CARBON NANOTUBE TREATED CARBON FIBRE PREFORMS FOR IMPROVED PROPERTIES OF AERONAUTICAL GRADE COMPOSITES

S.P. Fernberg[1*], R Joffe[1,2], F. Edgren[3]

[1] *Swerea SICOMP AB, Dept. of Materials and Manufacturing, P.O. Box 271, 941 26 Piteå, Sweden*
[2] *Luleå University of Technology, Division of Materials Science, 971 87 Luleå, Sweden*
[3] *Volvo Aero Corporation, Materials Technology, SE-461 81, Trollhättan, Sweden*
**patrik.fernberg@swerea.se*

Keywords: advanced carbon fibre composites, carbon nanotubes, electrophoretic deposition, toughening

Abstract

The current paper reports work on development of enhanced carbon fibre composites manufactured by resin transfer moulding (RTM). In particular, the possibility to obtain a toughened composite through deposition of carbon nanotubes (CNT) on the fibres is investigated. The hypothesis is that deposition of CNT on the fibre surface has two major advantages: a) filtering problems during manufacturing are eliminated and b) CNT can contribute to a local toughening in the vicinity of fibres, where stress concentrations often are high. Unidirectional and multi-axial composites, with and without CNT-modification, were manufactured using conventional RTM-technique and HexFlow®RTM6 epoxy resin. The composites were characterized by means of mechanical testing (interlaminar shear strength, ILSS) and microscopy. Significant improvements by 13 to37 % in ILSS values were achieved with the addition of CNT. Stiffness degradation tests were also performed. The results from these tests were not completely conclusive. Some treatments promoted stiffness degradation whereas others had no apparent effect.

1 Introduction

Current state-of-the-art polymeric composite materials exhibit a number of very good mechanical properties e.g. tensile stiffness and strength. Out-of-plane properties and interlaminar strengths however are usually lower and are often limiting the practical use of the materials. Improvement of these properties through enhancement of properties of resin and interface opens possibilities to more optimized use of carbon fibre reinforced polymers in high performance applications. Many previous and on-going research efforts are devoted to achieving such improvements through development of fibre composites with nanoparticle reinforced matrix phase. Some have been able to show that enhancement of materials properties are possible to achieve [1-4]. There is however some problems of practical nature associated with manufacturing of CNT-treated composites. Apart from the always occurring issues like difficulties in achieving a sufficiently good dispersion there are also problems due to high viscosities of nanocomposite resins and particle filtering during impregnation [5-6]. Already adding small amounts, like e.g. 0.5-1 % of CNT, gives a massive increase in resin

viscosity and filtering of CNT becomes a practical problem once fibre volume content is above 45%.

The work reported here is exploring the possibilities to manufacture CNT-doped fibre reinforced composite by applying CNT on to the fibres prior to infusion. In this way one avoids the mixing of particles into the viscous resin. The work is inspired by work where electrophoretic deposition (EPD) [7-11] is used to position CNT on fibres in composites. We have chosen to particularly evaluate the EPD process further. EPD is a comparably simple method that basically utilizes the fact that charged particles dissolved in a solvent moves towards a charged electrode when an electric field is applied. Then, in the second step they will deposit and accumulate at the deposition electrode once they reach the electrode. Thus, electrically charged CNT can be deposited on to carbon fibre tows or fabrics if fibres are used as one the deposition electrodes. The equipment used for this process, illustrated in Figure 1, is very simple, consisting of a vessel, two electrodes, a suspension, and a DC power supply.

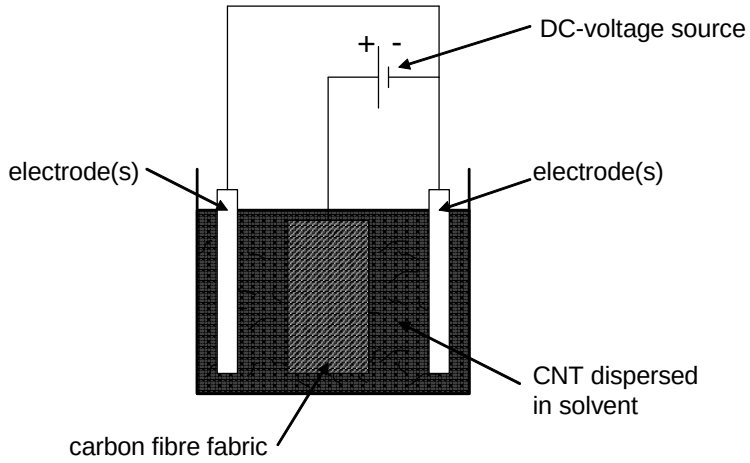

Figure 1. Sketch showing principals of EPD of CNT on to carbon fibre fabrics

The particular objectives of the work reported include:

- Establishing EPD on a small scale i.e. to use EPD to deposit CNT on individual fibre roving
- Scaling up the EPD treatment equipment and process so that it is possible to treat larger sheets of fabrics i.e. treatment on a semi-industrial scale
- Manufacturing of composite laminates with treated fabrics by means of RTM using a one-component epoxy resin
- Characterization of resulting composite laminates via mechanical testing and microscopy.

2 Materials

Multi-walled carbon nanotubes (MWCNT), Graphistrength CL1-020 produced by Arkema were used throughout the study. These CNT were supplied as pre-dispersed aqueous solution in concentration of 2wt% (2g CNT/100ml H_2O). A lower concentration was required in most of the manufacturing trials. Diluted solutions were obtained by addition and mixing of appropriate amounts of water. Carbon fibre tows (12K T700 from Toray) were initially studied during the small scale trials. An unidirectional weave with surface weight of 262 g/m^2 and based on Tenax-E HTS40 carbon fibres was used during large scale experiments and composite manufacturing. A monocomponent high T_g epoxy resin, HexFlow® RTM6 was used as matrix. This is a well known and established resin for the aeronautic industry.

3 Pre-form treatments

Three alternative carbon fibre treatments were evaluated. The first alternative was to perform electrophoretic deposition of CNT on individual sheets of fabric; this treatment is henceforth denoted *EPD* or *EPD-treated*. The second alternative was to manually impregnate a stack of multiple sheets with a diluted aqueous CNT-suspension and then dry the stack; this treatment is henceforth denoted *IMP* or *IMP-treated*. The third alternative was to use the carbon fibre textile as received; this treatment is henceforth denoted *REF* or *Reference*. A more detailed description of the treatments is presented in later section.

The composite samples were manufactured by conventional resin transfer moulding (RTM). This implies that the dry stack of reinforcement was placed inside a heated metal mould cavity. The cavity is subsequently filled and fibres impregnated by pressurized liquid epoxy resin. The resin is pre-heated to 80ºC before injection starts and kept at constant pressure (2 bar). The mould is kept at a constant temperature of 120ºC. The laminates were cured in the mould for more than 12h at 120ºC before demoulding. Finally a post-cure for 75 min at 165ºC and 2h at 180ºC followed. An overview of manufactured samples and their fibre architecture is presented in Table 1.

Preform treatment	**Cross-ply $[0/90_3]_S$**	**Quasi-isotropic $[45/0/-45/90]_{2s}$**
EPD	X	X
IMP	X	
REF	X	X

Table 1. Overview of samples and layups manufactured for different fibre treatments

4 Testing methods

Tensile loading-unloading experiments on cross-ply laminates were performed using an Instron 3366, 10 kN testing machine with constant loading rates of 2 or 3 mm/min. The maximum applied tensile strain during a cycle was incrementally increased with steps of 0.1% until a maximum strain above 1% was reached. Specimen edges were polished prior to testing enabling detection of transverse cracks growth using an optical microscope. The tensile stiffness is measured after each cycle and its relative decrease is related to the amount of damage accumulated during each cycle. The specimen was removed and cracks were counted under microscope after each completed loading-unloading cycle.

ILSS experiments were performed according to EN2563 standard (3P-bending of short specimens). Tests were performed with movement of machines cross-head of 1 mm/min on cross ply laminates. Load-deflection curves are recorded during the experiment. At least seven specimens were tested for each material.

Compression after impact (CAI) tests was made according to the ASTM D7136 standard on quasi isotropic laminates. Initially all materials are subjected to ultrasonic C-scan to determine the virgin state of each materials. EPD-treated composites were characterized using a wheel probe (RapidScan2, Sonatest), whereas the reference panels were characterized using a traditional immersion C-scan system. The panels were impacted with impact energy of 30 J using an impactor with diameter of 16 mm. C-scan was also used to determine the damaged area after impact. Finally samples were equipped with strain gages on both sides of the laminates before actual compression test was performed according to ASTM D7137. Swerea SICOMP and Volvo Aero performed CAI tests on EPD and REF composites respectively.

5 Results and Discussion

5.1.Small scale verification trials - EPD preform treatment

EPD of CNT on to carbon fibres was initially conducted on a small scale to verify the ability of the treatment. In these tests EPD was conducted in a glass vessel with dimensions: diameter 90 mm and height100 mm. The carbon fibre tow was used as the positive electrode while 100 mm^2 to 250 mm^2 large steel plates were used as negative electrode. The electrodes were separated a distance of 25 mm and a voltage of 20 V was applied. The Graphistrength electrolyte was diluted to give CNT-concentrations in ranges 0.03 to 0.5 mg/ml. Different deposition times were tested. After depositions the fibre was left to dry for at least 24h and studied with SEM.

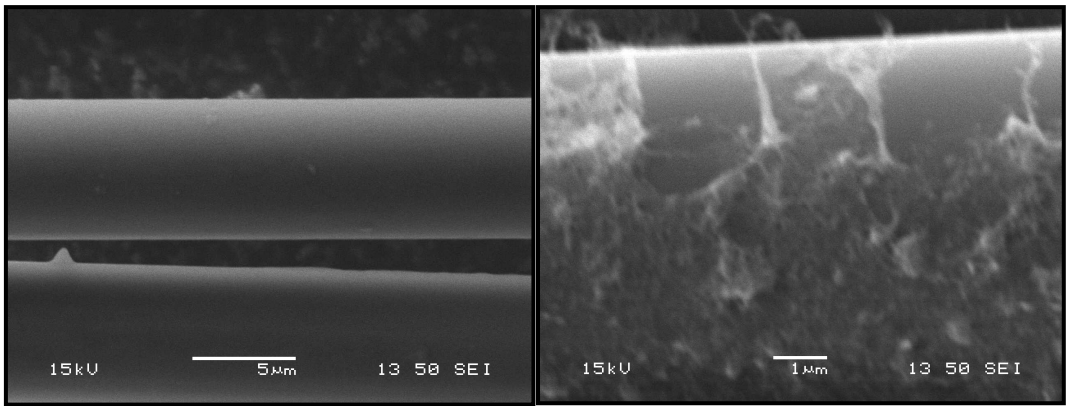

Figure 2. Images from SEM studies. Right: As received carbon fibre, 5000x. Left: carbon fibre surface after 4min EPD, 13500x.

The results from small scale EPD were encouraging since it was seen that a CNT layer is created on the surface of the fibres. This is evident from the comparison between the surface of an as received fibre and the CNT-coated surface seen in Figure 2. The best results during small scale EPD tests were obtained for 0.50 mg/ml concentration and deposition times of 3-4 minutes. Lower concentration solutions could also produce homogenous coatings but only if high deposition times were used. Besides providing useful guidance to appropriate processing parameters for larger scale EPD the small-scale test verified that the concept works with the selected constituents.

5.2 Large-scale EPD preform treatment

Larger sheets, of approximately A4 page size, of the UD carbon fibre fabric were EPD-treated using a specially designed and built glass tank. Photographs of the tank and the setup are presented in Figure 3. The tank is made from electrically insulating material (glass sheets) and it is approximately 350 mm high, 250 mm wide and 50 mm thick. Two metal plates (electrodes) are clamped onto both sides of the tank. The carbon fibre fabric is attached on a metal frame by copper clamps (for better electrical contact) at the top and bottom of the fabric. This metal frame is during EPD lowered and positioned in the middle of the electrolyte filled tank. The CNT electrolyte concentration was 0.01wt% (0.10 mg/ml). Negative electrodes, cathodes are attached to the metal plates while the metal frame and the carbon fibre are connected to the positive electrode, anode. During the actual EPD an electrical voltage of 10 V is applied to the system for 10 minutes. The treated and wet fabric is then removed from the tank and carefully transported directly to the RTM-tool, shown to the left in Figure 4. This procedure was repeated until the correct stacking sequence of the complete preform, was achieved. Drying of the preform was done inside the tool for 24h at 120ºC. The

RTM-manufacturing of the composite sample was performed according to procedures described earlier.

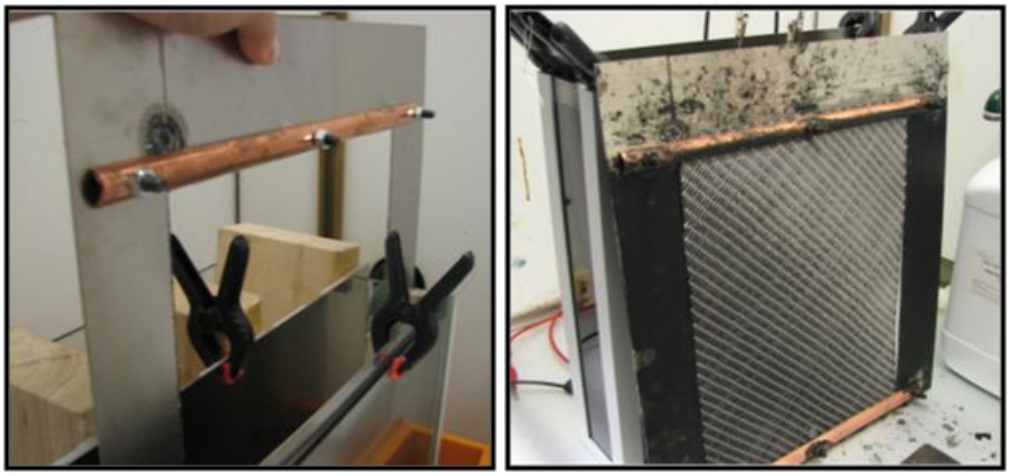

Figure 3. Images showing setup for large scale EPD preform treatment. Right: Metal frame (without carbon fibre fabric) under positioning in the EPD-treatment cell. Left: Metal frame (with fabric) in front of EPD-treatment cell before treatment.

5.3 IMP preform treatment

The IMP-treatment involved layer-by-layer manual impregnation of individual sheets with a diluted aqueous CNT-suspension while they were placed into the preform. The 0.2% CNT-dispersion was diluted in order to give a dispersion that both was dilute enough to fill the entire preforming cavity while still give a desired CNT-content in the laminate. Finally the preform was dried in the tool under closed lid for 24 hours at 120°C. The RTM-manufacturing of the composite sample was performed as described earlier.

Figure 4. RTM-mold used during manufacturing trials. Right: Manual impregnation of carbon fibre preform with dilute aqueous CNT-dispersion during IMP-treatment

5.4 Qualitative comparison between EPD and IMP

With the EPD-technique it is possible to quite accurately control the concentration of CNTs in the initial water solution. It is more difficult to directly control the amount of CNT eventually deposited on the fabric and therefore also in the ultimate composite. Impregnation treatment of fabrics implies more control over the amount of CNT in the final composite than EPD-treatment. It is however expected that EPD-treatment provides better control than IMP-treatment over the spatial distribution of CNT i.e. more evenly distributed CNT can be obtained with EPD. This statement remains to be confirmed experimentally. Despite some obvious difficulties in either controlling the amount of CNT (with EPD) or controlling the distribution (IMP) it is our opinion that the distribution of CNT on to the fibres offer

improved control of CNT compared to strategies where CNT are dispersed directly in resin prior to RTM or vacuum infusion. The obvious advantage with the latter strategy is that CNT can be thoroughly dispersed (by calendaring, ultrasonication or some other dispersing method) prior to infusion. This advantage is however often counteracted by the disadvantage of having excessive filtering of particles during mould filling of the laminates. Moreover, the dispersion in resin is impractical for highly reactive one-component epoxies like RTM6.

5.5 Stiffness degradation in cross-ply laminates

One of the first damage modes observed in multi-axial laminates is debonding of fibres from matrix and formation of cracks transverse to the loading direction. The initiation of transverse cracks and the rate of their accumulation are defined by adhesion between fibre and matrix. The extent of this damage is reflected in changes of the mechanical performance of laminate.

Results of the stiffness degradation tests on cross-ply laminates are presented in Figure 4 (stiffness is normalized with respect to the initial values for undamaged material). It can be noticed that the reference material shows no sign of stiffness degradation below 0.4% tensile strain. Both EPD- and IMP-treated material show a tendency towards reduced stiffness already between 0.3% and 0.4% strain. At higher strain levels, e.g. above 0.5%, there is a tendency that normalized stiffness values for EPD-treated composites coincide with the reference laminates. All values regarding EPD-treated composites are however uncertain because of the large scatter. This is to a large extent depending on the fact that only two samples were tested i.e. data for EPD in Figure 4 are based on two specimens. The data in Figure 4 for REF and IMP are based on 6 and 5 samples respectively which can be considered as a more acceptable base for statistical reasoning and conclusions. Thus it is appropriate to conclude that IMP-treated composites perform worse than REF in terms of stiffness degradation. The onset of stiffness degradation occurs at lower strains and the stiffness degradation at each strain level is always larger for IMP than for REF.

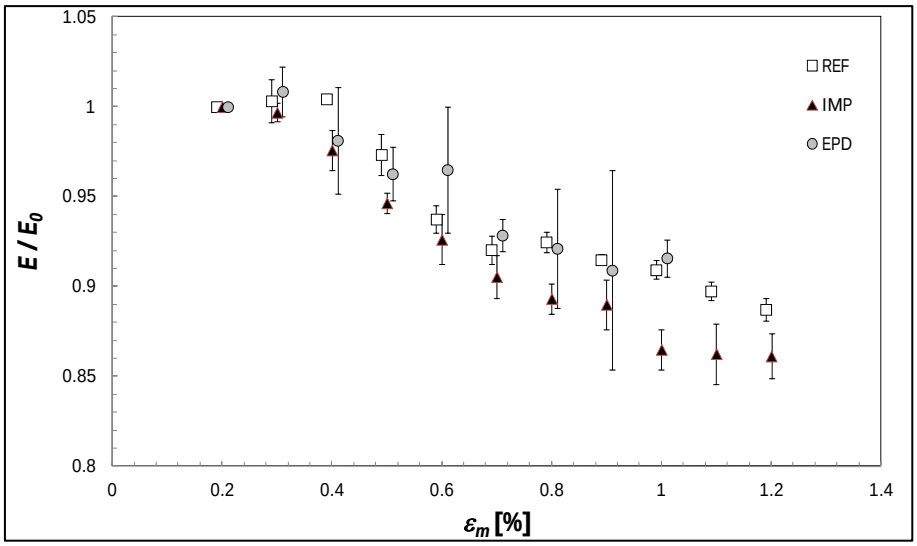

Figure 4. Tensile stiffness degradation from loading-unloading experiments. Average values from several tests. Error bars indicates confidence intervals at 90% confidence level.

5.6 Interlaminar shear strength (ILSS)

ILSS tests were performed for EPD, IMP and REF-laminates. The results presented in Table 2 show that treatment of preforms with CNT has a positive effect on ILSS. Both EPD and IMP perform better than REF. This is in support of the hypothesis that treatment of the carbon fibre preform contributes to a toughened interface/interphase and that such enhancement also contributes to improved fracture properties under certain loading conditions i.e. Mode-II

loading in this case. The increase for EPD-treated laminate compared to REF material is 37%, whereas a 13% increase is obtained for IMP-treated laminates.

Material	Average ILSS (MPa)	St. dev (MPa)	Increase from treatment [%]
EPD	75.6	7.1	37
IMP	62.4	1.8	13
REF	55.2	5.8	-

Table 2. Overview of samples and layups manufactured for different fibre treatments

5.7 Compression after impact, CAI

Typical C-scan images showing EPD-treated quasi-isotropic laminates after impact are presented in Figure 5. The damaged area was estimated based on such images. The values of these measurements and the results from CAI tests are presented in Table 3.

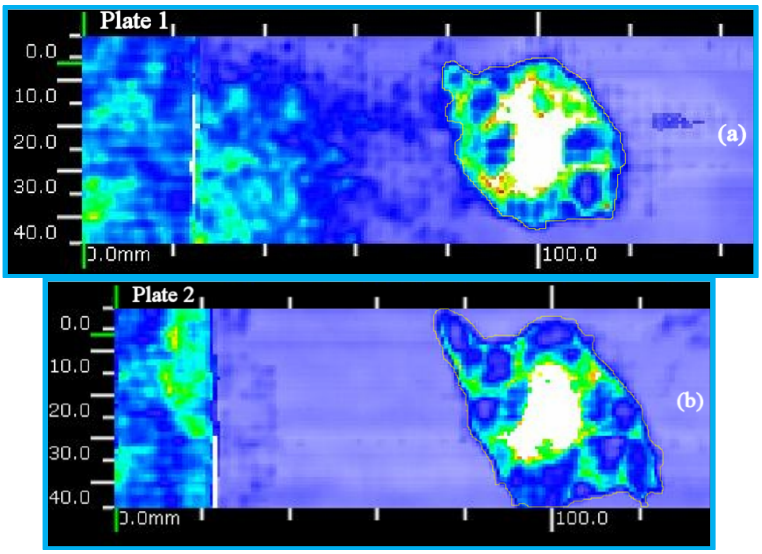

Figure 5. C-scan plots of EPD-treated composites after impact.

The results in Table 3 show that the damaged zone size is approximately 21% larger for EPD treated material compared to the reference material. It should be mentioned that optical microscopy of cross-sections of the EPD-treated quasi isotropic laminates indicated significant amount of voids. This may have led both to a more excessive damage initiation and propagation during impact but also to an uncertainty in the C-scan evaluation. The fact that different C-scan equipment was used also contributes to some discrepancy of results.

Material	Damage area (mm^2)	Failure strain (%)	CAI strength (MPa)	No of samples
EPD	1360	0.35	203	3
REF	1127	0.49	218	6

Table 3. Results from impact, C-scan and CAI-tests

CAI results show that compressive stress at failure for EPD treated laminates is slightly lower than values measured for reference laminates. The strain at failure for REF is significantly higher than that for EPD treated laminates. It should be mentioned once again that comparison of results is somewhat difficult since tests were performed at different laboratories.

It is worth noting that CAI strength values obtained of our laminates compare well with values from literature, obtained by Yokozeki et al [12] for prepreg based laminates. They

evaluated composites which werse doped with 5wt% and 10wt% of cup-stacked CNT. CAI strengths in a range 170 to 195 MPa was observed. Their results showed up to 8 % increase for doped laminates (10wt%) in comparison with their reference material. It should be noted that although these also were quasi-isotropic laminates, the stacking sequence $[0/90/45/-45]_{3S}$ is slightly different from the laminates used in current study.

6. Summary and conclusions

The main objective of the work was achieved: EPD treatment of carbon fibre with CNT was established both on a small and a larger scale. The results from the mechanical characterisation were encouraging since significant enhancement in the Mode-II dominated ILSS was observed for materials with CNT treatment. However, contrary to expectations, no significant improvement in the resistance towards the Mode-I dominated transverse cracking was observed with CNT treatment. The initiation of transverse cracks in the cross-ply composite with CNT occurred at similar or lower applied strain than in reference laminates. This indicates that Mode-I fracture toughness was not positively affected in the same manner as the onset of Mode-II damage in ILSS tests.

References

[1] Gojny F.H., Wichmann M.H.G., Kopke U., Fiedler B., Schulte K. Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content, Composites Science and Technology **64**, pp 2363–2371 (2004).

[2] Fidelus J.D., Wiesel E., Gojny F.H., Schulte K., Wagner H.D. Thermo-mechanical properties of randomly oriented carbon/epoxy nanocomposites Composites: Part A **36**, pp. 1555–1561, (2005).

[3] Lucas P., Roth T. LEO semi-solid film, JEC Composites Magazine 54, pp 53-55 (2010).

[4] Yokozeki T., Iwahori Y., Ishiwata S. Matrix cracking behaviors in carbon fiber/epoxy laminates filled with cup-stacked carbon nanotubes (CSCNTs), Composites: Part A, **38**, pp 917–924 (2007).

[5] Nordlund M, Fernberg S.P., Lundström T.S. Particle deposition mechanisms during processing of advanced composite materials, Composites: Part A, **38**, pp. 2182–2193 (2007).

[6] Nordlund M, Lundström T.S. An Investigation of Particle Deposition Mechanisms During Impregnation of Dual-Scale Fabrics with Micro Particle Image Velocimetry, Polymer Composites, **31**, pp. 1232-1240 (2009).

[7] Chou T.-W., Gao L., Thostenson E.T., Zhang Z., Byun J.-H. An assessment of the science and technology of carbon nanotube-based fibers and composites, Composites Science and Technology **70**, pp 1–19 (2010).

[8] Wicks S.S., Guzman de Villoria R., Wardle B.L. Interlaminar and intralaminar reinforcement of composite laminates with aligned carbon nanotubes, Composites Science and Technology **70**, pp 20–28 (2010).

[9] Boccaccini A.R., Cho J., Roether J.A., et al. Electrophoretic deposition of carbon nanotubes, Carbon **44**, pp. 3149–3160 (2006)

[10] Van der Biest O.O., Vandeperre L.J. Electrophoretic deposition of materials. Annual Review of Materials Science **29**, pp. 327–352 (1999).

[11] Bekyarova E., Thostenson E.T., Yu A., et al. Multiscale Carbon Nanotube - Carbon Fiber Reinforcement for Advanced Epoxy Composites, Langmuir. **23**, pp. 3970–3974 (2007).

[12] Yokozeki T., Iwahori Y., Ishiwata S., Enomoto K. Mechanical properties of CFRP laminates manufactured from unidirectional prepregs using CSCNT-dispersed epoxy, Composites: Part A, **38**, pp. 2121–2130 (2007).