

# Advanced manufacturing process for producing nanofiber yarns

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## ABSTRACT

AxNano, LLC, in collaboration with the Joint School of Nanoscience and Nanoengineering of North Carolina A&T State University, has developed a novel method for producing robust, high-volume, cost-effective carbon fibers in support of next-generation materials for structural composites. The advanced, high-throughput process yields yarns of bundled nanofibers and is designed to achieve greater structural perfection needed for leaps in mechanical strength and stability of carbon fibers. This project supports future innovative nanomaterial-based polymeric composites that have the potential to supplant conventional carbon fiber reinforced polymeric (CFRP) composites with applications in commercial space travel, air travel/cargo, and passenger vehicles/ground shipping industries.

Keywords: carbon fiber, nanofiber, yarns, advanced manufacturing

## 1 INTRODUCTION

### 1.1 Carbon Fiber Technology

Carbon fibers are long, thin strands of mostly carbon atoms oriented in a manner that results in a low density material (1.75-2.00 g/cm<sup>3</sup>) with impressively high strength (tensile strength of 3-7 GPa and modulus of 200-500 GPa).[2] Carbon fibers also exhibit excellent tolerance to extreme temperatures, chemical resistance and low thermal expansion. These unique properties have inspired the use of carbon fibers and carbon fiber-based composites in aerospace, defense, industrial and consumer industries.[3] The combined lightweight, high strength, and superior stiffness have made carbon fibers especially ideal for structural composites. For example, carbon fiber reinforced polymeric (CFRP) composites have been identified by

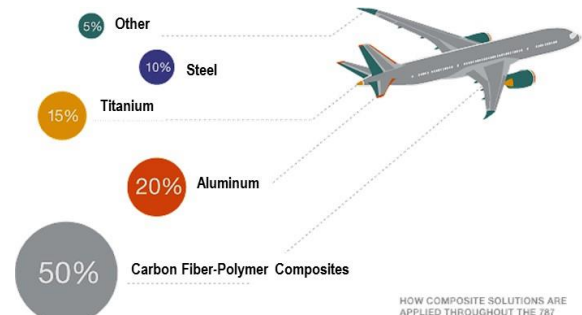


Figure 1. Boeing 787 is composed of 50% carbon fiber reinforce polymer composites.[1]

NASA as the material of choice for launch vehicles and spacecraft due to their high strength-to-weight ratio giving additional performance, reduced cost, and increased payload capacity of launch vehicles.[4] The private sector is also taking advantage of these advanced materials. For example, the Boeing 787 is composed of 50% CFRP (Figure 1), and Boeing cites another great advantage of using CFRP is significantly reduced maintenance requirements due to reduced risk of corrosion and fatigue compared to metal-based components.[1]

Carbon fibers are produced by first forming precursor fibers (typically from poly(acrylonitrile) (PAN)) that are then stabilized and carbonized by high temperature treatment. When scientists and engineers first produced carbon fibers over six decades ago, the tensile strength of carbon fibers (T300<sup>®</sup>) quickly reached 3 GPa. The strongest carbon fiber produced today (T1000<sup>®</sup>) has a tensile strength of ~7 GPa, still far below the theoretical tensile strength of 180 GPa. Extensive research indicates that the diameter, structural perfection, crystalline structure, and morphological and structural homogeneity of the precursor fibers are the most crucial factors impacting the strength of carbon fibers.[5] The “Size Effect” suggests that decreasing the diameter of the precursor fibers reduces structural imperfections and aligns graphitic crystallites yielding stronger carbon

fibers.[6] However, current commercial spinning techniques are inherently restricted to producing precursor fibers with diameters less than 5  $\mu\text{m}$ . As a result, significant research and development efforts have been focused on new spinning methods to produce fibers in sub-micron to nanometer range in hopes of producing higher strength carbon fibers.

## 1.2 Conventional Precursor Fiber Spinning Methods

Wet spinning and air gap spinning are the two most commonly used methods for producing PAN precursor fibers. In both methods, the spin dope (i.e., polymer solution) is extruded through a spinneret to produce filaments that are dispensed into a coagulation bath. In the coagulation bath, the filaments are dispersed in a non-solvent resulting in the formation of the solid PAN precursor fibers. In wet spinning, the spinneret is immersed in the coagulation bath. In air gap spinning, the spinneret is positioned a few millimeters above the coagulation bath. The placement of the spinneret allows for control over solvent diffusion and rate of fiber formation. The orifices in the spinneret will govern the diameter of the resulting fibers, and the size restrictions in their engineering limits the diameters of fibers produced by these methods to above 5  $\mu\text{m}$ .

## 2 TECHNOLOGY DESCRIPTION

AxNano, LLC has developed a novel polymer spinning technology that allows for the production of continuous nanoscale precursor fibers that are formed in weavable yarns. The method allows for precise control over precursor fiber diameters while still producing robust and high-volume carbon fibers in support of next-generation materials for structural composites. The ability to achieve nanoscale fiber precursors should improve the alignment and crystallinity of the resulting carbon fibers. As a result, significant improvements in mechanical strength and stability compared to current carbon fibers are possible. The technology is tunable and is compatible with a wide variety of polymer matrices. Moreover, the system is adaptable to allow the inclusion of additional nano-based moieties. To date, we have produced continuous polyacrylonitrile (PAN)-based carbon nanofiber yarns up to 50 feet in length, shown in Figure 2. These new CNFs are expected to exhibit reduced defects, increased uniformity, and much

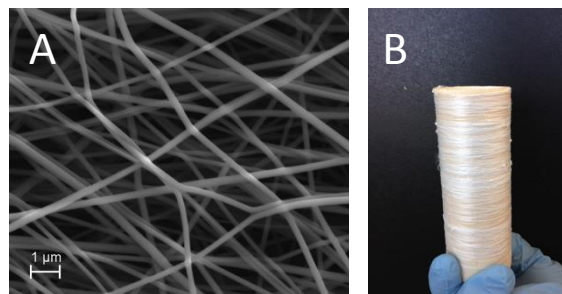


Figure 2. (A) Carbon fibers produced using AxNano technology have nanoscale morphologies and (B) are processed in a manner that can be spun into yarns.

higher strength than traditionally produced carbon fibers. This project supports future innovative nanomaterial-based polymeric composites that have the potential to supplant conventional carbon fiber reinforced polymeric (CFRP) composites as lightweight structural materials for aerospace and transportation applications.

## 3 EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 Optimization of polymer spin dope

We have repeatedly tested and altered the makeup of the PAN spin dope in order to find the optimum concentration for our novel spinning technology. Specifically we have found that the concentration of PAN regulates the integrity of our nanofibers by influencing (1) nanofiber formation; (2) nanofiber size; and (3) nanofiber strength. Lower PAN concentrations result in less uniform fiber formation, smaller fiber size and lower fiber strength. Higher

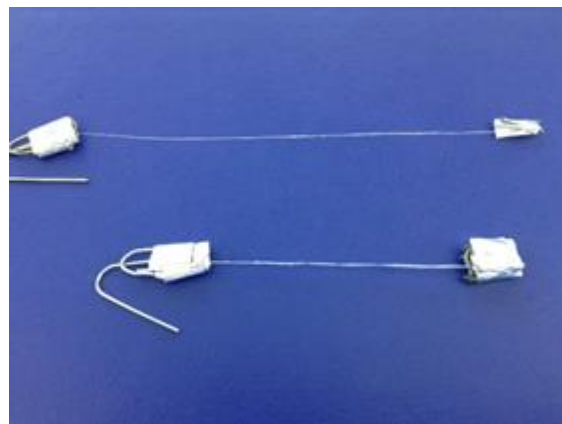


Figure 3. Stretched PAN nanofiber yarn vs as-collected PAN nanofiber yarn

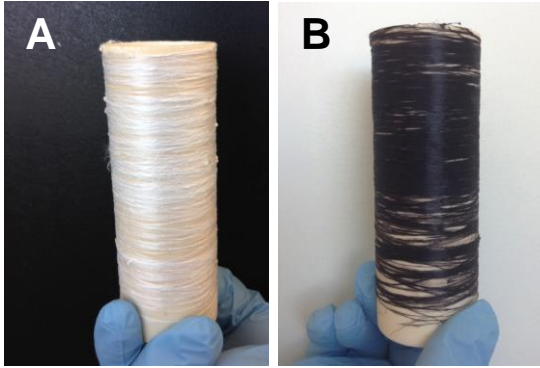


Figure 4. Spools of (A) precursor nanofiber yarns and (B) carbon nanofiber yarns after stabilization and carbonization.

PAN concentration in the spin dope results in more uniform fibers, thicker fibers and higher fiber strength. However, the latter is much more viscous and adversely affects processing. After multiple trials, the conclusion is 13% PAN (wt. %) brings the optimum balance of fiber size, strength, and post-processing.

### 3.2 Optimization of precursor fiber drawing method

The method by which the spun fiber precursor is drawn will directly affect the strength of the resulting carbon nanofiber. Drawing pulls the molecular chains within the fibers and orients them

along fiber axis, creating considerably stronger fibers. Inspired by conventional carbon fiber processing methods, our PAN nanofiber yarns were drawn through a series of steps at specific temperatures and humidity levels. As expected, the stretched PAN nanofiber yarns become longer and thinner compared to the as-collected fibers (Figure 3).

### 3.3 Fiber stabilization and carbonization

The conventional carbon fiber industry has developed optimized stabilization and carbonization conditions. A common procedure involves heating as-spun PAN fibers to approximately 300 °C in air, which breaks many of the hydrogen bonds, oxidizes, and cyclizes the material. The oxidized PAN is then placed into a furnace with an inert atmosphere of a gas such as argon, and heated to over 900 °C, which removes all elements other than carbon. We have employed these widely used methods with some modifications to stabilize and carbonize the nanofiber yarns produced from our advanced process. The resulting black carbon fibers are shown in Figure 4B.

### 3.4 Mechanical strength testing

Maximum load testing of as-spun, stretched, stabilized and carbonized single PAN nanofiber yarns was performed on an Instron testing machine located at the Material Testing Center of Gateway University

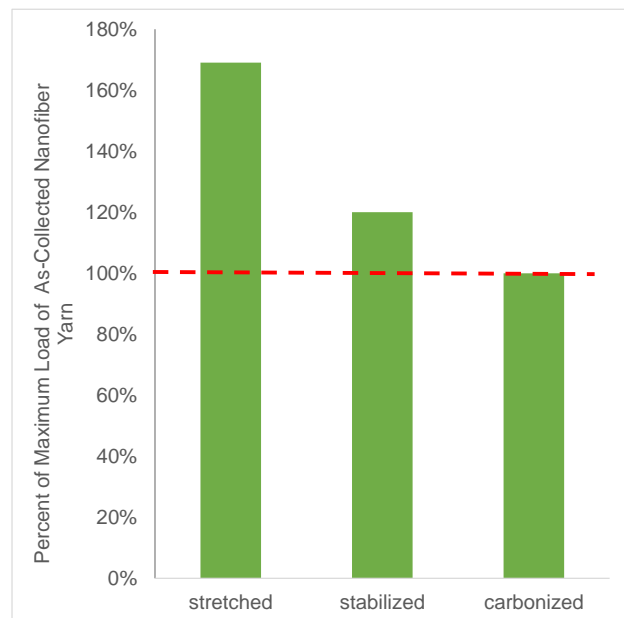
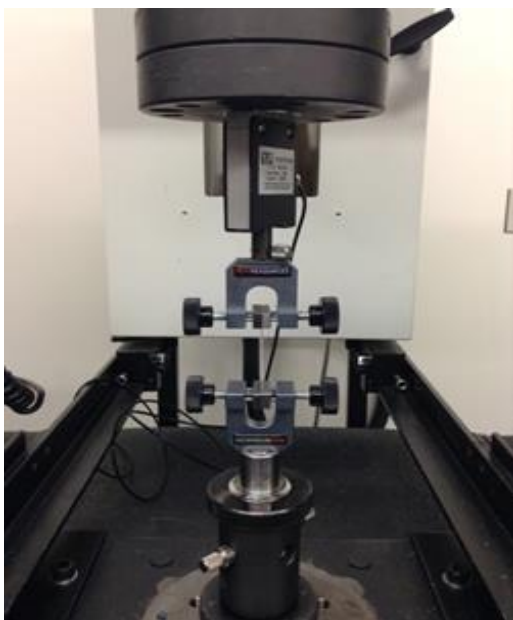


Figure 5. Strength testing of PAN nanofiber yarns on Instron testing machine (A) and effect of post-processing on strength of nanofiber yarns compared to as-collected (red-line).

Research Park with a 10 N load cell (accuracy 0.00001N) according to ASTM D3822 (Figure 5A).

Changes in the maximum load of the PAN nanofiber yarns following stretching, stabilization and carbonization compared to the as-spun yarns are shown in Figure 5B. After stretching, the maximum load increased by 68.6%. Stabilization reduced the maximum load by 28.8% compared to stretched PAN nanofiber yarns, but was still at a 20% increase compared to as-spun nanofiber yarns. Carbonization further reduced the maximum load by another 21.4% compared to stabilized PAN nanofiber yarns. There was not a statistically significant difference between the maximum load of the as-spun and the final carbonized nanofiber yarns. Current work is focused on measuring nanofiber cross-sectional areas in order to calculate tensile strength and compare to commercially available PAN-based carbon fibers.

The results of mechanical testing did show significant improvement on mechanical strength after stretching. The carbonized PAN nanofiber yarns exhibited comparable maximum load to as-spun PAN nanofiber yarns. This is due to two reasons: first, the nanofiber yarns shrunk significantly in size after carbonization, and secondly, the spin dope was composed of pure PAN, which is not a widely adopted carbon precursor for high strength carbon fibers. A copolymer of PAN with itaconic acid, methyl methacrylate, and others is normally employed for this purpose. Future work will investigate copolymer PAN precursors to improve the final carbon nanofiber yarn strength.

## 4 CONCLUSIONS

We have developed an advanced manufacturing method to produce continuous yarns of carbon nanofibers. Our novel method allows for control of fiber precursor on the nanoscale. We have investigated polymer dope concentration, drawing method, and stabilization and carbonization parameters of PAN-based carbon nanofibers using our method. The ability to create carbon fibers with nano scale diameters is expected to yield fiber strengths superior to those achieved with traditional carbon fibers that are restricted to diameters above 5  $\mu\text{m}$ . P-processing (i.e., stretching, stabilization and carbonization) the nanofiber yarns had direct effects on maximum load. Tensile strength calculations are underway as we design methods to measure nanofiber yarn cross-sectional area. Initial strength testing

indicates that copolymer precursors may be necessary to achieve superior strength. Future works aim to modify the polymer dope components as well as post-spinning processing to increase fiber strength.

Upon achieving carbon nanofibers yarns with superior strength to current commercially available carbon fibers, we will create carbon nanofiber yarn reinforced polymer (CNYRP) composites for use in a wide range of markets. An improved lightweight CNYRP structure has multiple commercial applications where there is a cost associated with moving any type of good or person. Lowering the weight of the underlying device that is moving the object will result in a tremendous cost savings. Three specific markets where the technology presents the best opportunity are the 1) commercial space travel, 2) air travel/cargo, and 3) passenger vehicles/ground shipping industries. All represent multi-billion dollar markets individually. Ultimately, this advanced manufacturing program will meet current and future composites application needs for the aerospace, wind power, and transportation industries to reduce weight, drive down costs, and ultimately reduce end product environmental impact through lower emissions.

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