Original Article

Improvement in the mechanical properties of neat GFRPs with multi-walled CNTs

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The present study focuses on fabrication and mechanical characterization of glass fiber reinforced polymers (GFRPs) filled with low specific carbon nanotube (CNT) contents. The epoxy resins were altered with 0.1%, 0.2%, 0.3% and 0.4% MWCNTs by weight to investigate the effects of CNTs on mechanical properties of GFRPs. Samples of GFRP reinforced with 0.3% MWCNTs had higher tensile (242.22 MPa) and flexural strength (332.53 MPa) as compared to neat GFRPs. Moreover, the hardness values agree with the tensile and flexural test results. The experimental results also reveal that MWCNTs plays a significant role in the enhancement of mechanical properties such as tensile strength, failure strain, and hardness. The morphology of the nanocomposites and fiber-matrix interfacial effects are perceived through scanning electron microscope (SEM).

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1. Introduction

Fiber-reinforced composite materials are one of the imperative materials and are used expansively in distinct engineering fields such as aerospace, construction, transportation, automotive, sports goods, etc. [1]. Among the fiber-reinforced composite materials, glass fiber reinforced composite materials (GFRP) are finding increased applications due to their high stiffness to density ratio, high endurance limit, high corrosive resistance, low coefficient of thermal expansion, near-net-shape and greater manufacturing feasibility over traditional engineering materials [2]. Specifically, GFRPs are extensively used in a radome of aircrafts and sports instruments such as golf shafts, bicycle helmets and so on. Carbon nanotubes (CNTs) were exposed in 1990s subsequent to the sighting of fullerenes and these emerged as best potential fillers to enhance the mechanical properties of nanopolymer composites [3]. In addition to the above investigations, it was observed that there was not a particular nature of CNTs, but plentiful ones depending ahead the numeral of tubes (shells can be rolled) like SWCNTs (single walled), DWCNTs (dual walled) and MWCNTs (multi-walled) on the display of the five-sided, six-sided rings along the tubular shell [4]. CNTs are important additives for the alteration of epoxy structures to improve the flexural modulus, flexural strength and flexural toughness of the epoxy-based nanopolymer composites. Experiments are being conducted to enhance the properties further with the addition of second reinforcement in the same matrix (hybridization) [5].
Sahoo et al. [6] discussed the issues related to the CNT/Epoxy composite fabrication and CNTs dispersion, alignment, and control of the CNTs in the epoxy matrix. CNTs are usually agglomerates due to van der Waals forces and it is extremely difficult to disperse and align in a polymer matrix. Not only dispersion but also the poor interfacial interaction between nanotubes and polymer matrix is very important for load transferring in nanocomposites. Sahoo also explained that there are several methods or techniques in the direction of the dispersion of nanotubes in the polymer matrix such as solution mixing, electrospinning, in situ polymerization, Sonication, calendaring and chemical functionalization of CNTs. These techniques improve the dispersion of nanotubes in epoxy resin and also progress the mechanical, thermal and physical properties of the CNT based nanocomposites.

Shekar et al. [7] employed a sonication technique for effective homogenous dispersion of MW CNTs into the polymers matrix. The author also pointed out that amino functionalized MW CNTs in the epoxy system escalates the flexural strength and flexural modulus of the nanocomposites. Gojny et al. [8] adopted a calendaring technique for homogeneous dispersion of DWCNTs in the epoxy resin. The addition of modest wt% of nanotubes leads to improve the mechanical properties compared to the same amount of carbon black filled in the epoxy resin. Gojny experimental results show that nanotube filled epoxy resin had enhanced tensile strength, fracture toughness, modulus of elasticity under the retention of the ductility. Karapappas et al. [9] focused on mechanical and fracture properties of CNT based composites, with the nano-filler contents of 0.1, 0.5, 1 wt% and also compared with neat epoxy. Based on the experimental observations, a significant improvement was achieved in fracture energy (about 60%) and fracture toughness with 1.0 wt% CNT into the carbon fibre reinforced polymers (CFRP). Tests revealed that further addition of nanofiller contents increases the toughness and glass transition temperature.

MWCNT-GFRPs are newly invented notable nanocomposites for an accurate application of aircraft fairings skins, which is the key structural part of the aircraft to produce a smooth outline surface, condense the drag and fills the gaps between the parts of the aircraft. MWCNT-GFRP nanocomposites are also used in wind farms to absorb the radar/radio frequency microwave energy. In particular, radar absorbing materials (RAM) or radar absorbing structures (RAS) are fabricated by plain-weave E-glass fiber cloth impregnated with epoxy matrix and carbon nanotube filler and this addition of CNT helps to disperse RF energy internally [10,11]. Chang [12] pointed out those mechanical properties of the FRP/epoxy composite laminates increased with the addition of MWCNTs. The flexural strength and impact strength properties of the MWCNT-GFRP composite laminates were enhanced up to 22.1% and 44.3% as compared to MWCNT-CFRP composite laminates. The fatigue cycles of MWCNT-GFRP composites were also increased from 959 cycles (neat GFRP) to 3232 cycles.

Zhang et al. [13] tried different low wt% of MWCNTs (0.4, 0.75, and 1.1) in the epoxy system of pre-stretched GFRP composites to enhance the mechanical properties in tension and quasi-static indentation. Among all samples, 0.75 wt% GFRP samples show higher tensile strength with limited damages and 0.4 wt% GFRP samples gives the advanced flexural strength, failure strain as compared to neat (0 wt%) GFRP samples. Consequently, 0.4 wt% GFRP and 0.75 wt% GFRP samples exhibit improved resistance to damage in the indentation. Mahato et al. [14] investigated the effect of MWCNTs addition (0.1, 0.3 and 0.5 wt. %) to the GFRP composites to identify the tensile behavior under different crosshead speeds (1, 10, 100 mm/min). During experimentation, the tensile strength has been increased steadily from 0.1 to 0.3 wt. % for all crosshead speeds, further extension of 0.3–0.5 wt% there is a slight decrement in tensile modulus due to the agglomeration of the CNTs in the polymer matrix system. Finally, 0.3 wt% GFRP samples show the optimum tensile properties as compared to control GFRP composites.

Wang et al. [15] conducted a series of impact tests on different epoxy-modified (0.1, 0.3 and 0.5 wt% of MWCNTs) GFRP laminates to improve the damage-resistant properties under low-velocity drop-weight impact loadings. The impact responses are improved in terms of material mechanisms, i.e., breakage, debonding, pull-out, etc., with MWCNTs addition to the epoxy system and damage factor also enhanced significantly with pre-stretched glass fabrics as compared to non-stretched fabrics. Oh et al. [16] determined the mechanical properties of low carbon black added GFRP composites, which are used as RAS (radar absorbing structure) material. The reported results revealed that the in-plane shear strain and compressive strength has been improved significantly, while the tensile strength and inter-laminar shear strength (ILSS) are decreased slightly by carbon black addition to the GFRP epoxy system. Seyhan et al. [17] studied the fracture toughness of MWCNTs (0.1 wt%) reinforced GFRP samples to evaluate the mode I and mode II fracture properties. The mode II fracture toughness and interlaminar shear strength values are improved significantly with an addition of MWCNTs to the neat GFRPs, while the mode I fracture toughness value is not affected as compared to neat GFRP samples.

According to the existing literature on FRP nanocomposites, laminates fabricated with modified epoxy resin by different CNT concentrations through different fabrication methods attain best mechanical properties compared to neat GFRP composites. The present study was mainly focused on the laminate (MWCNTs-GFRP) thickness, nanotube content and mechanical properties of modified and unmodified epoxy filled GFRP laminates. The hand lay-up fabrication method was employed to achieve the required thickness of the composite laminates for mechanical testing. The epoxy resins were modified with 0.1%, 0.2%, 0.3% and 0.4% multi-walled carbon nanotubes (MWCNTs) by weight to investigate the effects of CNTs on mechanical properties of GFRPs. The mechanical tests, i.e., tensile test, flexural test (three-point bending test) and hardness tests were organized for both modified and unmodified epoxy resins based on ASTM standards for evaluating as well as optimizing the MWCNT content and mechanical properties. Additionally, modified and unmodified epoxy based GFRP laminates were compared for better mechanical properties. The morphology, i.e., interfacial bond, fracture behavior, matrix deformation, fiber breakage, nanotube dispersion, crack propagation, etc., of the tested samples were examined by using the scanning electron microscope (SEM). From the literature [18] it is observed that with the addition of 0.4% MWCNTs to neat GFRPs, there is an
enhancement of mechanical properties and above it, there was a gradual decrease. Hence, in the present study, a humble attempt is made to observe the effect of lower CNT concentrations, i.e., 0.1%, 0.2%, 0.3% and 0.4% on the neat GFRPs.

2. Materials

For fabricating the MWCNT-GFRP nanocomposites, diglycidyl ether of Bisphenol-A type liquid epoxy resin (ARL-12) with triethylene tetramine (TETA) as a hardener (AH-312) was used, which were supplied by Atul Industries, India. The 7 Mil glass Cloth (200 gsm) used in this study was plain weave glass fabric with a filament diameter of 150 micrometers (μm) purchased from Suntech Fiber Pvt Ltd, Bangalore, India. Thin MWCNTs produced via the catalytic chemical vapor deposition (CCVD) process were procured from NanoCyl Company, Belgium. The average diameter and average length of these nanotubes were 10–20 nm and 1–10 μm respectively and a special surface area of 250–300 (m²/g). The MWCNTs had 90% carbon purity and transition metal oxide of <0.1%.

2.1. Fabrication of MWCNT incorporated GFRP laminates

As procured MWCNTs will be usually in agglomerated form. To de-agglomerate them, high purity ethanol was added and followed by sonication using an ultrasonic vibrator for 1 h at 40 kHz [19,20]. The MWCNTs are then added to the required quantity of liquid epoxy resin and the solution is thoroughly mixed using a magnetic stirrer at a speed of 900 RPM for 2 h at a temperature of 85°C. Later the suspension was sent to ball milling operation to improve the dispersion of CNTs into the epoxy matrix. This ball milling operation was performed with 4 mm diameter solid aluminum balls of 40 numbers about 120 min at 200 RPM.

The mechanical properties of polymer nanocomposites directly depend on the laminate geometry, specifically thickness. The laminate thickness plays a vital role while fabricating the fiber reinforced nanocomposites [21]. Based on ASTM standards, it is mandatory to maintain the laminate thickness of 4 mm for tensile and flexural property testing. For that purpose, 16 layers of glass fiber fabric with 80 g MWCNT-Epoxy suspension was used for obtaining a 4 mm thickness of MWCNT-GFRP laminates. After optimizing the number of piles, the ball milled MWCNT-Epoxy suspension was added to the hardener (AH 312) in the ratio of 10:1 and hand lay-up was done between mild steel plates with overhead projection (OHP) sheets on both sides. The OHP sheets are sprinkled with mold release agent to avoid the sticking of the laminate to the OHP sheets. Rathore et al. [22] also used hand lay-up technique for fabrication of MWCNT-GFRP composite for mechanical testing. The arrangement was pressurized under compression molding device at a pressure of 2.4 MPa for 18 h. Then the laminates are kept in industrial oven about 24 h for curing purpose. The fabricated MWCNTs-GFRP nanocomposites were nearly 4 mm thick and had about 52% volume fraction of glass fabric and 48% volume fraction of epoxy resin filled with a diverse of low weight percentage multiwall carbon nanotubes (0.0, 0.1, 0.2, 0.3 and 0.4). Fig. 1 shows the schematic representation of nanocomposite laminate preparation.

3. Experimental methods

The fabricated laminates were cut for the tensile, flexural and hardness tests, in accordance with ASTM standards. For the tensile test, the coupons had the geometry of 200 mm × 20 mm with 4 mm thickness followed by ASTM standard D3039/D3039M-14 [23]. The flexural test coupons had a standard span – thickness ratio of 16:1 and a standard coupon width of 13 mm with the specimen length of 20% greater than the support span length followed by ASTM D7264 standard [24]. In accordance with ASTM D785 standard, test samples were cut into 25 mm × 25 mm size for the hardness test [25].

The tensile, flexural and hardness tests were conducted by using Instron 8801 mechanical tester and TRSN model Rockwell hardness tester. The testing apparatus of tensile and flexural tests are as shown in Fig. 2(a) and (b). The accurate method for a finding of flexural properties, i.e., flexural strength and failure strain of the epoxy modified nanocomposites was three-point bending test and also provides the indentation structure failure of the nanocomposites laminates. In addition to the tensile and compressive forces, the lightweight nanocomposites structures (i.e., sports instruments, radar absorbing structures) may undergo indentation load. Moreover, it is essential to conduct the hardness test to assess the overall mechanical properties. Fig. 2(c) shows the testing apparatus of indentation test (hardness test). The failure mechanisms and structural integrity of tested specimens were identified by the scanning electron microscope (SEM, Model: ZEISS). In the specimen notation “#%CNT-GFRPs, # represents the MWCNTs weight fraction (wt%) in the epoxy resin”.

3.1. Tensile behavior

Fig. 3(a) shows the typical tensile stress-strain curves of Neat GFRP and GFRP with modified (0.1, 0.2, 0.3 and 0.4 wt% of MWCNTs) epoxy composite laminates. The variation of tensile strength with MWCNTs concentration is studied and it is found that the tensile strength follows an increasing trend with the addition of MWCNTs to the epoxy, except 0.2 wt%. This decrement at 0.2 wt% may be attributed to weak matrix-fiber interfacial interactions and random alignment of fiber in the epoxy system as shown in Fig. 4(a) and (b). The decrement can be also attributed to few air voids and agglomeration of CNTs. In a similar way, the higher tensile strength achieved with 0.3 wt% of MWCNTs in the epoxy matrix amongst all concentrations. This happened due to the rich interfacial interactions between CNTs and epoxy matrix and excellent nanotube dispersion with low agglomeration. The tensile strength of MWCNT-GFRPs increased from 178.05 MPa (neat GFRP) to 209.69 MPa (nearly 17.77%) with the addition of 0.1% of MWCNTs, increased marginally to 179.92 MPa (nearly 1.05%) when MWCNTs content was 0.2%, increased significantly to 242.22 MPa (nearly 36.04%) by the addition of 0.3% of MWCNTs and increased appreciably to
Fig. 1 – Schematic illustration of fabrication of MWCNT-GFRP composite laminate.

Fig. 2 – Testing apparatuses of (a) tensile test, (b) flexural test, (c) hardness test.
Fig. 3 – (a) Typical tensile stress–strain curves, (b) ultimate tensile strength and tensile modulus of elasticity, and (c) failure strain.

Fig. 4 – Glass fiber bundle (a) 0.2% CNT-GFRP, (b) 0.3% CNT-GFRP and (c) failure mode of fiber breakage in the composite after tensile test.
215.56 MPa (nearly 21.06%) with the addition of 0.4% of MWCNTs.

A variety of MWCNT concentrations were tried in the literature to find out the optimum tensile properties of the MWCNT-GFRPs. Siddiqui et al. [26] applied different coatings onto the glass fiber surface to improve the reinforcing effect of composites. The experimental results reveal that samples of functionalized 0.3% CNTs with glass fiber roving's gives the better tensile properties than un-functionalized samples. Genedy et al. [27] reported that modified GFRP/EP nanocomposites had elevated tensile properties (strength increased to 28%) with 0.5 wt% of MWCNTs in the epoxy system. This composite laminate was fabricated with 6% of EP/MWCNTs impregnated glass fabric cloths. Fig. 3(b) and (c) shows the effect of CNT addition on the ultimate tensile strength (σt, max), a tensile modulus of elasticity and failure strain (%). In Fig. 3(b), the tensile strength of the MWCNTs-GFRP coupons increases appreciably as compared to the neat GFRP and tensile modulus decreases smoothly with the increase of MWCNTs content. Fig. 3(c) specifies that the failure strain of 0.3% MWCNT-GFRPs increases considerably when compared to 0.4% MWCNT-GFRPs, which is attributed to decreased interfacial interactions and CNT agglomerations. Gomny et al. [28] also indicated that the failure strain (%) increases with a specific low content of nanotubes and decrease with the large content of nanotubes.

In Fig. 4(c), an extensive fiber influence and the failure mode of fiber breakage is observed in the MWCNTs-GFRP composites after the tensile test. It is also observed that the delamination is dominant in 0.0% and 0.2%, whereas the 0.1%, 0.3% and 0.4% MWCNT concentrations shows less delamination. This happened due to the resin rich portions, low shear forces between nanotubes and randomly aligned nanotubes in the 0.1%, 0.3% and 0.4% GFRPs. As illustrated in Fig. 5(a) and (b), a huge amount of epoxy resin remains to stick to the surface of the fiber of 0.3% GFRP, while the 0% GFRP fiber surface is softer. This result shows the improvement of the interfacial interactions between resin and fibers. Even though the tensile strength was optimum for 0.3% GFRP, there were few voids and agglomerates that Tehran study [29] also proves that CNTs enhance the interfacial interactions in between epoxy and CNTs in the load transferring of large area additions. Additionally, Fig. 5(d) displays uneven fracture surfaces and helps to avoid the crack propagation and skirt the crack.

The damaged tensile test specimens of Neat GFRP and GFRP-MWCNTs are shown in Fig. 6. Two types of damages, i.e., tensile or shear damage, are identified in all rest specimens. Shear damage is due to the tangential loading along the aligned direction of the nanotubes and perpendicular direction of the fracture plane of the glass fabric, which tends to fiber breakage and debonding between fabric cloth and modified epoxy. Shear damage is observed along the bias direction of the fabric cloth, which initiates interfacial crack propagation in the matrix, delamination and extending to the fiber breakage.

Finally, it was concluded that 0.3% MWCNTs/GFRP samples give enhanced tensile properties after the tensile test due to rich interfacial interactions between CNTs and epoxy matrix and excellent nanotube dispersion with low agglomeration. The obtained tensile properties are as shown in Table 1.

### 3.2. Flexural behavior

The typical flexural stress-strain curves of unmodified and modified epoxy with GFRP samples are as shown in Fig. 7(a). The dissimilarity of flexural strength is observed for MWCNT-GFRP samples and it is found that the flexural strength does not follow an increasing trend with the CNTs addition. Specifically, the 0.2% GFRP samples are getting very low flexural strength (decreases nearly 12.02%) as compared to neat GFRP samples. Fig. 8(b) is the causes for the deterioration of flexural properties of the 0.2% sample. The deterioration may be also attributed due to epoxy stacks on the GFRP samples and poor wettability. In a similar way, the rich interfacial interaction between modified epoxy and glass fiber, limited fiber breakage and fiber pullouts are the reason for the optimal flexural strength of the 0.3% GFRP samples.

Fig. 7(b) and (c) shows the influence of CNT addition on the flexural strength (MPa), failure strain (%) and flexural chord modulus (GPa). In Fig. 7(b), the flexural strength of MWCNT-GFRPs increased from 238.42 MPa (neat GFRP) to 269.51 MPa (nearly 13.01%) with the addition of 0.1% of MWCNTs and decreased slightly to 212.82 MPa (nearly 12.02%) when MWCNTs content was 0.2%. In the same way, the flexural strength of MWCNT-GFRPs increased significantly to 332.53 MPa (nearly 39.41%) with the addition of 0.3% of MWCNTs and increased appreciably to 272.59 MPa (nearly 14.33%) with the addition of 0.4% of MWCNTs. Ming-Chuen et al. [30] study also reveals the similar results of flexural strength increment (nearly 9.2%) with 0.75% MWCNT-GFRP samples as compared to neat GFRP samples. Rathore et al. [22] have studied the flexural behavior of MWCNT-GFRP samples at different in situ elevated temperatures. The 0.1% MWCNT-GFRP samples gave higher flexural strength (+32.8% over neat GFRP) and modulus (+11.5% over neat GFRP) among all CNT concentrations. Fig. 7(c) shows an enhancement of the flexural modulus with the addition of low nanotube content to the epoxy resin. This enhancement was due to the higher failure strain of the laminate and improved interfacial interaction between the glass fiber and epoxy resin.

Noticeably, the addition of 0.4%, 0.1% and 0.3% MWCNT concentrations gives an enhanced incremental failure strain, as well as flexural chord modulus values, are shown in Fig. 7(b) and (c). But whereas the CNT content of 0.2% exhibits very low flexural strain and modulus compared to neat GFRP. Pinho et al. [31] also reported that poor interfacial interaction between matrix and fiber at the specific low addition of MWCNTs to the epoxy resin decreases the failure strain which keeps samples to lower failure strain. In general, CNTs help to improve the interfacial interactions between matrix and fiber which leads to enriching the load transfer between matrix and fiber [32]. The samples of 0.3% MWCNTs exhibits enriched flexural strain and flexural chord modulus values among modified and unmodified epoxy samples. Additionally, the 0.3% MWCNTs in the epoxy resin alters the failure mode of the matrix-fiber interface as well as improves the load transferring capacity. In Fig. 8(a), the resin rich areas with considerable air voids and fiber breakages are also responsible for the optimum flexural properties with 0.3% GFRP samples. Additionally, increasing content of CNT increases the viscosity of the matrix, resulting in the very low wetting performance.
Fig. 5 – SEM images of fiber–matrix interface (a) neat GFRP, (b) 0.3% MWCNT-GFRP, (c) MWCNT pullouts and voids at the damages area (0.3% MWCNT), (d) fiber–matrix crack propagation.

Fig. 6 – Failure modes of GFRPs with 0.0%, 0.1%, 0.2%, 0.3% and 0.4% MWCNTs (a) with and (b) without CNTs.

**Table 1 – Tensile properties of samples with different CNT contents.**

<table>
<thead>
<tr>
<th>Sample code</th>
<th>CNT content (wt%)</th>
<th>Tensile strain (%)</th>
<th>Tensile modulus of elasticity (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%CNT-GFRP</td>
<td>0.0</td>
<td>1.88420</td>
<td>14.0</td>
</tr>
<tr>
<td>0.1%CNT-GFRP</td>
<td>0.1</td>
<td>2.58121</td>
<td>13.8</td>
</tr>
<tr>
<td>0.2%CNT-GFRP</td>
<td>0.2</td>
<td>2.57968</td>
<td>13.0</td>
</tr>
<tr>
<td>0.3%CNT-GFRP</td>
<td>0.3</td>
<td>5.42618</td>
<td>10.3</td>
</tr>
<tr>
<td>0.4%CNT-GFRP</td>
<td>0.4</td>
<td>4.44216</td>
<td>11.7</td>
</tr>
</tbody>
</table>
Fig. 7 – (a) Flexural stress–strain curves, (b) mean flexural strength and mean failure strain of without and with CNTs (0.0%, 0.1%, 0.2%, 0.3% and 0.4%) to GFRPs, and (c) flexural chord modulus.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>CNT content (wt%)</th>
<th>Failure strain (%)</th>
<th>Flexural chord modulus of elasticity (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%CNT-GFRP</td>
<td>0.0</td>
<td>2.198</td>
<td>14.05</td>
</tr>
<tr>
<td>0.1%CNT-GFRP</td>
<td>0.1</td>
<td>2.796</td>
<td>15.20</td>
</tr>
<tr>
<td>0.2%CNT-GFRP</td>
<td>0.2</td>
<td>2.558</td>
<td>10.21</td>
</tr>
<tr>
<td>0.3%CNT-GFRP</td>
<td>0.3</td>
<td>2.831</td>
<td>17.39</td>
</tr>
<tr>
<td>0.4%CNT-GFRP</td>
<td>0.4</td>
<td>2.659</td>
<td>14.34</td>
</tr>
</tbody>
</table>

of the epoxy matrix in the lay-up. The specific higher amount of CNT addition increases the viscosity, which establishes air voids and dislocations in the composite solution [33]. In summary, 0.3% CNT modified epoxy with GFRPs exhibits optimal flexural properties among all modified and unmodified epoxy matrix samples. The achieved flexural properties are as shown in Table 2.

The optimal MWCNT concentrations of tensile and flexural properties remains the same (0.3% MWCNTs) and it was concluded that MWCNTs reinforced GFRP samples with low specific nanotube contents are weaker in tension as compared to compression (flexural).

3.3. Indentation behavior

The hardness values of all samples were measured using Rockwell hardness tester. The hardness test was conducted by using steel ball indenter of 6.35 mm diameter with hardness L-scale. The major load of 60 kg was applied and an average of five hardness values was taken for each sample.

The mechanical properties such as tensile strength, modulus of elasticity, resistance to friction, abrasion, etc., are highly influenced by the hardness test results [34]. From the existing literature, it was concluded that the higher hardness of the materials offered greater mechanical properties. The reason for the improved higher hardness was due to the fully developed interfacial interactions and enriched CNT dispersion. The effect of CNT content on the hardness of the laminates is shown in Fig. 9(a). The hardness values of MWCNT-GFRP laminates were increased from HRL 66.8 (neat GFRP) to HRL 75.7, HRL 64.6, HRL 83.4 and HRL 72.7 with the addition of 0.1, 0.2, 0.3 and 0.4% MWCNT-GFRPs, respectively. The optimum value of the hardness was obtained for 0.3% MWCNT-GFRP laminate with an increment of 124.8% compared to the neat GFRP.

In Fig. 9(b), the tensile strength increases in accordance with the hardness values. Precisely, the peak hardness values achieved optimum tensile strength with the addition of 0.3% MWCNT-GFRP laminate. However, 0.2%-GFRP samples possess lowest strength values, which was almost equal to the neat GFRP. Whereas, in the flexural testing, the strength...
of the laminate was reduced drastically (decrement of 12.02%) for 0.2%-GFRP as shown in Fig. 9(c). Finally, it was concluded that mechanical behavior of the material directly depends on the hardness of the material.

The improvements in hardness of CNT reinforced laminates may be due to numerous reasons [35]. The primary reason for greater hardness is the high crystallinity of material which tends to have higher hardness [36]. The secondary reason for the higher hardness is the reinforcement effect of MWCNTs into epoxy resin. Subsequently, CNTs are high strain energy induced materials, the homogeneous dispersion of CNTs in the epoxy resin can improve the rigidity and hardness through interfacial interaction [37]. Due to the above reasons, MWCNTs reinforced GFRP laminates improve the hardness. Moreover, these hardness values agree with the tensile and flexural tests. In addition, the hardness values decreased internally with the addition of nanotubes. This happened due to the agglomeration and poor dispersion of nanotubes in the epoxy resin.

4. Conclusions

The present study reported the fabrication method and influence of MWCNTs content on the mechanical properties of GFRPs. The experimental results recommended that mechanical properties of GFRP laminates were enhanced with the low specific MWCNT concentrations. The fiber–matrix improvements, damage mechanisms and interfacial bonding and debonding effects were perceived under SEM. The experimental conclusions are as follows:

- A 4mm thickness of GFRP laminates were achieved by 16 layers of glass fabric cloth with modified and unmodified epoxy resins to investigate the mechanical properties.
- The tensile strength of MWCNT-GFRPs increased from 178.05 MPa (neat GFRP) to 242.22 MPa (nearly 36.04%) with the addition of 0.3% of MWCNTs but increases marginally to 179.92 MPa (nearly 1.05%) when MWCNT content was 0.2%.
- The failure strain of 0.3% MWCNT-GFRPs increases considerably when compared to 0.4% MWCNT-GFRPs, which is attributed to decreased interfacial interactions and CNT agglomerations as illustrated in the SEM figures.
- The flexural strength of MWCNT-GFRPs increased from 238.42 MPa (Neat GFRP) to 323.53 MPa (nearly 39.41%) with the addition of 0.3% of MWCNTs but decreased slightly to 212.82 MPa (nearly 12.02%) when MWCNTs content was 0.2%.
- The optimum value of the hardness was obtained by 0.3% MWCNT-GFRP laminate with an increment of 124.8% compared to the neat GFRP.

Fig. 8 – SEM images of fiber–matrix interface (a) resin rich portions of 0.3% CNT sample, (b) severe matrix deformation of 0.2% CNT sample, and (c) low wettability region.

In summary, 0.3% CNT modified epoxy with GFRPs exhibits optimum tensile, flexural and hardness properties among all samples.

Conflicts of interest

The authors declare no conflicts of interest.

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