

Incorporation of Carbon Nanotubes on Strategically De-Sized Carbon Fibers for Enhanced Interlaminar Shear Strength of Epoxy Matrix Composites

¹Muhammad Abdul Basit*, ¹Sybt-e-anwar Qais, ¹Muhammad Saffee Ullah Malik and ^{1,2}Ghufran Ur Rehman, ¹Faizan Siddique Awan, ¹Laraib Alam Khan and ¹Tayyab Subhani**

¹Department of Materials Science and Engineering, Institute of Space Technology, Islamabad 44000, Pakistan.

²School of Chemical Engineering and Analytical Science, University of Manchester, United Kingdom.
ab_saim@hotmail.com*; drtayabsubhani@ist.edu.pk**

(Received on 20th March 2018, accepted in revised form 20th December 2018)

Summary: Carbon fiber reinforced polymeric matrix composites are enormously used in aerospace and automotive industries due to their enhanced specific properties. However, the area of interlaminar shear properties still needs investigation so as to produce composites with improved through-the-thickness properties. To improve interlaminar shear properties of these composites, acid-functionalized multiwalled carbon nanotubes were deposited on de-sized carbon fibers through electrophoretic deposition. De-sizing of carbon fabric was performed through three different methods: furnace heating, acidic treatment and chloroform usage. As the acid-treatment provided better results than other two techniques, the acid-de-sized carbon fibers were coated with nanotubes and subsequently incorporated in epoxy matrix to prepare a novel class of multiscale composites using vacuum assisted resin transfer molding technique. Nearly 30% rise in the interlaminar shear strength of the composites was obtained which was credited to the coating of nanotubes on the surface of carbon fibers. The increased adhesion between carbon fibers and epoxy matrix due to mechanical interlocking of nanotubes was found to be the possible reason of improved interlaminar shear properties.

Keywords: Carbon fibers, Multiwalled carbon nanotubes, Electrophoretic deposition, Shear strength, De-sizing, Composites.

Introduction

Carbon fiber reinforced epoxy matrix (CF/EP) composites have been widely used as reinforcing material in polymer matrix composites (PMCs). These composites are preferred for various structural applications in engineering fields including aerospace, aviation and automobile industries because of their inspiring mechanical properties such as high strength, stiffness and low density [1]. The performance of CF/EP composites is largely dependent on the properties of the fiber/matrix interface [2, 3]. Indeed, the good interfacial properties are critical to ensure optimal load transfer on fiber through the matrix which helps to improve ultimate mechanical performance of the composite. One of the major failure modes in CF/EP composites is the delamination of fibrous lamina [4, 5]. The delamination may result due to poor interlaminar shear strength (ILSS) of composites, which ultimately causes due to weak interfacial strength. In CF/EP composites, ILSS may be enhanced by improving the interfacial adhesion between the fibers and the matrix [6, 7].

The important designing criteria like strength, weight and stiffness depend on the stress transfer mechanism exhibited by the composite, which in turn relies on the interactions at the interface between fibers and resin [8]. In case of CF/EP composites, one of the reasons of composite delamination is the presence of a

weaker adhesion between carbon fibers and epoxy which sometimes result in the reduction of strength and properties of composites leading to failures. Not only the properties of individual laminates affect ILSS but the orientation of these lamina also play a vital role [9, 10].

A range of techniques are used to enhance ILSS of epoxy matrix composites, i.e. plasma treatment [10], ammonia treatment [11], oxidation [12], anodization [13], acrylic acid treatment [14], ozone treatment [15], chemical grafting [16] and chemical vapour deposition of carbon structures like carbon nanotubes (CNTs), graphene nanoplatelets (GNPs), Graphene etc. [17]. One such method is the addition or coating of MWCNTs on the surface of CFs to increase the adhesion between CFs using the electrophoretic deposition (EPD) technique [18]. The addition of multiwalled carbon nanotubes (MWCNTs) improves mechanical interlocking, by improving the interfacial adhesion. However, commercially available CFs are coated with polymeric materials called sizing. This sizing makes the CFs inert and chemically stable towards reactions, also it helps in better adhesion between fibers and resin because sizing layer also being a polymeric coating, adheres to epoxy firmly compared to pristine carbon fibers. [18]. Disadvantageously, MWCNTs do not attach to such CFs unless a suitable

*To whom all correspondence should be addressed.

treatment is performed to de-size fibers. Different methods of de-sizing of CFs have been reported in literature depending upon the application.

In this work, we employed EPD technique to deposit functionalized MWCNTs on de-sized CFs so that the attachment of MWCNTs with CFs could increase the mechanical adhesion of MWCNT-coated carbon fibers with epoxy resin. It is worth-mentioning that the EPD set-up was designed and assembled in the workshop to carry out this research work. Through extensive scanning electron microscopic investigation of CFs de-sized by three techniques, we selected acid de-sized CFs to produce 6-ply and 8-ply CF/EP composites after the coating of MWCNTs through EPD. For reference, composites without the coating of MWCNTs were also prepared. Resultantly, the ILSS of composites increased by 30% which was affirmed and correspondingly elucidated using mechanical testing and effectual material characterization tools including fourier transformed infrared spectroscopy (FTIR), raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively.

Experimental

Materials

Polyacrylonitrile (PAN) based high strength 3K CFs with 232 twill weaves were obtained from CNME International, China. MWCNTs were obtained from Chengdu Organic Chemicals, China. The length of these MWCNTs was in the range of 60-200 μm and diameter ranged from 55-60 nm with a purity level

greater than 95% Epoxy resin used for the experiments was Araldite® 5052 purchased from Huntsman Advanced Materials, United States of America, with the curing agent having combined density of $2.25\text{g}/\text{cm}^3$.

Functionalization of MWCNTs

The functionalization of MWCNTs is necessary because the pristine MWCNTs showed lack of dispersion in the distilled water which was used as an electrolyte for the electrophoretic deposition. The functionalization was done using a mixture of sulphuric and nitric acids in 3:1 ratio [19]. As schemed in Fig. S1, 1g MWCNTs were added to 40ml acid mixture of Sulphuric acid and nitric acid in 3:1 ratio respectively and the process was carried out for 4h with constant stirring with 450-480 r/min at 90°C . The combination of these acids was used to introduce carboxylic acid functional groups on the surface of MWCNTs that would increase their suspension stability [19,20]. MWCNTs were filtered from the acid mixture after 4h followed by washing with distilled water till the pH was neutralized. Washed MWCNTs were filtered using centrifuge set to 1500 r/min and filtration assembly as shown in S1. MWCNTs were dried in oven at 110°C for 4h and then the dried MWCNTs were stored in acetone. Fig 2 shows the SEM images of pristine MWCNTs and CFs, TEM image and Raman spectroscopy of MWCNTs. These functionalized MWCNTs were characterized with FTIR to affirm the attachment of functional groups on their surface as represented in Fig 3.

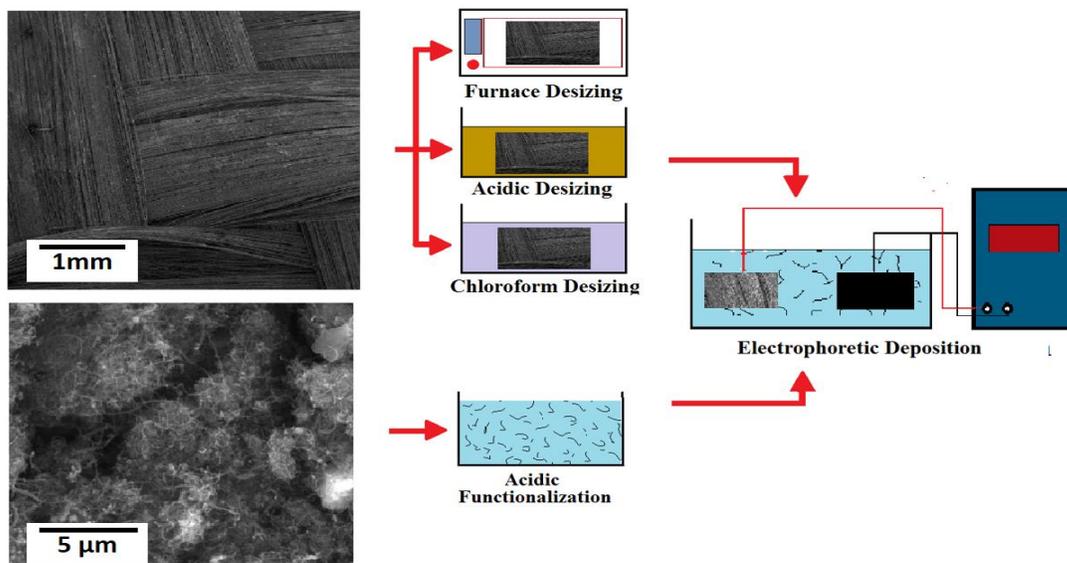


Fig. 1: Schematic illustration of different de-sizing methods and electrophoretic deposition process.

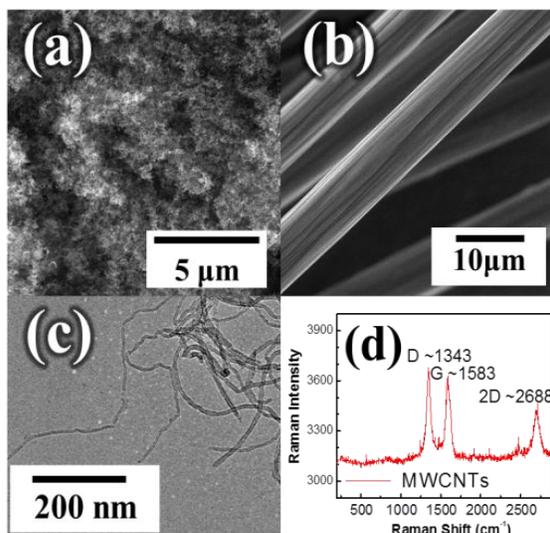


Fig. 2: Scanning electron microscope images of pristine (a) MWCNTs and (b) CFs. (c) Transmission electron microscopy image and (d) Raman spectroscopy of MWCNTs.

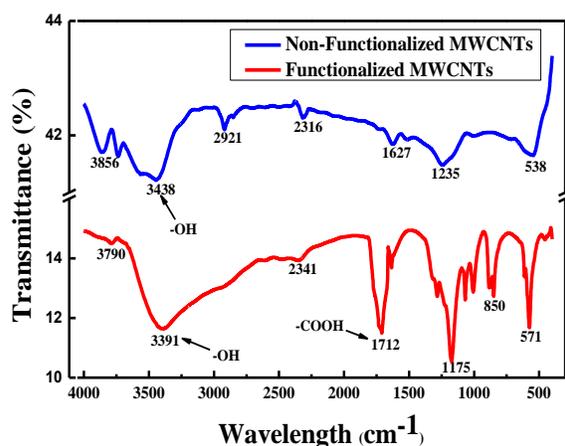


Fig. 3: FTIR spectra for non-functionalized (blue line) and functionalized (red line) MWCNTs.

De-sizing of CFs

The sizing of CFs is usually done to protect them from wear and tear during the manufacturing, transporting and storing [21]. In this study, CFs are de-sized using three common methods: furnace de-sizing, acid de-sizing and chloroform de-sizing (Fig. 1). The acid treatment of CFs was achieved by placing the carbon fabric in nitric acid at a constant temperature of 90°C for 4h [22, 23]. This process is also known as the chemical etching of the CFs.

Afterwards, CFs were removed and washed with distilled water and lastly dried in oven at 50°C.

The chloroform treatment was done by putting the carbon fibers in boiling chloroform at 61°C for 7min. After the treatment, the fibers were washed thoroughly with distilled water and then dried in oven for 2h at 110°C.

Furnace desizing of CFs was done by putting the CF sheets directly in oven for 2h at 400°C. The furnace heating of carbon fibers seemed to remove the sizing layer but some ash and residue appeared on the carbon fibers which were washed off and then the fibers were dried again in the oven at 50°C for 2hrs. The dried and de-sized carbon fibers were analyzed using SEM, as shown in Fig 4. The micrographs obtained from SEM were used to study the effect of each treatment on the sizing layer and carbon fibers.

Deposition of MWCNTs on CFs

Prior to EPD, a suspension of MWCNTs was prepared by adding functionalized MWCNTs in distilled water. The functionalized MWCNTs actually show a uniform stable dispersion in distilled water for longer time periods without forming agglomerates and settling down. Ultra-sonication was done using ultrasonicator model UP400S (Hielscher Ultrasound Technology, USA) for 4h to uniformly disperse the MWCNTs while keeping the cycle value to 0.5 and at an amplitude of 80%. This suspension acts as electrolyte for the electrophoretic deposition. After formation of a suspension, lab-scale EPD setup was designed and assembled. It consisted of an electrolytic tank with the electrodes mounted on a specially designed assembly to maintain a constant distance between them and the CF layers. The cathode is made of stainless steel plate while the carbon fabric is used as anode and both are placed at a distance of 2.5cm. EPD was done using functionalized MWCNTs while keeping an optimum distance between the electrodes in the EPD setup. [24]. During the deposition process, the bubbling out of gases (most probably carbon dioxide) from the tank was observed [25]. After the deposition, the layers were dried in oven at 60°C for 2h to remove moisture content.

Fabrication of Composites

Vacuum assisted resin transfer molding (VARTM) (Fig S2) was used to fabricate PMCs. The reference composites without MWCNTs were also fabricated having six and eight sheets of CFs for

comparison with composites containing deposited MWCNTs. The composites were left for curing for 24h after impregnation with epoxy under 0.8 bar vacuum pressure.

Characterizations

FTIR using Excalibur series FTIR spectrometer, (FTSW 300MX, BIO-RAD, USA) was performed to confirm the attachment and nature of functional groups introduced on the MWCNTs in the wave range of 4000-400 cm^{-1} . Extensive scanning electron microscopy (MIRA3, TESCAN, France) was used to observe the morphological details of MWCNTs, de-sized CFs and the fractured surfaces of the composites. Along with SEM, TEM (JEOL) was also performed to observe ILSS tests were carried out using load frame (INSTRON-5589, USA) while using the ASTM-D2344-84 standard for testing. A minimum of five specimens were used of each composite to obtain the average values of the shear properties.

Results and Discussion

Fig. 2 shows the SEM micrographs of pristine MWCNTs and CFs used in this research work. A Morphological image obtained using SEM (Fig. 2a) shows the entanglement of MWCNTs. To have better depiction of MWCNTs, TEM (Fig. 2c) is performed which reaffirmed the entanglement and further revealed that MWCNTs have nearly a diameter of 55-60 nm. Fig. 2b shows a SEM image of pristine CFs revealing the uniformity in diameters and relative smoothness due to wet spinning process used during their manufacturing as PAN-based CFs. In addition, the Raman spectra was obtained to reveal the pureness of MWCNTs (Fig. 2d), reflecting the D, G and 2D peak positions at nearly 1342 cm^{-1} , 1583 cm^{-1} and 2688 cm^{-1} .

Later, mixture of sulphuric and nitric acids ($\text{H}_2\text{SO}_4:\text{HNO}_3$) in 3:1 molar ratio is used to functionalize MWCNTs. The functionalization yields the attachment of functional groups on the surface of MWCNTs, which resulted in uniform dispersion of MWCNTs in distilled water [19]. Fig. 3 shows FTIR spectra of non-functionalized MWCNTs in comparison with functionalized MWCNTs. The peak at 3438 cm^{-1} depicts the presence of carbon-oxygen (C-O) bonds and the presence of hydrogen-oxygen (O-H) bonds. The carbon-oxygen (C-O) bonds could be due to single or double bonds. The single bonds

indicates the presence of hydroxyl (OH) groups attached on the surface of MWCNTs while the double bond reflects the presence of carboxylic (COOH) groups. A broad peak in the range of 3000-3600 cm^{-1} observed for functionalized MWCNTs show the same effect as shown by peak 3438 cm^{-1} for functionalized MWCNTs. In addition to the wide range peak for functionalized MWCNTs, a sharp peak was also seen at 1712 cm^{-1} which confirms the presence of double bonds between carbon and oxygen (C=O). It confirms the attachment of carboxylic (COOH) groups on MWCNTs while wide range peak reflects the presence of OH group. The presence of peak at 3438 cm^{-1} in blue curve suggests that a part of MWCNTs is oxidized due to moisture and thus hydroxyl groups were present on the surface of pristine MWCNTs [14]. It is worth mentioning that the presence of considerable amount of oxygen based functional groups indicates and plays an affirmative role by improving the interaction between CFs and epoxy matrix during subsequent stage of developing the composite.

Alongside the functionalization of MWCNTs, CFs are de-sized using furnace heating, chloroform treatment and acid treatment. In addition to the removal of sizing, such treatments of fibers create active sites for MWCNTs to attach and adhere with substrate. The resultant morphological effect is observed using SEM (Fig. 4). Pristine CFs have been compared with desized CFs as shown in Fig 4(a-d). Different desizing techniques revealed different results. Major change is observed in the furnace treated carbon fibers compared to other two techniques. Although the sizing layer seems to be removed by the three treatments but the acid-treatment of CFs proved much easier, convenient and effectual owing to its simplicity and quick accomplishment. It was also found that the morphology as well as diameter of CFs was relatively less altered because of acid de-sizing compared to the other two techniques. Further EPD of MWCNTs was carried out on acid de-sized CFs because it gave better results compared to other techniques and was relatively easier than other two methods. Resultant effect on the morphology of CFs caused by the removal of sizing layer is summarized in Fig. S4 which indicated that the diameter of CFs was reduced ominously after furnace de-sizing (Fig. 5b) while the least for acid de-sizing (Fig. 5d), which avowed that acid de-sizing is an appropriate technique to be employed for subsequent composite processing.

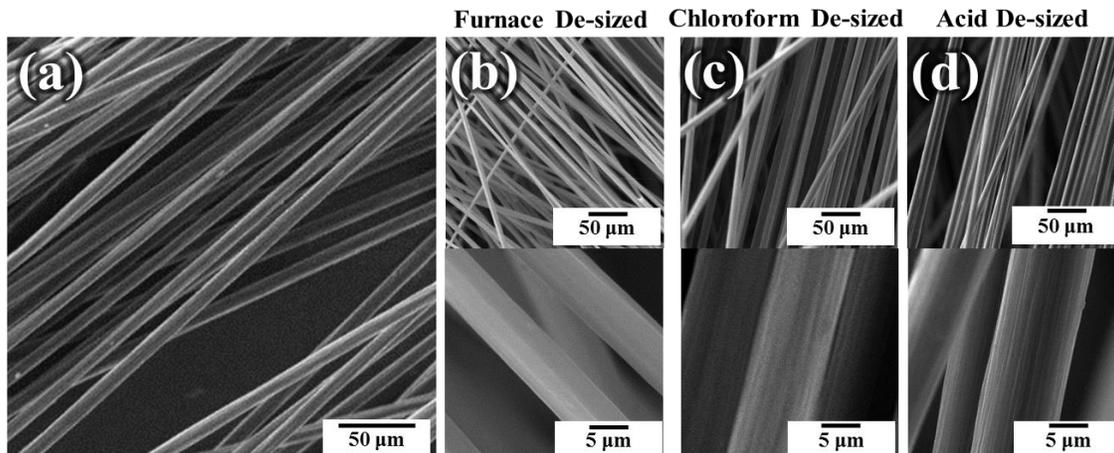


Fig. 4: Scanning electron microscopy images of (a) pristine CFs, (b) furnace de-sized CFs, (c) chloroform de-sized CFs and (d) acid de-sized CFs.

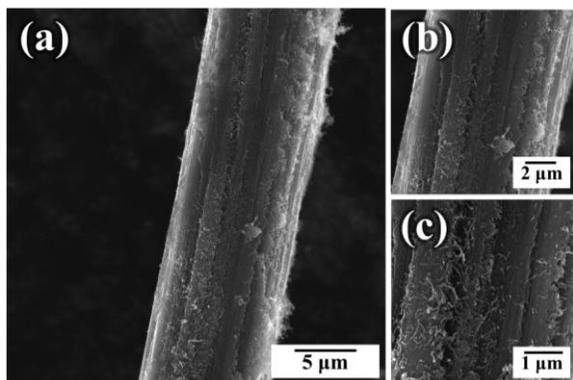


Fig. 5: (a-c) Scanning electron microscopy images of fibers showing successful deposition of MWCNTs at different magnifications

Fig. 5 reveals successful deposition of MWCNTs on CFs using EPD. Strongly and uniformly adhered MWCNTs on CFs having entangled appearance is in similarity with previous reports [23,27,28]. The MWCNT-deposited fibers were impregnated with epoxy to fabricate CF/EP composites. Finally the CF/EP composites were mechanically tested using interlaminar shear strength load frame and samples were made according to ASTM D2344-84 standard [29]. ILSS was determined using the following mathematical relation;

$$ILSS = 0.75 \left(\frac{P}{wh} \right)$$

where, P , w and h denote maximum applied load, width and thickness of the prepared samples with dimensions 24x9x4 mm respectively. The w and h

values were kept the same for all samples and thereafter a series of mechanical tests were performed to determine the average ILSS of CF/EP composites without MWCNTs, which acted as a reference sample for comparison. It was found that the reference composite made of eight and six layers of carbon fabric have average shear strength values of 30.7 ± 0.85 and 28.3 ± 1.84 MPa, respectively (Fig. 6a). It is well known for such composites that the strength increases with the number of ply layers. [31]. Therefore 8-ply composites of CF/EP exhibited considerably superior shear strength values than 6-ply composites in all three samples. However, when the effect of de-sizing was investigated over CF/EP composites with MWCNTs, it was found that the furnace de-sized CFs resulted even poor performance than sized CFs which is attributed the detrimentally decreased thickness of CFs as revealed by scanning electron microscopy images earlier, whereas the acid de-sized CFs appeared with best performance ensuing ~ 40 MPa ILSS value. Seeing the better ILSS value for 8-ply composite and for acid de-sized CFs, it is chosen as standard for further comparative studies to reveal the effect of time and voltage for EPD of MWCNTs on CFs against shear strength of CF/EP composites, shown in Fig. 7. It can be deduced (Fig. 7 a, b) that the time for EPD of MWCNTs played significant role at higher voltage (10V) to increase the shear strength value of standard composite from 30.7 ± 0.85 to 39.9 ± 0.80 MPa. Likewise, if the time for EPD of MWCNTs is kept shorter (5min), higher voltage is to be applied to obtain an equivalent increase (Fig. 7 c, d) in shear strength values of composites. These results affirmed that the incorporation of MWCNTs on acid de-sized CFs using EPD produces a significant increase of

~30% (from 30.7±0.85 to 39.9±0.85MPa) in the shear strength of CF/EP composites. Although the time and voltage can be further increased but higher voltage may lead to a decrease in the interlaminar shear strength according to earlier reports [32] as well as cost-effectiveness of the technique.

The study of fractured surfaces of such composites gives no clear reason for the increase of the shear strength [31]. Therefore, using SEM it was shown that epoxy was completely adhered to CFs containing deposited MWCNTs. Optimal load transfer on the carbon fibers is necessary and the failing of fibers before the failure of matrix yields good properties of the composites (Fig. 8). The strong adhesion of carbon fibers with the matrix from all sides (Fig. 8) helps in the load transfer mechanism. Therefore, it is inferred that the effectual attachment of MWCNTs on acid de-sized CFs increased the adhesion of resin and CFs which consequently increased the shear strength value [33]. The effectuality of incorporation of MWCNTs on CFs is schemed in Fig. 9. In the absence of MWCNTs, the CFs inside epoxy matrix are believed to have less interfacial adhesion. This is because presence of MWCNTs offers oxygen functional groups which increase interactions within epoxy matrix. In addition, MWCNTs facilitate the mechanical interlocking inside the composite (depicted by the area encircled in red). Our inference is equally endorsed from the fractured surfaces of composites (Fig. 10a) with optimal shear strength of 39.9MPa. It is shown that the load was transferred to de-sized CFs successfully due to the presence of MWCNTs as the fracture mode can be identified as fiber fracturing and bridging [34]. CF pullout depicts the toughening mechanism and the origin of increase of shear strength of composites (Fig. 10b).

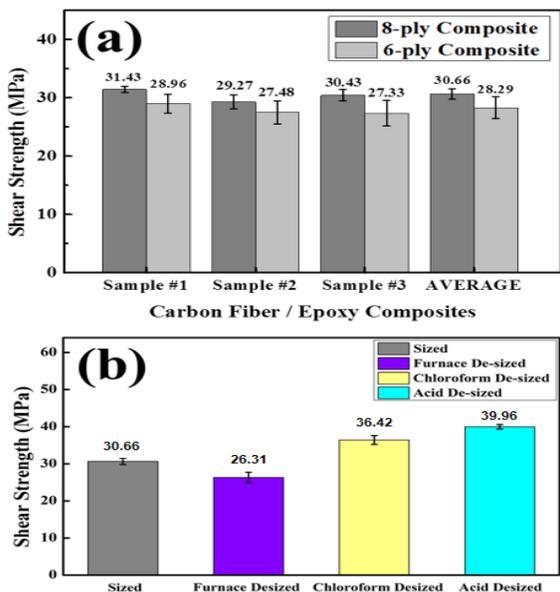


Fig. 6: Interlaminar shear strength (ILSS) of (a) CF/EP composites without MWCNTs comparison of 8-ply and 6-ply composites and (b) comparison of 8-ply composites with MWCNTs over differently de-sized CFs.

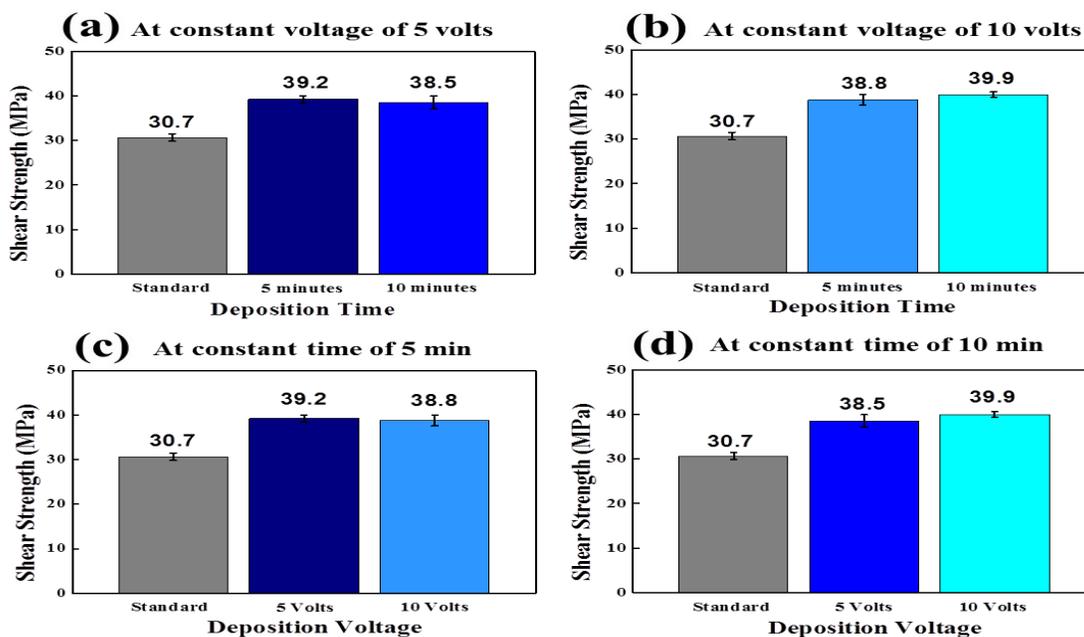


Fig. 7: Interlaminar shear strength of 8-ply CF/EP composites as a function of (a,b) time and (c,d) voltage for EPD of MWCNTs.

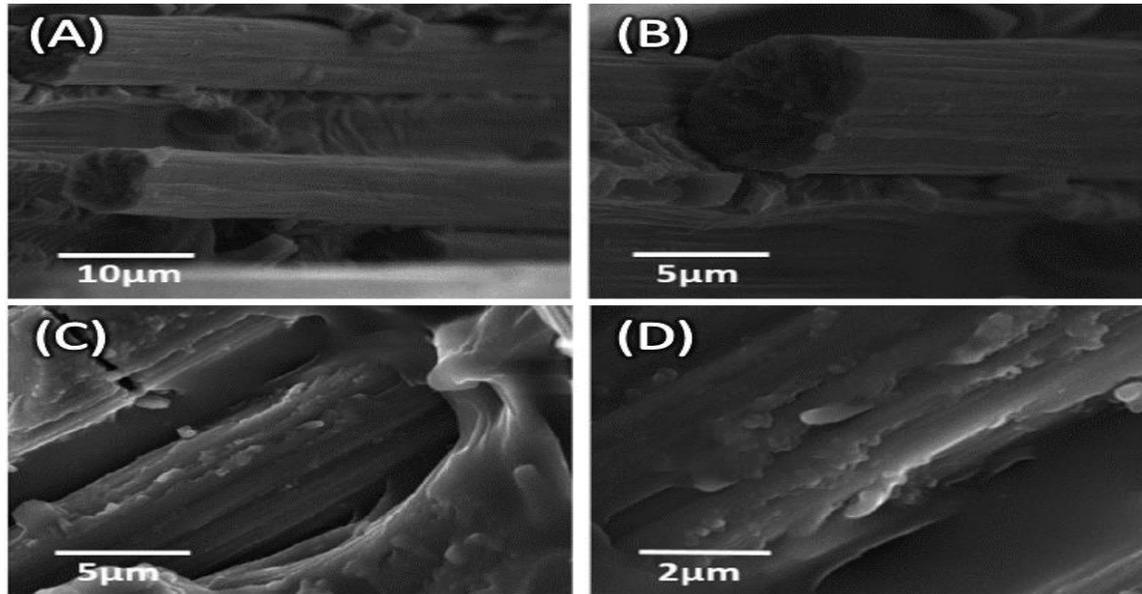


Fig. 8: (a-b) SEM images of CF/EP composites without MWCNTs showing lack of epoxy adhesion to CF surface, (c-d) CF/EP/MWCNTs composite showing good impregnation of CFs with epoxy resin due to presence of MWCNTs.

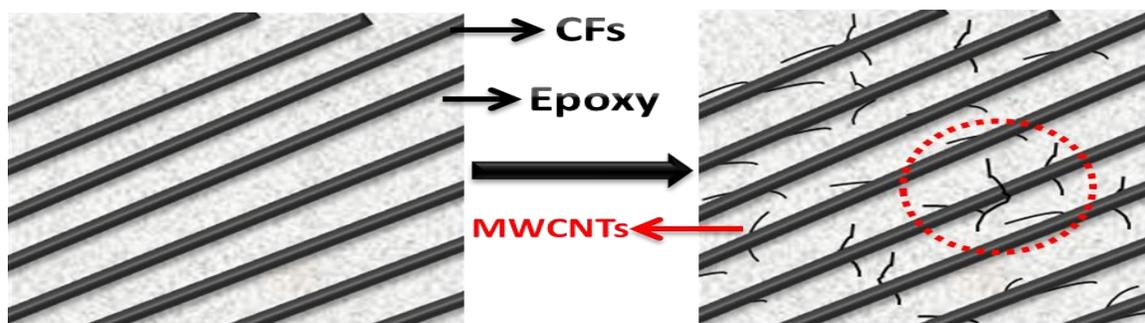


Fig. 9: Schematic illustration of effectuality of incorporating MWCNTs on de-sized CFs. The area encircled in red depicts the attachment of MWCNTs to the surface of CFs causing interlocking inside the epoxy matrix.

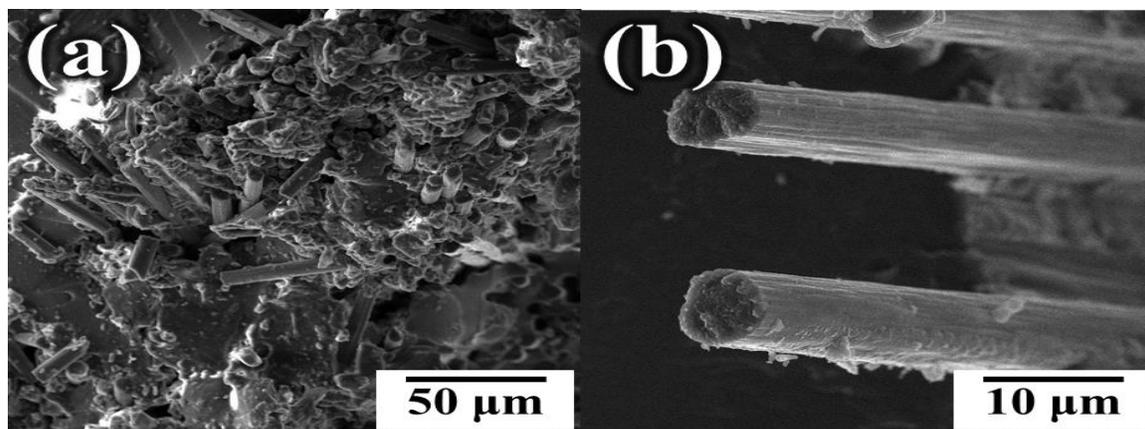


Fig. 10: (a-b) SEM images of fractured surfaces of CF/EP composites having EPD of MWCNTs.

Conclusions

We demonstrated the effectual conjunction of functionalized MWCNTs and acid de-sized CFs to enhance the ILSS of CF/epoxy composites. Among differently de-sized CFs, acid de-sized CFs exhibited minor morphological and dimensional deterioration and thus were successfully employed for electrophoretic deposition of MWCNTs prior to the development of CF/EP composite. EPD of MWCNTs on CFs increased mechanical interlocking between CFs and epoxy based matrix which results a maximum increase of 30% of the interlaminar shear strength of CF/EP composites. The results for CF/Epoxy composite without any MWCNTs reinforcement were almost 30.7 MPa whereas the composite with MWCNTs attached to CFs through EPD technique yielded a better ILSS result of 39.96 MPa. However, the parameters of EPD showed an anomalous behavior at 5 volt where the total strength of composite should have been higher for 10 mins EPD process time compared to 5 mins. Further research in the optimization and comparison of different parameters of EPD is necessary to improve the yield and results of the process. In addition to this, other methods of desizing of CFs must also be studied and compared to find an optimized and better approach.

References

1. M. Mrazova, Advanced Composite Materials of the Future in Aerospace Industry, *Incas Bulletin*, **5**, 139 (2013).
2. W. D. Callister, *Materials Science and Engineering. An Introduction*, John Wiley & Sons, 7th edition, 577-620 (2006).
3. L. T. Drzal,, *Interfaces and Interphases, Composites*, ASM International, **21**, 169-179 (2001).
4. L. Durão, J. Tavares, V. de Albuquerque, J. Marques and O. Andrade, Drilling Damage in Composite Material, *Materials*, **7**, 3802-3819 (2014).
5. A. G. M. António T. Marques and Luís M. Durão, Delamination Analysis of Carbon Fibre Reinforced Laminates, *16th International Conference on Composite Materials*, 1-10 (2007).
6. K. Li, L. Li, H. Li, Q. Song, J. Lu and Q. Fu, Electrophoretic deposition of carbon nanotubes onto carbon fiber felt for production of carbon/carbon composites with improved mechanical and thermal properties, *Vacuum*, **104**, 105-110 (2014).
7. Q. An, A. N. Rider and E. T. Thostenson, Electrophoretic deposition of carbon nanotubes onto carbon-fiber fabric for production of carbon/epoxy composites with improved mechanical properties, *Carbon*, **50**, 4130-4143 (2012).
8. C. Galotis, Continuous and discontinuous fibre model Composites By Laser Raman Spectroscopy, *Composites Science and Technology*, **48**, 15-28 (1993).
9. V. N. Murthy and C. B. N. Murthy, Mechanical & Thermal Properties of Carbon Fiber / Epoxy Composites with Different Fiber Orientation, *International Journal & Magazine of Engineering, Technology, Management and Research*, **2**, 1394-1403 (2015).
10. M. Sharma, S. Gao, E. Mader, H. Sharma, L. Y. Wei and J. Bijwe, Carbon fiber surfaces and composite interphases, *Compos. Sci. Technol.*, **102**, 35-50 (2014).
11. H. C. Wen K. Yang, K. K. Ou, W. F. Wu, C. P. Chou, R. C. Luo and Y. M. Chang, Effects of ammonia plasma treatment on the surface characteristics of carbon fibers, *Surf. Coatings Technol.*, **200**, 3166-3169 (2006).
12. J. Jian, C. Xu, Y. Su, Q. Gao, F. Liu, C. Deng, X. Yao and L. Zhou, Influence of Carbon Nanotube Coatings on Carbon Fiber by Ultrasonically Assisted Electrophoretic Deposition on Its Composite Interfacial Property, *Polymers*, **8**, 302-312 (2016).
13. S. J. P. S. J. Park and W. B. Park, XPS Analysis of Carbon Fiber Surfaces-Anodized and Interfacial Effects in Fiber-Epoxy Composites, *Journal of Colloid and Interface Sciences*, **215**, 167-169 (1999).
14. Z. Xu, L. Chen, Y. Huang, J. Li, X. Wu, X. Li and Y. Jiao, Wettability of carbon fibers modified by acrylic acid and interface properties of carbon fiber/epoxy, *European Polymer Journal*, **44**, 494-503 (2008).
15. H. J. Fu, Y. D. Huang and L. Liu, Influence of fibre surface oxidation treatment on mechanical interfacial properties of carbon fibre/polyarylacetylene composites, *Materials Science and Technology*, **20**, 1655 (2004).
16. H. Qian, A. Bismarck, E. S. Greenhalgh, G. Kalinka, and M. S. P. Shaffer, Hierarchical Composites Reinforced with Carbon Nanotube Grafted Fibers: The Potential Assessed at the Single Fiber Level, *Chemistry of Materials*, **20**, 1862-1869 (2008).
17. M. Kumar and Y. Ando, Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production, *Journal of Nanoscience and Nanotechnology*,

- 10, p. 3739-3758 (2010).
18. W. D. Bascom and L. T. Drzal, The Surface Properties of Carbon Fibers and Their Adhesion to Organic Polymers, *NASA Contractor report 4084*, 1-96 (1987).
 19. A. G. Osorio, I. C. L. Silveira, V. L. Bueno and C. P. Bergmann, $H_2SO_4/HNO_3/HCl$ -Functionalization and its effect on dispersion of carbon nanotubes in aqueous media, *Applied Surface Science*, **255**, 2485-2489 (2008).
 20. S. Hussain, Spectroscopic Investigation of Modified Single Wall Carbon Nanotube (SWCNT), *Journal of Modern Physics*, **2**, 538-543 (2011).
 21. Z. Dai, F. Shi, B. Zhang, M. Li and Z. Zhang, Effect of sizing on carbon fiber surface properties and fibers/epoxy interfacial adhesion, *Applied Surface Science*, **257**, 6980-6985 (2011).
 22. J. M. Clark and D. R. Secrist, Effect of Fiber Surface Treatment on the Properties of Carbon Fiber Reinforced Nylon Composites, *Journal of Thermoplastic Composite Materials*, **1**, 232-241 (1988).
 23. J. K. Ahmed, A. F. Hamzah, and A. Hamed, Thermal and Chemical Etching of Carbon Fiber, *International Journal of Engineering and Technology*, **7**, 519-526 (2017).
 24. S. Zhang, W. B. Liu, L. F. Hao, W. C. Jiao, F. Yang and R. G. Wang, Preparation of carbon nanotube/carbon fiber hybrid fiber by combining electrophoretic deposition and sizing process for enhancing interfacial strength in carbon fiber composites, *Composites Science and Technology*, **88**, 120-125 (2013).
 25. G. Wu, Y. Wang, D. Li, C. Lu, W.Z. Shen, X. Li and Z. Feng, Direct electrochemical attachment of carbon nanotubes to carbon fiber surfaces, *Carbon*, **49**, 2152-2155 (2011).
 26. M. B. Ehsan Moaseri, Majid Karimi and Morteza Maghrebi, 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*, **51**, 774-785 (2014).
 27. Z. Wu, C. U. Pittman and S. D. Gardner, Nitric acid oxidation of carbon fibers and the effects of subsequent treatment in refluxing aqueous NaOH, *Carbon*, **33**, 597-605 (1995).
 28. E. Moaseri, M. Karimi, M. Maghrebi and M. Baniadam, 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*, **51**, 774-785.
 29. T. Yokoyama and K. Nakai, Interlaminar and In-Plane Shear Strengths of a Unidirectional Carbon/Epoxy Laminated Composite under Impact Loading, *SEM Annual Conference and Exposition on Experimental and Applied Mechanics*, **3**, 191-196 (2006).
 30. A. C. Ancelotti Junior, L. C. Pardini, E. M. Bezerra and D. Roach, Use of the Mar-Lin criteria to determine the influence of porosity on the Iosipescu and short beam shear properties in carbon fiber polymer matrix composites, *Materials Research*, **13**, 63-39 (2010).
 31. A. Battisti, D. Esqué-de los Ojos, R. Ghisleni and A. J. Brunner, Single fiber push-out characterization of interfacial properties of hierarchical CNT-carbon fiber composites prepared by electrophoretic deposition, *Composites Science and Technology*, **95**, 121-127 (2014).
 32. P.-N. Wang, T.-H. Hsieh, C.-L. Chiang and M.-Y. Shen, Synergetic Effects of Mechanical Properties on Graphene Nanoplatelet and Multiwalled Carbon Nanotube Hybrids Reinforced Epoxy/Carbon Fiber Composites, *Journal of Nanomaterials*, **2015**, 1-9 (2015).
 33. W. Qin, F. Vautard, L. T. Drzal and J. Yu, Mechanical and electrical properties of carbon fiber composites with incorporation of graphene nanoplatelets at the fiber-matrix interphase, *Composites Part B Engineering*, **69**, 335-341 (2015).
 34. Z. Zha, K. Teng, N. Li, X. Li, Z. Xu, L. Chen, J. Niu, H. Fu, L. Zhao and Y. Liu, Mechanical, thermal and interfacial performances of carbon fiber reinforced composites flavored by carbon nanotube in matrix/interface, *Composite Structures*, **159**, 761-772 (2017).