



Preparation and Characterization of Carbon Nanotube Deposited Carbon Fiber Reinforced Epoxy Matrix Multiscale Composites

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ABSTRACT

In this study, desized carbon fibers were coated with carbon nanotubes using two diverse coating techniques, i.e. dip coating and spray up process and the factors affecting the coating techniques were investigated. The morphological study revealed better nanotube coating on carbon fibers from dip coating technique as compared to spray up process. Later, nanotube-coated fibers from dip coating were impregnated with epoxy to fabricate multiscale carbon fiber reinforced epoxy matrix composites. The nanotubes on fiber surface were expected to improve the interlaminar shear properties of the multiscale composites. According to short beam shear testing, 14% increase in interlaminar shear strength was observed in composite containing nanotubes as compared to reference composite. Microscopic observation under optical and electron microscopes confirmed the void-free impregnation of fibers with epoxy along with the presence of nanotubes on fibers and in matrix in the vicinity of fibers. Finally, the mechanisms involving the enhanced interlaminar properties were identified and discussed.

Keywords: Dip coating; Spray up; Multiscale composite; Carbon fiber; Epoxy; Carbon nanotubes; Interlaminar shear strength

1 Introduction

Carbon fiber reinforced polymer matrix (CFRPs) composites are widely used in aerospace and automobile industries due to their superior mechanical properties in comparison to conventional monolithic materials [1]. In CFRPs, the applied load transfers from matrix to fibers through an interface. Hence the presence of a strong interface plays a crucial role in determining the overall mechanical performance of CFRPs [2]. The use of carbon fibers as reinforcement is due to their high specific strength and stiffness while epoxy resin provides good wettability thus the synergy of carbon fibers with epoxy resin has been successful to produce a light weight material for a variety of engineering applications. Since the inception and utilization of CFRPs, attention has been focussed on continuous improvement in their mechanical properties. Along with other mechanical properties, the fiber/matrix interfacial properties are of significant importance especially in polymeric matrix composites wherein a strong interface is required for improved strength than weak interface as required in ceramic matrix composites for enhanced toughness [3]. As a result, studies have focused on improving the interfacial adhesion between fibers and matrix [4, 5]. Several mechanisms have been proposed to enhance the interfacial adhesion either by modifying the chemistry of the matrix [6] or modifying the surface properties of fibers [7]. Lately, the focus has been shifted toward modifying the surface properties of fibers. Fiber sizing [8], electrochemical processing [9] and more recently the incorporation of nanomaterials on the surface of micrometre-sized fibers [10] have gained special attention due to the ease of processing and the increase in the properties of CFRPs.



The introduction of nanomaterials such as carbon nanotubes (CNTs) in CFRPs can be achieved either by addition into matrix or direct deposition on fibers. The incorporation of nanomaterials in matrix has the advantage of their uniform distribution throughout the composite material while their deposition on micrometre-sized fibers can tailor the interfacial properties [11]. CNTs have been widely used and well-investigated as a key nano-reinforcement in polymeric matrices [12]. Especially the addition of CNTs along with micrometre-sized and nanometre-sized reinforcements has shown significant improvements in mechanical properties [13, 14]. The process of direct deposition can be achieved by various methods such as chemical vapour deposition (CVD) [10], electrophoretic deposition (EPD) [15], dip coating [7] and spray up methods [16]. CVD has the advantage of uniform deposition but several disadvantages are also associated with this method. CVD growth leads to damaged fiber surface due to high processing temperature [10]. Unlike CVD, EPD is a simple method for the deposition of nanomaterials and is not operated at high temperatures; however, the process requires functionalized nanomaterials and a closed setup for the deposition to take place [17]. Dip coating and spray layup are cost-effective and facile approaches for the deposition of nanomaterials [7, 16].

In this research work, the deposition of multiwalled carbon nanotubes (MWCNTs) on micrometre-sized carbon fibers has been achieved through dip coating and spray up processes. After deposition, the fibers were investigated under electron microscope to observe the quality of their deposition. The fibers coated from the process offering better MWCNT coating were used for the manufacturing of composites through vacuum bagging technique. Finally, the prepared composites were characterized for microstructural and interlaminar shear properties.

2 Experimental

2.1 Materials

High-strength PAN based 232 twill weave 3K carbon fabric was procured from CNME International, China (Figure 1a). MWCNTs of length 50–200 μm and diameter of ~ 60 nm with a purity level of $>95\%$ were procured from Chengdu Organic Chemicals, China (Figure 1b). Araldite® 5052 epoxy resin along with the curing agent was used as the matrix material.

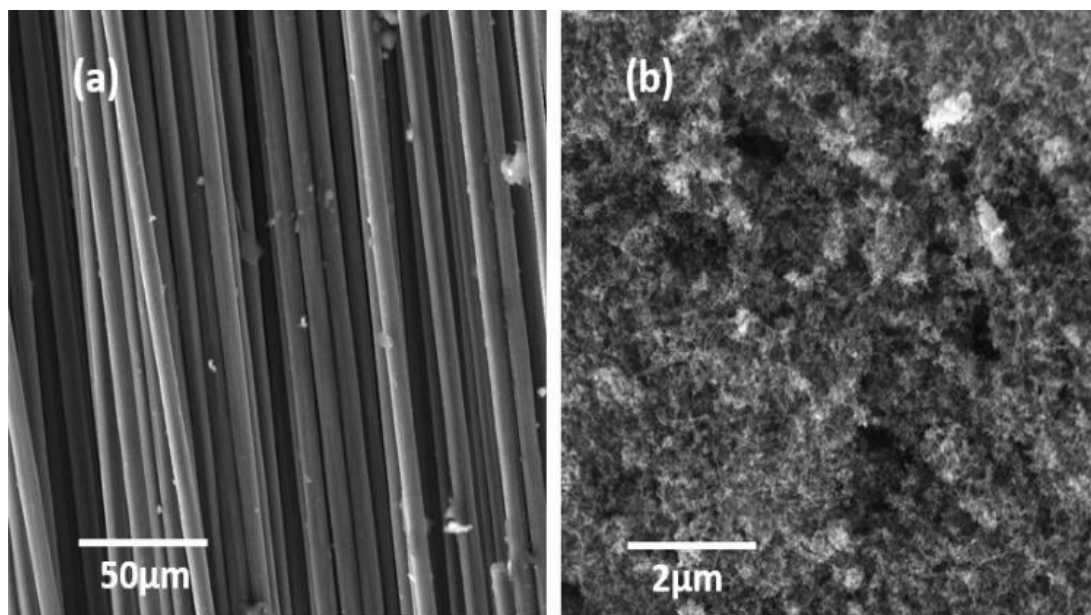


Figure 1: Materials used in the present study: (a) carbon fibers (b) MWCNTs

2.2 Manufacturing

2.2.1 Desizing of Carbon Fibers

Prior to coating of MWCNTs, the desizing of carbon fibers was performed. Fibers were washed with acetone. Later they were heated in an oven at 70°C for 15 min. Finally, the fibers were dried at room temperature. The aim of desizing was to remove polymeric sizing or any impurities present on surface of fibers so that MWCNTs could be coated on carbon fibers [18].

2.2.2 Functionalization of MWCNTs

Prior to deposition, MWCNTs were chemically functionalized with acid mixture of concentrated HNO₃ and H₂SO₄ in 3:1 ratio [19].

2.2.3 MWCNT Suspension

Before the two coating processes, equal quantity of functionalized MWCNTs was mixed in distilled water. After the addition, the mixture was sonicated for 2h in order to achieve uniform dispersion of MWCNTs (Figure 2).

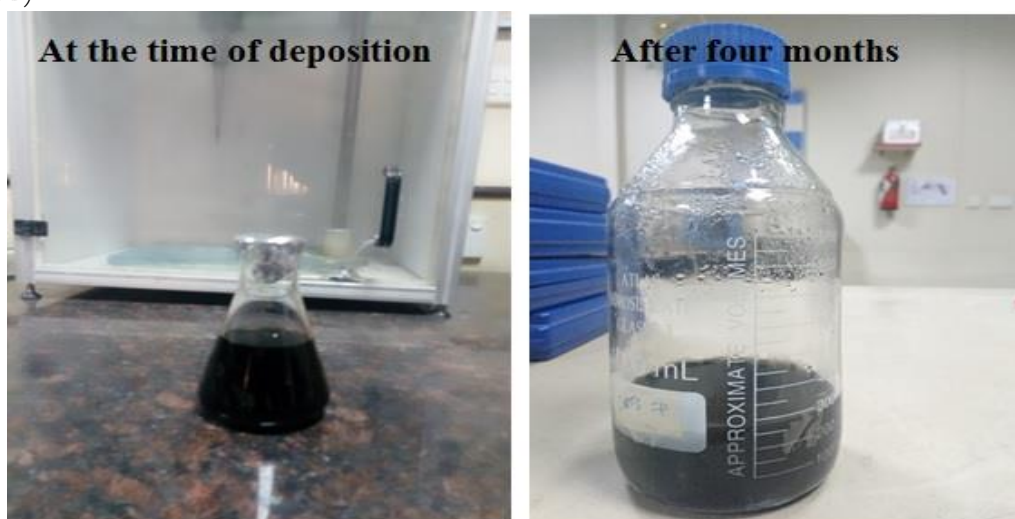


Figure 2: Photographs taken at the time of deposition and after four months showing the stability of MWCNTs suspension

2.2.4 Coating of MWCNTs on Carbon Fabric

Dip coating was the first technique used to deposit MWCNTs on carbon fibers. Twelve sheets of carbon fabric of similar size were dipped separately in glass containers containing functionalized MWCNT suspension for 12h. After coating, the fabric was dried in oven at 50°C for 30min (Figure 3).

In spray up process, MWCNTs were deposited on twelve sheets of carbon fabric through the operation of a manual spray gun. After spraying process, the fabric was dried in oven at 50°C for 30 min (Figure 3).

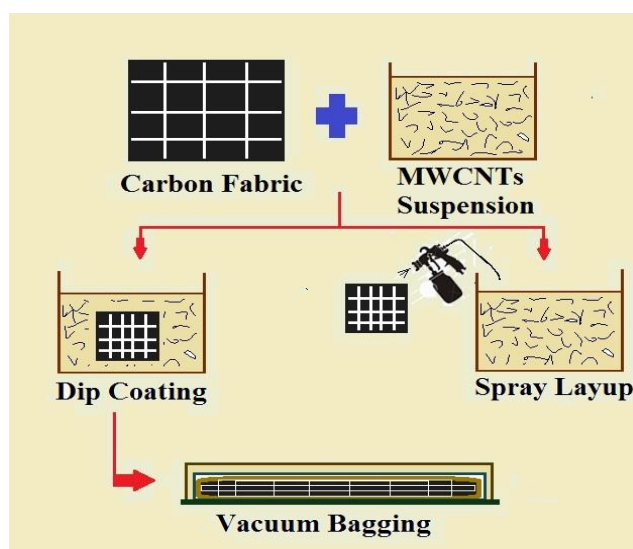


Figure 3: Schematic showing dip coating, spray up and vacuum bagging processes

2.3 Fabrication of Composites

After deposition of MWCNTs, carbon fibers were impregnated with epoxy resin using vacuum bagging technique. Twelve sheets of MWCNT-coated carbon fabric were stacked upon each other on an aluminium plate to prepare the setup for vacuum bagging process. An airtight nylon bag was placed over the setup and a vacuum pump was attached to generate a constant vacuum pressure. After the process, the composites were left for curing under vacuum for 24h. Finally, the cured composite were removed and cut into dimensions required for microstructural and mechanical property characterization.

2.4 Characterization

Optical micrographs of the composites were captured using an optical microscope (Metkon IMM 901, Metkon Instruments, Inc, Inc. Bursa Turkey) at magnifications up to 200x. Scanning electron microscopy (SEM) was performed on MWCNT-coated fabric and fractured surfaces of composite specimens. Field emission gun scanning electron microscope MIRA3 TESCAN was used in secondary electron imaging mode at an operating voltage of 5kV. To avoid charging during electron irradiation, the surface of the composite specimens was sputter-coated with carbon. To find interlaminar shear properties, short beam shear (SBS) testing was performed on specimens of dimensions 24x9x4mm in accordance with ASTM D-2344 on a universal testing machine (WDW-30, Jinan Testing Equipment IE Corporation, Jinan, China) at a crosshead speed of 1mm/min to obtain shear strength, modulus and fracture strain values. At least five specimens of multiscale and reference composites were tested to obtain average values of shear properties.

3 Results and Discussion

3.1 Microstructures

SEM was performed to witness the quality of coating of MWCNTs on carbon fibers by the two methods, as shown in Figure 4. MWCNT coating on carbon fibers after spray up process can be seen in Figure 4a and b, whereas Figure 4c and d are showing MWCNT-coated carbon fibers after dip coating. It can be observed that the spray up process led to non-uniform coating of MWCNTs along with the presence of their clusters; other carbonaceous impurities are also visible. On the other hand, a uniform coating of MWCNTs was obtained after dip coating process. Similar observation was reported in a different study where CNTs were grafted on glass fibers by dip coating [7]. After identification of the better deposition quality, twelve sheets of carbon fibers were coated with MWCNTs and later impregnated with epoxy resin to prepare multiscale composites by vacuum bagging technique. In addition, a reference composite without MWCNTs was also fabricated for comparison with multiscale composite.

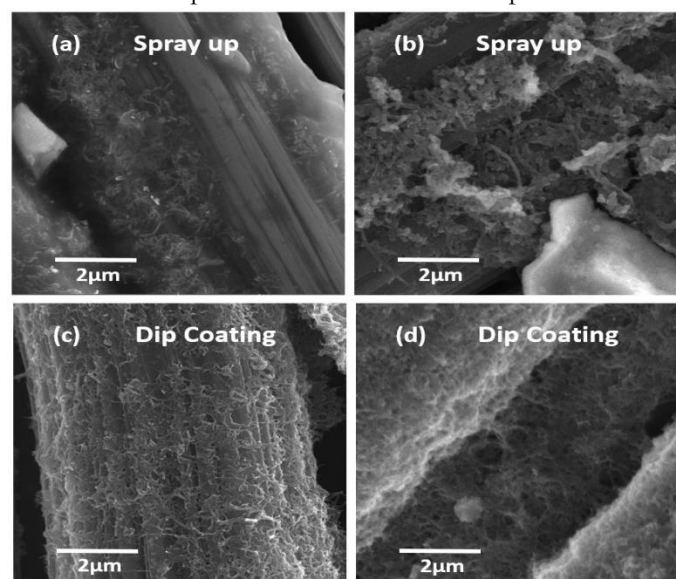


Figure 4: SEM images of MWCNT-coated carbon fibers by (a-b) spray up and (c-d) dip coating processes

Optical microscopy of the composites was performed to confirm the void free impregnation of carbon fibers with epoxy resin (Figure 5). While SEM of the composites confirmed the presence of MWCNTs in CFRP with pull out carbon fibers after fracture (Figure 6).

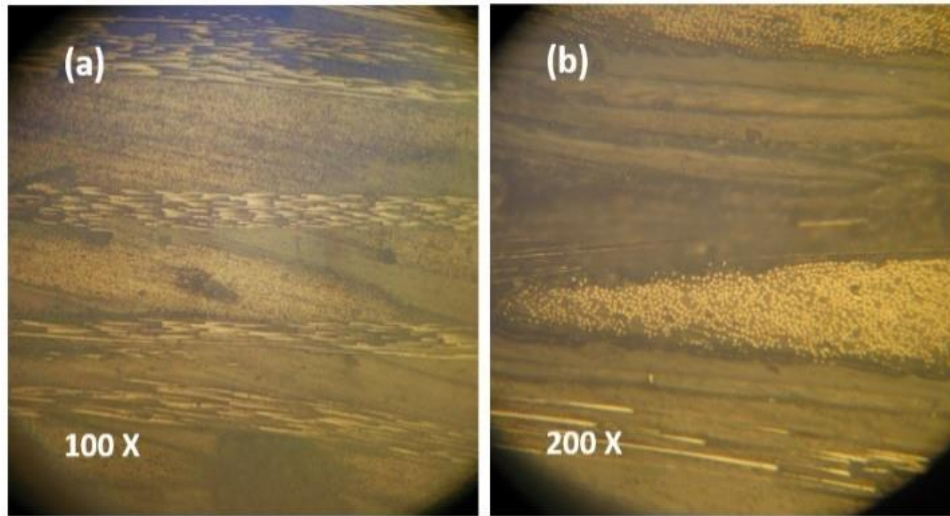


Figure 5: Optical micrographs of multiscale composite at two different magnifications showing the quality of impregnation of carbon fibers with epoxy

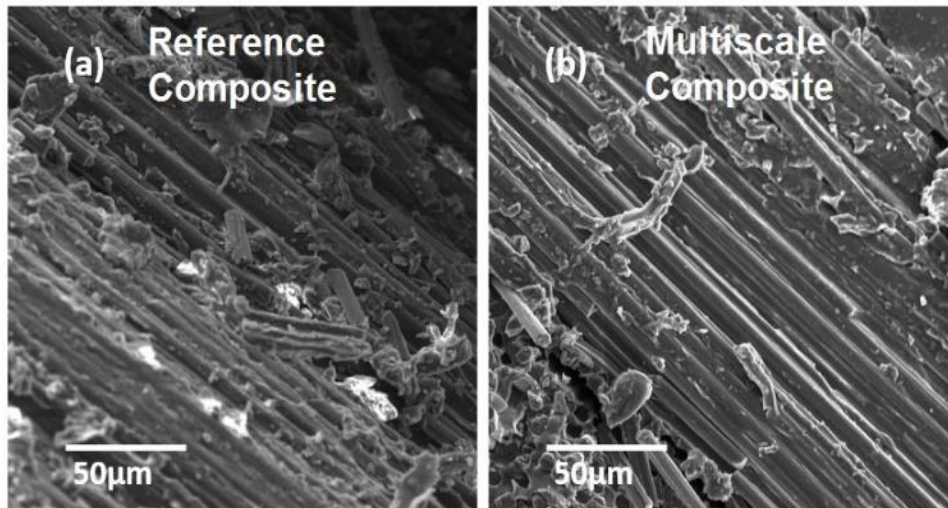


Figure 6: SEM images of (a) reference and (b) multiscale composites showing fracture morphology

3.2 Interlaminar Shear Properties

The interlaminar shear properties were determined to study the effect of MWCNT deposition on carbon fibers in multiscale composite. The determination of shear properties is based on Bernoulli-Euler beam theory. For a rectangular specimen, loaded cross-sectionally in a three-point bending, the maximum interlaminar shear stress occurs at the mid-thickness of the specimen between the center and end supports and is calculated as:

$$\tau = 0.75 \frac{L}{bt} \quad (1)$$

Where, L is load applied, b and t are width and thickness of the beam, respectively. In SBS, the load increases during bending until maximum load is reached. It is to be noted that if load drops by 30% or more just after the peak load, it is considered that sample is failed in shear loading and the maximum load is used to determine the shear strength [20].

The incorporation of MWCNTs increased interlaminar shear strength to $\sim 14\%$ from $33\pm 1\text{MPa}$ to $38\pm 2\text{MPa}$. Likewise the shear modulus was also increased from $2.2\pm 0.1\text{GPa}$ to $2.5\pm 0.2\text{GPa}$, showing an improvement of $\sim 12\%$. In addition, the deposition of MWCNTs on carbon fibers also improved fracture strain during shear loading from $2.0\pm 0.2\%$ for reference composite to $2.6\pm 0.2\%$ for multiscale composite (Figure 7). Similar results of improved interfacial properties were reported in a study, where glass fibers were coated by CNTs through dip coating method [7].

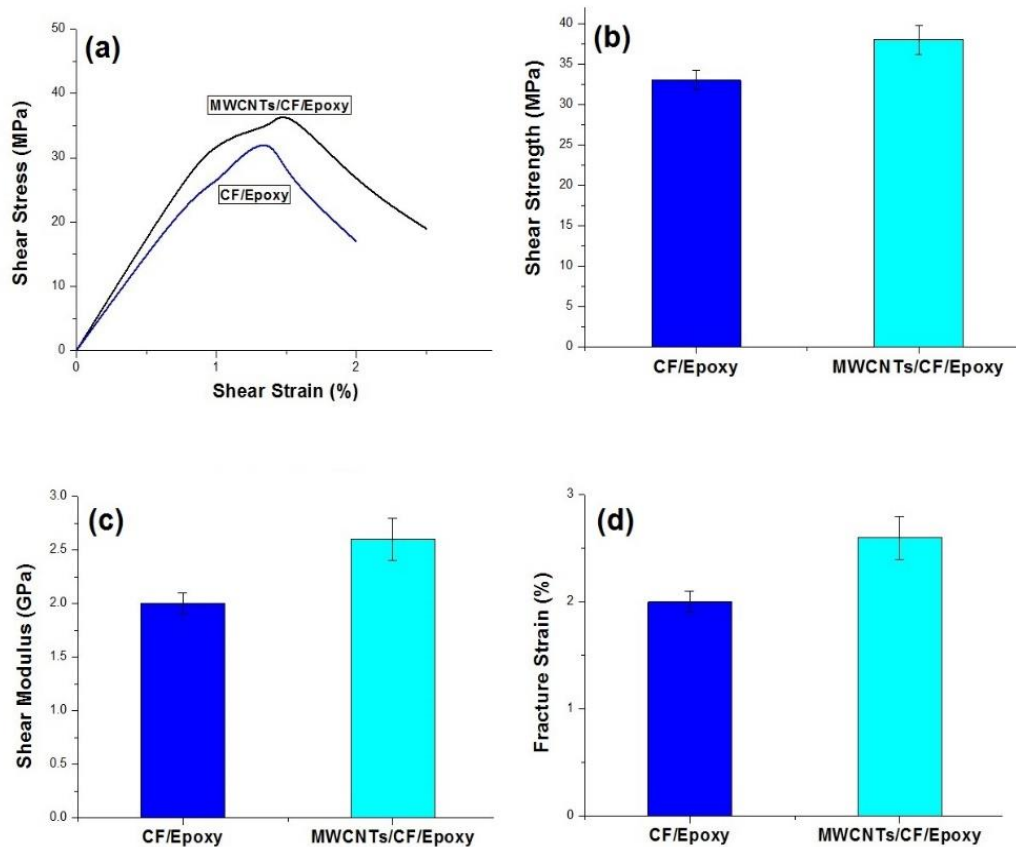


Figure 7: Interlaminar shear properties of reference and multiscale composites: (a) stress- strain curves, (b) shear strength, (c) shear modulus and (d) fracture strain during shear

3.3 Effect of Vacuum Bagging Process on Shear Properties

As stated earlier, the reference and multiscale composites were fabricated using the vacuum bagging method by infusing twelve layers of $10\times 10\text{cm}$ woven carbon fabric containing $3\text{wt}\%$ of MWCNTs in epoxy resin. It was found that adding MWCNTs to fibers increased the interlaminar shear properties of multiscale composites. As the vacuum bagging method does not generate shear flow in the thickness direction, MWCNTs were not preferentially aligned in any specific direction. By comparing the interlaminar shear properties of reference and multiscale composites, the effect of MWCNT orientation on the interlaminar shear properties can be studied. MWCNTs aligned in through-the-thickness direction would have greater impact on shear properties as compared to randomly oriented MWCNTs. In addition, other factors such as compaction and flow path may also affect the orientation and alignment of MWCNTs [20].

3.4 Influence of Deposited MWCNTs on Composite

The improvement in interlaminar shear properties of multiscale composite compared to reference composite are due to the emergence of some mechanisms, which ultimately explain the improvement in the overall performance of multiscale composite. The incorporation of MWCNTs on carbon fiber surface led to the bonding mechanisms that includes the presence of Van der Waals forces at interface due to

increased surface area, improved surface wettability of reinforcement with matrix, and mechanical interlocking at fiber/matrix interface; the localized stiffening and strengthening of matrix at fiber/matrix interface is another reason [21]. The carbon fibers are chemically inert; however, due to acetone desizing of carbon fibers, functional groups present on carbon fibers and MWCNTs may form chemical bonding. The Van der Waals forces, mechanical interlocking and improved wettability of fibers in composites play an important role in improving the interlaminar shear properties. These mechanisms will result in increased interfacial friction and restrict the movement at fiber/matrix interface. Figure 8a confirms the presence of MWCNTs at fiber surface and in matrix indicating Van der Waals binding due to increased fiber surface area. The roughness generated after MWCNT deposition is also visible in Figure 8a, which resulted in increased mechanical interlocking between fibers and matrix, thus providing a strengthening mechanism. Figures 8b and c confirm surface wettability; in general, epoxy resin has good wettability with carbon fibers, which was improved further by the addition of MWCNTs, which is a possible reason for improved interlaminar shear properties.

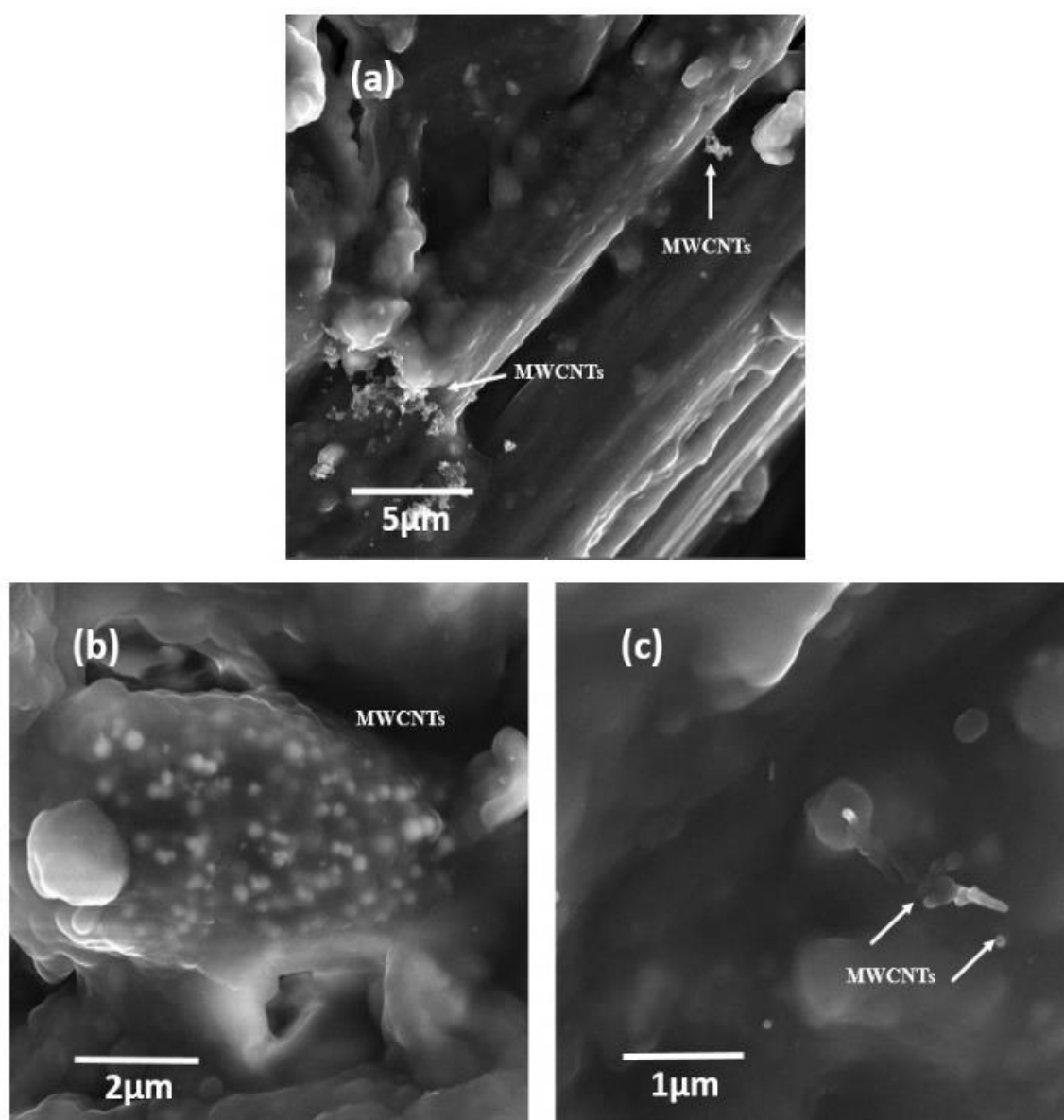


Figure 8: SEM images showing the presence of MWCNTs (a) on fibers and (b) in matrix indicating the (c) improved wettability of fibers with resin

4 Conclusions

Multiscale composites containing micrometre-scale carbon fibers and nanometre-scale carbon nanotubes in epoxy matrix were successfully prepared by vacuum bagging technique. Before incorporating carbon fibers in epoxy resin, these were coated with nanotubes to explore their effect on interlaminar shear properties. Two different coating techniques namely dip coating and spray up process were employed to coat nanotubes on carbon fibers. It was found that dip coating offered better coating of nanotubes while spray up process provided non-homogenous and thick nanotube coating on fibers, as witnessed under electron microscope. Dip coated carbon fibers were selected for subsequent incorporation in epoxy matrix to fabricate multiscale composites. It was observed that nanotubes were retained on carbon fibers after their impregnation with epoxy. The modification of carbon fiber/epoxy matrix interface due to the presence of nanotubes resulted in improved interlaminar shear properties. The interlaminar shear strength improved significantly up to 14%. The possible mechanisms influencing and enhancing the properties were identified as Van der Waals forces, mechanical interlocking of fibers and matrix due to nanotubes and increased wettability of fibers with polymer matrix. The prepared multiscale composites are potential candidates for aerospace structural materials possessing improved through-thickness strength in comparison to traditional carbon fiber reinforced polymeric matrix composites.

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References

- [1] Pathak, A.K., Borah, M., Gupta, A., Yokozeki, T., and Dhakate, S.R.: 'Improved mechanical properties of carbon fiber/graphene oxide-epoxy hybrid composites', *Compos. Sci. Technol.*, 2016, 135, pp. 28-38
- [2] Hughes, J.: 'The carbon fibre/epoxy interface—a review', *Compos. Sci. Technol.*, 1991, 41, (1), pp. 13-45
- [3] Subhani, T.: 'Silica and borosilicate glass matrix composites containing carbon nanotubes', Imperial College London, 2012
- [4] Kepple, K., Sanborn, G., Lacasse, P., Gruenberg, K., and Ready, W.: 'Improved fracture toughness of carbon fiber composite functionalized with multi walled carbon nanotubes', *Carbon*, 2008, 46, (15), pp. 2026-2033
- [5] Yao, X., Jiang, J., Xu, C., Zhou, L., Deng, C., and Wang, J.: 'Improved interfacial properties of carbon fiber/epoxy composites through graphene oxide-assisted deposition of carbon nanotubes on carbon fiber surface', *Fibers and Polymers*, 2017, 18, (7), pp. 1323-1329
- [6] Khurram, A.A., Khan, A., Gul, I.H., and Subhani, T.: 'Glass Fiber Epoxy Matrix Composites Containing Zero and Two Dimensional Carbonaceous Nanoreinforcements', *Polymer Composites*
- [7] Jamnani, B.D., Hosseini, S., Rahmadian, S., Rashid, S.A., and Balavandy, S.K.: 'Grafting carbon nanotubes on glass fiber by dip coating technique to enhance tensile and interfacial shear strength', *Journal of Nanomaterials*, 2015, 16, (1), pp. 306
- [8] Dai, Z., Shi, F., Zhang, B., Li, M., and Zhang, Z.: 'Effect of sizing on carbon fiber surface properties and fibers/epoxy interfacial adhesion', *Appl. Surf. Sci.*, 2011, 257, (15), pp. 6980-6985
- [9] Chun, B.-W., Davis, C.R., He, Q., and Gustafson, R.R.: 'Development of surface acidity during electrochemical treatment of pan-carbon fibers', *Carbon*, 1992, 30, (2), pp. 177-187
- [10] Kumar, M., and Ando, Y.: 'Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production', *Journal of nanoscience and nanotechnology*, 2010, 10, (6), pp. 3739-3758
- [11] Lee, J.U., Park, B., Kim, B.-S., Bae, D.-R., and Lee, W.: 'Electrophoretic deposition of aramid nanofibers on carbon fibers for highly enhanced interfacial adhesion at low content', *Composites Part A: Applied Science and Manufacturing*, 2016, 84, pp. 482-489
- [12] NI, A.B.: 'Carbon nanotube (CNT) reinforced glass and glass-ceramic matrix composites', *Ceramic Nanocomposites*, 2013, pp. 208
- [13] Subhani, T., Shaukat, B., Ali, N., and Khurram, A.A.: 'Toward improved mechanical performance of multiscale carbon fiber and carbon nanotube epoxy composites', *Polymer Composites*, 2015
- [14] Subhani, T., Latif, M., Ahmad, I., Rakha, S.A., Ali, N., and Khurram, A.A.: 'Mechanical performance of epoxy matrix hybrid nanocomposites containing carbon nanotubes and nanodiamonds', *Materials & Design*, 2015, 87, pp. 436-444
- [15] Cho, J., Konopka, K., Roźniatowski, K., García-Lecina, E., Shaffer, M.S., and Boccaccini, A.R.: 'Characterisation of carbon nanotube films deposited by electrophoretic deposition', *Carbon*, 2009, 47, (1), pp. 58-67
- [16] Davis, D.C., Wilkerson, J.W., Zhu, J., and Ayewah, D.O.: 'Improvements in mechanical properties of a carbon fiber epoxy composite using nanotube science and technology', *Compos. Struct.*, 2010, 92, (11), pp. 2653-2662

- [17] Boccaccini, A.R., Cho, J., Roether, J.A., Thomas, B.J., Minay, E.J., and Shaffer, M.S.: 'Electrophoretic deposition of carbon nanotubes', *Carbon*, 2006, 44, (15), pp. 3149-3160
- [18] Moaseri, E., Karimi, M., Maghrebi, M., and Baniadam, M.: 'Two-fold enhancement in tensile strength of carbon nanotube-carbon fiber hybrid epoxy composites through combination of electrophoretic deposition and alternating electric field', *International Journal of Solids and Structures*, 2014, 51, (3), pp. 774-785
- [19] Zhao, Z., Teng, K., Li, N., Li, X., Xu, Z., Chen, L., Niu, J., Fu, H., Zhao, L., and Liu, Y.: 'Mechanical, thermal and interfacial performances of carbon fiber reinforced composites flavored by carbon nanotube in matrix/interface', *Compos. Struct.*, 2017, 159, pp. 761-772
- [20] Fan, Z., Santare, M.H., and Advani, S.G.: 'Interlaminar shear strength of glass fiber reinforced epoxy composites enhanced with multi-walled carbon nanotubes', *Composites Part A: Applied Science and Manufacturing*, 2008, 39, (3), pp. 540-554
- [21] Li, M., Gu, Y., Liu, Y., Li, Y., and Zhang, Z.: 'Interfacial improvement of carbon fiber/epoxy composites using a simple process for depositing commercially functionalized carbon nanotubes on the fibers', *Carbon*, 2013, 52, pp. 109-121.

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