Nanoparticle type effects on flexural, interfacial and vibration properties of GFRE composites

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KEYWORDS
Flexural properties; GFRE composites; Interfacial bonding; Nanoparticles; Non-destructive vibration technique

Abstract Damping improvement in composite structures via introducing nanofillers generally has remarkable negative effects on the other mechanical properties. Therefore, in the present work, SiC and Al2O3 nanoparticles’ infusion effects on the flexural, interfacial and vibration properties of epoxy matrix and glass fiber reinforced epoxy (GFR/E) laminates were investigated. Unidirectional (UD-GFR/E) and quasi-isotropic (QI-GFR/E) laminates with [0/±45/90]s and [90/±45/0]s stacking sequences were hybridized by the optimum nanoparticles percentages. Results from off-axis flexural strengths of UD-GFR/E demonstrate good fiber/nanophased-matrix interfacial bonding. The interlaminar shear stress between the adjacent layers with different orientations/strains of ductile QI-GFR/SiC/E laminates results in decreasing the flexural strengths respectively by 24.3% and 9.1% for [0/±45/90], and [90/±45/0], stacking sequences and increasing the dissipated interfacial friction energy and thus the damping by 105.7% and 26.1%. The damping of QI-GFR/E, QI-GFR/SiC/E and QI-GFR/Al2O3/E laminates with [90/±45/0] stacking sequence was increased by 111.4%, 29.7% and 32.9% respectively compared to [0/±45/90] stacking sequence.

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1. Introduction

Recently, several studies related to the enhancement of the mechanical properties of epoxy matrix by introducing SiC1–7 and Al2O38–12 nanoparticles have been conducted. The nanophased epoxy matrix cannot be used alone for high-performance structural applications due to their limited mechanical properties. For that purpose a limited number of researchers have explored the SiC and Al2O3 nanoparticles impacts on the mechanical properties of nano-hybrid fiber reinforced composites, which is one of the objectives of this study. A key question is, to what extent the improvement in the damping properties of the nano-hybrid FRP composites can affect the other mechanical properties? To the best of the author’s knowledge, the answer to this question is not fully addressed yet in the literature and accordingly, is the subject of this study.

Chisholm et al.7 studied the influence of infusion of 1.5 wt % and 3 wt% of SiC nanoparticles into SC-15 epoxy on the
tensile properties of nanophased epoxy (nanocomposites) and nano-hybrid woven carbon fiber composite laminates. They reported that with 3 wt% loading of SiC nanoparticles the mechanical properties were degraded. They attributed this result to the agglomerate, which reduced the cross-linking density and increase void content in the nanocomposite. The enhancements in stiffness and strength of 1.5 wt% SiC-nanocomposite were 45% and 16% respectively compared to neat epoxy. For nano-hybrid woven carbon fiber composites, the improvements in the stiffness and strength were 23.5% and 11.6% respectively. The present work showed contrary behavior for the stiffness of glass fiber reinforced epoxy (Y 1092-1) infused with 1.5 wt% SiC nanoparticles.

Rodgers et al. investigated the effect of incorporation 0.5 wt%, 1 wt% and 1.5 wt% of SiC into SC-15 epoxy on the glass transition temperature ($T_g$) and flexural properties of the fabricated nanocomposites. Their results showed that the optimum loading of the SiC was about 1 wt% at which the best thermal and mechanical properties were observed. Their results also showed that the glass transition temperature (and thus chemical cross-linking density) of the modified epoxy with 1.5 wt% of SiC nanoparticles was decreased by 8 °C and there is hardly any gain in flexural strength. Faleh et al. attributed the decrease of cross-linking density to the fact that the presence of nanoparticles in epoxy resin develops a strong molecular interaction between them and epoxy molecules that hinder the interaction between epoxy resin and hardener molecules. This impedes the formation of the final cross-linked structure of the matrix during curing.

Uddin and Sun showed that introduction of 1.5 wt%–3 wt% of Al$_2$O$_3$ into DGEBA epoxy resin incorporates brittleness into the nanophased matrix (nanocomposite) and hence, the flexural strain at rupture was reduced by 6%–10% while, flexural modulus and strength were increased by 5%–9%. In that context, Zhao and Li showed that inclusion of 1.5 wt% Al$_2$O$_3$ nanoparticles in DGEBA epoxy resin has an insignificant effect on the glass transition temperature and thus chemical cross-linking density. In addition, rigid Al$_2$O$_3$ nanoparticles can act as physical cross-links for the epoxy molecular chains in the nanocomposites and accordingly, the fractured surfaces of Al$_2$O$_3$ nanocomposites show brittle failure. Mohanty et al. reported a contrary behavior to that reported by Uddin and Sun for Bondtite PL-41 epoxy resin filled with 1 wt%–5 wt% Al$_2$O$_3$ nanoparticles. From the literature it has been shown that incorporation of different nanofiller types onto epoxy resin can play a key role in the ductility/brittleness and thus the mechanical properties of nanocomposites, which are combined in the present work with the damping performance of the fabricated nanocomposites and nano-hybrid GFRE laminates was investigated.

The interfacial bonding plays a significant role in transferring the load from the epoxy matrix into higher strength/stiffness nanoparticles and hence, increasing the mechanical properties of the nanophased matrix. Several techniques can be used to characterize the interfacial bonding that includes microdebonding/microindentation technique and embedded single fiber test. For bulk composites, there are off-axis flexural and tensile tests, off-axis fracture toughness test, short beam shear test and the transverse Iosipescu shear tests. In the present study, the interfacial bonding was characterized via off-axis flexural tests of unidirectional GFRE laminates.

One promising approach to modify a brittle epoxy matrix is the incorporation of stiff nanoparticles like SiC, Al$_2$O$_3$, carbon nanotubes (CNT), which significantly improve the fracture toughness.\textsuperscript{8,13–15} Nanoparticle-related toughening mechanisms like crack deflection and crack pinning at the nanoparticles, nanoparticle pull-out, or nanoparticle-matrix debonding followed by plastic deformation of the matrix were observed depending on the nanoparticle type and morphology.\textsuperscript{14} These mechanisms enable the material to absorb more energy and accordingly, improve the damping properties. Improving the damping performance of the structural composite materials via introducing nanofillers generally has remarkable negative effects on the other mechanical properties. Therefore, any modifications in the constituent materials of the structural composites for optimizing their dynamic properties must be based on tradeoff between damping, stiffness and strength.\textsuperscript{13,16}

The objective of the present work is to investigate the effect of nanoparticle types on the flexural, interfacial and vibration properties of nano-hybridized GFRE laminates. To achieve this objective, a unidirectional and angle-ply GFRE laminates were hybridized with optimum weight percentages of SiC and Al$_2$O$_3$ nanoparticles. The interfacial bonding of the nano-hybrid GFRE laminates was investigated via off-axis flexural tests in which the failure is a matrix-dominated property. The effect of stacking sequences (0°/±45/90, and [90/±45/0] s) and the nanoparticle type on the flexural properties (strength, modulus and ultimate failure strain), and on the dynamic properties (damping, frequency, storage modulus) of the nano-hybrid GFRE laminates was investigated experimentally. The correlation between the flexural moduli determined by the static destructive test and the nondestructive vibration technique was investigated.

2. Experimental work

2.1. Materials

In the present work, twelve different composite materials with different configurations were fabricated from PY 1092-1 epoxy resin, Huntsman Advanced Materials Ltd. Details about the configurations of the fabricated panels and their constituent materials were illustrated in Table 1.

Eight of the fabricated materials were used to investigate the nanoparticles’ effect on the mechanical properties of both epoxy bulk composites and GFRE composite laminates with different configurations. In parallel, four control panels were also fabricated following similar routes without any nanoparticle infusion. The used nanoparticles materials were 1.5 wt% SiC and 1.5 wt% Al$_2$O$_3$. The selected weight percentages of the nanoparticles (1.5 wt%) were based on the optimum values that were determined earlier by Khashaba et al. In addition, this weight percentage showed enhancements in the mechanical properties of SiC/E and Al$_2$O$_3$/E nanophased epoxies by some investigators.\textsuperscript{4,7,9} The properties of the used nanoparticles are indicated in Table 2.

The epoxy resin was first modified by 1.5 wt% nanoparticles (SiC or Al$_2$O$_3$) using 750 W Ultrasonic Processor, Cole–Parmer, Inc., USA. Sonication parameters play a critical role in the dispersion of SiC and Al$_2$O$_3$ nanoparticles in epoxy resin. These parameters include the sonication temperature, sonication power and amplitude, sonicator probe diameter and immersing depth, sonication mode, sonication energy and container dimensions and materials. The contribution of each
parameter in the sonication processes was illustrated elsewhere. Details about the values of these parameters and the fabrication procedures of both the nano-based composite materials and the control panels were described earlier by Khashaba.

The fabricated nanophased materials include: SiC/E nanocomposite, Al₂O₃ nanocomposite, quasi-isotropic GFR/SiC/E with [0/±45/90]s and [90/±45/0]s stacking sequences, quasi-isotropic GFR/Al₂O₃/E with [0/±45/90]s and [90/±45/0]s stacking sequences, unidirectional UD-GFR/SiC/E laminates with 0°, 15°, 30° and 45° off-axis angles and unidirectional UD-GFR/Al₂O₃/E composite laminates with 0°, 15°, 30° and 45° off-axis angles. In parallel, the corresponding four control panels without nanoparticles in their composition were fabricated. Details about the fabrication procedures of the nano-hybrid composite laminates were illustrated earlier by Khashaba et al. The unidirectional laminates with different off-axis angles were used to characterize the interfacial properties through the off-axis flexural tests. The selected stacking sequence of the quasi-isotropic laminates exhibits all the typical failure modes (longitudinal, transverse, and shear), which are often present in the automotive and aerospace structural

![Table 1 Constituents of the investigated materials.](image)

<table>
<thead>
<tr>
<th>Material configuration and abbreviated name</th>
<th>Constituent material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Bulk neat epoxy (NE)</td>
<td>Epoxy part A (Resin): Araldite PY 1092-1 (100 part by weight)</td>
</tr>
<tr>
<td></td>
<td>Epoxy part B (Hardener): HY 1092 (45 part by weight)</td>
</tr>
<tr>
<td></td>
<td>Viscosity of epoxy (A and B) is 0.3 Pa s at 25 °C</td>
</tr>
<tr>
<td></td>
<td>Density (g/cm³) at 25 °C: 1.15 for Part A and 1.0 for Part B</td>
</tr>
<tr>
<td></td>
<td>Produced by Huntsman advanced materials specialty chemicals (Egypt) S.A.E</td>
</tr>
<tr>
<td>2-Bulk SiC/E</td>
<td>Epoxy: PY 1092-1/HY 1092</td>
</tr>
<tr>
<td></td>
<td>SiC: 1.5 wt% (epoxy parts A + B)</td>
</tr>
<tr>
<td></td>
<td>Outer diameter = 20 nm</td>
</tr>
<tr>
<td></td>
<td>Purity &gt;99.9wt%</td>
</tr>
<tr>
<td></td>
<td>SiC nanoparticles was manufactured by Timesnano, Chengdu Organic Chemicals Co. Ltd, Chinese Academy of Sciences</td>
</tr>
<tr>
<td>3-Bulk Al₂O₃/E</td>
<td>Epoxy: PY 1092-1/HY 1092</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃: 1.5wt% (epoxy parts A + B)</td>
</tr>
<tr>
<td></td>
<td>Outer diameter = 15 nm</td>
</tr>
<tr>
<td></td>
<td>Purity &gt;99.9wt%</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃ nanoparticles was manufactured by Timesnano, Chengdu Organic Chemicals Co. Ltd, Chinese Academy of Sciences</td>
</tr>
<tr>
<td>4-Unidirectional glass fiber reinforced epoxy (UD-GFR/E) with 0°, 15°, 50°, and 45° off-axis angles</td>
<td>Epoxy: PY 1092-1/HY 1092</td>
</tr>
<tr>
<td></td>
<td>E-roving glass-fiber linear density = 1.2 g/m</td>
</tr>
<tr>
<td></td>
<td>Produced by Nippon Electric Glass Ltd., Japan</td>
</tr>
<tr>
<td>5-Unidirectional glass fiber reinforced SiC/epoxy (UD-GFR/SiC/E) with 0°, 15°, 50°, and 45° off-axis angles</td>
<td>Epoxy</td>
</tr>
<tr>
<td></td>
<td>E-roving glass-fiber linear density = 1.2 g/m</td>
</tr>
<tr>
<td></td>
<td>SiC: 1.5wt% (epoxy parts A + B)</td>
</tr>
<tr>
<td>6-Unidirectional glass fiber reinforced Al₂O₃/epoxy (UD-GFR/Al₂O₃/E) with 0°, 15°, 50°, and 45° off-axis angles</td>
<td>Epoxy: PY 1092-1/HY 1092</td>
</tr>
<tr>
<td></td>
<td>E-roving glass-fiber linear density = 1.2 g/m</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃: 1.5wt% (epoxy parts A + B)</td>
</tr>
<tr>
<td>Quasi-isotropic glass fiber reinforced epoxy</td>
<td>Epoxy: PY 1092-1/HY 1092</td>
</tr>
<tr>
<td>7- [0/±45/90] s QI-GFR/E</td>
<td>E-roving glass-fiber linear density = 1.2 g/m</td>
</tr>
<tr>
<td>8- [90/±45/0] s QI-GFR/E</td>
<td></td>
</tr>
<tr>
<td>Quasi-isotropic glass fiber reinforced SiC/epoxy</td>
<td>Epoxy: PY 1092-1/HY 1092</td>
</tr>
<tr>
<td>9- [0/±45/90] s QI-GFR/SiC/E</td>
<td>E-roving glass-fiber linear density = 1.2 g/m</td>
</tr>
<tr>
<td>10- [90/±45/0] s QI-GFR/SiC/E</td>
<td>SiC: 1.5wt% (epoxy parts A + B)</td>
</tr>
<tr>
<td>Quasi-isotropic glass fiber reinforced Al₂O₃/epoxy</td>
<td>Epoxy: PY 1092-1/HY 1092</td>
</tr>
<tr>
<td>11- [0/±45/90] s QI-GFR/Al₂O₃/E</td>
<td>E-roving glass-fiber linear density = 1.2 g/m</td>
</tr>
<tr>
<td>12- [90/±45/0] s QI-GFR/Al₂O₃/E</td>
<td>Al₂O₃: 1.5wt% (epoxy parts A + B)</td>
</tr>
</tbody>
</table>

Table 2 Properties of the used nanoparticles.

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>𝜈深刻的 (GPa)</th>
<th>ρ深刻的 (g/cm³)</th>
<th>𝑤深刻 (%)</th>
<th>𝑉深刻 (%) Eq. (8)</th>
<th>𝐸深刻 (GPa)</th>
<th>σ深刻 (MPa)</th>
<th>G深刻 (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>0.19</td>
<td>3.210</td>
<td>1.5</td>
<td>0.521</td>
<td>476</td>
<td>310</td>
<td>179</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.27</td>
<td>3.835</td>
<td>1.5</td>
<td>0.436</td>
<td>393</td>
<td>280</td>
<td>152</td>
</tr>
</tbody>
</table>

parameter in the sonication processes was illustrated elsewhere. Details about the values of these parameters and the fabrication procedures of both the nano-based composite materials and the control panels were described earlier by Khashaba.

The fabricated nanophased materials include: SiC/E nanocomposite, Al₂O₃ nanocomposite, quasi-isotropic GFR/SiC/E with [0/±45/90]s and [90/±45/0]s stacking sequences, quasi-isotropic GFR/Al₂O₃/E with [0/±45/90]s and [90/±45/0]s stacking sequences, unidirectional UD-GFR/SiC/E laminates with 0°, 15°, 30° and 45° off-axis angles and unidirectional UD-GFR/Al₂O₃/E composite laminates with 0°, 15°, 30° and 45° off-axis angles. In parallel, the corresponding four control panels without nanoparticles in their composition were fabricated. Details about the fabrication procedures of the nano-hybrid composite laminates were illustrated earlier by Khashaba et al. The unidirectional laminates with different off-axis angles were used to characterize the interfacial properties through the off-axis flexural tests. The selected stacking sequence of the quasi-isotropic laminates exhibits all the typical failure modes (longitudinal, transverse, and shear), which are often present in the automotive and aerospace structural
2.2. Flexural characterization

The flexural properties of the fabricated materials were determined using three-point flexural test. The interfacial bond strength was characterized through the flexural tests on the unidirectional composite laminates with 15°, 30°, 45° and 90° off-axis angles. At least five specimens were prepared and tested for each composite type, in accordance with ASTM D790. Flexural moduli ($E_f$) of the fabricated materials were determined from the slope of the initial portion of the stress–strain curves, whereas the flexural strains ($\varepsilon_f$) and flexural stresses ($\sigma_f$) were estimated using simple beam theory.

2.3. Free vibration tests

Free vibration decay technique was used to determine the dynamic and elastic properties of the developed composite materials. The details about this technique were illustrated elsewhere and it is only outlined here. The test specimen with rectangular cross-section ((20 ± 0.1) mm width and (4.3 ± 0.1) mm thickness) was fixed as a cantilever with different lengths and excited by B&K impulse hammer model 2302-10 as shown in Fig. 1. The vibration response was measured using B&K accelerometer model 4507 B1. The hammer and the accelerometer were connected with B&K pulse analyzer model 3560c. The test parameters were: analyses range—500 Hz; acquisition time—200 ms; frequency resolution—2 Hz; sampling time—1 s and rectangular observation window. The free vibration of specimen setup (cantilever beam) was modeled as single degree-of-freedom and accordingly, the dynamic parameters were determined through the exponential decay response of free vibration curves using Eqs. (1)–(4). These parameters include logarithmic decrement ($\Delta$), loss factor ($\tan \delta$), apparent damping ratio ($\zeta$), and storage modulus ($E'$).

\[
\Delta = \ln \left( \frac{\delta_1}{\delta_2} \right) = \frac{1}{n} \ln \left( \frac{\delta_1}{\delta_n} \right) \tag{1}
\]

\[
\tan \delta = \frac{1}{n\pi} \ln \left( \frac{\delta_1}{\delta_n} \right) = \frac{\Delta}{\pi} \tag{2}
\]

\[
\zeta = \frac{1}{\sqrt{1 + \left( \frac{2n}{\pi} \right)^2}} = \frac{1}{\sqrt{1 + \left( \frac{2}{\tan \delta} \right)^2}} \tag{3}
\]

\[
E' = \frac{4\pi^2 f^3 L^3}{3I} \left( m_f + \frac{33}{140} m_b \right) \left( 1 - \frac{1}{\zeta^2} \right) \tag{4}
\]

where $\delta_1$ is the amplitude of the first peak, $\delta_n$ the amplitude after $n$ cycles in the free vibration decay curve, $m_b$ the mass of the cantilever specimen (kg), $m_f$ sum of the masses of the accelerometer and its mounting (kg), $L$ the beam length (m), $I$ the area moment of inertia (m$^4$), and $f$ the first modal frequency. The free vibration tests were repeated ten times for each material type and the average values were used for investigating the different relationships.

During the free vibration damping tests, the parasitic damping cannot be avoided due to the frictional interactions between the specimen and the fixture, the friction with the surrounding air and the interactions between the driving device and the specimen. Therefore, the following cares were taken to minimize the parasitic damping:

- Using free vibration technique with compatible B&K devices to minimize the interactions between the driving device and the specimen that can be observed between the specimen and the magnet in forced vibration technique.
- All the test specimens were mounted in the fixture through four M6 bolts with constant tightening torque of 5.2 N m using torque wrench. The resultant tightening force was not too much to damage the specimens owing to the compressive stress and it is enough to minimize the vibrational energy that can be transferred into the fixture.
- The free vibration tests were carried out in still air, to minimize the damping due to air friction.

3. Results and discussions

3.1. Flexural properties

3.1.1. Nanophased matrices

Fig. 2 shows the flexural stress–strain relationship of neat epoxy (NE), SiC/E and Al$_2$O$_3$ nanophased matrices. The results in the figure showed that the stress–strain curves have

![Fig. 1 Experimental setup of free vibration tests.](image-url)
A linear relationship up to about 60% of the ultimate load then followed by a nonlinear relationship. The used nanoparticles materials improve the strength and stiffness of the nanophased matrices. The higher stiffness of the Al₂O₃/E nanophased-matrix leads to reducing the strains at the ultimate and fracture stress compared to neat epoxy and SiC/E nanophased-matrix.

Table 3 shows the flexural properties (strength, modulus and strain at ultimate load) and the gain/loss percentages of SiC/E and Al₂O₃/E nanophased matrices (nanocomposites) compared to the neat epoxy (NE). The results in this table showed that the flexural properties of SiC/E and Al₂O₃/E nanophased matrices were respectively improved by 28.6% and 26.4% for flexural strengths and by 4.7% and 12.0% for flexural moduli compared to neat epoxy. The reason lies in that the dispersed nanoparticles in epoxy act as physical cross-links for the epoxy molecular chains.

Rodgers et al.² reported that the glass transition temperature (direct relationship with cross-linking density) of nanophased SC-15 epoxy with 1.5 wt% SiC nanoparticles was decreased by 8 °C compared to the neat epoxy. On the other hand, Zhao and Li¹⁰ showed that inclusion of 1.5 wt% Al₂O₃ nanoparticles in DGEBA epoxy resin has an insignificant effect on the glass transition temperature (chemical cross-linking density). In addition, rigid Al₂O₃ nanoparticles can act as physical cross-links for the epoxy molecular chains in the nanocomposites.¹⁰ A smooth fracture surface of Al₂O₃ nanocomposites was observed visually, which demonstrates the brittle failure.

### 3.1.2. Off-axis flexural properties (interfacial bond strength)

Off-axis flexural loading of a unidirectional composite laminate creates longitudinal, transverse and shear stresses, which can be predicted using several theories. In the present work, the off-axis flexural strengths (σₒ) of UD-GFR/E, UD-GFR/SiC/E and UD-GFR/Al₂O₃/E laminates were predicted using the Maximum Stress and Tsai-Hill theories as follows²⁶,²⁵:

\[
\sigma_0 = \begin{cases} 
\sigma_{0L} & \text{Longitudinal fracture} \\
\sigma_{0T} & \text{Transverse fracture} \\
\sigma_{0s} & \text{Shear fracture}
\end{cases}
\]

where σₒL and σₒT are the ultimate flexural longitudinal and transverse strengths respectively, and σₒs is the ultimate in-plane shear strength, which was calculated from the following equation²⁶:

\[
\sigma_{0s} = \tau_{LT} \left[ 1 - \left( \sqrt{V_f} - V_f \right) \left( 1 - \frac{G_m}{G_f} \right) \right]
\]

\[
G_m = \frac{E_m}{2(1 + v_m)}
\]

where \( V_f \) is the fiber volume fraction (=35%), \( G_f \) the shear modulus of the glass fiber (=28.841 GPa²), \( \tau_{LT} \) the shear strength of the matrix, \( E_m \) the Young’s modulus of the neat epoxy, \( v_m \) the Poisson’s ratio of the matrix and \( G_m \) the shear modulus of the neat epoxy that was calculated from Eq. (7).²⁷ The elastic properties of NE, SiC/E and Al₂O₃/E matrices are illustrated in Table 3 (\( E_m \)) and Table 4 (\( G_m \) and \( v_m \)). The longitudinal and transverse properties of the UD-composite laminates are presented in Table 5.

For the UD-GFR/SiC/E and UD-GFR/Al₂O₃/E laminates, the shear strengths and shear moduli of SiC/E and Al₂O₃/E nanophased-matrix respectively were used in Eq. (6) instated of \( \tau_{LT} \) and \( G_m \). The shear strengths of NE, SiC/E and Al₂O₃/E nanophased-matrix were respectively improved by 28.6% and 26.4% for flexural strengths and by 4.7% and 12.0% for flexural moduli compared to neat epoxy.

---

### Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>Static flexural property</th>
<th>Dynamic Property</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strength</td>
<td>Modulus</td>
</tr>
<tr>
<td></td>
<td>MPa</td>
<td>G/L (%)</td>
</tr>
<tr>
<td>NE</td>
<td>60.33</td>
<td>2.118</td>
</tr>
<tr>
<td>SiC/E</td>
<td>77.56</td>
<td>28.6</td>
</tr>
<tr>
<td>Al₂O₃/E</td>
<td>76.27</td>
<td>26.4</td>
</tr>
</tbody>
</table>

---

Fig. 2 Stress-strain curves of neat epoxy, SiC/E and Al₂O₃/E nanophased matrices in flexural test.
E were (22.225, 28.991, 30.117 MPa respectively) determined experimentally using Iosipescu shear test in accordance with ASTM D5379. Details about test procedure and specimen dimension were illustrated elsewhere.28,29 The elastic properties of NE, SiC/E and Al2O3/E matrices are presented in Table 4.

Based on the isotropy assumption, the shear moduli of SiC/E and Al2O3/E nanophased matrices were calculated from Eq. (7)27 in which the Poisson’s ratios of nanophased matrices (\(v_{\text{NP}}\)) were calculated using rule of mixtures, Eq. (8),29,30 and Young’s moduli were determined experimentally as shown in Table 2. Note: the subscript NP denotes nanoparticles (SiC or/and Al2O3).

\[
v_{\text{NP}} = v_{\text{NP}} V_{\text{NP}} + v_{\text{m}} (1 - V_{\text{NP}})
\]

where \(v_{\text{NP}}\) is the Poisson’s ratio of nanoparticles, \(v_{\text{m}}\) is the Poisson’s ratio of epoxy matrix (= 0.3628) and \(V_{\text{NP}}\) is the volume fractions of the nanoparticles that were calculated from the following equation31:

\[
V_{\text{NP}} = \frac{w_{\text{NP}}}{w_{\text{NP}}} + \left(\frac{\rho_{\text{NP}}}{\rho_{\text{m}}} - \frac{\rho_{\text{NP}}}{\rho_{\text{m}}}ight) w_{\text{NP}}
\]

where \(w_{\text{NP}} = 0.015\) is the weight fraction of the nanoparticles, \(\rho_{\text{NP}}\) the density of the nanoparticles (SiC and Al2O3) and \(\rho_{\text{m}} = 1.103\) g/cm³ the density of epoxy matrix. The values of \(v_{\text{NP}}, \rho_{\text{NP}}\) and \(V_{\text{NP}}\) are illustrated in Table 2.

(ii) Tsai-Hill theory

The Tsai-Hill failure theory is primarily derived from the von Mises distortional energy yield criterion for isotropic materials, which was modified to predict the off-axis strength of the anisotropic materials as follows32:

\[
\frac{1}{\sigma_{L}} = \cos^4 \theta \sigma_{L}^2 + \left(\frac{1}{\tau_{LT}} - \frac{1}{\sigma_{L}}\right) \cos^2 \theta \sin^2 \theta + \sin^4 \theta \sigma_{T}^2
\]

Fig. 3 shows the experimental results of UD-GFR/E, UD-GFR/SiC/E and UD-GFR/Al2O3/E composite laminates with different off-axis angles and the predicted off-axis flexural strengths of UD-GFR/SiC/E laminates. The results in the figure show that the Tsai-Hill theory gives a slightly better fit to the experimental results of UD-GFR/E than the Maximum Stress theory. Whereas, Maximum Stress theory has good agreement with the experimental results of the nano-hybrid laminates specially at 30° and 45° off-axis angles. This result was due to the fact that Maximum Stress theory provides an interaction between different modes of failures that may be arisen from using nanophased matrices in the hybrid composites.

Fig. 4 shows the improvement percentages of the off-axis flexural strengths of nano-hybrid unidirectional composite laminates compared to the control laminates. The experimental results in this figure reveal that the flexural strengths of both UD-GFR/SiC/E and UD-GFR/Al2O3/E composite laminates with off-axis angles ranging from 15° to 90° were significantly improved compared to the control laminates. This result demonstrates the improvement in the interfacial bonding between nanophased matrices and glass fiber, where the failures in these laminates are controlled by the matrix properties. The flexural strengths of both UD-GFR/SiC/E Table 4 Estimated values of \(v_{\text{m}}\) and \(G_{\text{m}}\) for NE, SiC/E and Al2O3/E matrices.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>(v_{\text{m}}), Eq. (8)</th>
<th>(G_{\text{m}}) (GPa), Eq. (7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE</td>
<td>0.360</td>
<td>0.826</td>
</tr>
<tr>
<td>SiC/E</td>
<td>0.3591</td>
<td>0.917</td>
</tr>
<tr>
<td>Al2O3/E</td>
<td>0.3588</td>
<td>0.873</td>
</tr>
</tbody>
</table>

Table 5 Mechanical properties of unidirectional laminate.

| Unidirectional laminate | Mechanical property | \(\sigma_{L}\) (MPa) | \(\sigma_{T}\) (MPa) | \(\tau_{LT}\) (MPa), Eq. (6) |
|-------------------------|---------------------|-----------------------|-----------------------|
| UD-GFR/E               | 488.822             | 24.499                | 21.601                |
| UD-GFR/SiC/E           | 490.295             | 28.154                | 22.317                |
| UD-GFR/Al2O3/E         | 494.922             | 27.915                | 22.852                |

Note: * Determined experimentally in the present work.

Fig. 3 Comparison between the experimental and predicted off-axis flexural strengths of UD-GFR/E, UD-GFR/SiC/E and UD-GFR/Al2O3/E laminates.

Fig. 4 Gain/loss percentages of off-axis flexural strengths of UD-GFR/SiC/E and UD-GFR/Al2O3/E laminates.
and UD-GFR/Al₂O₃/E laminates (with 0° off-axis) have the lowest improvement in flexural strength compared to other off-axis angles. This result was attributed to the fact that the failure of the unidirectional fiber reinforced composites is a fiber-dominated property. 13,20,33

The bigger improvements of the off-axis flexural strengths of UD-GFR/SiC/E laminates compared to UD-GFR/Al₂O₃/E laminates, Fig. 4, were justified by higher flexural strength of SiC/E nanophased-matrix compared to Al₂O₃/E nanophased-matrix as shown in Table 3.

The gained ductility/brittleness owing to incorporating different nanoparticles into GFRE laminates was discussed based on the fact that the brittle materials are weak in tension and flexural, have high stiffness and lower ultimate failure strain. Because the failure of off-axis composite laminate is a matrix-dominated property, the following observations demonstrate the acquired ductility and brittleness of the development of GFRE composites with SiC and Al₂O₃ nanoparticles respectively.

The off-axis flexural strengths and ultimate failure strains of UD-GFR/Al₂O₃/E were lower than those of UD-GFR/SiC/E composites as shown in Figs. 4 and 5 respectively. This result was due to increasing the cross-linking density and thus the brittleness of the Al₂O₃/E matrix. On the other hand, infusion of SiC leads to decreasing the cross-linking density that can be interpreted by their lower off-axis moduli and higher ultimate failure strains (ductile behavior) compared to UD-GFR/E and UD-GFR/Al₂O₃/E composites as shown in Fig. 6.

The amazing scanning electron microscope image of Fig. 7(a) shows large plastic deformation in the SiC/E matrix at the fibers boundary in flexural test. This result interprets higher off-axis ultimate failure strains and lower moduli of UD-GFR/SiC/E compared to the UD-GFR/Al₂O₃/E laminates as shown in Fig. 6.

3.1.3. Flexural properties of quasi-isotropic laminates with different stacking sequences

Fig. 8 shows stress–strain curves of both the control and nanohybrid quasi-isotropic laminates with different stacking sequences. Deviation from linearity was observed at about 35% of the ultimate stress of quasi-isotropic laminates with [90/±45/0]s stacking sequence owing to failure of 90° surface layers of the specimen. The specimen stiffness was decreased and the load redistributed between the ±45° layers resulting
The higher plastic deformation of the SiC/E matrix in flexural test interpreted the higher ultimate failure strains and lower moduli of UD-GFR/SiC/E compared to the UD-GFR/Al₂O₃/E laminates.

Fig. 7 SEM of hybridized laminates.

(a) SiC-laminate

(b) Al₂O₃-laminate

in further slowly increasing the stress in a nonlinear fashion up to the ultimate failure (at strain of about 6.5%) and then gradually decreasing up to the fracture of the unidirectional central layers that have minimum (or zero) stress.

The stress–strain curves of the [0/±45/90] s configurations showed almost linear relationship up to 75% of the ultimate stress, and then followed by a non-linear behavior up to the ultimate stress. Failures of quasi-isotropic laminates with [0/±45/90] s stacking sequences were characterized by catastrophic fracture owing to failure of the unidirectional (0°) surface layers on tension side of QI-GFR/SiC/E laminates and on compression side of QI-GFR/Al₂O₃/E laminates as shown in the visual examination image of Fig. 9.

Although the off-axis flexural strength (interfacial bonding) of UD-GFR/SiC/E showed higher improvement compared to the UD-GFR/E and UD-GFR/Al₂O₃/E, Fig. 4, the flexural strength of the QI-GFR/SiC/E composites showed reduction compared to the other laminates as shown in Fig. 10. This result was due to the fact that the ductility of the nanophased SiC/E matrix contrast plays a key role in the off-axis and quasi-isotropic flexural strengths of nano-hybrid composite laminates. Because the failure of off-axis laminates is a matrix dominated, their flexural strengths were improved with increasing matrix ductility. On the other hand, the ductility of SiC/E nanophased-matrix results in increasing the ultimate failure strains, Fig. 11, and reduction the stiffness (moduli), Fig. 12, of QI-GFR/SiC/E laminates with [0/±45/90] s and [90/±45/0] s stacking sequences. Therefore, the interlaminar shear stress between the adjacent layers with different orientations/strains was maximized as shown by the visual image of Fig. 9. The interlaminar shear stress between the adjacent layers with different orientations/strains reduces the specimen integrity and results in catastrophic fracture of the tension side and accordingly, the flexural strengths of [0/±45/90] s and [90/±45/0] s stacking sequences reduced by 24.3% and 9.1% respectively compared to control laminate and by...
31.4% and 11.5% compared to QI-GFR/Al2O3/E as shown in Fig. 10.

On the other hand, the stress–strain curves of QI-GFR/E and QI-GFR/Al2O3/E laminates showed stepped progressive catastrophic failures. This behavior was attributed to the failure of 0°/C176 surface layers of compression side. The stress–strain curves were further slightly increased due to redistribution of the load in ±45°/C176 layers and 0°/C176 surface layers in tension side up to another sudden failure owing to the failure of ±45° layers. Redistribution of the load between the 0°/C176 surface tension layers results in further slightly increases in the load up to the complete fracture of the specimen. Therefore, it can be concluded that the ultimate failure of quasi-isotropic laminates was controlled by ±45° layers for [90/±45/0], stacking sequence and by 0° surface layers of QI-GFR/SiC/E and QI-GFR/Al2O3/E laminates with [0°/±45/90], stacking sequences. The complete fracture of quasi-isotropic laminates was due to the failure of ±45° layers in both stacking sequences at strains of about 6.5% except QI-GFR/SiC/E with [0°/±45/90], stacking sequence, which has complete sudden fracture due to the interlaminar shear failure between the adjacent layers accompanied with complete fracture of the 0° layers on the tension side.

The ultimate failure strains of both the hybridized and the control GFRE laminates with [90°/±45/0], stacking sequence were about two times higher than that of [0°/±45/90], stacking sequence as shown in Fig. 11. On the other hand, the flexural strengths and moduli of both the hybridized and the control laminates with [0°/±45/90], stacking sequence were more than two times higher than that of the [90°/±45/0], stacking sequence as shown in Figs. 10 and 12 respectively. The reason lies in that the flexural properties of [0°/±45/90], stacking sequences were controlled by the higher strength/stiffness of the unidirectional (0°/C176) surfaces layers, compared to the 90° surfaces layers of the [90°/±45/0], stacking sequence. The reduction of the ultimate failure strains of QI-GFR/Al2O3/E laminates with [90°/±45/0], stacking sequence (24.3%) compared to QI-GFR/SiC/E laminates agrees with the off-axis ultimate failure strains in Fig. 6.

3.2. Dynamic mechanical properties

3.2.1. Nanophased-matrix

Table 3 shows the experimental values of the natural frequencies, damping ratios and storage moduli of neat epoxy, SiC/E and Al2O3/E nanophased-matrices and their improvement percentages compared to neat epoxy. The results in this table show that the frequencies were qualitatively in an agreement with the stiffness (storage moduli) of different matrices. It has been reported by several investigators that the “stick–slip” mechanism is responsible for the energy dissipation capability and therefore, controlling the dynamic properties of nanophased-matrix. Based on this concept, decreasing the cross-linking density of SiC/E nanophased-matrix leads to decreasing the storage modulus (stiffness) and natural frequency by 2.8% and 10.2% respectively as shown in Table 3. It was found that the SiC/E nanophased-matrix exhibits higher deflection (strain) and accordingly, higher interfacial frictional and energy dissipation compared to the Al2O3/E
nanophased-matrix at the same impulse load level. Therefore, the damping ratio of SiC/E nanophased-matrix was improved by 7.2% compared to neat epoxy and by 5.0% compared to Al₂O₃/E nanophased-matrix, which has the highest stiffness (storage modulus) and natural frequency as shown in Table 3.

3.2.2. Effect of beam free length

Fig. 13 shows the variation of natural frequencies versus beam free length of quasi-isotropic laminates with [0/±45/90]s stacking sequence. The results in this figure show that the natural frequency was increased with decreasing the beam free length as a result of increasing beam flexural stiffness (\(E/I/L\)). Similar observations were reported by some researchers for different composite materials.8,13,35,36 This behavior is clearly illustrated by the higher number of cycles per second (frequency) of free vibration curve of QI-GFR/SiC/E with short beam free length of 100 mm, Fig. 14(a), compared to the long beam free length of 200 mm, Fig. 14(b). Fig. 14 also shows that although the decay response of free vibration curves of the specimen with higher stiffness (\(L = 100\) mm) was more pronounced compared to the long one (\(L = 200\) mm), the change in the damping ratio was insignificant.

The storage moduli of quasi-isotropic laminates with [0/±45/90]s stacking sequence as a function of beam free length were illustrated in Fig. 15. It is obvious that the beam free length had a negligible effect on the storage moduli of both the hybridized and the control laminates, because the storage modulus is a materials’ property that should be constant, even if it has been determined using different methods.13 Therefore, the storage moduli of the fabricated panels (with and without nanoparticles) are correlated well (\(R^2 = 0.998\)) with the flexural moduli (\(E_f\)) that were determined using 3-point bending tests as shown in Fig. 16. Thus, it is recommended to use the dynamic nondestructive tests to determine the Young’s moduli of FRP composites instead of the destructive static techniques.

3.2.3. Effect of stacking sequences

Fig. 17 shows the storage moduli of the nano-hybrid QI-laminates with both [0/±45/90]s and [90/±45/0]s stacking sequences and their improvement percentages compared to the control laminate. Hybridization of quasi-isotropic laminates with Al₂O₃ results in increasing their stiffness (storage moduli) respectively by 1.6% and 12.3% for [0/±45/90]s and [90/±45/0]s stacking sequences compared to the control laminates, as shown in Fig. 17. On the other hand, the results in this figure show that the stiffness of the QI-GFR/SiC/E laminates with [0/±45/90]s and [90/±45/0]s stacking sequences were decreased by 22.3% and 8.3% respectively compared to the control laminates. The behavior of the nondestructive eval-
Evaluation of storage moduli in Fig. 17 was qualitatively agreed with that determined via distractive flexural tests in Fig. 12. For the same matrix type and nanoparticles loading percentage, the stiffness variation of QI-GFR/Al$_2$O$_3$/E and QI-GFR/SiC/E laminates was due to the cross-linking degree that played a key role in the static as well as dynamic properties of the developed materials.

Fig. 18 shows the natural frequencies of the nano-hybrid QI-laminates with both [0/±45/90]s and [90/±45/0]s stacking sequences and their loss/gain percentages compared to the control laminate. The results in this figure showed that the hybridization of composite laminates with both SiC and Al$_2$O$_3$ nanoparticles increase their natural frequencies respectively by 11.8% and 8.2% for [0/±45/90], stacking sequences and by 15.3% and 10.8% for [90/±45/0], stacking sequence. Increasing the natural frequencies of the hybridized composite laminates with [90/±45/0] stacking sequence was clearly observed by increasing the number of cycles per second of free vibration decay curve of QI-GFR/SiC/E compared to the control laminate as shown in Fig. 19a and b respectively.

Increasing the natural frequency with increasing the specimen stiffness as indicated by Eq. (4) cannot be generalized when comparing composite materials with different constituents. The results in Fig. 17 show that although the QI-GFR/SiC/E laminates with [0/±45/90], and [90/±45/0], stacking sequences have the lowest stiffness compared to the control laminates (QI-GFR/E) and QI-GFR/Al$_2$O$_3$/E composite laminates, the former laminates have the highest natural frequencies compared to the latter laminates as shown in Fig. 18. Similar observation was reported by Khan et al.\textsuperscript{36} for CFRE composites hybridized with MWCNTs. Also, Tsai and Chang\textsuperscript{37} reported that the flexural moduli of nanophased epoxy with 10 wt% Silica and 10 wt% CTBN, 10 wt% CSR, and 10 wt% CTBN were respectively 2.731, 2.474, 2.385 GPa (decreasing order) and the corresponding natural frequencies were increased by 24., 24.6, 24.65 Hz (increasing order).

The storage moduli, Fig. 17, and natural frequencies, Fig. 18, of QI-laminates with the same constituent materials and [90/±45/0], stacking sequence were significantly lower than those of [0/±45/90], stacking sequence. This result was due to the lower stiffness surfaces layers with 90$^\circ$ fiber orientation of the former stacking sequence, compared to the higher stiffness of 0$^\circ$ surfaces layers of the latter one. On the other hand, when the 0$^\circ$ degree layers are in the specimen center as exists in [90/±45/0], stacking sequence the damping ratios of QI-GFR/E, QI-GFR/SiC/E and QI-GFR/Al$_2$O$_3$/E laminates were increased by 111.4%, 29.7% and 32.9% respectively compared to [0/±45/90], stacking sequence as shown in Fig. 20. This result was attributed to the lower stiffness (storage moduli) of QI-laminates with [90/±45/0], stacking sequence, which leads to higher deflection (strain) compared to the [0/±45/90], stacking sequence at the same impulse load level. The higher deflection of QI-laminates with [90/±45/0], stacking sequence will maximize the dissipated interfacial friction energy owing to the stick-slip motions among the nanoparticles, epoxy matrix, glass fibers, nanoparticles themselves and the adjacent layers with different orientations.
and hence, the damping ratios are higher than those of \([0/\pm 45/90]\) stacking sequence.

Hybridization of quasi-isotropic laminates with SiC and Al\(_2\)O\(_3\) nanoparticles results in improving their damping ratios respectively by 105.7% and 62.3% for \([0/\pm 45/90]\) stacking sequence and by 26.1% and 2.0% for \([90/\pm 45/0]\) stacking sequence as shown in Fig. 20. The improvement of the damping ratio of the hybrid quasi-isotropic laminates with both \([0/\pm 45/90]\) and \([90/\pm 45/0]\) stacking sequences was due to the dissipated interfacial friction energy as a result of the stick-slip motions among the constituent materials, which have different strains within the layer and the various strains of the adjacent layers within the laminate.

The higher improvements of the damping ratios of QI-GFR/SiC/E laminates compared to QI-GFR/Al\(_2\)O\(_3\)/E laminates with both \([0/\pm 45/90]\) and \([90/\pm 45/0]\) stacking sequences were due to decreasing the stiffness (storage moduli) of former laminates by 22.3% and 8.3% respectively. The increased stiffness of the QI-GFR/Al\(_2\)O\(_3\)/E laminates by 1.6% and 12.3% respectively for \([0/\pm 45/90]\) and \([90/\pm 45/0]\) stacking sequences reduces the interlaminar shear deformation and hence the damping during bending vibration tests. Improving the ductility of the QI-GFR/SiC/E laminates leads to maximizing the interlaminar shear strains between the adjacent layers with different orientations at the same impulse load level. Therefore, the energy dissipative owing to the interfacial friction between the adjacent layers of QI-GFR/SiC/E laminates was higher than other laminates and accordingly, their damping ratios have the highest improvement percentage, as shown in Fig. 20. The higher improvements in the damping ratio of QI-GFR/SiC/E composite laminate were clearly observed in the free vibration decay curves that is more pronounced for QI-GFR/SiC/E laminate with \([90/\pm 45/0]\) stacking sequence, Fig. 19(a), compared to the control laminates, Fig. 19(b).

**4. Conclusions**

In the present work, nanoparticles infusion effects on the mechanical and dynamic properties of epoxy and GFRE laminates have been investigated experimentally and the following conclusions were drawn.

1. The flexural strengths of SiC/E and Al\(_2\)O\(_3\)/E nanocomposites were respectively improved by 28.6% and 26.4% while, the moduli were improved respectively by 4.7% and 12.0% compared to neat epoxy. The damping ratio of SiC/E nanophased-matrix was improved by 7.2% compared to neat epoxy and by 5.0% compared to Al\(_2\)O\(_3\)/E nanophased-matrix, which has the highest stiffness (storage modulus) and natural frequency.

2. The off-axis flexural strengths of both UD-GFR/SiC/E and UD-GFR/Al\(_2\)O\(_3\)/E laminates were significantly improved compared with the control laminates. This result demonstrates the improvement in the interfacial bonding between nanophased-matrices and glass fiber, where the failures in these laminates are matrix dominated.

3. The ductility of QI-GFR/SiC/E laminates maximized the interlaminar shear stress between the adjacent layers with different orientations/strains. Therefore, the integrity of the flexural specimens was reduced and hence, the flexural strengths of \([0/\pm 45/90]\) and \([90/\pm 45/0]\) stacking sequences reduced by...
24.3% and 9.1% respectively compared to control laminate and by 31.4% and 11.5% compared to QI-GFR/Al₂O₃/E laminate. In contrast, the higher interlaminar shear stress between the adjacent layers of QI-GFR/SiC/E laminates increases the energy dissipated in the interfacial friction and accordingly, improving the damping ratios of [0°/±45°/90°] and [90°/±45°/0°] stacking sequences by 105.7% and 26.1% respectively compared to control laminate and by 26.7% and 23.6% compared to QI-GFR/Al₂O₃/E composite laminate.

4. The storage moduli of the fabricated panels (with and without nanoparticles) are correlated well ($R^2 = 0.998$) with that determined using destructive flexural static tests. Thus, it is recommended to use the dynamic nondestructive tests to determine the Young's moduli of FRP composites instead of the destructive static techniques.

5. Although the QI-GFR/SiC/E laminates with [0°/±45°/90°] and [90°/±45°/0°] stacking sequences had the lowest stiffness compared to the control laminates (QI-GFR/E) and QI-GFR/Al₂O₃/E laminates, their natural frequencies were higher than those of the latter laminates. Therefore, increasing the natural frequency with increasing the specimen stiffness cannot be generalized when comparing composite materials with different constituents.

6. The storage moduli and natural frequencies of QI-laminates with [90°/±45°/0°], stacking sequence were significantly lower than those of [0°/±45°/90°], stacking sequence. This result was attributed to the lower stiffness of 90° surfaces' layers of the former stacking sequence, compared to the higher stiffness of 0° surfaces' layers of the latter one. On the other hand, when the 0° degree layers were in the specimen center as existed in [90°/±45°/0°], stacking sequence the damping ratio of QI-GFR/E, QI-GFR/SiC/E and QI-GFR/Al₂O₃/E laminates were increased by 111.4%, 29.7% and 32.9% respectively compared to [0°/±45°/90°], stacking sequence.

References

28. Khashaba UA, Sebaey TA, Mahmoud FF, Selmy AI, Hamouda RM. Experimental and numerical analysis of pinned-joints com-


U.A. Khashaba is a professor with Ph.D. degree in fatigue behavior of fiber composites (1993). His current research interests are related to the polymeric fiber composites in the following topics: fracture mechanics, fatigue, machining and machinability, vibration damping, mechanical behavior under combined loads, hybridization of the composite laminates with nanofillers, bolted joints, and adhesive joints/repairs.