Nanocomposites conductivity point measurement using Tunneling AFM (TUNA)

Marialuigia Raimondo[1*], *Liberata* Guadagno[1], *Luigi* Vertuccio[1], *Carlo* Naddeo[1], *Giuseppina* Barra[1], *Giovanni* Spinelli[2], *Patrizia* Lamberti[2], *Vincenzo* Tucci[2], and *Khalid* Lafdi[3]

[1]Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano (SA), Italy
[2]Department of Information and Electrical Engineering and Applied Mathematics, University of Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano (SA), Italy
[3]University of Dayton, 300 College Park, Dayton Ohio, 45440, USA

Abstract. Polymer-matrix composites containing conductive nanoparticles are a potential means for achieving an appealing combination of multifunctional properties for their use as structural parts in the aerospace field. Carbon nanofibers (CNFs) have been being looked forward to as the next generation of new and avant-garde aircraft structures because they are exceptionally coveted competitor materials to replace traditional metal components for lightning strike protection. In this regard, nanocomposites at low concentration of CNFs ranging from 0.05% up to 2% by wt to impart electron conduction in tetrafunctional epoxy resin have been prepared and characterized. The aim of this work concerns the use of Tunneling AFM (TUNA) as revolutionary tool able to correlate the electrical current map with the correspondent local morphology of CNF/resins. TUNA technique has proven to play a leading role in the identification of current paths and electrical interconnections, even without altering the morphology with usual treatments employed to create electrical contacts to the ground. Summing up, the good electrical performance together with the high mechanical properties due to a conductive cross-linked network of CNFs inside the resin demonstrate a charming applicative potential for the formulated nanocomposites as structural materials capable to provide a safe conductive path on the exterior skin, preventing serious damage to the aircraft.

1 Introduction

Polymer composites reinforced with carbon nanofibers (CNFs) have paved the way for new and exciting scenarios for multifunctional materials. In fact, carbon nanofibers are increasingly playing a leading role in the aeronautic field because they act as exceptional filler constituents providing overall improvement in mechanical, electrical, thermal properties and ease of processability of the polymer matrix material [1-4]. In particular, the low manufacturing cost and the remarkable electrical and thermal properties of CNFs offer

* Corresponding author: mraimondo@unisa.it

the possibility to effectively transfer the CNF intrinsic properties to the epoxy composites, thus determining the improvement of the final performance that goes beyond that provided by the individual nanoparticles, without sacrificing light weight. The tetrafunctional epoxy resin, tetraglycidyl methylene dianiline (TGMDA), cured with the aromatic diamine 4,4'-diaminodiphenylsulfone (DDS), is one of the most largely used epoxy matrices for the manufacture of high-performance fiber composites in the aircraft and spacecraft industries [5]. CNFs with extraordinarily high aspect ratios associated with low density have high electrical conductivity which makes them outstanding nanofillers for converting electrically non-conducting polymers into conductive materials useful for various and targeted applications, such as electromagnetic interference (EMI), photovoltaic devices, transparent conductive coatings as well as electro-actuating the shape memory polymer composites [6-8] and others [9,10]. The reduced electrical conductivity of the composites represents one inherent shortcoming in their use for aeronautic primary structures. This fact has raised concern over the performance of the composite structure during a lightning strike event that usually takes place during take-off and landing of an aircraft, as well as during passing through the storm clouds [11,12]. Lightning generally strikes a geometrically extremal point of an aircraft (like radome, wing tips, etc.) and travels through the structure along the shortest path, which is additionally the most conductive one, to exit at another geometrically extremal point [4]. During this process, several concomitant phenomena occur among which overpressure and resistive heating are the most significant. The current technology aimed at overcoming the drawback of the reduced electrical conductivity consists in reinforcing the composites with conductive metal fibers or metal screens in order to dissipate lightning currents. But many of these solutions add additional weight and reduce composite advantage. With the advances in the technology of this last decade, it is possible to overcome this critical point thanks to the recent development of new carbon nanostructured forms that can act as conductive nanofillers when incorporated into an epoxy matrix, replacing traditional metallic materials for lightning strike protection of aircrafts. The conductive fillers are preferably small in size (skin effect), have high electrical conductivity (for shielding by reflection) and high aspect ratio (lower percolation threshold). Aeronautic structures need to meet two criteria: high performance and lightweight. In this contest, conductive epoxy nanocomposites capable to fulfill tightened and compelling industrial requirements in the field of structural materials have been developed and characterized providing a safe conductive path on the exterior skin of the aircraft. With highly conductive skins, most of the lightning current remains on the exterior skin, without serious damage to the aircraft. The present study focused on the effect of CNF weight fraction on the conductive behavior of epoxy/CNF composites. It has been demonstrated that the electrical percolation threshold (EPT) is directly related to the dispersion of the fillers in the polymer matrix. Furthermore, the need for electrical characterization of surfaces on the nanometer scale in order to improve local conductivity measurements has led rapidly to a variety of scanning probe microscopy-based techniques. In fact, this paper focus on electrical characterization at nanoscale level using Tunneling AFM (TUNA), which is able to detect ultra-low currents ranging from 80 fA to 120 pA [13], as innovative tool for correlating the local topography with electrical properties of CNF/epoxy nanocomposites specifically designed to meet pressing industrial requirements in the field of structural materials. TUNA has proven to be a very effective means of investigation to identify conductive pathways and interconnections in CNF/resins, without undergoing the sample to any prior treatment with silver paint, which is usually employed to create electrical contacts to the ground [3]. In this work, Dynamic Mechanical Analysis (DMA) was used to analyze the effect of carbon nanofiber on the storage moduli and the loss factors (tanδ) of the developed nanocomposites. The detected values turned out suitable in the usual operational temperature range of structural materials. The high performance in mechanical properties strictly related to the high curing degree (almost 100%) reached with

the chosen formulation and curing treatment, together with the values in the electrical conductivity and the state of the nanofiller dispersion and interconnections (analyzed by TUNA technique), highlight an interesting applicative potential for the formulated material.

2 Experimental section

2.1 Materials and Methods

CNFs in the form of powders were from the Pyrograf III family. They were obtained by heat treatment at 2500°C starting from the as-received CNFs. The thermal treatment was found effective in providing the best combination of mechanical and electrical properties [3,14]. The epoxy matrix was prepared by mixing an epoxy precursor TGMDA (epoxy equivalent weight 117–133 g/eq) with a reactive diluent 1-4 butanediol diglycidyl ether (BDE). For this study, 4,4-diaminodiphenyl sulfone (DDS) was used as curing agent. All these products were obtained by Sigma-Aldrich. The epoxy formulation was obtained by mixing the TGMDA with the BDE at a concentration of 80%:20% (by wt) epoxide to flexibilizer. DDS was added at a stoichiometric concentration with respect to all the epoxy rings (TGMDA and BDE). This unfilled mixture will be named Epoxy in the following. The epoxy blend and the DDS were mixed at 120°C; the carbon nanofibers (named CNF in this work) were, then, added and incorporated into the matrix by using an ultrasonication for 20 min. An ultrasonic device, Hielscher model UP200S (200 W, 24 kHz) was used. In this study, then, the CNFs were dispersed within the epoxy mixture at the 0.05, 0.32, 0.64, 0.8, 1, 1.3 and 2wt % content. The nanocomposites are named Epoxy/X(%)CNF where X(%) represents the different CNF load percentage. For percentages up to 1.3% by wt, it is possible to obtain a homogeneous mixture for the formulated nanocomposites while percentages beyond 1.3% by wt determine an increase in viscosity [15]. All the epoxy mixtures were cured by a two-stage curing cycle: a first isothermal stage was carried out at the lower temperature of 125°C for 1 h and the second isothermal stage at higher temperatures up to 200°C for 3 h.
Dynamic mechanical properties of the unfilled epoxy matrix and CNF/nanocomposites were performed with a dynamic mechanical thermo-analyzer (Tritec 2000 DMA -Triton Technology). Solid samples with dimensions 2 x 10 x 35 mm^3 were tested by applying a variable flexural deformation in three points bending mode. The displacement amplitude was set to 0.03 mm, whereas the measurements were performed at the frequency of 1 Hz. The range of temperature was from -90°C to 310°C at the scanning rate of 3°C/min.
Micrographs of the CNF and Epoxy/1.3%CNF nanocomposite were obtained using Scanning Electron Microscope-SEM (mod. LEO 1525, Carl Zeiss SMT AG, Oberkochen, Germany). All samples were placed on a carbon tab previously stuck to an aluminum stub (Agar Scientific, Stansted, UK) and were covered with a 250 Å-thick gold film using a sputter coater (Agar mod. 108 A). Nanofilled sample sections were cut from solid samples by a sledge microtome. These slices were etched before the observation by SEM. The etching reagent was prepared according to a well-established procedure [3,13].
The conductivity mapping at nanoscale level of the nanofilled epoxy samples was performed by TUNA-AFM whose setup employs a conductive AFM probe, an external voltage source needed to apply a potential difference between the tip and the sample holder, and a current amplifier used to convert the (analogical) current signal into (digital) voltages that can be read by the computer. In particular, in our experiments, TUNA operated with a cantilever holder and an epoxy sample containing conductive CNFs, electrically connected to an external voltage source. Atomic force microscope (AFM) images were acquired in an ambient atmosphere (30%-40% humidity) with a Dimension 3100 coupled with a Bruker NanoScope V multimode AFM (Digital Instruments, Santa Barbara, CA) controller operating

in tunneling current mode (TUNA-AFM), using microfabricated silicon tips/cantilevers. The sample slices of the Epoxy/1.3%CNF were etched before the morphological observation. The TUNA-AFM measurements were performed using platinum-coated probes with nominal spring constants of 35 N m^{-1} and electrically conductive tip of 20 nm. TUNA -AFM operates in contact mode. In feedback mode, the output signal is the DC bias, adjusted to maintain the electric current setpoint. The following values of the TUNA control parameters are used: DC sample bias ranged from 1 V to 2 V, current sensitivity was 1 nA/V, current range was 200 nA, samples/lines determining the number of data points or pixels in X and Y were 256, scan rate that controls the rate at which the cantilever scans across the sample area was 0.9-1.5 Hz s^{-1}. In order to obtain repeatable results, different regions of the specimens were scanned. The images were analyzed using the Bruker software Nanoscope Analysis 1.80 (Build R1.126200).

3 Results and discussions

3.1 Dynamic Mechanical Analysis (DMA)

In this work, DMA analysis was performed in order to obtain fruitful information on the dynamic storage modulus, which is often associated with the "stiffness" of a material and is related to the Young's modulus, and the mechanical damping factor (tan δ) which is useful for determining the occurrence of molecular mobility transitions such as the glass transition temperature (Tg). Fig. 1 shows the storage modulus of the unfilled resin (Epoxy) and CNF/nanocomposites. We can observe for Epoxy/0.05%CNF sample a decrease in the storage modulus with respect to the unfilled resin (Epoxy) in the temperature range -50°C to about 250°C, even if the detected values are suitable in the usual operational temperature range of structural materials anyway. The lower value in the storage modulus of the epoxy sample Epoxy/0.05%CNF is most likely due to a lower crosslinking density. The neat resin (Epoxy) and Epoxy/0.8%CNF nanocomposite show almost the same trend in the storage modulus in the entire analyzed temperature range -90°C to about 260°C. For the epoxy samples loaded with percentages of 1% and 1.3% by wt of CNF, we can observe a general increase in the storage modulus with respect to the unfilled resin (Epoxy), which however becomes much more evident especially in the range between -90°C to about 60°C. In the epoxy nanocomposites Epoxy/1%CNF and Epoxy/1.3%CNF, the carbon nanofibers show a reinforcing effect up to 60°C. Fig. 2 shows the loss factor (tan δ) of the unfilled resin (Epoxy) and CNF/nanocomposites. The glass transition temperature (Tg) for the Epoxy/0.05%CNF sample decreases with respect to the unfilled epoxy formulation. The decrease observed in the temperature of the main peak of tan δ curve is most likely due to a lower density of the resin network that leads to easiest chain motion. As expected, no significant changes are observed in the glass transition temperature (Tg) for the formulations Epoxy and Epoxy/0.8%CNF, suggesting that the CNF content of 0.8% by wt does not hinder the motion of polymer segments. We can conclude that since Tg values are in the range between 260°C and 270°C and the value in the storage modulus is higher than 2000 MPa up to 110°C for all the analyzed samples, all the formulated nanofilled samples are suitable for a very wide range of structural applications.

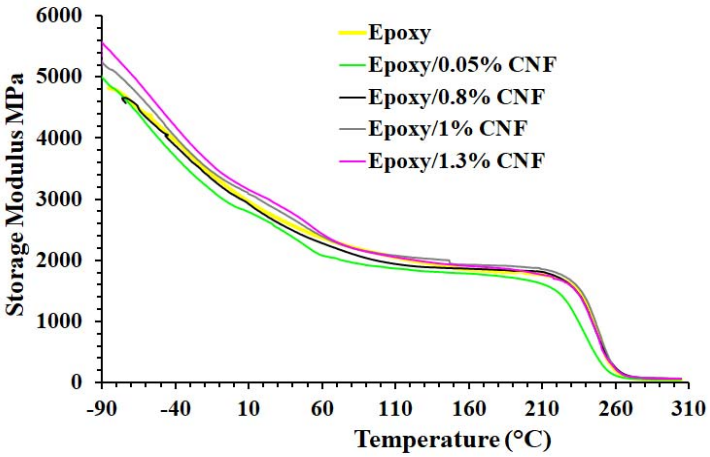

Fig. 1. Storage modulus of the unfilled resin (Epoxy) and CNF/nanocomposites.

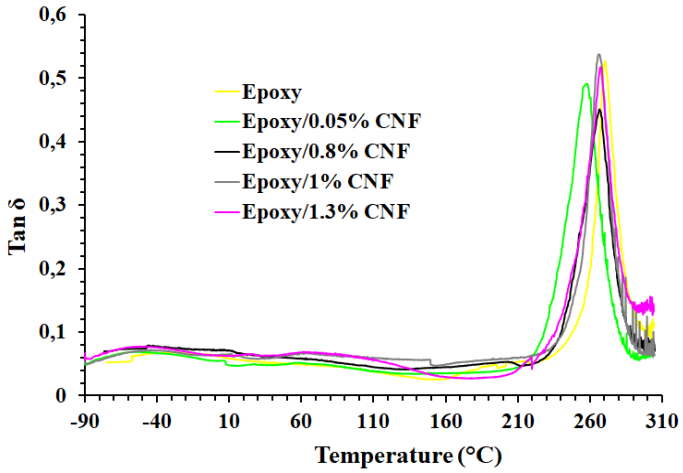

Fig. 2. Loss factor (tan δ) of the unfilled resin (Epoxy) and CNF/nanocomposites.

3.2 Morphological Analysis

3.2.1 Scanning electron microscopy (SEM) analysis

Fig. 3 shows the SEM images of the individual CNFs (see on the left) and the CNFs incorporated in the resin (see on the right). We can observe that the heat-treated CNFs are characterized by straighter walls where the nested configuration characteristic of the as made CNFs is not clearly visible [14]. In order to analyze the homogeneity of the nanofiller dispersion in the polymeric matrix, the epoxy nanocomposites were investigated by means of SEM. The analysis was carried out on etched samples to remove the resin surrounding the nanofibers, leaving them bare. SEM image (see Fig. 3 on the right) of the fracture surface of the Epoxy/1.3%CNF sample allows to distinguish a homogeneous structure where the CNFs appear uniformly distributed inside the resin also bringing to the fore the conductive network of carbon nanofibers strongly attached to the epoxy matrix. This explains the good dynamic mechanical properties and the electrical conductivity value of 1.37 S/m observed for this

sample [3]. It is worth noting that, in the dark zone of the SEM image, the etching procedure has enabled to foreground the presence of carbon nanofibers that form a continuous network in the matrix.

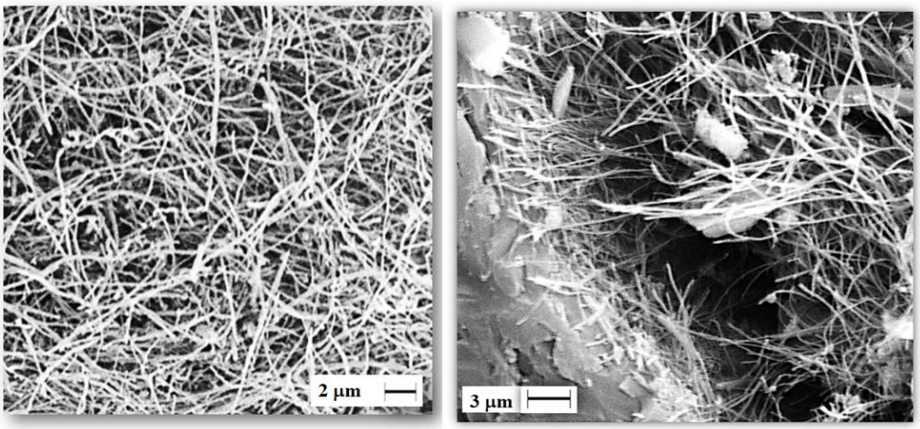

Fig. 3. SEM images of the CNF sample (see on the left) and fracture surface of Epoxy/1.3%CNF (see on the right).

3.2.2 Nanoelectrical characterization by TUNA-AFM

Fig. 4 shows the TUNA-AFM images, namely height, deflection error and tuna current (see on the top) and the corresponding 3D profiles (see on the bottom) of the Epoxy/1.3%CNF sample. These images distinctly show the morphological characteristics of the nanofilled sample providing complementary information that supports the reader to a more complete understanding of the observed electrical properties. We can clearly observe the conductive network of CNFs strongly anchored to the epoxy matrix, markedly visible in 2D and 3D tuna current images. In fact, the CNFs seem to be homogeneously distributed across the sample surface and, although they appear visible in almost all images, they are most resolved in the tuna current images that have been recorded at the same time as the height and deflection error images. The tuna current images show an increased contrast in the CNF morphological features. A clear correlation between the topography and the regions of high current was found whenever a measurable current can be recorded. In the case of the TUNA current image obtained at a bias voltage within a range of 1 to 2 V, conducting CNFs nanoparticles appear very bright in the light blue-green-yellow colour, thus demonstrating their high conductivity whereas domains with lower conductivity values appear darker. As it can be seen in the current profile, domains with different brightnesses present differences in the current value. A careful observation of the TUNA current profile of the Epoxy/1.3%CNF sample allows to confirm that the CNF/resins are intrinsically conductive. In fact, for the sample Epoxy/1.3%CNF, currents ranging from 122.8 fA to 1.1 pA were detected. The possibility to detect such low currents (ranging from fA to pA) in this nanocomposite, whose concentration is above the EPT, confirms the relative high value of the electrical conductivity (1.37 S/m) [3] and the effective conductive paths due to an optimal conductive nanofiller dispersion as it is highlighted by the strong contrast of the colors in the tuna current micrographs. Current flow through tunneling effect along the CNFs ensures a good transfer of electrical properties to the polymeric surface through a percolated filler network at nanoscale level, due to a critical minimum distance between CNFs, explainable on the basis of the stiffness and smoothness of CNF graphitized surface which determines a lower thickness of the insulating

epoxy layer around the fibers. It is worth noting that the EPT found for the CNF/nanocomposites falls in the narrow range [0.05÷0.32] wt% [3]. TUNA current images of Fig. 5 focus the attention on the distribution and characteristics of the network where very conductive areas, due to the presence on the sample surface of CNF filaments with greater brightness, are detectable.

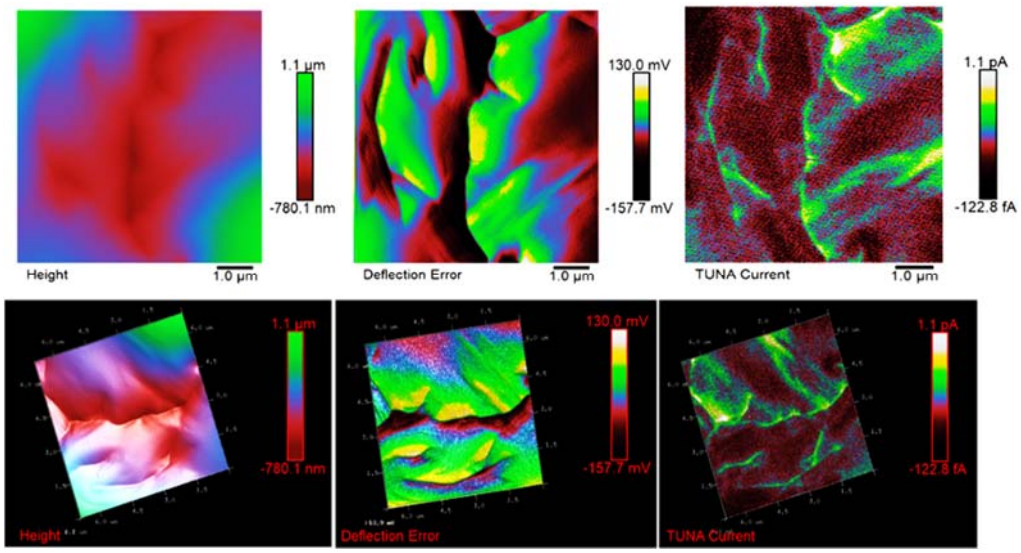

Fig. 4. TUNA-AFM micrographs (see on the top) of the fracture surface of the Epoxy/1.3%CNF sample and the corresponding 3D profiles (see on the bottom).

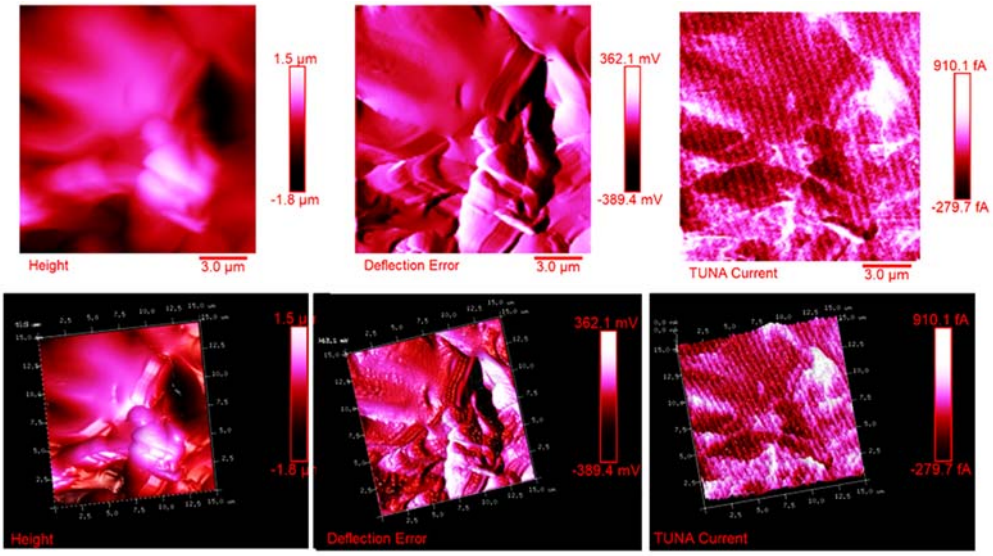

Fig. 5. Conductive network by TUNA-AFM micrographs (see on the top) of the fracture surface of the Epoxy/1.3%CNF sample and the corresponding 3D profiles (see on the bottom).

4 Conclusions

TUNA technique has proven to be an effective means of identifying the nanoscopic distribution of the conductive phase and characteristics of the charge conduction through the current pathways in carbon nanofiber reinforced resins, without carrying out any prior treatment with silver paint that is usually used to create electrical contacts to the ground. The developed CNF/epoxy nanocomposites are characterized by good electrical performance making them potentially suitable for aircraft lightning strike protection. Besides, the high mechanical properties confirm the real applicability of the conductive nanocomposites for aerospace structural applications.

Acknowledgments

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760940 – MASTRO.

References

1. S Bal, S Saha, IOP Conf Ser Mater Sci Eng **75**, 012018 (2015).
2. L. Guadagno, C. Naddeo, M. Raimondo, G. Barra, L. Vertuccio, S. Russo, K. Lafdi, V. Tucci, G. Spinelli, P. Lamberti, Nanotechnology **28**, 094001 (2017).
3. M. Raimondo, L. Guadagno, L. Vertuccio, C. Naddeo, G. Barra, G. Spinelli, P. Lamberti, V. Tucci, K. Lafdi, Compos B Eng **143**, pp. 148-160 (2018).
4. J. Gou, Y. Tang, F. Liang, Z. Zhao, D. Firsich, J. Fielding, Compos B Eng **41**, pp. 192-198 (2010).
5. L. Guadagno, M. Raimondo, U. Vietri, L. Vertuccio, G. Barra, B. De Vivo, P. Lamberti, G. Spinelli, V. Tucci, R. Volponi, G. Cosentino, F. De Nicola, RSC Adv **5**, pp. 6033-6042 (2015).
6. S. Yang, K. Lozano, A. Lomeli, H.D. Foltz, R. Jones, Compos Part A Appl Sci Manuf **36**, pp. 691-697 (2005).
7. F.H. Gojny, M.H.G. Wichmann, B. Fiedler, W. Bauhofer, K. Schulte, Compos Part A Appl Sci Manuf **36**, pp. 1525-1535 (2005).
8. J.M. Park, S.J. Kim, J.H. Jang, Z. Wang, P.G. Kim, D.J. Yoon, J. Kim, G. Hansen, K.L. DeVries, Compos B Eng, **39**, pp. 1161-1169 (2008).
9. L. Feng, N. Xie, J. Zhong, Materials, **7**, pp. 3919-3945 (2014).
10. J.M. Park, P.G. Kim, J.H. Jang, Z. Wang, J.W. Kim, W.I. Lee, J.C. Park, K.L. DeVries, Compos B Eng, **39**, pp. 1170-1182 (2008).
11. A. Katunin, Fatigue of Aircraft Structures, **1**, pp. 49-54 (2016).
12. S. Mall, B.L. Ouper, J.C. Fielding, J Compos Mater, **43**, pp. 2987-3001 (2009).
13. M. Raimondo, L. Guadagno, V. Speranza, L. Bonnaud, P. Dubois, K. Lafdi, Compos B Eng, **140**, pp. 44-56 (2018).
14. L. Guadagno, M. Raimondo, V. Vittoria, L. Vertuccio, K. Lafdi, B. De Vivo, P. Lamberti, G. Spinelli, V. Tucci, Nanotechnology **24**, 305704 (2013).
15. M.R. Nobile, M. Raimondo, K. Lafdi, A. Fierro, S. Rosolia, L. Guadagno, Polym Compos, **36**, pp. 1152-1160 (2015).