ELECTRICAL AND MECHANICAL PROPERTY INVESTIGATION OF FUZZY FIBRE-REINFORCED COMPOSITES

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ABSTRACT

The vertically aligned carbon nanotubes (CNTs) that are added into fiber reinforced polymer matrix composite can significantly improve not only mechanical but also electrical properties of composites and called as hybrid or nanoengineered composites (NECs). In this study, CNTs are directly grown onto advanced microfibers to fabricate fuzzy fiber reinforced nano-engineered composites (FF-NECs). In addition to fuzzy fibers, the polymer matrix is also toughened by CNT dispersion to achieve a combined mechanical and electrical enhancement on NECs. Mechanical property investigation is investigated by Mode-I fracture toughness and the electrical measurements in plane and out of plane is measured, as well. While steady-state toughness of NECs and FF-NECs exhibit almost same initiation toughness with increasing 113% and 119%, respectively, the electrical conductivity of NECs and FF-NECs are improved about 3 and 7-8 orders of magnitude respectively.

1 INTRODUCTION

Conventional continuous fiber-reinforced polymer composites have made a huge impact over the past half-century, particularly in the aerospace industry. Their superior mechanical properties and low weight, combined with their chemical and environmental resistance, make them ideal for many structural applications, including sporting equipment, aircraft, automotive, civil and marine structures, However, relatively weak compression and interlaminar properties of these composites still remain as major issues[1].

A carbon nanotube (CNT) is a tubular structure made of carbon atoms, although having nanometer order diameter, length of CNTs can be several micrometers. Since they were first described by Iijima [2], several CNT studies have been shown a dramatic increase because of advanced electrical, thermal, mechanical and optical properties [3, 4]. CNTs have shown great potential for use in a variety of applications, such as electrodes, actuators, filters, ultrafast photonics, structural fibers, and so forth [5]. In addition CNTs possess low density, well alignment, huge aspect ratio, a large surface area to volume ratio and low coefficient of thermal expansion. While the individual CNT shows excellent mechanical properties (Young's modulus of individual CNT over 1TPA and the strength between 11-63GPA), on the large scale composites which made using CNTs have shown some improvement not only in mechanical properties [6], and also electrical [7, 8] and thermal properties [9], making them attractive for enhancing a variety of polymer matrices. The main motivation for adding CNTs to conventional fiber composites is to overcome the existing limitations associated with the matrix dominated properties. For example, CNTs could offer both intralaminar and interlaminar reinforcement, thus improving delamination resistance and through-thickness properties, without compromising in-plane performance [1, 10]. These type composites could be called as hybrid, hierarchical or nano-engineered composites (NECs) in several studies in the literature.

Motivation of this study is to improve interlaminar fracture toughness and electrical properties of conventional composites using CNTs. High purity vertical aligned carbon nanotubes are synthesized on silicon wafer and glass fiber surfaces using thermal chemical vapor deposition (CVD) with different catalyst systems. In this study, two common methods;

- dispersion of CNTs into the polymer matrix
- growing of CNTs directly onto glass fiber (fuzzy)

are used to produce nano-engineered composites to exploit their multi-functional properties for improving traditional composite properties. The first method is focused on dispersing CNTs into a polymer matrix provides transferring the matrix loads to fibers and also to block crack propagation along crack route is an advantage of using CNT due to the high aspect ratio of them with almost no weight addition. In this method, most critical point is dispersion amount of CNTs without functionalization which is very limited due to CNTs agglomeration. In addition, the agglomeration of CNTs depend on matrix viscosity during composite production as well as dispersion method. Although adding CNTs enhances composite, only small enhancement in properties have been carried out because of difficulties in processing and controlling CNT orientation during manufacturing [6]. Growing CNTs onto the fiber directly provides oriantation control and homogeneous distribution of CNTs in advanced composites. This combined method with CNT dispersion in matrix and fuzzy fiber can improve mechanical [10], electrical [11] and thermal [9] properties of composites.

2 EXPERIMENTAL STUDIES

2.1. Synthesis and Characterization of Carbon Nanotubes

Although there are many different CNTs synthesis methods, only CVD method provides control on the CNTs orientation. A customized CVD system with a single zone Lindberg Blue M series tube furnace is used with a quartz tube of 2 inches diameter. CNTs are synthesized on Si wafer (coated with 10 nm Al_2O_3 and 1nm Fe by e-beam evaporation method) up to 2mm length by varying growth time. The furnace is heated to 750 °C under 1600 sccm and 1000 sccm of helium and hydrogen respectively.
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In order to investigate the orientation and the length of CNTs, SEM is used for morphological characterization. The image (Fig. 1a) shows the appearance of vertically aligned CNTs and with a zoomed view on right taken at higher magnifications and reveals wavy view of individual CNTs. As-grown A-CNTs would have <2% volume fraction after the growth procedure and the rest is air (~98%).

Raman spectroscopy (Fig. 1b) is one of the strongest methods for characterization of CNTs since non-destructive and fast analysis is possible without additional specimen preparation step. Two intensity ratio is a quantitative degree of purity and shows as I_G/I_D and obtained as 1.49 similar to multi-walled CNTs in the literature.

Thermogravimetric analysis (TGA) is a thermal analysis technique that measures the weight loss of the material depending on the temperature at desired atmospheric conditions. Especially it is widely used to measure the oxidation resistance of carbon-based materials. Oxidation resistance of the CNTs is an indication of its quality, so the thermogravimetric analysis was carried out at room temperature until 900°C using TA Instrument brand SDT Q600 DSC-TGA. The best decomposition temperature of CNTs is about 650°C at 5% weight loss and it shows as T_d (5%) (Fig. 1c).

2.2. Fabrication and Characterization of Fuzzy Fiber

To create fuzzy fiber, bi-directional glass cloth surfaces are coated with Fe catalyst particles to uniform aligned CNTs growth on fiber surfaces [12]. Firstly the cloth is dipped in a 50 mM solution of iron nitrate ($Fe(NO_3)_3$ 9 H_2O) in isopropyl alcohol (C_3H_8O) and then dried in a furnace at 30 °C at least 8 hours at controlled humidity conditions [6]. Clothes are cut according to furnace dimension as 4cm width and 22cm long and then the Fe-coated fabrics are positioned downstream of the furnace center [12]. Except growth temperature (650°C) the same recipe is used as CNTs synthesis. Fig. 2 shows optical images of glass fiber cloth before and after CNTs growth and scanning electron microscopy image of fuzzy fiber. The length and morphology of CNTs around the fibers depends on growth recipe, catalyst solution, sample position on tube and atmospheric conditions. According to these parameters, CNTs morphology can be tangled, partial, radial and Mohawk with different length [12].

In this study, the length of synthesized CNTs about 3μm and CNTs show homogeneous distributed radial morphology as seen in Fig. 2c. CNTs and growth temperature also effects cloth shape. As seen in Fig. 2b after CNTs growth, the rectangular cloth has a bit curvature with the effects of temperature and tube shape.

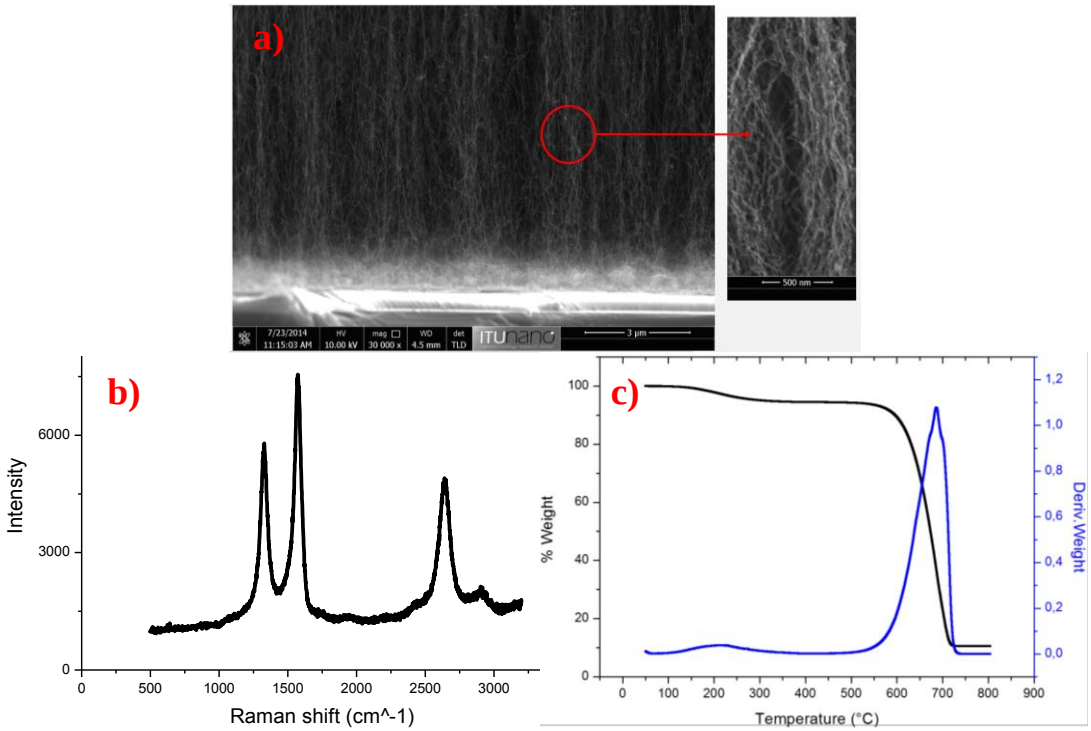

Figure 1: (a) SEM image, (b) Raman and (c) TGA graphs of CNTs.

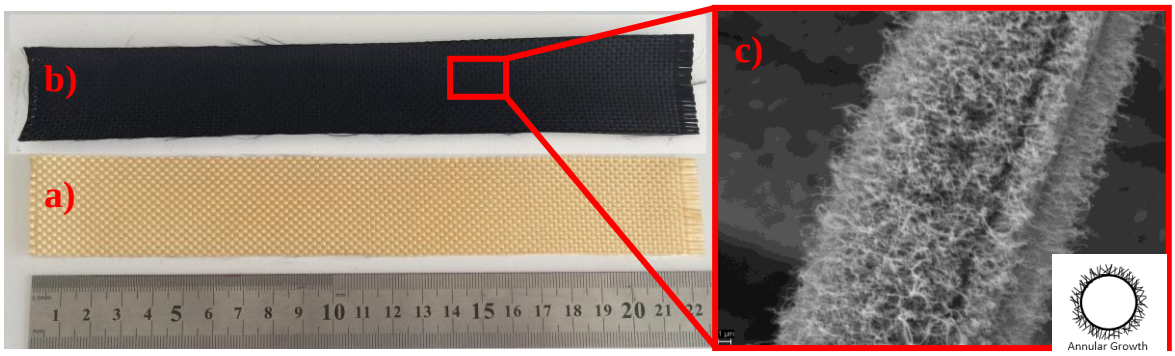

Figure 2: Glass fiber cloth before and after CNTs growth: (a) Fe coated glass cloth before CNTs growth, (b) after CNTs growth and (c) SEM image of fuzzy fiber.

2.3. Manufacture and Testing of FF-NECs

Baseline (no CNT), NECs (dispersed CNTs in the epoxy), and FF-NECs (dispersed CNTs in epoxy and CNTs are growth on fibers) laminates are manufactured 14 plies thick using vacuum infusion method. Aerospace (Hexcel RTM 6) type epoxy is used as matrix and this epoxy has a tensile strength of 75 MPa. Dispersion process is one of most critical part of CNTs loading as nano-fillers. In earlier studies, homogenizator, and horn sonicator were used for dispersion of CNTs in epoxy and IPA, respectively. Homogenizator method showed well CNTs dispersion, while the sonicator was indicating agglomeration at long CNTs loading (about 1.5mm). In this study, differently from these method, magnetic stirrer dispersion method is used for dispersion of CNTs in acetone. Firstly two magnetic stir bars and CNTs (0.04 wt%) are mixed in solvent. Secondly solvent is removed using a small space mesh, and then CNTs are dried in 30°C at least 8 hours due to evaporation of remain acetone and to achieve solvent dispersed CNTs which is also called as bucky paper. Then the obtained CNT bucky paper are dispersed in RTM 6 using mechanical mixer at about 1800 rpm at least 2 hours at 80 °C on a hot plate.

Schematic illustration of vacuum infusion process (VIP) is given in Fig. 3. While manufacturing of FF-NECs, internal middle 6 plies are selected from fuzzy fiber and 8 glass fiber plies are used as external plies, baseline and NECs specimens are manufactured using 14 glass fiber plies.The mold and

epoxy with CNTs loading are heated at 90°C and 80°C respectively. The wetting process is done under a 740mm Hg vacuum for straight and without tripping wetting. In order to obtain well wetted homogeneous composite, the wetting process have to done very slowly.

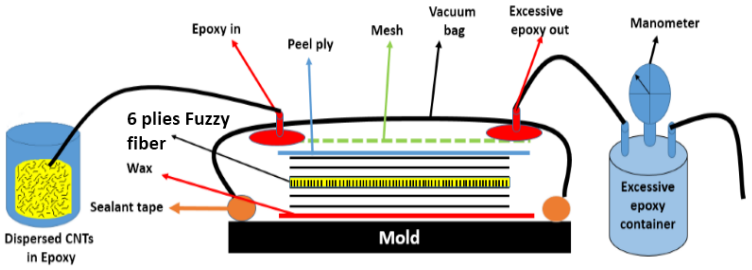

Figure 3: Schematic illustration of vacuum infusion process.

Mode 1 fracture testing is performed on specimens of baseline (no CNT dispersed) and short CNT fuzzy fiber with CNT dispersed in matrix. Baseline sample is manufactured as one rectangular plate with pure RTM 6. To fabricate double cantilever beam (DCB) laminates a 15 µm release film is placed between the middle two plies on the last 5 cm on one end of the laminate during lay-up, to form a starter pre-crack at the laminate centreline. All DCB specimens are cut 20mm width and 167mm length using 3D CNC. Specimen surfaces are roughened using sandpaper, cleaned with acetone and dried at 30 °C before pasting piano hinges at surfaces. The hinges is glued using Devcon 2 tone epoxy on specimen surfaces and to watch crack propagation, cross section surface of specimen is marked with white and red pen respectively (Fig. 5). DCB specimens are tested MTS test machine, and the specimens are loaded at 1mm/min and load, stroke, and crack propagation are recorded (ASTM D5528).

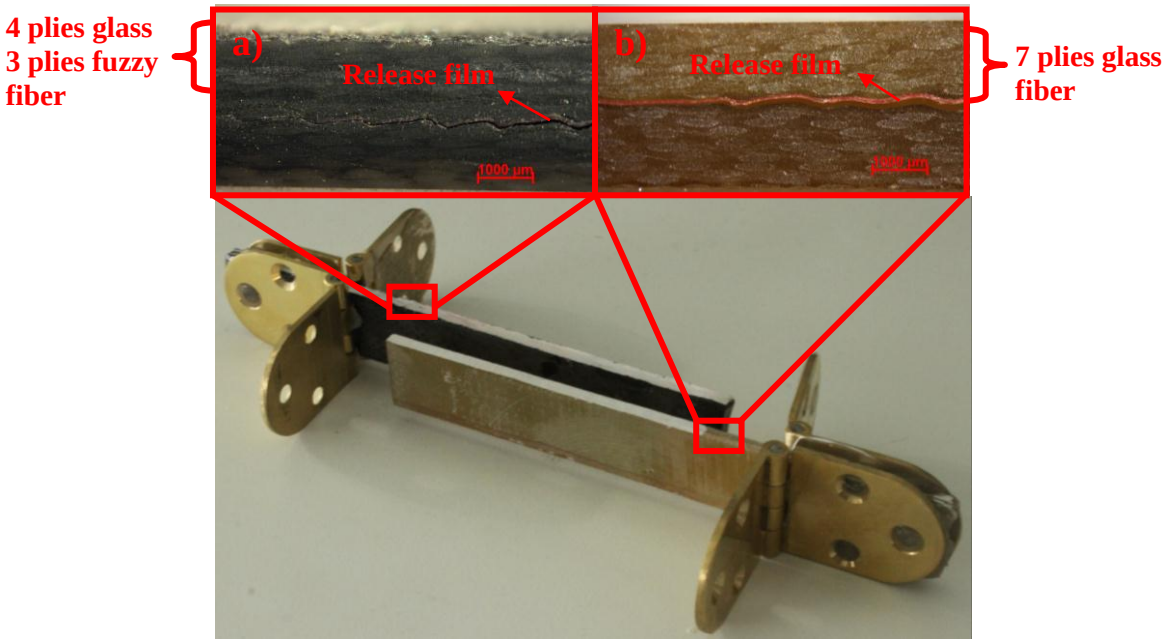

Figure 4: Cross section view of DCB specimens (a) FF-NECs and (b) baseline.

Electrical resistance was measured through thickness and in plane. The visual information about direction is exhibited in Fig. 5. The resistance measurement is provided to calculate electrical conductivity of NECs. The conductivities of cured samples are measured on rectangular specimens, 25 x 15 x 3 mm for baseline, NECs, and FF-NECs (laid 14 plies glass, glass, and fuzzy fiber, respectively).

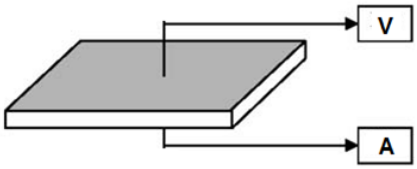

Figure 5: Schematic visualization of resistance measurement.

The DC electrical conductivity of the composites is measured by a standard two-probe electrode using Keithley 2400 in dry air at ambient temperature. The surfaces of the composite specimens are polished and silver conductive paste (Alfa Aesar 42469) which allow good electrical contact between the surfaces of the sample and electrodes is applied on probe contact surface and the samples are placed between two electrodes. Then voltage is applied to the electrodes between 0-40 V, I-V measurements are recorded, and the slope is linear fit. Then the conductivity of the samples is calculated using the formula;

$$\sigma(S/m) = \frac{l}{\Omega \times A} \qquad \textbf{(1)}$$

Where 'σ' is the electrical conductivity, 'Ω' is resistance, 'l' is the distance between probes in meters and 'A' is the area of contact of the electrodes with the sample in meter square.

3 RESULTS AND CONCLUSION

Mode I fracture toughness results are characterized by initiation and steady-state resistance curve (R-curve) as shown in Figure 6. Different R-curve shapes can be seen between baseline, NECs and FF-NECs, while the baseline showing almost same fracture toughness through crack propagation, NECs and FF-NECs has shown ups and downs especially FF-NECs. The modification of epoxy and fibers with CNTs change R- curve behavior from linear to non-linear. Mean initiation and steady-state toughness values are given in Figure 7. After crack initiation NECs and FF-NECs exhibit almost same initiation toughness with increasing 143% and 150%, respectively. This trend also continues at steady-state toughness. The average steady-state G_{Ic} of baseline, NECs, and FF-NECs means are calculated as 0.78, 1.66 and 1.7 kJ/m^2, respectively. Fracture toughness values are increased more than 2 fold with randomly dispersed CNTs loading and this long CNTs can be show bridging between plies. On the other hang it can be say that there is almost no effect of fuzzy fibers on Mode 1 fracture toughness because of short CNTs. The CNTs long are not enough to create bridging between plies.

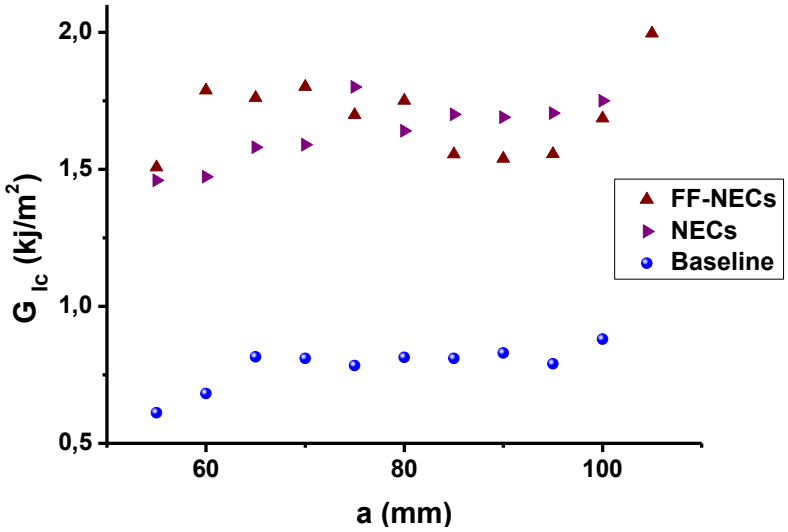

Figure 6: Steady-state R-curves of baseline, NECs, and FF-NECs.

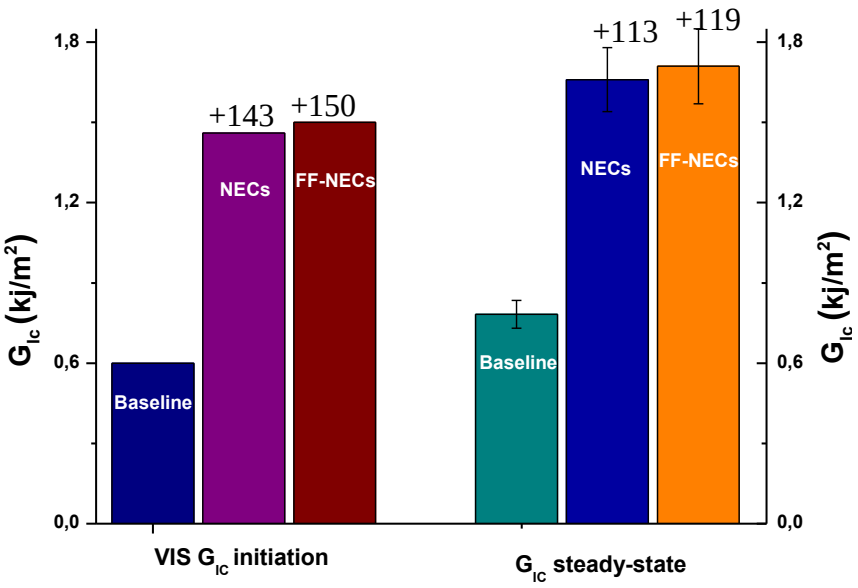

Figure 7: Mean strain energy release rate, G_{Ic}, of baseline, NECs, and FF-NECs.

To explain CNTs effects SEM images are investigated and are given in Figure 8. Smooth epoxy regions and exposed microfibers have control over baseline fracture surfaces (Fig. 8a). The fracture surfaces of NECs and FF-NECs are dominated by matrix cohesive failure, creating jagged, rough surfaces as given in Fig. 8b-c. On the other hand fracture surface of FF-NECs exhibit CNTs are pulled out a few microns, so CNTs create bridge interlaminar and this system contribute to increase of fracture toughness.

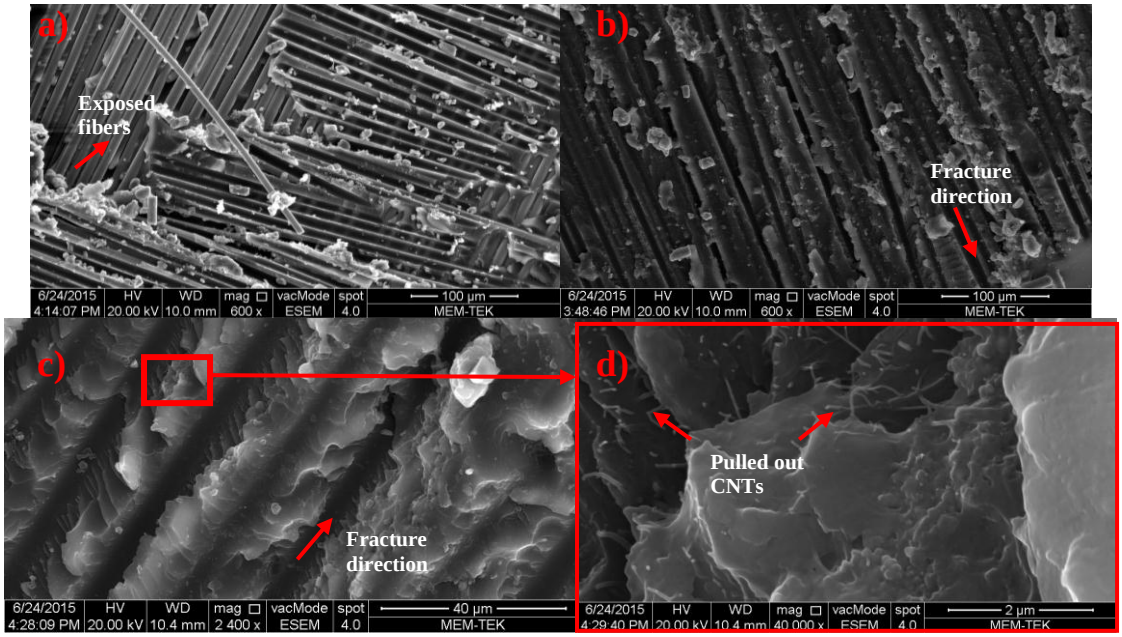

Figure 8: Example SEM fractography of (a) baseline, (b) NECs, and (c-d) FF-NECs.

CNTs addition in epoxy [13] and synthesis onto fiber surface [14] transform the insulating polymer to conducting composites even at a low CNTs content, due to their exceptional electrical properties. As shown in the Figure 9, FF-NECs and NECs electrical conductivity are rapidly and significantly increase with small amount of CNTs addition and fuzzy fiber, the electrical conductivity of FF-NECs and NECs are improved about 7-8 and 3 orders of magnitude, respectively, compared to the baseline through thickness and in-plane direction. In literature only a few high conductive glass fibers have been fabricated and one of them is achieved with high amount of conductive particles in glass fiber composite [15], but high amount of additive materials has potentially a higher tendency to

agglomerates. Additionally N. Yamamoto et al. successfully growth CNTs on alumina fibers and they achieved 13 S/m through-thickness and 142 S/m in-plane [9] and these results shows fuzzy fiber is one of the most effective method to increase electrical properties of composites without weight increase.

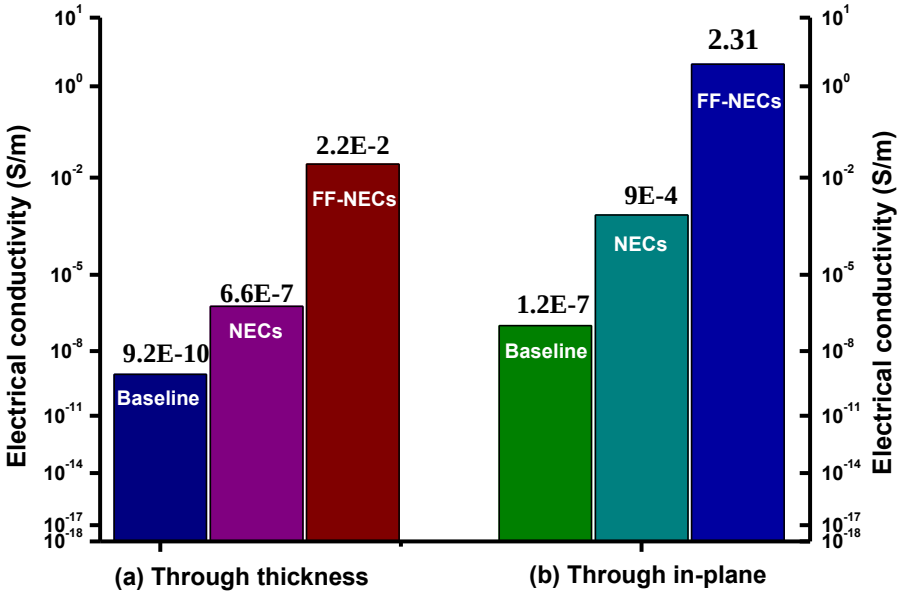

Figure 9: Electrical conductivity of baseline, NECs, and FF-NECs (a) through thickness and (b) in-plane.

DC electrical measurements of FF-NECs laminates show highly anisotropic electrical properties also. The conductivity in plane direction higher than through thickness because level of contact between neighboring fibers is governing parameter and packing of in plane direction denser than out of plane [16] and glass fibers may block continuous electrical pathways in the through-thickness direction [9].

4 REFERENCES

1. Qian, H., et al., *Carbon nanotube-based hierarchical composites: a review.* Journal of Materials Chemistry, 2010. **20**(23): p. 4751.
2. iijima, <*Helical microtubules of graphitic carbon*>. Natural, 1991(354): p. 56-58.
3. Shanov, V., et al., *CVD growth, characterization and applications of carbon nanostructured materials.* Surface and Coatings Technology, 2013. **230**: p. 77-86.
4. Chen, K.-R., *Optical-Electronic Properties of Carbon-Nanotubes Based Transparent Conducting Films.* Advances in Chemical Engineering and Science, 2013. **03**(01): p. 105-111.
5. Liu, L., W. Ma, and Z. Zhang, *Macroscopic carbon nanotube assemblies: preparation, properties, and potential applications.* Small, 2011. **7**(11): p. 1504-20.
6. Wicks, S.S., et al., *Multi-scale interlaminar fracture mechanisms in woven composite laminates reinforced with aligned carbon nanotubes.* Composites Science and Technology, 2014. **100**: p. 128-135.

7. Georgousis, G., et al., *Strain sensing in polymer/carbon nanotube composites by electrical resistance measurement.* Composites Part B: Engineering, 2015. **68**: p. 162-169.
8. Pozegic, T.R., et al., *Low temperature growth of carbon nanotubes on carbon fibre to create a highly networked fuzzy fibre reinforced composite with superior electrical conductivity.* Carbon, 2014. **74**: p. 319-328.
9. Yamamoto, N., R. Guzman de Villoria, and B.L. Wardle, *Electrical and thermal property enhancement of fiber-reinforced polymer laminate composites through controlled implementation of multi-walled carbon nanotubes.* Composites Science and Technology, 2012. **72**(16): p. 2009-2015.
10. Wicks, S.S., R.G. de Villoria, and B.L. Wardle, *Interlaminar and intralaminar reinforcement of composite laminates with aligned carbon nanotubes.* Composites Science and Technology, 2010. **70**(1): p. 20-28.
11. Garcia, E., et al., *Fabrication and multifunctional properties of a hybrid laminate with aligned carbon nanotubes grown In Situ.* Composites Science and Technology, 2008. **68**(9): p. 2034-2041.
12. Yamamoto, N., et al., *High-yield growth and morphology control of aligned carbon nanotubes on ceramic fibers for multifunctional enhancement of structural composites.* Carbon, 2009. **47**(3): p. 551-560.
13. Zeng, X., et al., *Mechanical reinforcement while remaining electrical insulation of glass fibre/polymer composites using core–shell CNT@SiO2 hybrids as fillers.* Composites Part A: Applied Science and Manufacturing, 2015. **73**: p. 260-268.
14. Veedu, V.P., et al., *Multifunctional composites using reinforced laminae with carbon-nanotube forests.* Nat Mater, 2006. **5**(6): p. 457-62.
15. Markov, A., B. Fiedler, and K. Schulte, *Electrical conductivity of carbon black/fibres filled glass-fibre-reinforced thermoplastic composites.* Composites Part A: Applied Science and Manufacturing, 2006. **37**(9): p. 1390-1395.
16. Reia da Costa, E.F., et al., *RTM processing and electrical performance of carbon nanotube modified epoxy/fibre composites.* Composites Part A: Applied Science and Manufacturing, 2012. **43**(4): p. 593-602.