ABSTRACT

This paper discusses the potential use of multi-walled carbon nanotubes (MWCNTs) to improve the mechanical properties of short glass fiber composites. Two methods to incorporate MWCNTs in short glass fiber composite fabrication were examined. First, Carboxylic-functionalized MWCNTs were dispersed in a silane fiber sizing material and then were allowed to bond to the surface of glass fibers. Second, MWCNTs were grown on the surface of glass fibers using the chemical vapor deposition (CVD) method. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were used to examine the significance of MWCNTs on fiber surface. Fourier Transform Infrared (FTIR) analysis was also used to identify chemical reactions between MWCNTs, the glass fiber surface, and the sizing material. Short MWCNTs-modified glass fiber reinforced epoxy composites were also fabricated. Mechanical properties of the MWCNTs-modified composites were compared with short glass fiber composites produced with neat fibers using dynamic mechanical analysis (DMA). The experimental investigation showed that dispersing MWCNTs in a silane sizing agent is more efficient than growing MWCNTs on the surface of glass fibers. A significant improvement in the storage elastic modulus was observed when MWCNTs were dispersed in silane. FTIR analysis confirmed the formation of chemical bonds between both COOH–MWCNTs and the glass fiber surface. No significant difference in the loss modulus (i.e. time dependent behavior) of the glass fiber composites was found with the different methods of incorporating MWCNTs during composite fabrication.

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INTRODUCTION

In recent years, fiber reinforced polymer composites have attracted significant interest for the purpose of fabricating lightweight structures for engineering applications, such as automotive [1] and aerospace parts [2]. Glass fibers, in particular, are widely used in making fiber reinforced polymer composites due to their relatively high strength, low density and relatively low cost [2]. Interfacial adhesion between glass fibers and polymer matrix critically influences the performance of composite materials. Many attempts have been made to improve fiber composites using carbon nanotubes (CNTs) because of the extraordinary mechanical properties of CNTs, such as a very high tensile strength (200 GPa) and elastic modulus (200–1 TPa) [3]. There are three methods to incorporate CNTs in such composites: dispersion of CNTs in polymer matrix [4], growing of CNTs on surface of the fibers [5], and dispersion of CNTs in a fiber coating material before sizing the fibers [6]. Aggregation of CNTs and the increased viscosity of the polymer matrix due to CNTs inclusion are among a few critical challenges met when using the first method [7]. On the other hand, significant enhancement in tensile, flexural and impact behavior of short glass fiber reinforced polypropylene composites was found when CNTs were grown uniformly on the surface of the glass fiber [8]. The high aspect ratio, large surface area and unique structure of surface grown CNTs provide effective load transfer due to the strong interfacial bonding between the CNTs and matrix, and thus, they improve the mechanical properties of composites [5, 8]. Du et al. [9] reported 70% improvement in interfacial shear strength of fibers with surface grown CNTs embedded in epoxy due to the good adhesion between CNTs and fibers. Lachman et al. [10] confirmed such findings, reporting a 20% increase in the interfacial adhesion owing to good fiber-matrix interfacial properties. Godara et al. [11] examined three methods for incorporating CNTs in glass fiber/epoxy composites; in fiber sizing, in matrix and in both fiber sizing and matrix and reported that incorporating CNTs in fiber sizing exhibited significant improvement (approximately 90%) in the interfacial shear strength compared with a combination of incorporating CNTs on the fiber surface and in the matrix. Several studies also reported remarkable improvement in mechanical properties of carbon nanotube-coated fiber reinforced composites either using electrophoretic deposition coating method [12] or spray coating method [13].

In this study CNTs are incorporated on the surface of short glass fiber composites using two methods: (1) dispersion of CNTs in the glass fibers sizing and (2) growing of CNTs on the surface of glass fibers using the chemical vapor deposition (CVD) method prior to fiber sizing. Our goal is to enhance the mechanical behavior of the short glass fiber composites by improving the interfacial adhesion between the CNTs-coated glass fibers and the epoxy matrix.

EXPERIMENTAL METHODS

Materials

Functionalized multi-well carbon nanotube (COOH-MWCNTs) was used in this study. The COOH-MWCNTs supplied by Cheap Tubes, Inc., USA. They had an outer diameter of 20-30 nm, an inside diameter of 5-10 nm, and a length of 10-30 µm. The carboxyl (COOH) groups were 1.23% by weight. Un-sized glass fibers used in this study were supplied by Jushi Egypt Co.
Ferrocene (98%) supplied by Sigma Aldrich was used for preparing the catalyst coating glass fiber materials. 3-minopropyltriethoxysilane (3-APTES) supplied by Sigma Aldrich was used for coating glass fiber materials. The epoxy used in fabrication was EPOTUF® 37-127 epoxy system supplied by U.S. Composites, Inc. The epoxy resin is low viscosity, 100% reactive diluted liquid based on Bisphenol-A containing glycidyl ether. The hardener was Aliphatic Amine EPOTUF® 37-614. The resin to hardener mixing ratio was 2:1.

**Growth of MWCNTs on surface of glass fiber via chemical vapor deposition**

A typical chemical vapor deposition (CVD) set-up was used for growing MWCNTs on the surface of un-sized glass fibers (Figure 1) using benzene as a carbon source and ferrocene as a catalyst. Typically, a bundle of glass fiber rods was located at the center of the quartz tube. Nitrogen gas was fed into the system with a flow rate of 100 sccm (standard cubic centimeters per minute) while the temperature was gradually raised up to 800 °C in a ramping rate of 25 °C/min. A solution of ferrocene catalyst was prepared (0.2 g in 50 ml of benzene) and was introduced into the system using a carrier gas (hydrogen) at a flow rate of 100 sccm while nitrogen flow was discontinued. Inside the quartz tube, thermal decomposition of ferrocene catalyst took place and produced iron nanoparticles in the hydrogen atmosphere. Consequently, these nanoparticles were deposited onto the glass fiber surfaces. In addition, benzene was thermally decomposed to metallic carbon which diffused through the iron catalyst and crystallized on the glass surface forming MWCNTs. In this way, MWCNTs grew on the surface of glass fibers in a time of 30~60 min.

![Figure 1. Schematic diagram of the reactor system.](image)

**Coating of Glass Fiber Surface with MWCNTs via Silane Coupling Method**

For the silane modification, 0.9 g COOH-MWCNTs were dispersed in a 2% 3-APTES solution, which was then added to 150 ml of an ethanol: water (95:5 v/v) solution. The mixture was stirred at 70 °C for 4 hours. The silanized-MWCNTs (S-CNTs) were separated by filtration.
using distilled water and were dried at 80 °C overnight. Figure 2 displays the hypothesized chemical modification of COOH-MWCNT by 3-APTES.

To size the glass fibers, 0.4 ml of 3-APTES were added to 100 ml of toluene and stirred for five minutes. Then the fibers were dipped into the solution. The fibers were left in the solution overnight while being continuously stirred at a slow rate. The glass fibers were removed from the solution and dried at 80 °C for 2 hours. Figure 3 displays a schematic of the hypothesized chemical modification of glass fibers by 3-APTES.

Figure 2. A schematic showing modification of COOH-MWCNTs by 3-APTES.

Figure 3. A schematic showing modification of the glass fiber surface by 3-APTES.
To disperse silaned-MWCNTs (S-CNTs) in silane, 0.5 g of S-CNTs were added to the above solution and mixed for another 5 minutes before dipping the glass fibers into the solution. Figure 4 displays a schematic of the chemical modification of glass fibers by S-CNTs dispersed in 3-APTES. Figure 5 shows (a) silaned-glass fiber (S-GF), (b) silaned-glass fiber coated with S-CNTs (S-CNTs-GF), and (c) glass fiber with surface grown MWCNTs (CNTs-GF), respectively.

Figure 4. A schematic showing chemical modification of glass fibers by S-CNTs dispersed in 3-APTES.

Figure 5. (a) Silaned-glass fiber (S-GF), (b) silaned-glass fiber coated with S-CNTs (S-CNTs-GF), (c) and glass fiber with surface grown MWCNTs (CNTs-GF).
Fabrication of Short Glass Fiber Composites

Three types of modified short glass fiber composites, each with glass fiber contents of 3.0 wt.% and 7.0 wt.%, were prepared. The choice of glass fiber contents was based on preliminary work by the authors with the intention to produce consistence specimens given the simple method used for producing the glass fiber composites. The same technique for producing the MWCNTs-coated glass fibers can be used for precise glass fiber composite fabrication using resin fusion or vacuum assisted methods. Nevertheless, the relatively low glass fiber weight content used here was chosen intentionally for a proof of concept. The modified short glass fibers were first hand-stirred into the epoxy resin and then sonicated using a probe sonicator for 5 minutes. The epoxy hardener was then hand-stirred into the mixture for 5 minutes, mold casted and left overnight. Specimens were then cured for 2.5 days at 100 °C to ensure complete curing. The specimens were prepared for various characterization methods. The test matrix is summarized Table I.

<table>
<thead>
<tr>
<th>Sample codes</th>
<th>Glass fiber composite type</th>
<th>Glass fiber wt.%</th>
</tr>
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<tbody>
<tr>
<td>A3</td>
<td>Silane-glass fiber-epoxy composite (S-GF)</td>
<td>3.0</td>
</tr>
<tr>
<td>A7</td>
<td>Silane-glass fiber-epoxy composite (S-GF)</td>
<td>7.0</td>
</tr>
<tr>
<td>B3</td>
<td>Silane-MWCNTs-glass fiber-epoxy composite (S-CNT-GF)</td>
<td>3.0</td>
</tr>
<tr>
<td>B7</td>
<td>Silane-MWCNTs-glass fiber-epoxy composite (S-CNT-GF)</td>
<td>7.0</td>
</tr>
<tr>
<td>C3</td>
<td>CVD grown MWCNTs-glass fiber-epoxy composite (CNT-GF)</td>
<td>3.0</td>
</tr>
<tr>
<td>C7</td>
<td>CVD grown MWCNTs-glass fiber-epoxy composite (CNT-GF)</td>
<td>7.0</td>
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</table>

Material Characterization

The morphological structure of the prepared glass fiber composites was characterized by Field Emission Scanning Electron Microscope (FESEM) (Quanta 250, FEI company, Netherlands) attached with EDX (Energy Dispersive X-ray Analyses) unit. Fourier Transform Infrared Spectra (FTIR) analysis was performed on COOH-MWCNTs and MWCNTs-APTES to confirm their functionalization using Nicolet IS-10 FTIR spectrophotometer-Thermo Fisher Scientific within the 400-4000 cm⁻¹ wave number range. For the mechanical properties of short glass fiber composites, three specimens, each with dimensions 20 mm × 11 mm × 3 mm were tested. Dynamic mechanic analysis (DMA) was performed on a Triton Instruments, operating in the 3-point bending mode at an oscillation frequency of 1 Hz. Data were collected from room temperature to 150 °C at a scanning rate of 10 °C/min and the effect of the synthesis method on storage and loss modulus was quantified.

RESULTS AND DISCUSSION

Figures 6 (a-c) present the SEM images of MWCNTs grown on glass fibers at 800 °C for 60 minutes. It can be observed that the MWCNTs were deposited randomly on the surface of glass fibers, i.e. CNTs islands were formed at different positions on the surface (Figure 6a). Figures 6b and 6c present the SEM images of the composite sample at higher magnification. It is shown that the morphology of the MWCNTs illustrates that the MWCNTs formed are entangled with each
other and possess curved and tubular shapes. From the SEM images at higher magnification (Figures 6b and 6c), the dimensions of the nanotubes were measured and were confirmed to be in the range of ~ 10 - 60 nm in diameter and several micrometers in length.

The elemental composition of the as-prepared CNT-GF material was characterized by energy dispersive X-ray spectroscopy (EDX). It is well-known that the EDX method for evaluating surface and bulk fiber composition is based on analyzing the characteristic X-rays emitted from elements after an electron beam has reached the material [14]. As illustrated in Figure 7, a strong peak attributed to the carbon element is detected at the beginning of the spectrum. This indicates that carbon deposition has occurred on the surface of the glass fibers. Moreover, several peaks related to the typical composition of pristine glass fibers were also detected. These peaks include O, Al, Si and Ca (Figure 7). The higher intensity of Si peaks is related to having silica (SiO₂) as the primary component of glass fibers. Aluminum oxide (Al₂O₃) and calcium oxide (CaO) are typically added to silica to reduce the working temperature during glass fibers manufacturing.

![Figure 6. SEM images of MWCNTs grown on GFs under (a) low magnification and (b, c) high magnification.](image)

![Figure 7. EDX spectrum of as-prepared MWCNTs/glass fibers composite material.](image)
FTIR analysis was performed on COOH-MWCNTs and silane-treated MWCNTs to confirm their functionalization. Figure 8 represents FTIR spectra of the COOH-MWCNTs and MWCNTs-APTES [15]. Figure 8(a) shows the FTIR spectrum of MWCNTs-COOH. A strong peak appears at wavenumber of 3430 cm⁻¹ which is assigned to the vibration of the OH group. The aromatic ring stretching of C=C shows peaks at the wavenumber of around 1550-1600 cm⁻¹. The peak that appears at 1200 cm⁻¹ is assigned to C-O bonding in the MWCNTs-COOH. Figure 8(b) presents the FTIR spectrum of MWCNTs-APTES. The peaks at wavenumbers of 1100 and 895 cm⁻¹ are assigned to the characteristic Si-O and Si-OH bonding, respectively. The chemical interaction between the amino group of APTES and the carboxylic group on the surface of MWCNT results in the formation of covalent (amide) bonds appearing at 1560 cm⁻¹ [16]. In addition, this prominent peak is also attributed to the existence of an amine bicarbonate salt formed by interaction with carbon dioxide and water vapor in the atmosphere [17]. The peak at 3420 cm⁻¹ is from an OH group, that at 1170 cm⁻¹ is from the out-of-plane vibration of C-O bonding and the peak at 1710 cm⁻¹ corresponds to C=O stretching. The peaks at 2900 and 2850 cm⁻¹ are attributed to C-H bonding. These results confirm the attachment of APTES onto the surface of MWCNTs.

![FTIR spectra of the COOH-MWCNTs and MWCNTs-APTES.](image)

Figures 9 (a-c) present SEM images of S-CNTs dispersed in the fiber sizing material. Figure 9b shows that the S-CNTs are well-dispersed on the surface of GFs, and there are some S-CNTs islands at different positions on the surface of GFs, as well. The elemental composition of S-CNT-GF is illustrated in Figure 10. Comparing with the EDX spectrum of CNT-GF shown previously in Figure 7, it can be observed in S-CNT-GF that also a strong carbon peak is detected at the beginning of the spectrum which indicates that MWCNTs have been attached on the surface of glass fibers. Other peaks related to the typical composition of pristine glass fibers, as discussed above, are also detected.
Finally, the DMA tests were performed to study the influence of the method of incorporating MWCNTs using surface growth or dispersion in silane on the mechanical properties of the glass fiber composites. Figure 11 shows the storage modulus of the different glass fiber composites (described by Table I) with the different methods of incorporating MWCNTs and the different glass fiber contents with A3 and A7 representing the reference glass fiber at 3 wt.% and 7 wt.% glass fiber, respectively. It is obvious that incorporating MWCNTs increases the storage modulus of glass fiber composites at 3 wt.% glass fibers from 900 MPa for type A3 to 1048.6 MPa for B3 and 1189.3 MPa for C3, representing an increase of 16.4% and 32%, respectively. On the other hand, incorporating MWCNTs in glass fiber composites at 7 wt.% glass fibers results in an increase of the storage modulus of glass fiber composites from 993 MPa for type A7 to 1567.8 MPa for B7 and to 1245.3 MPa for C7, representing an increase of 58% and 25.4%, respectively. The above results show that both methods for incorporating MWCNTs improved the storage modulus of glass fiber composites. While surface growing of MWCNTs improves the storage modulus due to
increased mechanical adhesion/friction of MWCNTs with the epoxy matrix, this improvement is limited and is not affected by the glass fiber content. On the contrary, an increased glass fiber content might diminish some of that effect. On the other hand, dispersion of MWCNTs in silane seems to produce a method to consistently improve the mechanical properties of glass fiber composites. A significant increase from 16.4% to 58% in the storage modulus of glass fiber composites was observed as the fiber content increased from 3.0 to 7.0 wt.%

![Figure 11. Storage modulus of different types of glass fiber composites.](image)

The improvement in the mechanical properties due to MWCNTs dispersion in silane before sizing glass fibers can be attributed to the chemical reaction between silane, MWCNTs and the epoxy matrix, resulting in strong interfacial bond strength with glass fiber. Figure 12 shows SEM images of type B3 (silane-MWCNTs-glass fiber-epoxy composite at 3 wt.% glass fibers). The right hand side sketch explains the chemical reaction between the surface of glass fiber, the sizing material (silane incorporated S-CNTs) and the epoxy matrix. Bond between the glass fiber surface and the silane-MWCNTs, as well as chemical reactions between silane functional groups grafted on the surface of MWCNTs and epoxide groups in the epoxy matrix, provides high bond strength (adhesion) and, thus, improves the elastic modulus of glass fiber composites. This reaction is confirmed by the FTIR results presented in Figure 8. The improvement of the storage modulus of B7 by 58% reflects the improved adhesion between glass fibers and epoxy matrix. On the other hand, in the case of surface growth MWCNTs, composite types C3 and C7, there are no chemical reactions between the surface grown MWCNTs and the epoxy matrix. The improvement in the storage modulus with the surface grown MWCNTs can be attributed to the mechanical interlock produced by the MWCNTs on the surface of glass fibers preventing slip. This enabled a good but limited increase in the elastic modulus of glass fiber composites. It is important to note that both C3 and C7 composites do not include silane sizing. Further research is warranted to examine the significance of silane sizing on bonds between epoxy matrix and glass fibers with surface grown
MWCNTs. Figure 13 shows an SEM image of glass fiber composite type C3 (CVD grown MWCNTs-glass fiber-epoxy composite at 3 wt.% glass fibers). The right hand side sketch shows a schematic of the no-chemical adhesion zone between the surface of the glass fiber and the epoxy matrix. This results in limiting the improvement gained by growing MWCNTs on the surface of glass fibers of the mechanical properties of glass fiber composites.

Figure 12. SEM images of type B3 of glass fiber composites with MWCNTs dispersed in silane. Right hand side sketch explains schematically the chemical reactions between the surface of glass fiber, the silane sizing material and the epoxy matrix.

Figure 13. SEM image of type C3 of glass fiber composites with MWCNTs grown on the surface of the glass fiber. Right hand side sketch shows schematically that there is no chemical reactions between surface of glass fiber and the epoxy matrix.
Figure 14. Loss modulus of different types of glass fiber composites.

Figure 14 shows loss modulus of the different glass fiber composites (described by Table I) with the different methods of incorporating MWCNTs and the different glass fiber contents (3.0 wt.% and 7.0 wt.%). The results show that incorporating MWCNTs using both methods did not show significant effects on the loss modulus of glass fiber composites.

CONCLUSION

Two methods of modification of glass fiber by introducing MWCNTs on fiber surface using direct growth of MWCNTs or dispersion of MWCNTs in sizing agent have been investigated. Limited increase in elastic modulus was observed for glass fiber composites with surface grown MWCNTs compared with composites incorporating glass fiber coated with silane-modified MWCNTs. Microstructural investigations demonstrated that chemical reactions took place between MWCNTs dispersed in sizing silane and epoxy matrix. These chemical reactions created strong bond and improved fiber-matrix interfacial adhesion and, thus, improved the elastic modulus of glass fibers. Inclusion of MWCNTs using both methods showed limited effects on the loss modulus of glass fiber composites. Further research is warranted to examine the effect of silane treatment on glass fibers with surface grown MWCNTs. Further research is also necessary to examine the significance of such treatments on glass fiber composites with high chopped glass fiber contents ranging between 25-35% similar to that used in industrial applications. The above study proved that dispersing MWCNTs in silane sizing material might be an effective way to enhance the mechanical properties of short glass fiber composites.
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