ORNL/TM-2022/2353

Oak Ridge National Laboratory CRADA Final Report Self-Sensing Fiber Reinforced Composite

CRADA No. NFE2008069

Christopher Bowland

DECEMBER 2021

ORNL/TM-2022/2353

Chemical Sciences Division

CRADA FINAL REPORT
SELF-SENSING FIBER REINFORCED COMPOSITE
(CRADA) NO. NFE2008069

Christopher Bowland

December 2021

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831-6283
managed by
UT-BATTELLE LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

LIST OF FIGURES

1.1 ABSTRACT

The project aimed to demonstrate a scalable coating process to adhere nanoparticles to the surface of fibers and fabricate composites with in-situ damage detection abilities and simultaneous mechanical performance enhancements. Carbon fiber (CF) composites have the inherent problem of hiding damage within the structure with no visual indications on the surface. Therefore, a technique to monitor for damage or excessive stress on the composite is necessary to ensure its safety and avoid catastrophic failure. This capability will be desired in future transportation vehicle designs, such as in cargo and surveillance drones developed by Dronesat, LLC, (Dronesat) who was the industrial partner on this project.

Prior work showed that silicon carbide nanoparticles embedded in a thin polymer layer on the surface of CF can result in multifunctional composites that have increased mechanical performance and enhanced self-sensing behavior [1]. Specifically, the composite's interlaminar shear strength was improved, which demonstrates better adhesion between the fiber layers. This fiber-to-fiber adhesion is typically the weak property of fiber-reinforced composites and is the mechanism for composites to fail catastrophically. The nanoparticles also enhanced the electrical resistance change of the bulk composite structure when subjected to applied stress, thus giving it better structural health monitoring capabilities. The nanoparticle deposition technique utilizes a continuous feed-through process that is compatible with existing commercial CF processing lines, thus enabling potential commercial deployment. This prior work resulted in a patent-pending fiber-coating technology titled, "Carbon Fiber-Nanoparticle Composites with Electromechanical Properties" (non-provisional patent application number 16/280,268). Within this project, the prior work was leveraged to extend the fiber coating process to another material system (i.e., titanium dioxide [TiO_2] nanoparticles on CF) to create composites with embedded active sensing abilities.

1.2 STATEMENT OF OBJECTIVES

This research work aimed to demonstrate self-sensing CF composites that can be deployed in transportation vehicles using a patent-pending process developed at Oak Ridge National Laboratory (ORNL). The embedded nanoparticles result in multi-functionalities that increase mechanical performance and enhance self-sensing behavior through electrical resistance change of the bulk composite structure when subjected to applied stress, thus giving it better structural health monitoring capabilities. The specific objectives include homogeneously coating CF with nanoparticles using a continuous processing method, improving mechanical performance through interlaminar shear strength characterization, and enhancing sensing capabilities by utilizing nanoparticles with piezoresistive behavior.

The main objective of this CRADA is to demonstrate a high-throughput nanoparticle deposition process to make fibers for multifunctional composites on size scales that are applicable in transportation vehicles, from unmanned drones to cars and trucks. These fibers will be used to fabricate fiber reinforced drone components that also serve as strain sensors to monitor the structural health of the aircraft.

Task 1 Coating, fabrication and design

ORNL will coat carbon fiber with silicon carbide nanoparticles using a continuous feed-through dip coating process. ORNL will use filament winding to fabricate unidirectional composites for short beam shear testing to characterize the interlaminar shear strength of the composites. Dronesat will design the drone components to be fabricated in later tasks using the nanoparticle coated fibers.

Task 2 Electrical system design and evaluation

ORNL will evaluate the change in electrical resistance during flexing and throughout a short beam shear test to monitor composite damage. Dronesat will design the electrical system for the drone for placement of the sensing composites throughout the structure.

Task 3 Prototype components

ORNL and Dronesat will fabricate prototype components (designed by Dronesat) via filament winding to demonstrate marketable, self-sensing composites.

Task 4 Final report

Completion of CRADA Final Report.

1.3 BENEFITS TO THE FUNDING DOE OFFICE'S MISSION

This work demonstrated multifunctional composites that could enhance the strength of composites and create integrated sensing capabilities. The enhanced strength helps achieve DOE's vehicle light weighting objective while the integrated sensing helps further progress the development and implementation of smart structures into infrastructure.

Dronesat offered its drone system as a testbed to demonstrate the application of multifunctional composites in real world scenarios This drone system is capable of round-the-clock surveillance that could provide an option for safe-guarding national assets. This system was also designed as a transportation vehicle that could significantly reduce the carbon emissions involved with traditional transportation networks.

1.4 TECHNICAL DISCUSSION OF WORK PERFORMED BY ALL PARTIES

1.4.1 Summary of ORNL Research Results

To achieve the project objectives, nanoparticles were coated on CF using a continuous feed-through process to be able to generate a sufficient length of fiber to fabricate into composites. This process consists of a two-step coating process. The bare CF was first submerged into an aqueous suspension of TiO_2 nanoparticles with subsequent drying. These coated fibers were then dipped in a second coating bath with a commercially sourced aqueous epoxy sizing emulsion. Sizing is a typical coating that is applied to CF in industrial settings. This polymer layer is 100–200 nm and serves multiple functions. It enhances the adhesion between the fiber and the matrix, protects the fiber surface during composite fabrication, and aids in handling of the fibers. This project aimed to utilize the sizing layer as a carrier matrix for nanoparticles in that the sizing helped bond the nanoparticles to the fiber surface. The goal of the nanoparticles was to enhance the mechanical interlocking at the composite interphase to increase the interlaminar shear strength, as well as increase the piezoresistive response of the composites. This piezoresistive response was quantified by measuring the electrical resistance of composite beams during repeated strain cycles.

The dip-coating procedure was successful in homogeneously dispersing TiO_2 nanoparticles on the surface of a CF tow and subsequently coating it with sizing as shown in Figure 1(a-e). This process allowed the concentration of TiO_2 nanoparticles to be easily modified by changing the concentration of nanoparticles in the coating bath. The fibers and composites in the figures are designated by the concentration of nanoparticles in the solution bath (i.e., the "1-wt%" fibers were dip coated through a water bath with 1-wt% nanoparticles). Fibers were dip coated with 0.1 to 4-wt% nanoparticle mixtures. Using these various fibers, unidirectional composites were fabricated using a filament winding technique followed by compression molding during epoxy curing. The resulting composites were short beam shear tested to quantify the interlaminar shear strength as summarized in Figure 2(a). For most composites, the nanoparticles enhanced the interlaminar shear strength with the most significant improvements in the 0.5 to 1.5 wt% composites as shown in Figure 2(b). Overall, the best performing sample was the 1-wt% composites, which was 14.7% stronger than the composites with no nanoparticles.

To characterize the structural health monitoring capabilities of the composites, the unidirectional composites were electroded in an out-of-plane through-thickness configuration, as observed in Figure 3(a) and placed in a dynamic mechanical analyzer using a single cantilever clamp. The composites were subjected to cyclic strain loading and unloading at different strain magnitudes, as shown in Figure 3(b), while capturing the change in electrical resistance, as shown in Figure 3(c). An overlay of the strain input and resulting electrical resistance change can be seen in Figure 3(d).

At least 10 strain cycles were repeated for each strain level and the corresponding electrical resistance change was averaged over the 10 cycles to create the plot in Figure 4(a), which shows the average electrical resistance change at each strain level for every composite. To quantify the structural health monitoring sensitivity, the gauge factor for each composite was calculated by dividing the relative electrical resistance change by the strain. The average gauge factor for each composite is shown in Figure 4(b), where a larger value represents a

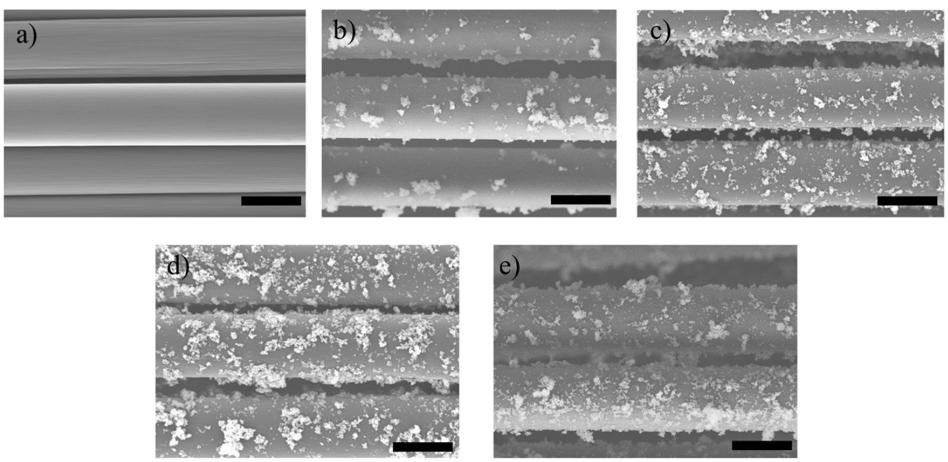

Figure 1. Scanning electron microscope images of TiO_2 on CF after a dip coating process with mixtures containing: (a) 0 wt%; (b) 1 wt%; (c) 2 wt%; (d) 3 wt%; and (e) 4 wt% TiO_2 nanoparticles. All scale bars are 5 µm. [2]

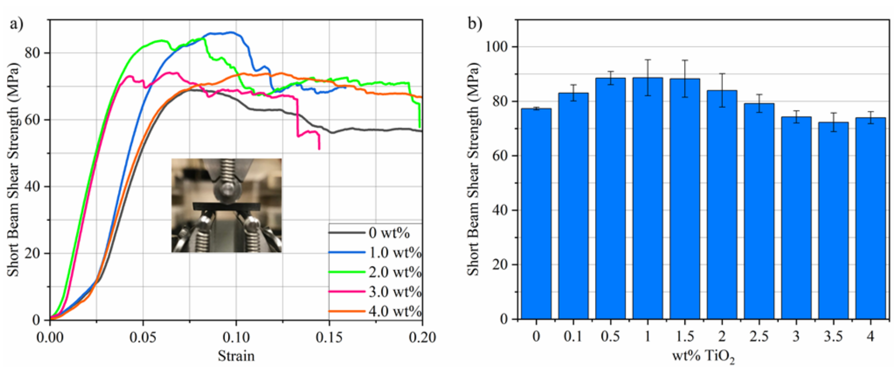

Figure 2. Results of the interlaminar shear strength testing showing (a) the representative strength vs. strain curves and (b) the average strength values versus the nanoparticle concentration in the coating mixture. The error bars signify one standard deviation. [2]

better performing composite. This showed that the composites with 1–3 wt% nanoparticles exhibited enhanced structural health monitoring sensitivity. The best performing sample in terms of gauge factor was the 2.5 wt% composite with a gauge factor of 7.14, which equates to 186% increase in sensitivity as compared to the composites without nanoparticles.

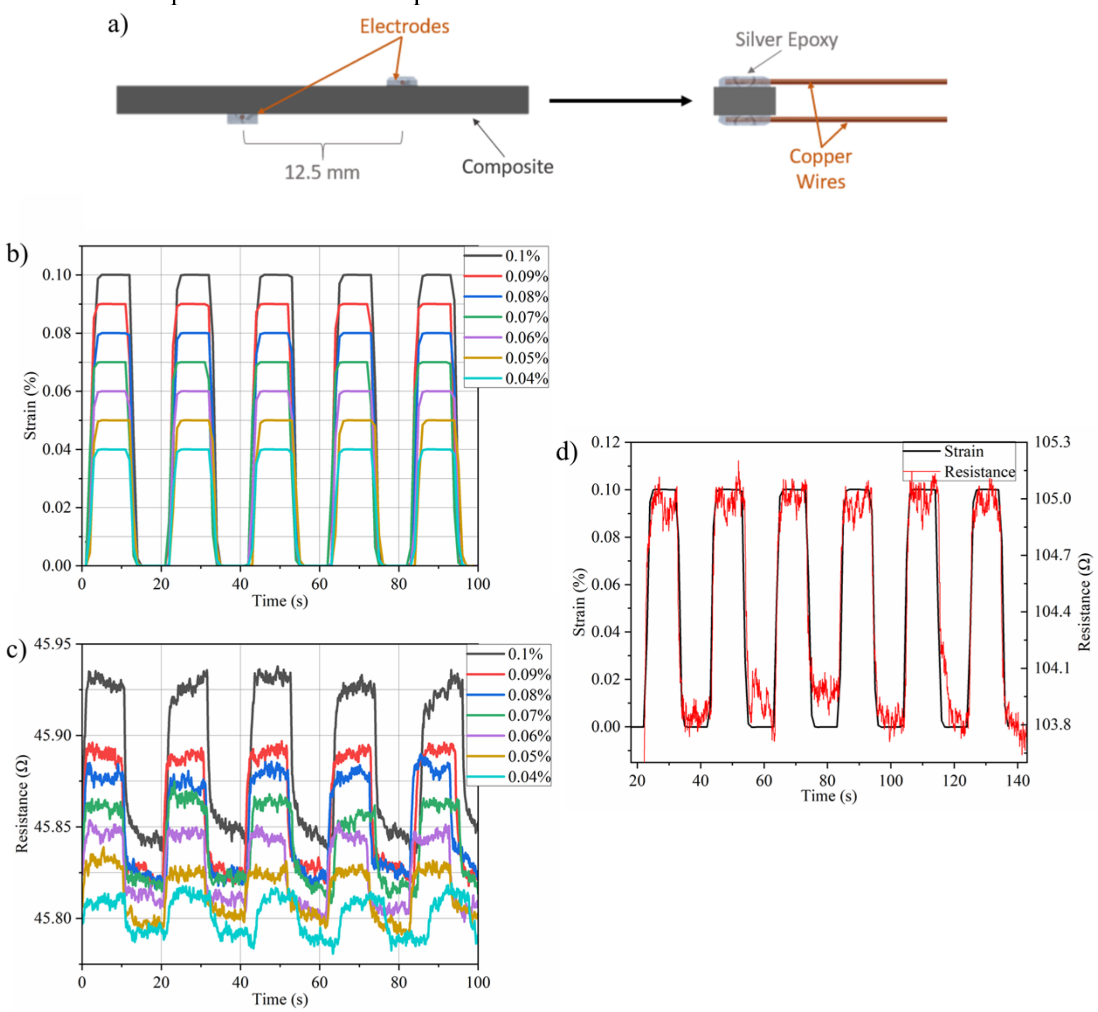

Figure 3. (a) Electroded sample schematic in which the carbon fibers run in the x-direction and the thickness is in the y-direction. (b) An overlay of the different strains placed on the composite beam. (c) Representative curves of the electrical resistance in response to the different strain cycles. (d) Overlap of a representative input strain and the electrical resistance response [2].

The overall performance of the composites is summarized in Figure 5, which plots both the interlaminar shear strength and gauge factor for each composite. The targeted area of the plot is the highlighted upper-right quadrant, which represents improvements in both mechanical and sensing performance as compared to the composites with no nanoparticles. As shown in Figure 5, the composites with 1–2.5 wt% nanoparticles saw enhancements in both properties. The best performing sample was the 1 wt% composite with improvements of 14.7% and 172% in interlaminar shear strength and gauge factor, respectively, as compared to the composites with no nanoparticles.

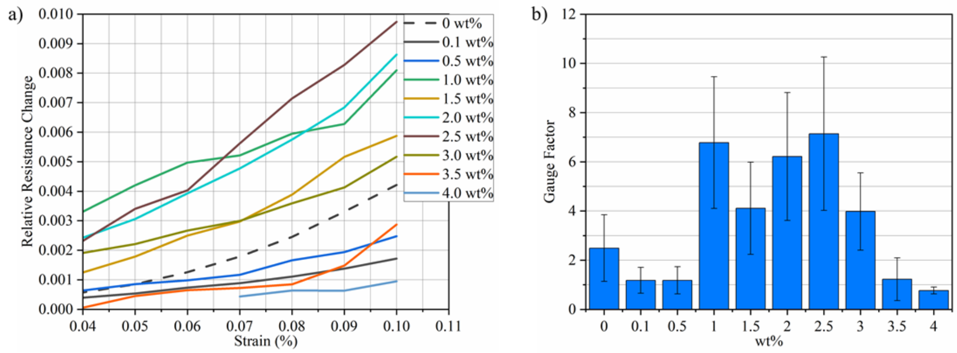

Figure 4. (a) Relative resistance change versus percent strain. (b) Gauge factor for each composite averaged over all the strain levels tested. Error bars signify one standard deviation. [2]

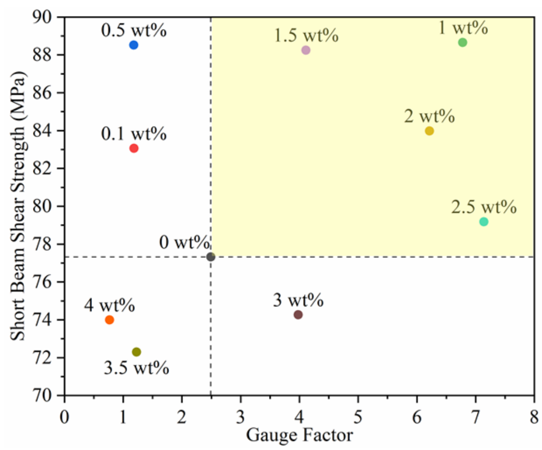

Figure 5. Plot of the different composites showing the average interlaminar shear strength versus the average gauge factor. The dashed lines show the values for the composite without nanoparticles with the highlighted region signifying simultaneous improvements in both properties [2].

As an extension of the dip coating process, barium titanate ($BaTiO_3$) particles were coated on basalt fibers. A unidirectional composite was fabricated with tows of $BaTiO_3$ coated basalt sandwiched between layers of bare carbon fiber tows and embedded in an epoxy matrix. The use of two different fibers within the same composite classifies this as a hybrid composite. Placing the basalt in the middle of the composite created a hybrid composite that was not electrically conductive through its thickness, thus enabling a passive sensor to be demonstrated. An electrically insulating composite is required to allow charge accumulation between the electrodes during excitation. For testing, the two carbon fiber layers were electroded with silver epoxy, as shown in the schematic in Figure 6(a). For the proof-of-concept of the power generation, a composite beam was clamped on one end and manually flexed by hand at the free end, Figure 6 (b). The resulting voltage generated during flexing was captured using a digital multimeter. Figure 6 (c) shows the voltage generated from different excitation events. It is seen that the composite has baseline noise vibration from the environment when not flexed, but when flexed at various magnitudes and frequencies, a corresponding voltage is generated. The zoomed-in plot in Figure 6(c) highlights the voltage generated during the excitation events. This final task of the project demonstrated that a passive sensing composite could be synthesized using the dip coating method developed throughout the project.

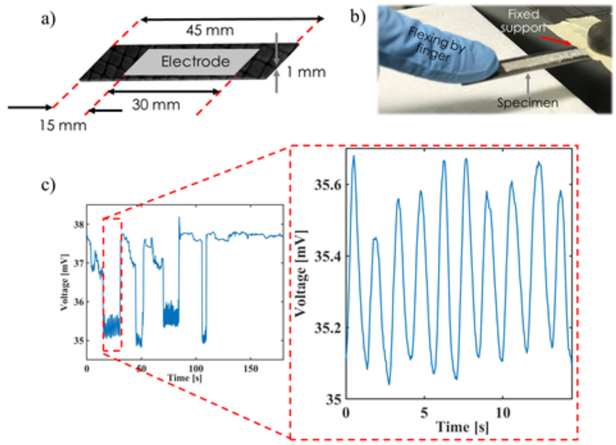

Figure 6. a) Schematic of the hybrid multifunctional composite. b) Picture of the flexing test method with c) the corresponding voltage output from the composite.

1.4.2 Summary of Dronesat, LLC Results

Dronesat has developed a tethered drone system for prolonged flight times for drones. To improve drone safety, Dronesat is wanting to integrate sensing composites into their drones to detect damage before catastrophic failure. They need this collaborative effort with ORNL to help integrate multifunctional composites into their structures, and Dronesat offers its drone system as a testbed to demonstrate the application of multifunctional composites in real world scenarios.

Working with Dronesat, this project also involved the design and initial fabrication of self-sensing composite components for a prototype drone. Dronesat has developed a tethered drone system for prolonged flight times. To improve drone safety, Dronesat wants to integrate sensing composites into their drones to detect damage before catastrophic failure. The ultimate result would reduce maintenance time by early detection of cracks or damage, thus mitigating costly effects of unexpected failures, which could result in vehicle loss. Materials that could detect damage and provide timely information about critical components—in particular, ducted fan blades, disks, open rotors, ducts, propellers, airframe, control surfaces, horizontal and vertical stabilizers, and wings—would be highly desirable for product safety. Dronesat collaborated with ORNL on this project to help integrate multifunctional composites into their structures, and Dronesat offered its drone system as a testbed to demonstrate the application of multifunctional composites in real-world scenarios. Dronesat has one of the most unique power infrastructure concepts for a drone in development that is positioning it to become a highly sought-after drone manufacturer. Safety is one of the biggest challenges in this type of drone market, so Dronesat partnered with ORNL to integrate sensors that could solve some of the safety challenges. To meet these safety challenges, ORNL has further developed the nanoparticle coating process within this project to achieve improved mechanical and sensing performance.

Dronesat designed the prototype components that could be made from the developed nanoparticle-enhanced composites. Figure 7 shows one example of many parts that were designed by Dronesat. The example here shows the fan blade assembly with different viewpoints. The critical part of this assembly would be the point at which the blade is attached to the base. This attachment point is the most prone to failure, so it was targeted as an ideal location to place the sensing composites. These nanoparticle-enhanced composites would both enable sensing of this joint and offer increased strength to reduce composite failure. The implementation of these composites in the drone prototypes is Dronesat's ongoing work. Dronesat designed other components within its patent pending drone system and developed testing fixtures to evaluate the self-sensing composites in different failure modes. The additional images of the components and test fixtures have been withheld from this report due to its proprietary nature.

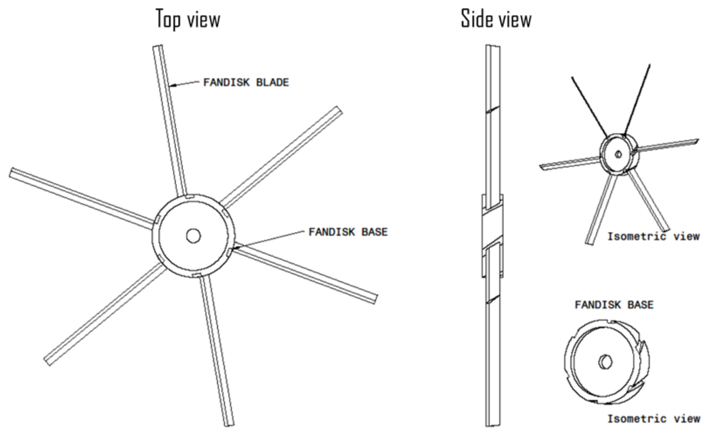

Figure 7. Schematic design of the fan blade assembly prototype where the multifunctional composites will be integrated.

1.5 SUBJECT INVENTIONS

This work involved the use of patent-pending fiber-coating technology titled, "Carbon Fiber-Nanoparticle Composites with Electromechanical Properties" (non-provisional patent application number 16/280,268).

1.6 COMMERCIALIZATION POSSIBILITIES

Dronesat is actively pursuing further funding for deployment of their drone system with the integrated sensing capabilities developed within this project. Commercialization is dependent on securing follow-on funds to build the full-scale system.

1.7 PLANS FOR FUTURE COLLABORATION

A collaboration between ORNL, Dronesat and the University of Arkansas for follow-on research are in the planning stages. Funding opportunities as a Technology Commercialization Fund Topic 2 project or SBIR projects are in the process of being put together to secure funding for more collaborative efforts.

1.8 CONCLUSIONS

This project demonstrated that the continuous fiber dip-coating process developed at ORNL could be used to homogeneously disperse TiO_2 nanoparticles on CF to produce multifunctional composites. The interlaminar shear strength was selected as the metric for mechanical performance. Most of the composites showed increased strength, and the highest performing composite was the 1 wt% nanoparticle composite, which showed a 14.7% increase. The structural health monitoring capabilities were evaluated by measuring the piezoresistive behavior of the composites and calculating the gauge factor for each composite. It was shown that composites with 1–3 wt% nanoparticles exhibited increased gauge factor with the highest performing sample being the 2.5 wt% composite, which had a 186% improvement. In comparing the performance of all the composites based on these two properties, the 1 wt% composite performed the best overall with 14.7% and 172% improvements in interlaminar shear strength and structural health monitoring sensitivity, respectively. The final tasks of the project showed that the dip coating process could be used with basalt fiber and $BaTiO_3$ microparticles to create a passive sensing hybrid composite. Therefore, this project produced CF coated with TiO_2 nanoparticles as well as basalt fibers coated with $BaTiO_3$ microparticles using a continuous feed-through dip-coating process that significantly enhanced the multifunctional performance of the composites and demonstrated both active and passive sensing composites.

REFERENCES

1. Bowland, C. C., N. A. Nguyen, and A. K. Naskar, 2018, "Roll-to-roll processing of silicon carbide nanoparticle deposited carbon fiber for multifunctional composites," ACS Applied Materials & Interfaces, 10, 26576-26585.
2. Rankin, S. M., M. K. Moody, A. K. Naskar, and C. C. Bowland, 2021, "Enhancing functionalities in carbon fiber composites by titanium dioxide nanoparticles," Composites Science and Technology, 201, 108491.