

Effect of Nanofillers on the Mechanical Properties of Vinyl Ester Resin Used as a Carbon Fiber Reinforced Polymer Matrix

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ABSTRACT

This article presents the results of research aimed at determining the influence of selected nanofillers of vinyl ester resin on the mechanical properties of the cured resin. The influence of the resin with nanofillers as a matrix on the properties of the unidirectional carbon fiber reinforced polymer (CFRP) composite was also investigated. Graphite, silicon oxide and titanium dioxide nanopowders were used as resin nanofillers. Each of the fillers was considered in two different contents, i.e. 1 wt.% and 2 wt.%. The variants with such nanofillers content were compared with the unfilled reference variant. The uniaxial tensile strength tests of the resin samples were carried out, showing the possibility of increasing the strength by 19.35% for the variant 1 wt.% of silica nanopowder content. For CFRP composites, the possibility of increasing the strength in the three-point bending test by 25.57% due to the use of a matrix reinforced with graphite nanopowder with a content of 1 wt.% was demonstrated. Based on the analysis of fracture surfaces performed using SEM microscopy, it was shown that the fillers used lead to a significant improvement in the adhesion of the matrix to the composite fibers.

Keywords: composites, nanofillers, vinyl ester resin, nano-reinforced polymers.

INTRODUCTION

Carbon fiber reinforced polymer (CFRP) composites are increasingly used in aerospace structures, wind power apparatus, automotive, marine engineering and others [1–4] due to a number of advantages. Properties that determine the increasing use of structures made on the basis of CFRP are, above all, high specific strength and stiffness, temperature stability (negligible thermal expansion), chemical and corrosion resistance [5–7]. Currently, high manufacturing costs are a limitation in the wider use of carbon fiber structures. In addition, some negative features limit their use in structures, these properties include, among others brittleness, low wear resistance and

poor resistance to crack propagation [8–10]. To ensure high strength fiber reinforced composites, it is essential to ensure a high strength adhesive bond between the fibers and the resin that forms the matrix of the composite. The adhesion between the fibers and the matrix is to ensure effective transfer of stresses to the reinforcement of the composite. Incorrect adhesion can significantly reduce the strength of the composite, causing delamination, shear, which is especially observed at bending loads. The adhesion is influenced by both the properties of the polymer resin and the surface properties of the fibers, including their surface energy [11, 12]. Various treatments are used to ensure high-strength adhesion between the fibers and the polymer matrix. The authors of the works

[13–16] described the modification of the epoxy resin constituting the matrix by adding nanofillers such as carbon nanotubes, nanofibers, nanoparticles of ceramic materials, which has been shown to improve the energy properties of the resin and thus improve adhesion to the fibers. In addition to modifying resins, there are also treatments improving the adhesive properties of the fiber surface, such as electro-chemical oxidation, plasma oxidation and others [17, 18]. Treatments such as deposition of the nanoparticles onto the fiber surface [19–22] are also used to modify the surface of the fibers in order to improve adhesion.

Focusing on the use of matrix nanofillers to improve the properties of fiber reinforced polymer (FRP) composites, the authors of [23–25] showed that the use of carbon nanotubes in the right amount can lead to a significant improvement in mechanical properties such as tensile strength and bending strength. The effective improvement of mechanical and thermal properties can also be obtained by using nanoclay as a filler [26]. At the same time, it is extremely important that the nanofillers are added in a strictly defined amount and are properly dispersed, because too high a content of nanoparticles and an inadequate mixing method may lead to the formation of aggregates and agglomerates, which in turn leads to the deterioration of mechanical properties [26–28]. The use of nanofillers may also lead to the improvement of aging resistances, as reported by the authors of the works [29–31].

This work presents the results of experimental studies aimed at determining the possibility of improving the mechanical properties of vinyl ester resin by using nanofillers. The tests of the cast resin samples were made on the basis of a static tensile test. After demonstrating the possibility of improving the mechanical properties of the resin itself, research was carried out on the possibility of improving CFRP composites made as unidirectional rectangular bars, in which a matrix modified with nanofillers was used. The research was carried out on the basis of the short-beam test. Interlaminar shear strength (ILSS) values were determined, which made it possible to determine the effect of nanofillers on the strength of the adhesive bond between the matrix and the fibers. Based on the analysis of fracture surfaces using SEM microscopy, a positive effect of the fillers used on the strength of the adhesive bond between resin and fibers was demonstrated.

MATERIALS AND METHOD

This paper aims to determine the possibilities of improving the vinyl ester resin used as a matrix of carbon fiber reinforced composites of the aircraft produced by the manufacturer of light-sport aircraft (LSA), the Ekolot company (Krosno, Poland).

The research on resin reinforcement consisted in the use of nanofillers of three different materials. The following nanoparticles were used:

- silica nanopowder with an average particle diameter of 20 nm, density 2.2 g/cm³ was supplied by Sigma-Aldrich Co. (Saint Louis, MO, USA);
- graphite nanopowder with an average particle diameter of 40 nm, density 1.8 g/cm³ was supplied by American Elements (Los Angeles, CA, USA);
- titanium oxide nanopowder with an average particle diameter of 30 nm, density 4.23 g/m³ was supplied by SkySpring Nanomaterials, Inc. (Houston, TX, USA).

Variants with the content of 1 wt.% and 2 wt.% according to the above-mentioned order of nanofillers were named: nanoGr-1%, nanoGr-2%, nanoSi-1%, nanoSi-2%, nanoTi-1% and nanoTi-2%. The variant without nanofillers was named Neat resin and is a reference.

The tested resin was vinyl ester resin, however, the detailed composition of the resin is a trade secret of the manufacturer.

The static strength tests in the uniaxial tensile test were carried out according to the guidelines presented in the PN-EN ISO 527-3: 2019-01 standard [32]. The tests were carried out at room temperature for samples with the shape and dimensions shown in Figure 1.

The samples were cast in molds made of MDF board. The procedure of preparing the unfilled vinyl ester resin composition was consistent with the technology used in the production process. As a good dispersion of the nanofiller in the polymer matrix is crucial for the properties of a final composite, we paid particular attention to determining the best conditions of the process. The resin compositions with nanofillers were prepared in the following sequential stages:

1. The resin was heated up to 50 °C in order to reduce its viscosity.
2. The purified nanofillers were added to the resins.

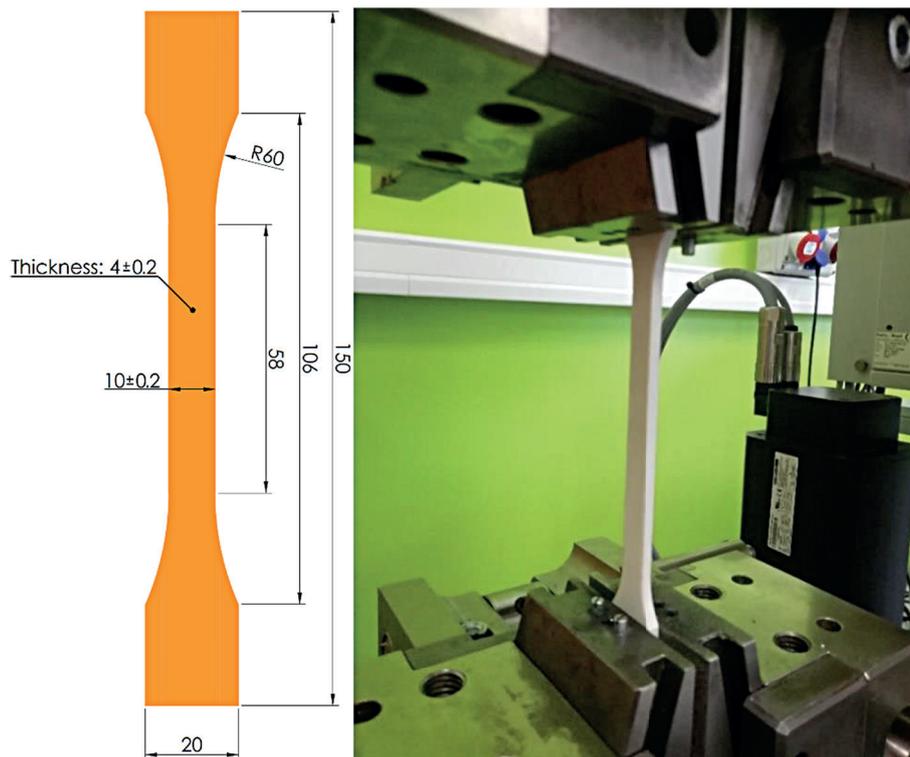


Fig. 1. Geometry of cured resin test specimen and view of the tensile test setup

3. Mechanical mixing for 60 min in an ultrasonic environment.
4. Sonification using ultrasonic homogeniser (UP400S, Hielscher – Ultrasound Technology, Germany).
5. Mixing of the resin with the nanofiller was carried out at a constant temperature of 50 °C for 60 min (maximum sonicator amplitude corresponded to the maximum sonotrode power (400 W)).
6. The right amount of hardener was added and mixed mechanically for 2 min.

After the samples were poured, a uniform procedure was followed for each of the options considered. After 24 hours, the hardened resin samples were removed from the molds, then they were subjected to aging for 3 weeks in the conditions prevailing in the production hall, i.e. ambient temperature 22 °C, air humidity 35%. The samples were then ground to remove flashes and the excess thickness using 240 grit sandpaper.

The static strength tests in the uniaxial tensile test were carried out on the Zwick/Roell Z100 testing machine, extensometers were used to precisely measure the deformation. The tests were carried out at a speed of 5 mm/min. The research was carried out for five repetitions.

Short-beam test of CFRP composites

The study also determined the influence of the modified vinyl ester resin used as a matrix on the properties of the CFRP composite. The research was carried out for unidirectional composites made of carbon roving, HTS 1600TEX carbon fibers by Toho Tenax Co., Ltd. (Tokyo, Japan) were used. The tests were carried out on the basis of the short-beam test, which is a normative test described in the ASTM D2344/D2344M-16 standard [33]. Samples with a rectangular cross-section of 14×16 mm and a length of 110 mm were tested. The dimensions of the cross-section of the samples result from the dimensions of the structural element, as these samples are part of the airplane wing spar.

In the 3-point bending test, the spacing of supports recommended by the standard, resulting from the thickness of the tested sample, was assumed to be equal to 5 times this dimension, i.e. 70 mm. The shape and dimensions of the samples used in the short beam test and the view of the stand used in the static three-point bending test are shown in Figure 2.

The tests were carried out on a Zwick/Roell Z100 testing machine at room temperature. A test speed of 5 mm/min was used. The bending strength was determined on the basis of the relationship:

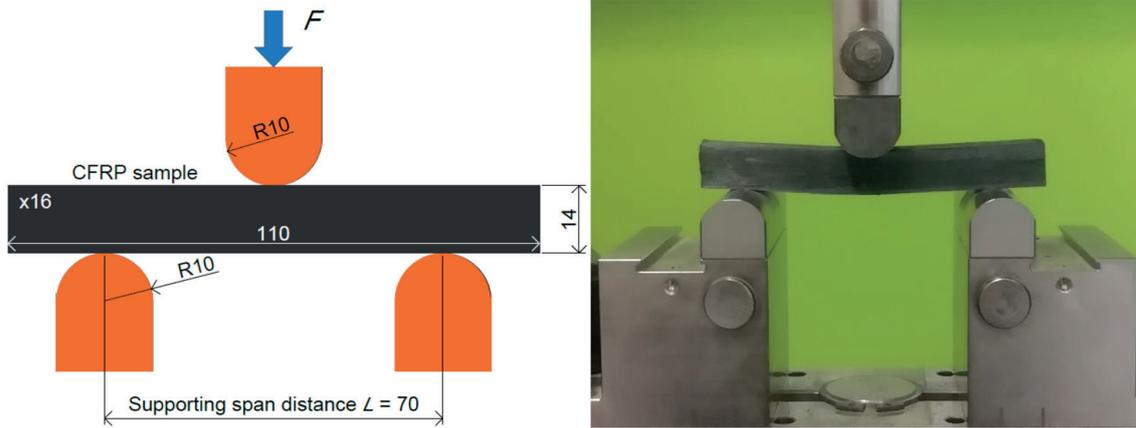


Fig. 2. Schematic diagram of loading of CFRP test specimen during the bending test and view of the test setup

$$\sigma = \frac{3F_{max}L}{2bh^2} \quad (1)$$

The interlayer shear stress was determined according to the formula:

$$\tau = \frac{3F_{max}}{4bh} \quad (2)$$

where: b and h – respectively, the width and height of the bent specimen;

F_{max} – value of the maximum force recorded during the bending test;

L – spacing of supports in the bending test.

Unidirectional carbon fibers in the form of roving supplied by Toho Tenax Co. Ltd., (Tokyo, Japan) were used as reinforcement of the composite samples. In the basic variant, the saturant used was the previously described vinyl ester resin in the Neat resin variant and resins filled with nanofillers, the same variants as described above. The same nomenclature of the variants was adopted, because the above-described variants of resins were used in this case as matrices of the CFRP composite.

The procedure for the preparation of resins as saturation of composite samples was identical to the above-described methodology of preparing resin samples with nanofillers. Composite samples were made by using a feeder through which the fiber bundles were pulled, saturating them with resin, and then the excess resin was squeezed out thanks to the appropriately selected mesh diameter.

The carbon fiber bundles, saturated in an appropriate proportion, were then placed in forms ensuring the shaping of samples with a cross-section of 14×16 mm and a length of 1000 mm. After

the appropriate number of roving strands were placed in the molds, they were covered with a vacuum bag, creating a negative pressure of about 0.07 MPa. After the resin has hardened, i.e. after 24 hours at room temperature, the samples were taken out of the molds, and then seasoned for 3 weeks under ambient conditions, i.e. temperature 22 °C, air humidity 35%. Then the samples were cut into sections equal to 110 mm, ie, the target length of the samples used in the short-beam test.

The morphologies of the fracture surfaces of the resins and composites were examined using an scanning electron microscope (SEM) Phenom ProX (Nanoscience Instruments, Phoenix, AZ, USA).

RESULTS AND DISCUSSION

Tensile strength of cured resins

Figure 3 shows typical tensile curves for individual variants of cured resin samples. On the basis of the curves, it can be seen that for each of the considered variants with the use of nanofillers, the strength and stiffness increased.

The graph presented in Figure 4 is a summary of the average values of static tensile strength for the considered variants, together with an indication of the standard deviation. The greatest increase in tensile strength in relation to the unfilled resin was demonstrated for the nanoGr-1% and nanoSi-1% variants, there was an increase in strength by 16.37% and 19.35%, respectively, which is undoubtedly a significant increase. At the same time, attention should be paid to the repeatability of tests for individual variants. For the unfilled resin, the standard deviation value was

1.87 N, slightly higher values of the standard deviation were shown for the variants filled with nanofillers with a weight content of 1%. For the nanoGr-1% variant, the standard deviation value was 2.54 N, for the nanoSi-1% variant it was 2.29 N, while the nanoTi-1% variant was characterized by a standard deviation value of 3.17 N. variants of increasing the dispersion of the results of static tests. In each variant with the nanofiller content equal to 2%, the standard deviation exceeded the value of 4.5. The significant increase in the standard deviation associated with the increase in the filler content may be

related to the uneven dispersion of the increased amount of fillers in the resin structure. It is a typical phenomenon that with a higher content of fillers, the mixture promotes the formation of aggregates of filler particles, then aggregates and agglomerates of nanoparticles are formed.

Table 1 summarizes the results of tensile strength and the values of elasticity modulus. According to the guidelines for determining the modulus of elasticity for polymeric materials, the initial modulus of deformation of 0.05% and 0.25% was determined. On the basis of the conducted research, an increase in the modulus of

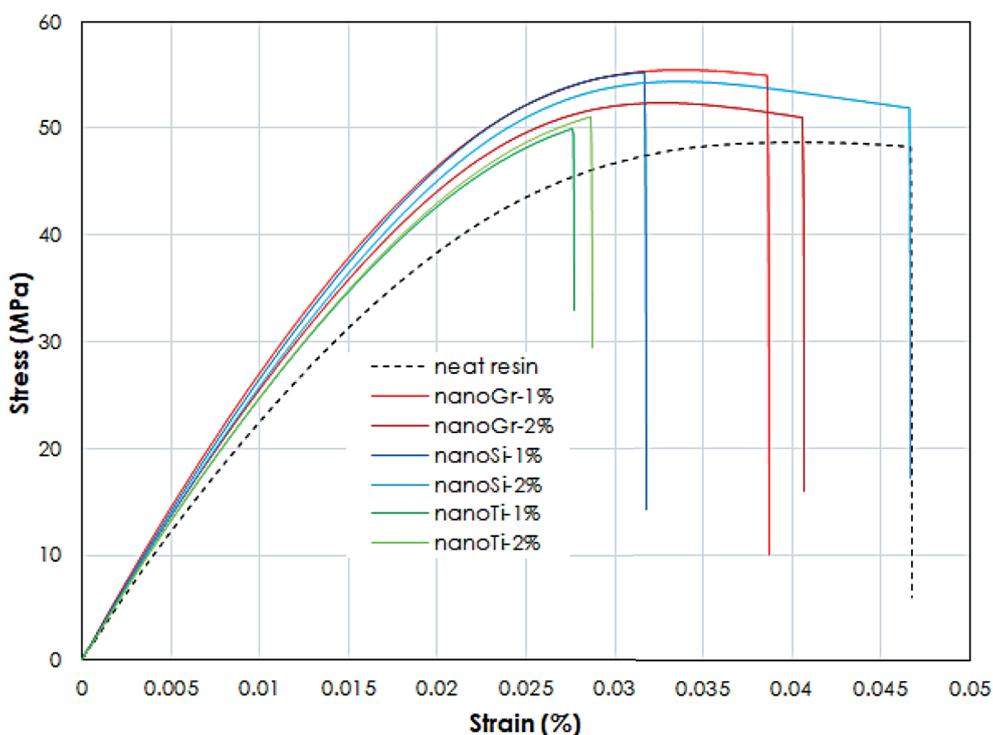


Fig. 3. Typical stress-strain test curves for resin samples studied

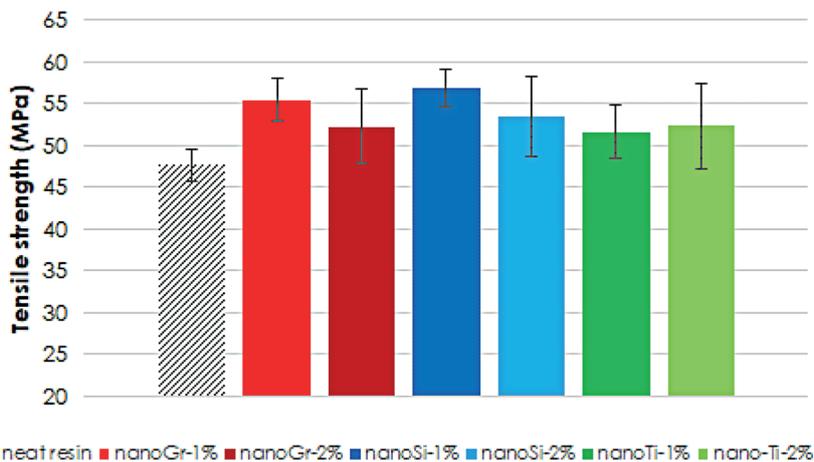


Fig. 4. Effect of type and content of nanofiller on the value of tensile strength of resin samples

Table 1. Tensile strength test results and modulus of elasticity for cured resin variants studied

Variant	Tensile strength (N) \pm SD	Percentage increase	Modulus of elasticity (MPa)	Percentage increase
Neat resin	47.62 \pm 1.87	-	2403.40	-
nanoGr-1%	55.41 \pm 2.54	16.37%	2956.18	23.12%
nanoGr-2%	52.25 \pm 4.21	9.72%	2811.13	16.96%
nanoSi-1%	56.83 \pm 2.29	19.35%	2884.98	20.04%
nanoSi-2%	53.47 \pm 4.84	12.28%	2808.46	16.85%
nanoTi-1%	51.65 \pm 3.17	8.47%	2705.99	12.59%
nanoTi-2%	52.38 \pm 5.12	10.00%	2693.87	12.09%

elasticity was clearly demonstrated for each of the variants with the addition of nanofillers. The highest increase of this parameter was recorded for the nanoGr-1% variant, which is an increase of 23.12% in relation to the unfilled resin.

For the unmodified resin, a brittle fracture, typical for thermosetting plastics, was demonstrated (Figure 5a and 5b), characterized by the fact that cracking is repeatedly initiated at the point of accumulation of stresses, this is the area at the edge of the cross-section, in its central axis, followed by cracking propagates evenly over the entire cross-section of the sample. The cleavage fracture initiation point is shown in Figure 5a.

A significantly different nature of the fractures was observed for samples with nanofillers.

On Figures 5 c–e shows the fracture surfaces of the resin samples with the considered nanofillers with the content of 1 wt.% for graphite fillers and silica over titanium oxide nanopowders, respectively, in each case for this filler content the greatest increase in strength was demonstrated. Fracture surfaces of reinforced resins revealed increase in the surface roughness that might be a sign of toughness enhancement.

The static strength tests showed a significant effect of the addition of nanofillers on the increase in the strength of the resin and the increase in the elasticity modulus. Based on the analysis of the fracture surfaces, it can be concluded about the mechanisms that improve the strength properties of resins.

Properly dispersed nanoparticles in the matrix structure lead to energy absorption during fracture. This is due to the absorption of the fracture energy by separating the filler particles from the matrix, the formation of voids in the vicinity of the voids and plastic deformation of the matrix in the area of nanoparticle deposition areas. Nanoparticles can also lead to changes in the direction of crack propagation and the forking of microcracks.

During the phenomenon of cracking in the uniaxial tensile test, nanometric particles of the resin filler lead to the formation of shear surfaces in the material structure, which also translates into energy absorption and thus counteracts the splitting cracking mechanism typical of duroplasts.

The higher described and imaged by scanning microscopy phenomena require energy, which resulted in an increase in the overall strength of the material with nanofillers. As shown, the highest increase in mechanical properties was obtained for the lowest of the considered nanofillers content (except for titanium oxide). The decreasing tendency of strength with a further increase in the content of nanofillers can be explained by the fact that the increased content of nanoparticles in the mixture with the vinyl ester resin in the liquid state promotes the compaction of particle clusters, which consequently leads to the formation of agglomerates and aggregates in the hardening resin matrix resulting from the combined clusters of nanoparticles.

Short-beam test of CFRP composites

In the next stage, research was carried out on the influence of the considered nanomaterials on the adhesive properties and on the interlayer shear strength of resins in a unidirectional CFRP composite, in which the above-described variants of resins were used as a matrix.

The diagram (Figure 6) shows representative force-displacement curves obtained in the static three-point bending test for the considered variants. On their basis, it can be concluded that nanofillers led to an increase in strength and stiffness of samples of unidirectional carbon-vinyl ester composites.

Table 2 summarizes the average values of the bending strength and the interlayer shear strength. Repeatable test results were obtained, as evidenced by relatively low and comparable values

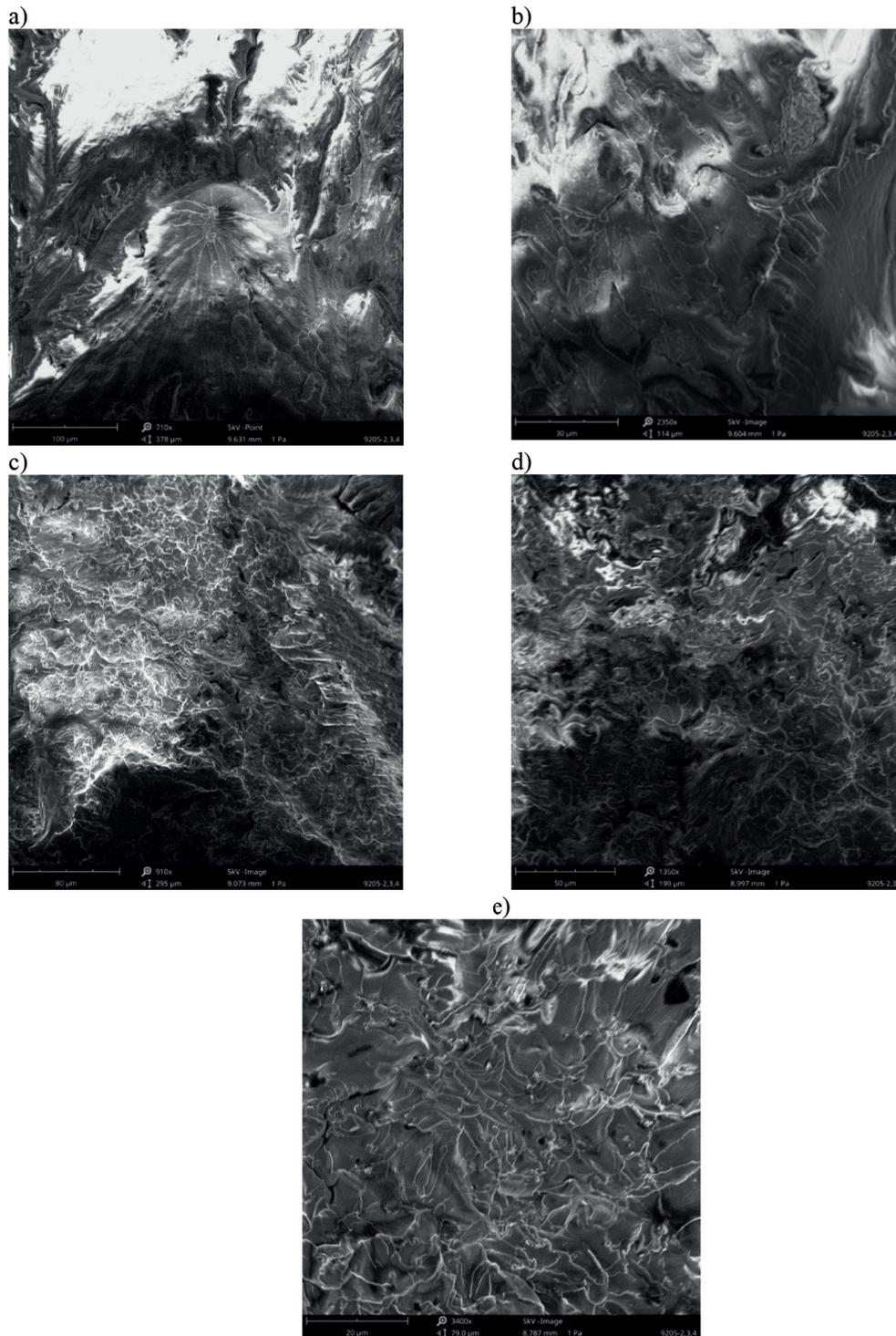


Fig. 5. SEM images of fracture surfaces of cured epoxy resin for variants: a, b) Neat resin, c) nanoGr-1%, d) nanoSi-1% and e) nanoTi-1%

of the standard deviation for each of the variants. A significant increase in the interlayer shear strength was demonstrated by filling the resins with nanopowders. For the nanoGr-1% variant it is an increase of 25.57%, and for the nanoSi-1% variant by 19.84% in relation to the variant of samples with an unfilled resin matrix (Figure 7).

Based on the analysis of the results of the three-point bending strength tests, it can be observed that 1% content of graphite nanopowder and nanosilica significantly increases the bending strength. A further increase in the content of the above-mentioned fillers also causes an increase in strength, but a downward trend can be

observed here, as it is an increase of 9.24% and 11.81% for the nanoGr-2% and nanoSi-2% variants, respectively. As for the third of the considered nanofillers, i.e. titanium dioxide nanopowder, research has shown that it does not improve

flexural strength. Similar results for nanofillers in the form of graphite and silica may be caused by their similar density, which is 2.25 g/cm³ for graphite and 2.65 g/cm³ for silica, respectively. In turn, titanium dioxide is characterized by a

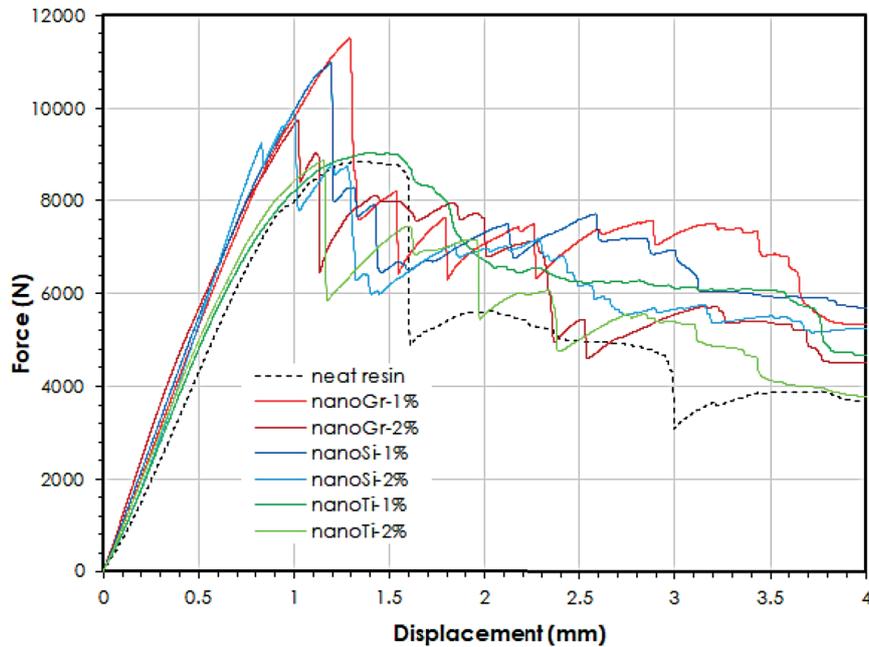


Fig. 6. Typical force-displacement test curves for CFRP composites samples studied

Table 2. Maximum load results and flexural strength for studied variants of CFRP samples

Variant	Maximum load (N) ± SD	Percentage increase	Flexural strength (MPa)	ILSS (MPa)
Neat resin	9007.2 ± 185.9	-	301.6	30.2
nanoGr-1%	11310.5 ± 378.5	25.57%	378.7	37.9
nanoGr-2%	9838.3 ± 657.0	9.23%	329.4	32.9
nanoSi-1%	10794.5 ± 299.2	19.84%	361.4	36.1
nanoSi-2%	9673.4 ± 692.8	7.40%	323.9	32.4
nanoTi-1%	9154.3 ± 465.7	1.63%	306.5	30.7
nanoTi-2%	8991.9 ± 792.9	-0.17%	301.1	30.1

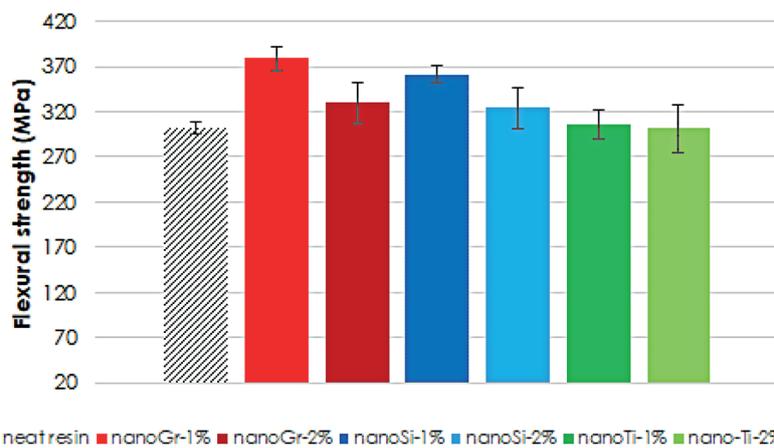


Fig. 7. Effect of type and content of nanofiller on the value of flexural strength of CFRP samples

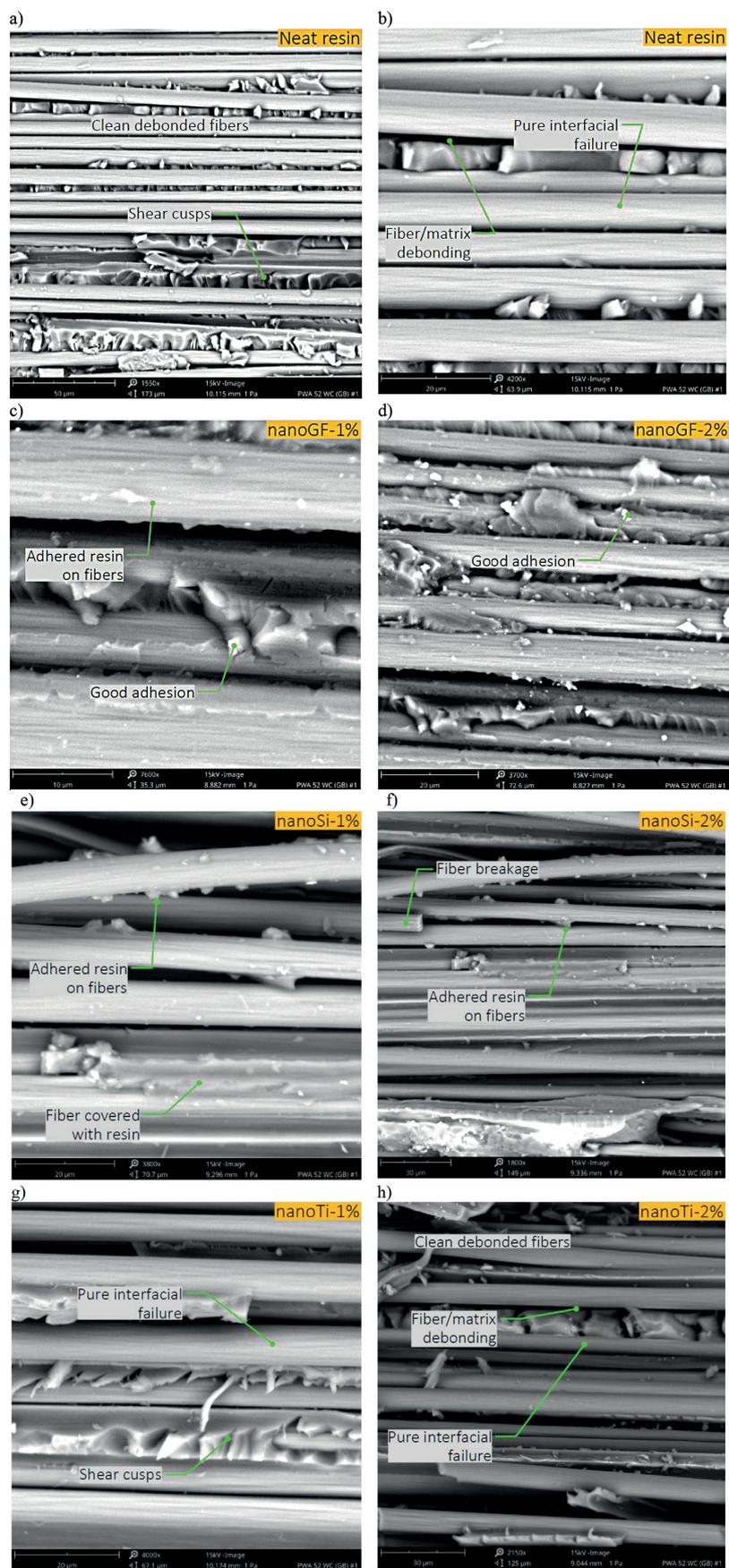


Fig. 8. SEM micrographs showing fracture surfaces after bending test for variants: a), b) Neat resin, c) nanoGr-1%, d) nanoGr-2%, e) nanoSi-1%, f) nanoSi-2%, g) nanoTi-1% and h) nanoTi-2% of studied CFRP composites

much higher density, equal to 4.25 g/cm^3 . Additionally, the properties of the composite are influenced by the adhesive properties. As part of the research, the discussion on the influence of nanofillers on the adhesive properties was undertaken on the basis of SEM fractography made on the shear surfaces of the layers after the bending tests. Figure 8 shows SEM images of the fracture surfaces of the CFRP samples considered after the bend tests performed.

Based on the fracture surfaces, a number of conclusions can be drawn. Figs. a,b present selected fragments of the shear surface of the composite in which the matrix is neat resin. Here, phenomena such as fiber-matrix debonding, shear cusps have been observed, and the surfaces of the fibers due to shear damage are smooth, devoid of resin residues, therefore pure interfacial failure has occurred. On this basis, it can be concluded that neat resin has a relatively low adhesion to carbon fibers. Moving on to the variant with nanofillers, a different nature of the destruction was noticed. Fig. 8c shows the fracture surface in which the nanoGr-1% resin variant was used as a matrix. In this case, a significantly better adhesion of the matrix to the fibers was observed, after the destruction of the composite structure on a significant surface of the fibers, the resin remained, which to a large extent proves the cohesive failure of the matrix. The higher content of graphite nanopowder in the resin also has a positive effect on the adhesion to carbon fibers (Fig. 8d). In the case of the filler in the form of nanosilica, similar adhesion improvement effects were demonstrated compared to the neat resin variant. Figs. 8e, f show the fracture surfaces for the nanoSi-1% and nanoSi-2% variants, respectively, here also resin residues on the fibers are visible, which proves a strong interfacial adhesion. In addition, the phenomenon of fiber breakage was observed here, which can also confirm the high strength of the adhesive bond in the composite between the matrix and the fibers.

Figure 8g and h show breakthroughs for composites in which the matrix was filled with titanium dioxide nanopowder with a content of 1% and 2%, respectively. In both of these cases, the nature of the destruction was similar to that of the neat resin variant. The bending strength tests also show that there were no significant changes in the failure mechanism.

It should be noted that the improvement of the composite properties through the use of resin nanofillers is influenced by a number of factors, such as the surface properties of the nanoparticles

enabling the formation of a high-strength adhesive bond with the resin, and the viscosity of the resin. An extremely important factor here is also the method of dispersion of nanoparticles in the resin volume, which should ensure their uniform distribution. The tendency to aggregate, i.e. agglomerates and aggregates by nanofiller particles is not a favorable phenomenon and does not lead to an improvement in properties. The formation of aggregates is favored by a higher filler content in the resin matrix, but also by individual properties of a given material.

CONCLUSIONS

The study investigated the influence of nanofillers on the properties of the matrix of the CFRP composite. Graphite, silica (SiO_2) and titanium dioxide (TiO_2) nanopowders were used as nanofillers. Each of the mentioned fillers was added to the vinyl ester resin in the amount of 1 wt.% and 2 wt.%, cast samples of such modified resin were tested, as well as unidirectional carbon fiber composite based on it. The results were compared with a reference material. The research results allow the following conclusions to be drawn addition 1 wt.% nanofiller for vinyl ester resin in the form of graphite nanopowder and silica nanopowder can lead to a significant increase in the tensile strength of the resin in the range of 16.37–19.35%. Fillers also increase the modulus of elasticity, as shown by the results of the research, an increase of 20.04–23.12% can be obtained. Higher content of these fillers, i.e. 2 wt.% has a smaller impact on improving strength and increasing the modulus of elasticity. Titanium dioxide nanopowder affects the resin reinforcement to a lesser extent, however, in the best case, an increase in tensile strength by 10% for 2 wt.% of nanopowder content. Fracture surfaces of reinforced resins revealed increase in the surface roughness that might be a sign of toughness enhancement. The use of reinforced vinyl ester resin through the considered nanofillers as a matrix of unidirectional carbon fiber composite enables the increase of the bending strength of such composites. It was shown that the content of 1 wt.% of graphite nanopowder and the same content of silica nanopowder increase flexural strength by 28.94% and 24.63%, respectively. On the basis of the research results, it was found that the third of the considered nanofillers, i.e. titanium dioxide, did not change the flexural strength of the composite.

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REFERENCES

1. Yang T., Lu S., Song D., Zhu X., Almira I., Liu J., Zhu Y. Effect of Nanofiller on the Mechanical Properties of Carbon Fiber/Epoxy Composites under Different Aging Conditions. *Materials*. 2021; 14(7810): 1–17.
2. Ge T., Zhao W., Wu X., Lan X., Zhang Y., Qiang Y., He Y. Incorporation of electroconductive carbon fibers to achieve enhanced anti-corrosion performance of zinc rich coatings, *J. Colloid. Interf. Sci*. 2020; 567: 113–125.
3. Zare Y., Rhee K.Y. Modeling of viscosity and complex modulus for poly (lactic acid)/poly (ethylene oxide)/carbon nanotubes nanocomposites assuming yield stress and network breaking time, *Compos. Part B Eng*. 2019; 156: 100–107.
4. He M., Xu P., Zhang Y., Liu K., Yang X. Phthalocyanine nanowires@GO/carbon fiber composites with enhanced interfacial properties and electromagnetic interference shielding performance. *Chem. Eng. J*. 2020; 388: 124255.
5. Ashrafi M., Hamadian M., Ghasemi A.R., Kashi F.J. Improvement mechanical and antibacterial properties of epoxy by polyethylene glycol and Ag/CuO nanoparticles. *Polym. Compos*. 2019; 40: 3393–3401.
6. Heng Z., Chen Y., Zou, H., Liang M. Simultaneously enhanced tensile strength and fracture toughness of epoxy resins by a poly(ethylene oxide)-block-carboxyl terminated butadiene-acrylonitrile rubber dilock copolymer. *RSC Adv*. 2015; 5: 42362–42368.
7. Flick E.W. *Epoxy Resins, Curing Agents, Compounds, and Modifiers: An Industrial Guide*; William Andrew: Norwich, NY, USA, 2012.
8. Shen X.J., Pei X.Q., Liu Y., Fu S.Y. Tribological performance of carbon nanotube–graphene oxide hybrid/epoxy composites. *Compos. Part B Eng*. 2014; 57: 120–125.
9. Jiang T., Kuila T., Kim N.H., Ku B.C., Lee J.H. Enhanced mechanical properties of silanized silica nanoparticle attached graphene oxide/epoxy composites. *Compos. Sci. Technol*. 2013; 79: 115–125.
10. Deng S.H., Zhou X.D., Zhu M.Q., Fan C.J., Lin Q.F. Interfacial toughening and consequent improvement in fracture toughness of carbon fiber reinforced epoxy resin composites: Induced by diblock copolymers. *Exp. Polym. Lett*. 2013; 7: 925–935.
11. Sharma M., Gao S., Mader E., Sharma H., Wei L.Y., Bijwe J. Carbon fiber surfaces and composite interphases. *Compos. Sci. Technol*. 2014; 102: 35–50.
12. Jin Z., Zhang Z., Meng L. Effects of ozone method treating carbon fibers on mechanical properties of carbon/carbon composites. *Mater. Chem. Phys*. 2006; 97: 167–72.
13. Han S., Lin J.T., Yamada Y., Chung D.D.L. Enhancing the thermal conductivity and compressive modulus of carbon fiber polymer-matrix composites in the through-thickness direction by nanostructuring the interlaminar interface with carbon black. *Carbon N.Y*. 2008; 46: 1060–1071.
14. Kim M.T., Rhee K.Y., Lee J.H., Hui D., Lau A.K.T. Property enhancement of a carbon fiber/epoxy composite by using carbon nanotubes. *Compos. B. Eng*. 2011; 42: 1257–1261.
15. Pathak A.K., Borah M., Gupta A., Yokozeki T., Dhakate S.R. Improved mechanical properties of carbon fiber/graphene oxide-epoxy hybrid composites. *Compos. Sci. Technol*. 2016; 135: 28–38.
16. Qin W., Vautard F., Drzal L.T., Yu J. Mechanical and electrical properties of carbon fiber composites with incorporation of graphene nanoplatelets at the fiber-matrix interphase. *Compos. B. Eng*. 2015; 69: 335–341.
17. Sharma M., Gao S., Mader E., Sharma H., Wei L.Y., Bijwe J. Carbon fiber surfaces and composite interphases. *Compos. Sci. Technol*. 2014; 102: 35–50.
18. Jin Z., Zhang Z., Meng L. Effects of ozone method treating carbon fibers on mechanical properties of carbon/carbon composites. *Mater. Chem. Phys*. 2006; 97: 167–72.
19. Karger-Kocsis J., Mahmood H., Pegoretti A. Recent advances in fiber/matrix interphase engineering for polymer composites. *Prog. Mater. Sci*. 2015; 73: 1–43.
20. Yue C.Y., Tang X.Z., Jiang Z., Yang J., Yu B. Enhanced interphase between epoxy matrix and carbon fiber with carbon nanotube-modified silane coating. *Compos. Sci. Technol*. 2014; 99: 131–40.
21. Bilotti E., Li Y., Huang Z., Zhang H., Wang H., Peijs T., et al. Synergistic effects of spray-coated hybrid carbon nanoparticles for enhanced electrical and thermal surface conductivity of CFRP laminates. *Compos. Part A Appl. Sci. Manuf*. 2017; 105: 9–18.
22. Xiao L., Ao Y., Zhang M., Liu L., Fu J., Li M. Layer-by-Layer electrostatic self-assembly silica/graphene oxide onto carbon fiber surface for enhance interfacial strength of epoxy composites. *Mater. Lett*. 2018; 236: 69–72.
23. Prusty R.K., Rathore D.K., Ray B.C. Water-induced degradations in MWCNT embedded glass fiber/ep-

- oxy composites: An emphasis on aging temperature. *J. Appl. Polym. Sci.* 2018; 135: 45987.
24. Bakis G., Wendel J.F., Zeiler R., Aksit A., Häublein M., Demleitner M., Benra J., Forero S., Schütz W., Altstädt V. Mechanical properties of the carbon nanotube modified epoxy-carbon fiber unidirectional prepreg laminates. *Polymers.* 2021; 13, 770.
25. Moon J.B., Kim M.G., Kim C.G., Bhowmik S. Improvement of tensile properties of CFRP composites under LEO space environment by applying MWNTs and thin-ply. *Compos. Part A.* 2011; 42: 694–701.
26. Firdosh S., Murthy H.N.N., Pal R., Angadi G., Raghavendra N., Krishna M. Durability of GFRP nanocomposites subjected to hygrothermal ageing. *Compos. Part B.* 2015; 69: 443–451.
27. Jeyakumar R., Sampath P.S., Ramamoorthi R., Ramakrishnan T. Structural, morphological and mechanical behaviour of glass fibre reinforced epoxy nanoclay composites. *Int. J. Adv. Manuf. Technol.* 2017; 93: 527–535.
28. Shettar M., Kini U.A., Sharma S., Hiremath P., Gowrishankar M.C. Hygrothermal chamber aging effect on mechanical behavior and morphology of glass fiber-epoxy-nanoclay composites. *Mater. Res. Exp.* 2020; 7: 015318.
29. Rodriguez-Gonzalez J.A., Rubio-Gonzalez C., Ku-Herrera J.D., Ramos-Galicia L., Velasco-Santos C. Effect of seawater ageing on interlaminar fracture toughness of carbon fiber/epoxy composites containing carbon nanofillers. *J. Reinf. Plast. Compos.* 2018; 1: 1346–1359.
30. Kattaguri R., Fulmali A.O., Prusty R.K., Ray B.C. Effects of acid, alkaline, and seawater aging on the mechanical and thermomechanical properties of glass fiber/epoxy composites filled with carbon nanofibers. *J. Appl. Polym. Sci.* 2020; 12: 48434.
31. Ibrahim M.H.I., Hassan M.Z., Ibrahim I., Rashidi A.H.M., Nor S.F.M., Daud, M.Y.M. Seawater infiltration effect on thermal degradation of fiber reinforced epoxy composites. *AIP Conf. Proc.* 2018; 1958: 020006.
32. PN-EN ISO 527-3:2019-01, *Plastics - Determination of tensile properties - Part 3: Test conditions for films and plates.* Published date: 01-19-2019, Publisher: Polish Committee for Standardization.
33. ASTM D2344/D2344M-16 (2016) Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates.