void inside each panel. SEM observations

(JEOL JSM840) were also performed to observe the dispersion of MWCNTs within the composite sample.

2.5 Electrical measurements

Electrical measurements were made on each manufactured sample in order to determinate the conductivity in the longitudinal and the through-the-thickness directions. Sample with two different MWCNT loadings for both processes were achieved: 0.5wt% and 1wt%. The longitudinal conductivity was measured with a four-probe technique (Fig. 2a). A DC current, controlled with a GPS-3303 power supply (Gwinstek) was gradually injected from 0 to 2.75 A. The voltage at each probe was measure with a PCI-6052E acquisition card (National Instrument). The through-the-thickness conductivity was measured by placing the same sample between two electrodes and injecting a DC current into the sample (Fig. 2b). Different voltages ranging from 0 to 10V were applied on the sample with a GPS-3303 power supply (Gwinstek) and electric current was measured with a PCI-6052E acquisition card (National Instrument) to calculate the electrical conductivity. Both conductivity measurement methods were based on ASTM D257-07 standard. Each electrical measurement has been repeated twice for each sample manufactured.

3. Result and discussion

3.1 Current diffusion in the composite panel

As preliminary results, a 2D simulation with Comsol 3.5 was achieved to investigate how the anisotropic electrical conductivity of carbon fiber/epoxy composite influences the current diffusion between each ply. In this simulation, a longitudinal conductivity of 1000 S/m and a transverse conductivity of 1 S/m were used. Fig. 3a shows the current density (arrows) and the heat generate for an applied voltage of 1 V (color shading). The current passes easily through the first plies, but it can hardly distribute through all the thickness of the panel. The high resistance between plies would lead to excessive heat generation especially near the electrodes and thermal material degradation. In comparison, Fig. 3b shows the same simulation but using an isotropic material with a conductivity of 1000 S/m. In that ideal case for the composite material, the current is able to diffuse through the thickness and the heat generated by Joule effects is more than 10 times lower.

3.2 Nanocomposite manufacturing

Fig. 4a shows a TEM picture of MWCNTs use for the experiment. TEM observations were performed in order to verify the specifications of the nanotubes and measure their dimensions. The average length of the nanotubes is 10 µm and the average diameter is 20 nm which respect the manufacturer specifications. Fig. 4b shows an optical image of the MWCNTs dispersion after three passes on the three rolls mixer. Images obtained with an optical microscope show a fairly good dispersion of the MWCNTs within the polymer resin with a maximum aggregate size of ~30 µm.

3.3 Composite panel constituents

Fig. 5a shows a cross-section optical image of a benchmark sample made by VARTM. These observations were done on each sample in order to verify if the sample has a fraction of void less than 2%. Fig 5b shows SEM observation of a multiscale composite sample with 1wt% of MWCNTs. It was possible to observe the presence of nanotubes bundles on fibers which could be a sign of filtration during the process.

Table 1 shows the measured density and fiber fraction for each panel made by VARTM and by hand lay-up. The electrical conductivity is also presented in this table in order to compare the two processes. The fiber fraction was approximately 35 vol.% and 30 vol.% for composite panels made by VARTM and by hand lay-up respectively.

4 Electrical measurements

4.1 Electrical conductivity of composite benchmarks

For comparison purposes, electrical measurements were made on carbon fiber/epoxy composite with no nanoparticle in the matrix. Fig. 6a shows the measured voltage between each probe as a function of current injected in the longitudinal direction for both composite samples (VARTM and hand lay-up). Three different phases can be distinguished. For currents between 0 and 2 A, the voltage increases in a linear manner and the electrical conductivity is constant. Conductivities of 1000±100 S/m and

800±80 S/m were calculated by linear regression for the linear part of the curve for composite panels made by VARTM and hand lay-up respectively.

For current higher than 2 A, the voltage increase becomes non-linear, probably due to a decrease of the electrical conductivity. Furthermore, the temperature of all samples has increased so high at this part of the experiment that degradation of the epoxy matrix was observed, accompanied with a decrease in electrical conductivity. Finally, when the intensity of injected current was progressively reduced back to zero, the voltage decreased in a linear manner, presuming that the samples conductivity did not change during the final stage of the experiments.

Fig. 6b shows electrical measurements in the through-the-thickness direction for both composite benchmarks made by VARTM and hand lay-up processes. Linear regression of this graph gives an electrical conductivity of 0.76 S/m for VARTM samples and 0.25 S/m for hand lay-up samples. Electrical conductivity in the through-the-thickness direction is found to be more than three orders of magnitude lower than in-plane conductivity probably due to the insulating matrix between each ply, which limits the current diffusion. For the electrical measurement through-the-thickness, the V-I curve maintained its linear behaviour and no significant heating effects were observed during those experiments.

For both in-plane and through-the-thickness directions, carbon fibers/pure epoxy composite samples made by the VARTM process showed an higher electrical conductivity than the composite panels made by the hand lay-up process. Analysis of the constituents shows that composite panel made by VARTM has a fiber fraction of 35 vol.%, which is slightly higher than that of the panel made by the hand lay-up process (30 vol.%). In the hand lay-up process, the resin was deposited on the carbon fibers before applying pressure causing a lower compaction of fibers. The fiber volume fraction of sample made by hand lay-up was lower and the electrical conductivity was lower.

4.2 Impact of MWCNTs on VARTM process

Fig. 7 shows electrical conductivity in the in-plane and in the through-the-thickness directions of composite panels made by VARTM for two different MWCNT loadings (i.e., 0.5 wt.% and 1 wt.%). At 0.5 wt.%, no significant difference was observed for the longitudinal conductivity. However, the conductivity of samples with 1 wt.% loading increases by 56% to reach 1560 S/m, as shown in Fig. 7a. This increase is mainly due to an increase of the electrical conductivity of the epoxy matrix which facilitates current diffusion within a single ply.

For the through-the-thickness direction, electrical conductivity increased by 29% and 33% for 0.5 wt.% and 1 wt.% MWCNT loadings respectively (Fig. 7b). Adding more nanotubes does not seem to have a great impact on the through-the-thickness conductivity of composite made by VARTM. However, tests with higher loadings need to be done to verify this conclusion.

4.3 Impact of MWCNTs on hand lay-up process

Fig. 7 shows the electrical measurements for the hand lay-up process. For the in-plane direction, samples with 0.5 wt.% of MWCNTs have a lower conductivity than the benchmark samples. However, electrical conductivity has increase by 18% with a MWCNT loading of 1 wt.%. Different parameters may have interfered during the experiment which could have led to a decrease of the conductivity such as the position of the probe for the voltage measurements and the roughness of the sample. Those parameters create large dispersion of the measured conductivity. More experiments should be carried out with the 0.5 wt.% loading in order to better understand the mechanisms that contribute to these variations in electrical conductivity.

For the through-the-thickness conductivity, there was no difference in the case of carbon fiber/epoxy composite with 0 or 0.5 wt.% loading of MWCNTs. For samples made with 1 wt.% loading, an increase of 53% in the electrical conductivity was apparent on the electrical conductivity. This suggest once again that the tests on the panel with 0.5 wt.% loading should be redone.

4.4 Comparison between the two processes

Samples made with VARTM process have a higher conductivity than those made with the hand lay-up process. During the VARTM process, compaction of fibers was higher and the fibers fraction was higher. A higher compaction reduces the resistance between each ply and is likely to improve the current diffusion between the plies. Thus, the in-plane conductivity of the bulk panel is directly related to the compaction and the fiber fraction.

In all cases though, the increase in electrical conductivity is much lower than what is desired in practice, and makes doubtful that any of the two processes investigated is suitable to increase the conductivity to useful levels. As mentioned before, isotropic materials are ideal to diffuse electrical current through the thickness. An increase of one or two order of magnitude of the through the thickness conductivity would be more suitable for electrical application.

In the through-the-thickness direction, an increase of the electrical conductivity with the addition of 1wt.% of MWCNTs was noticed for both processes. The increase was slightly more important for composite panels made by the hand lay-up process, although still very modest. In the VARTM, filtration of particle may have created a MWCNT-rich zone near the resin inlet. Cake filtration happens when the size of particles are larger than the porous media so nanoparticles cannot travel through the fiber plies. In case of multiscale composites, that kind of filtration doesn’t occur. Retention occurs when resin with nanoparticles flows through the fibers and particles are progressively deposited on fibers creating inhomogeneous fillers dispersion throughout the panel. The type of filtration might be present in the VARTM process. Thus, samples cut in the middle of the panel may have a MWCNTs’ loading lower than 1 wt.%, reducing the improvement of electrical conductivity.

In the hand lay-up process, epoxy reinforced with MWCNTs was manually deposited on each ply. With the absence of resin flow in the in-plane direction, MWCNTs are more likely to be uniformly dispersed within the composite panel. Furthermore, filtration could have been beneficial because MWCNT aggregates will remain stuck between each ply creating percolation paths.

However, it is too early to conclude that filtration is the principal reason of this better increase of the electrical conductivity in the through-the-thickness direction for the hand lay-up process. More tests need to be realized with higher MWCNTs’ loading (e.g., 2 wt.% and 5 wt.%), where filtration plays a more important role during the manufacturing process of composite panels.

5. Conclusion

Carbon fiber/epoxy composites panels with two different loadings of MWCNTs have been manufactured by two different processes: VARTM and hand lay-up. Four samples from each panel were characterized in terms of longitudinal and through-the-thickness electrical conductivity, for comparison purpose. In the through-the-thickness direction, increases of 33% and 53% were achieved at 1 wt.% for VARTM and hand lay-up processes, respectively. In the VARTM process, filtration may have decrease the impact of conductive nanoparticles However, further experiments at higher loadings should be carried out in order to confirm this hypothesis.

There was no major increased of the conductivity in the though-the-thickness direction and electrical anisotropy is still large. The random orientation of the MWCNTs in the matrix might be responsible for the poor to moderate reduction in electrical anisotropy. Future work will need to consider controlling the orientation of the MWCNTs during fabrication process, for instance by using an electric field, in order to create preferential percolation path between each ply. The quality of the electrical carbon fibers must also be improved in order to improve the diffusion of current through the thickness. Finally, composite materials with a higher electrical conductivity could lead to great impact in the aerospace industry, especially in application requiring electrical conduction and where heavy metallic parts are traditionally used. For example, conductive composite materials could reduce the weight of aircrafts and reduce their operating cost.

References

[1] F. H. Gojny, M. H. G. Wichmann, B. Fiedler, I. A. Kinloch, W. Bauhofer, A. H. Windle, and K. Schulte, "Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites," *Polymer*, vol. 47, pp. 2036-2045, 2006.

[2] S. Stankovich, D. A. Dikin, G. H. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, "Graphene-based composite materials," *Nature*, vol. 442, pp. 282-6, Jul 20 2006.

[3] G. A. Gelves, B. Lin, U. Sundararaj, and J. A. Haber, "Low Electrical Percolation Threshold of Silver and Copper Nanowires in Polystyrene Composites," *Advanced Functional Materials*, vol. 16, pp. 2423-2430, 2006.

[4] W. Bauhofer and J. Z. Kovacs, "A review and analysis of electrical percolation in carbon nanotube polymer composites," *Composites Science and Technology*, vol. 69, pp. 1486-1498, 2009.

[5] J. Qiu, C. Zhang, B. Wang, and R. Liang, "Carbon nanotube integrated multifunctional multiscale composites," *Nanotechnology*, vol. 18, p. 275708, 2007.

[6] F. H. Gojny, M. H. G. Wichmann, B. Fiedler, W. Bauhofer, and K. Schulte, "Influence of nano-modification on the mechanical and electrical properties of conventional fibre-reinforced composites," *Composites Part A: Applied Science and Manufacturing*, vol. 36, pp. 1525-1535, 2005.

[7] E. F. Reia da Costa, A. A. Skordos, I. K. Partridge, and A. Rezai, "RTM processing and electrical performance of carbon nanotube modified epoxy/fibre composites," *Composites Part A: Applied Science and Manufacturing*, vol. 43, pp. 593-602, 2012.

[8] Z. Fan, M. H. Santare, and S. G. Advani, "Interlaminar shear strength of glass fiber reinforced epoxy composites enhanced with multi-walled carbon nanotubes," *Composites Part A: Applied Science and Manufacturing*, vol. 39, pp. 540-554, 2008.

[9] D. Lefevre, S. Comas-Cardona, C. Binetruy, and P. Krawczak, "Coupling filtration and flow during liquid composite molding: experimental investigation and simulation," *Composites Science and Technology*, vol. 69, pp. 2127-34, 2009.

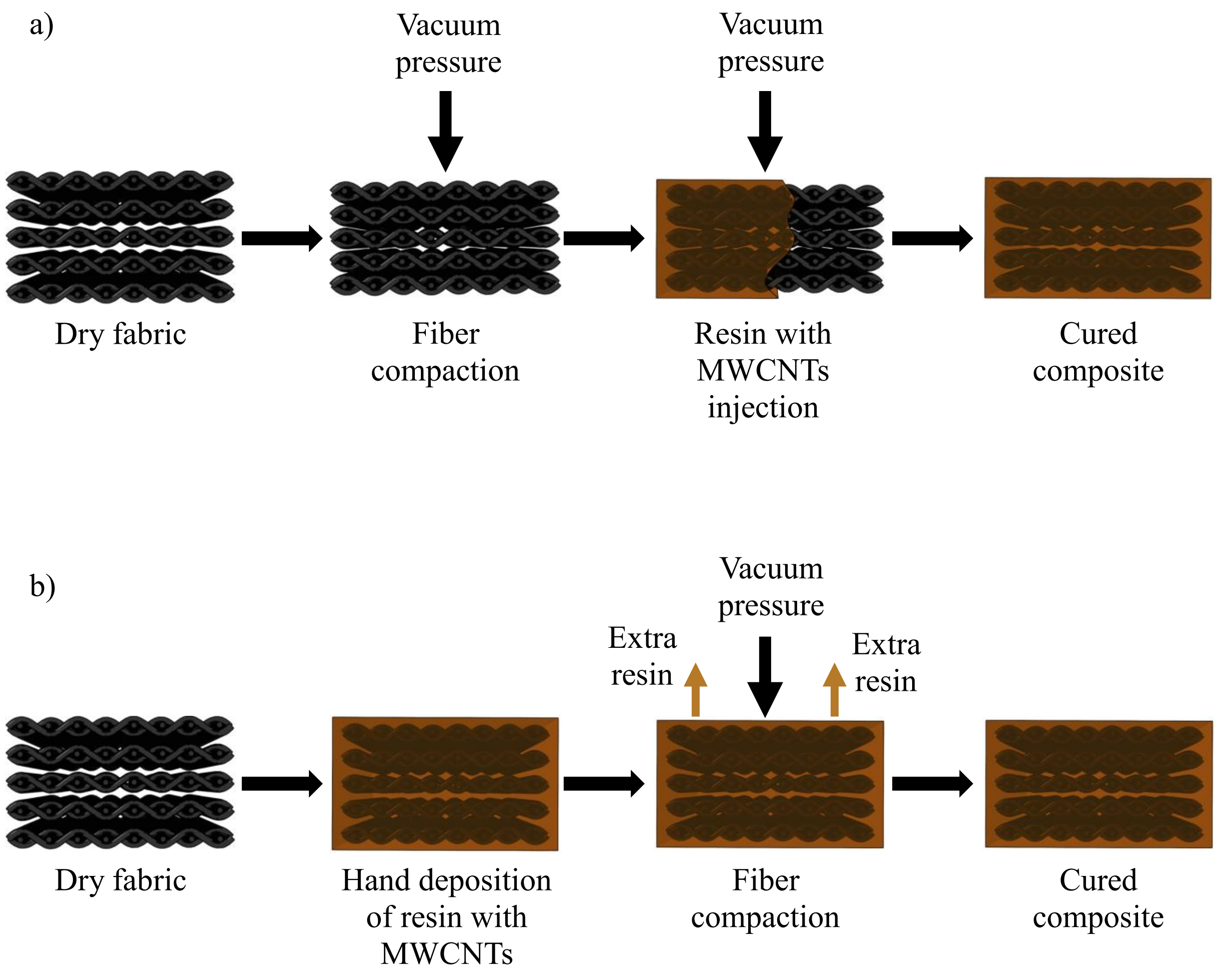

Fig. 1 Schematic of a) VARTM process; b) hand lay-up process

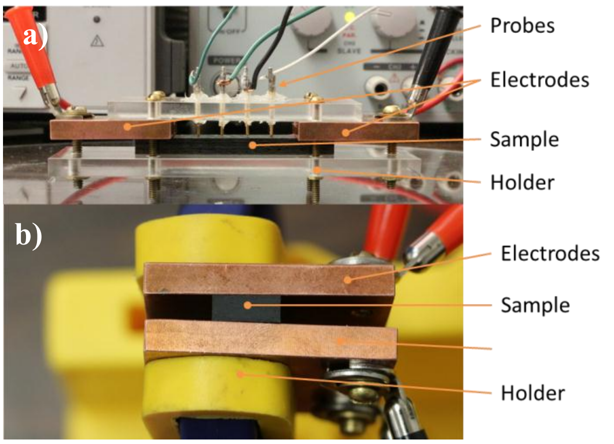

Fig. 2 a) Four probes setup for electrical conductivity measurement in longitudinal direction; b) Setup for electrical conductivity measurement in through-the-thickness direction;

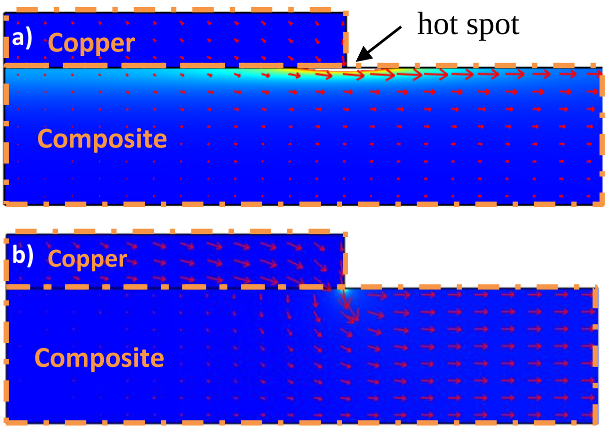

Fig. 3 Current density (arrows) and associated heat generation (color shading) simulated with COMSOL 3.5a in the case of a) an anisotropic composite material (current situation); b) an ideal isotropic material.

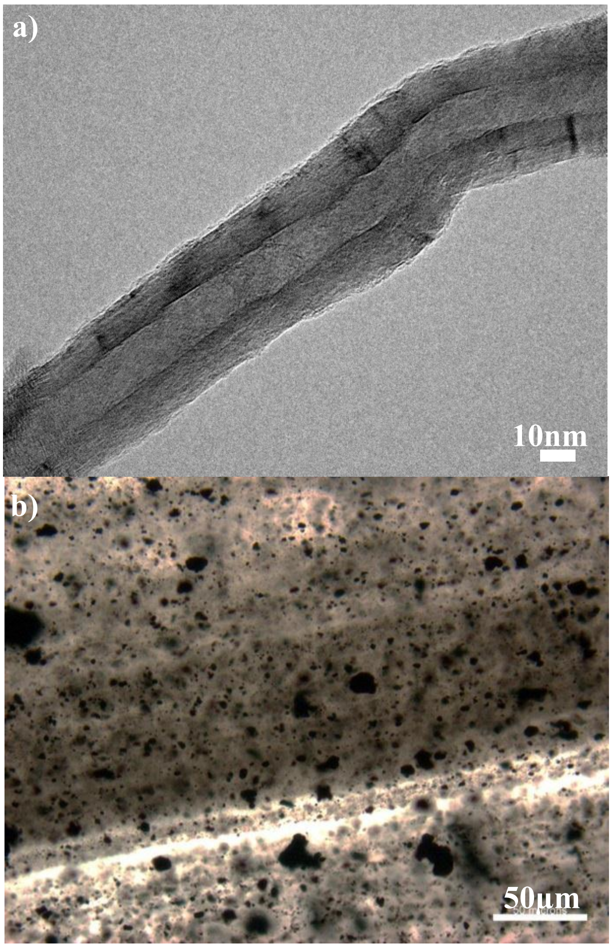

Fig. 4 a) TEM picture of a MWCNT used in multiscale composites; b) Optical microscopy of dispersed MWCNTs in epoxy

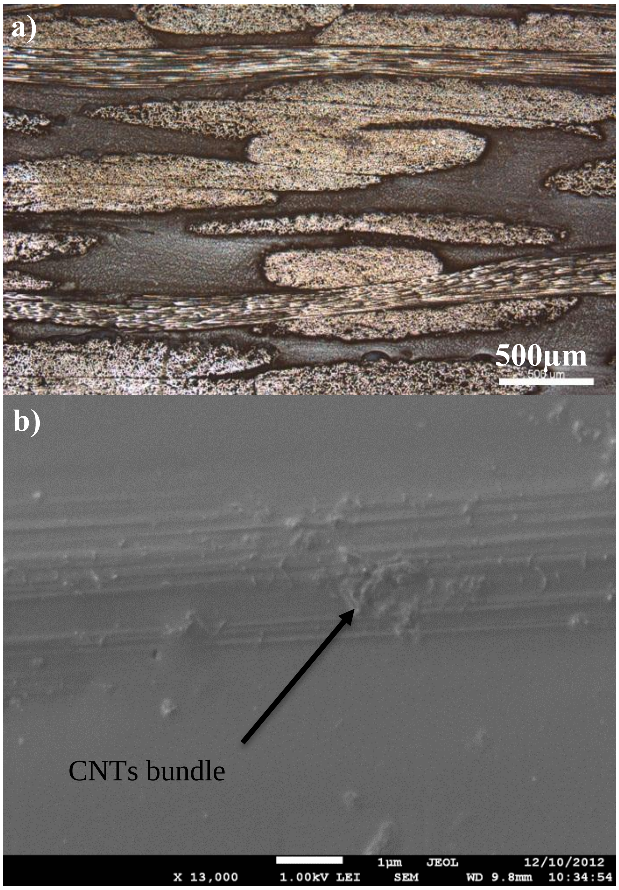

Fig. 5 a) Cross section images of a composite sample made by VARTM process; b) SEM images of a MWCNTs aggregates dispersed inside multiscale composite with 1wt.% loading

Table 1 Properties of manufactured composite panels by VARTM and hand lay-up processes

Process	MWCNT fraction (wt.%)	Density (g/cm^3)	Fiber fraction (vol.%)	In-plane conductivity (S/m)	Through the thickness conductivity (S/m)
VARTM	0	1.39	35	1000±100	0.76±0.1
VARTM	0.5	1.40	35	1010±200	0.98±0.1
VARTM	1	1.40	35	1560±150	1.01±0.1
Hand lay-up	0	1.37	30	799±80	0.25±0.1
Hand lay-up	0.5	1.37	30	591±150	0.24±0.2
Hand lay-up	1	1.38	30	944±100	0.38±0.06

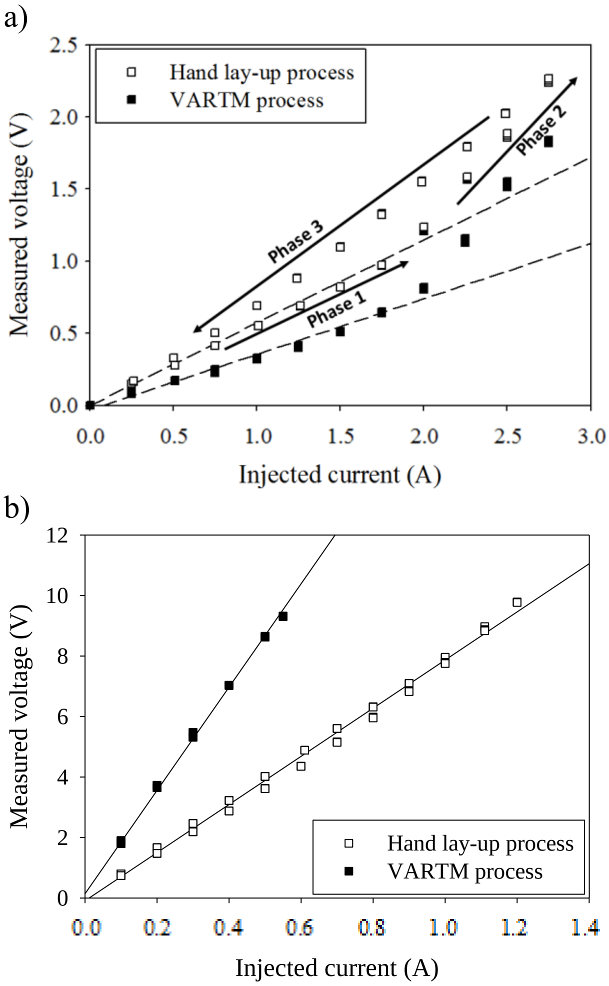

Fig. 6 Electrical measurements on benchmark sample (0 wt.%) made by VARTM and hand lay-up in: a) in-plane direction; b) through-the-thickness direction

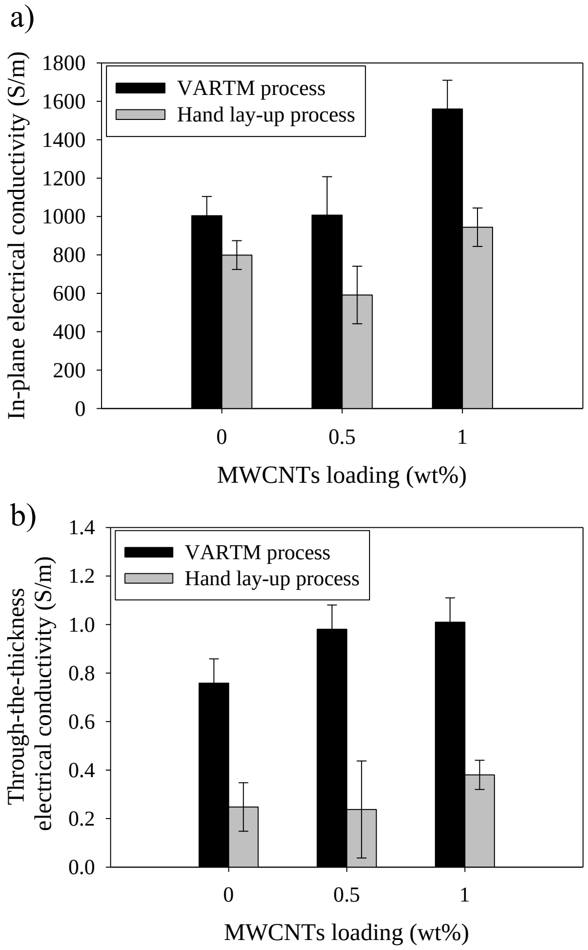

Fig. 7: Electrical conductivity for carbon fiber/epoxy composite reinforced with MWCNT in a) in-plane direction; b) through-the-thickness direction