

Preparation and Evaluation of Nano-Epoxy Composite Resins Containing Electrospun Glass Nanofibers

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ABSTRACT: In this study, electrospun glass (structurally amorphous SiO₂) nanofibers (EGNFs) with diameters of ~ 400 nm were incorporated into epoxy resin for reinforcement and/or toughening purposes; the effects of silanization treatment (including different functional groups in silane molecules) and mass fraction of EGNFs on strength, stiffness, and toughness of the resulting nano-epoxy composite resins were investigated. The experimental results revealed that EGNFs substantially outperformed conventional glass fibers (CGFs, with diameters of ~ 10 μm) in both tension and impact tests, and led to the same trend of improvements in strength, stiffness, and toughness at small mass fractions of 0.5 and 1%. The tensile strength, Young's modulus, work of fracture, and impact strength of the nano-epoxy composite

resins with EGNFs were improved by up to 40, 201, 67, and 363%, respectively. In general, the silanized EGNFs with epoxy end groups (G-EGNFs) showed a higher degree of toughening effect, while the silanized EGNFs with amine end groups (A-EGNFs) showed a higher degree of reinforcement effect. The study suggested that electrospun glass nanofibers could be used as reinforcement and/or toughening agent for making innovative nano-epoxy composite resins, which would be further used for the development of high-performance polymer composites. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 444–451, 2012

Key words: composites; nanofiber; mechanical properties; epoxy resins

INTRODUCTION

Fiber reinforced polymer composites are generally fabricated through impregnation of fiber fillers (with high strength and modulus) into polymeric resin matrices. The integration of filler and matrix phases results in excellent mechanical properties that cannot be achieved from either component alone. The high ratio of strength/modulus to weight makes the fiber reinforced polymer composites widely used in aircrafts, automobiles, sports utilities, and satellites.¹ The conventional fibers for making composites include carbon fibers, glass fibers, and polymer fibers (e.g., Kevlar fibers) with diameters typically in the range of a few to tens of microns. With the development of nanomaterials in recent years, innovative nanofibers have attracted growing interests in making polymer composites due to their

large specific surface areas that can lead to substantial improvement of interfacial bonding strength between fillers and matrices. To date, the majority of the reported research efforts on nanofiber reinforced polymer composites have been focused on vapor-grown carbon nanotubes/nanofibers.^{2–6}

The materials-processing technique of electrospinning provides a viable approach for convenient fabrication of polymer, ceramic, and carbon fibers (commonly known as “electrospun nanofibers”) with diameters ranging from nanometers to microns.^{7–10} Nevertheless, to the best of our knowledge, only limited research endeavors have been devoted to the development of polymer composites with electrospun nanofibers.^{10–14} The main reason is that in many cases, electrospun polymer and carbon nanofibers possess the mechanical properties that are lower than those of their conventional counterparts and vapor-grown carbon nanotubes/nanofibers; whereas electrospun ceramic nanofibers have been developed primarily for electronic and/or catalytic applications.¹⁵ It is noteworthy that electrospun glass (i.e., structurally amorphous SiO₂) nanofibers possess high mechanical strength and modulus, and they can be used for the fabrication of nanofiber reinforced polymer composites.^{16,17}

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Recent studies have indicated that continuous SiO₂ nanofibers with diameters of ~ 400 nm can be prepared through electrospinning a spin dope containing an alkoxide precursor of SiO₂ followed by pyrolysis at high temperature.^{18,19} These electrospun SiO₂ nanofibers are morphologically uniform and structurally amorphous, and they can retain their fiber morphology when subjected to vigorous ultrasonication; therefore, electrospun SiO₂ nanofibers are nanoscaled glass fibers. When these nanofibers were used to partially substitute (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 (WOF) of the resulting dental composites were considerably improved.²⁰

In this study, electrospun glass nanofibers (EGNFs) with diameters of ~ 400 nm were incorporated (at very low mass fractions of 0.5 and 1%) into epoxy resin for reinforcement and/or toughening purposes; and the motivation was for making the innovative nano-epoxy composite resins, which would be further used for the development of high-performance polymer composites. Two silane coupling agents with respective end groups of epoxy and amine including 3-glycidoxyl-trimethoxysilane (GPTMS) and 3-aminopropyl triethoxysilane (APTES) were selected for surface treatment of EGNFs. The surface treatment of EGNFs with GPTMS or APTES would improve the interfacial bonding strength between the fibers and the matrix, and also facilitate the uniform dispersion of EGNFs in the resin matrix. The effects of incorporation of EGNFs and the different silanization treatments on mechanical properties of the resulting nano-epoxy composite resins were investigated, and the results were compared to those acquired from the composite resins made from the conventional glass fibers (CGFs) with diameters of ~ 10 μm.

EXPERIMENTAL

Materials

The epoxy resin of SC-15A and the associated hardener of SC-15B were supplied by the Applied Poleramic (Benicia, CA). The conventional glass fibers (CGFs) were purchased from the Fisher Scientific (Pittsburgh, PA) in the form of glass wool. The silane coupling agents of 3-glycidoxylpropyl-trimethoxysilane (GPTMS) and 3-aminopropyl triethoxysilane (APTES) were purchased from ζ -Aldrich (St. Louis, MO).

Electrospinning

The detailed procedures and conditions for the preparation of EGNFs were reported in literature.^{18,19}

The EGNFs used in this study were prepared using the spin dope consisting of 13% (mass fraction) tetraethyl orthosilicate (TEOS) and 13% polyvinyl pyrrolidone (PVP) in a mixture solvent of DMF/DMSO (with volume ratio of 2/1) followed by pyrolysis at 800°C.

Silanization

Prior to silanization, the prepared EGNFs were first dispersed in water with the mass fraction of 5%; the suspension was then subjected to vigorous ultrasonication with a 100 W ultrasonic probe, purchased from the Branson Ultrasonics (Danbury, CT), for three 5-min time periods. The lengths of EGNFs after ultrasonication were a few to tens of micrometers. The CGFs were cut into short fibers with lengths of ~ 1–2 mm. The silanization was conducted by immersing either EGNFs or CGFs into 15% silane solution in ethanol, and the suspension was then heated to 50°C followed by being stirred for 1 h at 125 rpm using a Heidolph RZR 50 Heavy Duty Stirrer. The physically adsorbed silane molecules on fiber surfaces were removed through sonication in ethanol for 10 min followed by being thoroughly rinsed with ethanol. The GPTMS-treated fibers were desiccated under vacuum (~ 27.9 KPa) at room temperature, while the APTES-treated fibers were desiccated in an oven at 110°C for 15 min.

Fabrication of composites

EGNFs or CGFs (with or without silanization treatment) were first added into the SC-15A epoxy resin at the mass fractions of 0.5 and 1%; the mixtures were then mechanically stirred at 125 rpm for 12 h at 60°C followed by being sonicated for 30 min to uniformly disperse the glass fibers. Subsequently, the SC-15B hardener was added into each mixture; and the mass ratio of the epoxy resin versus the hardener was set at 100/30. After deaeration, each mixture was poured into an aluminum mold followed by being cured at 60°C for 2 h initially and postcured at 110°C for 5 h to obtain a composite panel with the length, width, and thickness being 100, 100, and 3 mm, respectively. Finally, specimens with the dimensions of 64 × 12.7 × 3 mm³ were cut from the composite panels for Izod impact test, while the dog-bone shaped specimens for tension test were machined according to ASTM D 1708.

Characterizations and evaluations

A Zeiss Supra 40 VP field-emission scanning electron microscope (SEM) was employed to examine the morphologies of fibers as well as the fracture surfaces of composite resins. Prior to SEM

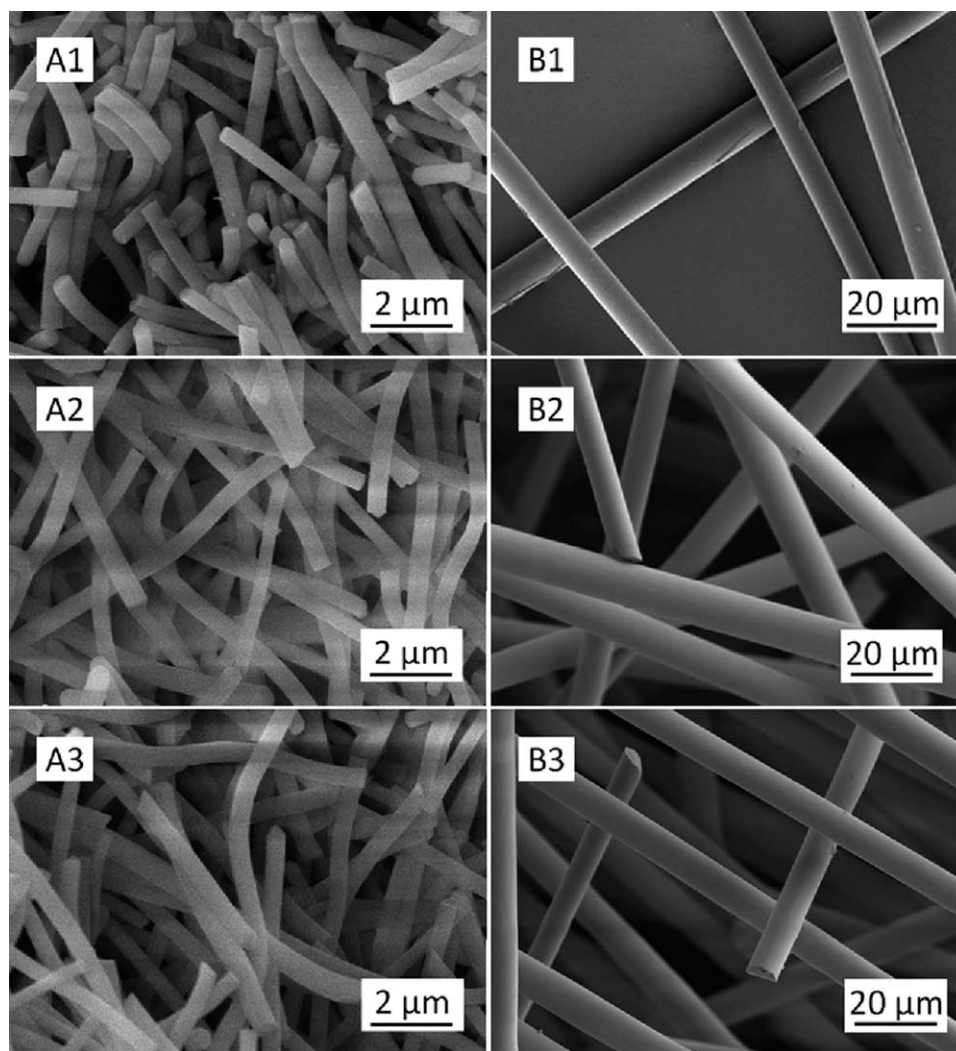


Figure 1 SEM images showing the representative morphologies of EGNFs after ultrasonication (A) and CGFs after being cut from glass wool (B). (1) Untreated fibers, (2) GPTMS-treated fibers, and (3) APTES-treated fibers.

examinations, specimens were sputter-coated with gold to avoid charge accumulations. Fourier transform infrared (FT-IR) spectra of EGNFs before and after silanization treatments with both GPTMS and APTES were acquired from the Bruker Tensor-27 FT-IR spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector; the samples were prepared by pressing the fibers with KBr, and the FT-IR spectra were acquired by scanning the samples (64 scans) from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . Measurements of mechanical properties were conducted at room temperature. The Izod impact test was carried out using a Tinius Olsen impact tester (Impact 104) according to ASTM D 256. The standard tension test was performed according to ASTM D 1708 at a strain rate of 1 mm/min using a computer-controlled universal mechanical testing machine (QTESTTM/10, MTS Systems, USA). Five specimens for each sample were tested and the mean values and standard deviations were calculated.

RESULTS AND DISCUSSION

Silanization

Both EGNFs and CGFs had the cylindrical shape with smooth surface; and their diameters were ~ 400 nm and ~ 10 μm , respectively, [Fig. 1(A1,B1)]; therefore, the EGNFs were approximately 25 times thinner than the CGFs. Two silane coupling agents, one with epoxy end group (GPTMS) and the other with amine end group (APTES), were used for surface treatment of both types of glass fibers. No appreciable difference on the morphology was identified for both types of glass fibers after silane treatments [Fig. 1(A2,A3,B2,B3)]. The reactions between the silane molecules and silanol (Si—OH) groups on the surface of fibers are illustrated in Figure 2, as evidenced by the following FT-IR results.

The FT-IR spectrum of EGNFs (Fig. 3) prior to silane treatments exhibited a broad peak centered at 3440 cm^{-1} that were attributed to Si—OH groups;

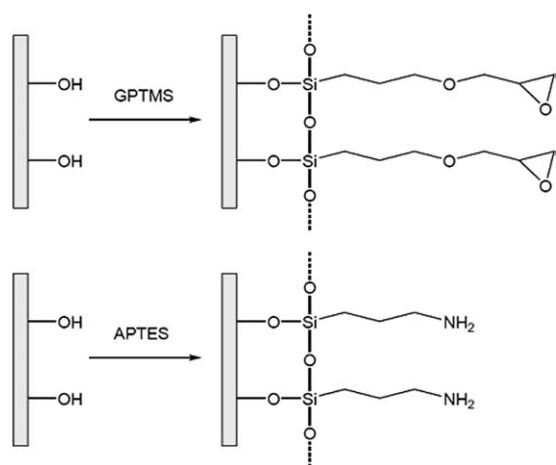


Figure 2 Schematic diagrams showing the reactions between silane coupling agents (of GPTMS and APTES) and silanol (Si—OH) groups on the surface of glass fibers (of EGNFs and CGFs).

the two strong peaks centered at 1060 and 1170 cm^{-1} were attributed to the vibration splitting of Si—O—Si asymmetric stretching. The other two peaks centered at 960 and 800 cm^{-1} were assigned to the Si—OH stretching and Si—O—Si bending.^{21,22} Because the silanization reaction only occurred to some of Si—OH groups on fiber surface, the epoxy and amino groups from the silane coupling agents of GPTMS and APTES were overwhelmed and/or overlapped with Si—O—Si and Si—OH absorptions in FT-IR spectra. Hence, the variations of Si—O—Si and Si—OH peaks before and after silanization could be used as evidence for the reaction. The peak centered at 800 cm^{-1} was selected as internal reference peak because it did not change appreciably before and after the silanization treatments; the reason was because this peak was related to Si—O—Si bending vibration, which would not vary substantially since the silanization only occurred on the fiber surface while the SiO_2 in the bulk of EGNFs did not change. Through comparison of FT-IR spectra of EGNFs, G-EGNFs, and A-EGNFs, it was evident that¹ the Si—OH absorption between 3000 and 3750 cm^{-1} , as well as the Si—OH absorption centered at 960 cm^{-1} , were distinguishably weakened; and² the Si—O—Si asymmetric vibration centered at 1170 cm^{-1} was shifted to higher wavenumbers after the silanization treatment; both indicated that the reactions between silanol groups on EGNFs and silane coupling agents of GPTMS and APTES did occur as shown in Figure 2. The CGFs used in this study were a commercial product and gave a complex FT-IR spectrum, probably due to additives in the CGFs; nonetheless, it was reasonable to expect that the silanization reactions occurring to EGNFs could also occur to CGFs.

Mechanical properties

Impact and tension tests on the epoxy composite resins containing low mass fractions (0.5 and 1%) of EGNFs or CGFs with or without silanization treatment were performed, and the acquired results are shown in Figure 4. The control sample was the neat epoxy resin that was prepared with the same processing conditions. G-EGNFs and G-CGFs represent the GPTMS-treated fibers, while A-EGNFs and A-CGFs represent APTES-treated fibers.

Strength

The incorporation of EGNFs or CGFs into the epoxy resin improved the tensile strength of the resulting composite resins, whereas EGNFs outperformed CGFs as the reinforcement agent [Fig. 4(A)]. The tensile strength of neat epoxy resin was 41.1 MPa; the incorporation of 0.5% EGNFs or CGFs resulted in 6.3 or 3.4% increase on tensile strength of the respective composite resins. With increasing the mass fraction of EGNFs or CGFs to 1.0%, the composite resins demonstrated 12 or 4.1% increase on tensile strength. G-EGNFs improved the tensile strength by 25 and 31% at the mass fractions of 0.5 and 1.0%, respectively; while G-CGFs resulted in merely 9.2% increase on tensile strength at the same mass fractions. The APTES-treated fibers showed the largest improvements on tensile strength: the tensile strengths of the resulting epoxy composite resins increased to 54.2 and 57.6 MPa (an increase of 32 and 40%) with incorporation of 0.5 and 1.0% A-EGNFs, respectively; while the tensile strengths merely increased by 8.5 and 18.5% with incorporation of the same mass fractions of A-CGFs.

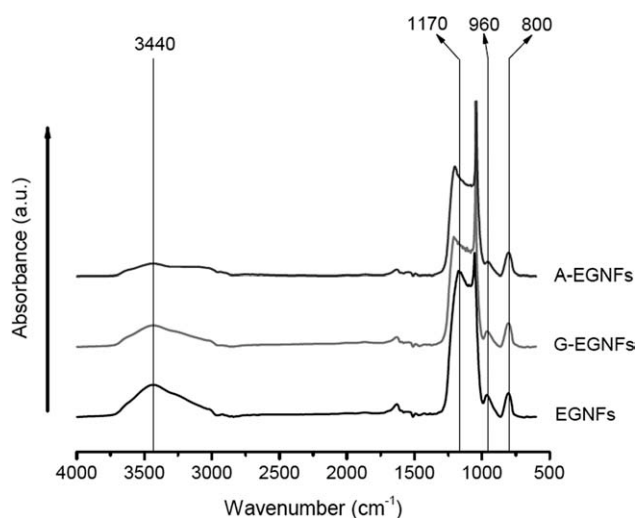


Figure 3 FT-IR spectra of EGNFs, GPTMS-treated EGNFs (G-EGNFs), and APTES-treated EGNFs (A-EGNFs).

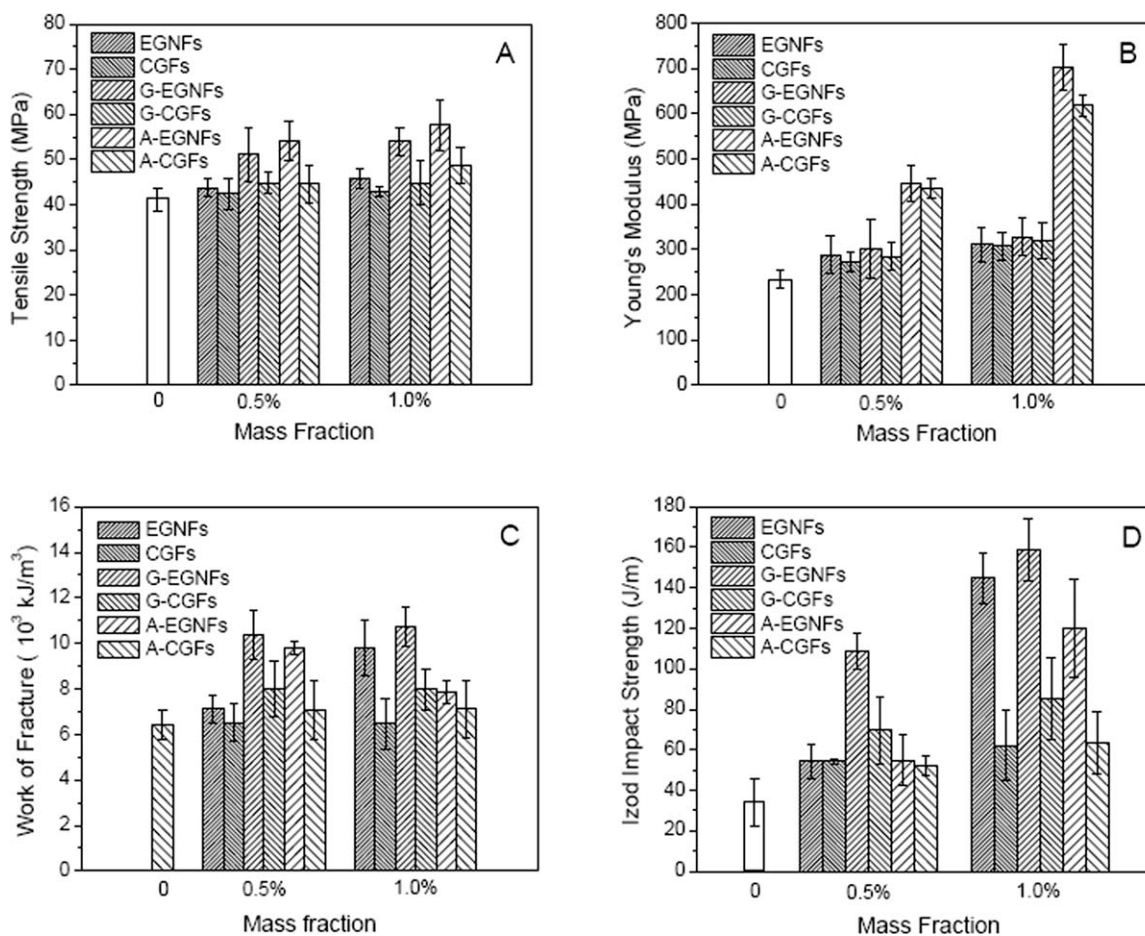


Figure 4 Tensile strength (A), Young's modulus (B), toughness (C), and impact strength (D) of the neat epoxy resin (control sample) and the composite resins containing EGNFs or CGFs. G-EGNFs and G-CGFs represent the GPTMS-treated fibers, while A-EGNFs and A-CGFs represent APTES-treated fibers.

Stiffness

Young's modulus was used as the measure of stiffness for the epoxy composite resins. EGNFs outperformed CGFs slightly on Young's modulus [Fig. 4(B)]. The neat epoxy resin exhibited the Young's modulus of 234 MPa, while the Young's moduli of epoxy composite resins increased with the amount of glass fibers. Incorporation of EGNFs resulted in 23 and 33% increases of modulus for the composite resins at mass fractions of 0.5 and 1.0%, respectively, while CGFs showed 16 and 31% increases correspondingly. G-EGNFs led to 29 and 40% improvements of modulus for the composite resins at mass fractions of 0.5 and 1.0%; for comparison, G-CGFs led to 22 and 37% improvements. The epoxy composite resins containing 1% A-EGNFs had the largest Young's modulus of 704 MPa, an increase by 201%, while the Young's modulus of the composite resin with 0.5% A-EGNFs increased by 91%; for comparison, the Young's moduli of the composite resins with 0.5 and 1.0% A-CGFs were increased by 86 and 165%, respectively.

Toughness

In general, the epoxy resin has relatively low toughness; the improvement on toughness for epoxy resin has continually been a goal of research efforts.^{23–25} The toughness of the prepared epoxy composite resins was characterized by measuring the area under the stress–strain curve (WOF) as well as the Izod impact strength.

Compared to the composite resins with CGFs, the composite resins with EGNFs exhibited higher WOF [Fig. 4(C)]. The WOF value of neat epoxy resin was 6.4×10^3 kJ/m³. Incorporation of EGNFs at the mass fractions of 0.5 and 1.0% resulted in 11 and 52% increases of WOF for the respective composite resins. As comparison, CGFs merely showed $\sim 1.5\%$ increase of WOF at these incorporation levels. The incorporation of 1% G-EGNFs further increased the value of WOF to 10.7×10^3 kJ/m³ (an increase by 67%); whereas the composite resin containing 1% G-CGFs showed merely 24% increase of WOF. Intriguingly, albeit the incorporation of APTES-treated fibers into the composite resins led to higher WOF than the incorporation of untreated glass fibers, the

improvements on WOF were not as much as the incorporation of GPTMS-treated fibers.

The Izod impact strength of neat epoxy resin acquired in this study was 34.3 J/m. As shown in Figure 4(D), the incorporation of EGNFs or CGFs into epoxy resin improved the impact strength of the resulting composite resins; and EGNFs outperformed CGFs. With incorporation of untreated EGNFs, the impact strength increased to 54.3 J/m (an improvement of 58%) at the mass fraction of EGNFs being 0.5%, while the impact strength increased to 145 J/m (an improvement of 322%) at the mass fraction of EGNFs being 1.0%. Correspondingly, the epoxy composite resins showed 58 and 81% increases of impact strength with 0.5 and 1.0% CGFs, respectively. Incorporation of GPTMS-treated fibers further improved the impact strength for the composite resin. The value of impact strength for the composite resin containing 0.5% G-EGNFs increased to 108 J/m, and the value further increased to 159 J/m with the increase of G-EGNFs to 1.0%; this represented 363% increase when compared with that of neat epoxy resin. For comparison, the impact strengths of the composite resins containing 0.5 and 1.0% G-CGFs were increased by 103 and 149%, respectively. The composite resins containing 0.5% APTES-treated fibers showed the similar values of impact strength as those containing the same amount of untreated fibers. At a higher mass fraction of 1.0%, however, A-EGNFs led to 250% increase of impact strength, while A-CGFs resulted in merely 85% increase of impact strength.

Effects on reinforcement and/or toughening

Through incorporation of EGNFs into epoxy resin, the resulting composite resins achieved simultaneous improvements on strength and toughness, and EGNFs outperformed its conventional counterpart of CGFs in both reinforcement and toughening. This was attributed to the high specific surface area of EGNFs. The average diameter of EGNFs was $\sim 1/25$ of that of CGFs; hence, the specific surface area of EGNFs was ~ 25 times larger than that of CGFs. The larger specific surface area would result in more fiber-epoxy interfacial interactions to facilitate the efficient transfer of stresses. Incorporation of higher amount of fibers from 0.5 to 1% would also result in more interfacial interactions, and in most cases showed more effective reinforcement and/or toughening.

The surface silanization treatments of fibers improved the interfacial bonding strength between the fiber filler and the resin matrix, and led to higher mechanical properties of the composite resins. Intriguingly, two types of silanized EGNFs exhibited different effects on strength/stiffness and toughness. The G-EGNFs showed a higher degree of

toughening effect, while A-EGNFs showed a higher degree of reinforcement effect. This was probably attributed to the different interfacial strengths resulted from the processing methods. During the preparation of composite resins in this study, the epoxy functional groups on G-EGNFs did not react with epoxy molecules in the matrix, and the chemical bonds between the filler of G-EGNFs fibers and the matrix of epoxy resin were not formed until the curing process through linking with hardener molecules; whereas the amine functional groups on A-EGNFs would react with epoxy molecules in the matrix and form chemical bonds prior to curing process, resulting in stronger fiber-matrix interfacial bonding strength than that of G-EGNFs.

Reinforcement effect

According to composite theory, the reinforcement of glass fibers for epoxy composites is attributed to the substantially higher strength and modulus of glass fibers than those of epoxy resin. However, the reinforcement potential of glass fibers can only be achieved if an effective load transfer from the epoxy matrix to the glass fibers is available. In regard to the mechanical properties of glass fiber reinforced epoxy composite resins, the fiber-matrix interfacial bonding strength is essential; and the strong bonding strength would result in high strength and modulus.

In general, the silane-treated EGNFs exhibited higher capability on reinforcement of composite resins than the untreated EGNFs; this is due to the improvement on fiber-matrix interfacial bonding strength. The stronger interface between A-EGNFs and epoxy resin led to more efficient load transfer from epoxy matrix to fiber filler; therefore, the higher tensile strength and modulus were observed in the epoxy composite resins containing A-EGNFs other than G-EGNFs.

Toughening effect

Fracture surfaces of composite resins can provide valuable information about fracture mechanisms and the influence of fiber surface treatment on fracture behavior. The fracture surfaces of impact test samples were examined by SEM (Fig. 5). The relatively smooth surface with oriented fracture lines initiated from sites of crack growth was observed on the fracture surface of the neat epoxy resin. The lack of plastic deformation and the smooth fracture surface were in agreement with the typical materials having low toughness. The epoxy composite resins containing EGNFs had rough features on their fracture surfaces, and jagged, short, and multi-plane fracture lines were observed on the fracture surfaces of the composite resin with 1.0% EGNFs; this indicated

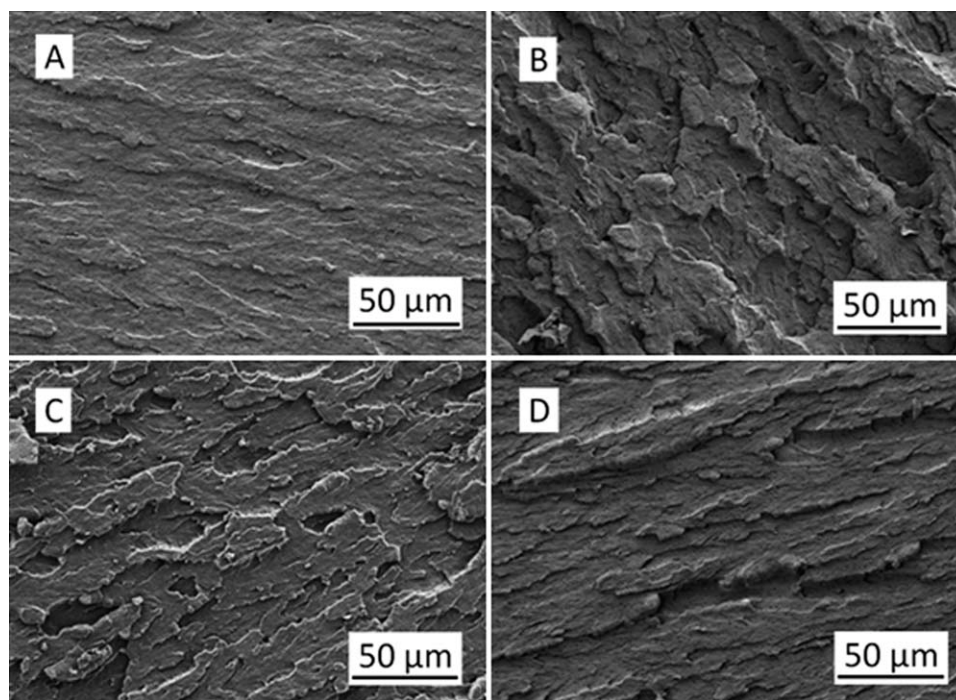


Figure 5 SEM images showing the representative fracture surfaces of the neat epoxy resin (A), the composite resins with 1% (mass fraction) EGNFs (B), 1% G-EGNFs (C), and 1% A-EGNFs (D).

that the crack fronts were deflected and kinked during growth. Thus, the main function of EGNFs in epoxy composite resins was probably to deflect the propagating cracks and force the crack growth to deviate from the existing fracture plane. Additional energy was then necessitated to continually drive crack growths, because the creation of additional fracture surface area would consume more energy. Increasing the mass fraction of EGNFs from 0.5 to 1.0% resulted in a higher degree of deflecting effect because of more EGNFs in the composite resin, which further improved the toughness. It is noteworthy that, due to the relatively weak interface between untreated EGNFs and epoxy, a small amount of energy was required to debond EGNFs from the epoxy matrix, leading to moderate improvement on toughness.

The epoxy composite resins containing silanized EGNFs had much improved fiber-matrix interface, and the required debonding energy was much higher; hence, the toughness of composite resins with silanized EGNFs was substantially higher than that of composite resins with untreated EGNFs. Additionally, A-EGNFs formed stronger bonding with the epoxy matrix, and thus interfacial debonding was more difficult to occur when compared with G-EGNFs. Consequently, G-EGNFs showed the largest improvement on toughness of the epoxy composite resins. The strong interfacial interaction between A-EGNFs and epoxy resin might enable more crack-bridging²⁵ in the fracture process instead of crack-deflecting.

This could be responsible for the fact that the fracture surface of epoxy composite resin containing A-EGNFs showed less deflecting lines [Fig. 5(D)].

CONCLUDING REMARKS

In this study, the nano-epoxy composite resins containing EGNFs (with diameters of ~ 400 nm) were prepared and evaluated for the first time. The incorporation of EGNFs into epoxy resin resulted in simultaneous improvements on both strength and toughness for the resulting composite resins; additionally, EGNFs substantially outperformed CGFs (with diameters of ~ 10 μm) in both tension and impact tests, and led to the similar improvements on strength, stiffness, and toughness of the composite resins at small mass fractions of 0.5 and 1%. The silanization treatment of EGNFs improved the fiber-matrix interfacial bonding strength, and resulted in higher mechanical properties of the corresponding composite resins. The silanized EGNFs with epoxy end groups (G-EGNFs) showed a higher degree of toughening effect, while the silanized EGNFs with amine end groups (A-EGNFs) showed a higher degree of reinforcement effect. Compared to the neat epoxy resin, the incorporation of 1% EGNFs increased the tensile strength by 12%, Young's modulus by 33%, WOF by 52%, and impact strength by 322%; the incorporation of 1% G-EGNFs increased the tensile strength by 31%, Young's modulus by 40%, WOF by 67%, and impact strength by 363%

and the incorporation of 1% A-EGNFs increased the tensile strength by 40%, Young's modulus by 201%, WOF by 22%, and impact strength by 250%. This study suggested that electrospun glass nanofibers could be used as reinforcement and/or toughening agent for making innovative nano-epoxy resins, which could be further used for the development of high-performance polymer composites.

References

1. Mallick, P. K. *Fiber Reinforced Composites: Materials, Manufacturing, and Design*; Marcel Dekker: New York, 1993, pp 1–11.
2. Hammel, E.; Tang, X.; Trampert, M.; Schmitt, T.; Mauthner, K.; Eder, A.; Potschke, P. *Carbon* 2004, 42, 1153.
3. Tibbetts, G. G.; Lake, M. L.; Strong, K. L.; Rice, B. P. *Compos Sci Technol* 2007, 67, 1709.
4. Jiang, H. X.; Ni, Q. Q.; Natsuki, T. *Polym Compos* 2010, 31, 1099.
5. Chou, T. W.; Gao, L.; Thostenson, E. K.; Zhang, Z.; Byun, J. H. *Compos Sci Technol* 2010, 70, 1.
6. Araújo, R. F.; Pederson, K. K.; Proença, M. F.; Silva, C. J. R.; Costa, C. M.; Lanceros-Méndez, S. *Polym Compos* 2010, 31, 369.
7. Dzenis Y. *Science* 2004, 304, 1917.
8. Greiner A.; Wendorff, J. H. *Angew Chem Int Ed* 2007, 46, 5670.
9. Fong, H. In *Polymeric Nanostructures and Their Applications*; Nalwa, H. S., Ed.; American Scientific Publishers: Los Angeles, 2005; Vol. 2, pp 451–474.
10. Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. *Compos Sci Technol* 2003, 63, 2223.
11. Fong, H. *Polymer* 2004, 45, 2427.
12. Lin, S.; Cai, Q.; Ji, J.; Sui, G.; Yu, Y.; Yang, X.; Ma, Q.; Wei, Y.; Deng, X. *Compos Sci Technol* 2008, 68, 3322.
13. Romo-Uribe, A.; Arizmendi, L.; Romero-Guzman, M. E.; Sepulveda-Guzman, S.; Cruz-Silva, R. *ACS Appl Mater Interfaces* 2009, 1, 2502.
14. Ozden, E.; Menciloglu, Y. Z.; Papila, M. *ACS Appl Mater Interfaces* 2010, 2, 1788.
15. Lu, X.; Wang, C.; Wei, Y. *Small* 2009, 5, 2349.
16. Jo, J. H.; Lee, E. J.; Shin, D. S.; Kim, H. E.; Kim, H. W.; Koh, Y. H.; Jang, J. H. *J Biomed Mater Res Part B* 2009, 91, 213.
17. Boccaccini, A. R.; Erol, M.; Stark, W. J.; Mohn, D.; Hong, Z.; Mano, J. F. *Compos Sci Technol* 2010, 70, 1764.
18. Liu, Y.; Sagi, S.; Chandrasekar, R.; Zhang, L.; Hedin, N. E.; Fong, H. *J Nanosci Nanotechnol* 2008, 8, 1528.
19. Wen, S.; Liu, L.; Zhang, L.; Chen, Q.; Zhang, L.; Fong, H. *Mater Lett* 2010, 64, 1517.
20. Gao, Y.; Sagi, S.; Zhang, L.; Liao, Y.; Cowles, D. M.; Sun, Y.; Fong, H. *J Appl Polym Sci* 2008, 110, 2063.
21. Almeida, R. M. In *Hand Book of Sol-Gel Science and Technology*; Sakka, S., Ed.; Kluwer Academic: Norwell, 2005; Vol 2, pp 65–90.
22. Xu, D.; Sun, L.; Li, H.; Zhang, L.; Guo, G.; Zhao, X.; Gui, L. *New J Chem* 2003, 27, 300.
23. Argon, A. S.; Cohen, R. E. *Polymer* 2003, 44, 6013.
24. Tjong, S. C. *Mater Sci Eng R* 2006, 53, 73.
25. Gojny, F. H.; Wichmann, M. H. G.; Fiedler, B.; Schulte, K. *Compos Sci Technol* 2005, 65, 2300.