

Using 3-Glycidoxypropyltrimethoxysilane Functionalized SiO₂ Nanoparticles to Improve Flexural Properties of Glass Fibers/Epoxy Grid-Stiffened Composite Panels

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Abstract—Lightweight and efficient structures have the aim to enhance the efficiency of the components in various industries. Toward this end, composites are one of the most widely used materials because of durability, high strength and modulus, and low weight. One type of the advanced composites is grid-stiffened composite (GSC) structures, which have been extensively considered in aerospace, automotive, and aircraft industries. They are one of the top candidates for replacing some of the traditional components, which are used here. Although there are a good number of published surveys on the design aspects and fabrication of GSC structures, little systematic work has been reported on their material modification to improve their properties, to our knowledge. Matrix modification using nanoparticles is an effective method to enhance the flexural properties of the fibrous composites. In the present study, a silane-coupling agent (3-glycidoxypropyltrimethoxysilane/3-GPTS) was introduced onto the silica (SiO₂) nanoparticle surface and its effects on the three-point flexural response of isogrid E-glass/epoxy composites were assessed. Based on the Fourier Transform Infrared Spectrometer (FTIR) spectra, it was inferred that the 3-GPTS coupling agent was successfully grafted onto the surface of SiO₂ nanoparticles after modification. Flexural test revealed an improvement of 16%, 14%, and 36% in stiffness, maximum load and energy absorption of the isogrid specimen filled with 3 wt.% 3-GPTS/SiO₂ compared to the neat one. It would be worth mentioning that in these structures, considerable energy absorption was observed after the primary failure related to the load peak. In addition, 3-GPTMS functionalization had a positive effect on the flexural behavior of the multiscale isogrid composites. In conclusion, this study suggests that the addition of modified silica nanoparticles is a promising method to improve the flexural properties of the grid-stiffened fibrous composite structures.

Keywords—Isogrid-stiffened composite panels, silica nanoparticles, surface modification, flexural properties.

I. INTRODUCTION

GRID-STIFFENED COMPOSITE (GSC) structures are used in many applications such as in aerospace, automotive, and aircraft components due to their specific characteristics such as high specific strength and stiffness, superior load bearing capacity, and excellent energy absorption capability. They are thin shell structures stiffened

with a network of helical or axial ribs. In these structures, the ribs are accounted as the main load bearing members. Also, the unidirectional nature of the ribs is very efficient because it leads to mass efficiency and very high reliability in these structures [1]. Studies related to the GSC structures have generated vast interest in the past decades. Numerous relevant investigations have attempted to improve the mechanical properties of the GSC structures through optimizing the design parameters such as rib cross section, rib angle, skin thickness, etc. [2], [3].

Because of the widespread usage of the fiber-reinforced polymers (FRPs), numerous research works have been conducted on their mechanical properties. The modification of the FRPs through the addition of nanoparticles can further increase their mechanical responses. This type of materials is called multiscale composites [4]. The multiscale composites often exhibited better mechanical properties compared to the neat fibrous ones. The introduction of nanofillers with micro-fiber reinforcement in a polymeric matrix can be obtained by dispersing the nanofillers in the matrix or reinforcing of fibers through growing of nanofillers on their surfaces [5], [6].

Nanosilica (SiO₂) particles are the most commonly used nanofillers in the fabrication of the nanocomposites due to their superior properties. However, due to very small dimensions and high surface free energy, they tend to be agglomerated in the matrix. Therefore, the final properties of the specimens will be declined. Surface treatment of the nanosilica with coupling agents is one of the best methods to eliminate their negative effects on mechanical response [7], [8].

In the present study, 3-glycidoxypropyltrimethoxysilane (3-GPTMS) was employed to functionalize the nonosilica particles and the effect of adding 3 wt.% nonosilica particles in matrix (with and without surface modification) on three-point flexural response of the E-glass/epoxy iso-GSC panels were assessed. The flexural properties of the specimens including stiffness, maximum load, and energy absorption were reported.

II. EXPERIMENTAL PROCEDURE

A. Materials

Epoxy resin utilized in this study was ML-506 resin (bisphenol-F). The curing agent was HA-11 (polyamine). ML-

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506 epoxy resin and HA-11 polyamine hardener were supplied by Mokarrar Engineering Materials Co., Iran. The spherical silica nanoparticles with a mean diameter of 65 nm (Fig. 1) and purity of more than 95% were provided by US-NANO, USA. In this research, unidirectional E-glass fibers (linear density: 2400 ± 120 g/km) supplied by LINTEX International Co., Ltd, China, were used as the fibrous reinforcement of the ribs. Also, two dimensional plain weave E-glass fibers were used for reinforcing the skin. Surface density of the fabric was 400 gr/m^2 . 3-Glycidoxypropyltrimethoxysilane (3-GPTS) was provided by Merck Chemical Co., Germany.

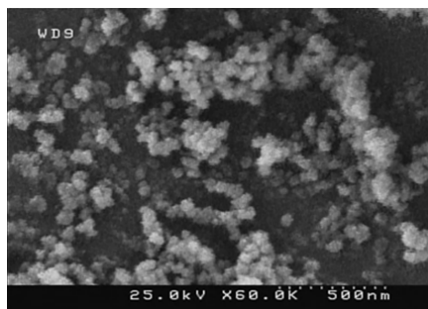


Fig. 1 SEM image of the silica nanoparticles

B. Silica Surface Treatment

2.0 g silica nanoparticles and 2.0 g 3-GPTS were added to 100 ml of 95% ethanol solution. Afterwards, this mixture was stirred for 10 min using a probe sonicator and then refluxed at 70°C for 12 h under constant low-speed magnetic stirring for 100 rpm. The pH value of the mixture was adjusted to be about 4-5, with the aid of 37% concentrated HCl. In the final stage, the nanosilica particles were centrifuged, and the precipitates were washed with ethanol for 3 h to remove the excess silane coupling agent absorbed on the silica surfaces.

C. Specimen Preparation

To fabricate the multiscale isogrid composites, the epoxy/silica mixture were first prepared. In all cases, the following procedure was conducted: At first, 3 wt.% nanosilica particles (treated or non-treated) was added to the epoxy resin. The mixture with adding acetone (100:15 by weight) was stirred by a high-speed mechanical stirrer (SDS-11D, Fintek Co., Korea) for 20 min at 2000 rpm. Then it was dispersed by a 14-mm-diameter probe sonicator (Ultrasonic homogenizer 400 W, 24 kHz, FAPAN Co., Ltd., Iran) for 90 min. After degasification, stoichiometry ratio of curing agent was added and the mixture was stirred manually for 5 min. Then it was quickly employed to fabricate the multiscale GSC structures. The specimens were manufactured using a manual filament winding method as shown in Fig. 2. Unidirectional E-glass fiber rovings were impregnated with the epoxy resin that modified with non-treated or silanized silica nanoparticles and then laid up into grooves of silicone mold layer by layer to form the ribs of grid structures (Fig. 2 (a)). In the next step, laying up the skin using 4 layers of E-glass woven fabrics was conducted (Fig. 2 (b)). The skin thickness of all the specimens was 1.8 mm. After completion of the manufacturing process, 3

h at room temperature was required until curing process of resin was performed. In order to conduct the ultimate curing and to achieve the maximum strength, the specimens were tested after 7 days of holding at room temperature. The specimens were characterized by length of 300 mm, width of 125 mm and thickness of 7.8 mm. The cross-section area of all ribs was $6 \times 6 \text{ mm}^2$. The total volume fraction of glass fibers was 44% and 48% in ribs and skin parts, respectively.

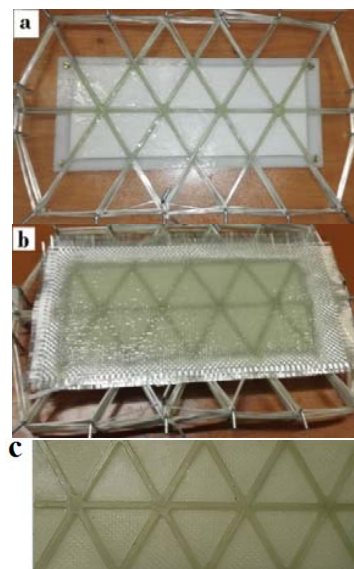


Fig. 2 Stages of GSC panel fabrication

D. Characterization

To characterize the functional groups on the silica surface, FTIR spectra of the non-treated and silanized silica nanoparticles were recorded on a Jasco FTIR spectrometer (FTIR-460 plus) through scanning small amounts of nanoparticles pressed into a pellet with potassium bromide (KBr). The specimens were scanned at wavelength range of $400\text{--}4000 \text{ cm}^{-1}$, with a resolution of 4 cm^{-1} .

Three-point flexural test was performed to investigate the flexural properties of isogrid composite specimens. Hounsfield test machine with a capacity of 25 KN was used for testing the specimens. The tests were performed based on the requirements of ASTM D7264. Loading rate of the machine was chosen 5 mm/min and span length kept to 250 mm. In this condition, the span-to-thickness ratio was 32:1. During the loading, load-displacement curve for each specimen was recorded in the Hounsfield testing system.

III. RESULTS AND DISCUSSION

Fig. 3 shows the FTIR spectra of the pristine silica, 3-GPTS, and silanized silica. The FTIR spectrum of 3-GPTS/silica nanoparticles shows additional peaks which are absent in the FTIR spectrum of the pristine silica. The bands at 692.3 cm^{-1} , 904.5 cm^{-1} , and 1400.1 cm^{-1} can be assigned to the epoxide ring vibration [9] and the bands at 2921.7 cm^{-1} and 2866.7 cm^{-1} correspond to the asymmetrical deformation of CH_3 and scissoring deformation of CH_2 [10], representing that

3-GPTS silane coupling agent has been successfully grafted onto the surface of silica nanoparticles after modification. This is in line with the results reported by other authors.

The flexural load-displacement curves for E-glass/epoxy isogrid specimen and multiscale composites based on unmodified and silanized silica nanoparticles are given in Fig. 4. For all of the specimens, three-point bending test was performed from the skin side until displacement of 80 mm. These graphs show a similar trend. Following an initial linear region, the specimens reached to a peak load, failed at this point with an abrupt drop in load and afterwards absorbed energy. It is interesting that in these structures, maximum energy absorption is obtainable after the primary failure occurring at the peak load point. As shown in Fig. 4, the introduction of silica nanoparticles and its surface functionalization have affected the flexural behavior of the E-glass/epoxy iso-GSC specimen. For better comparison the results, the flexural properties of the GSC specimens were compared in terms of stiffness, maximum load, and energy absorption. These properties are listed in Table I. With the addition of 3 wt.% functionalized silica nanoparticles, the stiffness and maximum load of the multiscale E-glass/epoxy/silica composite panel are enhanced by 16% and 14%, respectively, compared to that of neat E-glass/epoxy specimen, whereas the improvement is 10% and -12%, respectively, in the case of multiscale composite panel without silica surface treatment. It can also be seen from Table I that the energy absorption capability of the E-glass/epoxy grid specimen decreases through introduction of 3 wt.% untreated silica nanoparticles (19% decrease), whereas an increase of 26% was observed for the addition of 3 wt.% silanized silica nanoparticles.

The enhanced stiffness observed for the 3 wt.% 3-GPTS/silica loaded specimen is expected because of the higher modulus of the silica nanoparticles compared with the epoxy matrix. Another reason for observed trend is attributed to the restricting the mobility of the polymer chains under loading due to the presence of functionalized nanoparticles in the matrix [11]. However, it is noticeable that the stiffness of the specimen with 3 wt.% non-treated silica is 10% higher than that of the specimen without silica addition. This behavior is probably due to the poor interaction of epoxy matrix with non-treated silica nanoparticles.

The maximum load observed on the load-displacement curves was used as a favorable criterion for the comparison of the load-bearing capacity of the specimens. In an isogrid panel, fiber breakage and fiber microbuckling are two damage mechanisms occurring under transverse loading from the skin side. It can be mentioned that under flexural loading, longitudinal rib of isogrid composite panel along with skin sustains the maximum applied load. It seems that the observed increase in the maximum load of the multiscale specimen containing 3 wt.% silanized silica has two main reasons: First, when the matrix material is reinforced by silanized silica nanoparticles, the frictional slippage of fiber-matrix interface against applied load is restricted due to the presence of nanofillers [12]. This implies that in case of nanocomposite

matrix, the applied load can be effectively transferred from the matrix to the fiber reinforcement. Therefore, the load bearing capacity of nanocomposite specimens is higher than free-nanoparticle one. The second reason is attributed to the increasing the required stress level for fiber breakage and fiber microbuckling when the matrix is reinforced by silica nanoparticles. In fibrous composites, fibers (especially fiber skin) and fiber-matrix interface are accounted as stress concentration regions [13]. Introduction of silanized nanosilica to the matrix can effectively reduce the stress concentration onto the fibers during loading. This indicates the development of a strong interfacial bonding between the epoxy and the 3-GPTS/silica. When 3-GPTS/silica is added into the epoxy resin, epoxide groups of 3-GPTS and epoxy matrix can react in the presence of amine hardener, enhancing the interfacial interaction between them. On the contrary, in the case of reinforcing the GSC panel with the non-treated silica, a deleterious effect was observed and the maximum load of the multiscale composite was lower than that of neat E-glass/epoxy one. When epoxy matrix is reinforced with non-treated inorganic silica nanoparticles, a poor interfacial layer will be formed between them. As a result, the epoxy matrix cannot transfer the stress to the fillers well, reducing the maximum load of the multiscale specimen.

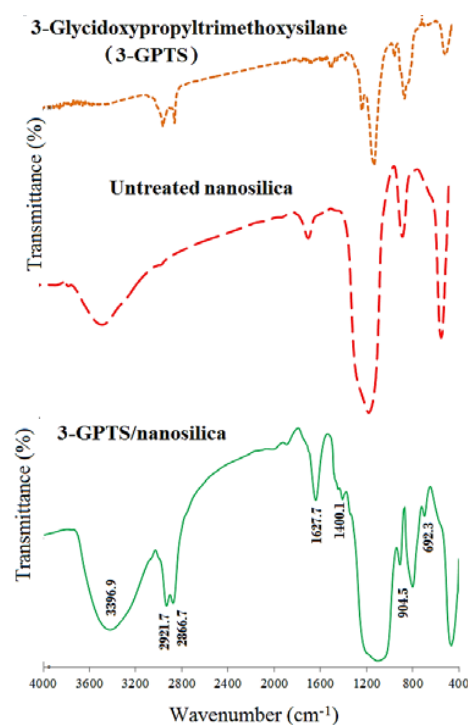


Fig. 3 FTIR spectra of the pristine silica, 3-GPTS, and silanized silica

Regarding Table I, the energy absorption follows the same trend as the maximum load because both of them are directly affected by the interfacial characteristics between the matrix and reinforcements. The value of energy absorption for the E-glass/epoxy iso-GSC specimen is 32.6 J, which shows 26% increase and 19% decrease in the case of specimens containing

3 wt.% of non-treated and 3-GPTS silica nanoparticles, respectively. The improvement in the energy absorption of the specimen containing 3-GPTS/silica is due to the crack deflection mechanism. Tilting and twisting of crack around the silica nanoparticles are occurred when the crack tip reaches to them [14]. This phenomenon leads to increasing the crack propagation path. When an epoxy matrix is filled with non-treated inorganic silica nanoparticles, a poor silica-matrix interfacial layer is formed between them. Consequently, it creates local cracks at the interface.

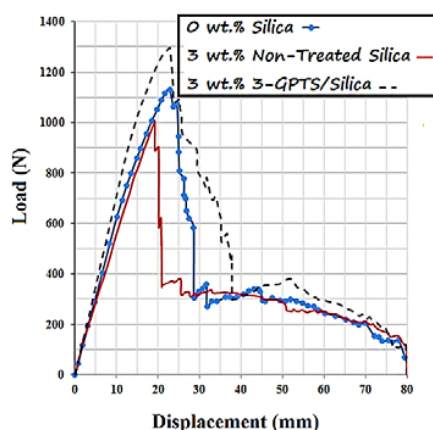


Fig. 4 Flexural load-displacement curves for the GSC panels studied in this study

TABLE I
FLEXURAL PROPERTIES OF THE GSC PANELS

Specimen	Stiffness (N/mm)	Maximum load (N)	Energy absorption (J)
0 wt.% silica	62.6	1131	32.6
3 wt.% non-treated silica	69.0	1004	27.4
3 wt.% 3-GPTS/silica	72.6	1296	41.4

From the results reported here, it is obvious that the functionalized silica nanoparticles create an effective impact on the flexural properties of GSC structures compared to untreated silica nanoparticles

REFERENCES

- [1] V. V. Vasiliev, and A. F. Razin, "Anisogrid composite lattice structures for spacecraft and aircraft applications," *Compos Struct*, vol. 76, pp. 182-189, 2006.
- [2] C. Gan, R. Gibson, and G. Newaz, "Analytical/experimental investigation of energy absorption in grid-stiffened composite structures under transverse loading," *Exp Mech*, vol. 44(2), pp. 185-194, 2004.
- [3] P. Jadhav, and P. R. Mantena, "Parametric optimization of grid-stiffened composite panels for maximizing their performance under transverse loading," *Compos Struct*, vol. 77, pp. 353-363, 2007.
- [4] M. M. Shokrieh, A. Saeedi, and M. Chitsazadeh, "Evaluating the effects of multi-walled carbon nanotubes on the mechanical properties of chopped strand mat/polyester composites," *Mater Des*, vol. 56, pp. 274-279, 2014.
- [5] A. Mirzapour, M. H. Asadollahi, S. Baghshaei and M. Akbari, "Effect of nanosilica on the microstructure, thermal properties and bending strength of nanosilica modified carbon fiber/phenolic nanocomposite," *Compos Part A*, vol. 63, pp. 159- 167, 2014.
- [6] M.F. Uddin and C. T. Sun, "Strength of unidirectional glass/epoxy composite with silica nanoparticle-enhanced matrix," *Compos Sci Technol*, vol. 68, pp. 1637-1643, 2008.
- [7] Kang S, Hong S, Choe C. R. et al. "Preparation and characterization of epoxy composites filled with functionalized nanosilica particles obtained via sol-gel process," *Polym*, vol. 42, pp. 879-887, 2010.
- [8] G. Y. Heo, and S. J. Park, "Effect of coupling agents on thermal, flow, and adhesion properties of epoxy/silica compounds for capillary underfill applications," *Powder Technol*, vol. 230, pp. 145-150, 2012.
- [9] D. K. Shukla, S. V. Kasisomayajula, and V. Parameswaran, "Epoxy composites using functionalized alumina platelets as reinforcements," *Compos Sci Technol*, vol. 68, pp. 3055-3063, 2008.
- [10] M. Mandhakini, T. Lakshmikandhan, A. Chandramohan, and M. Alagar, "Effect of nanoalumina on the tribology performance of C4-ether-linked bismaleimide-toughened epoxy nanocomposites," *Tribol Lett*, vol. 54, pp. 67-79, 2014.
- [11] M. Ayatollahi, E. Alishahi, and S. Shadlou, "Mechanical behavior of nanodiamond/epoxy nanocomposites," *Int J Fract*, vol. 170, pp. 95-100, 2011.
- [12] I. Srikanth, A. Daniel, S. Kumar, et al. "Nanosilica modified carbon-phenolic composites for enhanced ablation resistance," *Scripta Mater*, vol. 63, pp. 200-203, 2010.
- [13] S. Houshyar, A. Shanks, and A. Hodzic, "Modeling of polypropylene fiber-matrix composites using finite element analysis," *eXPRESS Poly Lett*, vol. 3, pp. 2-12, 2009.
- [14] A. J. Kinloch, and A. C. Taylor, "The toughening of cyanate-ester polymers-part I-physical modification using particles, fibers and woven-mats," *J Mater Sci*, vol. 37, pp. 433-460, 2002.