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Fabrication and mechanical properties of hybrid multi-scale epoxy composites reinforced with conventional carbon fiber fabrics surface-attached with electrospun carbon nanofiber mats

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This paper reports the fabrication and mechanical properties of hybrid multi-scale epoxy composites reinforced with conventional carbon fiber (CF) fabrics surface-attached with electrospun carbon nanofiber (ECN) mats. The ECNs were prepared via thermal treatments of polyacrylonitrile copolymer nanofibers, which were produced by the electrospinning technique and collected as overlaid mats on the T300 CF fabrics. The ECN-CF fabrics/mats were used as innovative reinforcement fillers for the fabrication of hybrid multi-scale composites (with SC-15 epoxy resin) through the composite-manufacturing technique of vacuum assisted resin transfer molding. Three-point bending test and short-beam shear test were carried out to evaluate the strengthening/toughening effects of ECNs on mechanical properties of the novel composites. The results indicated that out-of-plane mechanical properties of the ECN-CF/epoxy composites were considerably higher than the control sample of traditional CF/epoxy composites.

1. Introduction

Composite materials made of polymer resins reinforced with high-performance fibers (particularly carbon fibers) have a wide range of applications including, but not limited to, aerospace structures, ground vehicles, and sports utilities (e.g., golf clubs, tennis rackets, sailing boats). Compared to metallic materials, polymer composites possess a variety of advantageous properties such as high strength-to-weight ratio, excellent corrosion resistance, and favorable fatigue tolerance [1]. Due to the unique fiber architectures in laminated polymer composites, the resin matrices that function to bond and protect the reinforcement fibers dominate out-of-plane mechanical properties (e.g., interlaminar shear strength and delamination toughness), which are much lower than in-plane mechanical properties controlled by the reinforcement fibers [2]. In consequence, the interlaminar fracture (one of the typical failure modes) has been commonly detected in polymer composites; and its occurrence considerably deteriorates the mechanical performances of the composites in services [3]. To mitigate this problem, extensive research efforts have been devoted to interface-toughening of composites in the last several decades [4,5].

With the recent developments of nanomaterials/nanotechnologies, polymer composites reinforced with nanoscale fillers/agents have attracted growing interests among scientists and engineers. The polymer composites reinforced with nanotubes, nanofibers, and/or nanoparticles in matrices are expected to possess superior mechanical properties. However, due to several technological issues (e.g., inadequate dispersion/alignment and low volume fraction of nano-reinforcements, poor interfacial bonding strength and load transfer, etc.), the improvements of mechanical properties achieved so far are considerably lower than what have been predicted, in particular when compared to advanced composites reinforced with high-performance continuous fibers [6–12]. Albeit research endeavors are still in progress, it is unlikely that nanocomposites would replace conventional fiber-reinforced composites as bulk structural materials, at least in the near future. Nevertheless, recent investigations have revealed that nanoscale reinforcements could distinguishably enhance the toughness and damage tolerance of traditional structural composites used broadly in aerospace structures [13–17]. One promising approach is based upon incorporation of nano-reinforcement agents/fillers between composite laminas/prepregs to form hybrid multi-scale composites [13,14].

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It has been predicted in theory and validated in experiments that the hybrid multi-scale fiber-reinforced composites with uniformly distributed nano-reinforcement agents (between neighboring composite laminas/prepregs) would possess much enhanced mechanical properties [15–17]. Yet, the mechanical properties of many hybrid multi-scale composites that have been developed so far are not as high as expected due to the technological challenge on uniform dispersion of nanoscale fillers in highly viscous resins. Hence, it is important to study the processing methods/procedures to fabricate laminated polymer composites with uniformly dispersed nano-reinforcements in the interlaminar regions.

The top-down materials-processing technique of electrospinning provides a viable and versatile approach for convenient preparation of ultrathin fibers with diameters ranging from nanometers to microns [18,19]; nevertheless, only a few research efforts have been devoted to the development and evaluation of polymer composites reinforced with electrospun nanofibers [17,20–26]. Our recent studies have indicated that electrospun carbon nanofibers (ECNs) could be produced through thermal treatments of their precursors such as electrospun polyacrylonitrile (PAN) copolymer nanofibers. The electrospun PAN copolymer nanofibers possesses an extremely high degree of macromolecular orientation and a significantly reduced amount of structural imperfections; in addition, the diameter of nanofibers is approximately 100 times smaller than that of conventional counterparts, which effectively prevents the formation of structural inhomogeneity (particularly sheath/core structures) during stabilization and carbonization. As a result, the ECNs could possess superior mechanical properties that would unlikely be achieved through conventional approaches [27–29]. As continuation of this study, the hybrid multi-scale epoxy composites made of conventional carbon fiber (CF) fabrics with interlaminar regions containing mats of ECNs were fabricated; and the evaluation results indicated that the interlaminar shear strength and the flexural modulus of these innovative composites were appreciably higher than those of conventional CF/epoxy composites [20].

In this study, instead of preparing ECN mats in advance followed by sandwiching them between CF fabrics for the fabrication of hybrid multi-scale epoxy composites, PAN copolymer nanofibers were first electrospun directly onto the conventional T300 CF fabrics; thereafter, the nanofibers were converted into ECNs through thermal treatments of stabilization in air followed by carbonization in argon. Finally, the prepared ECN-CF fabrics/mats were used to fabricate hybrid multi-scale composites with an epoxy resin through the composite-manufacturing technique of vacuum assisted resin transfer molding (VARTM). The SC-15 epoxy resin was selected for this study due to its low shrinkage, excellent adhesion to carbonaceous materials, and high reactivity with a variety of chemical curing agents [30,31]. Mechanical properties of the hybrid multi-scale composites were evaluated by the three-point flexural test and the short-beam shear test to study the strengthening/toughening effects of ECNs. Additionally, the micro- and/or nano-scaled morphologies, the distribution of nanofibers, and the fracture surfaces of composites were characterized by scanning electron microscopy (SEM); the strengthening and/or toughening mechanisms were further correlated to the observed micro- and/or nano-structures of the novel hybrid multi-scale composites.

2. Experimental

2.1. Materials

Woven-fabrics of T300 carbon fibers (CFs) were provided by the Toray Industries, Inc. (Tokyo, Japan). Polyacrylonitrile (PAN) microfibers (SAF 3K fibers) were acquired from the Courtaulds, Ltd. (Nottingham, UK), and were used as the starting material to make electrospun PAN nanofibers. SAF 3K fibers were in the form of bundle with 3,000 individual microfibers of a PAN copolymer. The copolymer was synthesized from acrylonitrile together with 1.2 wt.% of itaconic acid and 6 wt.% of methyl acrylate. The epoxy resin of SC-15A and the associated hardener of SC-15A were supplied by the Applied Poleramic, Inc. (Benicia, CA). Acetone and *N,N*-dimethyl formamide (DMF) were purchased from the Sigma–Aldrich Co. (St. Louis, MO).

2.2. Preparation of electrospun ECN-CF fabrics/mats

Prior to electrospinning, SAF 3K microfibers were first immersed in acetone to remove the surface oil and then dissolved in DMF to prepare a solution with the concentration of PAN copolymer being 14 wt.%. Subsequently, the solution was filled in a 30-ml BD Luer-Lok™ plastic syringe installed with a stainless-steel needle having an 18-gauge 90° blunt end. The electrospinning setup included a high voltage power supply (model number: ES30P), purchased from the Gamma High Voltage Research, Inc. (Ormond Beach, FL), and a laboratory-made aluminum roller with the diameter of 25 cm. During the electrospinning process, a DC voltage of 25 kV was applied between the needle and the electrically grounded roller; a flow rate of 1 ml/h was maintained by a digital syringe pump (model number: KDS 200) purchased from the KD Scientific Inc. (Holliston, MA). The angular velocity of the roller (covered with aluminum foil) was set at 100 rpm; while the conventional CF fabrics with the length and width being 3 inches and 2 inches, respectively, were attached on the surface of roller. Electrospun PAN copolymer nanofibers were collected as almost randomly overlaid mats on the CF fabrics. The time periods for collection of nanofibers were set at 5, 10, 20, and 30 min, respectively. The stabilization and carbonization of PAN copolymer nanofibers (on CF fabrics) were conducted in a Lindberg 54453 heavy duty tube furnace purchased from the TPS Co. (Watertown, WI). The processing parameters and/or procedures for the preparation of ECNs from PAN copolymer (precursor) nanofibers were described elsewhere [20].

2.3. Fabrication of hybrid multi-scale epoxy composites

As illustrated in Fig. 1, the VARTM technique was adopted to process the hybrid multi-scale epoxy composites reinforced with ECN-CF fabrics/mats. The mass ratio of the epoxy resin versus the hardener was set at 100/30. Three composite panels were fabricated in this study, each of which was reinforced with six ECN-CF fabrics/mats (with the length and width being 3 and 2 inches, respectively); the ECN-CF fabrics/mats were prepared with the same nanofiber collection time (i.e., with the same thickness of ECN mats). A vacuum of 27 mmHg was applied during the initial curing, and the curing process was kept at room temperature of 22 ± 2 °C for 24 h; the obtained composite panels were further

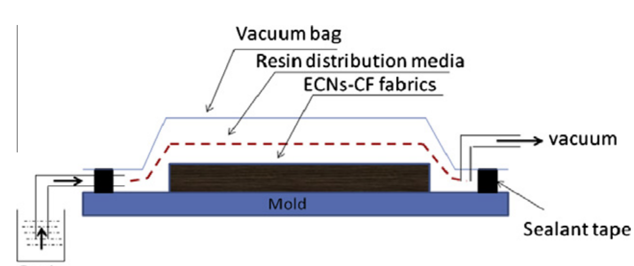

Fig. 1. Schematic representation showing the composite-manufacturing technique of vacuum assisted resin transfer molding (VARTM).

cured in an oven at 110 °C for 5 h before being characterized and evaluated. For the purpose of comparison, a composite panel with six CF fabrics alone was also fabricated as the control sample. For all of the fabricated composite panels, the thickness was controlled at approximately 1.6 mm.

2.4. Characterization and evaluation

A Zeiss Supra 40 VP field-emission scanning electron microscope (SEM) was employed to examine the morphologies of ECNs, the distribution of ECNs on the surface of CF fabrics, and the fracture surfaces of epoxy composites. Mechanical properties of the fabricated composites were evaluated at room temperature of 22 ± 2 °C, and all of the specimens (both three-point flexural specimens and short beam shear specimens) were cut from the fabricated composite panels by using a water-cooled diamond saw. To evaluate the strengthening/toughening effects of ECNs on the hybrid multi-scale composites, the three-point flexural test (with specimen dimensions of 50.8 mm in length, 12.7 mm in width, and 1.6 mm in thickness) was conducted on a QTESTTM/10 mechanical testing machine (MTS System Co., Eden Prairie, MN) in accordance with ASTM 790. During the test, a span distance of 25.4 mm and the strain rate of 0.01 mm/mm/min were adopted. To evaluate the toughening effect of ECNs on the interlaminar shear strength, short-beam shear specimens (8 mm in length, 4 mm in width, and 1.6 mm in thickness) were tested with the span-to-thickness ratio of 4 and the cross-head speed of 1 mm/min, according to ASTM D2344. Five specimens of each composite were evaluated; the mean values and the associated standard deviations of mechanical properties were calculated.

3. Results and discussion

3.1. Morphologies of CF fabrics and ECN-CF fabrics/mats

The SEM images in Fig. 2 show the morphologies of CF fabrics and ECN-CF hybrid fabrics/mats, in which Fig. 2A′-D′ and F′ are the corresponding images of Fig. 2A–D and F with higher magnifications, respectively. As shown in Fig. 2A and 2A′, the CF fabrics are woven-fabrics made of conventional CF bundles with fiber diameters of ~7 μm. Fig. 2B, B′, C, C′, D, D′, F, and F′ indicates the representative morphologies of ECN-CF fabrics/mats with the time periods for collection of electrospun PAN copolymer (precursor) nanofibers being set at 5, 10, 20, and 30 min, respectively. Under the adopted conditions for electrospinning and nanofiber collection, the ECN layers/mats with fiber diameters of ~500 nm can be uniformly attached onto the CF fabrics; in general, the thickness of ECN layers/mats are roughly proportional to the collection time when the time is less than 20 min. It is noteworthy that a few beads and/or beaded nanofibers can be identified in the low-magnification image of Fig. 2D, and it appeared that they could act as the structural defects in the fabricated composites (see the results of mechanical properties below). When the collection time further increased to 30 min (as shown in Fig. 2F), some of the ECN mats on the CF fabrics could be peeled off, and the density of ECN mats would be very low in some areas of CF fabrics (Fig. 2F′). As the result, the ECN-CF fabrics/mats with the collection time of 30 min were not selected to make the hybrid multi-scale epoxy composites.

3.2. Mechanical properties

3.2.1. Flexural properties

The three-point flexural test was carried out to measure the flexural strength (FS) and work of fracture (WOF) of the fabricated epoxy composites reinforced with conventional CF fabrics or hybrid ECN-CF fabrics/mats. FS is a material parameter to indicate the capability to against failure under external loading, while WOF is the energy dissipated to fracture a specimen, which can be determined by averaging the area under load-displacement curve over the cross-sectional area of the specimen. The FS and WOF values of the studied composites reinforced with CF fabrics or ECN-CF fabrics/mats (with different periods of collection time) were obtained, as shown in Fig. 3A.

In general, the FS and WOF values of the novel multi-scale epoxy composites reinforced with hybrid ECN-CF fabrics/mats were higher than those of their conventional counterparts reinforced with CF fabrics alone. As shown in Fig. 3A, the values of FS and WOF for the conventional CF/epoxy composite were (376.9 ± 11.8) MPa and (11.2 ± 0.5) kJ/m^2, respectively. However, for the hybrid multi-scale ECN-CF/epoxy composites, as the collection time at 10 min, the values of FS and WOF were (465.6 ± 38.4) MPa and (16.5 ± 1.8) kJ/m^2, respectively, which represented 23.5% and 47.3% improvements as compared to the CF/epoxy composite. Since the diameter of ECNs was much smaller and the specific surface area of ECNs was much larger than those of the T300 CFs, the interfacial bonding strength between ECN-CF fabrics/mats and epoxy resin can be much stronger than that between conventional CF fabrics and epoxy resin. In addition, ECNs could break and/or detach from the matrix of epoxy resin when the load was applied; this would dissipate the strain energy, prevent the failure of the composites, thus lead to higher values of FS and WOF. However, experimental results also showed that further increase of the collection time to 20 min did not improve the FS and WOF of the composites; instead, the values of FS and WOF decreased to (429.3 ± 27.2) MPa and (13.4 ± 1.2) kJ/m^2, respectively. This can probably be attributed to the presence of beads and/or beaded nanofibers (see Fig. 2D), which could function as the structural defects, leading to the reduction of mechanical properties of the composites. It is also noteworthy that, for the ECN-CF fabrics/mats with the collection time periods of 5 and 10 min, it was not easy to separate the ECN mats from the CF fabrics; whereas for the ECN-CF fabric/mat with the collection time period of 20 min, it appeared that the loose and multi-layer structure of ECNs was formed, resulting in the readiness of separating the ECN mat from the CF fabric. The ECN-CF/epoxy composite with the collection time of 10 min had higher mechanical properties than the one with the collection time of 20 min. In our previously reported study [20], five ECN mats (each with the thickness of ~40 μm) were prepared in advance followed by being sandwiched between six layers of CF fabrics, and then the epoxy resin was introduced by VARTM to fabricate the hybrid multi-scale epoxy composites; after that, the obtained composite was further cured in an oven at 110 °C for 5 h. According to Garcia's report [32], the thickness of nano-reinforcements between two laminas has significant effect on the mechanical properties of the resulting composites, and the maximal penetration to each laminar/ply by nano-reinforcements is ~10 μm. Hence, the optimal thickness of nano-reinforcements should be 20 μm or less. The thickness of ECNs in our previous study was ~40 μm [20], while the thickness of ECNs in this study was less than 20 μm, which could explain that the method adopted in this study would result in higher mechanical properties for the epoxy composite and outperform the method reported previously.

3.2.2. Interlaminar shear properties

Interlaminar shear strength (SS) and elastic modulus (EM) of the conventional CF/epoxy composite and the novel hybrid multi-scale ECN-CF/epoxy composites (with different collection time periods of 5, 10, and 20 min) are shown in Fig. 3B. The SS and EM values of the CF/epoxy composite were (27.5 ± 1.3) MPa and

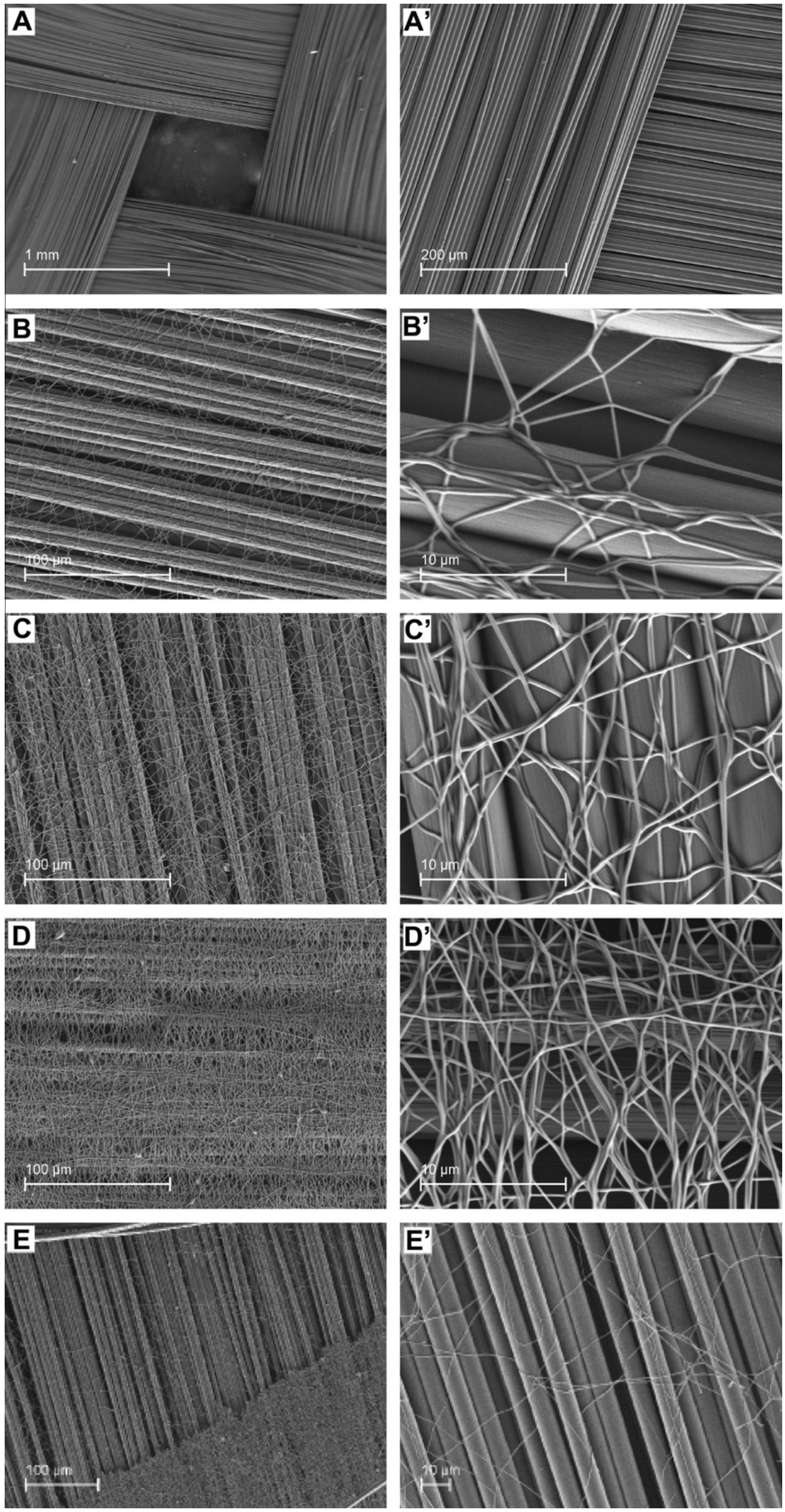

Fig. 2. Representative SEM images of CF fabrics and ECN-CF fabrics/mats. The time periods for collection of electrospun PAN copolymer (precursor) nanofibers on CF fabrics were set at (A) 0 min (i.e., CF fabrics without ECNs), (B) 5 min, (C) 10 min, (D) 20 min, and (F) 30 min, Figures A′, B′, C′, D′, and F′ are the corresponding SEM images of Figures A, B, C, D, and F with higher magnifications.

(12.1 ± 1.0) GPa, respectively. As the collection time at 10 min, the values of SS and EM for the ECN-CF/epoxy composite were (88.3 ± 5.8) MPa and (24.8 ± 3.9) GPa, respectively, representing 221.1% and 105.0% enhancements as compared to those for the

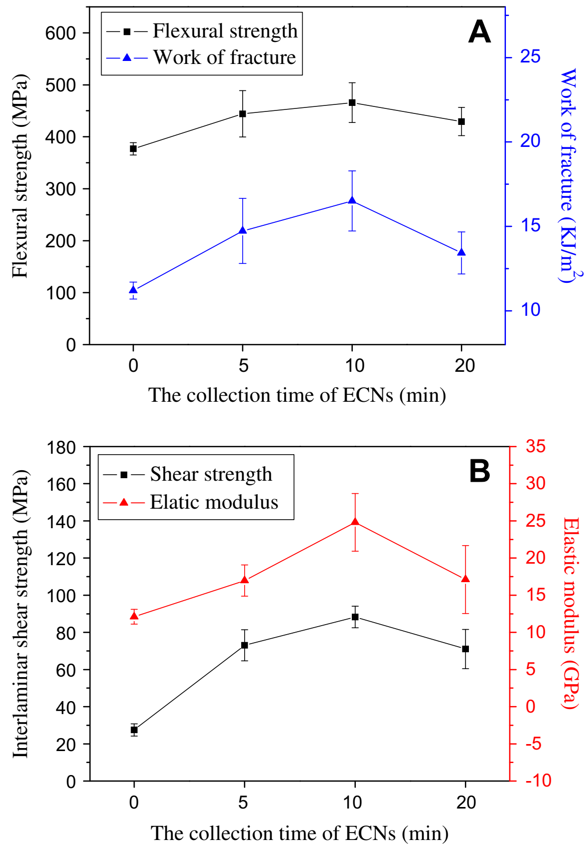

Fig. 3. Mechanical properties (A: flexural strength and work of fracture and B: interlaminar shear strength and elastic modulus) of epoxy composites reinforced with CF fabrics or ECN-CF fabrics/mats; the time periods for collection of electrospun PAN copolymer (precursor) nanofibers on CF fabrics was set at 0 min (i.e., CF fabrics without ECNs), 5 min, 10 min, and 20 min, respectively. Each datum provides the mean value of five specimens/tests with error bar representing one standard deviation.

control sample of CF/epoxy composite. However, the respective SS and EM values of ECN-CF/epoxy composite decreased to (71.0 ± 10.6) MPa and (17.1 ± 4.6) GPa, when the collection time was prolonged to 20 min. In general, the incorporation of ECN-CF fabrics/mats into the epoxy resin considerably improved the SS and EM of the resulting hybrid multi-scale ECN-CF/epoxy composite, since the ECN mats attached on the CF fabrics can function as nano-reinforcement in the interlaminar regions. In particular, the presence of ECNs could effectively mitigate the propagation of micro-cracks in the resin-rich interlaminar regions. If a micro-crack initiated in this region due to stress concentration, the ECNs remained intact across the crack plane and supported the applied load similar to the hooks and loops in Velcro [16]. As a result, the epoxy matrix was reinforced. Furthermore, it is well-known that the mechanical properties of fiber-reinforced composites are primarily determined by the mechanical properties and the volume fraction of reinforcement fibers. Thus, the incorporation of ECNs, with modulus much higher than that of the epoxy resin, resulted in the increase of SS and EM for ECN-CF/epoxy composites. On the other hand, the SS and EM showed a decreasing trend when the collection time was at 20 min. As explained before, there might be two reasons attributed to this decrease: (1) the formation of beads and/or beaded ECNs might act as structural defects and (2) with the collection time at 20 min, the ECN mats could be readily separated from the CF fabrics. In this study, the PAN copolymer (precursor) nanofibers were attached on the conventional CF fabrics during electrospinning. When the time for collection of nanofibers prolonged, the electric force between the jet and CF fabrics became weaker due to the residual charges on electrospun nanofibers; hence, the readiness for separation of precursor nanofibers from CF fabrics were different at different collection time. When the collection time was 20 min, the ECN mats could be easily separated from the CF fabrics. As shown in Fig. 2F and F′, when the collection time was further increased to 30 min, some of the ECN mats on the CF fabrics could be peeled off, and the density of ECN mats was low in some areas of CF fabrics.

3.3. Fracture surface and reinforcement mechanisms

During the interlaminar shear failure of laminated composites, the shear stress is typical transferred from layer to layer through resin matrix; thus, the delamination is one of the primary mechanisms responsible for the failure of composites [33,34]. Therefore, the fracture surfaces of laminated composites could provide vital information about the interfacial bonding strength between the fabrics/mats and the resin matrix. The SEM images of Fig. 4A–D show the representative fracture surfaces of conventional CF/epoxy composite and hybrid multi-scale ECN-CF/epoxy composites; among which, the collection time periods were set at 0, 5, 10, and 20 min, respectively; while Fig. 4A′, B′, C′, and D′ are the corresponding SEM images of Fig. 4A–D examined in different directions. For the CF/epoxy composite (Fig. 4A and A′), the epoxy resin was frequently detached from the CFs, as evidenced by that the CF surfaces were smooth without the remnants of resin. This suggests that the delamination was the dominant factor at the fiber/matrix interfacial regions due to weak adhesion. In contrast, as shown in Fig. 4B, B′, C, C′, D, and D′, fracture surfaces of ECN-CF/epoxy composites could be distinguished from the development of different interfacial microstructures and the matrix-resin deformations. Furthermore, for the ECN-CF/epoxy composites with the collection time periods of 5 and 10 min, the SEM images (Fig. 4B′ and C′) indicate that the carbon fibers were well embedded in and/or adhered with the epoxy resin; this indicates that the interfacial bonding strength between the filler and the resin has been improved through the incorporation of ECNs. As also observed in Fig. 4B and C, the fracture surfaces exhibited dimpled/scalloped features; this could explain the formation of tougher interface between the epoxy resin and ECN-CF fabrics/mats. Moreover, as shown in Fig. 4D and D′, the ECN-CF/epoxy composite with the collection time of 20 min exhibited the similar fracture features to those with the collection time periods of 5 and 10 min (Fig. 4B, B′, C, and C′). However, some voids and/or individual fibers could be identified in Fig. 4D and D′, which indicates the relatively weaker interfacial bonding strength between the epoxy matrix and this novel type of hybrid multi-scale ECN-CF fabrics/mats. Through examinations of the fracture surfaces of epoxy composites reinforced with CF fabrics and ECN-CF fabrics/mats, it was evident that the same conclusions could be drawn as those from the flexural and interlaminar shear properties; i.e., the ECN mats attached on the surfaces of CF fabrics could increase the interfacial bonding strength and improve mechanical properties of the resulting hybrid multi-scale ECN-CF/epoxy composites. Based upon the acquired experimental results, the optimal time period for collection of electrospun PAN (precursor) nanofibers appeared to be 10 min.

4. Concluding remarks

In this study, PAN copolymer (precursor) nanofibers were first electrospun directly onto conventional T300 CF fabrics; subsequently, the precursor nanofibers were converted into ECNs through thermal treatments of stabilization in air followed by carbonization in argon. Finally, the prepared ECN-CF fabrics/mats

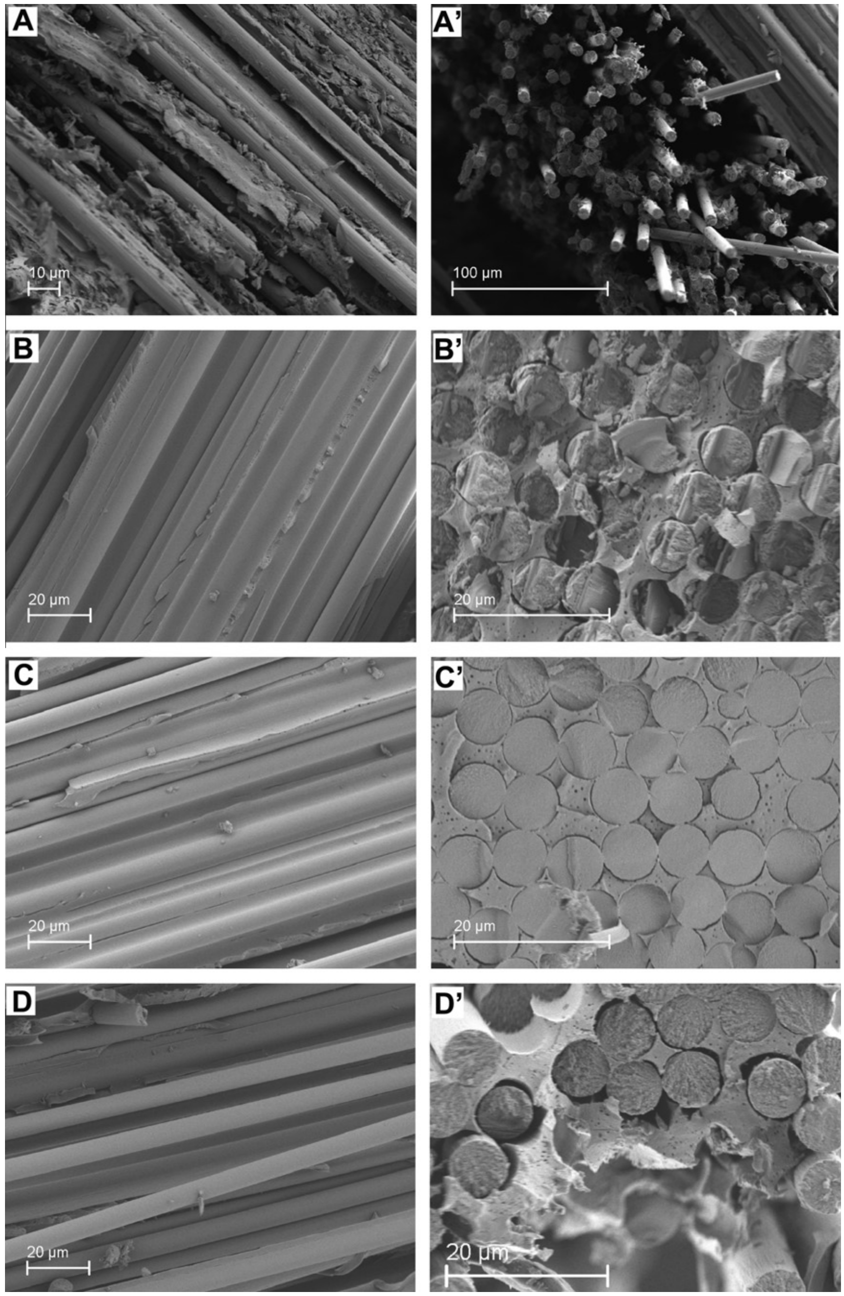

Fig. 4. Representative SEM images of fracture surfaces of epoxy composites reinforced with CF fabrics or ECN-CF fabrics/mats. The time periods for collection of electrospun PAN copolymer (precursor) nanofibers on CF fabrics were set at (A) 0 min (i.e., CF fabrics without ECNs), (B) 5 min, (C) 10 min and (D) 20 min; Fig. A′, B′, C′, and D′ are the corresponding SEM images of Fig. A, B, C, and D examined in different directions.

were used as novel reinforcement fillers for the fabrication of hybrid multi-scale composites with SC-15 epoxy resin through the VARTM technique. The hypothesis was that the impregnation of ECN-CF fabrics/mats would substantially improve the out-of- plane properties of the resulting hybrid multi-scale epoxy composites at small increase of weight, very low cost, and without substantial modification of the conventional fiber-composite processing procedure. The study revealed that the interlaminar mechanical properties of the ECN-CF/epoxy composites were enhanced considerably when compared to those of the traditional CF/epoxy composites. The improvement of mechanical properties was due to the high mechanical strength of ECNs, as well as the strong interfacial bonding strength between the ECN–CF fabrics/mats and epoxy resin. The acquired experimental results also indicated that, the optimal time period for collection of electrospun precursor nanofibers on CF fabrics appeared to be 10 min, and the corresponding hybrid multi-scale epoxy composites possessed the FS, WOF, SS, and EM of (465.6 ± 38.4) MPa, (16.5 ± 1.8) kJ/m^2, (88.3 ± 5.8) MPa, and (24.8 ± 3.9) GPa, respectively, which represented the improvements of 23.5%, 47.3%, 221.1%, and 105.0% as compared to those of the control sample of CF/epoxy composites. This study suggests that, the developed hybrid multi-scale ECN-CF/epoxy composite could replace conventional CF/epoxy composites as low-cost and high-performance structural composites with improved out-of- plane mechanical properties. The strengthening/toughening strategy formulated in this study indicates the feasibility of using the nanoscale reinforcements to further improve the mechanical properties of currently structured high-performance composites in the near- and medium-term time frame. In addition, the present study will significantly stimulate the long-term development of high-strength high-toughness bulk structural nanocomposites for broad applications.

Acknowledgments

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