Bitlis Eren Üniversitesi Fen Bilimleri Dergisi
BİTLİS EREN UNIVERSITY JOURNAL OF SCIENCE
ISSN: 2147-3129/e-ISSN: 2147-3188
VOLUME: 11 NO: 3 PAGE: 751-758 YEAR: 2022
DOI: 10.17798/bitlisfen.1076888

Effect of Silane-Coated SiO_2 Nanoparticles on the Hardness Values of Glass FRP Composites

Çağrı UZAY[1*], M. Safa KAMER[1]

[1]*Kahramanmaraş Sütçü İmam University, Dept. of Mechanical Engineering, Kahramanmaraş, Turkey (ORCID: 0000-0002-7713-8951) (ORCID: 0000-0003-3852-1031)*

Keywords: Nanoparticle, Silane-coated SiO_2, Fiber-reinforced polymer composite, Microhardness, Microstructure.

Abstract

In this study, silane-coated SiO_2 nanoparticles (as-received) were used as secondary reinforcement for glass fiber-reinforced polymer (FRP) composites, and the microhardness values of the developed composites were investigated. The nanoparticles were dispersed within the polymer epoxy at 1.5 and 3 wt.% ratios, respectively. Two different types of silane coating were used that were KH550 and KH570. The mixture of the epoxy resin and nanoparticles were subjected to ultrasonic homogenization to achieve a fine dispersibility of the SiO_2 nanoparticles. Then the matrix was prepared with a suitable hardener at a weight ratio of 100:25. The strengthened polymer matrix was reinforced by woven glass fiber fabrics (primary reinforcing element). The vacuum bag method was applied to produce silane-coated nano SiO_2 filled glass FRP composites. A digital microhardness testing device was used to determine the Vickers hardness values. While the pure glass/epoxy composite has resulted in a hardness of 20.69 HV, the maximum hardness value was recorded as 36.56 HV and it was obtained with 3 wt.% KH550-SiO_2 filled glass/epoxy. The incorporation of silane-coated SiO_2 nanoparticles has provided dramatic enhancements in terms of microhardness, approximately from 28 to 77%. The microscopic examination was also conducted via an optical microscope and the images were found helpful to explain the test results. Therefore, the findings of this study have shown that silane-coated nano SiO_2 filler can be used as secondary reinforcement where high hardness and better wear resistance are desired for glass/epoxy composite applications.

1. Introduction

Although the fiber-reinforced polymer (FRP) composites offer lightness, high strength, and stiffness, particularly for the weight-critical applications in automotive and aerospace, they still have some drawbacks such as delamination, sudden and brittle fracture [1]. The main reason could be the poor interfacial adhesion of the fiber and the matrix. Therefore, nano and microparticles, in very low contents, have been used as the reinforcing elements within the polymer matrix to overcome the FRPC's limitations and leading to obtaining better interfacial strength and so the high mechanical properties [2-5]. Reinforcing polymers with nano or microparticles is called the matrix toughening method [6, 7]. The mechanical, tribological, thermal, and dielectric properties could be improved with that method. The most commonly used particles that acted as filler material are titanium dioxide (TiO_2), silicon carbide (SiC), silica (SiO_2), boron carbide (B_4C), carbon nanotube (CNT), graphene oxide (GO), boron nitride (BN) [8-11].

The particle effects on the mechanical properties in terms of tensile, flexural and impact have highly been studied by many researchers [12-17]. However, the research on hardness instrumentation, wear resistance and tribology has been limited. Radhwan et al. [1] investigated the Vickers hardness values of the aluminum (Al) filled

*Corresponding author: cagriuzay@ksu.edu.tr
Received: 21.02.2022, Accepted: 07.07.2022

epoxy composites depending upon the particle content, and they found that 10% addition of filler yielded 14.5 gf/μm^2 hardness, whereas 40% addition of filler yielded 32.7 gf/μm^2 hardness value. The improvement was slowed down after 20% Al addition. Atiqah et al. [18] investigated the effects of honeycomb natural fiber addition into the epoxy polymer composite based on the Brinell hardness instrumentation. Except for 9 wt.% addition of fiber elements, the hardness values were reported in a decreasing trend for the additions of 3.wt%, 6 wt.%, and 12 wt.%, respectively. Reddy et al. [19] used tungsten carbide (WC) nanoparticles at weight ratios of 1, 2, 3, and 4% to reinforce the epoxy matrix. From 1 to 2 wt.% addition of WC nanoparticles increased the Vickers hardness value, but after 2 wt.%, the hardness values decreased. The reduction was attributed to the poor adhesion and agglomeration of the particles at relatively higher filler contents

The nano SiO_2 particles are inorganic and have a widespread usage area due to their low cost, availability, high surface area, heat resistance and insulative features [5, 14, 20, 21]. However, the use of pure nano SiO_2 particles may cause agglomeration easily, even at very low contents. Because the particles highly tend to react with water [17]. Therefore, silane coupling agents are generally used for surface treatments of the SiO_2 nanoparticles to avoid agglomeration. The synergistic effect of silanization and nano SiO_2 reinforcement has led to obtaining better mechanical and thermal properties [17, 22]. On the other hand, silanization is performed as an additional process for treating SiO_2 surfaces.

When the literature studies were examined, it can be inferred that the filler type, size, and content affect the polymer composites' hardness. In this study, silane-coated nano SiO_2 particles were supplied as received, and then they were used as a secondary reinforcement to modify the epoxy. The modified epoxy was reinforced by glass fibers. The developed nanofiller added glass FRP composites with different silane types (KH550 and KH570), and filler contents (1.5 and 3 wt.%) were subjected to microhardness instrumentation to reveal the effects of filler type and content on the hardness values. The microscopic examinations also confirmed that the composite parameters have significantly affected the results.

2. Material and Method

2.1. Materials

This study used glass fiber fabrics and epoxy resin set to manufacture glass fiber-reinforced polymer (FRP) composites. In addition, silane-coated SiO_2 nanoparticles (as received) were used as secondary reinforcement for the FRP composites. The glass fiber fabrics and epoxy resin set were supplied from Dost Kimya Inc. (Turkey), whereas the nanoparticles were supplied from Nano Grafi Inc. (Turkey). The materials' properties based on the manufacturers' technical data sheet are given in Tables 1 - 3. As seen in Table 3, two different types of silane coating were used that are KH550 (γ -aminopropyl-triethoxy silane) and KH570 (γ -methacryloxy propyl trimethoxy silane).

Table 1. Physical and mechanical properties of glass fibers

Property	Value
Fiber description	Plain woven fabric, 3K, 200 g/m^2
Density (kg/m^3)	2560
Tensile strength (MPa)	3400
Tensile modulus (GPa)	73
Tensile strain (%)	2.75

Table 2. Physical and mechanical properties of polymer matrix

Property	Value
Constituents	Epoxy resin (L160) + hardener (H160) (mixed at a weight ratio of 100:25)
Density (kg/m^3)	1180-1200
Tensile strength (MPa)	70-80
Tensile modulus (GPa)	3.2-3.5
Tensile strain (%)	5-6.5
Impact strength (kJ/m^2)	40-50
Compression strength (MPa)	80-100

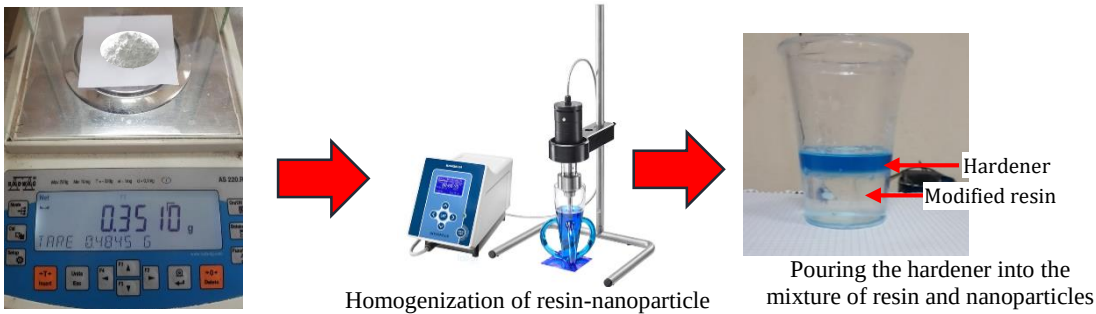
Table 3. Physical properties of silane-coated SiO_2 nanoparticles

SiO_2 nanoparticles	
Type	Nanoparticle
Particle size (nm)	18-35
Specific surface area (m^2/gr)	150-550
Amount of silane coating (%)	3-4
Purity of KH550-coated SiO_2 nanoparticles (%)	> 96.3
Purity of KH570-coated SiO_2 nanoparticles (%)	> 95.9

2.2. Silane-Coated Nano SiO_2 Filled Glass FRP Composite Manufacturing

The manufacturing of silane-coated nano SiO_2 filled glass FRP composites was carried out in two stages. Firstly, the polymer matrix was modified as follows;

- The nanoparticles were weighed according to the predetermined percent ratios (1.5 and 3 wt.%) of the matrix (Figure 1a),
- The nanoparticles were dispersed into the epoxy resin, and the mixture was subjected to homogenization by using an ultrasonic homogenizer (Figure 1b),
- A suitable hardener at a predetermined ratio was poured into the mixture (Figure 1c), and it was stirred manually.



Determination of the weight fraction silane-coated SiO_2 nanoparticles (a)

Homogenization of resin-nanoparticle mixture using ultrasonic homogenizer (b)

Pouring the hardener into the mixture of resin and nanoparticles (c)

Figure 1. Polymer matrix modification process

Four different modified matrix materials were prepared according to the types of silane coating and nanoparticle percent ratios. Then, the modified matrix materials were used to make glass fiber-reinforced laminates. The manufacturing process was based on the vacuum bagging method, as schematically presented in Figure 2. The lamination was conducted on an open mold, a tempered glass. The matrix impregnation of the glass fiber fabrics was performed by hand lay-up. A total of 21 glass fiber fabrics were stacked to achieve approximately 4 mm thickness of the composite structure. Then, a release film, a vacuum breather, and a vacuum bag were placed, respectively. Lastly, the composite system was sealed with sealant tape, and it was left for curing. The curing process was carried out at ambient temperature under a vacuum for 24 hours.

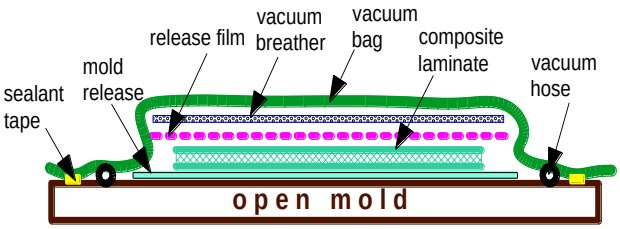


Figure 2. Vacuum bagging method for the lamination process

2.3. Hardness Test

Microhardness values of the produced composite materials were measured by applying the Vickers test method. In this method, the force is applied for 15 seconds by a diamond indenter, which inserts a pyramid form after the penetration of the indenter. Figure 3 shows the digital microhardness testing device used in the present study. Before the hardness measurements, the surface of the specimens was grounded with a 1200 grit size emery paper.

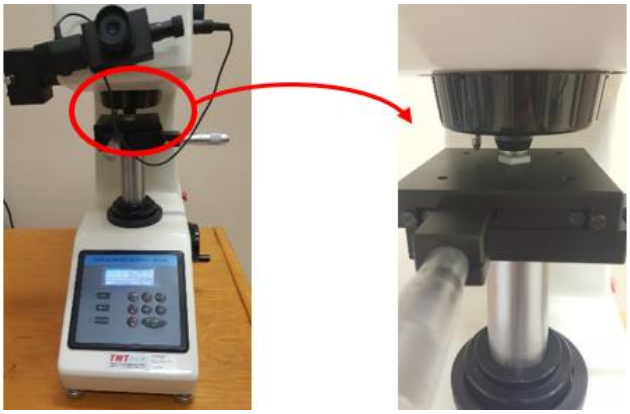


Figure 3. Digital microhardness testing device used in the present study

The Vickers hardness value (HV) can be calculated according to Equation (1) [23]. In the equation, F (N) is the applied force, and d (mm) is the arithmetic average of two diagonals of the pyramid. Both the F values of 1.962 and 2.942 N were used during the instrumentation.

$$HV \cong \frac{1.854 \times F}{d^2} \qquad (1)$$

Figure 4 shows an example of how the HV hardness value is determined. The microstructure of the composite specimen was examined with a microscope after the penetration of the indenter. Then

the diagonals of the pyramid form were measured. The recorded lengths of the diagonals were in μm. The digital microhardness testing device then determined the HV hardness value based on Equation (1).

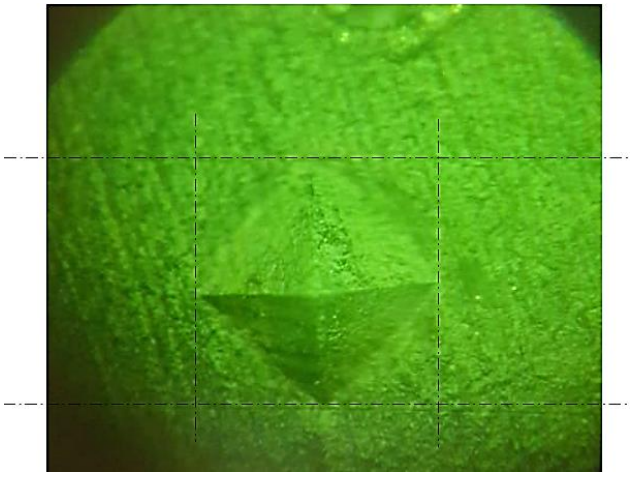


Figure 4. The examination of the pyramid's diagonals

3. Results and Discussion

3.1. Hardness Measurements

Pure glass FRP composite was firstly subjected to hardness measurement under two different loads that were 1.962 and 2.942 N. The reason to apply two different loads was to see the consistency of the results under different loads. Table 4 shows the hardness values of pure glass FRP composite. As seen in Table 4, the measurements yielded a hardness value of 20.997 and 21.177 HV, respectively. The difference between the two values is below 1%, and the standard deviations were found to be low and similar. Also, Singh et al. [24] found the glass FRP composite's HV hardness value as approximately 21.5, which is very close to the findings in the present study. Therefore, the microhardness measurements of the silane-coated nano SiO_2 filled glass FRP composites were carried out by applying 2.942 N. The results are given in Table 5.

Table 4. HV hardness values of the pure glass FRP composite

Applied load	Measurements			Arithmetic Average	Standard deviation
	1	2	3		
1.962 N	22.6	20.02	20.37	20.997	1.142
2.942 N	19.63	22.38	21.52	21.177	1.149

Table 5. HV hardness values of the silane-coated nano SiO_2 filled glass FRP composites

Composites	Measurements			Arithmetic Average	Standard deviation
	1	2	3		
1.5 wt.% KH550/SiO_2 - G/E	28.06	29.03	30.08	29.057	0.825
3 wt.% KH550/SiO_2 - G/E	37.00	35.08	37.61	36.563	1.078
1.5 wt.% KH570/SiO_2 - G/E	26.49	25.64	27.47	26.533	0.747
3 wt.% KH570/SiO_2 - G/E	30.39	30.53	31.69	30.870	0.582

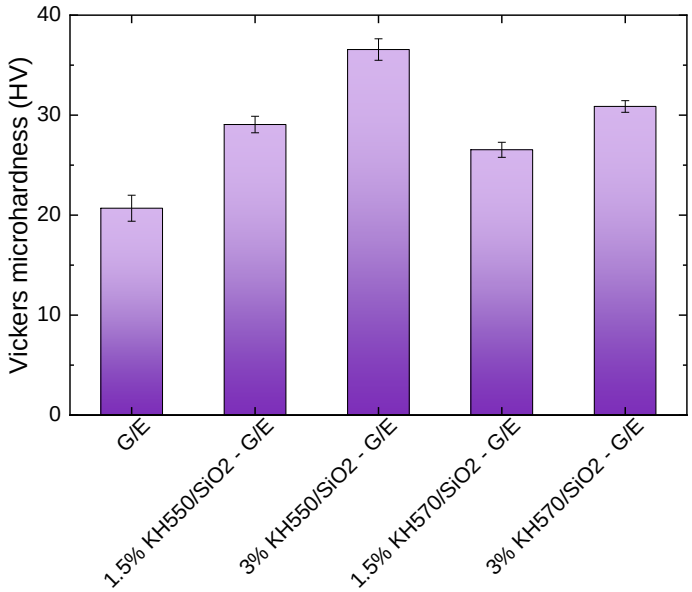
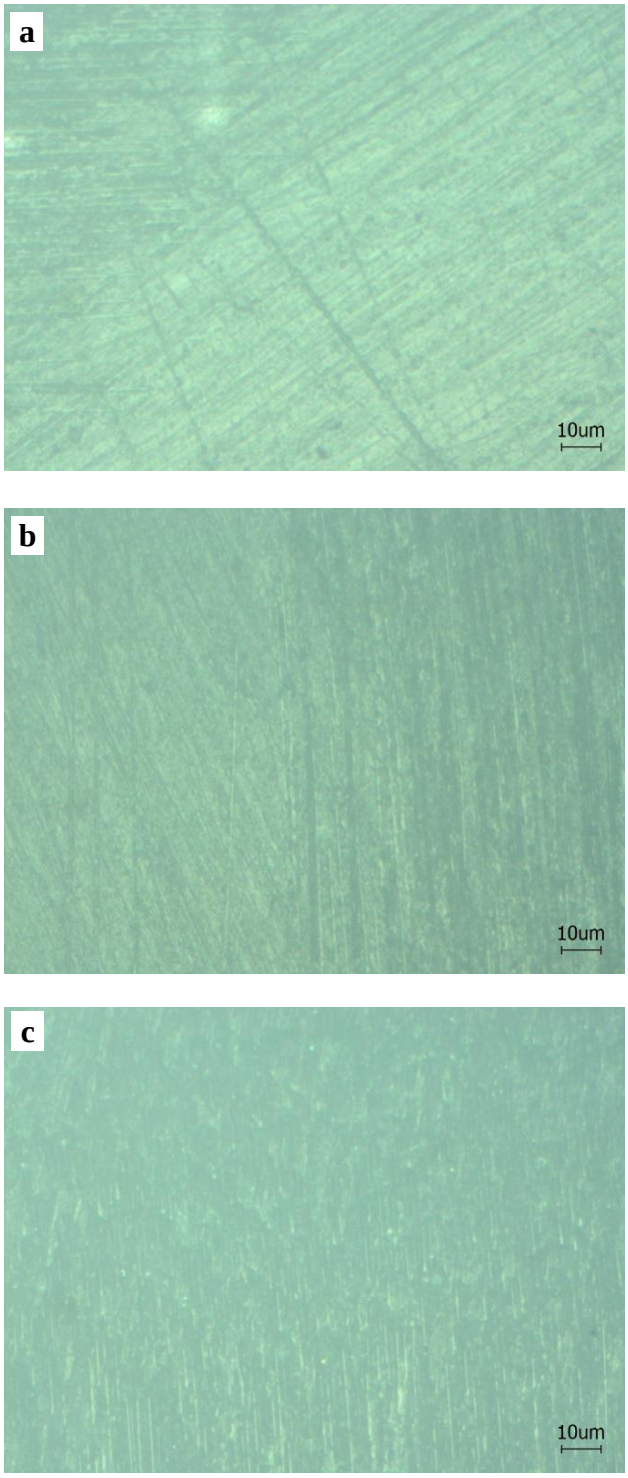


Figure 5. Comparison of Vickers microhardness values of pure and silane-coated SiO_2 filled glass FRP composites

As seen in Table 5, HV hardness values of the silane-coated nano SiO2 filled glass FRP composites were determined higher than that of pure glass FRP composite. This is because the presence of the nanoparticles did not allow the indenter to penetrate deeper [25]. However, the increments vary depending on both silane coating and filler percent within the polymer matrix. The KH550 silane coating has provided 37.21 (at 1.5 wt.% addition of SiO_2) and 72.66% (at 3 wt.% addition of SiO_2) higher HV hardness value, respectively, when compared to the results of pure glass FRP composite. On the other hand, KH570 silane coating has provided 25.30 (at 1.5 wt.% addition of SiO_2) and 45.77% (at 3 wt.% addition of SiO_2) higher HV hardness value, respectively. Therefore, it can be inferred that the silane type of KH550 has contributed more significant HV values than the KH570 silane coating of SiO_2 nanoparticles. The lower values might be attributed to the relatively poor adhesion bonding between the KH570 coated nanoparticles and the matrix [18]. The comparison of the pure and silane-coated SiO_2 filled glass FRP composites were presented in Figure 5.

3.2. Microstructural Examinations

The microstructural examinations of the pure and silane-coated SiO_2 filled glass FRP composites were carried out by utilizing an optical microscope. Figure 6 shows the microscope images that were magnified by 40X. When the pure glass FRP was examined (Figure 6a), it can be inferred that the surface of the specimen was observed smoother than the others. Also, the wear tracks of the emery paper can easily be seen. In Figure 6b, there is almost no wear track, and relatively fewer wear tracks were observed in Figure 6d, which could explain the higher wear resistance of the composite structures due to the presence of silanized SiO_2 nanoparticles. The surface of the specimens in Figures 6c and 6e were highly wavier due to the higher amount of nanoparticle contents. This is why 3 wt.% addition of nanoparticles has resulted in higher hardness values than that of 1.5 wt.% addition. However, KH550-coated SiO_2 filled glass FRP composite's wavy surface was observed more homogeneous than that of the KH570 coated SiO_2 filled glass FRP composite. The best wear resistance obtained by 3 wt.% KH550/ SiO_2-G/E composite could be due to homogeneous dispersibility and improved integration of the filler and the polymer matrix.



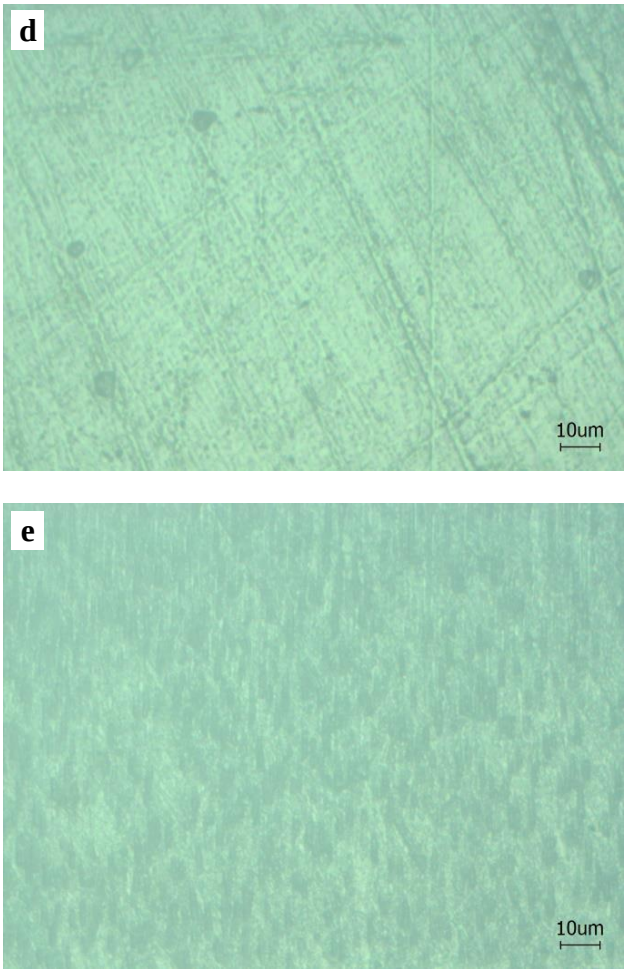


Figure 6. Optical microscope images (40X) of the glass FRP composites; a) pure, b) 1.5 wt.% KH550-SiO_2 filled, c) 3 wt.% KH550-SiO_2 filled, d) 1.5 wt.% KH570-SiO_2 filled, e) 3 wt.% KH570-SiO_2 filled

4. Conclusion

In this study, glass/epoxy composites were successfully strengthened with two different silane-coated SiO_2 nanoparticles that were KH550-coated SiO_2 and KH570-coated SiO_2. The Vickers microhardness measurements have shown that pure glass FRP composite resulted in the lowest hardness value (21.177 HV under 2.942 N). The addition of silane-coated SiO_2 nanoparticles into the polymer matrix considerably improved the hardness of the developed composite structures. The increments have varied according to both silane coatings and nanoparticle percent within the epoxy. Increasing the nanoparticle percent has dramatically enhanced the HV hardness values up to the 72.66%. However, KH550-coated nano SiO_2 filled glass FRP composites have contributed higher hardness values than KH570 coating. This could be attributed to the better integration of SiO_2 nanoparticles and the polymer matrix thanks to the KH550 silane coating. The optical microscope images also confirmed the findings.

The glass fibers offer cost-effective solutions and have widespread application areas such as automotive body parts, ship and boat building, wind turbine blades, and repair and maintenance. Therefore, dispersion of silane-coated SiO_2 nanoparticles at very low ratios into the epoxy improves the wear resistance of the glass/epoxy composites by increasing the structural hardness and can be cost-effectively used for the aforementioned industrial fields.

Acknowledgment

This study was supported by Kahramanmaraş Sütçü İmam University, Scientific Research Projects Coordination Unit under a grant number of 2020/9-32 M.

Authors' Contributions

Ç. Uzay contributed to the planning of the study, literature review, writing, evaluation of the results, and editing. M.S. Kamer carried out the experiments, evaluation of the results, and editing.

Statement of Conflicts of Interest

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The authors declare that this study complies with Research and Publication Ethics.

References

[1] H. Radhwan, S. Sharif, Z. Shayfull, M. A. Suhaimi, M. T. M. Khushairi, and K. Fathullah, "Experimental study mechanical behaviour of epoxy resin composites filled with aluminium particles," *AIP Conference Proceedings*, vol. 2129, no. 1, p. 020157, 2019.

[2] A. Elmarakbi, R. Ciardiello, A. Tridello, F. Innocente, B. Martorana, F. Bertocchi, F. Cristiano, M. Elmarakbi, and G. Belingardi, "Effect of graphene nanoplatelets on the impact response of a carbon fibre reinforced composite", *Mater Today Commun*, vol.25, 2020.

[3] C. Kostagiannakopoulou, X. Tsilimigkra, G. Sotiriadis, and V. Kostopoulos, "Synergy effect of carbon nano-fillers on the fracture toughness of structural composites," (in English), *Compos Part B-Eng*, vol. 129, pp. 18-25, 2017.

[4] S. K. Singh, A. Kumar, and A. Jain, "Mechanical and viscoelastic properties of SiO2/epoxy nanocomposites post-cured at different temperatures," *Plastics, Rubber and Composites*, vol. 50, no. 3, pp. 116-126, 2021.

[5] Z. J. Wu, M. Wang, and Z. Wang, "The gas phase SiO2/epoxy nanocomposites with enhanced mechanical and thermal properties," (in English), *High Perform Polym*, vol. 27, no. 4, pp. 469-475, 2015.

[6] M. Quaresimin, K. Schulte, M. Zappalorto, and S. Chandrasekaran, "Toughening mechanisms in polymer nanocomposites: From experiments to modelling," *Compos Sci Technol*, vol. 123, pp. 187-204, 2016.

[7] S. S. Vinay, M. R. Sanjay, S. Siengchin, and C. V. Venkatesh, "Effect of Al2O3 nanofillers in basalt/epoxy composites: Mechanical and tribological properties," (in English), *Polym Composite*, vol. 42, no. 4, pp. 1727-1740, 2021.

[8] İ. Aktitiz, K. Aydın, and A. Topcu, "Characterization of TiO2 Nanoparticle–Reinforced Polymer Nanocomposite Materials Printed by Stereolithography Method," *Journal of Materials Engineering and Performance*, vol. 30, no. 7, pp. 4975-4980, 2021.

[9] N. Geren, D. C. Acer, C. Uzay, and M. Bayramoglu, "The effect of boron carbide additive on the low-velocity impact properties of low-density foam core composite sandwich structures," *Polym Composite*, vol. 42, no. 4, pp. 2037-2049, 2021.

[10] P. S. Shuttleworth, A. M. Diez-Pascual, C. Marco, and G. Ellis, "Flexible Bionanocomposites from Epoxidized Hemp Seed Oil Thermosetting Resin Reinforced with Halloysite Nanotubes," *J Phys Chem B*, vol. 121, no. 11, pp. 2454-2467, 2017.

[11] J. Y. Zheng *et al.*, "Behavior of epoxy resin filled with nano-SiO2 treated with a Eugenol epoxy silane," *J Appl Polym Sci*, vol. 138, no. 14, 2021.

[12] J. Abenojar, J. Tutor, Y. Ballesteros, J. C. del Real, and M. A. Martinez, "Erosion-wear, mechanical and thermal properties of silica filled epoxy nanocomposites," *Compos Part B-Eng*, vol. 120, pp. 42-53, 2017.

[13] M. Landowski, M. Budzik, and K. Imielinska, "Water absorption and blistering of glass fibre-reinforced polymer marine laminates with nanoparticle-modified coatings," *J Compos Mater*, vol. 48, no. 23, pp. 2805-2813, Sep 2014.

[14] M. Megahed, A. A. Megahed, and M. A. Agwa, "The influence of incorporation of silica and carbon nanoparticles on the mechanical properties of hybrid glass fiber reinforced epoxy," *J Ind Text*, vol. 49, no. 2, pp. 181-199, 2019.

[15] J. C. Santos, L. M. G. Vieira, T. H. Panzera, M. A. Schiavon, A. L. Christoforo, and F. Scarpa, "Hybrid glass fibre reinforced composites with micro and poly-diallyldimethylammonium chloride (PDDA) functionalized nano silica inclusions," *Materials & Design (1980-2015)*, vol. 65, pp. 543-549, 2015.

[16] C. Su, X. Wang, L. N. Ding, and Z. S. Wu, "Enhancement of mechanical behavior of FRP composites modified by silica nanoparticles," *Constr Build Mater*, vol. 262, 2020.

[17] L. H. Wang, C. Tang, X. B. Wang, and W. Zheng, "Molecular dynamics simulation on the thermodynamic properties of insulating paper cellulose modified by silane coupling agent grafted nano-SiO2," *Aip Adv*, vol. 9, no. 12, 2019.

[18] A. Atiqah, M. N. M. Ansari, and L. Premkumar, "Impact and hardness properties of honeycomb natural fibre reinforced epoxy composites," *Materials Today: Proceedings*, vol. 29, pp. 138-142, 2020.

[19] M. Reddy, S. Valasingam, and K. Srinadh, "Micro Hardness and Erosive Wear Behavior of Tungsten Carbide Filled Epoxy Polymer Nano Composites," *International Journal of Mathematical, Engineering and Management Sciences*, vol. 5, pp. 405-415, 2020.

[20] Bagci, H. Imrek, and O. M. Khalfan, "Optimization of Test Parameters That Influence Erosive Wear Behaviors of Glass Fiber-Reinforced Epoxy Composites by Using the Taguchi Method," *J Tribol-T Asme*, vol. 137, no. 1, 2015.

[21] A. K. Pun, Siddhartha, and A. K. Singh, "Thermo-mechanical and Erosion Wear Peculiarity of Hybrid Composites Filled with Micro and Nano Silicon Dioxide Fillers - A Comparative Study," *Silicon-Neth*, vol. 11, no. 4, pp. 1885-1901, 2019.

[22] S. Safi, A. Zadhoush, and M. Ahmadi, "Flexural and Charpy impact behaviour of epoxy/glass fabric treated by nano-SiO2 and silane blend," *Plastics, Rubber and Composites*, vol. 46, no. 7, pp. 314-321, 2017.

[23] G. Vander Voort and G. Lucas, "Microindentation hardness testing," *Metal Progress*, vol. 154, pp. 21-25, 1998.

[24] V. Singh, P. Kumar, and V. K. Srivastava, "Influence of cement particles on the mechanical and buckling behavior of laminated GFRP composites with variation of end conditions of buckling," *Mater Res Express*, vol. 5, no. 6, 2018.

[25] T. Ahmad, R. Ahmad, M. Kamran, B. Wahjoedi, I. Shakoor, F. Hussain, F. Riaz, Z. Jamil, S. Isaac, and Q. Ashraf, "Effect of Thal silica sand nanoparticles and glass fiber reinforcements on epoxy-based hybrid composite," *Iran Polym J*, vol. 24, no. 1, pp. 21-27, 2015.