Materials Research Proceedings 35 (2023) 342-349 https://doi.org/10.21741/9781644902714-41

Effect of carbon nanotube content on the mechanical behaviour of CFRP composite materials

Marina Andreozzi[1,a], Iacopo Bianchi[1,b], Archimede Forcellese[1,c], Serena Gentili[1,d*], Luciano Greco[1,e], Tommaso Mancia[1,f], Chiara Mignanelli[1,g], Michela Simoncini[1,h], Alessio Vita[1,i]

[1]Università Politecnica delle Marche, Dipartimento di Ingegneria Industriale e Scienze Matematiche, Via Brecce Bianche 12, 60131, Ancona, AN, Italy

[a]m.andreozzi@pm.univpm.it, [b]i.bianchi@pm.univpm.it, [c]a.forcellese@staff.univpm.it, [d]s.gentili@pm.univpm.it, [e]l.greco@pm.univpm.it, [f]t.mancia@pm.univpm.it, [g]c.mignanelli@pm.univpm.it, [h]m.simoncini@staff.univpm.it, [i]alessio.vita@staff.univpm.it

Keywords: Composite Materials, CFRP, Carbon Nanotubes, Mechanical Performances

Abstract. The present investigation aims at studying the effect of carbon nanotubes (CNTs) content on the mechanical performances of carbon fiber reinforced polymer (CFRP) composite materials. To this purpose, percentages of carbon nanotubes, ranging from 0.5 to 4%, were dispersed in the epoxy resin used to impregnate carbon fibers. Tensile and flexural tests were performed in order to evaluate the effect of CNTs content on the tensile and flexural performances of CFRP composites reinforced using different percentages of carbon nanotubes. Furthermore, a scanning electron microscopy analysis was carried out in order to analyze the dispersion of the CNTs in the composite laminates. The results showed that the addition of nanofillers up to the value of 3% leads to an improvement in the tensile and flexural performances of CFRP composites.

Introduction

Carbon Fiber Reinforced Polymer (CFRP) are increasingly used in the field of advanced materials for a wide range of sectors due to their high specific mechanical properties [1-4]. The most common CFRPs are obtained by combining thermosetting matrix with continuous carbon fibres. The properties of these materials can be further enhanced by the addition of nanoparticles dispersed within the CFRP polymer matrix [5]. Among others, carbon nanotubes (CNTs) are receiving most of the attention due to their remarkable reinforcement properties. Nanotubes can be single-walled (SWCNT) or multi-walled (MWCNT) [6]; the latter are easier and less expensive to produce than the former; furthermore MWCNTs have excellent properties in terms of stiffness, strength, thermal and electrical conductivity [7, 8].

Several studies have highlighted how the dispersion of CNTs within thermosetting matrix significantly improves the matrix properties in terms of strength, modulus and interlaminar shear strength [9-11]. In addition, the use of CNTs can improve the fatigue resistance of CFRP composites, making them stronger and more durable. For these reasons, the addition of CNTs to CFRP composite materials can offer several benefits and innovations in various industrial fields, including aerospace, automotive and sport equipment. CFRP composites with CNTs can be lighter than traditional composites and can lead to more efficient and sustainable components in service. Costs could also be lowered by dispersing carbon nanotubes within CFRP composites, as the improved mechanical behaviour of the materials [12] can reduce the amount of material required to achieve the desired performance. However, the high potential of CNT reinforced polymer composites can be exploited through the definition of the proper CNTs content; furthermore, the agglomeration of CNTs in the polymer matrix must be avoided since the agglomerates can lead to stress concentration that weakened the interface between CNT and matrix [13]. Several methods can be used to obtain a high quality dispersion, such as solution-assisted dispersion, tip/bath sonication, three-roll milling and thermal agitation [14].

Another problem presented by CNTs is the filtering effect that occurs during the manufacturing process of CFRPs, as it exploits long resin flows. This happens because the reinforcement retains the nanofiller during the matrix flow, preventing uniform dispersion. Then, the dispersion of CNTs in the matrix enhances its thixotropic behaviour, making the impregnation and the curing processes more complicated [13]. Therefore, the CNTs content must be carefully defined to improve mechanical performances and to guarantee uniform mechanical properties of the component, without promoting the agglomerates formation and avoiding the CNTs filtering effect. For this reason, even though some studies have been already presented on this topic, it is of extreme important to enrich the literature with a comprehensive study of the reinforcement effect of CNTs on composite laminates, especially at high dispersion concentrations. To do this, composite panels have been realized exploiting the liquid infusion process and varying the CNTs volume fraction in an epoxy matrix from 0 to 4%, with steps of 0.5%. This allows to evaluate both the filtering and the agglomerating processes of CNTs and how these affect the mechanical properties of laminates.

The characteristic of the CFRP composite laminates have been evaluated in terms of tensile and flexural behaviours and fractured surfaces were analysed by means of scanning electron microscopy. In addition, void contents in each composite panel have been measured in order to investigate the processability of unfilled and nanofilled matrices.

Materials and Experimental Procedures

Materials

The CNTs used in the present research are industrial-grade -OH functionalized multi-walled carbon nanotubes supplied by Nanoamor. The reinforcement used in the composite material is a TWILL-type carbon fiber, realized with an aerial weight of 200 g/m2. The thermosetting matrix is a high performing and low viscosity two component epoxy resin (EC157) and W152 amine hardener provided by Elantas. This matrix is widely used in the high-performance composites industry due to its outstanding mechanical properties that make it suitable for racing and aerospace applications. The CNTs were dispersed in the liquid resin through a patented three-roll milling process [15] developed by Nanotech S.p.A; different weight contents, ranging from 0.5 to 4% were investigated. After the dispersion, the liquid nanofilled resin was collected and mixed with the hardener in a mixing ratio of 100:30, as reported in the technical datasheet.

Manufacturing Process of Composite Laminates

The manufacturing processes used to fabricate the composite laminates is the liquid infusion, by which the matrix is heated to decrease the viscosity and, by means of a vacuum pump, is flowed inside the fibrous reinforcement, suitably disposed over a mold and closed in a vacuum bag. In order to facilitate the impregnation and to accelerate the process, a grid with high permeability is laid above the laminate, in this way it uniforms and speeds up the flow of resin, limiting the possibility of the formation of voids or dry areas.

Once the impregnation process is completed, the composite material is placed in an autoclave to allow the resin solidification under pressure. The process, according to the matrix data sheet, was carried out at 120°C for 6 hours at a pressure of 4 bar. Once the autoclave cycle was completed, a post-curing process was carried out at 120°C for 6 hours in an oven to achieve complete cross-linking. Figure 1 schematically shows the steps of the manufacturing process of the composite laminates reinforced by CNTs. This manufacturing process has been repeated to obtain composite laminates with different CNTs dispersion.

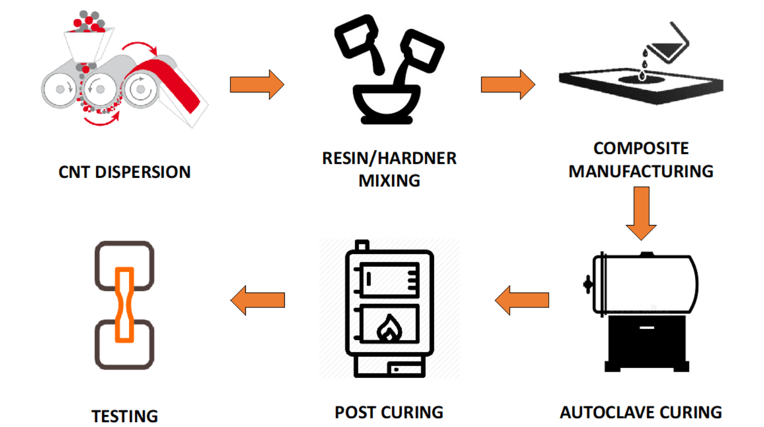


Fig. 1 Scheme of the manufacturing process of composite laminates with carbon nanotubes.

Void quantity analysis

The presence of voids in composite materials, that strongly reduces the material strength [16], was detected by performing the resin digestion test, according to the ASTM D3171 standard - procedure B “matrix digestion using sulfuric acid/hydrogen peroxide”. This procedure allows the quantification of the constituent materials of the composite (matrix and fiber). This test, in addition to allowing the determination of the fiber-to-matrix ratio, allows the quantification of the void volume percentage, a key parameter in identifying the quality of a composite and its manufacturing process. In fact, void percentages greater than 2% are typically considered unacceptable in high demanding sectors, thus leading to laminate nonconformity [17].

Mechanical tests

In order to evaluate the effect of carbon nanotubes content on the mechanical performances of CFRP composite materials, tensile and flexural tests were performed at room temperature, according to the ASTM D3039 and ASTM D7264 – Procedure A standards, respectively. Such tests were carried out on the MTS 810® servo-hydraulic testing machine, with a load cell of 250 kN. The specimens were extracted from cured laminates, at different CNTs contents, by means of waterjet cutting operations. The tensile samples were characterized by a nominal length, width and thickness equal to 250, 15 and 1 mm, respectively. In order to reduce stress concentrations that can be caused by the clamping system of testing machine and to avoid premature failure, tabs in composite material, with a thickness of 1.5 mm, were bonded to each end of the tensile specimens using two components epoxy adhesive. Tensile tests were carried out at a loading rate of 2 mm/min. During tests, the load and nominal strain along the loading direction were acquired using the load cell and an extensometer; such results allowed to plot tensile stress vs. tensile strain curves, by which the maximum value of tensile strength was obtained.

In order to investigate the effect of CNTs content on the flexural behavior of the CFRP composite laminates, flexural tests were performed by three-point bending tests, carried out at a constant crosshead motion of 1 mm/min. To this purpose, rectangular specimens, 154 mm in length, 13 mm in width and 4 mm in thickness, were cut by laminates at different values in percentage of CNTs contents. Tests were carried out until fracture using an equipment consisting in a loading nose and two supports, characterized by cylindrical contact surfaces, finely ground surfaces free of indentation and burrs, with all sharp edges relieved. The diameter of the loading nose and supports span are respectively 5.0 ± 0.1 mm and 57.5 mm. The force applied to the specimen and resulting specimen deflection at the center of span was measured and recorded until the sample failure occurs on the outer surface. The experimental results were plotted as flexural stress vs. flexural strain curves, derived after the acquisition of punch load and punch stroke (ps) during experimental tests.

To guarantee the repeatability of the results, five tensile and flexural tests were performed for each experimental condition investigated. The results obtained by tensile and flexural tests on samples obtained using different CNTs contents were compared to the mechanical behavior of the CFRP sample obtained using the net resin, in order to evaluate the influence of the CNTs content in percentage.

To evaluate more precisely the results obtained at different CNTs contents, a normalization process with respect to the fiber volume fraction was performed. As a matter of fact, the variation of fiber content in the composite laminate leads to significant changes in the mechanical properties of the laminates. Therefore, the results obtained from the mechanical tests were normalized to a quantity of fiber volume fraction equal to 60%, by taking into account the results of the resin digestion, as reported in composite materials [18].

Scanning Electron Microscopy

The fracture surfaces of tensile specimens in CFRP composite material, at different CNTs contents, were analyzed using the scanning electron microscope FESEM ZEISS SUPRA TM40, with compact GEMINI® objective lens, in order to acquire high magnification three-dimensional topography of materials and to evaluate the effect of the dispersion of the CNTs in the composite laminates. The samples for SEM investigation were coated by means of a metallization process in order to make it conductive for the analysis.

Results and Discussion

The presence of voids in laminates significantly reduces the strength of the material, degrading the physical and chemical properties of the fibers due to the consequent moisture absorption and crack propagation. As far as the evaluation of the void contents is concerned, typical results of resin digestion test, conducted according to ASTM D3171- Procedure B, are shown in Table 1, in which the results of the resin digestion test are reported.

Table 1: Results of the resin digestion

MEASURE	SAMPLES								
	0% CNT	0.5% CNT	1.0% CNT	1.5% CNT	2.0% CNT	2.5% CNT	3.0% CNT	3.5% CNT	4.0% CNT
Composite density [g/cm^3]	1.506	1.492	1.477	1.457	1.449	1.462	1.451	1.516	1.467
Fiber volume fraction Vf [%]	50.85	50.17	47.92	46.35	43.20	47.22	46.21	52.12	46.16
Matrix volume fraction Vm [%]	48.78	49.06	51.25	51.97	56.16	52.17	51.97	46.85	53.11
Void volume fraction [%]	0.37	0.77	0.83	1.68	0.64	0.61	1.82	1.03	0.73

It can be observed that, irrespective of the CNTs content, the value of the void volume fraction in nano-reinforced composite materials is always higher than the unreinforced composite. Such a result can be attributed to the higher viscosity of the matrix, which makes the impregnation process more difficult. As the viscosity increases, resin flow between the fibers becomes more challenging, resulting in air trapping and void formation in the cured composite. In addition, the consolidation process that occurs in the autoclave is less effective when using high viscosity resins because their flow towards the breather and bleeder is lower. However, it should be noted that all measured values are below 2%, which is considered the maximum acceptable value for high-performance applications.

In Fig. 2, typical tensile stress vs. tensile strain curves and flexural stress vs. flexural strain curves are shown. As can be seen, the increase of CNTs content leads to an increase in both strength and stiffness of the laminates. This effect is more marked as the quantity of CNTs is the highest, whilst at values of 0.5 and 2% the mechanical performances improvement is limited.

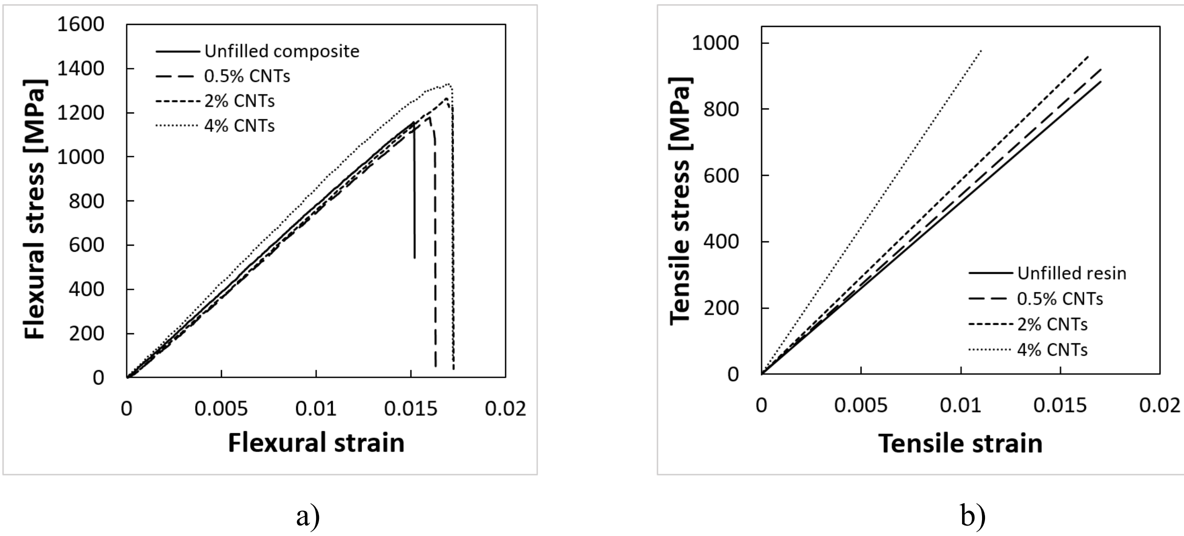
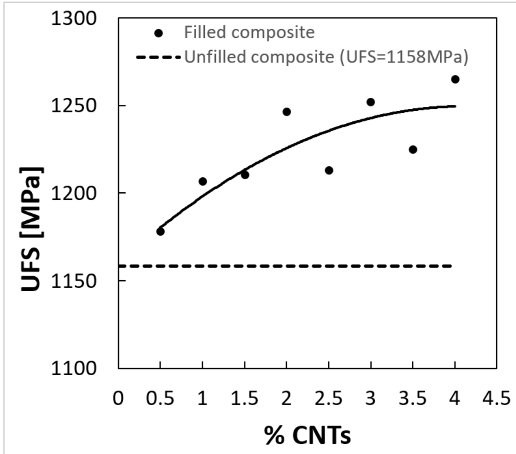


Fig. 2 Typical a) tensile and b) flexural stress strain curves for 0, 0.5, 2 and 4% CNTs concentration

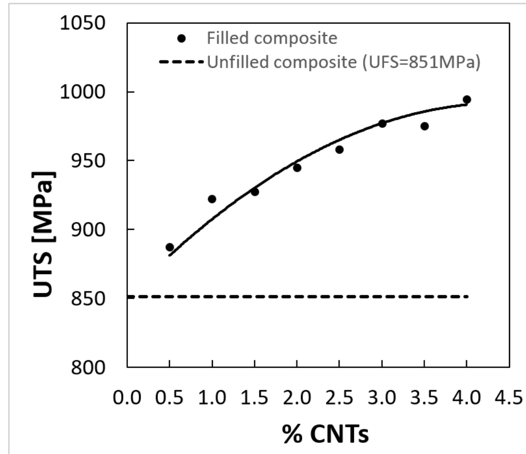
Fig. 3a shows that, irrespective of the CNTs content, the ultimate tensile strength is higher than the one of the unfilled composites. Such increase can be attributed to the reinforcement effect of carbon nanotubes on the matrix, which results both in a higher strength at the matrix fiber interface which leads to an improved load transfer mechanism, and in a stiffening effect on the matrix. Furthermore, the elongation to failure tends to decrease with increasing CNTs content, resulting in a reduction of about 50% with respect to the unfilled composite at the highest CNTs content investigated. In the literature, it has been shown that for low CNTs content agglomerate formation is not observed; as an example, Forcellese et al. [19] demonstrates that samples reinforced using a multiwalled carbon nanotube content of 1% did not exhibit evident agglomerates. However, for higher CNTs content dispersed, conflicting results are reported. In one hand, some studies, such as the one carried out by Hong et al. [15], show an increase in mechanical performances, while in the other hand other research show a decrease due to the formation of agglomerates as the content of CNTs increases [20].

In this study, as far as the slope of the UTS vs. % CNTs curve is concerned, a decrease with increasing carbon nanotubes content is reported; such behavior is more evident as the CNTs content is higher than 2%. This effect can be related to the formation of agglomerates due to the occurrence of CNTs filtering effect. In fact, as the CNTs content increases, the strengthening effect produced by CNTs is mitigated by the weakening effect caused by the CNTs agglomerates.

Materials Research Proceedings 35 (2023) 342-349 https://doi.org/10.21741/9781644902714-41



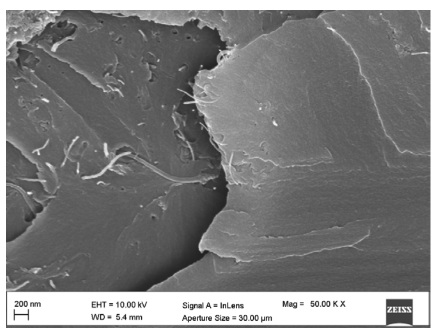
a)



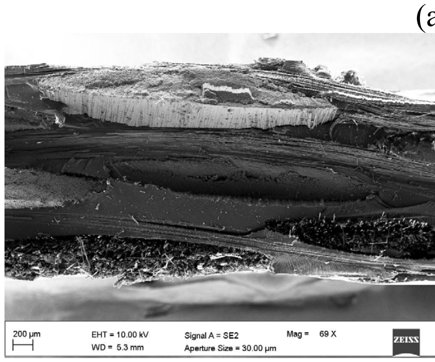
b)

Fig. 3 (a) Maximum tensile stress values of CFRP composite material as a function of CNTs, (b) Maximum flexural stress of CFRP composite material as a function of CNTs

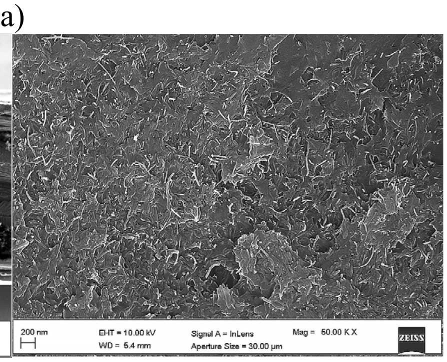
As far as the ultimate flexural strength (UFS) is concerned, a trend similar to the one exhibited by UTS is shown. As a matter of fact, Fig. 3b shows that UFS values of nanofilled composite are higher than the unfilled one; in addition, the UFS vs. % CNTs curve is characterized by a decrease in the slope with increasing CNTs content.



(a)



(b)



(c)

Fig. 5 SEM of fractured tensile specimen characterized by a CNTs content of: (a) 0.5, (b) 2 and (c) 4%.

Fig. 5 shows the SEM microscopies of the fracture surface of filled laminates at different CNTs contents. It can be observed that the CNTs tend to form agglomerates with the increase in CNTs content (Fig.s 5b and 5c). Such agglomerates lead to stress concentration and weakened CNT-matrix interfacial adhesion, resulting in a reduction of mechanical properties of the filled CFRP laminate. Furthermore, the matrix results in rough and jagged surface, denoting an increasingly ductile behavior as the CNTs content increases. On the other hand, at the lowest CNT content investigated, the surface appears smooth, indicating a more brittle failure of matrix (Fig. 5a).

Conclusion

The present study aimed at investigating the effect of carbon nanotube content on the mechanical properties of carbon fiber reinforced composites. Carbon nanotubes were dispersed in an epoxy resin using a patented process, and carbon fiber composites were realized by using resin infusion with an autoclave curing process. Laminates characterized by different CNTs weight contents (ranging from 0.5% to 4% in steps of 0.5%) were tested to evaluate tensile and flexural behavior and to measure void content. Fracture surfaces were analyzed using SEM images, to analyze the effect of CNTs content on failure mechanisms.

The main results can be summarized as follows:

- the increase in CNTs content leads to an increase in void quantities, due to the increase in resin viscosity, and a consequent poor fiber - matrix impregnation;
- the CNTs dispersion in composite laminates results in an improvement in tensile and flexural properties as compared to the unfilled composite;
- the ultimate tensile and flexural strength increase with CNTs content with a decreasing rate; such behavior tends to be more marked when a CNTs content of 2% is exceeded;
- SEM images showed that high CNTs content resulted in the formation of agglomerates, which caused stress concentration and weakened CNT-matrix interfacial adhesion.

Future research will focus on optimizing CNTs dispersion through appropriate processing techniques to minimize void formation and optimize the composite's mechanical properties.

References

[1] S. J. Jitha, A. Saritha, W. Runcy, J. Kuruvilla, G. Gejo, O. Kristiina, An introduction to fiber reinforced composite materials, Fiber Reinforced Composites: constituents, compatibility, perspectives and applications, Woodhead Publishing, (2021),1-24. https://doi.org/10.1016/B978-0-12-821090-1.00025-9

[2] M. Sreejith, R.S. Rajeev, Fiber reinforced composites for aerospace and sports applications, Fiber Reinforced Composites: constituents, compatibility, perspectives and applications, Woodhead Publishing, (2021), 821-859. https://doi.org/10.1016/B978-0-12-821090-1.00023-5

[3] A. Oludaisi, M. Thokozani, Industrial and biomedical applications of fiber reinforced composites, Fiber Reinforced Composites: constituents, compatibility, perspectives and applications, Woodhead Publishing, (2021), 753-783. https://doi.org/10.1016/B978-0-12-821090-1.00004-1

[4] I. Bianchi, A. Forcellese, M. Simoncini, A. Vita, Life cycle impact assessment of safety shoes toe caps realized with reclaimed composite materials, J Clean Prod, vol. 347, (2022) https://doi.org/10.1016/j.jclepro.2022.131321

[5] I. Bianchi, S. Gentili, L. Greco, M. Simoncini, Effect of graphene oxide reinforcement on the flexural behavior of an epoxy resin, Procedia CIRP, vol. 112, (2022) pp. 602-606. https://doi.org/10.1016/j.procir.2022.09.057

[6] M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, R. S. Ruoff, Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load, Science (1979), 287 no. 5453 (2000) 637-640. https://doi.org/10.1126/science.287.5453.637

[7] E. W. Wong, P. E. Sheehan, C. M. Lieber, Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nanotubes, Science (1979), 277 no. 5334 (1997), 1971-1975. https://doi.org/10.1126/science.277.5334.1971

[8] M. M. J. Treacy, T. W. Ebbesen, J. M. Gibson, Exceptionally high Young's modulus observed for individual carbon nanotubes, Nature, 381 (Jun. 1996) 678-680. https://doi.org/10.1038/381678a0

[9] A. Pantano, Mechanical Properties of CNT/Polymer, in: R. Rafiee (Eds.), Carbon Nanotube-Reinforced Polymers: From Nanoscale to Macroscale, Elsevier Inc., (2017), pp. 201-230. https://doi.org/10.1016/B978-0-323-48221-9.00009-1

[10] S. Imani Yengejeh, S. A. Kazemi, A. Öchsner, Carbon nanotubes as reinforcement in composites: A review of the analytical, numerical and experimental approaches, Comput Mater Sci, 136 (Aug. 2017) 85-101. https://doi.org/10.1016/j.commatsci.2017.04.023

[11] T. Glaskova-Kuzmina, A. Aniskevich, M. Zarrelli, A. Martone, M. Giordano, Effect of filler on the creep characteristics of epoxy and epoxy-based CFRPs containing multi-walled carbon nanotubes, Compos Sci Technol, vol. 100, (Aug. 2014) pp. 198-203. https://doi.org/10.1016/j.compscitech.2014.06.011

[12] A. Forcellese, M. Simoncini, A. Vita, A. Giovannelli, L. Leonardi, Performance analysis of MWCNT/Epoxy composites produced by CRTM, J Mater Process Technol, (2020). https://doi.org/10.1016/j.jmatprotec.2020.116839

[13] A. Forcellese, A. Nardinocchi, M. Simoncini, A. Vita, Effect of Carbon Nanotubes Dispersion on the Microhardness of CFRP Composites, Key Eng Mater, vol. 813, (2019). https://doi.org/10.4028/www.scientific.net/KEM.813.370

[14] S. N. Bhattacharya, M. R. Kamal, R. K. Gupta, Polymeric nanocomposites: Theory and practice, Polymeric Nanocomposites: Theory and Practice, pp. 20061-383.

[15] S. K. Hong, D. Kim, S. Lee, B. W. Kim, P. Theilmann, and S. H. Park, Enhanced thermal and mechanical properties of carbon nanotube composites through the use of functionalized CNT-reactive polymer linkages and three-roll milling, Compos Part A Appl Sci Manuf, vol. 77, (Oct. 2015), pp. 142-146. https://doi.org/10.1016/j.compositesa.2015.05.035

[16] P. Olivier, J. P. Cottu, and B. Ferret, Effects of cure cycle pressure and voids on some mechanical properties of carbon/epoxy laminates, Composites, vol. 26, no. 7, (1995). https://doi.org/10.1016/0010-4361(95)96808-J

[17] K. Naresh, K.A. Khan, R. Umer, W.J. Cantwell, The use of X-ray computed tomography for design and process modeling of aerospace composites: A review, Mater. Des, (2020). https://doi.org/10.1016/j.matdes.2020.108553

[18] Department of defense, handbook composite materials handbook vol. 1, Polymer matrix A.

[19] A. Forcellese, M. Simoncini, A. Vita, A. Giovannelli, and L. Leonardi, Performance analysis of MWCNT/Epoxy composites produced by CRTM, J Mater Process Technol, vol. 286, Dec. 2020, p. 116839. https://doi.org/10.1016/j.jmatprotec.2020.116839

[20] M. Tarfaoui, K. Lafdi, and A. El Moumen, "Mechanical properties of carbon nanotubes based polymer composites," Compos B Eng, vol. 103, (Oct. 2016), pp. 113-121. https://doi.org/10.1016/j.compositesb.2016.08.016