OAK RIDGE
NATIONAL LABORATORY

MANAGED BY UT-BATTELLE
FOR THE DEPARTMENT OF ENERGY

**NFE-10-02991**

**Materials Science & Technology**

# CRADA Final Report
# For
# CRADA Number
# NFE-10-02991

# Development and Commercialization of Alternative Carbon Precursors and Conversion Technologies

**Robert Norris, Felix Paulauskas, Amit Naskar, Michael Kaufman, Ken Yarborough**
**Oak Ridge National Laboratory**

**Chris Derstine**
**The Dow Chemical Company**

**Prepared by**
**Oak Ridge National Laboratory**
**Oak Ridge, TN 37831**
**managed by**
**UT-BATTELLE, LLC**
**For the**
**U.S. Department of Energy**
**Under contract DE-AC05-00OR22725**

**October 2013**

**Approved for**
**Public Release**

UT-BATTELLE

ORNL-27 (4-00)

**DOCUMENT AVAILABILITY**

Reports produced after January 1, 1996, are generally available free via the U.S. Department of Energy (DOE) Information Bridge.

***Web site*** http://www.osti.gov/bridge

Reports produced before January 1, 1996, may be purchased by members of the public from the following source.

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
***Telephone*** 703-605-6000 (1-800-553-6847)
***TDD*** 703-487-4639
***Fax*** 703-605-6900
***E-mail*** info@ntis.gov
***Web site*** http://www.ntis.gov/support/ordernowabout.htm

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and International Nuclear Information System (INIS) representatives from the following source.

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
***Telephone*** 865-576-8401
***Fax*** 865-576-5728
***E-mail*** reports@osti.gov
***Web site*** http://www.osti.gov/contact.html

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## CONTENTS

**LIST OF FIGURES** ..... **V**

**ACKNOWLEDGMENTS** ..... **VII**

**1. ABSTRACT** ..... **1**

**2. BACKGROUND** ..... **2**

**3. STATEMENT OF OBJECTIVES** ..... **4**

**4. BENEFITS TO THE FUNDING DOE OFFICE'S MISSION** ..... **6**

**5. TECHNICAL DISCUSSION OF WORK PERFORMED BY ALL PARTIES** ..... **8**

**5.1 Precursor Development** ..... **8**

**5.2 Scaleup and Enhancement of Advanced Conversion Processes** ..... **14**

**5.2.1 Processing Modeling as Supported via Dielectric Measurement System** ..... **14**

**5.3 Microwave-Assisted-Plasma (MAP) System Scaling** ..... **16**

**5.4 MAP Energy Balance** ..... **25**

**5.5 Alternative Process Investigations** ..... **26**

**6. SUBJECT INVENTIONS (AS DEFINED IN THE CRADA)** ..... **34**

**7. COMMERCIALIZATION POSSIBILITIES** ..... **36**

**8. PLANS FOR FUTURE COLLABORATION** ..... **38**

**9. CONCLUSIONS** ..... **40**

**LIST OF FIGURES**

Fig. 1 TGA thermogram of a crosslinked polymer precursor. It indicates requirement of secondary functionalization. ..... 9
Fig. 2 Stress-strain profiles of a functionalized polymer precursor. ..... 10
Fig. 3 Stress-strain profiles of a neat and stretched polymer precursor. ..... 10
Fig. 4 Thermomechanical thermograms of two different functionalized precursors ..... 11
Fig. 5 Thermomechanical thermograms of a functionalized precursor at different applied stress levels. ..... 12
Fig. 6 SEM images of fracture surfaces of fibers with the best tensile strength for a sample (process ID 110606T4) carbonized under low tension (a) and the same precursor sample (process ID 110616T1) carbonized under high tension (b). ..... 12
Fig. 7 ORNL diagnostic measurement cavity with associated heating system. ..... 15
Fig. 8 The loss tangents as a function of temperature of selected materials that are of interest in microwave processing of carbon fiber. ..... 15
Fig. 9 The current density shown inside the plasma column for two different values of plasma conductivity. ..... 16
Fig. 10 Maximum temperature of quartz tube and of gas at outlet vs. gas inlet pressure. ..... 17
Fig. 11 Commercial filter-trap installed on the MAP vacuum line. ..... 18
Fig. 12 Geometry of the tows within the vacuum tube. The red dotted circles are the extent of the old, smaller tube used for 3-tow experiments in 2011. The dashed circle prescribes the radius of the outermost tows prior to the 5-tow experiments. (a ..... 19
Fig. 13 Intra-tow tension differences in oxidized PAN feedstock. Part of the tow is under very little. 20
Fig. 14 Tow orientations within MAP applicator. (a) Orientation in pre-2012 multi-tow experiments. Heating is very uneven. (b) Attempted tow orientation in 3Q2012 campaign. (c) Tow orientation after applicator rotation for 5-tow experiment in early F. ..... 20
Fig. 15 (a) The MAP line after rotating the applicator. Microwave coupling is now from below. (b) The MAP line exit feed-throughs are shown fully strung with five tows in the horizontal configuration. ..... 20
Fig. 16 Time trace of 5-tow, 2+ hour milestone run. Shown are the forward and reflected power, the nominal maximum vacuum tube temperature, the outlet gas temperature, and the tube gas pressure. At t=17 minutes, the microwave generator tripped. ..... 21
Fig. 17 Mechanical properties from selected MAP runs. The orange, red and cyan points are from three 5-tow runs. Fiber properties in the shaded region meet or exceed programmatic targets. Large variance is due to single-filament mechanical testing. ..... 22
Fig. 18 Mechanical properties and relative positions of a single 5-tow MAP run for the horizontal configuration (left) and the “smiley-face” configuration (right). ..... 23
Fig. 19 Proposed multi-cavity MAP applicator. Each cavity should be nominally uncoupled from the others, unlike the plasma zones in the side-wall coupled applicator. ..... 24
Fig. 20 The new single-cavity MAP applicator. ..... 25
Fig. 21 A plasma test with a single tow in the v4 MAP applicator. ..... 25
Fig. 22 Energy and mass inputs and outputs for the MAP process. ..... 26
Fig. 23 Atmospheric pressure plasma torch operating with oxidized tow. ..... 27
Fig. 24 Temperature profiles with respect to the axial distance from the plasma torch nozzle. ..... 28
Fig. 25 Atmospheric pressure plasma torch operating with an oxidized tow under inert atmosphere. The copper coil at the upper center is a heat exchanger for the “bell jar” enclosure. ..... 29
Fig. 26 Heating a carbonized fiber via induction heating. ..... 30
Fig. 27 Atmospheric plasma carbonization experimental setup at ReMaxco. ..... 31
Fig. 28 Version 6 of the benchtop carbonization unit. ..... 32

Fig. 29 Samples of partially processed/vaporized OPF. ..... 32

## ACKNOWLEDGMENTS

Research sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office and co-funded by the Vehicle Technologies Program for the advanced carbonization portion, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

There is no proprietary data contained within this report.

## 1. ABSTRACT

The overall objective of the collaborative research performed by the Oak Ridge National Laboratory (ORNL) and the Dow Chemical Company under this Cooperative Research And Development Agreement (CRADA NFE-10-02991) was to develop and establish pathways to commercialize new carbon fiber precursor and conversion technology. This technology is to produce alternative polymer fiber precursor formulations as well as scaled energy-efficient advanced conversion technology to enable continuous mode conversion to obtain carbonized fibers that are technically and economically viable in industrial markets such as transportation, wind energy, infrastructure and oil drilling applications. There have been efforts in the past to produce a low cost carbon fiber. These attempts have to be interpreted against the backdrop of the market needs at the time, which were strictly military aircraft and high-end aerospace components. In fact, manufacturing costs have been reduced from those days to current practice, where both process optimization and volume production have enabled carbon fiber to become available at prices below $20/lb. However, the requirements of the lucrative aerospace market limits further price reductions from current practice. This approach is different because specific industrial applications are targeted, most specifically wind turbine blade and light vehicle transportation, where aircraft grade carbon fiber is not required. As a result, researchers are free to adjust both manufacturing process and precursor chemistry to meet the relaxed physical specifications at a lower cost. This report documents the approach and findings of this cooperative research in alternative precursors and advanced conversion for production of cost-effective carbon fiber for energy missions. Due to export control, proprietary restrictions, and CRADA protected data considerations, specific design details and processing parameters are not included in this report.

## 2. BACKGROUND

ORNL is a world leader in the development of new materials and processes for the manufacture of carbon fibers. For close to a decade, ORNL has been developing alternative precursors, advanced conversion processes, and other technology aimed at reducing the cost of commercial grade carbon fibers. Alternative precursors under development by ORNL with US Department of Energy (DOE) sponsorship include textile grade polyacrylonitrile-based fibers, lignin-based precursor fibers, and polyolefin-based precursor fibers. ORNL possesses world-class expertise and unique physical resources for carbon fiber research and development.

The Dow Chemical Company is the world's largest manufacturer of polyolefin resin, and a world leader in chemistry, materials science, engineering and manufacturing excellence. For example, Dow Chemical Company's ASPUN™ and ENGAGE™ polyolefin fibers are commercially available and used today in a range of products, but existing forms are not appropriate for use as carbon fiber precursors. Development of new, value-added products targeting low cost carbon fiber manufacture from polymers designed with the cost and performance requirements of carbon fiber in mind will generate additional, sustainable revenue for the Company.

Dow Chemical Company objectives were to accelerate ongoing developmental efforts to achieve commercialization within five years. This will require a dramatically accelerated research, development, demonstration, and deployment program. This CRADA addresses the accelerated research with detailed fundamental understanding, development, and demonstration of advanced conversion processes and polyolefin-based carbon fiber precursor production.

Polyolefin fibers, such as polyethylene and polypropylene can easily be melt-spun. Dow Chemical Company utilized both Michigan Center of Energy Excellence (COEE) and in-kind contributions to invest in polymer precursor development, including building out fiber spinning capability in Michigan. Plans were to initiate this program with an open consideration to all types of polyolefinic fiber formulations and spinning techniques that are available to allow for the development of a wider class of low-cost polymer precursor fiber. Then, after selecting a preferred family of material chemistries, the CRADA participants down-selected to the most cost-effective means of preparing the precursor fiber and converting the precursor into carbon fiber.

Conventional conversion employs a thermal pyrolysis process that is slow, energy intensive, and space intensive. This advanced conversion portion of this project is based upon a discovery by the principal investigator that microwave energy could likely be used as a means to rapidly convert polyacrylonitrile (PAN) precursor fibers into finished carbon fibers while potentially reducing energy usage substantially. Early in the project, the researchers determined that the best approach was to use a combination of single-frequency microwaves and plasma, or microwave-assisted plasma (MAP), to carbonize and graphitize oxidized PAN fibers. MAP processing feasibility was demonstrated in a batch reactor. Continuous operation was then demonstrated in a low-speed single-tow reactor, which was subsequently scaled to achieve high-speed single-tow operation, and finally three-tow operation. The researchers demonstrated a significantly reduced residence for the advanced process versus the conventional baseline.

Federal funding for this integrated project addressing alternative precursors and advanced conversion was provided by the U.S. Department of Energy's Advanced Manufacturing Office and Vehicle Technologies program and activities executed via this collaboration agreement. ORNL and Dow agreed to work together to accelerate development and commercialization of low-cost polymer-based carbon fiber precursors and advanced conversion processes. This work built on the foundation and substantial efforts of ORNL staff that had been funded through the U.S. DOE Vehicle Technologies program.

## 3. STATEMENT OF OBJECTIVES

The production cost of commercial grade carbon fiber is about equally split between raw materials and the conversion process; therefore it is necessary to attack both materials and conversion costs to meet the cost targets specified by US DOE. The specific objectives for this work include:

1. Develop polyolefin precursors
    a. Commercial polyolefins and blends
    b. Molecularly designed polyolefin fiber (such as that based on polyethylene or polypropylene) that can be crosslinked prior to carbonization
2. Demonstrate accelerated crosslinking route(s) for chemically functionalized precursor fibers
3. Obtain carbonized fiber from the inert precursors by applying optimal conventional and advanced conversion parameters
4. Characterize the carbon fiber and show that the mechanical properties are satisfactory for future product development in composite industries
5. Scale-up efforts will leverage the pilot line currently under development in the laboratories of the Contractor
6. Evaluate materials, sealing, and atmospheric pressure solutions
7. Estimate energy requirement for various scales
8. Determine preferred microwave/plasma parameters and profiles
9. Scale to ≥ five large tows
10. Determine long-term, continuous operability
11. Develop design specifications to facilitate scale-up of this approach for implementation in the ORNL Demonstration Facility

At the conclusion of this CRADA, objectives were for the team to have identified and demonstrated one or more formulations for an alternative carbon fiber precursor and the spinning and conversion protocols necessary to manufacture a carbon fiber that meets mechanical property and economic targets identified as adequate for production scale up. The team will also have developed equipment and process knowledge adequate to produce specifications for the scale-up of an advanced carbonization process for demonstration in the ORNL Carbon Fiber Demonstration Facility. These accomplishments represent a significant step in the commercialization process bridging a large portion of the gap between bench-scale research and pre-production-scale demonstration.

## 4. BENEFITS TO THE FUNDING DOE OFFICE'S MISSION

The U.S. Department of Energy funds the research, development, and demonstration of highly efficient and innovative manufacturing technologies. The Advanced Manufacturing Office (AMO) partners with industry, small business, universities, and other stakeholders to identify and invest in emerging technologies with the potential to create high-quality U.S. manufacturing jobs, enhance global competitiveness, and reduce energy use by encouraging a culture of continuous improvement in corporate energy management. The Vehicle Technologies Program develops and deploys efficient and environmentally friendly highway transportation technologies that will enable America to use less petroleum. These technologies will provide Americans with greater freedom of mobility and energy security, while lowering costs and reducing impacts on the environment. Both offices focus on R&D that has high impact, uses project diversity to spread risk, targets nationally important innovation at critical decision points, and contributes to quantifiable energy savings.

Carbon fiber manufacturing has been identified as a technology of strategic importance to the United States. In addition to aerospace and defense importance, it is generally conceded that carbon fiber composites have potential to make significant impact in energy missions such as vehicle lightweighting, enabling longer and more efficient wind turbine blades, enhanced structural capacity for offshore oil and gas exploration and production structures, etc. For example, studies have shown that for 10% structural weight reduction in automotive applications would typically provide a 5-7% improvement in gas mileage. However, cost of the carbon fiber itself has been a limiting factor for applications in these areas. In a cost analysis study conducted by Kline and Company, it has been shown that the carbon fiber cost to manufacture can be reduced toward $5 - 8/lb if low-cost precursors and advanced technology such as plasma oxidation and Microwave Assisted Plasma (MAP) carbonization routes are adopted.[2] The study also revealed that manufacturing process costs make up more than 50% of the total cost of commercially available carbon fibers. This is primarily due to the low carbon yield of the precursors (<50% of the mass of the precursor becomes carbon fiber). Prior work conducted by Hexcel researchers (2004) indicated 78% carbon yield from polyolefin precursor; therefore, about 50% increase in production rate could be expected if polyolefin-based precursors are considered for low-cost carbon fiber (LCCF) production.1 Work in advanced conversion has demonstrated a 2X improvement in residence time that would translate into smaller equipment per unit of production capacity with inherently less energy required in processing. In summary, there is a very high potential that LCCF can be economically produced from polyolefin precursors with advanced conversion techniques at a substantial cost reduction over other alternative precursor materials and utilizing conventional manufacturing processes.

In addition to the higher carbon yield, polyolefinic precursors offer significant advantage in that they are melt-spun versus requirement for PAN-based precursors to be solution spun. Melt spinning offers significant advantages in terms of overall throughput, much more favorable environmental conditions without need for solvent recovery and handling, smaller footprint without needs for solvent recovery space, and reduced energy consumption primarily due to the higher throughput and reduced solvent processing needs.

All of the above factors directly address portions of DOE mission goals. The alternative precursor and advanced conversion processes use energy more efficiently on a per unit mass basis. Environmental issues are mitigated. Most importantly the increased implementation of carbon fiber made possible through cost reduction enhances energy production and efficiency of energy utilization in application.

---

1 M. G. Abdallah, B. Hansen, G. Jacobsen, Low Cost Carbon Fiber (LCCF) Development Program, Phase-1 final submitted to U.S. DOE/OTT Automotive Lightweighting Materials Division (Contract Sponsor) via the Oak Ridge National Laboratory (Technical Administrator for DOE/OTT) (2004)

## 5. TECHNICAL DISCUSSION OF WORK PERFORMED BY ALL PARTIES

Although groundwork had been initiated in continuing discussions with our partners Dow Chemical Company and the Michigan Economic Development Corporation, actual funded work on this project began at ORNL in April of 2010. ORNL and Dow exchanged several visits and numerous teleconferences to define and refine specific approaches and metrics for materials of interest to this program. Based on previous ORNL work and studies conducted as part of this work, a better understanding was developed between Dow and ORNL on the underlying economics of material and process choices impacting portions of the technical approaches. This information and these discussions were utilized to develop a basic agreement on division of tasks and task responsibilities. Contracts personnel at both organizations were apprised of this general agreement and consulted as to the best mechanism or mechanisms for formalizing the agreement into the appropriate legal documentation. Although not required by either organization or funding agencies, it was determined that a Cooperative Research and Development Agreement (CRADA) was indeed the appropriate format for the formal agreement and the CRADA document was completed in October of 2010.

As has been the case for related work in carbon fiber development, ORNL has found an effective working arrangement to be establishment of a critical leadership core of permanent researchers with significant background and experience in this area (carbon fiber alternative precursor and advanced conversion development) to be augmented with postdoctoral researchers bringing specific skills to this project. Through detailed analysis of project requirements and extensive recruiting efforts, most of the defined needs for these postdoctoral researchers have been identified and these personnel are being relocated to ORNL to support this activity. Likewise, a need for rheology evaluation via extrusion was defined and equipment necessary for this work is being specified for near-term procurement. Effort is also underway to develop work plans for a subcontractor with extensive background and experience in the area of atmospheric plasma processing in carbon fiber oxidation to extend on-going collaboration with ORNL to work in the carbon fiber carbonization process.

Significant development and demonstration in precursor and advanced conversion process development represent a significant step in the commercialization process bridging a large portion of the gap between initial technology development and feasibility demonstration and the scale-up to pre-production volumes and operational time periods necessary to justify market entry. Activities and accomplishment in these areas are described as follows:

### 5.1 PRECURSOR DEVELOPMENT

Polyolefin fibers, such as polyethylene and polypropylene can easily be melt-spun. However, a wider variety of polymers and copolymers are capable of being solution-spun (wet-spinning), and may not be amenable to melt spinning. Any polymer that can be put into solution can, in principle, be prepared by solution-means into a fiber. Therefore, plans were to initiate this program with an open consideration to all types of fiber spinning that are available to allow for the development of a wider class of low-cost polymer precursor fiber. Then, after selecting a preferred family of material chemistries, the most cost-effective means of preparing the precursor fiber were to be down-selected. A protocol for screening polyolefin precursor composition suitable for carbon fiber research & development by the team was developed and processing parameters to obtain precursor fibers from selected compositions determined. Solutions for precursor fiber crosslinking were proposed and feasibility of specific candidates producing adequate material properties evaluated. As necessary, accelerated crosslinking route(s) for chemically functionalized precursor fibers were developed culminating in demonstrated production of carbonized fiber from cross-linked precursors following conventional and microwave-assisted plasma conversion processes.

A key objective of this work was to develop technologically designed fiber-forming precursor materials.

Parameters for the precursor screening metrics were identified during initial project work. Precursor screening parameters include melt-processability of the precursor resin (in terms of melt-flow index), crystallinity in filament, film, or bulk material, and ability to convert the precursor to thermally stable form. ORNL researchers worked with Dow to develop this selection procedure. Characterization of a different type of cross-linked precursor (common for high voltage cable insulation) was conducted. A representative TGA thermogram of the material is displayed in Fig. 1. The material appeared non-carbonizable. Chemical functionalization is necessary. Because of CRADA protection, details of various identified precursor candidates are not disclosed.

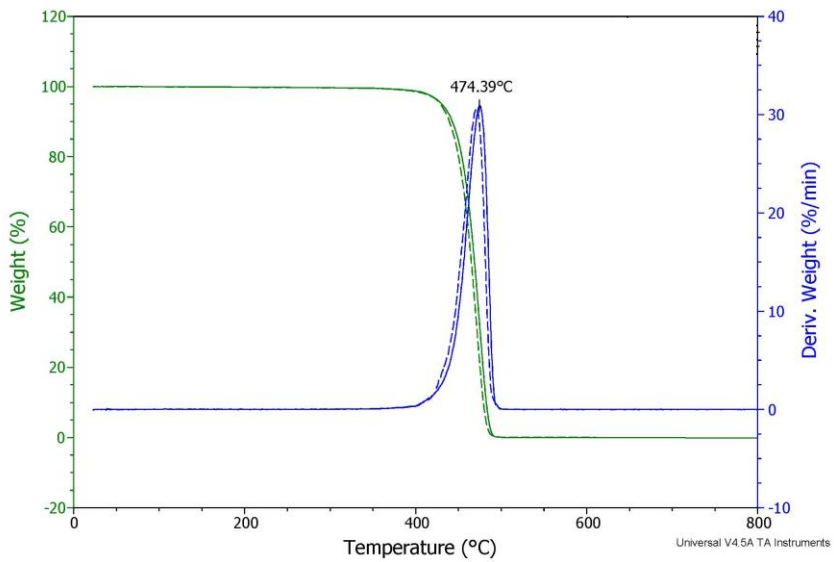


**Fig. 1 TGA thermogram of a crosslinked polymer precursor.** It indicates requirement of secondary functionalization.

Another key objective of this work was to find processing parameters for functionalized precursors. Precursor fibers at various degrees of functionalization were investigated and the thermo-mechanical properties of those fibers studied. A protocol for establishing fiber stress-strain profiles at various temperatures was developed to understand the role of functionalization and dimensional stability during the conversion process of these new types of precursors. Stress-strain profiles of representative functionalized and neat samples are shown in Figure 2. These data are important to establish the conversion (heat treatment and carbonization) protocol. With increase in temperature the modulus of functionalized fiber decreases but ultimate elongation is not significantly affected in comparison to neat fibers. This indicates that the functionalized fibers have higher tolerance to heat treatment compared to that of the neat fibers. Thus, this functionalization offered dimensional stability in the precursor and such stability is needed prior to carbonization.

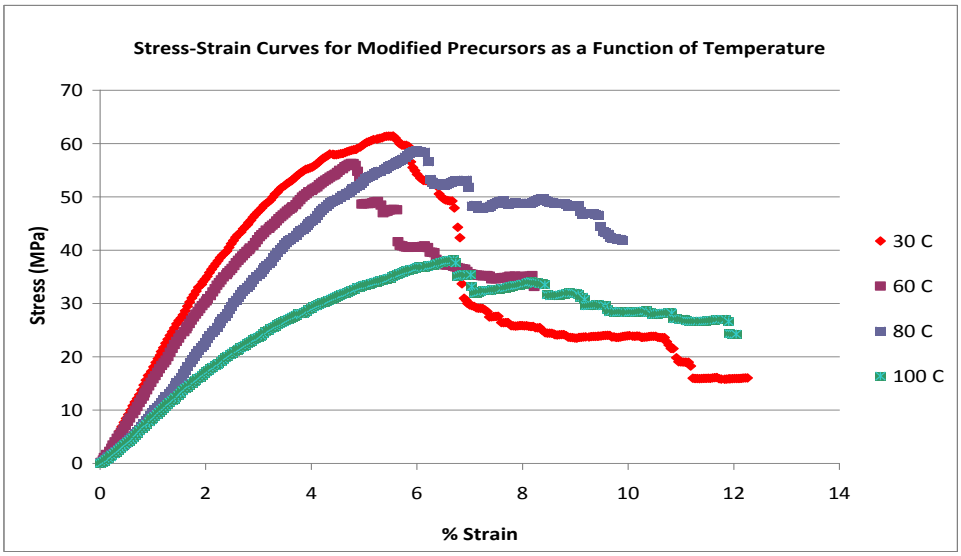


**Fig. 2 Stress-strain profiles of a functionalized polymer precursor.**

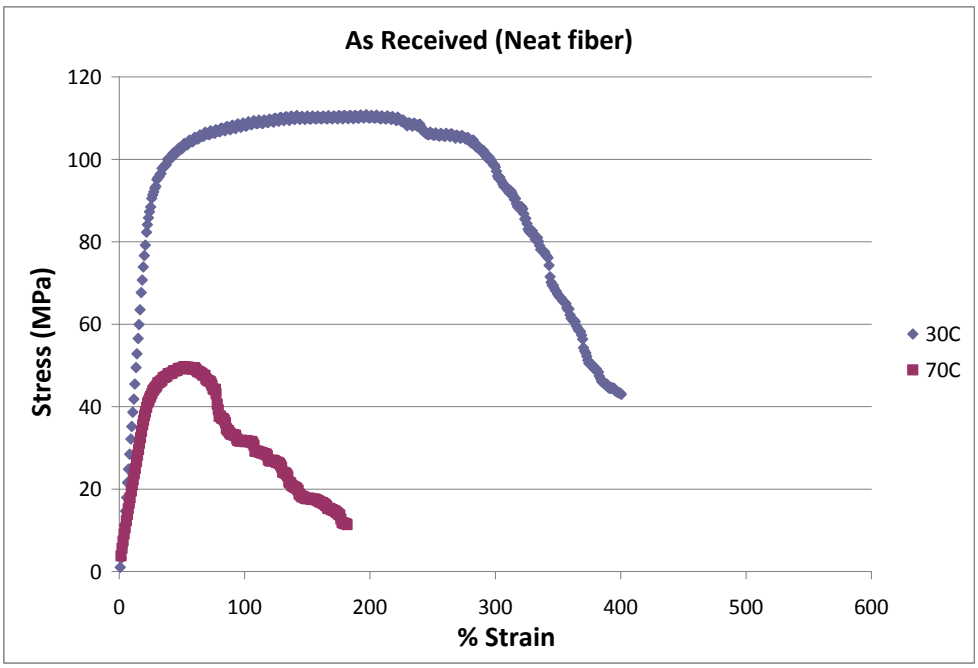


**Fig. 3 Stress-strain profiles of a neat and stretched polymer precursor.**

Originally, it was intended to initiate this program with an open consideration to all types of fiber spinning (solution and melt-spinning) that are available to us to allow for the development of a wider class of low-cost polymer precursor fiber. However, based on early results and availability of wide varieties of melt-processable precursor, it was decided to focus on melt-processable plastics unless unforeseen limitations downstream were uncovered. The criteria for screening these polyolefin precursors suitable for carbon fiber research & development has been set up based on initial conversion results from commercially available polyethylene fibers and tentative processing parameters to obtain precursor fibers from selected compositions determined.

Protocols for dynamic mechanical analysis of the fiber tow were established to understand the molecular dynamics of the neat polymer precursor and its chemically functionalized derivatives in fiber form. Similarly, protocols for thermo-mechanical analyses of a tow were developed to understand dimensional stability of the fibers before and after functionalization.

ORNL and Dow researchers selected various possible fiber forming linear polymers. Dow researchers produced fibers from 3 of those precursors. Protocol for characterization of the fiber tow was established earlier to understand the molecular dynamics of the neat polymer precursor and its chemically functionalized derivative in fiber form. Figure 4 shows thermo-mechanical thermograms of 2 different functionalized fibers showing differences in their shrinkage behavior at different temperatures. The shrinkage level at both low and high temperature regions of one sample is better than the other. Obviously, one is dimensionally more stable than the other one. This differential behavior is due to differences in degree of crosslinking, degree of crystallinity, and processing parameter (tension, time, etc.) during functionalization step. Therefore, it can be fairly assumed that the optimal processing parameters for different precursor candidates will be different.

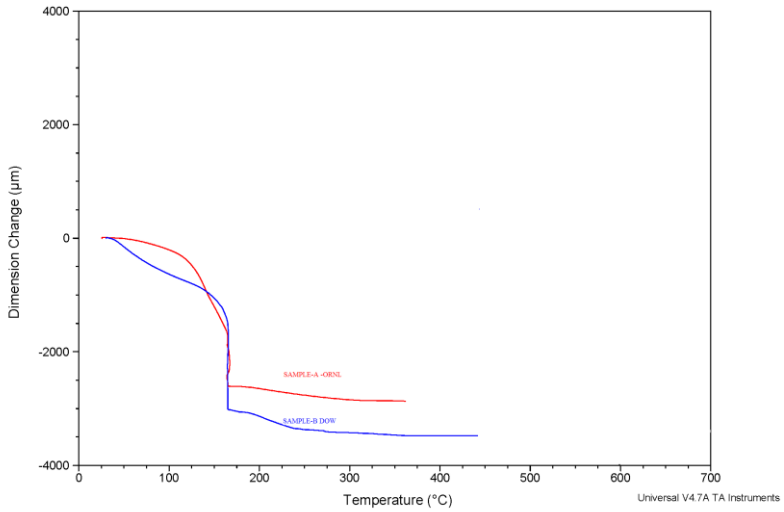


**Fig. 4 Thermomechanical thermograms of two different functionalized precursors**

Thermo-mechanical analysis was used to determine convertibility of treated precursor into carbonized form by applying certain tension and to identify processing parameters that enhance mechanical properties. Figure 5 shows that fiber shrinkage decreases with increasing applied stress during thermal treatment. However, very high shrinkage stress causes tow breakage. Fiber breaks during heat treatment step at <200 °C at high stress levels.

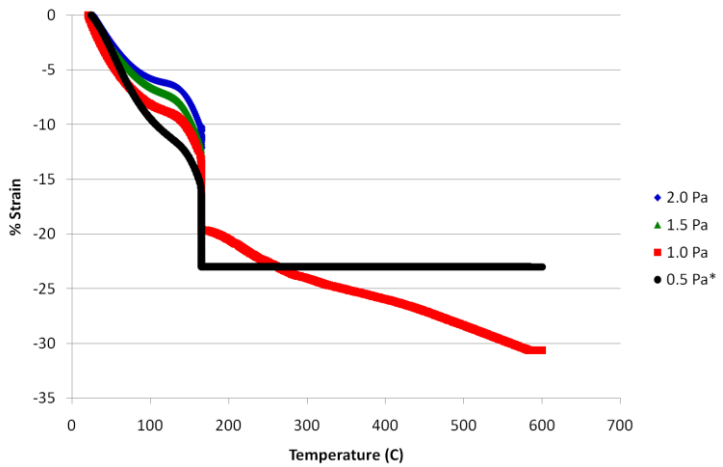


**Fig. 5 Thermomechanical thermograms of a functionalized precursor at different applied stress levels.**

Various characterization methods including thermal analysis tools, electron microscopy, and mechanical testing protocols were employed to identify better precursor fibers. Melt-spun fibers of 4 different precursors were obtained. Among those, two different polyolefin candidates were studied extensively and their optimal degrees of functionalization have been established. The lead precursor candidates exhibit > 60% carbon yield and demonstrate < 1 h processing time for the maximum possible degree of functionalization. Carbonized filaments from those precursors were also produced. Thus the baseline performance of the two precursors candidates was evaluated against the identified metrics.

Early on the research team found that with increase in the applied tension during carbonization the resulting carbon fiber's failed surface becomes rougher with multiple tear paths. At low tension during heat treatment the carbon fiber exhibits mostly smooth failure surface likely due to poor alignment of carbon microstructures along the fiber axis. Higher work of rupture as shown by multiple tear paths in Figure 6 below is evident for the sample carbonized at significantly higher tension. This confirms that tension during carbonization, which is well known in PAN-based carbon fiber processing, has the same effect in LLDPE-based carbon fiber.

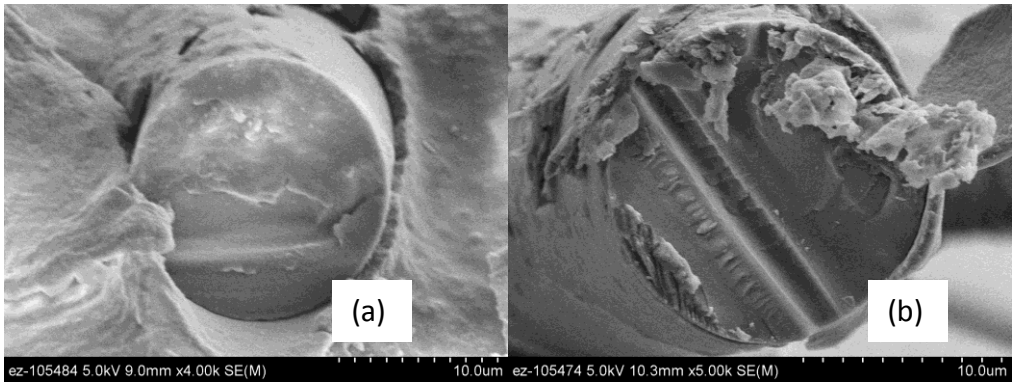


**Fig. 6 SEM images of fracture surfaces of fibers with the best tensile strength for a sample (process ID 110606T4) carbonized under low tension (a) and the same precursor sample (process ID 110616T1) carbonized under high tension (b).**

During the latter portion of 2011, a precursor tow free of fused filaments was sulfonated continuously and

carbonized at lower temperature under constant tension inside thermo-analysis equipment. This carbonized sample has a modulus of 10 Msi and a tensile strength of 155 ksi. The same sulfonated precursor was shipped to Dow and was carbonized to the maximum heat treatment temperature at that time, under suitable tension. This sample exhibited a modulus of 15 Msi and a tensile strength of 154 ksi as measured by Dow. To establish consistent tensile test protocols, a round-robin testing series was conducted by the team members utilizing standard (commercial) carbon fibers. The primary difference between the ORNL process and the Dow process at the time of this work was that Dow could only carbonize samples in a batch process under a moderate heating rate whereas ORNL's continuous carbonization process could provide a rapid heating rate (>100 °C/min). Although a slow heating rate yields higher modulus carbon fiber, it isn't economically feasible. Later on, work continued to achieve higher carbon fiber properties using conventional continuous, scalable carbonization processes. One approach was to vary the stabilization/sulfonation conditions so as to begin low-temperature carbonization during the sulfonation step. Although a similar protocol was used for testing in two different labs, more rigorous comparison of testing methods and data was done with appropriate samples as the project continued.

In a separate study, continuously-sulfonated precursor was heat treated to different temperatures to determine the effect of carbonization temperature on carbon fiber properties. In previous experiments, somewhat lower than expected carbon fiber properties were observed at an intermediate carbonization temperature whereas expectations were that properties would increase with increasing temperatures. It was hypothesized that the difference was mainly due to a change in furnace for higher temperature operation. In the continuous study, the high-temperature furnace was used with relatively wide temperature ranges. The result was more consistent improvement in properties with higher temperatures as evident in the data discussed below. These data were obtained on a precursor that was sulfonated and carbonized in a continuous manner at ORNL.

During the last quarter of FY2012, Dow provided precursor samples in short lengths (12 inch) as well as in spools (continuous tow of length > 2 m) for carbonization trials at ORNL. These samples were successfully converted and yielded targeted mechanical properties. Heat treatment at >1800°C was necessary to achieve the desired modulus. Temperature optimization was the next focus with the Dow precursor candidates. ORNL had previously achieved properties of 202 ksi tensile strength and 22 Msi modulus (at ORNL's maximum temperature process condition) with a polyolefinic precursor material produced using specialized spinning conditions not considered for focus in the CRADA due to scalability issues. These samples were shared with Dow researchers and they confirmed the properties. With multiple sets of Dow-stabilized samples, properties of 20 Msi (138 GPa) modulus and 200 ksi (1.38 GPa) tensile strength were achieved. Researchers demonstrated fibrillar morphology in stabilized fibers (which was key for mechanical property management) and that 5% elongation was achievable. Such morphology allowed tensioning during conversion.

Work continued to build in understanding how to improve and exploit these characteristics toward higher tensile strength for automotive and potentially other applications. Subsequently Dow continued development of their own precursor composition and process control parameters. In the first half of 2013, Dow prepared the next batches of sulfonated (crosslinked and pyrolyzable) samples and those were carbonized at lower temperature than the previous runs both at ORNL and at Dow's newly installed high temperature furnace. Depending on the processing history, samples exhibited tensile strength in the range of 145-350 ksi (1.0-2.4 GPa) and modulus in the range of 16-29 Msi (110-200 GPa). A couple of batches of samples show < 1.0% ultimate elongation and those are being correlated with the processing history of the fibers. Thus, while meeting a milestone for properties, a structure-property-processing relationship is being developed in order to better optimize properties versus economics of the process for the specific Dow formulations being utilized in the CRADA work. This completed one of the last major milestones for precursor development in the CRADA.

An alternative gas-phase sulfonation-based stabilization process for polyolefin fibers was proposed by ORNL and preliminary work initiated. This processing methodology was demonstrated to provide adequate stabilization of the fibers for the subsequent carbonization step. A 6" long tow of fibers was processed using this method that does not require a contact with liquid prior to washing with deionized water. Fibers exhibited >65% carbon yield when pyrolized at higher temperature in a thermogravimetric analyzer. Carbonization under tension had not been optimized at the conclusion of this work, as it required longer pre-processed tow than was available for key experiments. Although this work was discontinued before definitive results were obtained, a modified gas-phase reactor was designed and utilized for initial experimental work that did provide encouragement that the gas-phase approach is technically feasible for stabilization of polyolefinic precursors.

As the team was approaching the final property milestones established for CRADA completion, updated economic projections at Dow indicated that although cost benefits were expected, the projected level of the benefits was likely not sufficient to entice the large capital investment projected for commercial-scale implementation of the baseline sulfonation process utilized for much of this work. Although minimum programmatic property targets were achieved and the precursor development work was on schedule to meet final property milestones, alternative processing routes are desirable to mitigate investment risks. Therefore, the precursor development work was placed on hold pending resolution of Dow assessment of alternatives and plans forward in this area.

## 5.2 SCALEUP AND ENHANCEMENT OF ADVANCED CONVERSION PROCESSES

In previous work funded by the DOE Vehicle Technologies Program, ORNL researchers have carbonized a single 50k tow at 5 m/min, or < ½ of conventional residence time, and 3 x 50k tows at 1 m/min, or < 2 X conventional residence time. Currently, the system is not robust and cannot approach the required uptime. We propose to begin scaling and proving the MAP carbonization process. The principal tasks of this portion of the project are:

- Evaluate materials, sealing, and atmospheric pressure solutions;
- Estimate energy requirement for various scales;
- System modeling
- Determine preferred microwave/plasma parameters and profiles necessary to minimize residence time;
- Scale to ≥ five large tows;
- Determine long-term, continuous operability.
- Develop information necessary to produce a robust advanced technology carbonization unit to be built and operated in the ORNL Carbon Fiber Demonstration Line.

### 5.2.1 Processing Modeling as Supported via Dielectric Measurement System

A microwave cavity diagnostic for measuring dielectric properties has been constructed as shown in Figure 7 and has been utilized to provide key information on the sensitivity of the precursor to microwave exposure as a function of the exposure temperature and degree of conversion to carbon fiber. The process control software for this system is also a candidate for use as an in situ diagnostic on the MAP line. The associated heating system allows for precise control of fiber temperatures up to approximately 700C. The measurement of loss tangent with respect to temperature was also used along with the modeling information to evaluate a hybrid conversion approach. An example data plot is shown in Figure 8.

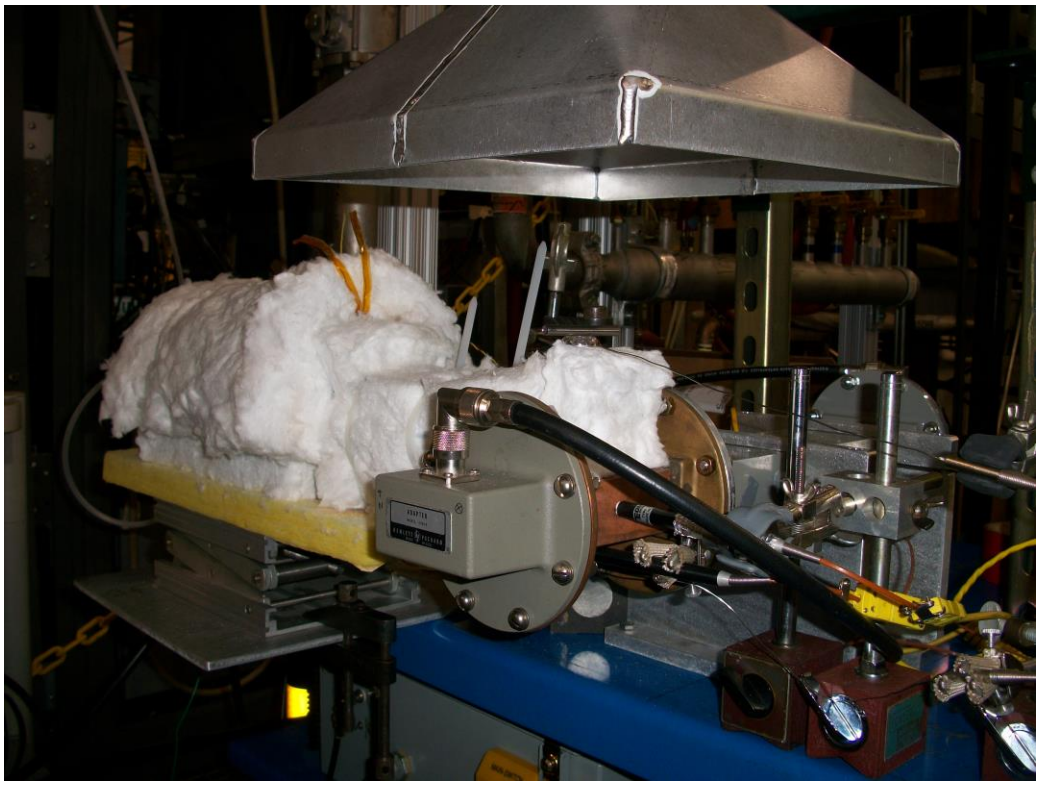

**Fig. 7 ORNL diagnostic measurement cavity with associated heating system.**

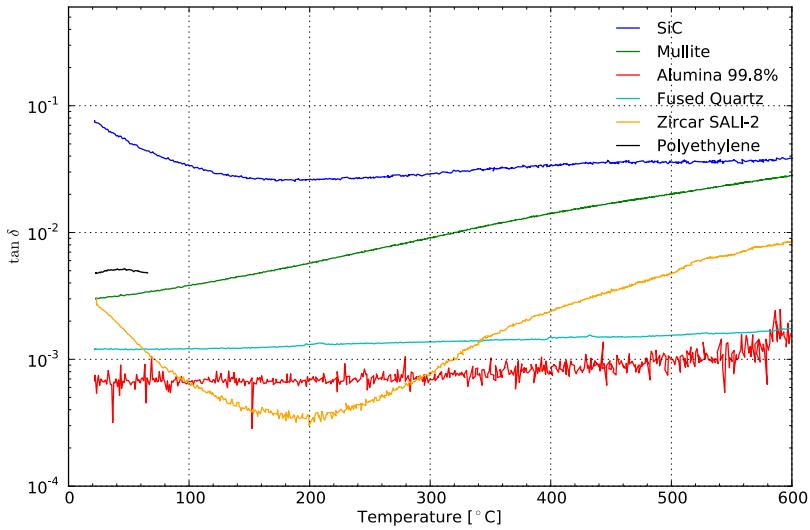


**Fig. 8 The loss tangents as a function of temperature of selected materials that are of interest in microwave processing of carbon fiber.**

A pair of finite element codes was used to model the MAP system. CST Microwave Studio (MWS) software is a 3D EM simulation tool that solves Maxwell's equations with the finite integration technique and finite time differencing. COMSOL is a multi-physics finite element package that can couple rf and microwave power inputs with heat transfer models. A 3D model of the system was created and includes the material properties of the waveguide and quartz tube. The initial model used a uniform material with a high permittivity to simulate the plasma. The tow was assumed to be uniform and given a density, resistivity and diameter consistent with that of a carbon fiber tow post graphitization.

A Drude dielectric dispersion model was developed to more accurately model the plasma including segmenting the plasma into 1-2 inch sections to account for the non-uniformity observed in the MAP plasma. Additionally, the tow was partitioned into smaller segments to account for changes in density, resistivity, diameter and position within the quartz tube. Dielectric data from the cavity diagnostic described previously was utilized to more accurately model the tow parameters.

Given the intra-tow variance in the mechanical properties, the modeling effort was revisited to understand the causes. Treating the plasma as a poorly conducting metal, the plasma current density profile corresponding to the processing power as function of location was modeled. Figure 9 shows two simulations of a plasma column in an applicator analogous to the MAP. At higher conductivity, the current profile changes shape considerably to become hollow. This may explain the relative lack of processing on the interior tows.

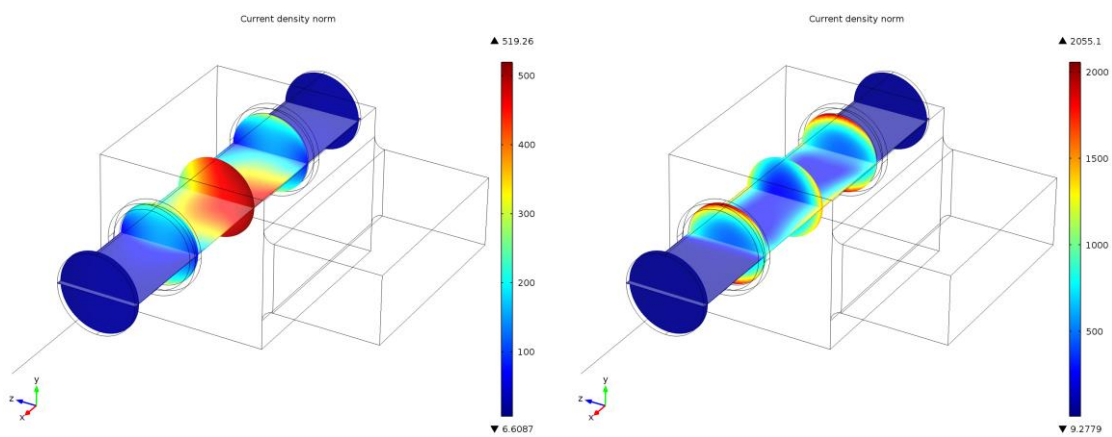


**Fig. 9 The current density shown inside the plasma column for two different values of plasma conductivity.**

### 5.3 MICROWAVE-ASSISTED-PLASMA (MAP) SYSTEM SCALING

The baseline MAP system runs in the low-to-medium vacuum regime. This operating regime requires the use of vacuum pumps and seals that have been the focus of engineering improvements to reduce cost and enhance reliability as the system was scaled to handle more tows. A series of plasma-only baseline measurements were taken in order to develop a set of optimized operating conditions for carbonization. For example, Figure 10 shows the how the temperature of the vacuum chamber and the working gas varies as the inlet pressure is varied. Similar experiments have been done for chamber pressure and rf input power. Later experiments added the tow to determine the effect of effluent emission during carbonization

as well as the modified rf absorption profile in the chamber due to the tow.

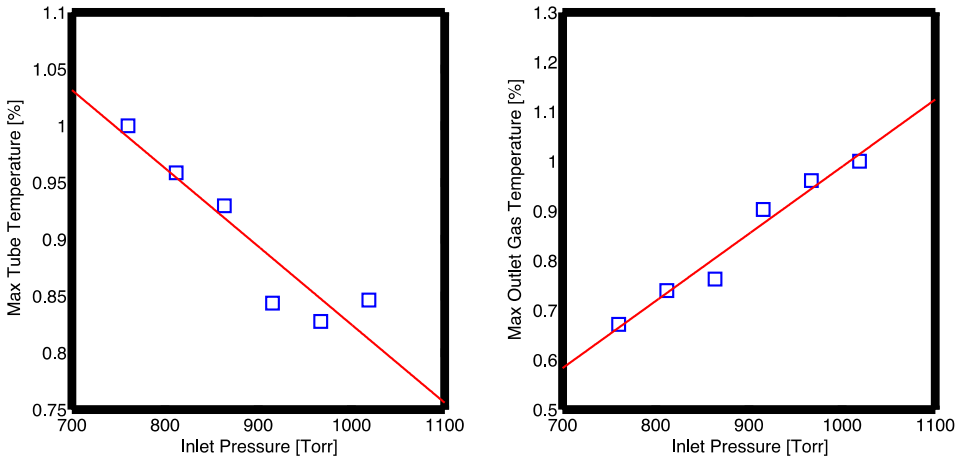


**Fig. 10 Maximum temperature of quartz tube and of gas at outlet vs. gas inlet pressure.**

As the carbonization was being scaled, effluent tar buildup in the vacuum foreline, mesh filters, and vacuum pumps that led to a loss of pumping speed was noted after only several hours of processing. The loss of pumping speed meant that the chamber pressure could not be maintained for long processing runs in that configuration, and the buildup of tar in the pumps led to extensive downtime for maintenance and rebuild. A commercial filter as shown in Figure 11 was installed to evaluate a simple approach to removing this buildup. While the conductance through the filter had slowly reduced over time as the filter gauze fills up, the conductance was still easily high enough to maintain pumping speed even after three times the processing time required to saturate the previous mesh filter. In addition, an inspection after a significant amount of run-time revealed that far less of the effluent tars were making it past the new filter-trap, better protecting the pumps. Even with these improvements, subsequent experiments with higher throughput show that pump protection is not fully resolved.

**Fig. 11 Commercial filter-trap installed on the MAP vacuum line.**

A larger diameter processing tube was installed in early stages of the scale-up. Another issue was identified in initial runs with the larger tube: a hot spot appeared on the tube itself resulting in melting of the tube. This had been noticed before in the regions of highest plasma temperature and had been mitigated with active air cooling of the tube in these regions. To solve this new problem, three additional sources of air cooling were added to the MAP line. Comparing runs before and after the installation of the extra cooling shows no significant differences in mechanical properties. The extra cooling appeared to have solved the melting problem as was verified at the next direct inspection of the tube. Active air cooling of the tube has eliminated significant deformation of the tube and significantly increased its lifetime.

In continuing implementation and evaluation of hardware upgrades to the MAP line, the metal-to-glass transition of the vacuum tube was shown to be less durable than is required for industrial use. To combat the fragility of the graded vacuum seal, an alternative mechanism using an o-ring seal was designed and installed. Replacement vacuum tubes now require just a length of tube instead of an additional pair of expensive and fragile graded seals. As an added bonus, the tube replacement time has been reduced by at least 75%.

To prepare for the 5-tow experiments, the pumping sections of the MAP line were increased again in diameter to accommodate larger eyelet plates and facilitate stringing multiple tows through the line. The glass eyelets were replaced with metal eyelets. This change reduces the fragility of the system as well as eliminates the small level of residual rf leakage that was present at the exit of the MAP line. Given some earlier results from tow geometry experiments indicating under processing for tows positioned farther away from the rf windows, it was decided to orient the 5 tows in a vertical line centered in the vacuum tube. To accommodate the additional tows, however, the eyelets had to be placed closer together as shown in Figure 12a.

During the shakedown of the new system, certain issues with experimental material form and processing

configuration had to be overcome. The large 50K tow band obtained by the project team for the experimental work appeared to have different levels of stretch as it was wound onto the spools. (The oxidized tow being used was from a commercial manufacturer, but was provided as an experimental sample and is not representative of how that manufacturer would have produced the same tow specifically for commercial application.) It was found that different parts of the tow drooped more or less under gravity as it is tensioned going through the system as shown in Figure 13. In the vertical configuration, it was found that with adjacent tows, parts of the upper tow would droop down into the one below it. As the tows become more conductive as they're processed, the electric field tended to arc across the tows forming a very localized plasma leading to inevitable breakage. Additionally this intra-tow droop leads to the lowest tow-position to drag on the bottom of the vacuum tube. Whereas much more uniform tow would be expected in actual production, this non-uniformity does help in development of a more robust process to enable handling of perturbations in product form. As a work-around, the tows were repositioned to a horizontal linear orientation as shown in Figure 12b. It was found after testing that the innermost and outermost tows do not touch the vacuum tube and adjacent tows do not appear to interact in the same way as in the vertical configuration.

To meet an 8 hour intermediate level milestone run requirement, three tows were placed horizontally as in Figure 1(b). There was a concern that the outer tows farther away from the rf input might be under processed, but this position allowed for expediently evaluating hardware durability and vacuum feed-through issues more critical to long-term success. A continuous 8½ hour run was successfully completed with the 3 tows. There were no problems at all with the vacuum tube or the pumping systems. Inline linear resistance measurements during the run indicate that as expected, the outermost tow is less processed that the other two. Average mechanical properties for these tows did meet project targets.

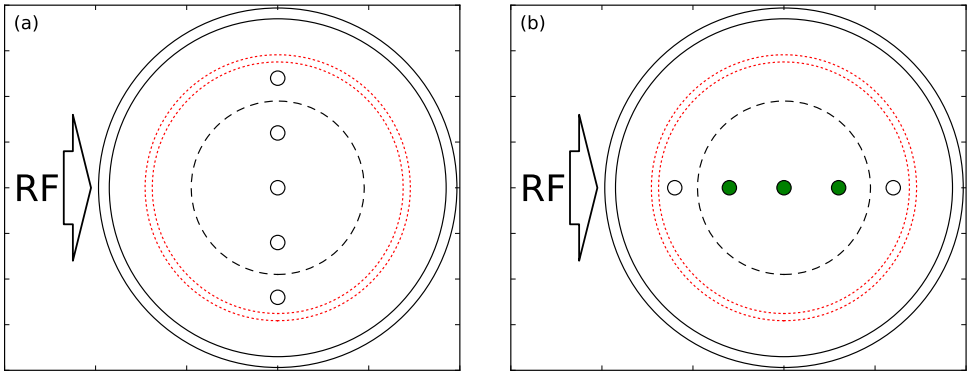


**Fig. 12 Geometry of the tows within the vacuum tube.** The red dotted circles are the extent of the old, smaller tube used for 3-tow experiments in 2011. The dashed circle prescribes the radius of the outermost tows prior to the 5-tow experiments. (a

**Fig. 13 Intra-tow tension differences in oxidized PAN feedstock. Part of the tow is under very little.**

Initial work with 5 tows in the applicator indicated that the horizontal tows are not processed evenly, with the tow farthest from the coupled rf inadequately processed as shown in Figure 14. The solution to this issue was to rotate the rf applicator itself so that the tows are still horizontal to avoid gravity effects, but with all the tows a similar distance from the rf source. This orientation is shown in Figure 14c. This rotation was completed and the updated configuration is shown in Figure 15.

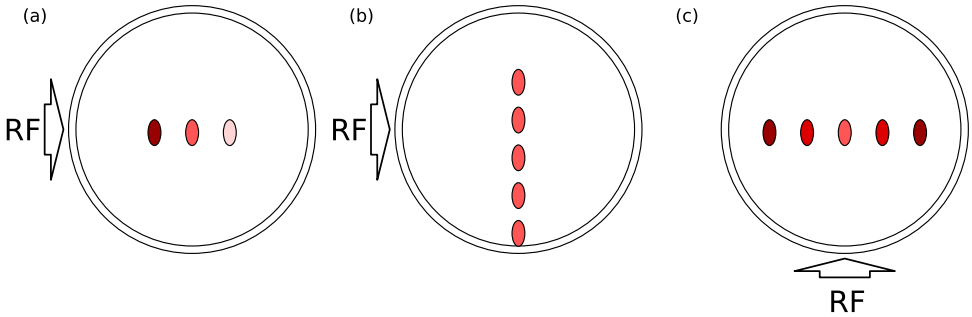


**Fig. 14 Tow orientations within MAP applicator. (a) Orientation in pre-2012 multi-tow experiments.** Heating is very uneven. (b) Attempted tow orientation in 3Q2012 campaign. (c) Tow orientation after applicator rotation for 5-tow experiment in early F.

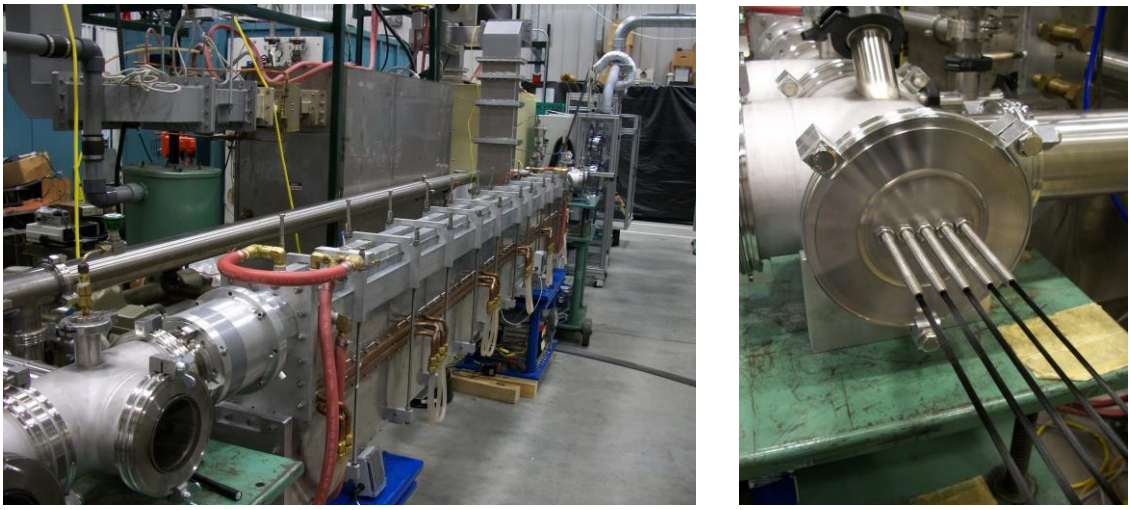

**Fig. 15 (a) The MAP line after rotating the applicator.** Microwave coupling is now from below. (b) The MAP line exit feed-throughs are shown fully strung with five tows in the horizontal configuration.

Moving forward with the new configuration and five tows in the applicator, the plasma was stable over a larger operating space than had seen under 3-tow operation. Reflected power was on average several percent lower than in 1 or 3-tow operations as well, which raises the efficiency of the process. However, preliminary experiments found that tow-to-tow processing is not as uniform as had been hoped. The outer tows seem to be processed more than the inner tows, but the variance is not as drastic as was seen in the 3-tow experiments with the rf coupling from the side. Another internal milestone was completed with a two hour MAP run with five tows. Several parameters are shown in Figure 16. For the most part this was a smooth run, with the exception that at about 17 minutes into the run, the microwave generator tripped off. The cause is unknown, but is not believed to related to the MAP process itself. After resetting, the team was able to achieve the prior operating conditions about two minutes later. (Actually it is believed that the ability to stop, start, and change parameters rapidly as necessary is one of the inherent advantages of the MAP approach over conventional processing.) After the reset, the run continued uninterrupted for another two hours and six minutes before shutting down normally.

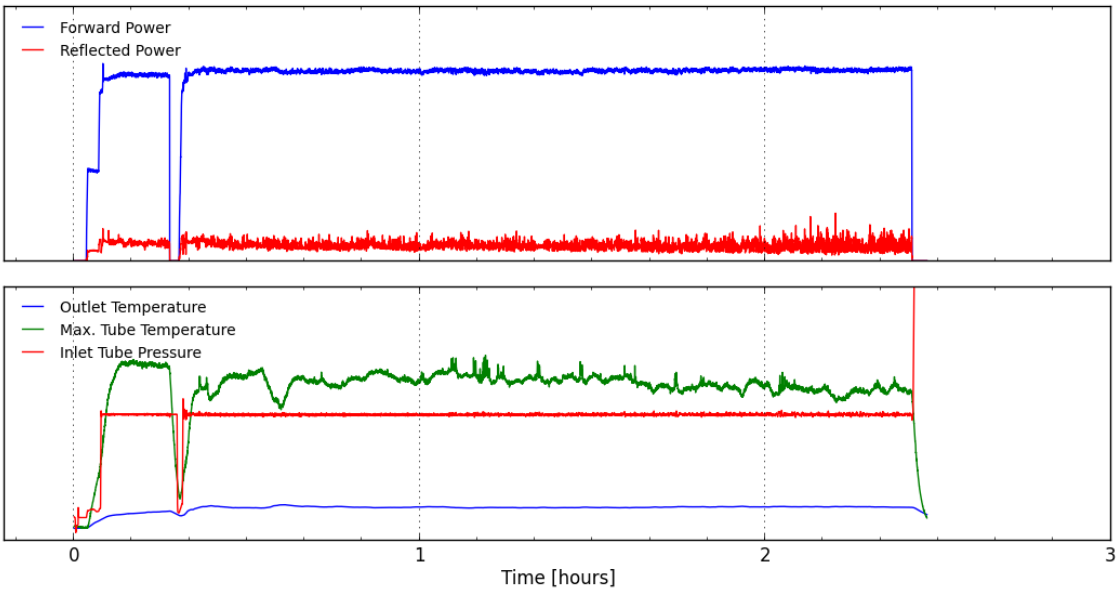


**Fig. 16 Time trace of 5-tow, 2+ hour milestone run.** Shown are the forward and reflected power, the nominal maximum vacuum tube temperature, the outlet gas temperature, and the tube gas pressure. At t=17 minutes, the microwave generator tripped.

Since implementing the larger processing chamber tube and transitioning to 5-tow operation, operations continued to improve allowing focus on issues such as factors influencing capability of the system to produce larger quantities of fiber at higher rates and capability to produce more consistent materials. Figure 17 gives a compilation of results in running with 5 tows including indication that mechanical properties are approaching targets even at 500% increased throughput over previous 3 tow operation. In terms of variability, the mechanical properties of the interior tows were significantly lower than for the exterior tows in the initial work with 5 tows. A run with similar operating parameters, but at 50% more speed demonstrated some degradation of properties, but the property levels were in ranges comparable with earlier experiments where relatively small modifications to processing parameters allowed achievement of targets. Indeed, by altering the operating parameters at the lower speed, the team was able to increase the tensile strength and modulus to a point where the target specification for all tows as shown by the cyan points in the Figure was met.

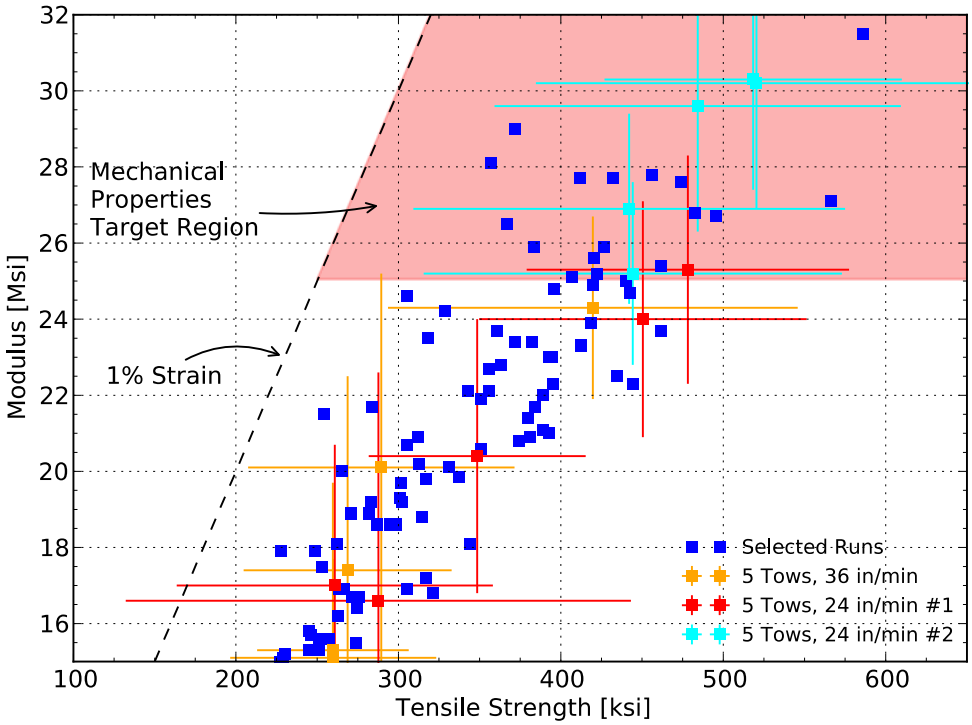


**Fig. 17 Mechanical properties from selected MAP runs.** The orange, red and cyan points are from three 5-tow runs. Fiber properties in the shaded region meet or exceed programmatic targets. Large variance is due to single-filament mechanical testing.

Multiple experiments have been performed to determine routes for improving tow-to-tow variability. Several approaches were identified and upgrades to the MAP system were completed to demonstrate effectiveness of the identified approaches including changing the tow configuration in the processing chamber and modifying the microwave energy introduction and management approach as described below.

Previous five-tow experiments have been able to exceed the programmatic mechanical property targets; however, it was found that the tows suffer from a tow-to-tow variability with the central tow just meeting the modulus target while the outer tows exceeded the modulus target by over 20%. Guided by energy deposition modeling and observation that some wall heating might be affecting level of processing, tow configuration changes have been implemented. Figure 18 shows the results of a previous experiment on the left and an experiment with the modified "smiley-face" configuration on the right, with both experiments using SGL Panox 50K tows at approximately the same operating parameters including a tow movement speed of 24 in/min. As shown in the figure, the resulting data shows average properties improved overall in the new configuration, but the configuration changes resulted in reversed trends: the mechanical properties have now switched positions with the middle tows experiencing greater conversion and the outer tows processed less thoroughly. Mechanical properties were not measured along the fiber length, but density and resistivity measurements along the fiber length indicate consistent uniformity. This result indicates that shifting the tows radially can indeed influence the inter-tow properties and we expect that making the configuration a little less "smiley" should even up the mechanical properties even more. From the data differences, it is surmised that any wall heating is a second order effect.

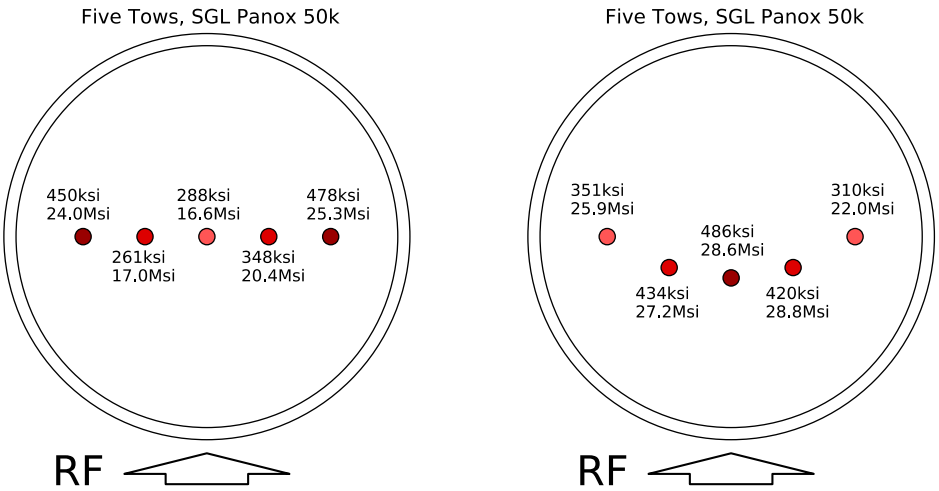


**Fig. 18 Mechanical properties and relative positions of a single 5-tow MAP run for the horizontal configuration (left) and the "smiley-face" configuration (right).**

Perhaps having the greatest potential impact in process management, among the modified approaches implemented for evaluation during the fourth quarter of FY2013 was an alternative technique based on existing microwave technology and relatively standard hardware that exploits modular microwave-plasma cavities. To validate the approach prior to reconfiguring the entire processing system, a single unit was tested in the MAP system initially.

Plasma stability and reproducibility has long been a focus in moving the MAP line to a dependable industrial process. The number of zones and relative power and location of the multiple plasma zones in the side-walled coupled waveguide MAP applicator are highly interdependent. System stability is a function of the input power and pressure as well as the location and presence of the carbon fiber in the applicator. If one could uncouple the plasma zones from each other, then the heating profile can be more easily tailored and also the plasma can be made more stable under a variety of operating conditions. Figure 19 shows a proposed multi-cavity applicator method that utilizes commercially demonstrated hardware to replace the side-wall coupled design for the MAP. Each cavity is driven separately and can be matched to provide the desired cavity-to-cavity heating profile.

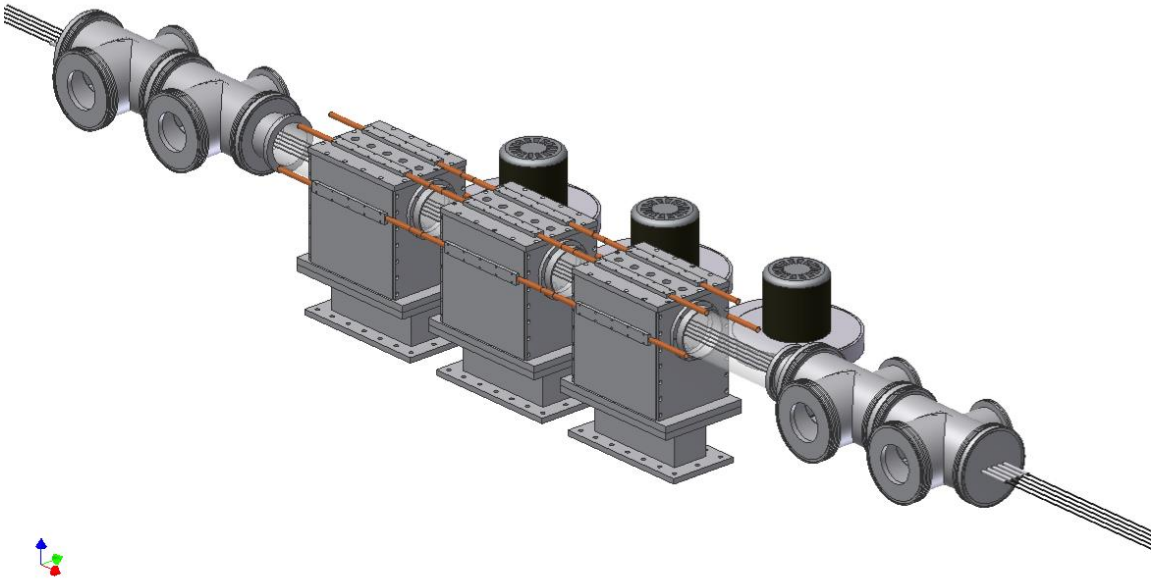

**Fig. 19 Proposed multi-cavity MAP applicator. Each cavity should be nominally uncoupled from the others, unlike the plasma zones in the side-wall coupled applicator.**

In order to demonstrate feasibility of this concept, a single unit cavity was obtained, installed and tested. Figure 20 shows the new single unit applicator. Medium power rf tests demonstrated excellent directivity and plasma tests at low power provided excellent coupling and an ability to maintain what is expected to be attractive processing parameters even at low input power. Figure 21 shows a plasma in the cavity running a single 50k tow. Mechanical testing of the 50k tow running at 24 in/min yielded 376 ksi tensile strength and 23 Msi modulus — slightly lower than our programmatic targets. However, this is extremely encouraging as the results were achieved with only a single cavity with un-optimized processing parameters.

With these results the team decided to go forward and add two or three additional cavities to the applicator for full carbonization capability. The key hardware was on order at the time of CRADA conclusion with plans for installation, testing, and demonstration to potential commercialization partners during the final stages of the overall project.

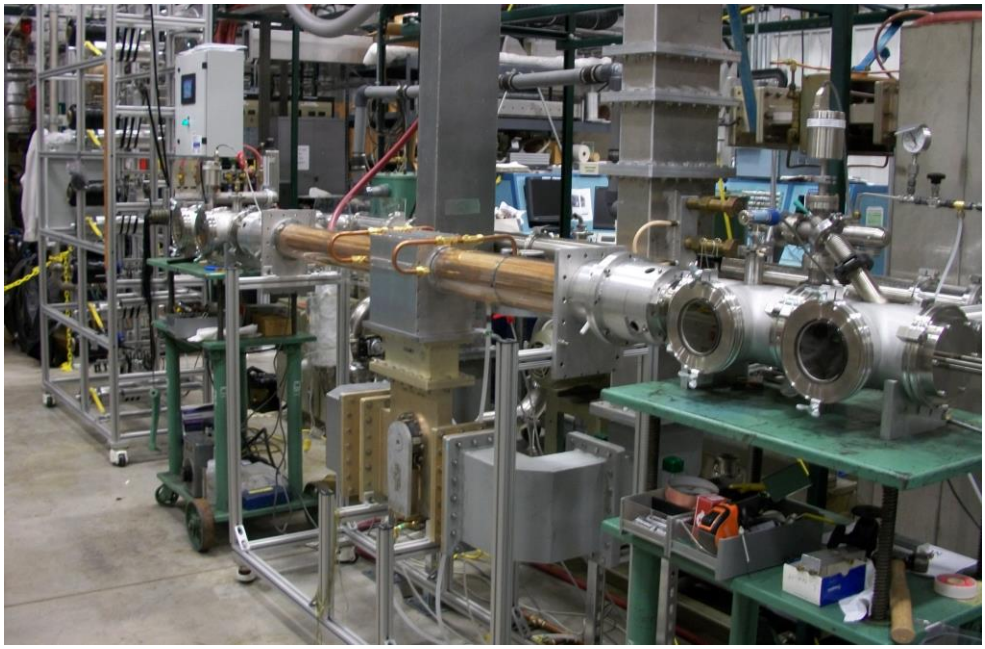

**Fig. 20 The new single-cavity MAP applicator.**

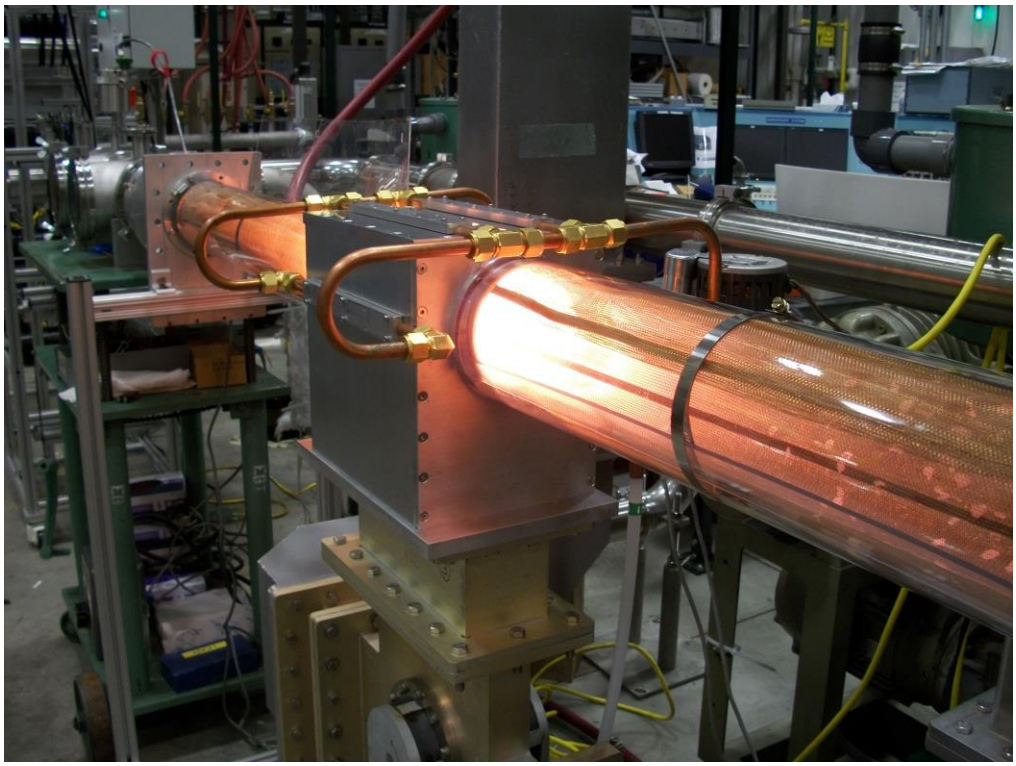

**Fig. 21 A plasma test with a single tow in the v4 MAP applicator.**

### 5.4 MAP ENERGY BALANCE

To effectively take MAP processing to an industrial scale, we must have data regarding energy usage as well as the various precursors and products. A schematic of the MAP system is shown in Figure 22. In addition to the oxidized fiber precursor, inputs include a cover gas to maintain an inert atmosphere, water

and air for cooling and electrical power. The water is circulated through a heat exchanger and is in a closed loop. For the milestone energy balance calculation, the power consumed by the heat exchanger is not computed. Instead the amount of power removed by the water is measured. This value will set the requirements for a future dedicated cooling system for an industrial-scale MAP. The other outputs are cooling air, the carbonized fiber, and residue and exhaust gases.

The required electrical power is used for microwave generation, cooling fans, vacuum pumping, and diagnostics. For the baseline energy balance, the power for the microwave generator comprises about 65% of the total electrical input. The exhaust consists of the cover gas output as well as any gaseous byproducts of the conversion process. The residue consists of any other non-gaseous vapors (the tars mentioned previously) of the effluent. Data from conventional processing shows that this residue is approximately 20% by mass of the oxidized precursor fiber.

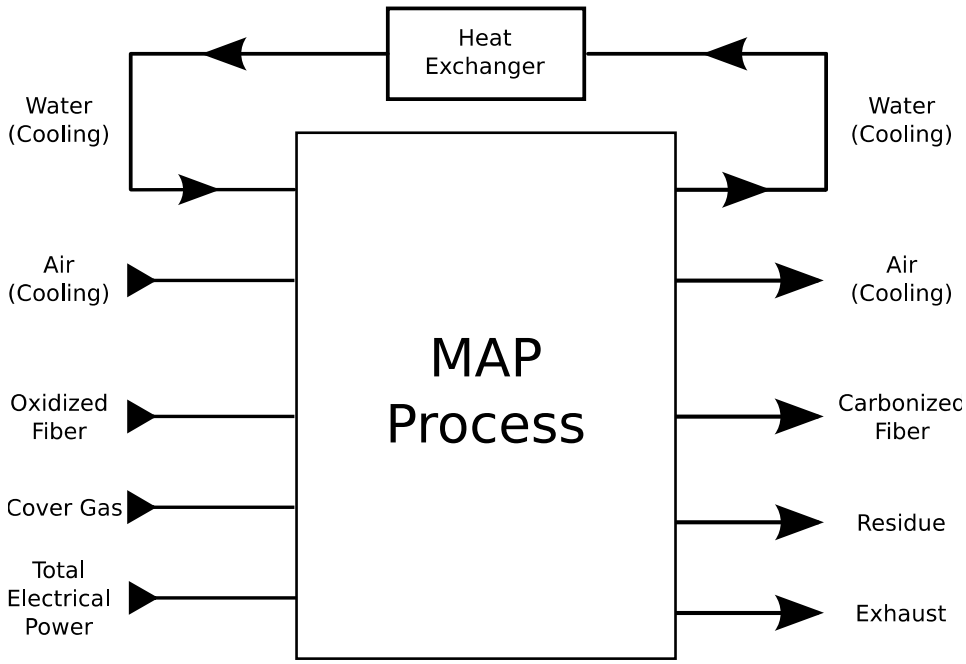


**Fig. 22 Energy and mass inputs and outputs for the MAP process.**

It remains to be seen exactly how processing efficiency scales. Multi-tow experiments show that doubling the throughput of the MAP line required only ~15% more RF input power to maintain equivalent mechanical properties. This figure corresponds to a ~6% increase in the overall electrical power needs of the current MAP system. As tows are added to a single applicator (read module), we should expect favorable kW/lb. scaling. The energy balance calculation will continue to be refined as parameters are tuned to optimize performance and the system is scaled up.

### 5.5 ALTERNATIVE PROCESS INVESTIGATIONS

In parallel to this work, the team also evaluated the feasibility of some atmospheric pressure alternatives to significantly reduce or eliminate the sealing issue altogether. A review of the current literature indicated that the use of a plasma torch or set of plasma torches might be a promising avenue of research. As with the baseline MAP process, any such solution must be evaluated with an eye toward the possibility or

difficulty of industrial scale-up. Previous attempts to perform carbonization/graphitization at atmospheric pressure did not prove fruitful. There were potentially several reasons for this lack of positive results, the most pressing being that the torch power was limited to greater than 1kW in order for the torch to operate in a stable manner. More recently published work with both the earlier inductively coupled plasma (ICP) type torch and the more recent microwave waveguide type torches has allowed the power levels to be reduced by more than an order of magnitude while still maintaining stable operation. An array of such low power torches might be necessary for scale-up to multiple tows if single tow operation and control could be demonstrated.

A low power atmospheric pressure plasma torch based on the "surfaguide" concept was constructed as shown in Figure 23. Initial tests have demonstrated that the torch can be operated with argon with low as 80 W of input power. Some axial temperature profiles are shown in Figure 24. A plasma was successfully formed with nitrogen as the fill gas; however, the minimum power obtained was 100 W before the plasma self-terminated. Additionally, certain plasma instabilities with nitrogen were observed that might be due to the torch design.

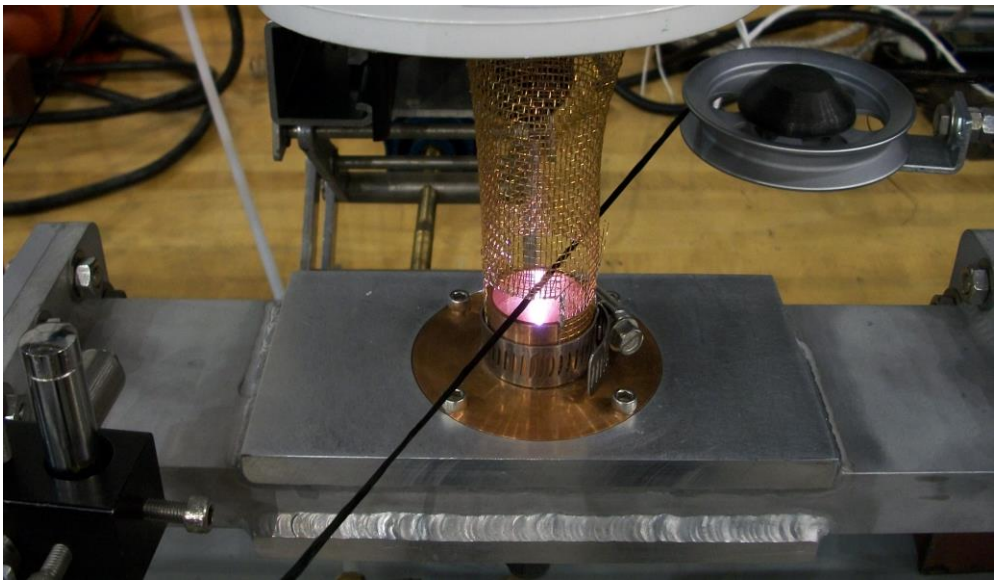

**Fig. 23 Atmospheric pressure plasma torch operating with oxidized tow.**

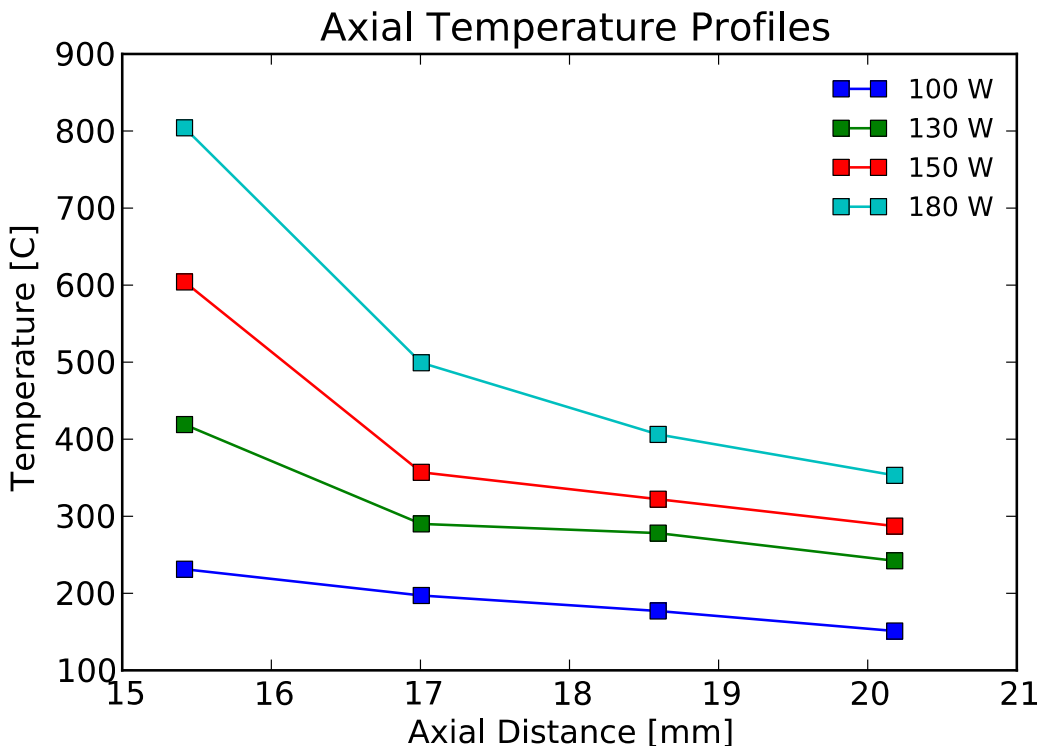


**Fig. 24 Temperature profiles with respect to the axial distance from the plasma torch nozzle.**

A static test of carbonization with an oxidized tow ~20 mm above the torch nozzle at 200W showed no degradation. Slowly moving the tow through the flame quickly frayed and broke the tow, an indication that too much oxygen was present in the vicinity of the flame. Subsequent tests with a partial nitrogen blanket did not prevent the destruction of the tow. The experiment was modified to provide for a completely inert atmosphere near the plasma flame. To do so, a "bell jar" was designed and fabricated to keep the torch under an inert atmosphere. The improved design is shown in Figure 25. With a nitrogen blanket at <30 ppm $O_2$, a preliminary experiment with a fully carbonized tow was performed. At modest line speeds, the temperature of the tow was measured to be ~700°C, sufficient for low-temperature carbonization. This was accomplished with minimal fraying and <100 W of input power.

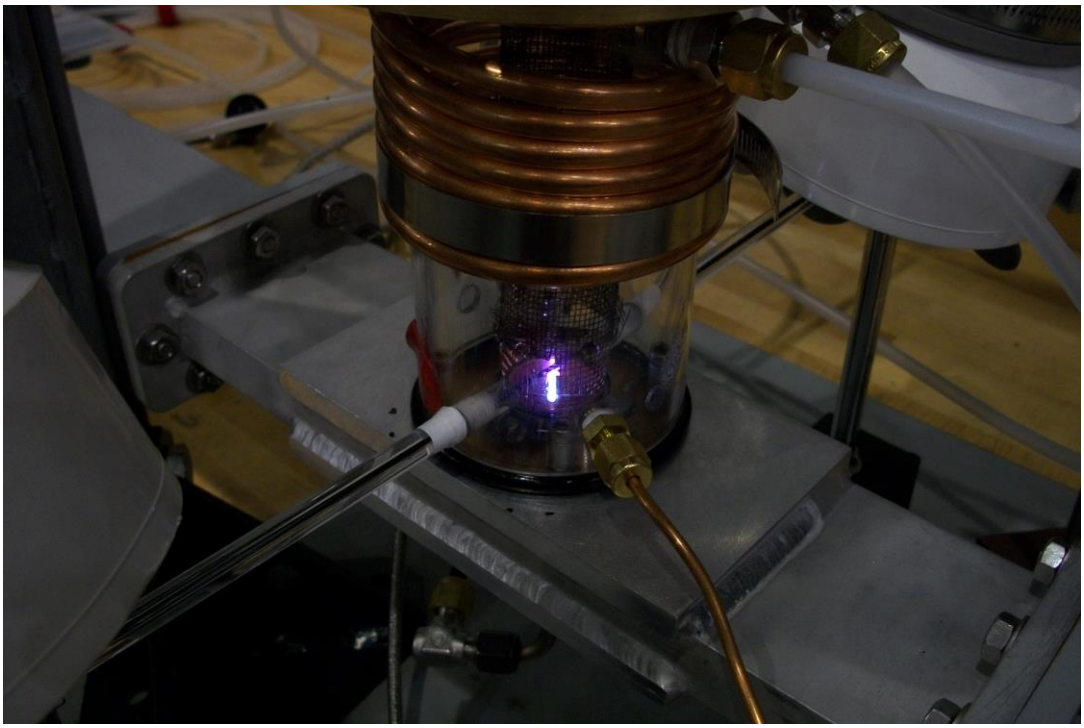

**Fig. 25 Atmospheric pressure plasma torch operating with an oxidized tow under inert atmosphere.** The copper coil at the upper center is a heat exchanger for the "bell jar" enclosure.

An initial experiment with oxidized fiber showed fiber temperatures of ~400°C at ~70 W of input power. However, increasing the power led to the destruction of the tow as unfortunately, oxidized fiber placed in the torch was quickly destroyed. Several follow-up experiments were performed after upgrading the seals to further reduce oxygen contamination. At ~80 W, diagnostics indicated the presence of HCN in the exhaust, so we it was concluded that some amount of thermal processing is taking place. However, the temperature of the tow remained below the threshold of the diagnostic, about 400°C. Increasing the power past 100 W results in the disintegration of the tow, with no apparent increase in tow temperature before destruction. With no obvious path forward, the decision was made to end efforts to carbonize fiber with a "surfaguide" plasma torch.

Preliminary experiments were also conducted to determine if processing via induction heating could act as a viable pre- or post-heater to the MAP process. The first experiment as shown in Figure 26 used a fully carbonized 12k fiber whose low resistivity allows for maximum current flow through the fiber.

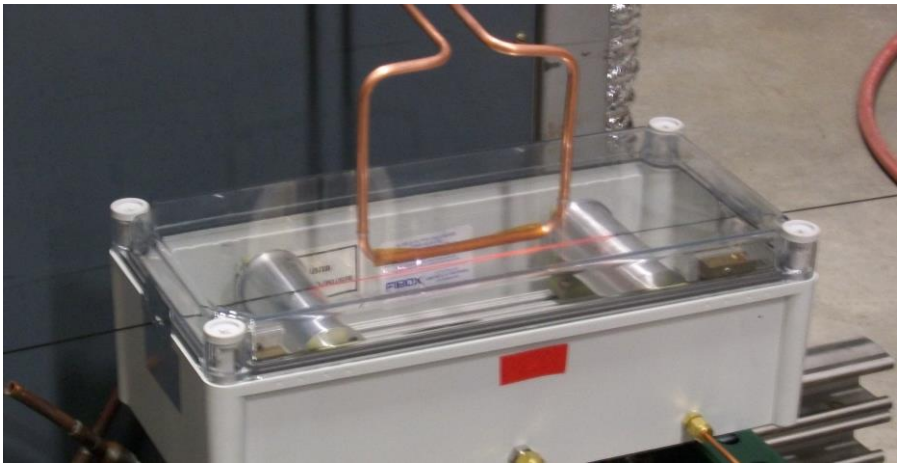

**Fig. 26 Heating a carbonized fiber via induction heating.**

As shown in the Figure, an antenna oriented axially to the fiber can excite enough current to heat the tow to dull red, and by increasing the power to the antenna, the fiber glows incandescent. Though no direct temperature measurement has been done, the temperatures achieved should be hot enough for mid-to-high temperature carbonization. In the preliminary experiments, several issues were encountered several. First, some filament breakage was experienced at the interface between the tow and electrode/rollers when the tow was hot. This is probably due to the abrupt temperature gradient of the tow at the electrode. This breakage could be mitigated either by heating the electrode or by directing cooler cover gas at the electrode-tow interface. Second, arcing between the tow and antenna was also observed, some of which is due to broken filaments acting as coronal enhancers. Most of the arcing was eliminated by placing a dielectric material between the antenna and tow, and some success was achieved in initial experiments.

After the successful preliminary experiment with fully carbonized fiber, experiments were conducted with less processed fiber. Unfortunately, at the maximum power available with the induction heater, partially processed fiber could not be heated to carbonization temperatures. The resistivity of these feedstocks is simply too high to inductively heat. After this difficulty, the feedstock was switched to tow that had been partially processed with the MAP line. Part of this tow did heat effectively with the induction heater, but a majority of the tow did not. Because of the current level of filament breakage and tensioning issues with MAP-processed fiber, most of the tow in these preliminary experiments did not make good electrical contact with the electrode, preventing a closed circuit. Thus, only the part of the tow under tension was heated. The setup was modified in order to mitigate this problem, but significant advantage was not achieved. At the point that this work was concluded, the experiments to date did show some processing capability for induction heating. However, it was determined that the energy consumption and overall footprint requirements would likely be too high for replacing major portions of the carbonization process and at best this approach would only be applicable in final portions of processing already partially carbonized fiber.

The primary alternative processing approach evaluated in this project was based on atmospheric plasma technology developed and demonstrated in collaboration with an ORNL partner for oxidative stabilization of precursor. (Oxidative stabilization is not applicable to the polyolefinic precursors of focus in this CRADA.) In work at partner ReMaxCo on the atmospheric plasma approach, the initial investigation into producing a high intensity plasma discharge with sufficient power density to carbonize oxidized PAN fiber utilizing inductive coupling resulted in the conclusion that 1) generating such a plasma was technically possible, however 2) scaling the resulting optimized apparatus to the industrial scale needed for commercialization would not be economical. Based on this conclusion, the development team switched to

the second approach largely employing capacitively coupled plasma. Preliminary analysis indicated that this approach could be scaled to industrially relevant levels in similar fashion to the plasma oxidation technology.

ReMaxco designed and built necessary hardware to investigate the feasibility of the new fiber carbonization mechanism utilizing near-field capacitively-coupled RF plasma with integrated electromagnetic heating. Significant research into the power electronics portion of this novel processing apparatus was necessary to determine the optimal power signal conditioning and matching to the fiber treatment chamber equipment. Working at this combination of frequency and voltage level has not been done before for this type of application. After extensive experimentation with a wide variety of custom-built power electronics equipment, a solution has been found that provides very good matching and conditioning to the load cell, and which takes advantage of the distributed element (transmission line) domain physics demanded by the operating frequency. This custom piece of equipment as shown in Figure 27, designed and fabricated at ReMaxco, was built to provide sufficient voltage and power to generate the heating and processing necessary for carbonization of a single 3k tow of oxidized PAN fiber in a batch process.

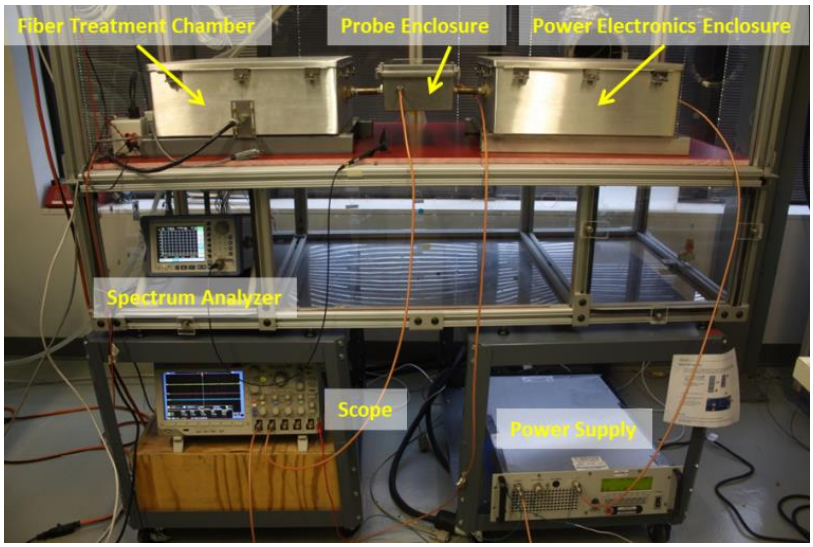


**Fig. 27 Atmospheric plasma carbonization experimental setup at ReMaxco.**

Version 6 of the carbonization system is shown in Figure 28 below, and can process 4 x 24k OPF tows. The research team was successful at heating the fiber to nearly 500C using this experimental technique. This temperature measurement probably did not capture the maximum temperature actually experienced by the OPF being tested, and as Figure 29 shows, portions of the fiber were vaporized. This occurred in less than a minute while consuming 50-60W of power.

**Fig. 28  Version 6 of the benchtop carbonization unit.**

**Fig. 29  Samples of partially processed/vaporized OPF.**

It is difficult to accurately measure the density of a very small amount of material, even with liquid density columns.  Fortunately, ReMaxCo has been working on a technique utilizing FTIR spectroscopy to measure density of OPF that requires only milligrams of material, and allows for sectioned measuring of OPF density along a tow length (in this case, 7 – 1mm length cuts from a 15cm section of processed 24k OPF tow).  Utilizing FTIR also allows for the study of the chemistry of the processed fiber.  Results did show an increase of density in certain areas.

This approach is promising. It is flexible, economical, and scalable. It operates at atmospheric pressure. It appears that the temperature requirements for Low Temperature (LT) carbonization can easily be achieved, and high temperature carbonization is possible. Shielding for EMI will be required given the frequency range this system operates in, but this is not a major issue. The entire system can be segmented to tune the system to the various stages of processing. The primary deficiency in the system is the generation of hot spots although the research team has proposed three methods of reducing this issue. The plasma component of the system needs to be studied in greater detail to determine exactly its effect on the carbonization process. Once the heating mechanism is optimized, plasma effects can be singled out by proper design-of-experiments methodologies.

Results confirmed that, at the very least, this technique accomplishes "low temperature" carbonization (conventionally in the 500-700C range of processing). The final design (for this project) has been termed the Close-Proximity Plasma Electromagnetic-Heating (CP2E) carbonization technique. The project team concluded that the new technique is feasible for assisting in low temperature carbonization, but not adequately advanced for implementation in the scope of this project. It is intended to revisit this approach later for longer-term development and demonstration as funding becomes available for next generation technology.

## 6. SUBJECT INVENTIONS (AS DEFINED IN THE CRADA)

ORNL intellectual property contributions were brought into performance of the CRADA as Background IP. Naskar & Paulauskas filed an invention disclosure with ORNL, "Microwave Processing of Functionalized Polyolefin Fibers" in September of 2010. Based on the initial feasibility studies on the atmospheric plasma investigation, an invention disclosure entitled "Atmospheric Plasma Carbonization of Pre-Stabilized/Oxidized Precursors" as been submitted for patent filing considerations. If adequate supporting data can be produced, the team intends to file an invention disclosure at a later date on the modified applicator approach as described in earlier sections.

As a result of the research conducted under this CRADA, Dow has filed patent applications for the following subject inventions:

| Title | US Serial # | Date |
|---|---|---|
| Process for Preparing Carbon Fibers Using Sulfur Trioxide in a Halogenated Solvent | 61/670802 | 7/12/2012 |
| Process for Preparing Caron Fibers Using Gaseous Sulfur Trioxide | 61/670810 | 7/12/2012 |
| Tow-Step Sulfonation Process for the Conversion of Polymer Fibers to Carbon Fibers | 61/670821 | 7/12/2012 |

## 7. COMMERCIALIZATION POSSIBILITIES

Utilizing DOE funding outside of this CRADA, ORNL completed and commissioned a 25-tonne-per-year Carbon Fiber Technology Facility (CFTF) during latter stages of the CRADA. This initiative will enhance demonstration of carbon fiber technologies at near-production scale in order to facilitate commercialization of these technologies. The Dow/ORNL team moved substantially towards material selection and process approaches that lend themselves to commercialization upon successful completion of this project and other related activities. A more recently formed team of Dow, Ford, ORNL has been awarded a grant from the DOE/AMO Integrated Manufacturing Initiative to scale up the alternative precursor approach developed in this CRADA for market scale demonstration. At the conclusion of this project, scale-up activities were on hold pending review of capital equipment cost assumptions for the sulfonation process versus alternative approaches.

The ORNL team has identified microwave generator and vacuum system suppliers who could be potential partners. The team also has fielded inquiries from existing manufacturers of carbon fiber conversion equipment and others interested in entering this business on potential partnerships for scaling up carbonization systems. At this point, it is not appropriate to commit to specific partners, especially considering that the issues regarding the potential for atmospheric plasma approaches and specifics of multi-chamber versus single chamber MAP approaches have not yet been resolved. Two major industrial companies as well as others have expressed interest. A formal request for expressions of interest requiring potential partners outline their proposed approaches is being planned. This activity will be completed during the first half of FY 2014.

Although the formal CRADA agreement with Dow expired prior to the end of the funded effort at ORNL, ORNL plans for completing this work include evaluation of potential partners and partnership arrangements for scaling the technology to the pre-production scale demonstration comparable with the 25-tonne-per-year scale currently being implemented at the Carbon Fiber Technology Facility in Oak Ridge. A deliverable of the ORNL project is technology documentation adequate for specifying the equipment in this size range. Equipment and process details can be demonstrated and discussed with potential partners allowing for development of collaborative proposals for moving to the next scale level and eventual commercialization. ORNL will solicit input from various commercial sources as to interest in this area and work with the Program Office(s) to formalize planning for acquiring adequate resources for the following phases of this work.

## 8. PLANS FOR FUTURE COLLABORATION

Dow and ORNL have ongoing interaction and plans for extensive collaboration in carbon fiber development and demonstration leading to commercialization. In 2012, a major initiative was announced involving Dow, Ford, and ORNL working together to scale and demonstrate market development scale production of carbon fiber composites targeted towards vehicle applications. This initiative, funded by substantial investments of Department of Energy and the Michigan Economic Development along with in-kind contributions of Ford and Dow, intends to take technology developed in the program described here-in and related work in low cost carbon fiber and composites of the partners to the level necessary for evaluation of technology maturity and economic justification for full scale-up opportunities. Plans are for Dow to scale precursor production to a level approximately consistent with production levels present at the CFTF and then produce carbon fiber at this level for demonstration of composites appropriate for automotive application in lightweighting for enhanced fuel economy. Successful demonstration would be a step towards commercialization of this value stream in a key energy mission area.

## 9. CONCLUSIONS

ORNL and Dow have combined in this CRADA to make substantial inroads in the development of new carbon fiber precursors and conversion technology and towards establishing pathways to commercialization of these interrelated technologies. The technology to produce alternative polymer fiber precursor formulations as well as scaled energy-efficient advanced conversion technology will facilitate commercialization of carbon fibers that are technically and economically viable in industrial markets such as transportation, wind energy, gas storage, infrastructure and oil drilling applications. Although there have been efforts in the past to produce a low cost carbon fiber, current carbon fiber production techniques are currently derived from historical needs of military aircraft and high-end aerospace components which are not conducive of meeting cost targets of commercial energy-related missions. This approach is different the researchers were free to adjust both manufacturing process and precursor chemistry to meet the different physical specifications at a lower cost.

During the course of the CRADA, the precursor development team moved from utilization of commercially available sources of polyolefinic materials identified prior to the CRADA by ORNL to specific formulations chosen by the team as most likely to meet technical and economic goals of the project from the vast reservoir of Dow sources. The team developed appropriate screening criteria that was implemented and adjusted as appropriate in making materials selection. The sulfonation process previously utilized in batch form by ORNL was implemented in continuous from by the CRADA team and property versus property relationships were established. With enhanced knowledge and experience of the team, the best formulation alternatives were identified and Dow provided fibers custom spun and stabilized through sulfonation for conversion and testing by ORNL and Dow. Properties were advanced to levels approaching program targets when Dow economic analyses indicated that the sulfonation approach made large-scale economic advantages marginal versus assumed risks. At this point, the polyolefin development work was suspended while Dow assesses possibilities for alternative stabilization techniques.

Work on the advanced conversion process was continuing at the time of CRADA expiration and compilation of this report. Various alternative approaches to atmospheric plasma processing using plasma torch approaches as well as inductively and capacitively coupled plasmas have been considered. Although encouraging results were achieved with the capacitively-coupled approach, this technique was considered not sufficiently mature for scaling at this time, but with further development, may be reconsidered in the future. A non-plasma inductive technique for preheating and/or post-processing was evaluated as well, but did not provide significant advantages for further exploitation at this time. At the time of this report, the pilot-scale demonstration unit was being constructed with a single low pressure processing chamber fed with multiple microwave cavities integrated for enhanced energy deposition control.

Utilizing advances described in this report, low pressure sealing techniques have been improved and external cooling and effluent trapping approaches demonstrated to enhance process durability. In addition to better understanding of energy deposition itself, the modeling work has assisted in better understanding of how tow placement impacts process uniformity. Minimum property level targets have been consistently achieved at each stage of the hardware advancements described and property uniformity appears within reach when adequately uniform precursor is available. A baseline energy balance has been developed to assist in evaluation of economics of the final demonstration system with semi-optimized processing conditions. The team plans to demonstrate the advanced conversion approach to potential commercialization partners as specifications are developed for pre-production scale equipment.

During the course of the CRADA, ORNL completed and commissioned the 25-tonne-per-year CFTF with DOE funding outside this CRADA. This capability will enhance demonstration of carbon fiber technologies at near-production scale in order to facilitate commercialization of these technologies. It is intended for this capability to be utilized in paving the pathway forward for introduction of low cost

precursors such as polyolefins and as a location for demonstration of the next-scale for the advanced conversion process.