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Research Article

Influence of seawater on mechanical properties of SiO₂-epoxy polymer nanocomposites

Halil Burak Kaybal^{*a,1}, Hasan Ulus^{b,2}, Ahmet Caner Tatar^{c,3}, Okan Demir^{d,3}, Ahmet Avci^{e,4}

¹Department of Mechanical Engineering, Amasya University, Amasya, Turkey.

²Huglu Vocational High School, Selcuk University, Konya, Turkey

³Department of Mechanical Engineering, Konya Technical University, Konya, Turkey

⁴Department of Biomedical Engineering, Necmettin Erbakan University, Konya, Turkey

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Abstract

In this study, dispersion of nano SiO₂ in epoxy composite aged in seawater and its effect on mechanical properties were studied. The SiO₂-epoxy polymer nanocomposite materials were kept in seawater for a total of six months to be tested every two months. Tensile and bending tests were applied to composite materials as a mechanical test. According to the mechanical test results, there was less decrease in strength in SiO₂-epoxy polymer nanocomposite material compared to unmodified material. In usage of seawater, the mechanical properties were observed to be the best in 3 % added SiO₂-epoxy nanocomposite material.

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1. Introduction

Epoxy resins are thermoset materials widely used (used widely) in structural and composite materials due to their properties such as high strength, low shrinkage, effective electrical insulation, excellent adhesion, chemical and solvent resistance, low toxicity and low cost. Moreover, it has high hardness, heat and wear resistance (1-3). Also, epoxy resins are generally used as coatings, casting materials, binders and adhesives application (4). The use of nanoparticles is a common method used to improve the strength of epoxy resins. Nanoparticles can enhance interfacial area between fillers and polymer (5). Thus, an increment in performance on the properties of epoxy resin is observed (5, 6). In the literature, boron nitride, CNT (7), nano clay (8), silica (9), graphene (10), nano-Al₂O₃, nano-SiO₂, nano-CaCO₃ (11-16) nanoparticles are commonly used to improve composite material properties. For instance, Zhai et al. improved adhesion properties with 2 wt % of nano-Al₂O₃ in epoxy matrix (11). Bauer et al observed that the epoxy's glass transition temperature and viscoelastic properties changed with the addition of nano-sized silica, alumina and titania (12). Zhang et al. introduced different rates of Nano SiO₂ to the epoxy polymer. They increased the toughness of the Epoxy/ SiO₂ composite as a result of impact test (13). Suraj and Raman investigated the effect of nano and micro sized aluminum

*Corresponding author: hburak@amasya.edu.tr

^a orcid.org/0000-0002-2312-7106; ^b orcid.org/0000-0001-8591-8993; ^c orcid.org/0000-0003-4470-7801;

^d orcid.org/0000-0001-9411-775X; ^e orcid.org/0000-0003-3434-1711

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particles in epoxy polymer on fracture toughness. They found that enhancement on (of) fracture toughness and highest values for increase in fracture toughness of epoxy is found for addition of 20 -100 nm aluminum particles (14). Park and Jana achieved to increase the tensile and impact strength of composite materials with nano clay reinforcement (17). It is known that polymeric resins can be influenced by water in marine applications. The interface of filler-polymer or fiber-polymer may weaken when the resin absorbs water (18). Wei et al. examined the effect of seawater on the tensile and bending strength of fiber reinforced composite materials. They observed that these strengths decreased with the effect of seawater (19). Li and Weitsman concentrated on seawater induced damage in composite sandwich structures, gaining weight, expansion strain, and on possible deterioration in the properties of the materials (20). Davies et al. studied on four different thermoset resins and their glass fiber reinforced composite under three immersion conditions (21). In other studies conducted in the literature, it is stated that moisture and salt water absorption directly affects the mechanical, physical and chemical properties of composite materials (20-23).

In this research, the influence of seawater aging on the mechanical performance of epoxy nanocomposites filled with different proportions from 1 wt % to 5 wt % of nano-SiO₂ have been studied for marine application. The nanocomposites were submerged in seawater for up to six months at room temperature for the first time in the literature. The specimens were mechanically examined every two months. Tensile and bending tests were evaluated as mechanical properties according to the related standard methods. The experimental results illustrate that the SiO₂ nanoparticles left a positive influence on the mechanical performance of the nanocomposites in the sea water conditioning.

2. Material and Methods

2.1. Material

The diglycidylether of bisphenol-A (DGEBA) epoxy resin (L160 code) and suitable curing agent (H160 code) supplied by Momentive Hexion Inc. as the commercially available. The SiO₂ nanoparticles, have a specific surface area of 650 m²/g, was purchased from MKnano Canada Company and average primary particle diameter of 15 nm. It can be seen powder SiO₂ in Fig 1.

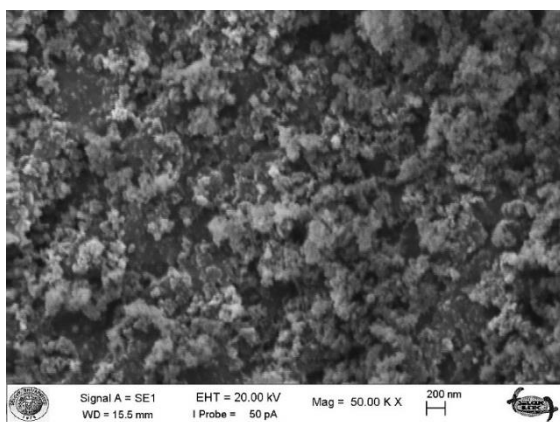


Fig. 1. SEM image of powder SiO₂

2.2. Production of Composites

Nanocomposite materials were manufactured at rates of 1 % to 5 % nano- SiO₂. These ratio values are taken in accordance with the literature (13). Epoxy and powdered nano-SiO₂ were mixed with the ultrasonicator for 30 minutes in the ice bath. After dispersing process curing agent was added in to epoxy and the mixture was degassed at 25 °C and 0.6 bar at approximately 20 min. Steel molds are covered with mold release in Fig 2(a). The epoxy mixture was cast into steel molds. Curing was performed firstly at 80 °C for approximately 1 h, then at 120 °C at approximately 2 h. After that it was slowly cooled to room temperature in the oven. Subsequently, the specimens were removed from the steel molds in Fig 2(b). All samples conventionally polished with SiC sandpapers with grit numbers of 800 to minimize effect stress concentration caused by sharp edges. The produced composite materials were transported to seawater environment and kept in seawater for 6 months.



Fig. 2 a) Steel mold b) Test specimens

2.3. Test procedure

Bending and tensile tests were performed as a mechanical test in the study. The ASTM D7264/ D7264M-07 standards were used for the bending test and the ASTM D4762 - 11a standards for the tensile test, respectively. The specimens were tested every two months. Shimadzu test machine which has 1 kN load cell was used for mechanical test. Tensile tests were carried out with 2 mm·min⁻¹ tensile speed and bending tests were performed under 1 mm·min⁻¹.

3. Results and Discussions

In a previous study, we conducted that stress-displacement curves of different proportions of nano SiO₂ containing epoxy composites are shown for dry conditions in Fig. 3. It can be seen highest enhancement of the tensile strength and bending force is achieved with the 3 wt. nano % SiO₂ adding in Fig. 3 (a) and (b), respectively. Furthermore, mechanical properties of 1 wt. % and 2 wt. % epoxy/SiO₂ added nanocomposite are also increased. However, these figures shows that the tensile and bending properties are getting worse at 4 and 5 wt. % nano SiO₂ addition. We know that tensile properties decrease occurs due to the agglomerations of nano SiO₂ (24). Then, the composite specimens, aged under sea water condition, were tested every two months. Fig. 4 illustrated that curves of tensile and bending tests for SiO₂/Epoxy nanocomposite in seawater condition. It is clear that the all of composite specimens are negatively affected by sea water when the tensile strength and

bending force are examined. In addition, it is seen that nano reinforced composites are less effected than 0 wt. % epoxy/SiO₂. According to all curves, reinforcement of 3 wt. % SiO₂/Epoxy has better mechanical performance than the other proportions. In the end of 6th month, we did not get any results for bending test, due to excessive displacement in the nanocomposites.

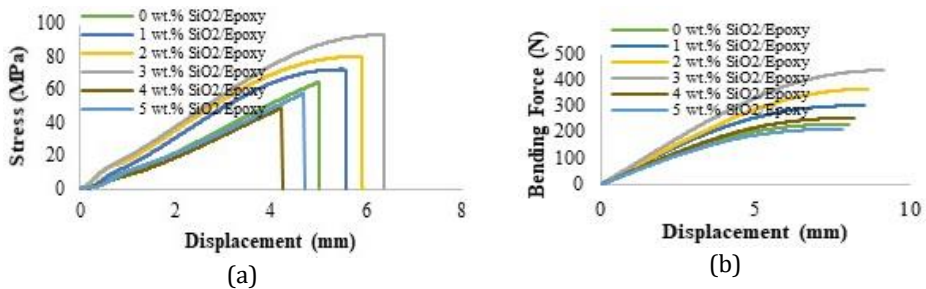


Fig 3. (a) Tensile curve (b) Bending curve in dry condition (24)

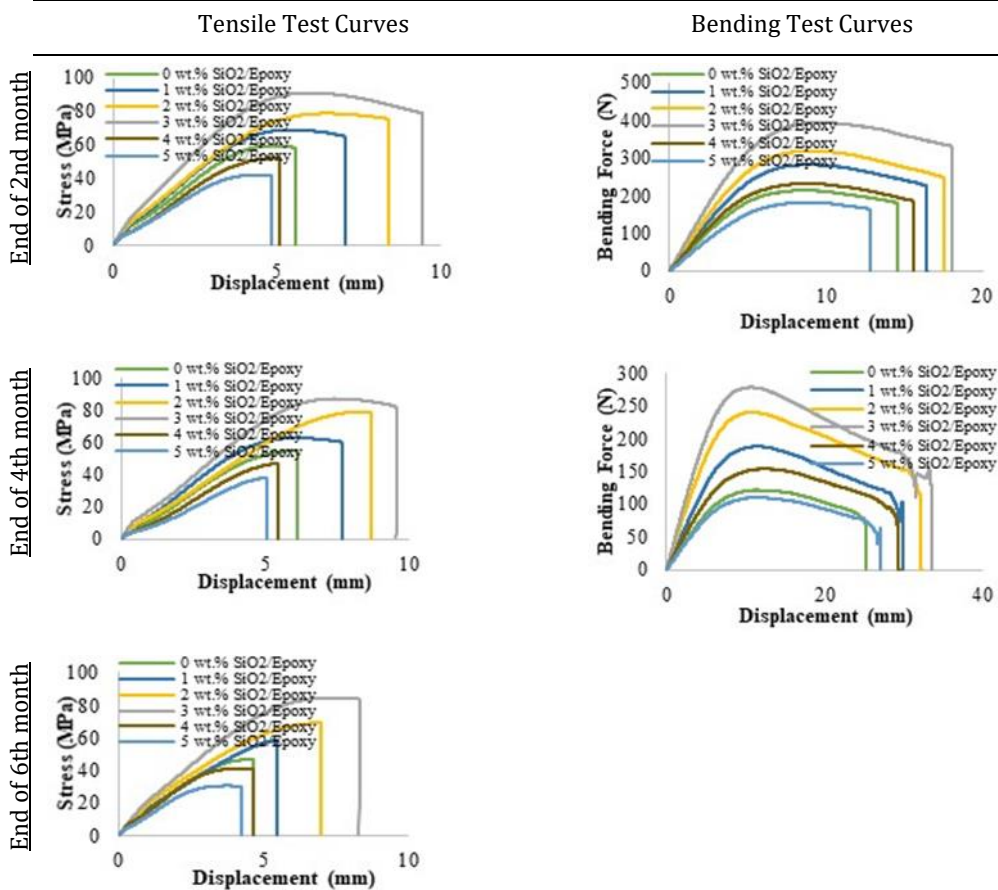


Fig 4. Tensile and Bending Curves in sea water condition for SiO₂/Epoxy nanocomposite

The nano-SiO₂ particles incorporated into the epoxy polymer have caused absorbing or deflection of the cracking in the matrix. The cracks in the epoxy have compelled to break and debonding the nano-SiO₂ particles. Since the composite needs more energy to achieve this event, the tensile strength and bending force values of the nanocomposite specimens are higher than neat composites. Fig. 5 gives an information about toughening mechanisms of nanocomposite materials such as crack deflection and particle debonding. The reduction of tensile strength and bending force in high proportions of nano-SiO₂ such as 4 and 5 wt. % is caused by the agglomeration of the particles. Fig. 6 demonstrates agglomeration of the SiO₂ nanoparticles in epoxy nanocomposites.

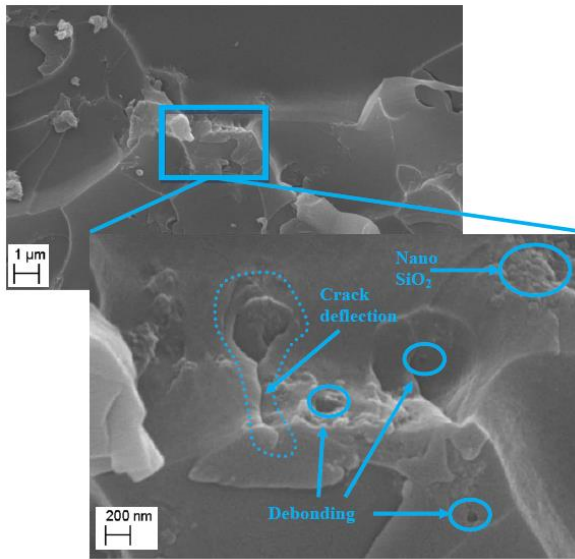


Fig 5. 3 wt. % SiO₂/Epoxy Nanocomposite (24)

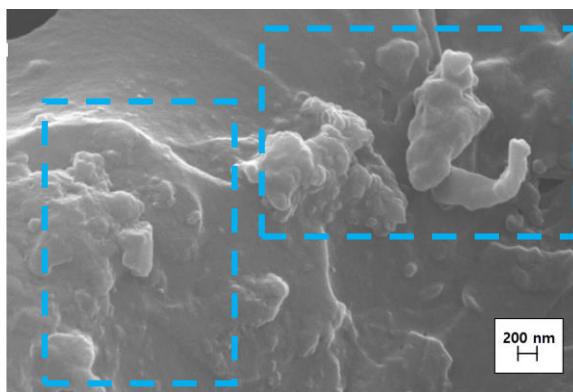


Fig 6. 5 wt. % SiO₂/Epoxy Nanocomposite (24)

Compared to 0 wt. % SiO₂/Epoxy composite, the mechanical properties of 3 wt. % SiO₂/Epoxy nanocomposite are presented in Table 1. Although SiO₂ nanoparticles are enhanced the performance of tensile strength and load bending capacity in dry condition,

the particles cannot be prevented decrement of these mechanical performances after aging due to the detrimental effect of the absorbed seawater. Nevertheless, SiO₂ nanoparticles are succeeded in delaying the damage mechanisms when the numerical results in Table 1 are considered.

Table 1. Results of mechanical test for 0 wt.% and 3 wt.% SiO₂/Epoxy nanocomposite.

Mechanical Properties	Condition				
	Dry	Sea water			Nanocomposites
		2nd	4th	6th	
Tensile Strength (MPa)	65.2	59.4	54.9	46.7	0 wt.% SiO ₂ /Epoxy
	93.9	90.8	87.4	84.4	3 wt.% SiO ₂ /Epoxy
Bending Force (N)	233	213.5	121.2	-	0 wt.% SiO ₂ /Epoxy
	438.5	393.7	277.9	-	3 wt.% SiO ₂ /Epoxy

The mechanical properties of the composite specimens under the seawater effect are reduced in Fig. 3 and Fig. 4. In addition to the reduced load carrying capacities under the influence of seawater, the displacements under stress are increased in both of composites. In composite specimens immersed in seawater, the absorbed water interacts chemically with the epoxy polymer by way of Van der Waals and hydrogen bonds. This chain mobility causes polymerization and reducing mechanical strength for tensile and bending in the composite material (25). The minimum reducing mechanical strength is obtained for nanocomposite specimens. The fracture surfaces of tested specimens were observed by Scanning Electron Microscope (SEM) for 0 wt. % epoxy/SiO₂ composite and 3 wt. % epoxy/SiO₂ nanocomposite in Fig. 7. Polymerization and degradation areas of 0 wt. % epoxy/ SiO₂ composite in seawater condition are shown in Fig. 7(a). Besides, strengthening mechanism of the 3 wt. % epoxy/ SiO₂ nanocomposite are seen in Fig. 7(b). Larger polymerization areas in composite material are seen compared to the nanocomposite material. Nano- SiO₂ particle debonding in fracture surface is ensured that nanocomposite is swallowed more energy and is increased its strength.

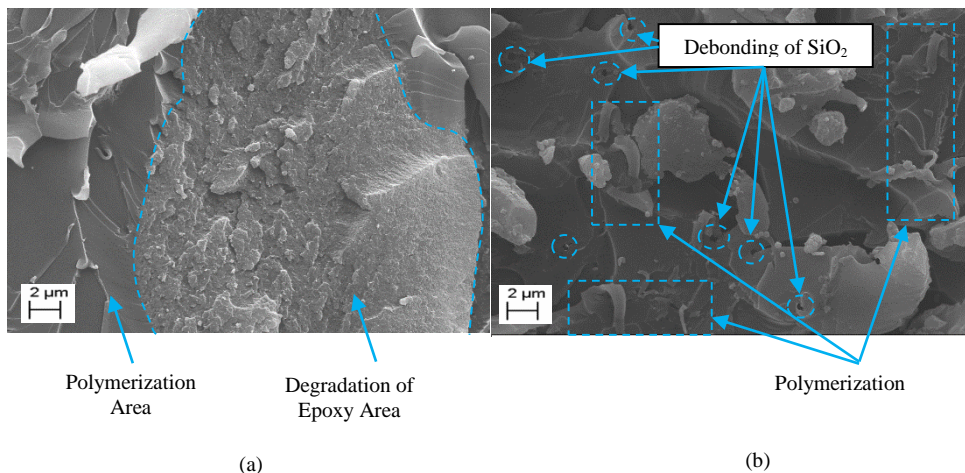


Fig. 7 SEM images of fracture surface (a) 0 wt. % epoxy/SiO₂ composite (b) 3 wt. % epoxy/SiO₂ nanocomposite

3. Conclusion

Consequently, the studies on the mechanical properties show that the reinforcement of SiO₂ nanoparticles in the epoxy matrix polymer has significant positive or negative influences on nanocomposites for both of dry and seawater conditions. From the results of this study, the following conclusions can be drawn:

- High proportions of SiO₂ nanoparticles (e.g. 4-5 wt. %) have shown weak performance in load capacity due to agglomeration of particles.
- The other proportions of SiO₂ nanoparticles in epoxy matrix polymer are demonstrated superior properties in both of condition.
- According to result of mechanical test, sea water absorption is weaken both tensile strength and bending force. But, SiO₂ added nanocomposites are less affected after aging than the others.
- At the end of the sixth month of bending test results, a displacement exceeding the device capacity has occurred.
- The reducing mechanical strength is fewest for 3 wt. % epoxy/SiO₂ in seawater condition.

References

- [1] Kalogerias IM, Roussos M, Christakis I, Spanoudaki A, Pietkiewicz D, Brostow W, et al. Dielectric properties of cured epoxy resin+ poly (ethylene oxide) blends. *Journal of non-crystalline solids*. 2005;351(33-36):2728-34. <https://doi.org/10.1016/j.jnoncrysol.2005.03.066>
- [2] Maity T, Samanta B, Dalai S, Banthia A. Curing study of epoxy resin by new aromatic amine functional curing agents along with mechanical and thermal evaluation. *Materials Science and Engineering: A*. 2007;464(1-2):38-46. <https://doi.org/10.1016/j.msea.2007.01.128>
- [3] Shi H, Liu F, Yang L, Han E. Characterization of protective performance of epoxy reinforced with nanometer-sized TiO₂ and SiO₂. *Progress in Organic Coatings*. 2008;62(4):359-68. <https://doi.org/10.1016/j.porgcoat.2007.11.003>
- [4] Boyle MA, Martin CJ, Neuner JD. Epoxy resins. *ASM Handbook Volume 21 Composites*. 2001:78-89.
- [5] Zheng Y, Zheng Y, Ning R. Effects of nanoparticles SiO₂ on the performance of nanocomposites. *Materials Letters*. 2003;57(19):2940-4. [https://doi.org/10.1016/S0167-577X\(02\)01401-5](https://doi.org/10.1016/S0167-577X(02)01401-5)
- [6] Song G. Polymeric nano-metered composites. *Mater Rep*. 1996;4(1):57-60.
- [7] Ulus H, Şahin ÖS, Avcı A. Enhancement of flexural and shear properties of carbon fiber/epoxy hybrid nanocomposites by boron nitride nano particles and carbon nano tube modification. *Fibers and Polymers*. 2015;16(12):2627-35. <https://doi.org/10.1007/s12221-015-5603-4>
- [8] Wang L, Wang K, Chen L, Zhang Y, He C. Preparation, morphology and thermal/mechanical properties of epoxy/nanoclay composite. *Composites Part A: Applied Science and Manufacturing*. 2006;37(11):1890-6. <https://doi.org/10.1016/j.compositesa.2005.12.020>
- [9] Liu Y-L, Hsu C-Y, Wei W-L, Jeng R-J. Preparation and thermal properties of epoxy-silica nanocomposites from nanoscale colloidal silica. *Polymer*. 2003;44(18):5159-67. [https://doi.org/10.1016/S0032-3861\(03\)00519-6](https://doi.org/10.1016/S0032-3861(03)00519-6)

- [10] Rafiee MA, Rafiee J, Srivastava I, Wang Z, Song H, Yu ZZ, et al. Fracture and fatigue in graphene nanocomposites. *Small*. 2010;6(2):179-83. <https://doi.org/10.1002/sml.200901480>
- [11] Zhai L, Ling G, Li J, Wang Y. The effect of nanoparticles on the adhesion of epoxy adhesive. *Materials Letters*. 2006;60(25-26):3031-3. <https://doi.org/10.1016/j.matlet.2006.02.038>
- [12] Bauer F, Decker U, Ernst H, Findeisen M, Langguth H, Mehnert R, et al. Functionalized inorganic/organic nanocomposites as new basic raw materials for adhesives and sealants Part 2. *International journal of adhesion and adhesives*. 2006;26(7):567-70. <https://doi.org/10.1016/j.ijadhadh.2005.11.001>
- [13] Zhang X, Xu W, Xia X, Zhang Z, Yu R. Toughening of cycloaliphatic epoxy resin by nanosize silicon dioxide. *Materials Letters*. 2006;60(28):3319-23. <https://doi.org/10.1016/j.matlet.2006.04.023>
- [14] Zunjarrao SC, Singh RP. Characterization of the fracture behavior of epoxy reinforced with nanometer and micrometer sized aluminum particles. *Composites Science and Technology*. 2006;66(13):2296-305. <https://doi.org/10.1016/j.compscitech.2005.12.001>
- [15] Yu H, Wang L, Shi Q, Jiang G, Zhao Z, Dong X. Study on nano-CaCO₃ modified epoxy powder coatings. *Progress in Organic Coatings*. 2006;55(3):296-300. <https://doi.org/10.1016/j.porgcoat.2006.01.007>
- [16] Li H, Zhang Z, Ma X, Hu M, Wang X, Fan P. Synthesis and characterization of epoxy resin modified with nano-SiO₂ and γ -glycidoxypropyltrimethoxy silane. *Surface and Coatings Technology*. 2007;201(9-11):5269-72. <https://doi.org/10.1016/j.surfcoat.2006.07.143>
- [17] Park JH, Jana SC. The relationship between nano-and micro-structures and mechanical properties in PMMA-epoxy-nanoclay composites. *Polymer*. 2003;44(7):2091-100. [https://doi.org/10.1016/S0032-3861\(03\)00075-2](https://doi.org/10.1016/S0032-3861(03)00075-2)
- [18] Silva R, Aquino E, Rodrigues L, Barros A. Curaua/glass hybrid composite: the effect of water aging on the mechanical properties. *Journal of reinforced plastics and composites*. 2009;28(15):1857-68. <https://doi.org/10.1177/0731684408090373>
- [19] Wei B, Cao H, Song S. Degradation of basalt fibre and glass fibre/epoxy resin composites in seawater. *Corrosion Science*. 2011;53(1):426-31. <https://doi.org/10.1016/j.corsci.2010.09.053>
- [20] Li X, Weitsman YJ. Sea-water effects on foam-cored composite sandwich lay-ups. *Composites Part B: Engineering*. 2004;35(6-8):451-9. <https://doi.org/10.1016/j.compositesb.2004.04.012>
- [21] Davies P, Mazeas F, Casari P. Sea water aging of glass reinforced composites: shear behaviour and damage modelling. *Journal of composite materials*. 2001;35(15):1343-72. <https://doi.org/10.1106/MNBC-81UB-NF5H-P3ML>
- [22] Marcovich NE, Reboredo MM, Aranguren MI. Dependence of the mechanical properties of woodflour-polymer composites on the moisture content. *Journal of Applied Polymer Science*. 1998;68(13):2069-76. [https://doi.org/10.1002/\(SICI\)1097-4628\(19980627\)68:13<2069::AID-APP2>3.0.CO;2-A](https://doi.org/10.1002/(SICI)1097-4628(19980627)68:13<2069::AID-APP2>3.0.CO;2-A)
- [23] Adams R, Singh M. The effect of immersion in sea water on the dynamic properties of fibre-reinforced flexibilised epoxy composites. *Compos Struct*. 1995;31(2):119-27. [https://doi.org/10.1016/0263-8223\(95\)00007-0](https://doi.org/10.1016/0263-8223(95)00007-0)
- [24] Kaybal HB, Ulus H, Demir O, Tatar AC, Avci A. investigations on the mechanical properties of the nano sio₂ epoxy nanocomposite. *Applied Engineering Letters*. 2017, 2(4); 121-124.
- [25] Prolongo S, Gude M, Urena A. Water uptake of epoxy composites reinforced with carbon nanofillers. *Composites Part A: Applied Science and Manufacturing*. 2012;43(12):2169-75. <https://doi.org/10.1016/j.compositesa.2012.07.014>