High sensitivity and versatility fiber sensors based on carbon nanomaterials for in situ monitoring of composites manufacturing

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ABSTRACT

Sensor technology based on carbon nanomaterials (CNM) provides a variety of promising strategies for implementing the self-sensing and diagnostic functionalities of next-generation layered composites. Compared to the study of excess composite structure deformation and cracking, the technology for monitoring the manufacturing stage of composites using CNM is rather limited. This paper systematically investigates carbon nanotubes (CNTs) coated, graphene coated and carbon fiber enabled sensors for monitoring the complete molding process of composites through acquiring the real-time resistance change of sensors. In comparison to graphene-coated and carbon fibers with densely and continuously packed graphitic structures, the CNT coated fiber sensor with the entangled and loosely packed porous network shows far superior performance for sensing different processing stages of composites, including resin infiltration, gelation and curing.

1. Introduction

The next-generation fiber-reinforced polymeric composites (FRPs) are impending to possess built-in functionality to continually monitor and diagnose their own health states. Carbon nanomaterials (CNM) enabled sensors or sensor systems are emerging as one of the most promising technology for self-sensing, identifying, quantifying and deciding the health states of FRPs by virtue of their excellent mechanical robustness, structural non-invasiveness, interfacial conformability and high piezoresistive sensitivity[1]. Basically, the strategies to hybridize CNMs in FRPs include coating, depositing, sandwiching and mixing various types of carbon nanomaterials, e.g. carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene, graphite nanoplatelets (GNPs) and carbon blacks onto/into the surface, interlamination, fiber/matrix interface and resin matrix of composites. For instance, CNT twisted yarns[2,3], CNT/PVA coagulated fibers[4,5] and CVD grown fuzzy fibers[6,7] were explored as 1D sensors by assembling and embedding them in composite matrix. CNT thin films[8,9], CNT/polymer hybrid films[10], buckypapers[11] and graphene ribbons[12] have been served as 2D sensors by attaching them on surface or in between prepreg layers. In addition, 3D sensors have been widely utilized by dispersing and distributing CNMs particles in resin matrix to enable the conducting/reinforcing dual functionality[13,14].

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The current CNMs technology for SHM applications of FRPs is majorly concerned for detecting deformations, cracks and failure modes in service stages of composites. For examples, Abot et al. utilized CNT/PVA coagulated fiber sensors to monitor fracture modes of composites through the process of three point bending[3]. Thostenson et al. dispersed CNTs in resin matrix and systematically studied its capability for sensing cracks and failure of glass fiber composites under tensile deformations[13]. Compared to service stage detections, advanced SHM technology for monitoring manufacturing stages of FRPs is equally important to detect and control events that may induce quality degradations and part-to-part variations during the inline manufacturing process such as non-uniform flow front and problematic flow defects (e.g. dry spots)[15]. Zhang et al. raised the possibility to correlate electrical resistance of CNT networks with properties of epoxy resin including glass transition temperature[16]. Gnidakouong[17], Lu[18,19] and Ali et al.[20] respectively utilized spray coated CNT networks, buckypapers and graphene coated fabrics to detect resin flow and cure states of polymeric composites. The obtained gain factors (percentage of the maximum resistance change) of the sensor subjected to resin infusion and gelation is ~160[17], ~240[19] and ~30[20].

Given the progress being made, the current CNM technology for process monitoring of composites is principally focusing on establishment of sensor fabrications and evaluation of sensor properties. Here, this paper reports on three different types of CNMs based sensors, namely, CNT coated fiber sensors (CNT-FS), reduced graphene oxide coated fiber sensors (rGO-FS) and carbon fiber sensors (CFS) for monitoring the whole event of vacuum assisted resin transfer molding (VARTM) process of composites. Upon SEM imaging, we first observed a significant difference on the microscopic morphology and packing structure of sensors made of different materials. Compared to CFS with a continuous and densely packed graphitic structure, rGO-FS and CNT-FS with different nanoparticles coated on fiber cores respectively present a thin platelet stacking structure and a loosely packed rope-like network. As the packing structure changes from loose to compact, we indeed observed the clearly hierarchical performance of sensors with the resistance gain factor increased from ~7.5 (CFS) to ~37 (rGO-FS) and 1600 (CNT-FS) during resin infusion and curing. This strong structure-dependent sensing performance was explained by different levels of resin infiltration to alter the tunneling resistance and density of conducting pathways in the sensor network. This result demonstrates the capability of CNT-FS for quality assurance.

2. Experimental

2.1 Fabrication and Characterization of CNM Sensors

To fabricate CNT-FSs and rGO-FSs, high-quality dispersion of nanomaterials was first prepared. The CNT dispersion was processed by dispersing 300 mg multi-walled carbon nanotube (MWCNT, General Nano LLC.) in 100 mL of deionized water with 8 mL of nonionic surfactant triton X-100 (CAS # 9002-93-1, Sigma-Aldrich) in an ice bath using a Ultrasonics FS-600N probe sonicator (20 kHz). The graphene oxide (GO) dispersion was processed by dispersing 300 mg GO (synthesized by the modified Hummer’s method[21]) in 100 mL of deionized water following the same sonication setup. The sonicator was operated in a pulse model (on 10 s, off 10 s) with the power set at 480 W for 1 h. The as-sonicated dispersion was then mildly centrifuged (Eppendorf Centrifuge 5418) at 3000 rpm for 10 min to remove large bundles and aggregations. To be consistent with composites, a fiberglass roving (10 m in length) extracted from the plain woven cloth (290 g/m², part # GF-PL-290-100, Easy Composites Ltd.) was selected and used as the substrate of CNT-FSs and rGO-FSs. Similarly, a 15 cm long carbon fiber roving cut from the fiber spool (3000 filaments, 200 mg/m, part # CF-PL-210-100, Easy Composites Ltd.) was served as the CFS.

An in-house developed continuous dip coating and fiber winding system was set up for roll-to-roll fabrication of CNT-FSs and rGO-FSs. The key elements for this system is composed of a
computer controlled stepper motor (Silverpak 17C, Lin Engineering Corps.) and a series of pulley modules for conveying the fiber roving sequentially through a CNT or GO bath with 200 mL of CNT/GO dispersion, a surfactant removing reservoir with 500 mL of deionized water, and a heating station (HG-301A, Master Heat Gun) for drying. In a typical coating process, the motor winding speed was set at 1 cm/min and the drying temperature was set at 200 °C. After the coating process, the CNT coated fiberglass with 15 cm in length was cut from the continuous roving and coined as CNT-FS. The GO coated fiberglass was further treated by a reduction process carried out by immersing the roving into a HI acid solution (CAS # 10034-85-2, Sigma-Aldrich) placed in a thermostatted oil bath at 85 °C for 30 min. The as-reduced graphene fibers were cleaned in ethanol and water to remove excessive HI solution. Then, it was coined and used as rGO-FS.

The structures of different fiber sensors were examined by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) and Raman spectroscopy. SEM was performed with JEOL JSM-7001F at 10 kV for examining morphologies and packing structures. Samples were sputter coated with platinum prior to SEM imaging. The same instrument was used to acquire EDX spectrum for elemental analysis. A Horiba HR800 Raman microscope was also used for collecting the Raman spectra of varied sensors with a 532-nm excitation laser at the power of 5 mW.

![Figure 1. Photographs of (a) the as-produced fiber sensors, (b) the fiberglass fabrics with braided single or multiple (inset) fiber sensors, and (c) the experimental setup of VARTM process with the embedded fiber sensor and the composite part after manufacturing with multiple sensors integrated (inset).](image)

**2.2 Process Monitoring of CNM Sensors in Polymeric Composites**

To embed the fiber sensor in composites and in situ monitor the whole manufacturing process, three different sensors were carried out by the same VARTM process. The fiber sensor was first manually braided in a single layer of plain woven cloth with the trimmed dimension of 15 cm × 15 cm along its center line. The sensor embedded layer along with another two neat fabric layers were stacking together on top of a PMMA substrate. Assisted by conductive silver paint (SPI®, Structure Probe Inc.), two copper electrodes were connected to each end of the fiber sensor for electrical measurements. A nylon medium (RESINFLOW 90 HT, Airtech Ltd.) for uniform distribution of resin flow and a composite release film (ELS60100, Airtech Ltd.) were also laid on top of the fabrics. A vacuum bagging film (WL5400, Airtech Ltd.) and a double-sided sealant tape (AT200Y, Airtech Ltd.) were then used to seal the preform in a confined space for resin infusion from two nylon hoses connected as inlet and outlet.

Subsequent to sensor integration and preform lay-up, the resin infusion process was operated by a vacuum pump to generate one standard atmospheric pressure (0.1 MPa) in ambient temperature or 60 °C controlled in a vacuum oven. Under the vacuum pressure, the mixture of polyester resin (IP2, Easy Composites Ltd.) catalyzed by 1.5 wt.% of methyl ethyl ketone peroxide (MEKP, CAS # MEKP-05, Easy Composites Ltd.) was automatically infused, infiltrated and filled. The infused fluid was then de-gassed for 5 min to remove entrapped air bubbles before clamping the hose. The following curing process was isothermally maintained for 24 h as recommended by the vendor. During the whole process of VARTM, real-time resistance of the embedded sensor was recorded by a Keithley 2450 Sourcemeter® programmed...
by a homemade LabVIEW user interface\cite{22}. For simultaneous recording of multiple sensors, a Keithley switch control system 3706A-SNFP was assisted. For comparison, the curing process of the same resin used above was test using DSC (Q-100, TA Instruments) by monitoring heat flow of the resin isothermally controlled at 25 °C or 60 °C.

3. Results and Discussions

3.1 Structural Characterization of Varied CNM based Fiber Sensors

Figure 2. Comparison of SEM images of CNT-FSs (a-c), rGO-FSs (d-f) and CFSs (g-i) at varied magnifications for examining the packing structure of nanoparticles on the fiber roving.

As described in the Experiment section, different types of fiber sensors, including CNT-FS and rGO-FS were successfully fabricated through the continuous winding and coating process. The optical photograph of a pristine fiberglass roving, a fiber roving coated by graphene oxide (GO) particles, and the graphene fiber sensor after the reduction process is shown in Figure 1(a). Comparing to the ivory white color of the bare glass fiber bundle, the as-coated GO fiber roving appears shiny grey. After 20 min reduction treatment with hydroiodic acid, the as-produced graphene fiber sensor (rGO-FS) shows a pitch black appearance. The CNT coated fiber sensor (CNT-FS) also shows a very dark appearance even without the intermediate reduction process. The clear change of colors as revealed in Figure 1(a) is a good indication of efficient coating process as well as the sufficient reduction process. It is believed that the capillary force formed by pores and micro-channels in the roving would drag, trap and coat nanoparticles onto surface of fibers\cite{23}. 


Following the roll-to-roll process, the fiber sensor was integrated in dry fabrics by braiding, as shown in Figure 1(b). It clearly demonstrates that the manual braiding won’t interrupt the configuration and density of fibers in the plain woven fabric. In addition to single fiber integration, the inset picture of Figure 1(b) further proves the scaled-up configuration of multiple sensors to form a 5×5 fiber sensor network for possible local mapping applications. The single and multiple fiber sensor configurations were also demonstrated either in the course of VARTM process or in the cured composite part, as shown in Figure 1(c). Owing to continuous and flexible sensor fabrication and deployment, we can certainly expect that, with the assistant of robotic machines such as 2D and 3D co-braiding equipment, this technique can be further scaled up for large-scale manufacturing of smart composite structures with customized sensor configurations.

In addition to visual inspection, morphology and microstructure of representative CNT-FS, rGO-FS and CFS specimens were systematically examined and compared by SEM imaging. Figure 2(a) to 2(c) unveils the microstructure of CNT-FSs under different magnifications. The low magnified images (2a and 2b) confirm the uniform CNT coating by observing the nanoparticle arrested throughout the surface of fiber cores. Additionally, the high magnified image (2c) restores the detailed packing structure of CNT network, in which the rope-like nanotubes were twisted and entangled to form a porous network. The pore size of the CNT network was visually estimated in the range from several tens to several hundred nanometers. This typical spaghetti-like structure of CNT thin coating can also be found on a large-area 2D or 3D substrate.[24,25]. Similar to CNT-FSs, the graphene coating of rGO-FSs is also uniform and conformal as shown in Figure 2(d) – 2(f). Especially in Figure 2(e), it clearly shows the ultra-thin and flexible nature of graphene flake/sheet with large lateral dimension that is able to completely cover and wrap the fiber surface with obvious ripple and wrinkle texture. The similar structure also can be seen elsewhere in a common rGO thin film[26,27]. Comparing to CNT-FS and rGO-FS with stacking of nanoparticles on fiber surface, the CFS itself is the graphitized structure which is continuously and densely packed by a random arrangement of flat or crumpled graphitic sheets with invisible voids[28], as shown in Figure 2(g) – 2(i). In general, the CNT network is relatively loose-packed compared with the flake-wrapping structure of rGO and the continuous structure of carbon fiber.

![Figure 3](image)

**Figure 3.** Comparison of (a) Raman and (b) EDX spectrum of CNT-FSs, rGO-FSs and CFSs under various fabrication stages, including the neat fiber stage, the as-coated stage and the post-treatment stage.

To further examine the structure of various fiber sensors under different fabrication stages, Raman and energy-dispersive X-ray (EDX) spectroscopy measurements have been performed. In Figure 3(a), comparing to the featureless spectrum of neat glass fibers, the signature Raman features – D-band around 1360 cm⁻¹, G-band around 1590 cm⁻¹, and the two-component 2D-
band around 2650 cm\(^{-1}\) have been identified to confirm the CNT or graphitic structures existed in CNT-FSs, GO coated fibers (GO-F), rGO-FSs and CFSs. As an indication of graphene production by reducing GO, the clear increase (from 0.27 to 0.58) in the intensity ratio of the 2D to G peak \((I_{2D}/I_G)\) strongly suggests the restoration of sp\(^2\) carbon in rGO\(^{29}\). Due to the high percentage of sp\(^3\) carbon in GO, the reduction process was further proved by increase (from 1.13 to 1.28) of the intensity ratio of the D to G peak \((I_D/I_G)\), relating to the quantity of structural defects\(^{30}\). In addition to Raman inspection, the EDX spectra (Figure 3b) clearly show the substantial increase of the normalized carbon atoms from 12.21 wt.% (Neat-GF) to 30.88 wt.% (CNT-FS), 28.22 wt.% (rGO-FS) and 22.39 wt.% (GO-F), indicating the successful coating of nanoparticles. Again, the increased ratio of the carbon to oxygen peak from 0.49 (GO-F) to 0.75 (rGO-FS) confirms the effective removing of oxygen-containing groups.

### 3.2 Sensing Performance of Varied CNM based Fiber Sensors

Figure 4. Comparison of the real-time resistance change of CNT-FS, rGO-FS and CFS for \textit{in situ} monitoring the (a) overall, (b) infusion stage, (c) equilibrium stage, and (d) curing stage of composites manufacturing.

To reveal the valuable insights of \textit{in situ} process monitoring of composites and explore the underlying structure-property relationship, the sensing performance of varied CNM based fiber sensors were systematically evaluated and compared. As the VARTM process started, the real-time resistance change \((dR/R_0)\) of each fiber sensor was continually measured until the end of resin curing under ambient temperature around 25 ºC. By collecting the electrical signal data
under the vendor suggested 24 h for complete VARTM process, Figure 4(a) compares the time dependent resistance change ($dR/R_0$) of CNT-FS, rGO-FS and CFS. The electrical resistance of CNT-FS throughout the process shows the highest variation, which is about 2 orders of magnitude higher than rGO-FS and about 3 orders of magnitude higher than CFS.

To systematically analyze the data, we divided the complete molding process into three stages: 1) Infusion stage (0 – 0.5 h) for resin injection until filling the pre-vacuumed bag; 2) Equilibrium stage (0.5 – 1 h) for the low viscous resin staying in the bag before gelation; 3) Curing stage (1 – 24 h) for polymer cross-linking reaction after gelation. Figure 4(b) first shows the sensor performance in the infusion stage. In addition to different absolute change of $dR/R_0$ in CNT-FS (0 – 1641.8 %), rGO-FS (0 – 38.7 %) and CFS (0 – 7.9 %), the trend of $dR/R_0$ in this stage shows high degree of similarity, in which a swift increase (0 – 0.1 h) of $dR/R_0$ was followed by a milder increase (0.1 – 0.3 h) to gradually approach to stabilization (0.3 – 0.5 h).

Combined with previous works for studying electrical properties of CNMs upon resin infiltration\cite{17,19}, we strongly believe the simultaneous inter- and intra-roving flow of the resin competes with each other to dominate the observed phenomenon. For the first 0.1 h, the resin was quickly introduced into the vacuumed bag to wet the roving surface and fill the voids of the woven fabric. During this period, resin molecules would also penetrate and expand the conducting network of CNMs to alter their original structural configurations such as to increase the tunneling distance and even break the particle/particle contacts. Thus, the initial resistance increased with high ramping rate. After filling majority of the voids existed inter rovings, the resin would continuously infiltrate intra rovings with a much lowered impregnation speed because of the micro- or nanoscaled intra-roving space\cite{14}. As a result, the conducting network of CNMs was further interrupted by observing a milder increase of resistance.

Following the infusion stage, Figure 4(c) shows the electrical behavior of various sensors in the equilibrium stage. It can be seen that the value of $dR/R_0$ from 0.5 to 1 h for all types of sensors kept almost constant after it reached the maximum in infusion stage. This clearly confirms the end of resin flow so the sensor and the surrounding resin were basically staying in an equilibrium state. Although the viscoelastic property of resin was actually changing in this stage, the low viscous and low cross-linked structure of resin would not further interrupt the configuration of the sensing network.

Right after the infusion stage, the resistance of sensors started to decrease enormously, which can be seen in Figure 4(d). Confirmed by the identical upturn moment of damping factor acquired by dynamic mechanical analysis (DMA), Lu’s recent work argued that the moment that the resistance of CNT paper starts decaying is related to gelation time\cite{19}. Based on this significant discovery, we further attribute the complete decaying behavior of CNM sensors to the physical/chemical changes in cross-linking reaction as well as the development of matrix shrinkage caused by phase transformation of gelation and vitrification. To specify, drastic increases of viscosity and volumetric shrinkage were concomitantly happening after gelation of resin with high levels of cross-linking density\cite{31}. Consequently, the inflated sensing network with infiltrated resin would shrink constantly to cause conductive particles and paths closing together with improved electron transport. Accordingly, the $dR/R_0$ was respectively decaying in CNT-FS (from 1594.8 % to 517.8 %), rGO-FS (from 36.36 % to 27.38 %) and CFS (from 7.43 % to 3.99 %) after 4 hours of gelation. As slowing down of curing for the rest of the process, it is thus straightforward to expect a gentle decay of $dR/R_0$ from 5 h to 24 h. Figure 4(d) indeed shows the intended electrical behavior in CNT-FS (from 517.8 % to 399.5 %) and CFS (from 3.99 % to 3.23 %). For rGO-FS, nevertheless, an interesting increase of $dR/R_0$ has been observed from 27.38 % to 34.18 %. With the rationale of graphene with ultrathin and flexible nature, we believe the shrink effect of resin cross-linking would generate certain levels of internal stress to introduce reorientation and bending of the fiber roving as well as the stacked graphene nanosheets. As a result, fissures and ruptures may be introduced in the graphene network to degrade its electrical property.
3.3 Structure Dependent Sensing Mechanism of Varied CNM based Fiber Sensors

Recapitulated from previous sections, the three different types of fiber sensors possess extremely similar sensing behavior for monitoring resin infusion and curing. However, the sensing sensitivity, i.e. the level of electrical resistance change varies substantially. Based on comparative study of microstructure and performance, we are confident about the existence of an underlying structure-property relationship in fiber sensors assembled by different CNM strategies. For one thing, the structure of conducting network is formed by packing of particles or fibers, so they are all subjected to dynamic structural inflation and shrinkage as resin infusion and curing. For another thing, the micro- and nano-scaled structural properties, such as particle dimension, pore size distribution, packing density and coating thickness are vastly different. This will inevitably result in different degrees of resin infiltration to interrupt the conducting network. To elucidate this idea, Figure 5 shows the schematics to illustrate the structure dependent sensing mechanism(s). For CNT-FS, it is naturally easy for resin molecules to migrate into the conducting network due to the comparatively loose-packed structure of CNTs with big pores. Thus, the achieved sensitivity is the highest. For rGO-FS, because of the large lateral dimension of graphene sheets which is comparable (or larger) to diameter of a single glass fiber, its network structure is almost poreless. As a result, only a small portion of resin molecules can penetrate into the fissure-like gap between the overlapped nano-flakes to cause a much weaker inflation effect. For CFS, its graphitic structure is continuous and densely-packed with negligible voids, so resin molecules could hardly penetrate inside a single fiber but could affect inter-fiber contacts. Due to the continuous length of carbon fibers with high structural integrity, nevertheless, the variation of inter-fiber contacts hardly contributes on the overall resistance change. Thus, its sensitivity is reasonably the lowest.

![Figure 5](image)

Figure 5. Schematic diagrams of different packing structures and/or conducting networks of CNT-FS (top), rGO-FS (middle) and CFS (bottom) under different processing stages of composites.

4. Conclusions

In summary, three representative CNMs, i.e. CNT, rGO and CF have been selected and compared to assemble the embeddable fiber sensors for in situ monitoring and evaluating the health states of composites during the whole manufacturing process. With varied microstructure and sensing performance, the integrated CNM sensors are capable of monitoring different stages of VARTM, including resin infusion, gelation and curing, which is highly valuable and critical for quality assurance of the host composites. Systematically studied through SEM, Raman and EDX, detailed morphology and packing structure of varied sensor assemblies have been
revealed for understanding the substantial difference in sensing performance. Comparing to CF and rGO with continuous and densely packed graphitic structure, we believe the loosely packed CNT network with comparatively large pore size is the major contribution for the markedly enhanced sensitivity. The multipurpose sensing capabilities in conjunction with their unique scalability and noninvasiveness make CNM fiber sensors highly valuable for next-generation smart composites with life-long self-sensing capabilities.

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References


