

Mechanical and Thermal Enhancements of Benzoxazine-Based GF Composite Laminated by *In Situ* Reaction with Carboxyl Functionalized CNTs

Mingzhen Xu, Jinquan Hu, Xingqiang Zou, Mengdie Liu, Shihua Dong, Yanke zou, Xiaobo Liu

Research Branch of Functional Materials, Institute of Microelectronic & Solid State Electronic, High-Temperature Resistant Polymers and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu, People's Republic of China

Correspondence to: X. B. Liu (E-mail: liuxb@uestc.edu.cn)

ABSTRACT: An easy and efficient approach by using carboxyl functionalized CNTs (CNT-COOH) as nano reinforcement was reported to develop advanced thermosetting composite laminates. Benzoxazine containing cyano groups (BA-ph) grafted with CNTs (CNT-g-BA-ph), obtained from the *in situ* reaction of BA-ph and CNT-COOH, was used as polymer matrix and processed into glass fiber (GF)-reinforced laminates through hot-pressed technology. FTIR study confirmed that CNT-COOH was bonded to BA-ph matrices. The flexural strength and modulus increased from 450 MPa and 26.4 GPa in BA-ph laminate to 650 MPa and 28.4 GPa in CNT-g-BA-ph/GF composite, leading to 44 and 7.5% increase, respectively. The SEM image observation indicated that the CNT-COOH was distributed homogeneously in the matrix, and thus significantly eliminated the resin-rich regions and free volumes. Besides, the obtained composite laminates showed excellent thermal and thermal-oxidative stabilities with the onset degradation temperature up to 624°C in N₂ and 522°C in air. This study demonstrated that CNT-COOH grafted on thermosetting matrices through *in situ* reaction can lead to obvious mechanical and thermal increments, which provided a new and effective way to design and improve the properties of composite laminates. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2629–2637, 2013

KEYWORDS: mechanical properties; thermal properties; composites

Received 22 November 2012; accepted 31 December 2012; published online 30 January 2013

DOI: 10.1002/app.38988

INTRODUCTION

Fiber reinforced polymer composites, combined the advantageous properties offered by polymer matrices including easy processing, recyclability, and good chemical resistance with the high specific stiffness and strength of fibers, have been extensively used in high-performance applications such as aerospace, aircraft, sports, and military industry.¹ Nevertheless, technological advances have imposed additional requirements such as further mechanical properties and thermal stabilities on these materials.

Extensive researches and improvements in glass fiber (GF)-reinforced composites have led to remarkable developments in the mechanical properties of the composites, which especially exhibited excellent in-plane properties, but generally showed poor out-of-plane performance, which was dominated by the polymer matrix.^{2–5} In addition, the poor impregnation of most polymer matrices with fibers will often bring about weak fiber-matrix interfacial adhesions between fibers and polymer matrices, and consequently reduce the ultimate performances of the composites.

To solve these problems, some researchers are dedicated to employ two kinds of polymer matrices: one matrix provides main mechanical and thermal properties while the other one acts as wetting agents to promote infiltration and interfaces between fibers and polymer matrices. Of them, epoxy resins have been generally utilized as such agents for their good wetting abilities, low viscosities, high activities, excellent mechanical properties, and fracture toughness. Due to the improved impregnation of the matrices and fibers, remarkable enhancements in mechanical properties of the composites have been reported in many epoxy/fiber systems.^{6–9} For example, Xu Y et al. reported that small amount of nanoclay added into carbon fiber/epoxy composites can enhance the flexural strength by 38%.¹⁰ Bekyarova E et al. prepared a kind of carbon fiber-reinforced epoxy composites by introducing carbon nanotubes (CNTs) showed outstanding interlaminar shear strength (~50 MPa).¹¹ In our previous work, a kind of high thermal resistant resin benzoxazine containing cyano groups was reinforced by GF to prepare the fiber-reinforced composite laminates. Epoxy

resin was utilized to enhance the interfacial adhesions because of its excellent impregnation. The results indicated that the ultimate performance of the composite laminates improve significantly as a result of the incorporation of epoxy.¹²

Admittedly, these researches did achieve successes in improving the interfacial adhesions between fibers and polymer matrices. However, the limits of improving composite properties made of traditional micrometer-scale fiber have been reached, since the composite properties, especially the mechanical properties, generally involve compromises.^{10,11} One problem in these composites is that the presence of matrix-rich and free-volume regions was found in the gaps between the interlaced fiber bundles. These regions and gaps, where cracks easily initiate and propagate, are difficult to be reinforced with traditional microscale fiber.¹¹ Therefore, nano-fillers are expected to play critical roles in the reinforcements of the composite laminates.

In recent years, interest has been attracted in improving the fiber-reinforced composites by the incorporation of nano-fillers.^{13–19} Gojny et al. have reported that the incorporation of multi-walled CNTs into the epoxy matrix, even in a small content (e.g. 0.3 wt %), can significantly increase the interlaminar shear strength of the GF reinforced composites.¹⁴ The remarkable improvement effect of nanoclay on the mechanical properties in GF reinforced composites also has been found.¹⁵ CNTs, suggested as the ideal candidate for selective nano-reinforcement of matrix-rich interlaminar regions and the poor adhesion of long fiber and matrix is because of their nanoscale diameter, high aspect ratio, excellent mechanical strength, electrical, and thermal properties.^{20–25} However, most of the studies have utilized the approach that dispersing the pristine CNTs into the polymer matrix by high-shear mixing. Obviously, the nonreactive nature of CNTs would ultimately leads to a weak interfacial interaction with the polymer matrix that resulted in the phase separation. Furthermore, the method of dispersing CNTs into polymer matrix by direct mixing makes CNTs hard to be distributed homogeneously.

B-ph is a novel kind of phthalonitrile resin containing benzoxazine rings. Excellent processability (low melting point, low viscosity) and outstanding thermal property have made BA-ph resin attract increasing interest and attention in the field of composites compared with the traditional heat resisting resins. In comparison with traditional biphenyl type phthalonitrile resin, BA-ph possesses longer molecular distances derived from the bisphenol-A, which are conducive to the toughness of the composites. In addition, the cost-effective BA-ph is potential in the widely application of phthalonitrile resin in future. Thus, in the current study, we prepared carboxyl functionalized carbon nanotubes (CNT-COOH) and grafted onto the BA-ph molecular by the opening-ring polymerization. Through *in situ* reaction, CNT-COOH would be connected with the BA-ph molecules by chemical bonds, which would help CNTs disperse homogeneously in the matrix and prevent phase separation by chemical bonds. Then, based our previous report, 40 wt % epoxy resin was introduced as active diluents to reduce the viscosity of BA-ph matrix, which would improve the impregnation of matrix in the preparation of the multi-scale CNT/GF/benzoxazine containing cyano groups (BA-ph) laminate composites.¹² Then, the mechanical

and thermal measurements have been performed to evaluate the effects of carboxyl CNT on the composite laminates. Also, the fracture surfaces of the composite laminates have been investigated to confirm the strong bonding interaction between fiber and matrix resulted from the carboxyl CNT.

EXPERIMENT

Materials

CNTs (diameters: 10–30 nm, purity: >95%) were supplied by Chengdu Organic Chemistry Co., Chinese Academy of Sciences, Chengdu, China. Carboxyl functionalized CNTs (CNT-COOH) were prepared as reported before²⁶: raw CNTs were sonicated in a mixture of concentrated sulfuric and nitric acid (3:1 by volume) for 1 h at 60°C. The solid was centrifugalized and dried in a vacuum. Bisphenol-A, paraformaldehyde, 1, 4-dioxane, and toluene were obtained from Tianjin BODI Chemicals Co., Tianjin, China. Epoxy resin (diglycidyl ether of bisphenol A) with epoxide equivalent weight of 213–244 was kindly supplied by Blue Star New Chemical Material Co., Beijing, China. The model of the GF fabric is EW170-100 provided by Shenyang Gaote glass fiber Co., Shenyang, China. All the chemicals and reagents were used without further purification. 3-Aminophenoxyphtalonitrile (3-APN), benzoxazine containing cyano groups (BA-ph) was synthesized and purified according to the procedure reported before.^{12,27}

In Situ Preparation of CNT-g-BA-ph

3-APN, bisphenol-A, paraformaldehyde, and 1,4-dioxane and toluene were mixed under a stirrer at a speed of 300 rpm according to Ref. ¹². After being refluxed at 100°C for 2 h, various CNT-COOH contents (0 wt %, 2 wt %, 4 wt %, 6 wt %, and 8 wt %) were incorporated into the solution and continued to be refluxed for another 3 h. Herein, the CNT-g-BA-ph resin-impregnated solution was prepared with various CNT-COOH content. To confirm the component of the resin-impregnated solution, certain amount of the reaction mixture was cooled to room temperature and slowly poured into distilled water to precipitate. The solid was filtered and washed five times with distilled water. Then the grey solid was dried in a vacuum at 60°C overnight.

Preparation of the CNT-g-BA-ph/GF Composite Laminates

To promote infiltration and interfaces between fibers and polymer matrices, epoxy resins had been adopted and our previous work¹² indicated that introduction of 40 wt % epoxy resin had significantly improved the interfacial wettability and enhanced the mechanical properties. Hence, the as-prepared CNT-g-BA-ph viscous solution was mixed with 40 % (by weight of the CNT-g-BA-ph matrix) epoxy resin and was used directly to impregnate the GF fabric. The GF fabric (20 × 20 cm²) was brush-coated with the viscous solution obtained above and dried at room temperature (25°C) for 24 h. It was designed to give a prepreg of 40% polymer matrix and 60% GF by weight. Twenty layers of GF prepreg fabric were placed in a stainless steel mold and hot-pressed under a pressure of 20 MPa at 200°C for 2 h, 230°C for 3 h, 260°C for 3 h, and 280°C for 3 h, respectively.

Characterizations

FTIR spectra were recorded with Shimadzu FTIR8400S Fourier Transform Infrared spectrometer in KBr pellets between 4000 and 400 cm^{-1} in air. The flexural tests of the composite laminates were performed with a SANS CMT6104 series desktop electromechanical universal testing machine at room temperature. Flexural tests (three-point bending mode) were held according to the GB/T9341-2008 standard test method with a crosshead displacement speed of 10 mm/min, and the test fixture was mounted in a 10 kN capacity. The samples (dimensions: 80 mm \times 15 mm \times 2 mm) were tested with a support span/sample thickness ratio of 15:1, and gained an average value for every three samples. The morphology of the fractured surfaces of the composites was observed by SEM (JSM2 5900LV) operating at 20 kV. Thermogravimetry (TGA) was performed on a TA Instruments TGA Q50 with a heating rate of 20°C/min (under nitrogen or air) and a purge of 40 mL/min.

RESULTS AND DISCUSSIONS

In the previous work reported in Ref. ¹², BA-ph resin has been synthesized and copolymerized with epoxy resin. Then the copolymer system has been explored to prepare the GF-reinforced composite laminates through hot-press forming technology. The results indicated that polymerization of BA-ph/EP copolymers was progressing at the ranges from 180 to 200°C. EP/BA-ph copolymer exhibited better processing advantages than pure BA-ph while the compatibility of EP/BA-ph copolymers with the fiber fabrics improved compared with the pure BA-ph matrix. The mechanical, morphological, and thermal properties of the GF-reinforced BA-ph/EP composite laminates were also investigated. Compared with those of BA-ph/GF laminates, the flexural strength and flexural modulus of EP/BA-ph/GF composites with 40 wt % EP content were 564 MPa and 28 GPa, increased by 10.4% and 9.6%, respectively. Such mechanical enhancements can be attributed to primary component and the effect of EP on the interfacial interactions. Thermal properties revealed that all EP/BA-ph/GF composites could stand high temperature up to 470°C in N_2 and 510°C in air. In terms of these developments in processability, as well as mechanical and thermal properties of the composite laminates, carboxyl CNT was introduced through *in situ* reaction with BA-ph matrix to further improve the BA-ph-based GF-reinforced composite laminates.

Characterization of CNT-COOH Grafted with BA-ph Matrix

The preparation of CNT-COOH was carried out according to Ref. ²⁶. It is well known that the carboxyl groups on the CNT-COOH make itself negatively charged, which can further bond to the BA-ph via the *in situ* reaction. The carboxyl-catalyzed ring-opening via cationic mechanism has been reported before.^{28,29} It is evidently known that the carboxylic acid groups of CNT-COOH have been bonded to the BA-ph. Figure 1(a) shows the illustration of the possible synthesis process of CNT-g-BA-ph molecules. Figure 1(b) illustrated the further polymerization of the as-prepared CNT-g-BA-ph with epoxy resin at elevated temperature. According to Refs. ^{12, 30-32}, the carboxylic acid groups on the surface of CNT-COOH and the hydroxyl generated from the ring-opening of epoxy would catalyze the ring-opening of the benzoxazine rings, and consequent form

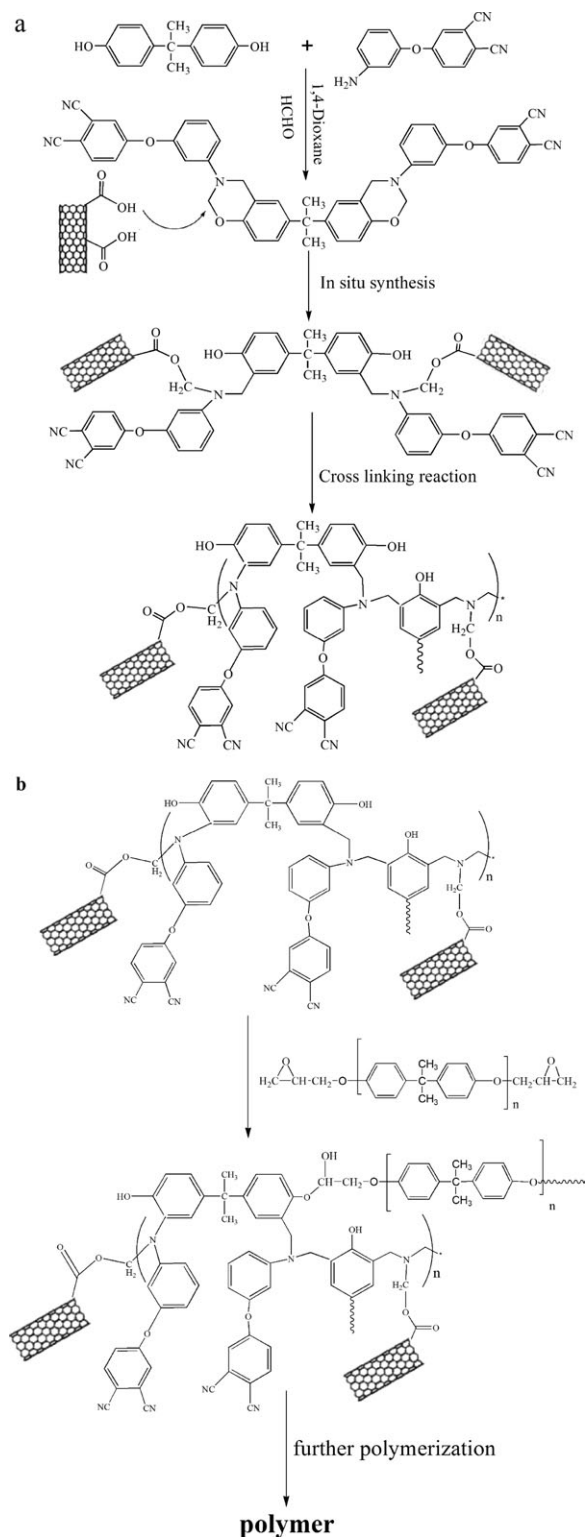


Figure 1. (a) Probable structures of the CNT-COOH bonded to BA-ph molecule and (b) the cross linking process of CNT-g-BA-ph with epoxy resin.

ester bonds with the BA-ph molecules. Then the prepolymerized CNT-g-BA-ph resin was self-catalyzed and catalyzed by epoxy resin to further polymerization through the heat treatment in

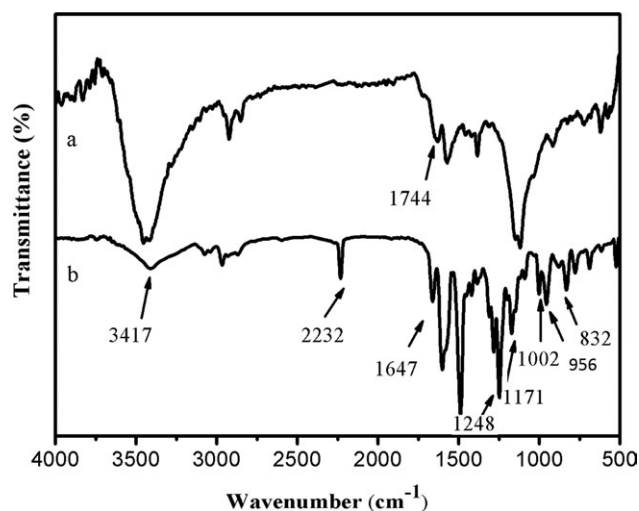


Figure 2. FTIR spectra of CNT-COOH and CNT-g-BA-ph prepared via *in situ* synthesis.

the hot-press process. Underwent the stage curing process, the CNT-g-BA-ph matrix with epoxy resin would gradually cross-link and polymerize to finally form the high-density network with CNTs being entangled in the matrix. According to the Ref.,¹² the structure and the cross-linking of CNT-g-BA-ph and epoxy resin were thoroughly illustrated in Figure 1.

To further understand the structure of CNT-g-BA-ph through *in situ* reaction of CNT-COOH with BA-ph, the CNT-COOH and the obtained CNT-g-BA-ph were confirmed by FTIR spectra as shown in Figure 2(a,b), respectively. In Figure 2(a), it provided clear evidence for the linkage of the carboxylic acid groups in the CNTs after being acid treated [Figure 1(a)]. The CNT-COOH exhibited two absorption bands at 3417 and 1744 cm^{-1} [Figure 2(a)], which were assigned to the hydroxyl ($-\text{OH}$) and carbonyl ($-\text{C}=\text{O}$) stretch of the carboxylic acid groups attached to the open ends of CNT.³³ Then, the as-prepared CNT-COOH was introduced into the synthesis solution of BA-ph molecules and the CNT-g-BA-ph molecules were obtained.

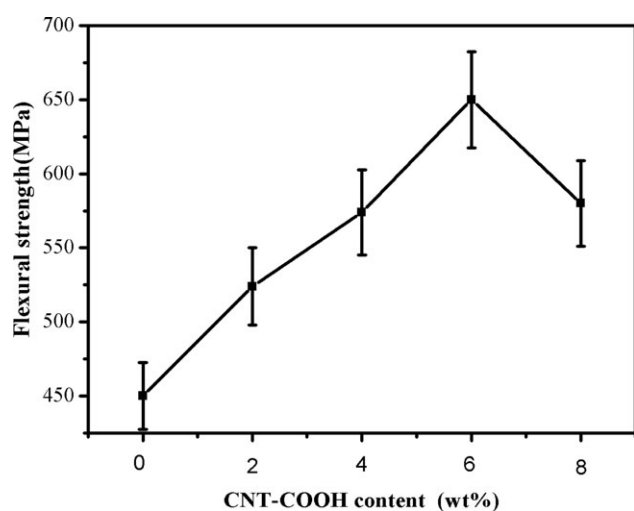


Figure 3. Flexural strength of CNT-g-BA-ph/GF composite laminates.

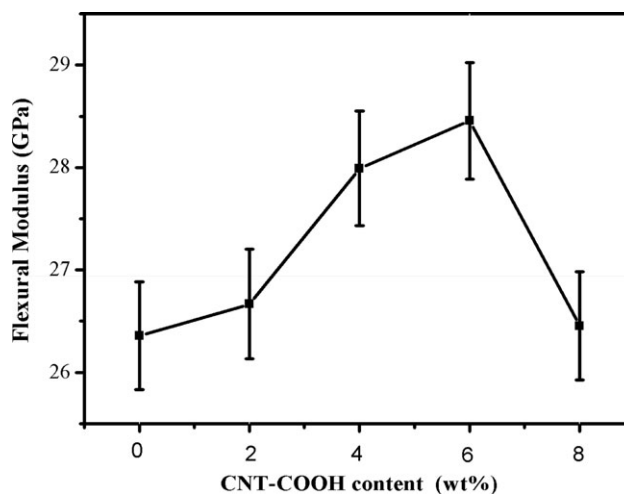


Figure 4. Flexural modulus of CNT-g-BA-ph/GF composite laminates.

In Figure 2(b), the shift of the carbonyl absorption band of CNT-COOH from 1744 to 1647 cm^{-1} indicated the formation of chemical bonds between the CNT-COOH and the BA-ph. Meanwhile, several characteristic absorption bands of BA-ph remained after the *in situ* reaction with CNT-COOH. The absorption band of cyano groups ($-\text{CN}$) at 2232 cm^{-1} was detected in Figure 2(b).^{27,34} The absorption bands at 956 (tri-substituted benzene ring attached with oxazine ring), 1171, and 832 cm^{-1} (stretch $\text{C}-\text{N}-\text{C}$), 1248, 1002 cm^{-1} (stretch, $\text{C}-\text{O}-\text{C}$),¹² confirmed the successful synthesis of benzoxazine molecules. Hence, the obtained CNT-g-BA-ph resin has been utilized to prepare fiber-reinforced composite laminates undergoing the heat treatment. In the process of the hot-press forming, the CNT-g-BA-ph resin gradually polymerized and eventually the final expected composites were obtained.^{35–38}

Mechanical Properties of BA-ph/GF and CNT-g-BA-ph/GF Composites with Various Content of CNT-COOH

Mechanical tests were performed to evaluate the effect of CNT-COOH content on the mechanical properties of the multi-scale hybrid composite laminates. Flexural tests were explored and the results were integrated and showed in Figures 3 and 4. The flexural strength of the BA-ph/GF composite laminates with and without CNT-COOH is shown in Figure 3. As can be seen, flexural strength of CNT-g-BA-ph/GF composite laminates dramatically increases with the increasing of CNT-COOH loading. With a small addition of CNTs (2 wt %), the flexural strength increases from 450 MPa in the BA-ph/GF composites to 524 MPa in the CNT-g-BA-ph/GF laminates, leading to 16.4% increase. As CNT-COOH content increases, the flexural strength of CNT-g-BA-ph/GF composites increase firstly and decrease afterward; it reach the maximum when CNT-COOH content was 6 wt %. At that point, CNT-g-BA-ph/GF composites show a flexural strength as high as 650 MPa, increased by 44.4% in comparison with that of BA-ph/GF composite laminates without CNT-COOH. However, CNT-g-BA-ph/GF composites with more CNT-COOH (8 wt %) show the decreased flexural strength. The flexural strength of the CNT-g-BA-ph/GF composite laminate for 8 wt % content CNT-COOH is 580 MPa,

decreased by 10.7% compared with that of composite with 6 wt % CNT-COOH. Although the decrease, the composite laminates with 8 wt % content CNT-COOH exhibits better mechanical property in comparison with that of composite without CNT-COOH. The flexural modulus of the composite laminates is given in Figure 4. Similarly, with the increase of CNT-COOH content, the flexural modulus of the composite laminates continuously increases and reaches its climax as high as 28.4 GPa when the CNT-COOH content is 6 wt %, which is increased by 8% compared with laminates without CNT-COOH. Many other researchers have studied the impact of CNTs on the flexural properties of the laminate composites and have also observed the enhancement.^{39–43} For example, Bekyarova et al. have reported the 10% enhancement of flexural strength in the SWNT-reinforced epoxy/CF nanocomposites.¹⁵ Gojny et al. have reported that CNT-filled epoxy/GF nanocomposites showed 20% enhancement of the shear strength as compared to that of epoxy/GF composites.⁴³

It is well known that the mechanical properties of polymer composite depended on the properties of each primary component, the nature of the interfacial surface, and the locus of the filler-matrix interaction between the matrix resins and GFs.⁴⁴ In this work, all of the CNT-g-BA-ph/GF composite laminates exhibited outstanding mechanical properties, which are apparently attributed to the primary component of GF and matrix themselves, since that GF is well known for its high specific strength and stiffness both in tension and in compression, while CNT and BA-ph are also traded for their high mechanical performances.^{41,42} However, with increasing the content of CNT-COOH, the mechanical properties of the composite laminates increased to the maximum (with 6 wt %) and then decreased (with 8 wt %). The results are largely due to the role of CNT-COOH that plays in the whole systems.

It is noteworthy that resin matrix cracking, fiber pull-out, and debonding and delamination are the primary failure modes responsible for interfacial failures.^{45,46} Thus, CNT-COOH, performed as the nano-reinforced fillers, was introduced into the matrix through *in situ* reaction to mitigate the drawbacks. First, homogeneously scattered in the matrix, the CNT-COOH is efficient to eliminate the resin-rich regions, where cracks easily initiate and propagate. In these regions, the CNT-COOH serves as the site of stress concentration, would lead to high energy absorption and deflect the micro-cracks during the cracks propagation process. When the strain energy was dissipated, the initiation and propagation of cracks were significantly controlled and eliminated. Second, owing to the high aspect ratio and high surface area, as well as the polar hydroxyl groups, the CNT-COOH was easy to adhere to the surface of fibers. The presence of CNT-COOH on the fibers would effectively prevent the fibers from pull-out and debonding, which avoids the voids/holes in the interface of fiber and matrix. Third, the cross linking polymerization of CNT-COOH with BA-ph matrix during curing could contribute to the formation of strong bonds between fibers and matrices, resulting in the improvement of interfacial bonding strength, consequently, the enhancement of the flexural strength of the composite laminates. Additionally, it has been generally adopted that the increased stiffness and strength of the

polymer matrix endowed by the nano-reinforcements is usually associated with the nano-fillers possessed superior mechanical performances.¹⁴ Nevertheless, the decrease of flexural strength and modulus of the CNT-g-BA-ph/GF composite laminates with 8 wt % content CNT-COOH have been detected. Combining the aforesaid factors, the reduction may be attributed to the aggregation of the excess CNT in the matrix, which significantly weakened the effective surface areas of the CNTs. Furthermore, the efficient interfacial stress transfer channels have been destroyed owing to the aggregation, thus results to the increase the local stress concentration along the fiber/matrix interface.¹³ In addition, the excess CNTs in BA-ph matrix may refrain from crosslinking of the matrix host and results to the decrease of the density of cross-linked network, which consequence leads to the decreased stiffness and strength of the composite laminates.

SEM Images of BA-ph/GF and CNT-g-BA-ph/GF Composites with Various Content of CNT-COOH

SEM analysis was conducted to examine the morphology of the fracture surfaces of the BA-ph/GF composite laminate and CNT-g-BA-ph/GF composite laminates with various content of CNT-COOH. Figure 5 shows the representative morphologies of fracture surfaces of the composite laminates with and without CNT-COOH. Figure 5(a) shows that in the BA-ph/GF composite laminates, the fracture surfaces are very smooth. The fibers are exposed and there does not seem to have resin protruding from the surface of the fibers during fracturing which indicates the existence of fiber/matrix interfacial debonding. Similar phenomenon was also observed in the EP/CF composite laminates and the authors thought this kind of morphology be attributed to the characteristic of brittle epoxy and relative weak interfacial bonding strength.⁴⁷ In this study, some free volumes between fiber and BA-ph matrix also can be observed, this may be indicate that it's hard to significantly improve the interfacial adhesions between the traditional micrometer-scale fiber and the matrix relying on the impregnation of the polymer matrix improved by epoxy dilution merely. Additionally, resin-rich regions are also detected in the gaps between fibers. In contrast, a much better interfacial adhesion between fibers and matrices can be observed in the composite laminates containing CNT-COOH. It can be seen in Figure 5(b) that most of the fibers are embedded in the matrix, the surfaces of the fibers are covered by layers of matrix and no exposed fibers are detected. In Figure 5(c), it is obvious that the CNT-COOH is existed at the fiber/matrix interface as well as in the matrix inter-fiber regions. It is clearly to see from the micrograph of the fiber/matrix interface in Figure 5(d) that CNT-COOH is strongly attached to fibers which significantly improve the interfacial adhesion between fibers and matrices, resulting to the excellent integration of fibers into the matrices. Furthermore, the CNT-COOH homogeneously disperses in the matrix-rich regions between fibers is visible in all the fracture surfaces of composite laminates with CNT-COOH in Figure 5(b–f). Compared with the neat BA-ph/GF composite laminates, no voids/holes and resin-rich regions between fiber and matrix are observed in all the fracture surfaces of composites with CNT-COOH. Figure 5(e) (with 6 wt % CNT-COOH) is the high-level micrograph of the narrow region between fibers, it can be seen that the CNT-COOH in the

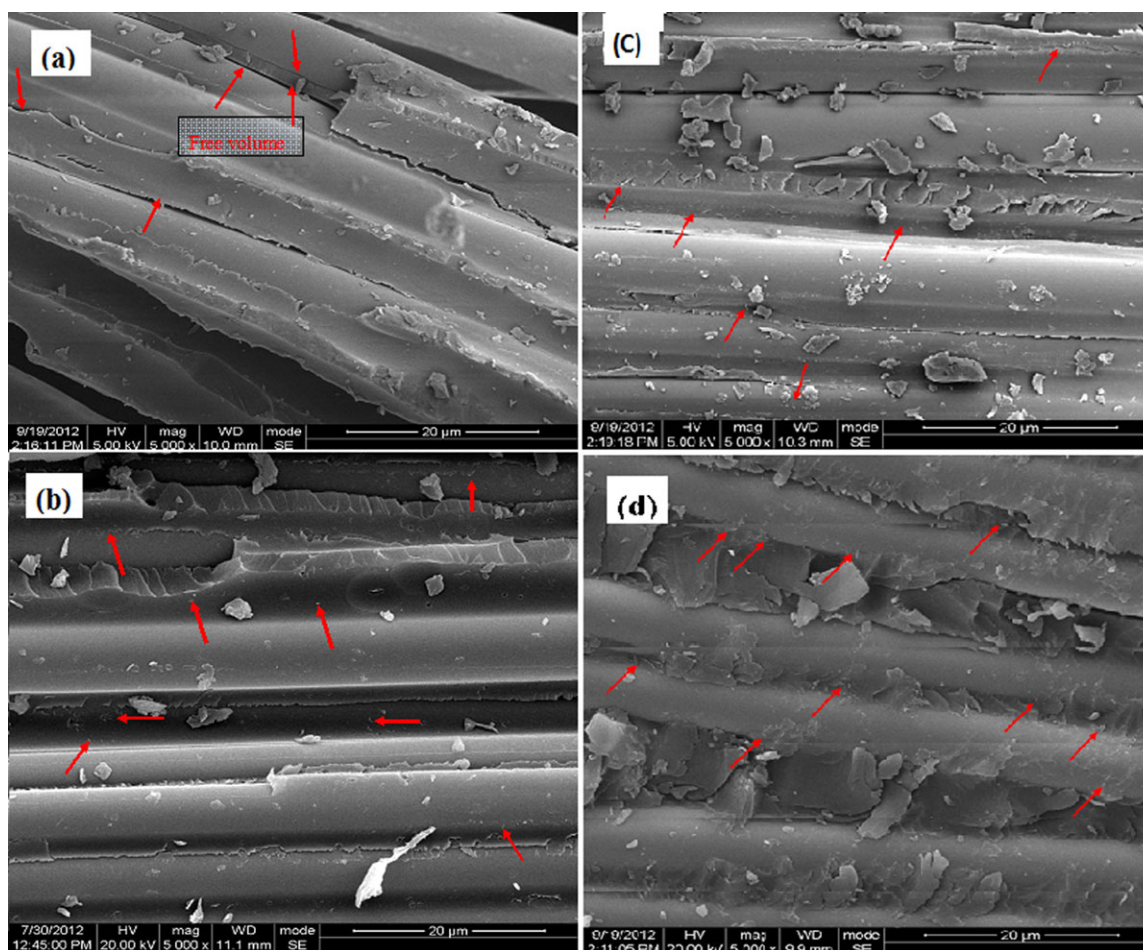


Figure 5. SEM images of (a) BA-ph/GF composite laminates without CNT-COOH, (b) CNT-g-BA-ph/GF composites with 2 wt % CNT-COOH, (c) CNT-g-BA-ph/GF composites with 4 wt % CNT-COOH, (d) & (e) CNT-g-BA-ph/GF composites with 6 wt % CNT-COOH, and (f) CNT-g-BA-ph/GF composites with 8 wt % CNT-COOH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

matrix is distributed homogeneously which significantly eliminate the resin-rich regions. Simultaneously, matrices attracted strongly to fibers are detected obviously which is differentiated from the interfacial adhesion of the BA-ph/GF composite laminate. A micrograph of a fracture surface with 8 wt % of CNT-COOH is presented in Figure 5(f), in which the excellent adhesions between fiber and the matrix are clearly visible. However, the gaps between fibers caused by the breakage of the matrix rather than debonding of fiber and matrix are also detected. The gaps and free volumes are formed centralized in the resin-rich regions which may be attributed to the comparatively low level dispersion when more CNT-COOH (8 wt %) is introduced.

As is well known, during the typical three-point flexural tests of the laminated composites, resin matrix cracks and fiber pull-out and debonding are the main failure mode which are resulted from the extension of strain, stress in the resin-rich regions and the poor interfacial adhesions between fibers and matrices. It is observed that for the BA-ph/GF composite laminates, the fractures and cracks usually occurred in the resin-rich regions and the interfaces of fiber and matrix. The fracture surfaces are relatively smooth with oriented and resulted from the extension of micro-cracks initiated at the location of stress concentration.

With the introduction of CNT-COOH into the matrix, the resin-rich regions have been eliminated significantly as can be seen in Figure 5(b–f). The fracture surfaces of CNT-g-BA-ph/GF composites are much rougher without identifiable fracture lines, which attributed to the deflection of micro-cracks due to the presence of CNT-COOH in the matrix. The CNTs serve as the effective interfacial stress transfer channel in the matrix, and consequently reduce the stress concentration in interface between fiber and matrix. As the cracks break away from the fibers, the kinked and rougher fracture surfaces are visible, suggesting more strain stress dissipation during the propagation of cracks. Additionally, no voids and free volumes are observed on the fracture surfaces of the composites with CNT-COOH in the matrix due to fiber pull-out and debonding. The results indicated that the interfacial bonding strength has been great improved by the CNT-COOH, which ultimately enhance the flexural strength and modulus.

Thermal Stabilities of BA-ph/GF and CNT-g-BA-ph/GF Composites with Various Contents of CNT-COOH

TGA has been carried out to estimate the thermal and thermal-oxidative stabilities of BA-ph/GF composite laminates and CNT-g-BA-ph/GF composite laminates. Additionally, the influence of CNT-COOH with the thermal stabilities of the

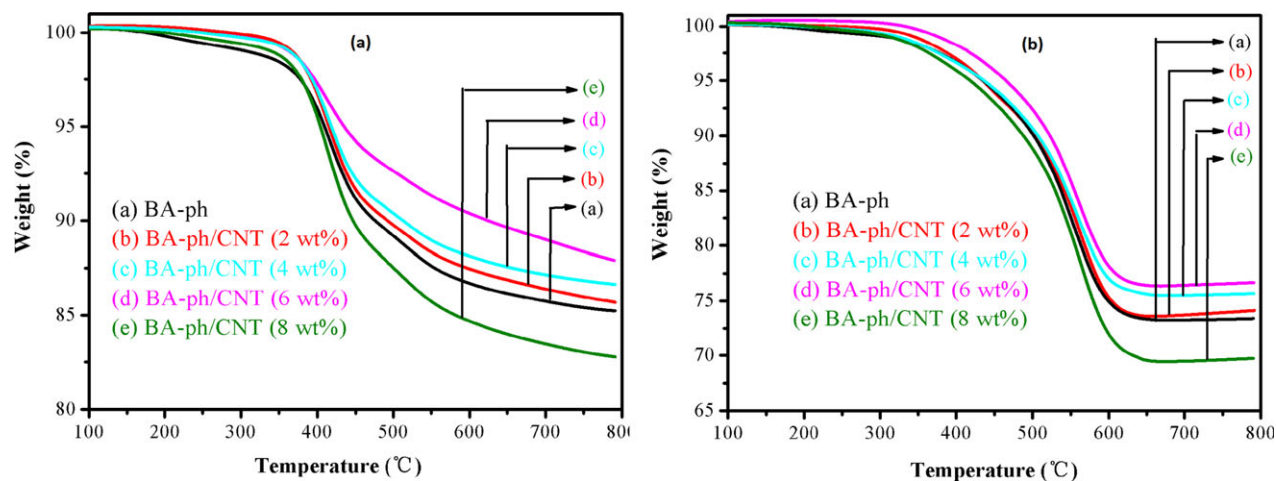


Figure 6. TGA curves of CNT-g-BA-ph/GF composite laminates with and without CNT-COOH (a) in N_2 and (b) in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composite laminates has been discussed. To show the effects of CNT-COOH on the thermal and thermal-oxidative stabilities of the composite laminates, the main TGA results (Figure 6) were summarized in Table I, in which the initial decomposition temperatures at weight loss of 5%, 10% ($T_{d5\%}$, $T_{d10\%}$) and char residue at 800°C were displayed. Overall, thermal and thermo-oxidative stabilities of CNT-g-BA-ph/GF composite laminates in N_2 and air atmosphere were increased by the increasing CNT-COOH content. It can be seen in Figure 6 that the composites containing 2 wt % and 4 wt % CNT-COOH show slightly increment in the initial decomposition temperatures at weight loss of 5% ($T_{d5\%}$) and 10% ($T_{d10\%}$). This may be because that the CNT-COOH cross-linked with BA-ph matrix only accounts precious little of the composite materials, the low CNT-COOH content in the composites would not be expected to affect the thermal stabilities significantly. Nevertheless, dramatic increments of $T_{d5\%}$ and $T_{d10\%}$ are observed in CNT-g-BA-ph/GF composite laminates containing 6 wt % CNT-COOH. For the 6 wt % CNT-g-BA-ph/GF composite laminates, $T_{d5\%}$ and $T_{d10\%}$ are up to 435°C and 624°C in N_2 , increased 25.8°C and 149°C compared with those of BA-ph/GF composites, respectively. The increments, on one hand, can be attributed to due to the intrinsic merits of CNT-COOH and fiber such as nice barrier effect. On the other hand, the homogeneous dispersion of CNT-COOH in the matrix host would contribute uniform heat transport channels and make heat transfer effectively in the matrix,

eventually retarding thermal degradation of the composites. In addition, the thermal-oxidative stability of the composite laminates was consistent with the amount of CNT-COOH addition, as well as the char residue at 800°C in N_2 and in air atmosphere. As shown in Figure 6 and Table I, the thermal degradation temperatures of the CNT-g-BA-ph/GF composite laminates with 8 wt % CNT-COOH has decreased, which is analogous to that tendency of the mechanical properties. This may be due to the aggregation of excess CNTs in the matrix [Figure 5(f)], which collect heat in some regions, resulting to no effective heat transport channels, then the concentration of heat would accelerate the thermal degradation. Also, the reduction of the char residue at 800°C is attributed to two factors, on one hand, existence of great amounts CNTs wrecks the consummate cross-linking structure to some extent due to the space hindrance resulted from the congeries of excess CNTs in the BA-ph matrix, resulted to low-density of cross-linked network. On the other hand, the reduction of char residue are mainly attributed to the worsening matrix-filler interaction resulted from the aggregation of excess CNT in the matrix. The aggregation of CNTs results in less effective heat transport in the matrix, eventually reducing the char residue.

CONCLUSIONS

Significant improvement in the mechanical and thermal properties of GF-based thermosetting composites or laminates can be

Table I. Thermal and Thermal-Oxidative Stabilities of CNT-g-BA-ph/GF Composite Laminates

CNT-COOH content (wt %)	N_2			Air		
	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	Char residue (%)	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	Char residue (%)
0%	409.3	475.7	85.2	435.3	501.5	73.4
2%	415.2	492.1	85.7	435.1	503.1	74.1
4%	418.3	512.9	86.6	436.7	507.1	75.7
6%	435.1	624.7	87.9	465.2	522.7	76.7
8%	403.9	446.6	82.8	418.3	488.0	69.7

achieved by inducing CNT-COOH via *in situ* polymerization reaction. The flexural strength and modulus of CNT-g-BA-ph/GF composite laminates with 6 wt % CNT-COOH are as high as 650 MPa and 28.4 GPa, which are increased by 44.4% and 8% compared with those of BA-ph/GF composite laminates, respectively. Based on the SEM micrograph analysis, such mechanical enhancements are due to the dissipation of strain and stress during the propagation of cracks and the improved interface between CNT-COOH and BA-ph matrix. Thermal and thermal-oxidative stability study revealed that the $T_{d5\%}$ and $T_{d10\%}$ of 6 wt % CNT-filled CNT-g-BA-ph/GF composite laminates was as higher as 149°C and 21.2°C compared with those of BA-ph/GF composites, respectively. The functionalization of CNTs and the distribution of CNT-COOH into the polymer matrix by *in situ* reaction would be a novel solution to solve the problems of the CNTs aggregation and the poor interfacial adhesion between fibers and polymer matrix. It is expected that the multi-scale composites reinforced by CNTs with outstanding mechanical properties and thermal-oxidative stabilities would be further explored for the development of advanced structural composites.

ACKNOWLEDGMENTS

The authors wish to thank for financial support of this work from the National Natural Science Foundation (No. 51173021) and “863” National Major Program of High Technology (2012A A03A212).

REFERENCES

- Benmokrane, B.; Chaallal, O.; Masmoudi, R. *Constr. Build. Mater.* **1995**, *9*, 353.
- Gojny, F. H.; Wichman, M. H. G.; Kopke, U.; Fiedler, B.; Schulte, K. *Compos. Sci. Technol.* **2004**, *64*, 2363.
- Liu, H.; Uhlherr, A.; Bannister, M. K. *Polymer* **2004**, *45*, 2051.
- Ren, Y.; Fu, Y. Q.; Liao, K.; Li, F.; Cheng, H. M. *Appl. Phys. Lett.* **2004**, *84*, 2811.
- Shenogin, S.; Xue, L. P.; Ozisik, R.; Koblinski, P.; Cahill, D. G. *J. Appl. Phys.* **2004**, *95*, 8136.
- May, C. A.; Tanaka, G. Y. *Epoxy resin chemistry and technology*; New York: Marcel Dekker; **1973**.
- Baur, R. S. *American Chemical Society*; Washington (DC); **1979**.
- Potter, W. G. *Epoxide Resins*; Springer: New York; **1970**.
- McAdams, L. V.; Gannon, J. A. *Wiley-Inter science*; New York; **1986**, 322.
- Xu, Y.; Hoa, S. V. *Compos. Sci. Technol.* **2008**, *68*, 854.
- Bekyarova, E.; Thostenson, E. T.; Yu, A.; Kim, H.; Gao, J.; Tang, J. *Langmuir* **2007**, *23*, 3970.
- Xu, M. Z.; Yang, X. L.; Zhao, R.; Liu, X. B. *J. Appl. Polym. Sci.* **2012**, DOI:10.1002/app.38422.
- Hsiao, K. T.; Alms, J.; Advani, S. G. *Nanotechnology* **2003**, *14*, 791.
- Gojny, F. H.; Wichmann, M. H. G.; Fiedler, B.; Bauhofer, W.; Schulte, K. *Compos. Part A Appl. Sci. Manufac.* **2005**, *36*, 1525.
- Wichmann, M. H. G.; Sumfleth, J.; Gojny, F. H.; Quaresimin, M.; Fiedler, B.; Schulte, K. *Eng. Fract. Mech.* **2006**, *73*, 2346.
- Haque, A.; Shamsuzzoha, M.; Hussain, F.; Dean, D. J. *Compos. Mater.* **2003**, *37*, 1821.
- Kornmann, X.; Rees, M.; Thomann, Y.; Necola, A.; Barbezat, M.; Thomann, R. *Compos. Sci. Technol.* **2005**, *65*, 2259.
- Siddiqui, N. A.; Woo, R. S. C.; Kim, J.-K.; Leung, C. K. Y.; Munir, A. *Compos. Part A Appl. Sci. Manufac.* **2007**, *38*, 449.
- Kostopoulos, V.; Tsotra, P.; Karapappas, P.; Tsantzalidis, S.; Vavouliotis, A.; Loutas, T. H.; Paipetis, A.; Friedrich, K.; Tanimoto, T. *Compos. Sci. Technol.* **2007**, *67*, 822.
- Calvert, P. *Nature* **1999**, *399*, 210.
- Yu, M. F.; Files, B. S.; Arepalli, S.; Ruoff, R. S. *Phys. Rev. Lett.* **2000**, *84*, 5552.
- Che, J. W.; Cagin, T.; Goddard, W. A. III. *Nat. Nanotech.* **2000**, *11*, 65.
- Osman, M. A.; Srivastava, D. *Nanotechnology* **2001**, *12*, 21.
- Thostenson, E. T.; Li, W. Z.; Wang, D. Z.; Ren, Z. F.; Chou, T. W. *J. Appl. Phys.* **2002**, *91*, 6034.
- Yang, X. L.; Zhan, Y. Q.; Yang, J.; Zhong, J. C.; Zhao, R.; Liu, X. B. *J. Polym. Res.* **2012**, *19*; DOI: 10.1007/s10965-011-9806-0.
- Zhan, Y. Q.; Zhao, R.; Meng, F. B.; Lei, Y. J.; Zhong, J. C.; Yang, X. L.; Liu, X. B. *Mater. Sci. Eng. B* **2011**, *176*, 779.
- Yang, X. L.; Lei, Y. J.; Zhong, J. C.; Zhao, R.; Liu, X. B. *J. Appl. Polym. Sci.* **2011**, *119*, 882.
- Dunkers, J.; Ishida, H. *J. Polym. Sci. A* **1999**, *37*, 1913.
- Chutayothin, P.; Ishida, H. *Macromolecules* **2010**, *43*, 4562.
- Riess, G.; Schwob, J. M.; Guth, G.; Roche, M.; Lande, B. In *Advances in Polymer Synthesis*; Culbertson, B. M., Mc Garth, J. E., Eds.; Plenum: Advances in polymer synthesis, New York: Plenum, **1985**. p. 27.
- Ning, X.; Ishida, H. *Polym. Sci. Part A: Polym. Chem.* **1994**, *32*, 1121.
- Ning, X.; Ishida, H. *Polym. Sci. Part B: Polym. Phys.* **1994**, *32*, 921.
- Bekyarova, E.; Thostenson, E. T.; Yu, A. P.; Itkis, M. E.; Fakhruddinov, D.; Chou, T. W.; Haddon, R. C. *J. Phys. Chem. C* **2007**, *111*, 17865.
- Keller, T. M. J. *Polym. Sci. Part A: Polym. Chem.* **1988**, *26*, 3199.
- Guoping, C.; Wenjin, C.; Xiaobo, L. *Polym. Degrad. Stab.* **2008**, *93*, 739.
- Guoping, C.; Wenjin, C.; Junji, W.; Wenting, L.; Xiaobo, L. *Express Polym. Lett.* **2007**, *1* (8), 512.
- Ning, X.; Ishida, H. *J. Polym. Sci. Part A: Polym. Chem.* **1994**, *32*, 1121.

38. Ishida, H.; Ohba, S. *Polymer* **2005**, *46*, 5585.
39. Allaoui, A.; Bai, S.; Cheng, H. M.; Bai, J. B. *Compos. Sci. Technol.* **2003**, *62*, 1993.
40. Bai, J. B.; Allaoui, A. *Compos. Part A: Appl. Sci. Manufac.* **2003**; *34*:689–94.
41. Liao, Y. H.; Marietta-Tondin, O.; Liang, Z.; Zhang, C.; Wang, B. *Mater. Sci. Eng. A* **2004**, *385*, 175.
42. Miyagawa, H.; Drzal, L. T. *Polymer* **2004**, *45*, 5163.
43. Park, S. J.; Joeng, H. J.; Nah, C. *Mater. Sci. Eng. A* **2004**, *385*, 13.
44. Prashantha, K.; Soulestin, J.; Lacrampe, M. F.; Claes, M.; Dupin, G.; Krawczak, P. *Express Polym. Lett.* **2008**, *2*, 735.
45. Li, J.; Sham, M. L.; Kim, J. K. *Compos. Sci. Technol.* **2007**, *67*, 296.
46. Hibbs, M. F.; Tse, M. K.; Bradley, W. L. In *Toughened Composites*, ASTM STP, 937; Johnston Norman, J. Ed.; Toughened composites, ASTM STP, 937. American Society for Testing and Materials, **1987**, p. 115.
47. Jiang, Z. Y.; Zhang, H.; Zhang, Z.; Murayama, H.; Okamoto, K. *Compos. Part A: Appl. Sci. Manufac.* **2008**, *39*, 1762.