The Effect of Nano-Sized Zirconium Oxide (ZrO_2) Particles on the Tensile Behaviour of Glass Fiber Reinforced Polymer (GFRP) Composites

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Abstract: Tensile properties, such as tensile strength and tensile modulus, are highly desirable mechanical properties for any Conventional Fiber Reinforced Polymer (FRP)-based composite material intended for various structural applications in aircraft, automobiles, and marine vehicles. In this work, we demonstrate the development of a nano-modified polymer-based fiber-reinforced composite material with superior tensile strength and tensile modulus.In the first stage, Zirconium Oxide (ZrO_2) nano powder is synthesized using a solution-combustion process. In the second stage, the synthesized ZrO_2nano powder is uniformly mixed into a matrix system, and the mixture is used to create the nano-modified FRP composite laminates. To establish baseline data, composite laminates are also developed using an unmodified matrix in combination with glass fabrics. Tensile tests are performed on both the neat FRP composite and the nano-modified FRP composite using a Universal Testing Machine (UTM). The results show that the fracture point of the nano-modified FRP composite occurs earlier than that of the neat FRP composite, likely due to the increased brittleness of the composite after the addition of ZrO_2nano-powder. The toughness of the nano-modified FRP composite laminate was reduced by 8.1% compared to that of the neat FRP composite; however, there was an increment in the fracture point.The composite exhibited improved tensile strength and tensile modulus due to the addition of 1.0wt% of ZrO_2nano-powder in the matrix, with a % enhancement of strength and modulus at 8.33% and 16.17%, respectively. Scanning Electron Microscope (SEM) micrographs showed strong fiber-matrix bonding and less fiber pull-out in the nano-modified samples. The extensive surface area of the synthesized ZrO_2nano powder seems to have provided a strong interface between the matrix and the fibers, resulting in enhanced tensile properties.

Keywords:*Zirconium Oxide (ZrO_2), Glass Fiber, Polymer Matrix, Tensile Properties.*

1. Introduction

Due to their superior mechanical characteristics, such as specific strength, specific stiffness, and ease of manufacturing, fiber-reinforced polymer (FRP) composites are widely used in various structural applications, including aircraft structures, automobiles, and marine vehicles [1]. Researchers are actively exploring various techniques to enhance the mechanical properties of these conventional FRP composites. One such method is the incorporation of nano-fillers into polymers during the production of composite laminates, which has shown promising results in improving their mechanical properties.The existing literature on polymer-based composites containing nano-materials as additional fillers has inspired researchers to include nano-sized materials in the production of FRP composites [2-5]. The significant specific surface areas (SSA) of nanomaterials make them promising fillers for the development of polymer-based composites. Nanomaterials provide a large interfacial area that enhances the bonding ability of the matrix [6].Recent studies have reported both positive and negative effects of nano-fillers on the mechanical properties of FRP composites. These effects depend on the geometry of the nanomaterials, the production techniques, the quantity of fillers used, and their dispersion quality within the matrix. Nano-fillers come in various geometries, including fibers, flakes, and spherical particles, with dimensions ranging between 1–100 nm [7].

A very few authors have demonstrated the potential for improving the properties and performance of polymer-based fiber-reinforced composites by incorporating nanomaterials as additional reinforcements. Layered silicates, initially introduced by researchers from Toyota [8], hold promise as nanomaterials. In the case of glass-fiber/epoxy resin composites, a significant improvement in interlaminar shear strength, flexural strength, and fracture toughness was observed at 1 wt.% of layered silicate content. Enhanced interfacial bonding was evident on the fractured surfaces of the test samples [9].For carbon-fiber/polymer composites, an increase in flexural strength and flexural modulus by 14% and 9%, respectively, was noted at 2 wt.% of nano clay [10]. Carbon nanotubes (CNTs) opened up new possibilities for creating low-weight composites with exceptional mechanical characteristics. Studies on tensile properties, such as tensile strength and tensile modulus of Carbon Nanotubes (CNTs) filled polymer-based composites, demonstrated a proportional enhancement in these properties with the addition of CNTs (up to 1.75% of the mass fraction) in the polymer. However, adverse effects were reported for composites containing more than 1.75% of the mass fraction of CNTs [11].Similarly, adverse effects on tensile strength, tensile modulus, and failure strain were also reported for composites with a high volume fraction of Carbon Nanotubes (CNTs) in the polymer [12]Composites exhibited increased resistance to crack propagation upon the addition of Carbon Nanotubes (CNTs) to the polymer [13]. Micro- and macro-mechanical studies demonstrated that the inclusion of silica nanoparticles in FRP composites led to significant improvements in the interfacial bonding between carbon fibers and the matrix. This improvement was attributed to a toughened matrix that enhanced stress transfer and dissipated more deformation energy [14].The mechanical properties, including tensile strength, flexural strength, and compressive strength, of basalt fiber-reinforced epoxy composites were found to be enhanced by the addition of Graphene Oxide Nanoplatelets (GNOP) at very low weight percentages. Microscopic studies of the nano-modified composites revealed enhanced interfacial adhesion between the basalt fibers and the matrix [15]. The introduction of Carbon Nanotubes (CNTs) into the polymer resulted in improved interlaminar shear and flexural properties of the glass-fiber-reinforced nano-polymer-based composites [16].Vibration and damping studies on glass-fiber/polymer composites filled with various Carbon-Nanomaterials showed enhanced damped natural frequencies of the composite [17]. Researchers have developed nano-modified polymer-based fiber-reinforced composites using various methods. They have demonstrated the production of nano-polymer-based FRP composites with enhanced mechanical characteristics, even with very low loadings of various nanofillers. Additionally, several methods have been showcased for processing and characterizing nano-polymer-based FRP composites [18].

Thus far, the incorporation of nanomaterials in FRP composites has demonstrated potential, but extensive research is still required to comprehend the impacts of various nanomaterials on the mechanical and physical characteristics of FRP composites. This paper presents the utilization of antimony oxide nanoparticles as reinforcing fillers in the fabrication of conventional glass-fiber-reinforced polymer hybrid composites. It introduces a novel composite material with exceptional mechanical properties, well-suited for structural applications in the automotive, aerospace, and marine industries

2. Methods

In the present study, Zirconium Oxide nano-fillers were synthesized in the laboratory and subsequently used as nano-fillers in the fabrication of fiber-reinforced polymer-based composites. Glycine was employed as the fuel, and Zirconyl nitrate served as the oxidizer for synthesizing zirconium oxide nano powder via the solution combustion method. Both chemicals were dissolved in de-ionized water (25 ml), and the stoichiometric composition of the redox mixtures was placed in a crystalline dish, which was then introduced into a pre-heated muffle furnace maintained at 400°C. The homogeneous solution began to boil, releasing gases over 4-5 minutes, resulting in the formation of ZrO_2nano powder at the conclusion of the combustion process. The obtained cubic ZrO_2nano powder was finely ground.

In the second stage, synthesized ZrO_2nano powder (1.0 wt. %) is dispersed in the base resin, di-glyceryl ether of bisphenol (DGEBA), using a mechanical stirrer. It is then subjected to strong ultrasonication to break down the agglomerates of ZrO_2 nanoparticles in the matrix. The hardener, tri-ethylene tetramine (TETA), is subsequently mixed into the nano-modified base resin and uniformly stirred.Furthermore, two different sets of composite laminates are produced. The first set consists of neat FRP composite (a), and the second set comprises nano-modified FRP composite (b). Neat/unmodified matrix systems are used for the first set, while ZrO_2nano-modified matrix systems are employed for the second set. In the process, unidirectional glass fabric sheets with a weight of 220 GSM are placed in the mold, and the matrix (neat/nano-modified) is applied over them. The sheets are laid one above the other to achieve the desired thickness. After laying up the sheets, the wet laminate is subjected to vacuum bagging to eliminate unwanted air bubbles from the laminates. The laminates are then cured at ambient temperature for 24 hours.Test specimens are prepared from two different sets of composite laminates: a) neat FRP composites and b) nano-modified FRP composites by machining the laminates to the required dimensions. Table 1 provides details of the two sets of composite laminates fabricated: a) neat FRP composites and b) nano-modified FRP composites.

Table 1 gives details of two sets of composite laminates fabricated

Specimen no.	**Specimen Type**	**Glass fibre (Wt. %)**	**Epoxy (Wt. %)**	**Zirconium Oxidenanoparticles (wt. %)**
1	Neat FRP Composite	48	52	0.0
2	Nano-modified FRP composite	48	51	1.0

The tensile properties of the two sets of composite laminates, a) neat FRP and b) nano-modified FRP, are investigated following ASTM D-3039 guidelines. Tensile tests are conducted using a Universal Testing Machine (UTM) with a cross-head speed of 1 mm/min.

3. Results and Discussion

Synthesized Zirconium Oxide nano powder is examined under Scanning Electron Microscopy (SEM), and the micrograph is shown in Figure 1. The micrograph clearly shows that the powder is porous and exhibits a large surface area, with the average particle size ranging from 70 nm to 100 nm.

Fig. 1 SEM image of Sb_2O_3 nano-powder

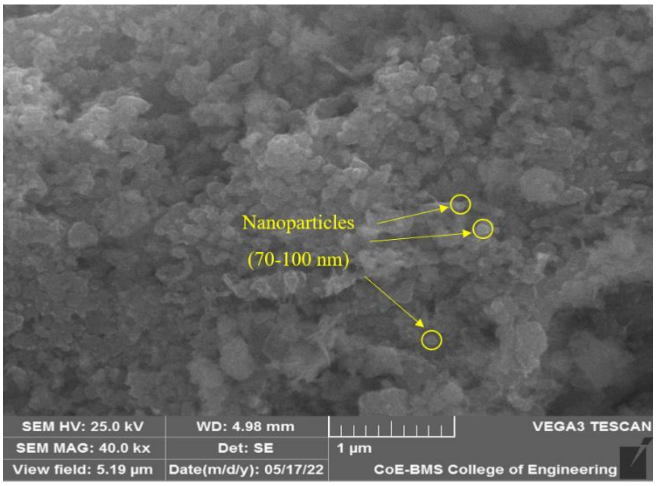

Fig. 2 displays the X-ray diffraction (XRD) pattern of the synthesized Zirconium oxide nanoparticles, with XRD scans conducted in the 2θ range from 20° to 80°. The XRD pattern reveals distinct peaks at 300, 350, 500, and 600, characteristic of zirconium oxide nanoparticles.The Specific Surface Area (SSA) of the synthesized zirconia was determined using nitrogen physisorption and a NOVA 1000 Quanta chrome high-speed gas adsorption analyzer (ver3.7). Approximately 0.0050 gm of powdered material served as the test sample. This sample was placed in a chamber filled with helium gas (pressure ≈ 30 mmHg). Nitrogen was incrementally introduced into the chamber while withdrawing helium, and the sample was maintained in the chamber for 4 hours at 120°C to facilitate absorption. After 4 hours, the deposition of liquid nitrogen on the surface of the test sample powder, forming a monolayer, allowed the determination of the sample's SSA based on the quantity of deposited nitrogen.The results revealed that the specific surface area (SSA) of the synthesized zirconia nano-powder was 25.40 m²/gm.

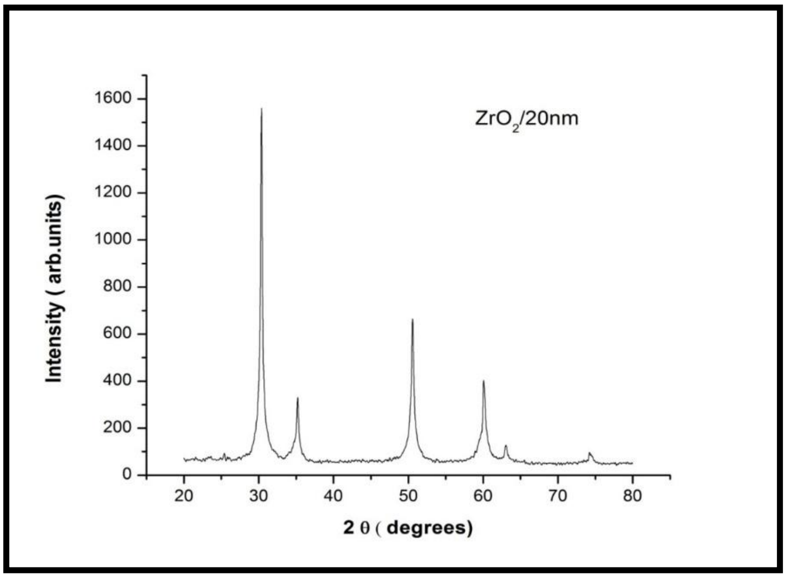

Fig. 2 XRD pattern of zirconium oxide nanoparticles (20 nm)

Composite laminates were successfully developed using conventional glass fabric sheets. Two different sets of composite laminates, (a) neat FRP composites, and (b) nano-modified FRP composites, were produced using unmodified matrix systems and ZrO_2nano-modified matrix systems, respectively. Test samples were machined from both composites, and tensile tests were conducted on these samples. The recorded tensile strength and tensile modulus are displayed in Figures 3a and 3b, respectively.

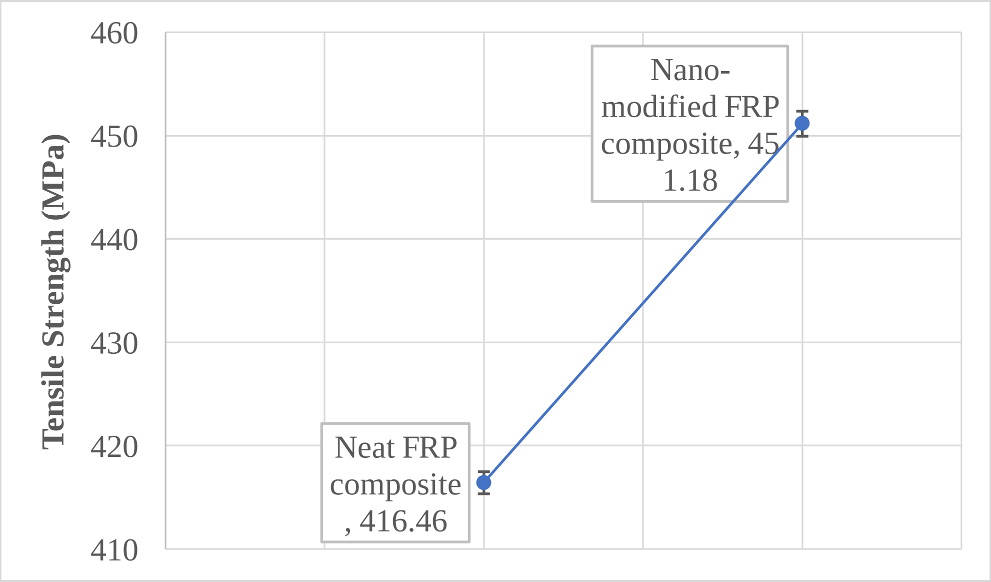

Fig. 3a. Tensile strength of a) Neat FRP composite and (b) Nano-modified FRP composite test samples

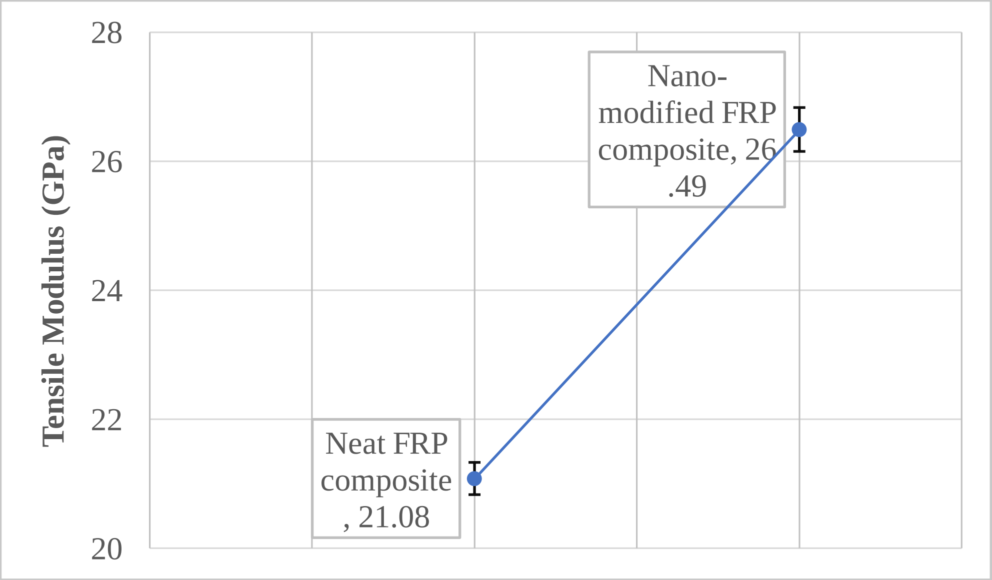

Fig. 3b. Tensile modulus of a) Neat FRP composite and (b) Nano-modified FRP composite test samples

The composite exhibited improved tensile strength and tensile modulus due to the addition of 1.0 wt.% of the ZrO_2nano-powder in the matrix. In particular, the tensile strength and tensile modulus of the composite increased from 416.46 ± 1.07 MPa to 451.18 ± 1.21 MPa and from 21.08 ± 0.45 GPa to 24.49 ± 0.74 GPa, respectively. The % enhancement of strength and modulus was 8.33% and 16.17%, respectively. The uniform dispersion and exfoliation of the ZrO_2nano-powder in the matrix are the reasons for these enhancements in the composite properties. The presence of ZrO_2nano-powder seems to have improved the reinforcing efficiency of the matrix because of its high specific surface area. During the polymer curing process, the ZrO_2nano-powders get entrapped in the cross-links of the polymer and provide strong adhesion between fibers and the matrix. Figure 4 (a & b) shows SEM micrographs of (a) neat FRP composite and (b) nano-modified FRP composite test samples.

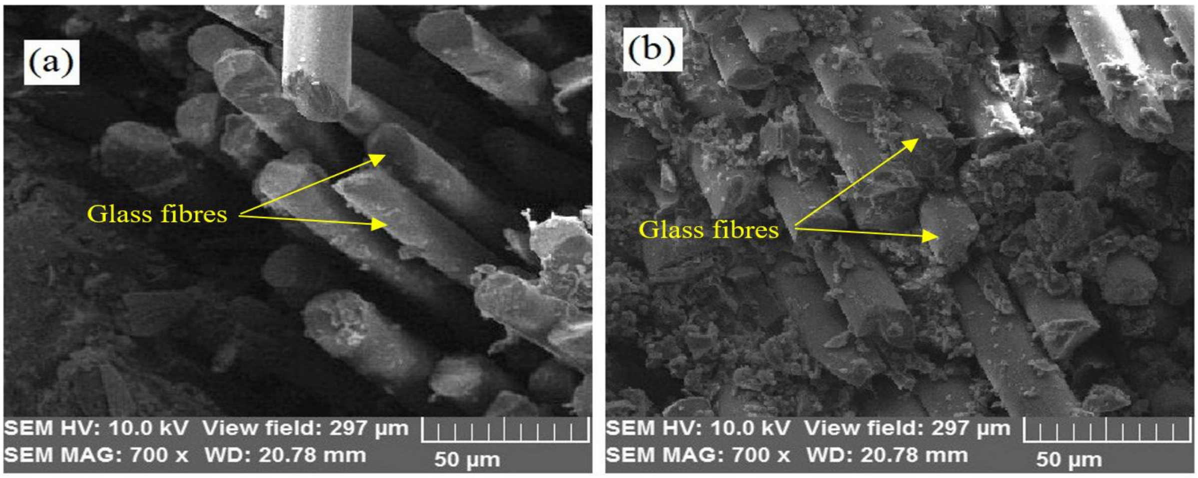

Fig. 4 SEM micrographs of (a) neat FRP composite and (b) nano-modified FRP composite test samples.

SEM micrograph of nano-modified FRP composite test sample (Fig. 4.b) shows enhanced fibre–matrix interface bonding. Uniform dispersion of the ZrO_2nano-powder in the matrix offer good adhesion between fibres and the matrix resulting in improved delamination resistance.A very large fibre pull-out can be seen in the SEM image (Fig. 4.a) of neat FRP composite indicating a weak fibre–matrix interface bonding. In contrary, a very strong fibre–matrix interface bonding can be seen in the SEM image (Fig. 4.b) of nano-modified matrix-based composite. Surface of fractured test specimen appear to be rougher, showing a higher energy requirement for the propagation of the crack. However, the fracture point of the nano-modified FRP composite is earlier than that of the neat FRP composite due to the increased brittleness of the composite after the addition of the ZrO_2nano-powder. The toughness (area under stress-strain curve) of the nano-modified FRP composite laminate was reduced by 8.1% compared to that of neat FRP composite.

Conclusions

1. In this work, the tensile behavior of a newly developed nano-modified FRP composite laminate is presented. In the first stage, Zirconia (ZrO_2) nano-powder is synthesized by the solution-combustion process. The SEM micrograph of the synthesized Sb_2O_3nano-powder clearly shows that the powder is porous and provides a large surface area, with an average particle size ranging from 70 nm to 100 nm. XRD studies revealed diffraction peaks corresponding to the characteristic peaks of ZrO_2nano-powder.

2. The two different sets of composite laminates, (a) neat FRP composite and (b) nano-modified FRP composite, were successfully developed using conventional glass fabric sheets. Tensile tests were performed on specimens machined from both the neat FRP composite and the nano-modified FRP composite laminates. The results of the tensile tests show that the fracture point of the nano-modified FRP composite occurs earlier than that of the

neat FRP composite due to increased brittleness, resulting in an increment in the fracture point. The toughness of the nano-modified FRP composite laminate was also reduced compared to that of the neat FRP composite.

3. The composite exhibited improved tensile properties, such as tensile strength and tensile modulus, due to the addition of 1.0 wt% of ZrO_2nano-powder in the matrix. The presence of ZrO_2nano-powder in the polymer matrix seems to have facilitated good adhesion between fibers and the matrix during the polymer curing process. The SEM micrograph of the nano-modified FRP composite test sample confirmed the enhanced fiber-matrix interface bonding with very little matrix cracking and fiber pull-out. The surface of the fractured test specimen appears rougher, indicating a higher energy requirement for crack propagation.

This study demonstrates that the unmatched levels of specific stiffness and specific strength of FRP composites can be further enhanced by additional reinforcements, such as nano-fillers, to achieve the best possible characteristics suitable for various structural applications.

Declarations

The datasets used and analysed during the current study are obtained during experimentation and are available from the corresponding author if required.

4. References

[1] Autar K Kaw, "Mechanics of Composite Materials", Second Edition, (2005), CRC Press.

[2] T. Kashiwagi, E. Grulke, J. Hilding, R. Harris, W. Awad, J. Douglas, Macromol. Rapid Comm. 2002, 23, 761.

[3] J. Njuguna, K. Pielichowski, Adv. Eng. Mater. 2004, 6, 193.

[4] J. Njuguna, K. Pielichowski, Adv. Eng. Mater. 2004, 6, 204.

[5] R. Andrews, D. Jacques, M. Minot, T. Rantell, Macromol. Materials Eng... 2002, 287, 395

[6] N.G. Sahoo, S. Rana, J.W. Cho, L. Li, S.H. Chan, Polymer nanocomposites based on functionalized carbon nanotubes, Prog. Polym. Sci. 35 (2010) 837–867.

[7] J. Njuguna, 'Epoxy-Based Fibre Reinforced Nanocomposites: Current Status', advanced engineering materials, volume 9, issue 10, page 835-847, October 2007

[8] Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, O. Kamigaito, *Mater. Res. Soc. Proc.* **1990,** 171, 45.

[9] Haque, M. Shamsuzzoha, F. Hussain, D. Dean, *J. Compos. Mater.* **2003,** 37, 1821.

[10] F. H. Chowdhury, M. V. Hosur, S. Jeelani, *Mater. Sci. Eng A.* **2006,** 421, 298.

[11] Liang, S.; Jia, C.; Tang, Y.; Zhang, Y.; Zhang, J.; An-qiang, P. Mechanical and electrical properties of carbon nanotube reinforced epoxide resin composites. Trans. Nonferrous Met. Soc. China **2007**, 17, 675–679.

[12] Wong, M.; Paramsothy, M.; Xu, X.J.; Ren, Y.; Li, S.; Liao, K. Physical interactions at carbon nanotube–polymer interface. Polymer 2003, 44, 7757–7764.

[13] Zhou, Y.; Pervin, F.; Lewis, L.; Jeelani, S. Fabrication and characterization of carbon/epoxy composites mixed with multi walled carbon nanotubes. Mater. Sci. Eng. A 2008, 475, 157–165.

[14] Tian, Y.; Zhang, H.; Zhang, Z. Influence of nanoparticles on the interfacial properties of fiber-reinforced-epoxy composites. Compos. Part a Appl. Sci. Manuf. 2017, 98, 1–8.

[15] Jamali, N.; Rezvani, A.; Khosravi, H.; Tohidlou, E. On the mechanical behavior of basalt fiber/epoxy composites filled with silanized graphene oxide nanoplatelets. Polym. Compos. 2018, 39, E2472–E2482.

[16] Lal, A.; Markad, K. Thermo-mechanical post buckling analysis of multiwall carbon nanotube-reinforced composite laminated beam under elastic foundation. Curved Layer. Struct. 2019, 6, 212–228.

[17] Rafiee, M.; Nitzsche, F.; Labrosse, M.R. Fabrication and experimental evaluation of vibration and damping in multiscale graphene/fiberglass/epoxy composites. J. Compos. Mater. 2019, 53, 2105–2118.

[18] Mostovoy, A. Fiber-Reinforced Polymer Composites: Manufacturing and Performance. Polymers 2022, 14, 338.