



Hybrid multi-scale composites developed from glass microfiber fabrics and nano-epoxy resins containing electrospun glass nanofibers

Qi Chen^a, Lifeng Zhang^a, Yong Zhao^a, Xiang-Fa Wu^{b,*}, Hao Fong^{a,*}

^a Department of Chemistry, South Dakota School of Mines and Technology, Rapid City, SD 57701, USA

^b Department of Mechanical Engineering, North Dakota State University, Fargo, ND 58108, USA

ARTICLE INFO

Article history:

Received 12 March 2011
Received in revised form 26 June 2011
Accepted 22 August 2011
Available online 28 August 2011

Keywords:

A. Polymer–matrix composites (PMCs)
A. Glass fibers
B. Mechanical properties

ABSTRACT

In this study, hybrid multi-scale composites were developed from glass microfiber fabrics (GFs) and nano-epoxy resins containing electrospun glass nanofibers (EGNFs). The hypothesis was that, through dispersing a small amount of EGNFs into epoxy resin, mechanical properties (particularly out-of-plane mechanical properties) of the resulting hybrid multi-scale composites would be significantly improved. The composites were fabricated by the technique of vacuum assisted resin transfer molding (VARTM). The interlaminar shear strength, flexural properties, impact absorption energy, and tensile properties of the composites were evaluated, and the results were compared to those acquired from GFs/epoxy composite as well as GFs/epoxy composites containing chopped glass microfibers (GMFs); additionally, the reinforcement and/or toughening mechanisms were investigated. The study revealed that the nano-epoxy resin with 0.25 wt.% of EGNFs resulted in substantial improvements on mechanical properties of the resulting hybrid multi-scale composites.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Composites made of high-performance fibers (e.g., carbon and glass fibers) embedded in compliant polymeric resins have been used in a wide range of fields such as aerospace engineering and sports utilities. The major advantages of these composites include high specific strength and toughness, superior manufacturability, as well as excellent corrosion resistance and fatigue tolerance [1]. In general, fiber reinforced composite laminates exhibit excellent in-plane properties; whereas the resin matrices dominate out-of-plane properties (e.g., interlaminar shear strength and delamination toughness), which are substantially lower than in-plane properties [2]. To improve the properties (particularly the out-of-plane properties) of fiber reinforced composite laminates, nanoscale materials have been introduced into matrix resins for the development of hybrid multi-scale composites [3–5]; and numerous research efforts have indicated that the properties of these composites, in which nanoscale materials are dispersed as the second phase of matrices, are significantly higher [6–8]. Several types of nanoscale materials including graphite nanofibers, carbon nanotubes/nanofibers, exfoliated graphite nano-platelets, activated carbon, organo-clay, and silica nanoparticles have been studied to reinforce the

matrix-rich interlaminar regions due to their high mechanical properties and large surface-to-mass ratios [9–13].

The materials-processing technique of electrospinning provides a viable approach for convenient preparation of polymeric, ceramic, and carbonaceous fibers (commonly known as “electrospun nanofibers”) with diameters in the range from nanometers to micrometers [14]. Morphologically uniform and structurally amorphous silica (SiO₂) fibers with diameters of ~500 nm (i.e., glass nanofibers) can be readily prepared by electrospinning a spin dope consisting of tetraethyl orthosilicate (TEOS, the alkoxide precursor for making SiO₂) and polyvinylpyrrolidone (PVP, the carrying polymer) in *N,N*-dimethyl formamide (DMF, the solvent) followed by pyrolysis at 800 °C [15,16]. Our previously reported study revealed that, when electrospun glass nanofibers (EGNFs) were used to partially replace (up to a mass fraction of 7.5%) the conventional dental glass filler (i.e., the dental glass powder with particle sizes ranging from tens of nanometers to a few microns), the flexural strength, elastic modulus, and work of fracture of the resulting dental composites were considerably improved [17].

Herein, we report our recent studies on the reinforcement and/or toughening effects of EGNFs on the epoxy composites containing the conventional glass microfiber fabrics (GFs). Fig. 1 is a schematic representation of the hybrid multi-scale composites that have been developed and evaluated in this study. The hypothesis was that, through dispersing a small amount of EGNFs into epoxy resin, mechanical properties (particularly out-of-plane mechanical properties) of the resulting hybrid multi-scale composites would be

* Corresponding authors. Tel.: +1 701 231 8836; fax: +1 701 231 8913 (X.-F. Wu), tel.: +1 605 394 1229; fax: +1 605 394 1232 (H. Fong).

E-mail addresses: Xiangfa.Wu@nds.edu (X.-F. Wu), Hao.Fong@sdsmt.edu (H. Fong).

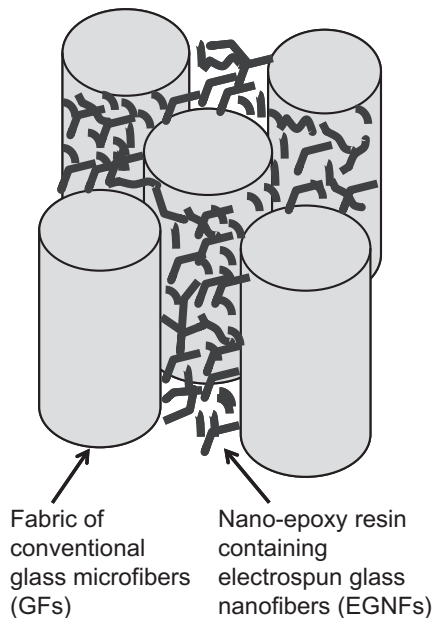


Fig. 1. Schematic representation of hybrid multi-scale composites developed from glass microfiber fabrics and nano-epoxy resins containing electrospun glass nanofibers.

significantly improved. To test the hypothesis, the commonly used composite-manufacturing technique of vacuum assisted resin transfer molding (VARTM) was adopted for fabrication of the composites; and the reinforcement and/or toughening effects of EGNFs on mechanical properties of the hybrid multi-scale composites were studied. For comparison, the short fibers chopped from a commercially available glass wool (*i.e.*, glass microfibers, GMFs) were also incorporated into the epoxy resin for making composites. Mechanical properties (including interlaminar shear strength, flexural properties, impact adsorption energy, and tensile properties) of the prepared composites were evaluated, and scanning electron microscopy (SEM) was employed to examine the micro- and nano-scaled morphologies as well as the fracture surfaces to study the failure mechanisms.

2. Experimental

2.1. Materials

The epoxy resin of SC-15A and the associated hardener of SC-15B were purchased from the Applied Poleramic Inc. (Benicia, CA). The plain-woven fabrics of conventional glass microfibers (S-glass, 6 osy) and the glass wool, with respective morphologies being shown in Fig. 2A–C, were purchased from the Fisher Scientific (Pittsburgh, PA). TEOS (with purity of 98%), PVP ($M_w = 13,00,000$), DMF (with purity of 99%), and dimethyl sulfoxide (DMSO, with purity of 98%) were purchased from the Sigma–Aldrich Co. (Milwaukee, WI) and used without further purification.

2.2. Preparation of electrospun glass nanofibers

The detailed procedures and conditions for the preparation of EGNFs were described in a previous publication [17]. The EGNFs for this study (as shown in Fig. 2D) were prepared using a spin-dope consisting of 13% (mass fraction) TEOS and 13% PVP in a mixture solvent of DMF/DMSO (mass fraction: 2/1) followed by pyrolysis at 800 °C.

2.3. Preparation of nano-epoxy resins

EGNFs with four mass fractions (*i.e.*, 0.05, 0.1, 0.25 and 0.5 wt.%) were dispersed into the SC-15A epoxy resin by stirring at 125 rpm for 12 h using a Heidolph RZR 50 Heavy Duty Stirrer followed by being sonicated (using a 100 W digital ultrasonic probe, purchased from the Branson Ultrasonics Corp.) for 30 min to achieve the uniform dispersion of the nanofibers in the resin [18]. Subsequently, the SC-15B hardener was added with the mass ratio of the hardener versus the epoxy resin being set at 30/100, and the mixtures were then hand-mixed for 5 min. After deaeration for 20 min under vacuum (~ 27 mm Hg), the prepared nano-epoxy resins were used for the fabrication of hybrid multi-scale composites using the VARTM technique. For comparison, chopped GMFs were also dispersed in the epoxy resin using the same procedure to prepare the micro-epoxy resins.

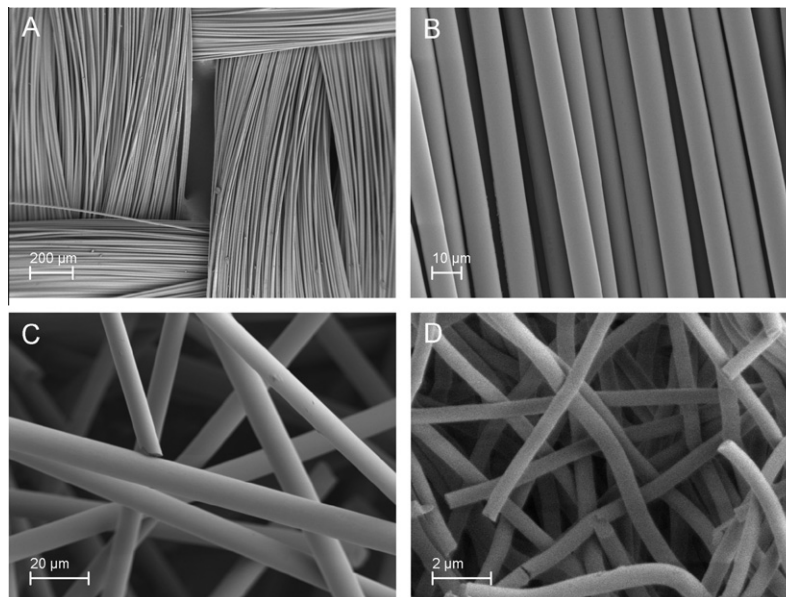


Fig. 2. SEM images showing the representative morphologies of (A) S-glass fabrics, (B) a microfiber bundle in the fabrics, (C) chopped glass microfibers, and (D) electrospun glass nanofibers.

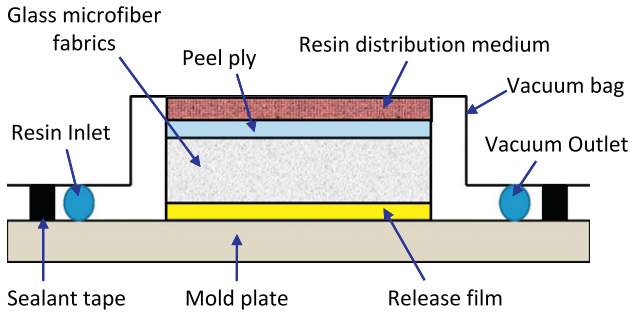


Fig. 3. The schematic of vacuum assisted resin transfer molding (VARTM).

2.4. Fabrication of hybrid multi-scale composites

The (micro- and) nano-epoxy resins were infused into a vacuum bag containing six plies of woven glass fabrics (GFs) using the VARTM technique, as schematically shown in Fig. 3. It is noteworthy that, with even a small amount of glass fibers (including both EGNFs and chopped GMFs) incorporated into the epoxy resin, a considerable increase of viscosity would be observed; to improve the fluidity, the colloidal suspension was kept at 50 °C, and the vacuum of 27 mm Hg was applied during the initial curing at room temperature for 24 h. The obtained composites were further cured in an oven at 110 °C for 5 h prior to the following characterization and evaluation. For comparison, the conventional composite made

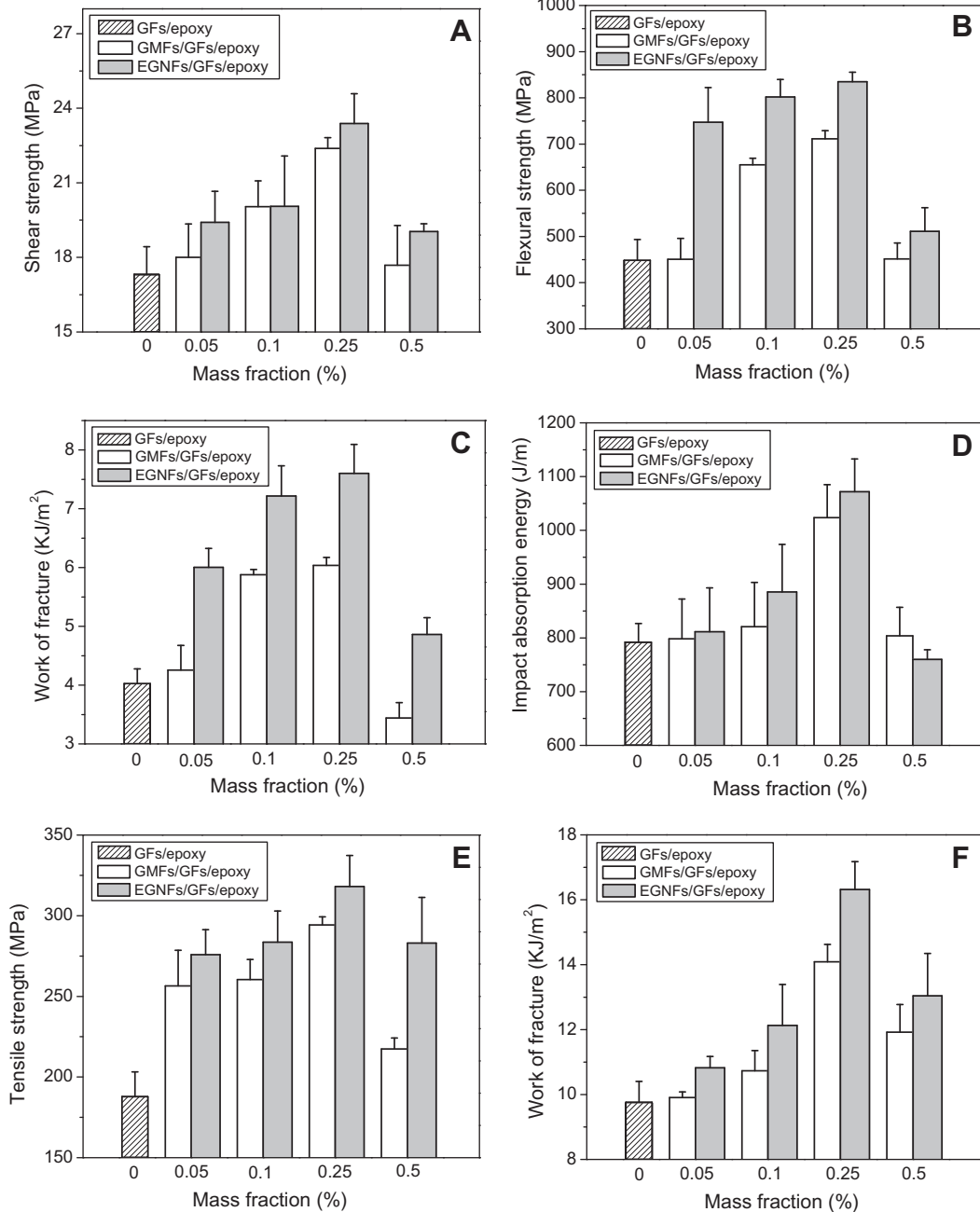


Fig. 4. Mechanical properties of the composites acquired from the short-beam shear test, three-point bending test, Izod impact test, and tension test: (A) shear strength, (B) flexural strength, (C) flexural work of fracture, and (D) impact absorption energy, as well as (E) tensile strength and (F) tensile work of fracture.

of six layers of GFs and epoxy resin (without EGNFs and/or chopped GMFs) was also fabricated and evaluated.

2.5. Characterization and evaluation

A Zeiss Supra 40 VP field-emission scanning electron microscope (SEM) was employed to examine morphologies of the fibers as well as fracture surfaces of the composites. Prior to SEM examinations, the specimens were sputter-coated with gold to avoid charge accumulations.

Mechanical properties of the fabricated composites were tested at room temperature. The impact specimens (64 mm in length, 12.7 mm in width, and 1.6 mm in thickness), the flexural specimens (50.8 mm in length, 12.7 mm in width, and 1.6 mm in thickness), and the short-beam specimens (8 mm in length, 4 mm in width, and 1.6 mm in thickness) were cut from the prepared composite panels by water-jet. The impact tests were performed on a Tinius Olsen impact tester (Impact 104) according to the ASTM D256. The specimens for flexural and short-beam tests were prepared and evaluated in accordance with ASTM D790 and ASTM D2344, respectively. The three-point flexural test with the span distance of 25.4 mm was conducted to fracture the specimens at the strain rate of 0.01 mm/mm/min on a QTESTTM/10 mechanical testing machine purchased from the MTS Systems Co. (Eden Prairie, MN). The short-beam test was carried out at the span-to-thickness ratio of 4 and the cross-head speed of 1 mm/min until the specimens failed. Five specimens of each composite were evaluated, and the mean values and the associated standard deviations of the mechanical properties were calculated.

3. Results and discussion

3.1. Interlaminar shear strength

The short-beam shear test was carried out to measure the interlaminar shear strength of the fabricated composites. Interlaminar shear strength is to describe the composite's resistance against the failure under shear stress; herein, the interlaminar shear strength is calculated according to an approximate formula:

$$\tau_s = 0.75 \frac{P_m}{b \times h} \quad (1)$$

where τ_s is the (short-beam) interlaminar shear strength in MPa, P_m is the maximum load (recorded in the test) in N, b is the specimen width in mm, and h is the specimen thickness in mm.

As shown in Fig. 4A, the values of interlaminar shear strength were increased with the increase of GMFs or EGNFs amounts up to 0.25 wt.%. The value for the control sample (i.e., the epoxy composite with GFs only) was (17.3 ± 1.1) MPa; for the GFs/epoxy composites containing 2.5 wt.% GMFs or EGNFs, the respective values were (22.4 ± 0.4) MPa and (23.4 ± 1.2) MPa. Thus, the interlaminar shear strength was improved by 29.5% and 35.3%, respectively. Nonetheless, when the epoxy resins contained 0.5 wt.% GMFs or EGNFs, the interlaminar shear strength decreased; this was probably due to the agglomeration of GMFs or EGNFs at the higher concentration. It is known that the agglomerates would act as mechanical weak points (structural defects) in the composites.

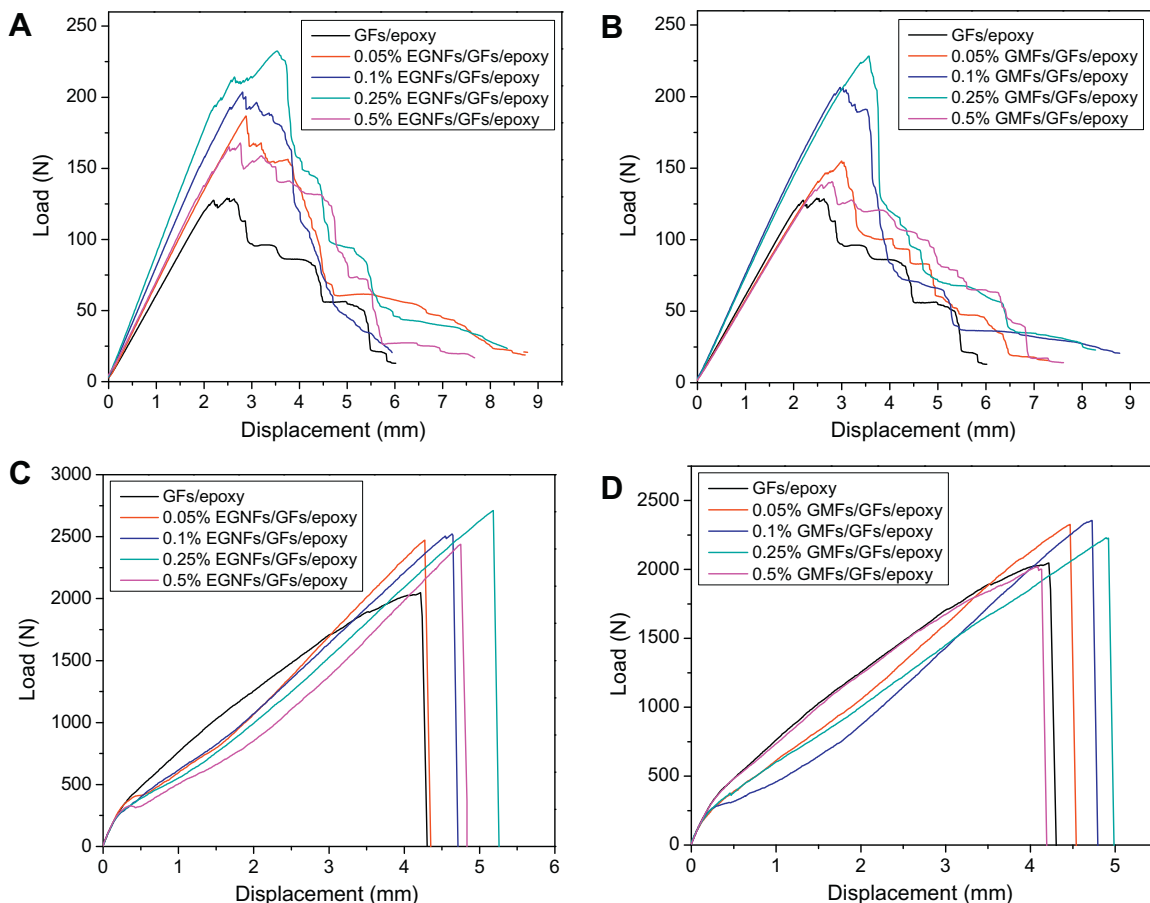


Fig. 5. Typical experimental load–displacement curves recorded from the three-point bending test (A and B) and tensile test (C and D) for the GFs/epoxy composites containing varied amounts of GMFs or EGNFs.

3.2. Flexural properties

Fig. 5A and B shows the typical load–displacement curves acquired experimentally for the composites with and without GMFs or EGNFs. It was evident that the incorporation of GMFs or EGNFs substantially increased the flexural rigidity (stiffness) and failure load, which would reach the maximum values when the amount of GMFs or EGNFs was 0.25 wt.%. The flexural strength and work of fracture (WOF) of GFs/epoxy composites containing varied mass fractions of GMFs or EGNFs were measured, and the results are shown in Fig. 4B and C. The values of flexural strength and WOF were substantially increased by the incorporation of small mass fractions (up to 0.25 wt.%) of GMFs or EGNFs into the GFs/epoxy composites; if the incorporation amount was too high (e.g., 0.5 wt.%), the values would decrease. The flexural strength and WOF for the control sample of GFs/epoxy composite were (448.4 ± 45.1) MPa and (4.0 ± 0.3) kJ/m², respectively. For the GFs/epoxy composite with 0.25 wt.% GMFs, the flexural strength and WOF were increased to (711.5 ± 17.6) MPa and (6.0 ± 0.1) kJ/m². Thus, the flexural strength was improved by 58.7%, and the work of fracture was improved by 50% respectively. For the GFs/epoxy composite with 0.25 wt.% EGNFs, the measured values of flexural strength and WOF were (835.0 ± 20.5) MPa and (7.6 ± 0.5) kJ/m², representing the improvements of 86.2% and 90% compared to the values acquired from the control sample respectively. Further increase of the incorporation amount of GMFs or EGNFs did not result in higher mechanical properties. For the GFs/epoxy composite with 0.5 wt.% GMFs, the respective values of flexural strength and WOF were (451.2 ± 34.5) MPa and (3.4 ± 0.3) kJ/m²; while for the GFs/epoxy composite with 0.5 wt.% EGNFs, the values were (511.2 ± 50.6) MPa and (4.9 ± 0.3) kJ/m², respectively. These results indicated that both micro- and nano-epoxy resins could substantially improve flexural properties of the resulting composites when the incorporation amount of GMFs or EGNFs was low (e.g., 0.25 wt.%), whereas EGNFs (and the resulting nano-epoxy resins) outperformed GMFs (and the resulting micro-epoxy resins). This is primarily due to the following two reasons including (1) the mechanical strength of ceramic fibers (such as glass fibers) is inversely proportional to the square root of diameter, assuming that the fibers (with different diameters) possess the same density and distribution of structural defects [1], thus the EGNFs

might be stronger than GMFs; and (2) the smaller the fiber diameters are, the larger the total surface areas will be; this would result in the improvement on interfacial bonding strength. It is noteworthy that GMFs or EGNFs have to be distributed uniformly in the epoxy resin to achieve the reinforcement effect; as described before, if GMFs or EGNFs exists as agglomerates, which would act as mechanical weak points (structural defects), the mechanical properties of the corresponding composites would be low.

3.3. Three-point bending fracture surface and the reinforcement mechanism

It is well-known that the shear stress is typically transferred from layer to layer through resin matrix during the interlaminar shear failure and three-point flexural failure of the laminated composites. Thus, the main failure mechanism is related to interfacial bonding between the resin and the fibers; while the deformation/fracture of resin matrix may also contribute to the failure [2]. To understand the reinforcement mechanism of EGNFs, the fracture surfaces of three-point bending specimens were examined by SEM. Representative fracture surfaces of the GFs/epoxy composites with 0.25 wt.% GMFs or EGNFs as well as the control sample are shown in Fig. 6. For the control sample, the matrix completely detached from the surface of GFs due to weak adhesion, and the failure surfaces of fibers were smooth without the remnants of resin (Fig. 6A). In comparison, the specimens with GMFs or EGNFs could be distinguished from significantly different interfacial microstructure and the deformation of matrix, as shown in Fig. 6B–D. These SEM micrographs showed that the fibers of GMFs or EGNFs were surrounded by and adhered to the resin, indicating that the interfacial bonding between the glass fabrics and the epoxy matrix could be improved by the micro- or nano-epoxy resins. These results suggested that the presence of GMFs or EGNFs could deflect the micro-cracks, and thus the resistance to crack growth was increased. Additionally, GMFs and EGNFs could also be broken and/or detached from the epoxy resin when the load was applied; this would dissipate the strain energy, preventing the failure of the composites and leading to the higher value of work of fracture. Nonetheless, as shown in Fig. 6D, the EGNFs appeared to form agglomerates in the GFs/epoxy composite with 0.5 wt.% EGNFs; this was probably the reason that such a composite had

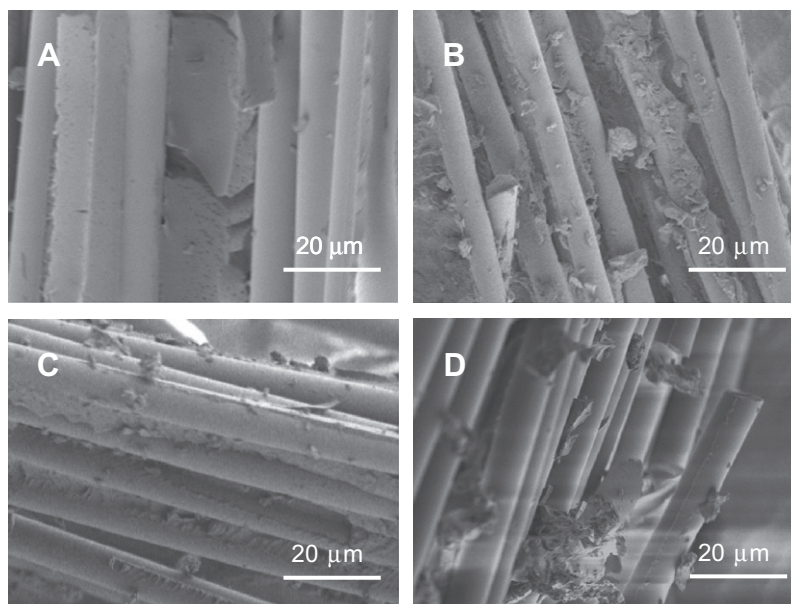


Fig. 6. SEM images showing the representative three-point bending fracture surfaces: (A) the GFs/epoxy composite (control sample), (B) the GFs/epoxy composite with 0.25 wt.% GMFs, (C) the GFs/epoxy composite with 0.25 wt.% EGNFs, and (D) the GFs/epoxy composite with 0.5 wt.% EGNFs.

lower mechanical strength. For the same mass fraction of GMFs or EGNFs (as described before, the mechanical strength of EGNFs might be considerably higher than that of GMFs) in the epoxy resin, the smaller the fiber diameters are, the larger the total surface areas will be; this would result in the improvement on interfacial bonding strength, leading to higher mechanical properties (including strength, modulus, and work of fracture) of the composites.

3.4. Impact property

The Izod impact test of notched specimens was conducted to examine fracture behaviors of the fabricated composites through measuring the energy absorption to break the specimens at high strain rates. Upon impact, the total energy can be divided into two components including (1) the elastic energy stored in specimen in the form of mechanical vibrations, part of which is reflected back to the impactor, and (2) the dissipated energy associated with plastic deformation of resin, generation of cracks in matrix, as well as detachment of fibers from resin matrix in the interfacial regions [19].

As shown in Fig. 4D, the values of impact absorption energy were increased when the incorporation amount of GMFs or EGNFs was up to 0.25 wt.%; the values were then decreased when the incorporation amount was further increased. The impact absorption energy of the control sample of GFs/epoxy composite was (791.9 ± 35.0) J/m. For the composites containing 0.25 wt.% GMFs or EGNFs, the respective impact absorption energies were increased to (1023.7 ± 61.2) J/m and (1072.0 ± 61.0) J/m; thus, the

impact absorption energies were improved by 29.3% and 35.4%, respectively, and it appeared that EGNFs slightly outperformed GMFs by 5.0%. Nonetheless, the impact absorption energies of the composites with 0.5 wt.% GMFs or EGNFs were decreased to (803.8 ± 53.2) J/m and (759.9 ± 18.0) J/m, respectively; and this was also attributed to the formation of agglomerates of GMFs or EGNFs.

3.5. Impact fracture surfaces and the toughening mechanism

In general, the impact absorption energy may result in delamination of composites, breakage and/or pull-out of fibers, and deformation of resin matrices. Upon impact, if the energy is lower than the critical value, no impact failure will occur, while the energy will only lead to (elastic) deformation of resin matrix. As the incident impact energy increases, delamination starts to occur and/or propagate until the maximum delaminated area is reached. When the impact energy is further increased, (localized) failures such as breakage and/or pull-out of fibers as well as complete delamination will occur.

The SEM images in Fig. 7 show the representative impact fracture surfaces of (A) GFs/epoxy composite, (B) GFs/epoxy composite with 0.25 wt.% GMFs, and (C) GFs/epoxy composite with 0.25 wt.% EGNFs; the images on the left (A1, B1, and C1) show the regions within composite laminae, while the images on the right (A2, B2, and C2) show the interlaminar regions. As shown in Fig. 7 (A1), the interface between (neat) epoxy resin and glass fabrics had the lowest impact resistance, as evidenced by smooth fiber

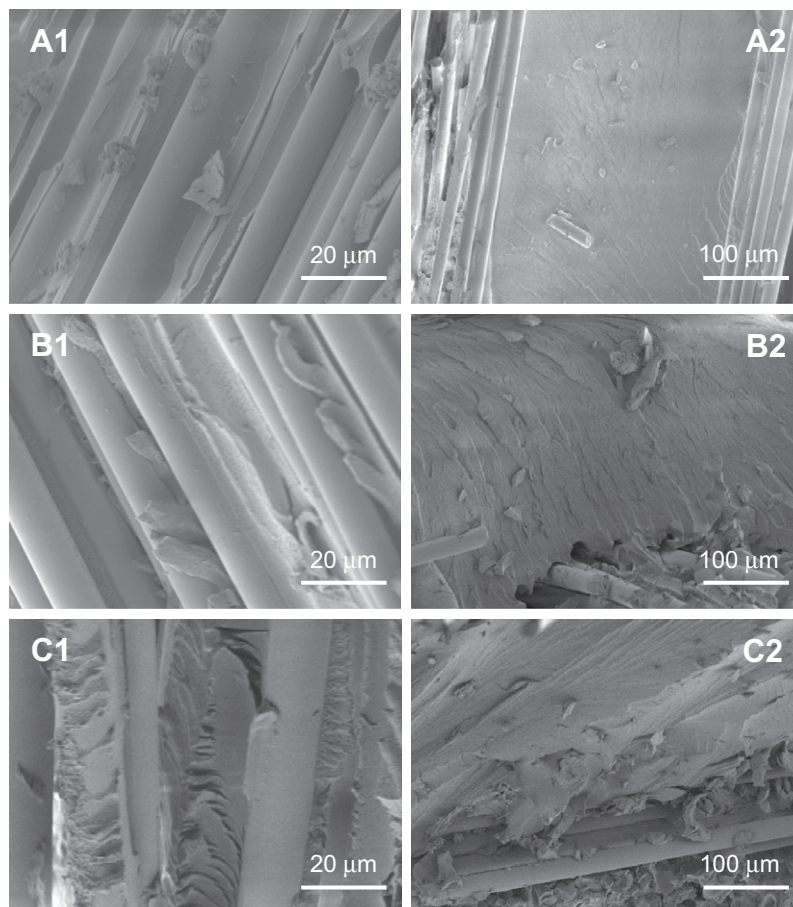


Fig. 7. SEM images showing the representative impact fracture surfaces: (A) the GFs/epoxy composite (control sample), (B) the GFs/epoxy composite with 0.25 wt.% GMFs, and (C) the GFs/epoxy composite with 0.25 wt.% EGNFs. The images on the left (A1, B1, and C1) showing the regions within composite laminae, while the images on the right (A2, B2, and C2) showing the interlaminar regions.

surfaces upon debonding failure. As shown in Fig. 7 (A2), the fracture surface in the interlaminar regions was smooth with oriented fracture lines due to extension of crazings initiated from the locations of stress concentration. In contrast, Fig. 7 (B1) and (C1) exhibited dimpled/scalloped fracture features; this could explain the formation of tougher interface between epoxy matrix and glass fabrics due to the presence of GMFs or EGNFs. Meantime, the fracture surfaces of the matrix regions, as shown in Fig. 7 (B1) and (C1), were rougher without clearly identifiable fracture lines; and the fracture surface of the composite with EGNFs was rougher than that of the composite with GMFs. These results suggested that the (micro- and) nano-epoxy resins could increase the matrix deformation and crack length considerably during the impact fracture, making the delamination more difficult to occur (*i.e.*, more energy would be required for impact fracture). When the cracks finally broke away from the fibers, kinked fracture surfaces were created, suggesting more strain-energy dissipation during cracking, which led to the increase of impact strength/resistance.

3.6. Tensile properties

The typical load–displacement curves of tensile tests for the composites with and without GMFs or EGNFs are shown in Fig. 5C and D. Similar to the ones shown in Fig. 5A and B, the hybrid multi-scale composite with 0.25 wt.% EGNFs had the highest stiffness and failure load. Based upon all of the load–displacement curves acquired experimentally, the tensile strength and WOF of GFs/epoxy composites containing varied amounts of GMFs or EGNFs were acquired, as shown in Fig. 4E and F. Each datum in the plots provided the mean value of five measurements with the error bar representing one standard deviation.

As shown in Fig. 4E and F, the values of tensile strength and WOF were significantly increased when the (micro- and) nano-epoxy resins were employed. The tensile strength and WOF for the conventional GFs/epoxy composite were (187.8 ± 15.4) MPa and (9.8 ± 0.6) kJ/m², respectively. For the composite with 0.25 wt.% of GMFs, the tensile strength and WOF were (294.3 ± 5.0) MPa and (14.1 ± 0.5) kJ/m², respectively; thus, the tensile strength was improved by 36.2%, and the WOF was increased by 43.9%. For the composite with 0.25 wt.% EGNFs, the respective tensile strength and WOF were (318.1 ± 19.2) MPa and (16.3 ± 0.9) kJ/m²; thus, the tensile strength and WOF were improved by 69.4% and 66.3%, respectively, compared to the control sample of GFs/epoxy composite. It was also evident that EGNFs (and the resulting nano-epoxy resins) outperformed GMFs (and the resulting micro-epoxy resins). As explained previously, this might be attributed to the following two reasons including (1) EGNFs might possess higher mechanical strength than GMFs, since the mechanical strength of glass fibers would be inversely proportional to the square root of diameter; and (2) the smaller the fiber diameters are, the larger the total surface areas will be; and this would result in the improvement on interfacial bonding strength. Similar to other tests, the mechanical properties of composites with 0.5 wt.% GMFs or EGNFs were lower than those of composites with 0.25 wt.% GMFs or EGNFs due to the formation of agglomerates.

4. Concluding remarks

In this study, hybrid multi-scale composites were developed from glass microfiber fabrics (GFs) and nano-epoxy resins containing electrospun glass nanofibers (EGNFs); for comparison, chopped glass microfibers (GMFs) were also studied for the preparation of micro-epoxy resins. The hypothesis was that, through dispersing a small amount of EGNFs into epoxy resin, mechanical properties (particularly out-of-plane mechanical properties) of the resulting

hybrid multi-scale composites would be significantly improved. The composites were fabricated by the technique of vacuum assisted resin transfer molding (VARTM). The interlaminar shear strength, flexural properties, impact absorption energy, and tensile properties of the hybrid multi-scale composites were tested, and the results were compared to those of conventional GFs/epoxy composite as well as the GFs/epoxy composites with GMFs. The study revealed that the epoxy resins containing EGNFs or GMFs would result in substantial improvements on mechanical properties of the resulting composites, while EGNFs outperformed GMFs on the improvements. This was due to higher mechanical strength of EGNFs as well as stronger interface between EGNFs and epoxy resin. The study also indicated that, the optimal amount of EGNFs or GMFs in the corresponding nano- or micro-epoxy resins was ~0.25 wt.%; when the amount of EGNFs or GMFs was higher, the agglomerates would be formed. These agglomerates would act as mechanical weak points and/or structural defects, leading to lower mechanical properties. The study suggested that EGNFs had the potential to be utilized as innovative reinforcement and/or toughening agent for the development of nano-epoxy resins, which would further be used for the fabrication of high-performance epoxy composites with fabrics of conventional glass microfibers.

Acknowledgments

The research conducted at the South Dakota School of Mines and Technology (SDSM&T) was supported by the National Aeronautics and Space Administration (NASA) of the United States (Grant No.: NNX07AT52A) and by the U.S. Air Force Research Laboratory (AFRL) under the Cooperative Agreement Number of FA9453-06-C-0366. The study conducted at the North Dakota State University (NDSU) was supported in part by the New Faculty Research Initiative Grant and the NDSU Development Foundation.

References

- [1] Mallick PK. Fiber-reinforced composites: materials, manufacturing, and design. New York: Marcel Dekker, Inc.; 1993. p. 1–11.
- [2] Zhu J, Imam A, Crane R. Processing a glass fiber reinforced vinyl ester composite with nanotube enhancement of interlaminar shear strength. *Compos Sci Technol* 2007;67:1509–17.
- [3] Bekyarova E, Thostenson ET, Yu A. Multiscale carbon nanotube – carbon fiber reinforcement for advanced epoxy composites. *Langmuir* 2007;23:3970–4.
- [4] Kulkarni M, Carnahan D, Kulkarni K, Qian D, Abot JL. Elastic response of a carbon nanotube fiber reinforced polymeric composites: a numerical and experimental study. *Composites: Part B* 2010;41(5):414–21.
- [5] Zhamu A, Zhong WH, Stone JJ. Experimental study on adhesion property of UHMWPE fiber/nano-epoxy by fiber bundle pull-out tests. *Compos Sci Technol* 2006;66:2736–42.
- [6] Gaicia EJ, Wardle BL, Hart AJ. Joining prepreg composite interfaces with aligned carbon nanotubes. *Composites: Part A* 2008;39:1065–70.
- [7] Gojny FH, Wichmann MHG, Fiedler B. Influence of nano-modification on the mechanical and electrical properties of conventional fiber-reinforced composites. *Composites: Part A* 2005;36(11):1525–35.
- [8] Wichmann MHG, Sumfleth J, Gojny FH. Glass fiber-reinforced composites with enhanced mechanical and electrical properties-benefits and limitations of a nanoparticle modified matrix. *Eng Fract Mech* 2006;73(16):2346–59.
- [9] Thostenson ET, Li WZ, Wang DZ, Ren ZF, Chou TW. Carbon nanotube/carbon fiber hybrid multiscale composites. *J Appl Phys* 2002;91:6034–7.
- [10] Tsai JL, Wu MD. Organoclay effect on mechanical response of glass/epoxy nanocomposites. *J Compos Mater* 2008;42(6):553–68.
- [11] Park JK, Do IH, Askeland P. Electrodeposition of exfoliated graphite nanoparticles onto carbon fibers and properties of their epoxy composites. *Compos Sci Technol* 2008;68:1734–41.
- [12] Allaoui A, Bai S, Cheng HM. Mechanical and electrical properties of a MWNT/epoxy composites. *Compos Sci Technol* 2002;62:1993–8.
- [13] Kinloch AJ, Masania K, Taylor AC. The fracture of glass-fiber-reinforced epoxy composites using nanoparticle-modified matrices. *J Mater Sci* 2008;43:1151–4.
- [14] Dzenis Y. Spinning continuous fibers for nanotechnology. *Science* 2004;304:1917–9.
- [15] Liu Y, Sagi S, Chandrasekar R, Zhang L, Hedin NE, Fong H. Preparation and characterization of electrospun SiO₂ nanofibers. *J Nanosci Nanotechnol* 2008;8:1528–36.

- [16] Wen S, Liu L, Zhang L, Chen Q, Zhang L, Fong H. Hierarchical electrospun SiO₂ nanofibers containing SiO₂ nanoparticles with controllable surface-roughness and/or porosity. *Mater Lett* 2010;64:1517–20.
- [17] Gao Y, Sagi S, Zhang L, Liao Y, Cowles DM, Sun Y, et al. Electrospun nano-scaled glass fiber reinforcement of Bis-GMA/TEGDMA dental composites. *J Appl Polym Sci* 2008;110:2063–70.
- [18] Inam F, Peils T. Transmission light microscopy of carbon nanotube–epoxy nanocomposites involving different dispersion methods. *Adv Compos Lett* 2006;15(1):7–13.
- [19] Schrauwen B, Bertens P, Peijs T. Influence of hybridization and test geometry on the impact response of glass-fiber-reinforced laminated composites. *Polym Polym Compos* 2002;10(4):259–72.