7. Low-Cost Carbon Fiber

A. Low Cost Carbon Fiber from Renewable Resources

Project Contact: F. S. Baker, N. C. Gallego, D. A. Baker
Oak Ridge National Laboratory
Post Office Box 2008
Oak Ridge, TN 37831-6087
(865) 241-1127; e-mail: bakerfs@ornl.gov

Team Members:
Nidia C. Gallego and Darren A. Baker - Oak Ridge National Laboratory
Dr. Kendall (Ken) Pye - Lignol Innovations
Mlle Jessica Charland Labonté, Kruger Wayagamack, and Dr. Peter Axegård
Innventia (STFI Packforsk)

Technology Development Manager: Dr. Carol Schutte
(202) 287-5371; e-mail: carol.schutte@ee.doe.gov

Field Technical Manager: C. David Warren
(865) 574-9693; e-mail: warrencd@ornl.gov

Contractor: Oak Ridge National Laboratory
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Objectives

- The cost of the precursor material currently accounts for about 50% of carbon fiber manufacturing cost; therefore, emphasis in the ORNL research work is on the development of processes utilizing low cost precursor materials, notably textile grade polyacrylonitrile (PAN) and lignin, a renewable resource material.
- The goal of this project is to identify at least one precursor formulation, comprising both renewable and recycled materials, which could be used to produce industrial grade carbon fiber at a cost in the DOE target range of $5-7 per pound.

Approach

- Working with lignin materials furnished by the industrial collaborators, develop a viable process for production of carbon fiber meeting the cost and mechanical property targets for large scale automotive use.
- Provide feedback to the industrial collaborators as necessary for the refinement of the respective procedures used to isolate lignin to obtai n a material that exhibits the chemistry, physical properties, and purity necessary to produce the target carbon fiber properties.

- Pursue intellectual property to cover novel technologies developed and to facilitate technology transfer to industry.
- Promote the ORNL work at appropriate venues, including commercialization workshops at ORNL, to identify business opportunities for commercialization of the low cost carbon fiber technologies.
- Derive the fundamental data required to establish melt spinning conditions for the continuous production of lignin-based carbon fiber meeting target properties.
- Using research and pilot-scale carbon fiber production lines, construct the technical data base necessary to facilitate commercial production of lignin-based carbon fiber, including knowledge in the following respects:

    1. Isolation and purification of lignin to obtain appropriate precursor properties for carbon fiber production.
    2. Melt spinning technology, including compounding/pelletization of precursor feed material, extruder and spinneret configuration, spinning conditions, co-polymers, and plasticizing agents.
    3. Thermal processing of precursor fiber into carbon fiber.
    4. Advanced processing of lignin-based carbon fiber.
    5. Mechanical properties of lignin-based carbon fibers.
    6. Surface treatment and sizing technology for relevant resin systems.
    7. Development of process flow sheets for lignin-based carbon fiber production, including process economics, for presentation to companies considering entering the business of low cost carbon fiber production.

- Industrial partners and collaborators: Lignol Innovations (Vancouver, BC, Canada); Kruger Wayagamack (Trois-Rivières, Quebec, Canada); and INNVENTIA, formerly STFI Packforsk, (Stockholm, Sweden).

FY'09 Milestones, Metrics and Accomplishments

- Demonstrated a melt spinning speed of 1500 meters/minute (m/min) for 12-filament lignin fiber tow; 1500 m/min is the mechanical limit of the winder on the melt spinning equipment. 1500 m/min is 2.5 times the baseline speed of 600 m/min assumed in the Kline economic model, and almost 4 times the commercial solution spinning speed of PAN-based fibers. With appropriate spinning equipment, higher lignin melt spinning speeds of upwards of 5000 m/min appear within reach.
- Demonstrated sustained, continuous melt spinning of lignin precursor fiber tow of target filament diameter (10 μm) from two distinct sources of lignin, both of which met purity specifications as isolated from the biomass; i.e., without need for subsequent purification procedures. Coupled with the demonstration of 2.5 times the target spinning speed, these developments represent a significant beneficial impact on the economics of lignin-based carbon fiber production.
- Demonstrated that softwood lignin crosslinks more readily than hardwood lignin, and that this can be exploited to enhance the rate of stabilization of lignin-based carbon fiber; e.g., an 80/20 blend (by weight) of Organosolv-pulped hardwood lignin and Kraft-pulped softwood lignin could be stabilized at 10 times the rate of the 100% Organosolv (only) lignin fiber.

- Implemented work on the continuous processing of lignin precursor fiber into carbon fiber, using the precursor evaluation line. Preliminary means of transporting the fiber through the line were developed (by Amit Naskar in the Polymer Matrix Composites Group), but improvements are needed to reduce partial fusion of the fibers during thermal processing.
- Identified a major deficiency occurring during the thermal processing of lignin-based carbon fibers; namely, the development of a high degree of nano-dimension porosity in the carbon fiber as a result of in situ carbon gasification (in the inert atmosphere of the furnace). This is detrimental from a carbon fiber standpoint (for composites), but potentially commercially exploitable for high surface area activated carbon fiber production for many applications, notably electrical energy storage.

Future Direction

FY'10

A. Identification of appropriate blends (alloys) of lignin with synthetic polymers and pitches.

Milestone: Establishment of melt spinning conditions for one or more appropriate blends of Alcell lignin with copolymers; process into carbon fibers and measure properties.

Gate: If mechanical properties are significantly improved over current 100% lignin-based fibers, focus on the most promising blend and optimize conversion conditions to assess potential for achieving target carbon fiber properties.

Decision: If Strength >150ksi, Modulus >20 Msi, continue this approach; if not, stop approach.

Timing: FY'10, 4th Quarter

FY'11

A. Substantial enhancement of lignin molecular weight.

Milestone: Establishment of melt spinning conditions for one or more lignin materials with a molecular weight of at least 7,000 (weight average); process into carbon fibers and measure properties.

Gate: If mechanical properties are significantly improved over current 100% lignin-based fibers, focus on the most promising high molecular weight lignin material and optimize conversion conditions to assess potential for achieving target carbon fiber properties.

Decision: If Strength >150ksi, Modulus >20 Msi, continue this approach; if not, stop approach.

Timing: FY'11, 2nd Quarter

B. Continuous conversion of lignin-based precursor fiber into carbon fiber using the precursor evaluation line.

Milestone: Establishment of processing conditions for conversion of one or more types of lignin precursor fibers into carbon fiber on the precursor evaluation line; measurement of mechanical properties of the carbon fibers.

Gate: Focus on the most promising type of lignin precursor material and optimize continuous conversion conditions to assess potential for achieving target carbon fiber properties.

Decision: If Strength >150ksi, Modulus >20 Msi, continue this approach; if not, revisit selection of processing conditions (assuming batch furnace processing resulted in "go" decision).

Timing: FY'11, 4th Quarter (to be coordinated with Polymer Matrix Composites Group)

Introduction

The DOE Vehicle Technologies-funded work at ORNL is directed to the development of processes for the low cost production of carbon fibers, including the use of advanced processing techniques such as plasma oxidation, carbonization, and "graphitization" of the precursor fiber. Carbon fibers have the potential for substantial weight saving in vehicles because of their remarkable high strength, high modulus, and low density.

To place the potential increase in fuel economy into perspective, body-in-white modeling indicates that over 60% of the steel in a vehicle could be replaced with carbon fiber composite materials without impacting vehicle crash worthiness. However, carbon fiber is currently too expensive for large scale automotive use, which necessitates a large reduction in cost of industrial grade carbon fiber from about $20/lb to the DOE target range of $5-7/lb; furthermore, the current supply of carbon fiber is far too limited to meet the projected demand for automotive use. The cost of the precursor material currently accounts for about 50% of the cost of manufacturing carbon fibers, and therefore emphasis in the ORNL research work is being placed on the development of processes utilizing low cost precursor materials, notably textile grade polyacrylonitrile (PAN) and lignin (a renewable resource material) to manufacture carbon fiber with mechanical properties appropriate for automotive use (tensile strength, 250 Ksi; modulus, 25 Msi).

Lignin has a significant potential cost advantage over even textile grade PAN as a precursor material for low cost carbon fiber production. Whereas the cost of PAN is almost directly proportional to the cost of oil, the cost of lignin is largely independent of oil price, and essentially is based on its fuel value of about 5¢/lb. On the downside, however, relatively little is known about how to transform lignin into a carbon fiber. Furthermore, as currently isolated by the only commercial manufacturer of Kraft lignin-based products worldwide (MeadWestvaco), the lignin by-product from the Kraft pulping of wood is not suitable for carbon fiber production and requires purification before it can be properly used for this purpose, which increases its cost but not prohibitively. On the upside, though, other pulp and paper companies are considering isolating lignin from Kraft black liquor, and one company (Kruger Wayagamack) has already demonstrated isolation of a softwood lignin material that comes close to meeting the purity specifications for melt spinning and subsequent carbon fiber production.

Currently, chemical pulping of wood is the only large scale source of lignin in the USA, but as biomass refineries come on-stream the lignin by-product from cellulosic ethanol fuel production will represent a valuable resource material for carbon fiber production. Work on biomass lignins produced from the Oganosolv pulping of wood, the first step in cellulosic ethanol production, has demonstrated that such lignins are readily melt-spinnable as isolated and are of a much higher purity level than lignins derived from the chemical pulping of wood for paper production. In this context, Lignol Innovations is furnishing 100 kg quantities of its Alcell™ lignin product (derived from waste hardwood materials). Lignol has recently brought on-stream a one ton (biomass)/day pilot scale biorefinery, from which it will produce modified lignin materials for this project, and it has been awarded one of the DOE contracts ($30 MM) for construction of a demonstration scale biorefinery in Colorado.

Depending on species, lignin comprises about 15-30 wt% of wood, compared to about 38-48 wt% cellulose (on a dry wood basis); switch grass has a similar content of lignin. Thus, wood and switch grass contain significant amounts of lignin (about half the amount of cellulose), which if utilized for the production of value-added products, such as carbon fiber, would offset the high cost of producing cellulosic ethanol from biomass. Furthermore, utilization of the lignin

by-product for carbon fiber production (and other value-added chemicals) would result in real benefits in the contexts of increased energy efficiency, reduced environmental pollution, and enhancement of national security interests (e.g., reducing dependence on imported fossil fuels).

Lignin is already utilized in transportation applications on a large scale. For example, as emulsifying agents for asphalt road surfaces; similarly, as a dispersing agent for cement and concrete mixes, much of which is utilized in the construction of roads and bridges. Lignin is used as an "expander" (of active species surface area) in the negative plates of lead-acid batteries, the large majority of which are used for starting, lighting, and engine ignition (SLI) functions on vehicles. Lignin derivatives are used as economical adhesives for carbon black, 70% of the world production of which is used in the compounding of rubber for vehicle tires.

Summary of FY'09 Research

- The mechanical properties of 100% Alcell lignin-based carbon fibers are currently falling well short of the target properties (50% of target), but each new spinning run on the Alcell material resulted in a greater understanding of the properties of this very different, but promising type of lignin. Emphasis in the work has been shifted from 100% lignin to blends of the Alcell lignin with appropriate polymers, including PAN, PET, PEO, polyolefins, and also with the Kruger softwood lignin. Also, work was implemented in FY 2009 on the continuous conversion of lignin precursor fibers into carbon fibers, using the small scale precursor evaluation line.

- Carried out a paper study of Hildebrand and Hansen (respectively) solubility parameters of lignin materials, polymers, and pitches to better predict the most suitable additives to blend with lignin to enhance melt spinnability and conversion of the precursor fiber to carbon fiber. Implemented evaluation of spinning of Alcell lignin blends with polyethylene terphthalate (PET), polyethylene (PE), Polyacrylonitrile (PAN), mesophase pitch (MPP), and softwood lignin, respectively.

- Established more detailed relationships between the conditions of devolatilization of Alcell lignin (removal of residual solvents) and the glass transition temperature (Tg), melting point (Tm), and viscosity of the lignin. Each of these properties of the lignin is sensitive to the amount of residual solvent on the lignin, and as such influences the melt spinnability of the lignin. On one hand, reducing the level of residual solvent to low level (< 0.05 wt %) raises Tg and Tm substantially, which permits a faster rate of stabilization of the precursor fiber at higher temperatures. On the downside, however, the higher Tg and Tm require higher melt spinning temperature, which induces crosslinking in the lignin during the extrusion/spinning operation; this leads to unstable spinning conditions and, in the worst case scenario, loss of spinnability entirely (the lignin crosslinks in the extruder, thereby terminating flow of lignin through the spinneret). In essence, the challenge is to find the best balance between lignin spinnability and subsequent processing of the lignin precursor fiber.

- More knowledge has been gained of the inter-relationships between the fundamental properties of the lignin precursor fiber, notably Tg, stabilization conditions and carbon yield, and the ultimate yield and mechanical properties of the carbon fiber obtained under various combinations of stabilization and carbonization conditions. Because of the sensitive nature of carbon fiber processing information, specific conditions will not be cited here in a publicly-accessible document, but Figure 1 provides an indication of how thermal processing conditions impact the structural integrity of lignin-based carbon fibers and thereby the mechanical properties of the fibers. When carbonized relatively quickly, structurally sound carbon fibers were obtained (left hand SEM image); in marked contrast, when carbonized relatively slowly many defects were introduced into the carbon fiber (right hand SEM image), which was reflected by lower mechanical properties.

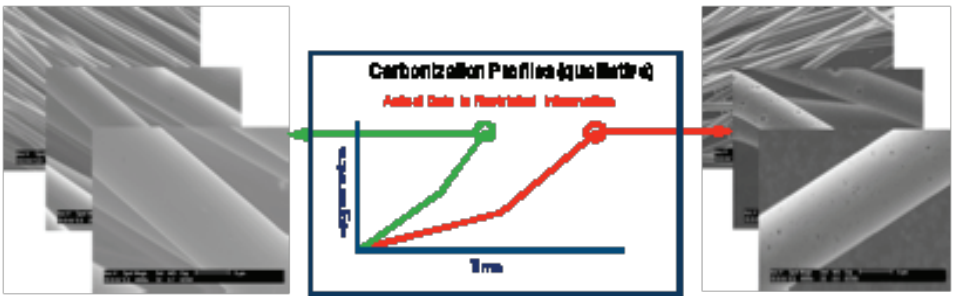


Figure 1. Influence of carbonization heating rate on structure of Alcell lignin carbon fiber.

Regardless of the rate of carbonization (in a batch furnace) though, mechanical properties of all the lignin-based carbon fibers still fell well short of target; i.e., even when the SEM images revealed an apparently structurally sound fiber (solid line and upper SEM image in Figure 1). To probe the structure of the carbonized fibers on a much smaller scale, nitrogen adsorption measurements were carried out on selected fibers representing "good" and "bad" conditions of carbonization; i.e., to test for the presence of porosity much smaller in dimension than can be imaged by SEM analysis.

The nitrogen adsorption data revealed a surprisingly high amount of surface area in pores of 1-5 nm in width. In fact, in the worst case of the fibers carbonized slowly (dotted line and lower image in Figure 1), the BET surface area of the carbon fibers was almost 1000 m^2g^{-1}; i.e., well into the range of activated carbon fibers! Even the fibers carbonized relatively quickly (solid line and upper SEM image in Figure 1) possessed a significant surface area of 550 m^2g^{-1}. Surface area of the same batch of lignin-based carbon fibers carbonized rapidly (< 3 minutes), using the continuous precursor evaluation line, fell to a minimum of 30 m^2g^{-1}. In this context, it should be noted that PAN-based carbon fibers produced on the precursor evaluation line exhibited no measureable surface area or nano-dimension porosity; also, that they readily met target mechanical properties.

- Demonstrated that softwood lignin crosslinks more readily than hardwood lignin, and that this can be exploited to enhance the rate of stabilization of lignin-based carbon fiber; e.g., an 80/20 blend (by weight) of Alcell hardwood lignin and Kruger softwood lignin could be stabilized at 10 times the rate of a 100% Alcell (only) lignin fiber.

- Implemented work on the continuous processing of lignin precursor fiber into carbon fiber, using the precursor evaluation line (late FY 2009).

- Established collaborative relationship with INNVENTIA, formerly STFI Packforst (Stockholm, Sweden). STFI will furnish ORNL with higher molecular weight Kraft lignin materials that meet the purity specifications and with Tg and Tm characteristics more favorable for melt spinning and fiber stabilization. STFI is the world's leading institution with respect to lignin materials, and bringing it on-board the project will help to accelerate progress on the development of lignin-based carbon fibers as well as promote the ORNL research effort to a larger and more diverse industry base of potential lignin suppliers. Attention is being given in Sweden to the conversion of less profitable (smaller) Kraft pulp and paper mills to the pulping of wood for lignin properties, where cellulose would be the by-product and would be used for cellulosic ethanol fuel production.

Conclusions from FY'09 Work

- Lignin meeting the purity specifications for melt spinning and conversion into carbon fiber can be isolated from either Kraft black liquor or processes for production of cellulosic ethanol fuel; i.e., relatively expensive purification processes are not necessary, which further enhances the economics of carbon fiber production from lignin materials.

- The chemistry of softwood lignin favors stabilization of lignin-based fibers and subsequent processing into carbon fiber with high yields (55% +), but softwood lignins are not readily melt spinnable and require the addition of a plasticizing (alloying) agent. The converse is the case for hardwood lignin, with slightly lower carbon yield (50-55%).
- Certain hardwood lignins are excellent plasticizing agents for the melt spinning of softwood lignins.
- Certain softwood lignins will substantially enhance the stabilization rate of hardwood lignin fiber, and by a degree significantly greater than the mass proportion of softwood lignin.
- Because of the substantial release of water and carbon dioxide during carbonization of lignin, substantial surface area and porosity is introduced into the fiber as a result of gasification of the carbon by these molecules (well known gasification agents); this is exacerbated by slow carbonization times, which increases exposure of the carbon to the higher temperatures at which gasification occurs. At this point in time, this is believed to be detrimental to the mechanical properties of the carbon fibers, albeit the same phenomenon could be exploited to produce low cost activated carbon fibers; e.g., for electrical energy storage.
- "Graphitization" of carbonized fibers (100% Alcell lignin) at temperatures up to 2700°C did not result in enhancement of mechanical properties of the carbon fibers. However, given the above conclusion, this begs the question of whether the precursor fiber was stabilized and carbonized, respectively, under the best conditions"?
- A substantial enhancement of lignin molecular weight is necessary to help achieve carbon fiber target properties. This will be tackled through a multi-front approach by the lignin suppliers and ORNL, including in situ increase of molecular weight through manipulation of pulping conditions and/or conditions of isolation of the lignin.
- Mechanical properties of lignin-based carbon fibers are currently about 50% of target.

Awards/Publications/Presentations/Patents (FY 2008 thru May 2009)

Awards

Elected as the American Carbon Society Graffin Lecturer for 2008/2009. (The American Carbon Society's Graffin Lectureship is endowed by Asbury Carbons in honor of George D. Graffin, a pioneer in the natural graphite industry. Each year, the American Carbon Society selects a lecturer who has made distinguished contributions to carbon science and engineering. The lecture is made available to North American universities, companies, and government agencies, and all travel expenses for the lecture tour are picked up by the American Carbon Society. The Graffin Lecture for the 2008/2009 period comprises two parts, each about one hour duration: 1. "Low Cost Production of Carbon Fibers from Renewable Resource Materials," and 2. "Nanoporous Carbon Materials - How They Benefit Our Lives and the Environment".)

Publications and Presentations - (* Presenting author)

1. C. D. Warren, F. L. Paulauskas, F. S. Baker, C. C. Eberle, A. Naskar, "Development of Commodity Grade, Lower Cost Carbon Fiber – Commercial Applications," SAMPE Journal, Mar-Apr 2009 Issue.
2. Graffin Lectures at Lawrence Technological University, MI (12/08); City University of New York, NY (3/09); GrafTech International, OH (5/09); Kruger Wayagamack, Canada (7/09); University of Washington, WA (11/09).

3. Frederick S. Baker,* “Carbon Fibers from Renewable Resources,” invited panel presentation at the 6th World Congress on Industrial Biotechnology and Bioprocessing, Montreal, Canada, July 19-22, 2009.

4. Frederick S. Baker,* Nidia C. Gallego, and Darren A. Baker, “Low Cost Production of Carbon Fibers from Lignin Materials,” CARBON 2008 World Conference on Carbon, Biarritz, France, June 14-19, 2009.

5. Darren A. Baker*, Nidia C. Gallego, and Frederick S. Baker, “Low Cost Production of Carbon Fibers from Lignin Materials,” SAMPE’09 Conference, Baltimore, MD, May 18-21, 2009.

6. Cliff Eberle,* Amit K. Naskar, Felix L. Paulauskas, Charles David Warren, Robert E. Norris, and Frederick S. Baker, “Low Cost Carbon Fiber Composites for Energy Applications,” 2009 ASM-TMS Annual Symposium: Materials Challenges for Alternative Energy, Niskayuna, New York, May 11-12, 2009.

7. Darren A. Baker*, Nidia C. Gallego, and Frederick S. Baker, “Carbon Fiber Production from a Kraft Hardwood Lignin,” Fiber Society Annual Meeting and Technical Conference, Boucherville, Quebec, Canada, October 1-3, 2008.

United States Patents (involving carbon fiber)

1. “Lightweight, Durable Lead-Acid Batteries,” US-2009-0269666-A1, Application published October 29, 2009, Edgar Lara-Curzio, Ke An, Jim Kiggans, Nancy J. Dudney, Cristian I, Contescu, Frederick S. Baker, and Beth L. Armstrong.

2. “Carbon Nanotubes Grown on Bulk Materials and Methods for Fabrication,” Paul A. Menchhofer, Frederick C. Montgomery, and Frederick S. Baker, U.S. Application No. 12/417,887, Filed April 3, 2009.

3. Baker, F. S., “Production of Composite Cellulose/Carbon Fiber Filters for HVAC Systems,” Invention Disclosure, Dec 9, 2008.

B. Advanced Oxidative Stabilization of Carbon Fiber Precursors

Principal Investigator: Felix L. Paulauskas
Oak Ridge National Laboratory
P.O. Box 2008; Oak Ridge, TN 37831-8048
(865) 576-3785; e-mail: paulauskasfl@ornl.gov

Participants:
Cliff Eberle, Amit K. Naskar, Soydan Ozcan, and Kenneth D. Yarborough - Oak Ridge National Laboratory
Professor Joseph Spruiell - University of Tennessee
Truman Bonds - Sentech

Technology Area Development Manager: Dr. Carol Schutte
(202) 287-5371; e-mail: carol.schutte@ee.doe.gov

Field Technical Monitor: C. David Warren
(865) 574-9693; e-mail: warrencd@ornl.gov

Contractor: Oak Ridge National Laboratory (ORNL)
Contract No.: DE-AC05-00OR22725

Objectives

- Develop an improved technique for oxidizing carbon fiber (CF) precursor with reduced residence time, CF cost, and equipment footprint.
- Verify that finished fiber properties satisfy automotive requirements.
- Provide data for the preliminary evaluation of the cost impact of the new oxidation technique.
- Investigate interfaces and compatibility with other advanced conversion processes.

Approach

- Develop a process for polyacrylonitrile (PAN) precursor oxidation using atmospheric-pressure plasma.
- Develop fiber handling protocols for continuous processing.
- Conduct parametric studies and perform diagnostics to correlate processing parameters and fiber properties.
- Characterize fibers to confirm that they satisfy program requirements.

Accomplishments

- Completed recovery from a key partner's bankruptcy-induced exit. Transitioned critical knowledge base and equipment to a new subcontractor and restored effective experimental operations with the new partner.

- Relocated advanced oxidation equipment to a new facility and resumed experimental operations there.
- Constructed first multiple-tow plasma oxidation reactor and conducted multiple-tow experiments.
- Evaluated multiple-tow reactor performance and modified reactor system.
- Evaluated spatial uniformity of key process parameters in the multiple-tow reactor.
- Commenced design of materials compatibility test stand.

Future Direction

- Continue refining and scaling the reactor design and processing protocols to achieve high speed, multiple large tow, semi-continuous (multiple pass) plasma oxidation process.
- Acquire and implement new diagnostic tools. Conduct parametric studies and fiber characterization to better understand process effects and the processing window and to quantify fiber properties.
- Conduct rate-effect studies and update cost analysis.
- Investigate oxidation of alternative precursors.
- Investigate interface with microwave-assisted plasma carbonization process
- Scale the process and equipment, and integrate into an advanced technology pilot line.

Introduction

The advanced oxidative stabilization project is a critical element in the low cost carbon fiber program in terms of meeting ultimate technical and economic goals. As previously stated, the objective of this project is to develop an improved technique for oxidizing carbon fiber (CF) precursor with reduced residence time, carbon fiber cost, and equipment footprint. In order to meet these objectives, technology developed in this project should be capable processing economically attractive precursor fiber chemistries and of being scaled to process sufficiently large tow sizes and numbers of tows such that the entire integrated material and process system can meet program goals for fiber performance and costs. Significant advancements in demonstrating process feasibility have been achieved at the bench scale as documented in this and previous reports.

The purpose of this project is to develop a plasma processing technique to rapidly and inexpensively oxidize PAN precursor fibers. Conventional oxidation is a slow thermal process that typically consumes more than 80% of the processing time in a conventional carbon fiber (CF) conversion line. A rapid oxidation process could dramatically increase the conversion line throughput and appreciably lower the fiber cost. A related project has already demonstrated the potential for significantly accelerating carbonization. The oxidation time must be greatly reduced to effect fast conversion. This project will develop a plasma oxidation technology that integrates with other advanced fiber conversion processes to produce inexpensive CF with properties suitable for use by the automotive industry. Critical technical criteria include (1) $\geq$ 25 MSI tensile modulus, $\geq$ 250 KSI breaking strength and $\geq$ 1.0% ultimate tensile strain in the finished fiber; (2) uniform properties over the length of the fiber tow; (3) repeatable and controllable processing; and (4) significant unit cost reduction compared with conventional processing.

Previous proof-of–principle work demonstrated that individual fibers of precursor could be oxidized and stabilized using advanced processing methods in small batches. This effort is aimed at further developing those technologies to be able to continuously process small tows of fiber for short periods of time (hours) and achieve properties equivalent to industrial grades of carbon fiber. This is being done by using a 3K commercial precursor, processing it in the advanced oxidative stabilization and then carbonizing it conventionally. The goals also include significantly reducing the time required for oxidative stabilization (conventionally 90-120 minutes) which will permit greater fiber production rates and improved economics. Once this project is concluded, the scientific basis will be sufficiently mature to allow for the development of processes using lower cost precursors in larger tow sizes on a continuous basis.

Project Deliverable

At the end of this project, the researchers will have developed an advanced oxidation process with residence time much shorter than that typical of conventional CF conversion lines. The program target is a residence time of no more than 2/3 that of conventional oxidative stabilization, however, it is believed that residence times less than ½ of conventional methods are achievable. The advanced oxidation process will be sufficiently well understood and documented that the team can commence scaling it up to develop a multiple, large-tow oxidation module for an advanced technology pilot line.

Technical Approach

The researchers are investigating PAN precursor fiber oxidation using nonequilibrium, nonthermal plasma at atmospheric pressure. As illustrated in Figure 1, conventional oxidative stabilization produces “core-shell” geometry with a distinct interphase between the (slowly growing) fully oxidized shell and the (shrinking) stabilized inner core. Plasma processing enhances oxygen diffusion and chemistry in the PAN oxidation process, accelerating the oxidized layer growth rate and oxidizing the fiber more uniformly, with a considerably less pronounced interface between the two regions.

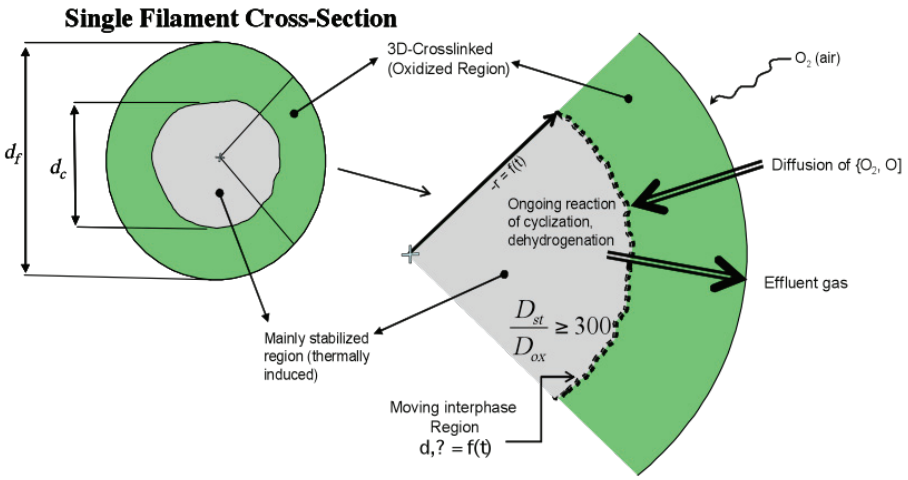


Figure 1. Single filament cross-section during conventional oxidative stabilization process

Atmospheric-pressure plasma provides better control over the thermal environment and reaction rates than evacuated plasma. It greatly reduces the sealing challenges inherent to evacuated plasma processing. Various fiber characterization tools and instruments are used to conduct parametric studies and physical, mechanical, and morphological evaluations of the fibers to optimize the process.

Experimental Results

To date, a reduction in oxidation residence time of about two-thirds has been demonstrated. Mechanical properties of various plasma oxidized samples are shown in Table 1. With increase in density, the ultimate elongation decreased. The mechanical properties could be tailored depending on the degree of oxidation. Tensile data show strength and elongation can vary from 17-45 KSI and 2-18%, respectively.

Table 1. Mechanical properties of plasma oxidized fibers

Fiber ID #	Density (D) (g/cm3)	Tensile Strength (Ksi)	Tensile Modulus (Msi)	Ultimate Elongation (%)
AGT 1411	1.3515	29.8 ± 3.4	0.77 ± 0.21	5.86 ± 1.19
AGT 1427	1.3378	31.7 ± 3.1	0.88 ± 0.16	6.10 ± 1.39
AGT 1552	1.3839	33.2 ± 3.0	0.84 ± 0.17	14.58 ± 3.81
AGT 1586	1.3769	35.1 ± 2.4	0.82 ± 0.16	18.02 ± 4.52
AGT 1750	1.5028	20.0 ± 3.7	0.70 ± 0.30	3.15 ± 0.60
AGT 1496	1.3914	42.6 ± 3.4	0.90 ± 0.30	18.5 ± 4.3
AGT 1723	1.5719	20.2 ± 1.9	1.1 ± 0.20	2.02 ± 0.37
AGT 1752	1.4799	21.5 ± 4.2	1.2 ± 0.30	2.23 ± 0.55
AGT 1754-1755	1.5182	17.1 ± 1.7	0.60 ± 0.20	3.27 ± 0.59
Conventional-Hexcel 3k 4 hours	1.4651	39.3 ± 5.4	0.93 ± 0.33	10.35 ± 1.87
Conventional-Hexcel 3k 24 hours	1.6333	26.2 ± 2.6	0.09 ± 0.20	3.62 ± 0.66

Single-filament mechanical properties of plasma oxidized, partially carbonized fibers are shown in Figure 2 (in some cases plasma oxidation was combined with electron beam pre-stabilization). The results are approaching required properties, which is encouraging at this stage of the development program. This work has been carried out using a small tow aerospace precursor. The next phase of the work will concentrate on increasing the material throughput and move toward using a commodity grade carbon fiber precursor.

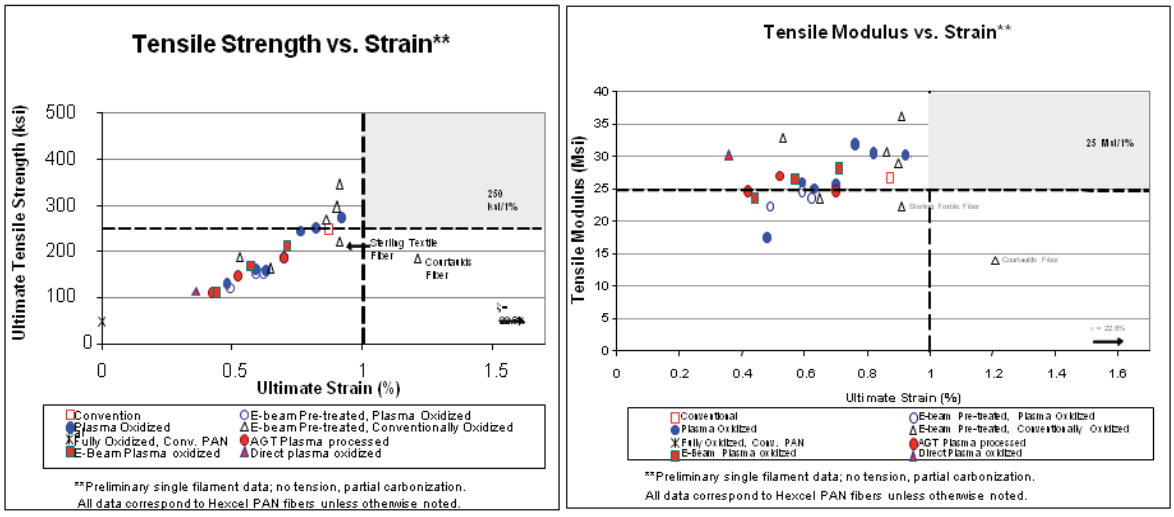


Figure 2. Mechanical properties of CFs stabilized and oxidized by various routes then conventionally carbonized at low temperature. The oxidation routes included conventional thermal oxidation, plasma oxidation, e-beam oxidation, conventional pre-oxidation, and e-beam pre-oxidation treatments. There was no tensioning, controlled stretching, or tow spreading during conversion. Conventional data points are for thermally shocked and thermally ramped heating protocols.

Scaling to multiple large tows is a major objective of this research. The first scaling step was taken by the construction and initial experimental operation of a multiple-tow reactor. In early FY 2009, the project team achieved single-tow line speed in the multi-tow reactor roughly equivalent to that previously demonstrated in the single-tow reactor. A photograph of the samples obtained in this reactor is displayed in Figure 3.

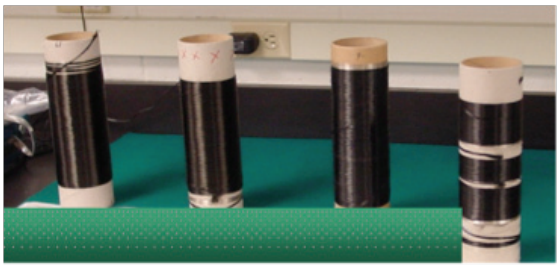


Figure 3. Photograph of samples processed in advanced oxidation reactors

X-ray diffraction (XRD) data of the plasma oxidized samples are shown in Figure 4. XRD data indicate that there is less degree of order for the advanced oxidized fibers (sharpness of the peak due to precursor fiber orientation is reduced) in comparison to the conventionally oxidized fibers e.g., textile and Hexcel fibers with densities 1.37 g/cm^3 and 1.42 g/cm^3, respectively. This is due to higher degree of oxidation in advanced processed fibers and lack of proper tensioning during the advanced oxidation of these fibers. The lower peaks indicate a higher degree of oxidation. Standard production material oxidation is indicated by the yellow curve. All three plasma oxidized curves exhibit a greater degree of oxidative stabilization than the standard production sample and were produced using the same precursor.

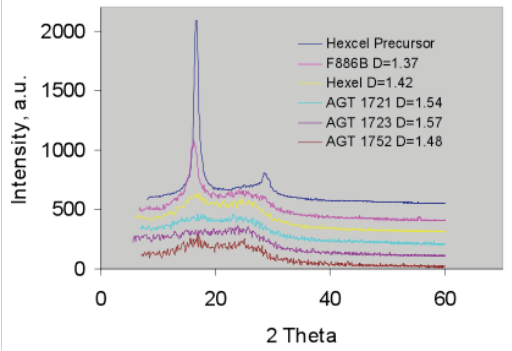


Figure 4. Wide angle XRD data of oxidized PAN

Multiple-tow reactor optimization was a significant task in the last half of FY 2009. The reactor was relocated to the new Sentech facility in February and March, followed by shake-down tests and resumption of operations in April. In June, we demonstrated first operation with multiple tows. Figure 5 shows a multiple-tow reactor experiment. Parametric evaluations revealed issues that were addressed by upgrades in July, followed by further modifications in August. These upgrades resolved unstable temperature profiles, insufficient concentration and flows of reactive species and non-homogenous processing within the equipment.

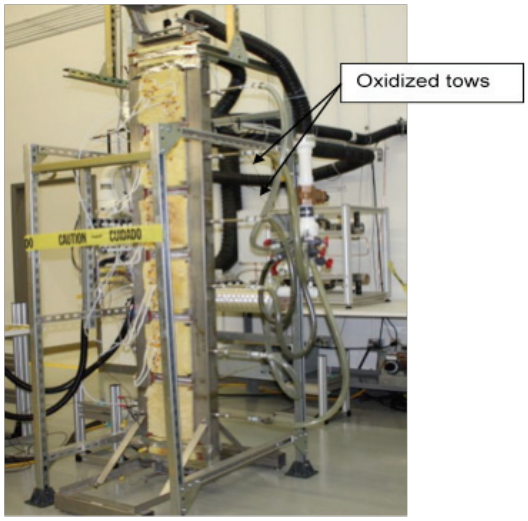


Figure 5. Reactor operation with two tows

Operating temperature is a key parameter governing reactor performance. Best performance requires good control of the temperature value, gradient, and stability throughout the reactor. Figure 6 shows temperature distribution across the reactor at two different locations, before and after hardware modifications to improve flow distribution, heating logic, etc.

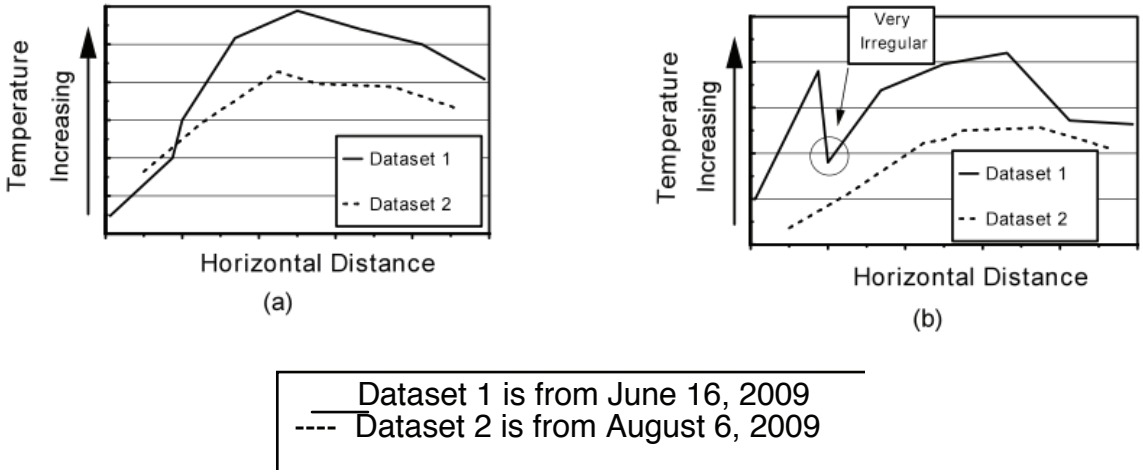


Figure 6. Temperature distributions across the reactor at two different locations

Figure 7 shows another type of measurement made to the multiple-tow reactor. In an effort to make a temperature measurement which accurately reflects the temperatures the precursor experiences (not including exothermic input from the precursor), the following method was used. A long thermocouple wire with a junction on one end was wound on the tension roller, with provision made for its opposite end to be connected to the data acquisition system and the resulting temperature recorded. The thermocouple was then pulled through the reactor in the same position that the precursor tow is pulled. For the test in this figure, varying speeds were used to determine the thermal inertia of the thermocouple junction, so that this could be cancelled out of subsequent measurements. Differences in the measured temperatures vs. speed were readily apparent, and later tests incorporated a thermocouple junction with less inertia.

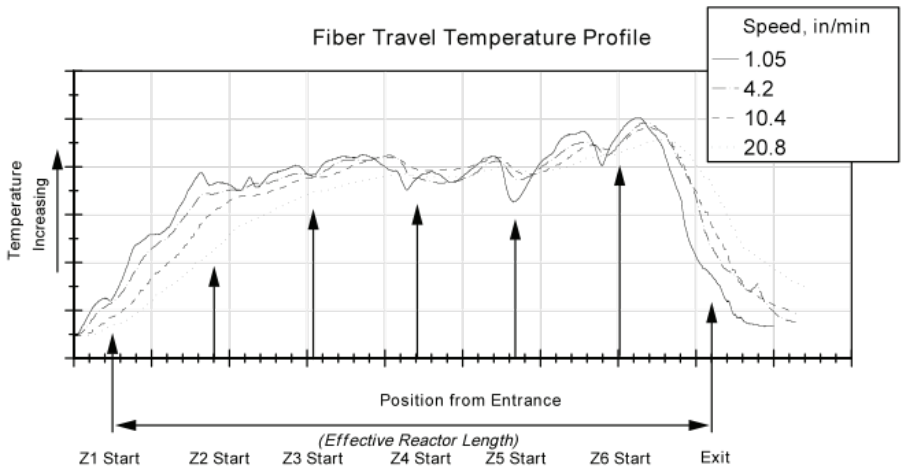


Figure 7. Temperature observed on the fibers while processing from entrance to exit of the reactor as a function of linear tow speed

The same test method was used to evaluate the temperature nonuniformity caused by gas injection. Figure 8 shows the measured axial temperature profile during gas injection, with the arrows indicating where the feed gas is being injected. While the previous data shows a relatively smooth progression of temperature, the new data shows sharp drops in temperature at the gas injection points. This issue will be addressed by redesigning the gas injection system.

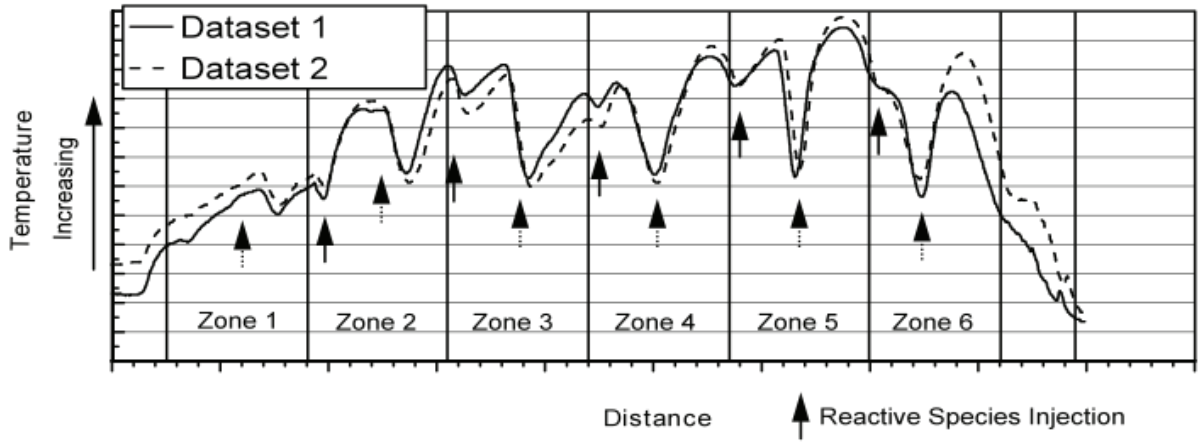


Figure 8. Axial temperature profile during gas injection

Figure 9 illustrates how the researchers believe the ideal axial temperature profile would appear based upon the pre-heating and post-heating sections, temperature profiles in the reactor, the level of reactive species along the reactor and past experience in processing with this type of equipment. To achieve this profile, we need to (i) improve the initial heating in region 1; (ii) make a smoother transition in region 2; (iii) increase the axial temperature gradient in region 3; (iv) develop a better defined temperature gradient in all regions which will eliminate or reduce sudden temperature shifts; and (v) moderate the cooling in region 5. Gentler temperature gradients will result in more uniform fiber processing, less fiber damage and more consistent final properties.

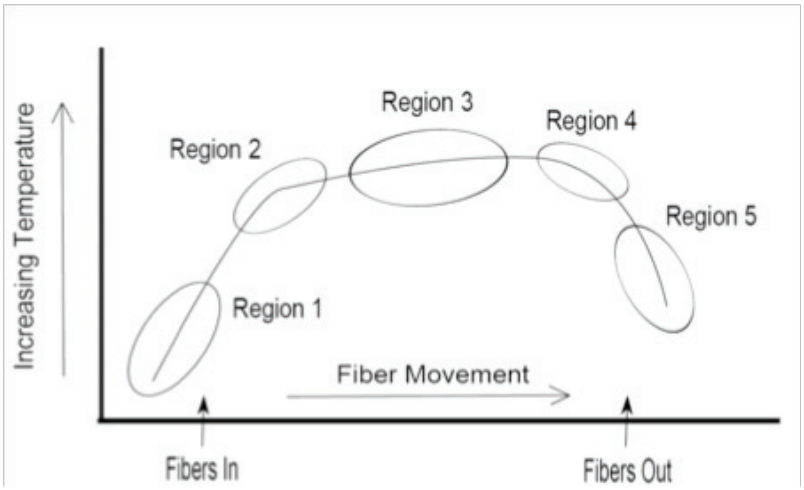


Figure 9. Ideal axial temperature profile

The concentration and spatial distribution of reactive species is the dominant parameter influencing the oxidized fiber properties. Measurement of this distribution is performed by pulling gas samples from the reactor at various fixed test points. Gas analyzers were used to allow for real time analysis of species concentration. Figure 10 shows average concentrations across the reactor, at various measurement points along the reactor length. The research team is currently working on approaches to improve the spatial uniformity of reactive species. Better processing can be achieved by a more uniform distribution of reactive species within each region of the unit both from entrance to exit of the region and also from side to side of each region. Failure to maintain uniformity will result in different tows being processed with different resulting properties simply due to their location.

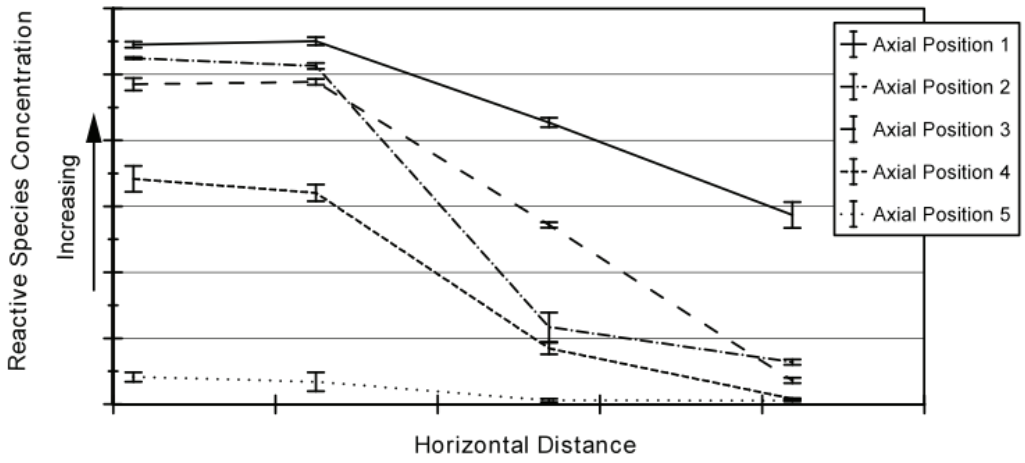


Figure 10. Reactive species concentration across the reactor at various axial locations

Oxidized fiber densities of >1.6 g/cc were previously achieved in the single-tow reactor (for reference, the commonly accepted optimal density of oxidized fibers is ~ 1.38 g/cc for the production of carbon fiber). When the multiple-tow reactor was first put into operation, densities greater than 1.28 g/cc could not be achieved. With consistent experimental work and analysis of data such as is presented in this report, discoveries led to the modifications previously mentioned and allowed the production of oxidized fiber with densities >1.4 g/cc. Parametric studies are now concluding related to all equipment input and output characteristics. From the results of this study, current equipment performance will be optimized and validated by evaluation of carbonized fibers produced using this method. By the end of FY2010, fiber properties are to be achieved which meet or exceed program requirements. The fibers will be oxidatively stabilized using the equipment and techniques developed in this project and then

conventionally carbonized. Fiber properties and processing conditions will then be evaluated to determine the economic viability of this process.

If satisfactory fiber properties and economics are achieved the next phase of this development effort will commence. That phase will consist of four main goals:

1. Develop the ability to use lower cost commodity grade carbon fiber precursors rather than aerospace grades.
2. Develop the ability to use larger tow precursors. Tows greater than 3K will be used with a goal to eventually process 24K tows.
3. Develop the ability for long term operation of the equipment without the need for frequent stoppages while simultaneously achieving consistency in fiber properties from location to location in the equipment (side to side) and along the length of the fiber.
4. Develop the ability to run larger numbers of tows simultaneously through the system. Since it is envisioned that this follow on phase will conclude with the design of a pre-production size unit, the goal will be to run six tows simultaneously.

For patent protection and export control reasons, detailed equipment design and process parameters are not published in DOE reports or the open literature, but they are periodically disclosed to the relevant program managers in oral briefings.

Future Direction

The future project direction will focus on improving the uniformity and control of reactor parameters; scaling to several large tows; achieving improved properties of carbonized fibers; oxidation of alternative precursors; process and equipment reliability; integration with other conversion process modules; and transitioning the technology to an industrial partner for ultimate commercialization.

Significant work remains to demonstrate the technology is adequately robust for eventual commercialization. Near term plans include demonstrating the ability to oxidize multiple large tows in ~1/2 of conventional residence time, with low variability in carbonized fiber mechanical properties; demonstrating that filament count and line speed are scalable by increasing equipment size, and demonstrating plasma oxidation scaling with non-conventional precursor (e.g., textile PAN, lignin, etc.). Key elements of these intermediate targets are continuing and advancing efforts to understand and utilize results of process stoichiometry investigations as a function of configuration adjustments, updating reactor and related hardware materials compatibility studies to capture longer-term operational experience, process conditions are continually optimized to assure that properties of plasma oxidized, conventionally carbonized tows satisfy or exceed program requirements, plasma oxidation of various formulations of textile PAN and/or other unconventional precursors are evaluated as available; and key economics drivers are reassessed, specifically residence time and energy demand per unit output.

At the conclusion of this project, the researchers will be positioned to procure, install, test, and operate a pilot scale plasma oxidation module in an advanced technology pilot line. The follow-on of this project will be the design and construction of the advanced technology pilot line that will then be installed in the Carbon Fiber Technology Center. It will be used to validate system performance and scalability as well as to produce the required quantities of advanced technology carbon fibers to support LM program's advanced development activities.

Conclusions

Plasma oxidation of PAN fibers continues to progress toward the goal of reducing the cost of CF manufacture. The ability to use the advanced oxidation method is being scaled from single filaments to small tows and satisfactory oxidative stabilization levels have been achieved. It has now been used to simultaneously produce multiple tows. To date, researchers have reduced oxidation residence time by about two-thirds compared to conventional oxidation. It is believed that further optimization is possible to reduce the residence time to ½ of that that is required by conventional thermal methods. Parametric studies are being conducted to bring this to fruition. Critical process and oxidized fiber characterization was conducted during this period, and scale-up began to receive significant attention with the completion and initial operation of the first multi-tow plasma oxidation reactor.

Patents and Publications

One new invention was disclosed from this project during this reporting period. Multiple articles based on the entire carbon fiber research work at ORNL were published in a variety of forums.

Investment in the Carbon Fibre Business for Commercial Grade Low Cost Composites; Proceedings of the Carbon Fibre 2008 Conference; September 30 – October 2, 2008; Hamburg, Germany.

Producing Low-Cost, High Volume Fibres for Commercial Applications; Proceedings of the Carbon Fibre 2008 Conference; September 30 – October 2, 2008; Hamburg, Germany.

Development of Lower Cost Carbon Fiber for High Volume Applications; Proceedings of the Composites + Polycon 2009 Conference; January 15-17, 2009; Tampa, FL.

Novel Precursor Materials and Approaches for Producing Lower Cost Carbon Fiber for High Volume Industries, Presented at and published in the proceedings of 17th International Committee on Composite Materials ICCM-17, July 27-31, 2009, Edinburgh, Scotland, UK.

Non-Traditional Precursor Materials and Conversion Approaches for Lower Cost Carbon Fiber for Multiple Industries, Presented at and published in the proceeding of the 17th International Conference on Composites/Nano Engineering, ICCE-17, July 25 – August 1, 2009, Honolulu, HI.

Low Cost Carbon Fiber Composites for Energy Applications, Presented at and published in the proceedings of the 2009 ASM/TMS Annual Symposium Materials Challenges for Alternative Energy, May 11-12, 2009, Niskayuna, NY.

Developing Lower Cost Carbon Fiber for Multiple High Volume Industries - Automotive, Wind Energy, Infrastructure, Ground-Based Defense, Gas Storage, Energy Production and Power Transmission, Keynote Address given at the SAMPE '09 Conference, 18-21 May 2009, Baltimore, MD.

High Volume Lower Cost Carbon Fiber for Multiple Industries – A National Initiative Critical to Maintaining US Leadership, Presented at and published in the proceeding of the 17th International Conference on Composites/Nano Engineering, ICCE-17, July 25 – August 1, 2009, Honolulu, HI.

Low Cost Carbon Fiber Composites for Energy Applications, at the 2009 Regional ASM/TMS Annual Symposium on Materials Challenges for Alternative Energy, 11-12 May 2009.

Development of Commodity Grade, Lower Cost Carbon Fiber-Commercial Applications, SAMPE Journal, 24(2), 2009, 24-36.

Education

Materials characterization has been conducted in partnership with the University of Tennessee's (UT's) materials science department. UT graduate students were engaged to provide characterization support to the project.

Partners

ORNL gratefully acknowledges contributions to this project by Hexcel and TohoTenax America. Both have generously provided raw materials and offered technical consultation. Additionally, technical and programmatic consultation has been provided by the Automotive Composites Consortium. We also acknowledge the research partnership with Sentech.

C. Precursor and Fiber Evaluation

Principal Investigator: Cliff Eberle
Oak Ridge National Laboratory
Oak Ridge, TN 37831-8048
(865) 574-0302; e-mail: eberlecc@ornl.gov

Principal Team Members:
Amit K. Naskar, Robert E. Norris, Jr., Soydan Ozcan, Felix L. Paulauskas, C. David Warren, and Kenneth D. Yarborough - Oak Ridge National Laboratory

Technology Area Development Manager: Dr. Carol Schutte
(202) 287-5371; e-mail:carol.schutte@ee.doe.gov

Field Technical Monitor: C. David Warren
(865) 574-9693; e-mail: warrencd@ornl.gov

Contractor: Oak Ridge National Laboratory
Contract No.: DE-AC05-00OR22725

Objectives

- Provide capability for production of small quantities of fiber or composite material samples.
- Provide capability to test the convertibility of alternate precursors and develop their conversion protocols.
- Provide capability to test new concepts that can potentially lower carbon fiber cost.

Approach

- Maintain and operate Oak Ridge National Laboratory's (ORNL) conventional pilot line for production of fiber or composite material samples.
- Maintain and operate ORNL's microwave-assisted carbonization unit for demonstration and materials sampling purposes.
- Maintain, upgrade, and operate ORNL's precursor evaluation system.
- Use the aforementioned facilities to test new concepts that can potentially lower carbon fiber cost.

Accomplishments

- Evaluated textile PAN, polyolefin, and proprietary precursors in the precursor evaluation system.
- Acquired new 1750 °C carbonization furnace, five-pass box oxidation oven to simulate the configuration and conditions of industrial oxidation ovens and acquired tensioning/stretching equipment for precursor evaluation system.

- Received and commenced installation of a 2500 °C furnace for precursor evaluation system.
- Constructed a storage mezzanine and began permanent relocation of precursor evaluation system into a larger laboratory space.

Future Direction

- Upgrade, operate, and maintain the facilities as needed to support Low Cost Carbon Fiber initiative.

Introduction

The purpose of this project is to perform the general evaluations that support the Low Cost Carbon Fiber (LCCF) initiative. The key aspect of this project is maintenance, intelligent upgrading, and wise use of the critical facilities that have been developed in previous or current projects. The use of these facilities includes evaluation of alternate precursor convertibility, production of fibers and/or composite specimens for evaluation by the Automotive Composites Consortium (ACC) and other interested parties, and new concept evaluations. The primary facilities supported by this project are the precursor evaluation system, the 1:20 scale conventional carbon fiber pilot line, and the microwave-assisted plasma (MAP) carbonization unit.

ORNL's conventional pilot line enables the production of order 1-10 lb/day of 50k tow. Therefore, it is useful for making small quantities of fiber for tow and composite evaluations. It can also be used to conventionally oxidize or carbonize tows that are partially converted by advanced processes. Minimum material requirements for evaluation on the pilot line are hundreds of feet of ≥ 1K tow, and startup time for the high temperature carbonization furnace is ≥ 10 hours.

The precursor evaluation system is designed to complement the conventional pilot line, in that it is designed for single-shift evaluation of very small precursor quantities. During precursor development, initial batches tend to be a few short filaments. The precursor evaluation system is useful for evaluating the feasibility of converting alternative precursors and then determining the process parameters for converting those precursors into carbon fibers. After the conversion process parameters are determined, the conversion protocols can be validated on the pilot line and evaluation quantities of fiber produced there. The precursor evaluation system can be used to convert a single filament or a single tow up to ~ 80k filaments.

The MAP carbonization unit was developed in the MAP carbonization project and continues to be maintained and operated for demonstration purposes. In the future, the current MAP carbonization unit will be the starting point for development of an advanced technology demonstration line.

Project Deliverables

The primary project deliverables are samples of converted carbon fibers or composite specimens fabricated from fibers converted at these facilities. Short lengths of tow or mechanical test data from converted fibers would be a typical deliverable from the precursor evaluation system. Small spools of fiber would be typical deliverables from the pilot line and MAP carbonization unit. On rare occasions, the deliverable may be a few kilograms of fiber or composites made from fiber converted at these facilities.

Current Status

The conventional pilot line, the MAP carbonization module, and the precursor evaluation system are currently operational. The precursor evaluation system was used to evaluate textile PAN, polyolefin, and proprietary precursors during the reporting period. A new project to develop polyolefin-based precursors has been started based on data from polyolefin precursor evaluations in the precursor evaluation system. The precursor evaluation system will be further utilized in the polyolefin precursor development project, especially in the project's early stages.

A 2500ºC water-cooled graphite tube furnace, shown in Figure 1, was received and its installation is ongoing in the precursor evaluation system. Precise pressure control over the cooling water has required the procurement and installation of a new pump system to isolate the furnace from the plant process water system's pressure, which could potentially be too high. The pressure isolation system procurement and installation was underway but not yet complete at the end of this reporting period. A new 1750ºC furnace was also procured for the precursor evaluation system and is shown in Figure 2. Other new capabilities include a five-pass box oven to simulate the configuration and conditions of industrial scale oxidation ovens (Figure 3), as well as transport, tensioning, and stretching equipment. This enables detailed evaluation of the effects of molecular orientation vs. thermal relaxation in the precursor fibers.

Figure 1. 2500ºC graphite tube furnace.

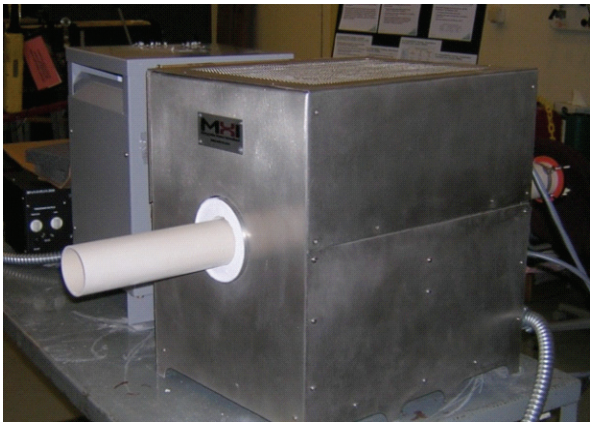


Figure 2. 1750ºC carbonization furnace.

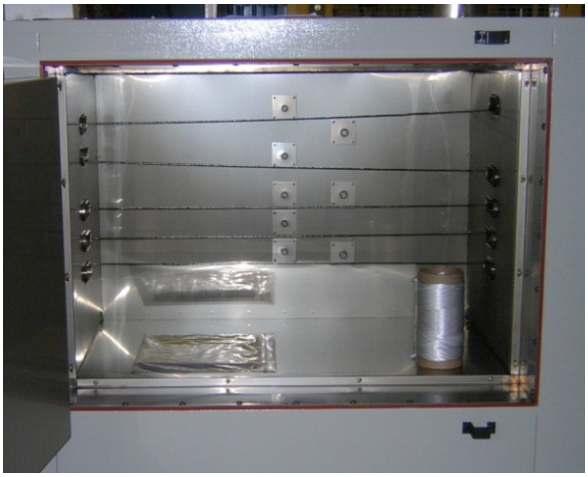


Figure 3. Five-pass oxidation oven.

A transparent oxidation oven that had been unavailable for an extended period was returned to service. Because it allows visual observation of the oxidation process, it is ideal for investigating the oxidation of a few filaments in the early stages of precursor evaluation.

With the continuing addition of new hardware and capabilities, the precursor evaluation system has outgrown the lab space in which it was housed. Therefore, in the last quarter of FY 2009 a mezzanine was constructed in ORNL's composites processing lab to increase the available lab space and we began relocating the precursor evaluation system into the larger space. At the end of FY 2009, the new lab space was not quite ready for permanent occupancy as adequate power was not yet available for all of the precursor evaluation equipment. We expect to complete permanent equipment relocation in the first half of FY 2010. Figure 4 shows the precursor evaluation system configured in the new lab space.

Figure 4. Precursor evaluation system configuration in new labo ratory space.

The conventional pilot line was used extensively for processing textile PAN. A "dancer" system to independently tension multiple tows (Figure 5) was installed in the pilot line. We also continued the development of specifications for equipment upgrades to add differential stretching to the conventional pilot line's oxidation module and increase its line speed. We were still finalizing plans for that upgrade at the end of this reporting period. No modifications were made to the MAP system during this reporting period. Its operation was frequently demonstrated for guests, and its potential deployment is a topic of interest to several prospective partners that visited ORNL during this reporting period.

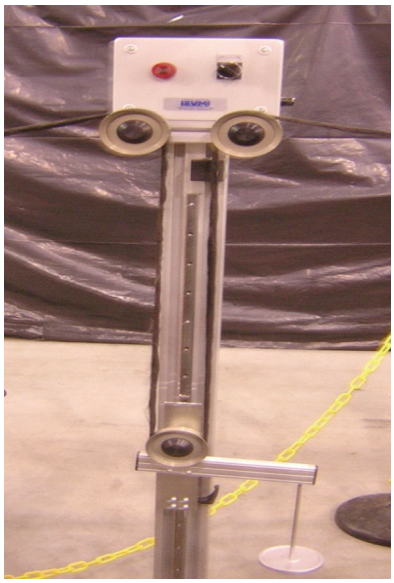


Figure 5. Dancing tension controller.

Projects those were benefited by use of the precursor evaluation system are summarized in Table 1.

Table 1. LCCF projects that utilized precursor evaluation system during FY 2009.

Projects	Project ID
Full Scale Development of Commercial Textile Precursors (PAN-VA) using Chemical Pretreatment – FISIPE	ALM-16622
Low-Cost Carbon Fiber from Renewable Resources	ALM-8987
Carbon Fiber Precursors from Polyolefins	ALM-18899
Corporate proprietary project-A	ORNL-CRADA
Advanced Oxidative Stabilization of Carbon Fiber Precursors	ALM-9442

Future Direction

The precursor evaluation system and pilot line continue to function as essential tools for the development and validation of new precursor technology, having been used for the initial evaluation and/or development of polyolefin, textile PAN, and proprietary precursors. Significant new capabilities have been acquired for the precursor evaluation system with installation underway, as well as equipment relocation to a more spacious laboratory. Important upgrades to the pilot line are in the specification stage. These facilities will continue to be maintained and operated as needed to support the development of Low Cost Carbon Fiber.

Conclusions

The precursor evaluation system, conventional pilot line, and MAP carbonization unit have been upgraded, maintained, and operated to continue the development of Low Cost Carbon Fiber.

D. Commercialization of Textile Precursors (FISIPE S.A.)

Principal Investigators: Felix L. Paulauskas and C. Cliff Eberle
Oak Ridge National Laboratory
Oak Ridge, TN 37831-8048
(865) 576-3785; e-mail: paulauskasfl@ornl.gov
(865)574-0302; e-mail: eberlecc@ornl.gov

Principal Team Members:
Cliff Eberle, Amit K. Naskar, Soydan Ozcan, C. David Warren, Kenneth D. Yarborough - Oak Ridge National Laboratory
Mohamed Abdallah - MGA Advanced Composites and Engineering
Ana Paula Vidigal - Paolo Correira, José Contreiras, FISIPE SA

Technology Area Development Manager: Dr. Carol Schutte
(202) 287-5371; e-mail:carol.schutte@ee.doe.gov

Field Technical Manager: C. David Warren
(865) 574-9693; e-mail: warrencd@ornl.gov

Contractor: Oak Ridge National Laboratory
Contract No.: DE-AC05-00OR22725

Objectives

- Develop textile based polyacrylonitrile (PAN) precursors for conversion into carbon fiber.
- Develop all processing parameters needed for conversion of textile PAN precursors.
- Scale-up FISIPE production facilities to commercially produce textile based carbon fiber precursor.
- Aid current and future carbon fiber producers in the incorporation of new textile precursors into manufacturing plants.
- Transfer time-temperature-tension profiles to users of alternate precursors. Assist in optimization of the manufacturing parameters.
- Produce small quantities of finished carbon fiber.

Approach

- Work with FISIPE S.A. to develop lower cost textile PAN precursors.
- Determine the time-temperature-tension conversion profiles for converting alternative precursors into carbon fiber.
- Work with potential carbon fiber manufacturers to incorporate the alternative precursors into current or future carbon fiber production facilities.
- Assist FISIPE with industrial scale-up, tow splitting and final product verification.

Milestone, Metrics and Accomplishments

- Initiated work on full scale development of a textile PAN precursor.
- Completed a technical evaluation of the pilot line and laboratory capabilities of Portuguese textile PAN fiber manufacturer FISIPE SA, and entered into a partnership with them to scale up and commercialize textile PAN precursor technology.
- Down selected a preferred textile PAN/VA chemical composition from among numerous candidate chemical compositions.
- Developed the conversion protocols for converting the textile precursor into carbon fiber.
- Incorporated chemical pretreatment into one of FISIPE's large production lines.
- Developed initial tow splitting technology for reducing tow sizes to 40,000 or 20,000 filament tows, in plant.
- Achieved current best fiber properties for strength of 388 KSI on full scale tows. Program requirement is 250 KSI.
- Achieved current best fiber properties for modulus of 34 MSI on full scale tows. Program requirement is 25 MSI.
- Met with Zoltek, Hysoung, SGL, Dupont, Great Lakes Carbon Fiber and others protected by secrecy agreements to scope out possible collaborative efforts to commercialize textile and lignin based precursors.
- Determined the apparent precursor aging issues did not negatively affect final carbon fiber properties.

Future Direction (If Further Funding is Received)

- Continue to optimize the FISIPE precursor processing conditions. Will require adding pre-stretching and tensioning to the pilot line to yield more precise fiber stretching during stabilization and oxidation.
- Pursue commercialization of lower cost precursors with current industrial carbon fiber suppliers.
- Evaluate potential collaboration with new entrants into the carbon fiber market.
- Incorporate textile precursors into Carbon Fiber Technology Center demonstration line.
- Scale-up textile precursor technology from pilot line scale to production line scale at the FISIPE plant in Portugal.

Introduction

During the past several years, the Automotive Lightweighting Materials (ALM) Program has been developing technologies for the production of lower cost carbon fiber for use in body and chassis applications in automobiles. Program requirements target materials that have tensile strengths in excess of 250 KSI and modulus of at least 25 MSI. Past work included the development of alternate, lower cost precursors and alternate, lower cost methods for manufacturing precursors into finished carbon fiber. The purpose of this project is to take one precursor technology, textile based polyacrylonitrile (PAN), from the technical feasibility, stage

and scale-up to manufacturability demonstration. The technology being pursued for the textile based precursor is the chemical modification of textile PAN containing vinyl acetate using a proprietary solution bath while the fiber is still in the un-collapsed state.

This project will result in the determination of the best concentration-temperature-exposure profiles to render the fiber carbonizable by conventional processes but also readily and inexpensively manufacturable in existing textile PAN plants. Successful completion of this project will result in a manufacturer being ready to sell to producers and ORNL providing to those producers specific instructions for precursor conversion, subject to export control limitations. Deliverables include spools of fully carbonized carbon fiber. As time and funding permit, the program researchers will work with future carbon fiber manufacturers to design factories and specify equipment for future carbon fiber lines.

Background

Previously, under a separate contract as part of the ALM program, Hexcel Corporation developed the basic science necessary to render textile based PAN polymers carbonizable. That science included subjecting the textile precursor to a chemical pretreatment bath while the fiber was still in the un-collapsed state. That work was conducted off-line from the textile fiber manufacturing. Fiber samples were split off from the line by hand, packaged and shipped to Hexcel's Decatur, Alabama plant for processing in their lab. Hexcel obtained satisfactory samples but under only one set of processing conditions and with one specific textile fiber. Certain issues needed to incorporate the technology into manufacturing plants were not addressed but are being addressed for vinyl acetate (VA) containing precursors in this project. They include:

1. How and when in the production line to split the precursor into manageable sizes that would be used by the automotive industry. A specific "standard" tow size of approximately 24,000 filaments is the current program goal.

2. Determination of the necessary chemical absorption required to create a sufficient shift in the DSC curves to render the precursor stabilizable in an acceptable amount of time. The shift in the DSC curves is tied to both the absorption of the pretreatment chemical by the fiber and the diffusion of the elements into the fiber.

3. Acceleration of the chemical prê-treatment to make the chemical treatment readily amenable to textile fiber production processes without slowing down the production process and thus adding cost to the precursor.

4. Design, manufacturing and installation of the chemical treatment equipment.

5. Determination of the required processing conditions for converting the precursor into finished carbon fiber. Early samples are being processed using ORNL's precursor evaluation equipment. Later materials are being processed using ORNL's 1/20th scale carbon fiber line and the precursor evaluation system. (Figure 1.)

Figure 1. Conventional pilot line installation at ORNL

6. Assistance is to be given to current and future users of the alternative precursors to help them specify equipment and design carbon fiber lines that will most efficiently convert the precursors into carbon fiber. The main goal is reduce the technical risk for incorporation of alternative precursors into the industry.

Items 1-5 have been completed and item 6 may be proposed as a commercialization effort.

Project Deliverables

At the end of this project, lower cost precursors will have been made from textile grade polyacrylonitrile in textile mills. The precursors will have been chemically pretreated and methods for converting them into carbon fiber will have been fully developed. The technology for accomplishing these activities will have been integrated into a commercial manufacturing facility. In order to accomplish the goal of commercialization the following tasks will have to have been completed:

- (C) Development of suitable formulations of textile PAN;
- (C) Development of chemical pretreatment methods for textile PAN;
- (C) Design and installation of chemical pretreatments in a textile plant;
- (C) Determination of time-temperature-tension processing profiles for textile PAN;
- (C) Determination of methods of splitting and/or maintaining splits in textile based precursors during the spinning process;
- (I) Development (if necessary) of alternate material formats that may be required by higher volume industries;
- (I) Assistance given to current and future carbon fiber manufacturers to incorporate alternative precursors into their manufacturing facilities;
- (C) Upgrades completed to pilot line to allow for more optimization of final carbon fiber properties from alternative precursors;
- (I) Upgrades completed to pilot line to allow for production of larger amounts of lab-scale produced fiber from alternative precursors;

Tasks that are already completed are indicated by (C) and those in-process are indicated by (I). Completion of these tasks should allow for the lowest risk commercialization of alternative precursors into conventional carbon fiber manufacturing facilities.

Current Status

ORNL has established a highly interactive and mutually beneficial partnership with a Portugese textile fiber manufacturer FISIPE SA, who produces vinyl acetate co-monomered PAN for textile applications. FISIPE is a high volume manufacturer who produces a commodity fiber that is roughly one-half the cost of conventional acrylic carbon fiber precursors. Our efforts are aimed at developing a chemical pretreatment to be added in their manufacturing line to render one of their textile formulations oxidizable and carbonizable and satisfactory as a carbon fiber precursor.

The first step in development of the precursor was to evaluate the DSC curves of more than 30 potential formulations that FISIPE made with a variety of proprietary additives. The onset of the exotherms, seen in the DSC curves, is indicative of the onset of stabilization and the steepness

of the curves and is indicative of the severity of the exotherm during oxidative stabilization. Less steep curves indicate a less severe exotherm which correspondingly could result in more rapid stabilization.

Once candidate precursors were selected, FISIPE installed a chemical treatment unit in their pilot line and began generating chemically pretreated samples. ORNL has conducted extensive characterization of chemically modified precursors and polymer samples generated by FISIPE, as well as conversion trials on filaments and tows generated by FISIPE from selected precursor chemical compositions. An example DSC characterization is shown in Figure 2. We have selected a preferred chemical composition that is the baseline for future work. By the end of FY 2007, FISIPE was making multiple spools of chemically treated 26.6k tow at 1 – 2 kg of fiber per spool. This fiber has subsequently been used for conversion trials in ORNL's precursor evaluation system and pilot line.

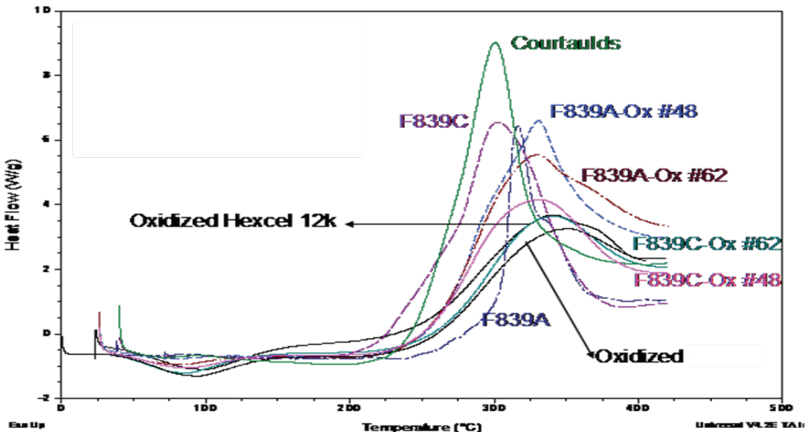


Figure 2. DSC characterization of various oxidized textile PAN precursor compositions, and comparison to oxidized commercial precursors. Final formulations are not shown for proprietary reasons.

The first step was to determine oxidation temperatures to obtain optimal processing conditions. This was done using the precursor evaluation line and measuring the oxidation density while targeting values that would be close to conventional carbon fiber precursors that were fully oxidized. Oxidized densities slightly higher than industrial grade precursors and slightly lower than aerospace grade precursors have been obtained.

Over the next several months, (the period of this report) ORNL has been using both the precursor evaluation line and the pilot line to determine time-temperature-tension processing profiles for the FISIPE precursor. Program requirements are to develop fibers with strengths of at least 250 KSI and moduli of at least 25 MSI. Figures 3 and 4, respectively, show the evolution of the strength and modulus during development of processing conditions over time. We have currently reached strengths of 450 KSI which exceeds program goals and are also well above program goals on modulus with a current value of 35 MSI.

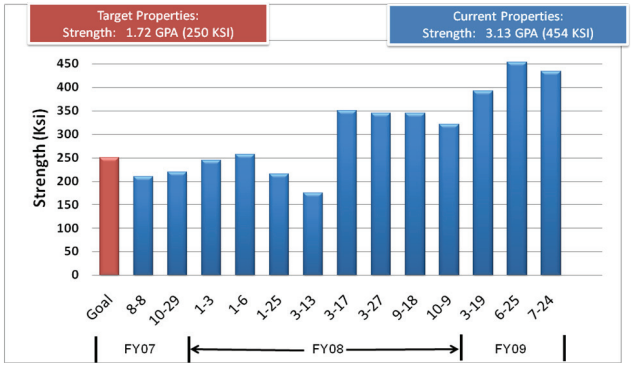


Figure 3. Obtained strength (KSI) of carbon fiber produced from FISIPE precursor during development of the processing protocol as a function of time.

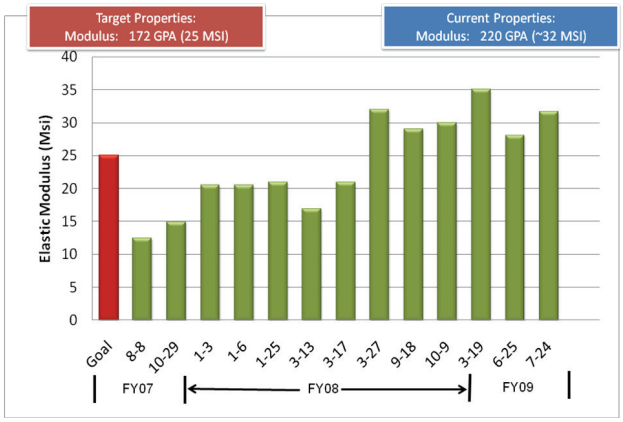
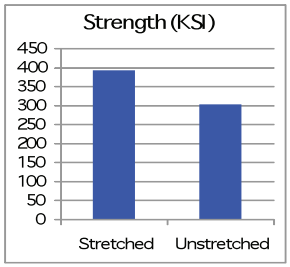
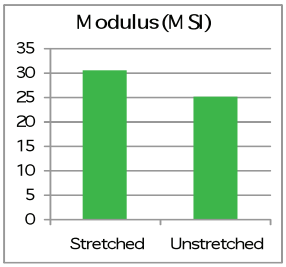


Figure 4. Obtained modulus (MSI) of carbon fiber produced from FISIPE precursor during development of the processing protocol as a function of time.

The addition of tensioning during upgrade of the pilot line was projected to yield significant improvement in the ability to align graphene planes and increase modulus. Figures 5A and 5B show the effects of adding tensioning during the preprocessing stages of production, just before the precursor enters the first oxidation oven. As can be seen from these figures, a significant increase in properties was obtained. If differential tensioning is added during the various oxidation stages, further increases in properties can be expected.





Figures 5A and 5B. The effects of pretensioning on the obtained strength (A) and modulus (B) of the FISIPE precursor.

Figures 6 and 7, respectively, show manufacturing of the carbon fiber on the precursor evaluation line and the resultant carbonized fiber tows.

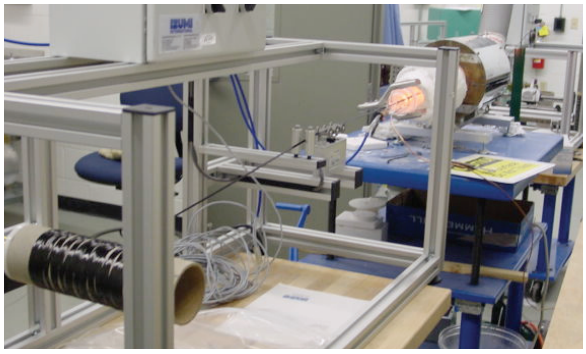
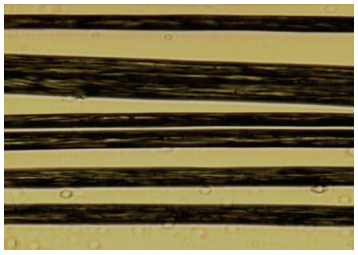


Figure 6. Processing of FISIPE precursor using ORNL's precursor evaluation line.

Figure 7. Carbon fibers produced from FISIPE precursor.



At the end of FY 2008, ORNL delivered spools of fully carbonized textile precursor based carbon fiber to Ford, General Motors and Chrysler meeting the program milestone and property requirements. Chemical pretreatment and tow splitting capabilities have been added to the FISIPE production line enabling them to enter the market as a precursor supplier.

Future Direction

This project terminated at the end of FY 2009 with all of the technical goals reached. The technical progress allows the precursor fiber to be produced from commercial grade PAN by adding only a few cents a pound to the production cost. Selling price of the precursor will depend upon market supply and demand. Complete commercialization will require the completion of several steps including:

1. Complete development of textile VA-PAN with FISIPE.
2. Begin development of MA-PAN with at least one company (preferable two - to eliminate the reliance on single source).
3. Optimize current precursor processing parameters.
4. Do preliminary work on processing of an improved precursor formulation based upon what was learned from the current work.
5. Assist carbon fiber manufacturers or potential manufacturers with the conversion protocol necessary to use textile precursors via a separate commercialization project.
6. Complete in-plant tow pre-splitting from 80K down to 20K or 40 K tows.

These activities will be the topic of discussion for potential future projects.

Conclusions

The development of vinyl acetate polyacrylonitrile textile precursors is well ahead of schedule. Strength values (450 Ksi) exceed program requirements (250 Ksi) and modulus values (35 Msi) are above program requirements (25 Msi). The chemical pretreatment equipment has been installed in the production facility and final verification of production quality material is being scheduled.

Presentations/Patents/Publications

1. Investment in the Carbon Fibre Business for Commercial Grade Low Cost Composites; Proceedings of the Carbon Fibre 2008 Conference; September 30 – October 2, 2008; Hamburg, Germany.
2. Producing Low-Cost, High Volume Fibres for Commercial Applications; Proceedings of the Carbon Fibre 2008 Conference; September 30 – October 2, 2008; Hamburg, Germany.
3. Development of Lower Cost Carbon Fiber for High Volume Applications; Proceedings of the Composites + Polycon 2009 Conference; January 15-17, 2009; Tampa, FL.
4. Novel Precursor Materials and Approaches for Producing Lower Cost Carbon Fiber for High Volume Industries, Presented at and published in the proceedings of 17th International Committee on Composite Materials ICCM-17, July 27-31, 2009, Edinburgh, Scotland, UK.

5. Non-Traditional Precursor Materials and Conversion Approaches for Lower Cost Carbon Fiber for Multiple Industries, Presented at and published in the proceeding of the 17th International Conference on Composites/Nano Engineering, ICCE-17, July 25 – August 1, 2009, Honolulu, HI.

6. Low Cost Carbon Fiber Composites for Energy Applications, Presented at and published in the proceedings of the 2009 ASM/TMS Annual Symposium Materials Challenges for Alternative Energy, May 11-12, 2009, Niskayuna, NY.

7. Developing Lower Cost Carbon Fiber for Multiple High Volume Industries - Automotive, Wind Energy, Infrastructure, Ground-Based Defense, Gas Storage, Energy Production and Power Transmission, Keynote Address given at the SAMPE '09 Conference, 18-21 May 2009, Baltimore, MD.

E. Commercialization of Low-Cost Carbon Fiber Composites and Carbon Fiber Precursors

Principal Investigator: Cliff Eberle
Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, TN 37831-8048
(865) 574-0302; e-mail: eberlecc@ornl.gov

Primary Participants:
Frederick S. Baker, Alexander G. DeTrana, Amit K. Naskar, Robert E. Norris, Jr.,
Felix L. Paulauskas, and C. David Warren - Oak Ridge National Laboratory

Technology Area Development Manager: Dr. Carol Schutte
(202) 287-5371; e-mail:carol.schutte@ee.doe.gov

Field Technical Monitor: C. David Warren
(865) 574-9693; e-mail: warrencd@ornl.gov

Contractor: Oak Ridge National Laboratory (ORNL)
Contract No.: DE-AC05-00OR22725

Objectives

- Achieve industrial scale deployment and commercialization of low cost carbon fiber composites technology.
- Produce small quantities of finished carbon fibers using the new precursors.

Approach

- Publicize Low Cost Carbon Fiber technology, especially by publication and presentation at selected conferences, symposia, and workshops.
- Identify prospective industrial partners and develop partnerships to commercialize low cost carbon fiber composites technology.
- Work with industry partners to establish technology development needs, exit criteria, and stage-gated transition strategy; continue executing technology development projects to pass through the stage gates.
- Develop an intellectual property portfolio and licensing strategy that delivers competitive advantage and profitability to commercialization partners while fostering marketplace conditions needed to achieve DOE goals.
- Provide the capability to develop and test conversion protocols for new polymer precursors.
- Provide the capability to melt spin low-cost precursor, and convert it by either conventional or advanced conversion processes, in volumes needed for material and process evaluations/ qualifications by end users and/or their suppliers.

Accomplishments

- Commenced evaluation of textile polyacrylonitrile (PAN) precursor made on full-scale textile fiber line by Portuguese partner and fiber manufacturer FISIPE SA.
- ORNL staff participated in several conferences, chaired one international conference on carbon fibers and made featured presentations at multiple conferences. Additionally, a member of ORNL's carbon fibers research team serves as the Carbon Society's 2008/2009 Graffin Lecturer, and delivered five invited lectures in that capacity.
- ORNL terminated negotiations with one prospective partner for the development and commercialization of lignin-based fibers, when it became evident those mutually agreeable terms, consistent with the DOE program goals, would not be reached. ORNL is in continuing discussions with other prospective partners.
- ORNL hosted an international Workshop on Low Cost Carbon Fiber Composites for Energy Applications on 3-4 March 2009, attended by seventy-eight representatives from industry and government.
- ORNL continues to identify and engage prospective commercialization partners. ORNL has engaged at a significant level with over 30 companies that were exploring a potential partnership.
- ORNL has commenced developing an integrated portfolio valuation and licensing strategy for low cost carbon fiber composites intellectual property.

Future Direction

- Conduct an educational workshop at the Carbon Fiber 2009 conference in San Diego.
- Continue scaling textile PAN precursor with FISIPE as one piece of the overall low-cost carbon fiber technology development and transition strategy.
- Continue outreach efforts at conferences, symposia, and other strategic venues.
- Continue the development of partnerships on low cost carbon fibers and composites.
- Capture and maintain momentum generated by the Workshop on Low Cost Carbon Fiber Composites for Energy Applications. Follow up on relationships and strategies that resulted from the workshop.
- Develop partnerships to address fiber spinning. Work with those partners to develop the capability to spin low-cost precursor, and convert it by either conventional or advanced conversion processes, in volumes needed for material and process evaluations/qualifications by end users and/or their suppliers. Again this is one part of an overall low-cost carbon fiber technology development and transition strategy.
- Negotiate and execute multiple (vertically integrated) partnerships to complete development of low cost carbon fiber composites technology and commercialize it into multiple industries.
- Broaden the low cost carbon fiber composites funding base beyond the DOE-EERE Vehicle Technologies Program to create an integrated low cost carbon fiber composites program with financial support spanning multiple offices or agencies.

Introduction

During the past several years, the DOE-EERE Vehicle Technologies Program has been developing technologies for the production of lower cost carbon fibers for use in body and chassis applications in automobiles. Program requirements target materials that have tensile strengths in excess of 250 KSI and modulii of at least 25 MSI. Past work included the development of alternate, lower cost precursors and alternate, lower cost methods for manufacturing precursors into finished carbon fibers. The purpose of these projects is to take low-cost precursor technologies from the technical feasibility stage and scale up to a manufacturability demonstration with conventional conversion. Likewise, the advanced conversion processes under development are being initially developed with conventional precursors, but will ultimately be developed for alternate precursors.

The technologies under development must be successfully transitioned and achieve widespread, high volume commercial use to realize the mission goals of the DOE-EERE sponsor. The new materials and processing methods under development in this program are now reaching a sufficient level of maturity that commercialization is on the horizon for the more mature technologies.

Project Deliverables

The ultimate deliverable of this project is the successful transition to commercial application of low cost carbon fiber composites into multiple high volume passenger automobile platforms produced and sold in the US. In the most optimistic scenario, this goal is many years away. Therefore other important deliverables on the path to that goal include: (i) the creation of formal partnerships focused on achieving the commercialization of low cost carbon fiber composites; (ii) demonstration of low-cost carbon fiber technology scalability; and (iii) providing low-cost carbon fiber samples to OEM's and their suppliers in sufficient quantities for material and process evaluation/qualification.

Current Status

- ***Textile PAN Fibers***

ORNL has established a highly interactive and mutually beneficial partnership with Portuguese textile fiber manufacturer FISIPE SA, which produces textile PAN fibers with an inexpensive co-monomer. FISIPE is a high volume manufacturer that produces a commodity fiber that is roughly one-half the cost of conventional acrylic carbon fiber precursors. The current project is aimed at developing, scaling, and commercializing a chemical pretreatment for the FISIPE manufacturing line that will render one of its textile formulations oxidizable and carbonizable and thus satisfactory as a carbon fiber precursor. During FY08, satisfactory formulations were developed on FISIPE's pilot scale precursor fiber line, and were then converted into carbon fibers at ORNL with mechanical properties exceeding the program requirement. During FY09, FISIPE began scaling to its full-scale production line and recently delivered to ORNL for evaluation the first textile grade precursor fibers it had made at full production scale. The FISIPE effort is a separately funded project. Outreach to commercialize the results of that project is conducted under this effort.

- ***Lignin-Based Fibers***

ORNL continues the development and work towards commercialization of lignin-based precursors. For many months, ORNL and DOE conducted extensive discussions with a large U.S. company regarding potential collaboration on developing and commercializing lignin-based precursors and carbon fibers made from them. In the last half of FY2009, it became evident that

mutually agreeable terms that were consistent with DOE program goals could not be reached. Negotiations with this company were therefore terminated. Several other companies have also expressed interest in lignin-based precursors and fibers, and the ongoing discussions include the development of strategies for developing multiple complementary partnerships and/or projects.

- ***Outreach***

ORNL publicizes its work by publication in the open literature and presentations at conferences, symposia, workshops, and other selected venues. During this reporting period, ORNL staff participated in multiple relevant conferences, chaired one international conference on carbon fibers and delivered featured presentations at multiple conferences. Additionally, a member of ORNL's carbon fibers research team serves as the Carbon Society's 2008/2009 Graffin Lecturer and delivered five invited lectures in that capacity.

ORNL continues to identify and engage prospective commercialization partners with interests in any or all of the technologies under development. At the conclusion of this reporting period, ORNL has engaged at a significant level (hosting a visit or receiving substantial project support) from over 30 companies that were exploring a potential partnership. Most of them are currently in active discussions or a higher level of engagement. A small number of companies have indicated intent to locate staff in ORNL's Science and Technology Park. We also anticipate broadening the low cost carbon fiber composites funding base beyond the DOE-EERE Vehicle Technologies Program to create an integrated low cost carbon fiber composites program with financial support spanning multiple offices or agencies. For example, we have won a small project funded by DOE-EERE's Wind and Water Program, and have also begun developing plans to work with DOE-EERE's Industrial Technologies Program to develop energy-efficient manufacturing technologies that cross-cut multiple industries and EERE Programs.

- ***Workshop on Low Cost Carbon Fiber Composites for Energy Applications***

On 3 – 4 March 2009, ORNL hosted a technology development scoping workshop that addressed low-cost carbon fiber reinforced composites for energy applications. Specifically, the workshop goals were to

- Develop information on the research, development, and demonstration needs for government and industry to reduce the cost of carbon fiber reinforced composites; and
- Identify market issues and challenges for widespread deployment and manufacturing scale-up of these composites; and
- Examine implementation approaches to support future activities that would address the needs, issues, and challenges identified.

Experts in a broad range of end-use industries as well as both technical and business representatives from all aspects of the carbon fiber and composite materials value chain were invited to provide insight on commercialization challenges of these materials. Seventy-eight people attended the workshop, including representatives of the wind, oil and gas, marine, automotive, and aviation industries; DOE; other national laboratories; universities; carbon fiber manufacturers; precursor providers; carbon fiber conversion equipment manufacturers; and composite materials manufacturers.

Workshop attendees were provided a common contextual framework through a series of opening presentations on current carbon fiber and composite materials production and manufacturing processes; current market potential; advanced manufacturing and processing technologies under development; and an overview of technology applications and markets in the wind and automotive industries as well as general industrial applications. The attendees then formed into small break-out groups to consider specific topics.

1. Research, development, and demonstration (RD&D) needs
2. Identification of key RD&D activities to address needs
3. Market issues and challenges
4. Identification of key deployment and scale-up activities to address market issues and challenges
5. Implementation approaches

There were three technical breakout groups and one business breakout group. All three technical breakout groups addressed topics 1, 2, and 5 above. The business breakout group addressed topics 3, 4, and 5.

- ***Summary of Workshop Findings***

Technical Breakout Groups

The three technical groups stressed that a systems approach is needed to achieve lower cost carbon fiber composites. Diversity of application is a challenge that can best be overcome by interaction and cooperation between disciplines and industries.

RD&D needs identified by all three groups were

1. Alternative and/or new lower cost precursor materials and processes.
2. Faster processes and technologies for fiber conversion.
3. Reduced composite parts manufacturing cycle time.

Additional RD&D needs identified as important to lower cost carbon fiber were

1. Fundamental knowledge of precursor structure-property relationships.
2. Optimization of fiber-resin interface
3. Modeling of the fiber production and composite manufacturing processes.

Two of the groups identified key activities supporting development of precursor material and processes; a common finding was that a pilot line is needed in the mid-term (1-4+ years) capable of handling multiple precursors. A pilot line was also indicated for feasibility and processing scale-up of advanced fiber conversion processes. Only one group quantified resource requirements; that group estimates approximately $30M to address alternative and/or new lower cost precursor materials and processes.

Business Breakout Group

This group identified cost, return on investment (ROI), risk reduction, and standards development as key market issues and challenges. Key activities to reduce cost and improve ROI were identified as improving manufacturing technologies and “leaning” the value chain through identification of key technologies and processes, establishment of cost/quality/performance goals by market segment, and developing a technology process improvement plan. Ensuring material availability will reduce the effects of price fluctuations, and may be achieved in part through materials diversity. Other issues noted were regulatory barriers and over-specification.

- ***Implementation Approaches***

All breakout groups were asked to consider the advantages and disadvantages of at least three implementation approaches: a national demonstration facility; horizontally integrated technology

development and deployment (i.e., at specific points within the value stream); and vertically integrated technology development and deployment. Common findings are listed below.

National Demonstration Facility

Advantages

1. Risk mitigation.
2. Resource sharing, critical mass of expertise.
3. Capability to evaluate and compare materials and processes.

Disadvantages

1. Hard to get long-term funding commitment because of the large capital investment required.
2. May be underutilized over time and if inadequately funded.
3. Concentration of talent in fiber spinning and conversion; not able to have all important technologies located at facility.

Horizontal Integration

Advantages

- Focuses on key technologies, high-potential points in value chain.
- Lower risk: secures intellectual property, increases chances of success on specific items.

Disadvantages

- Incremental, only a small jump forward.
- A non-systems approach, not looking at all possibilities and interactions.

Vertical Integration

Advantages

- Connects supply chain to market.
- Feedback mechanism for system improvement; ability to learn from failures.

Disadvantages

- Significant coordination needed: determining who will pay; different requirements from different industries and stakeholders; requires a paradigm shift in industry thinking (not the "normal" way of doing things).
- Doesn't guarantee scale-up, risk of having minor impact across a broad industry.

One of the groups proposed a fourth, two-phase implementation approach. Phase I would be a modular facility focusing on technology validation and verification at pilot scale. Phase II would scale up to full production volume (estimated 1,000-ton line) focusing on technology application to end uses. Funding would be shared by industry and government; this approach would require commitment from all parties. Advantages of this approach include risk mitigation and industry involvement in moving toward domestic large-scale production. Disadvantages include high capital investment and perceived threat by the carbon fiber industry.

The workshop generated tremendous awareness and interest in low cost carbon fiber composites. ORNL, DOE, and their partners are engaged in follow-up discussions with several of the workshop participants. One workshop finding that has generated substantial further discussion is the need for a facility with the capability to spin precursor fibers from various candidate precursor materials, and convert them into finished fibers, with sufficiently high output volume to satisfy the material and process qualification demands of end users.

- *Intellectual Property Management*

Intellectual property management is invariably a high priority topic in partnership discussions. To date, we have fielded a small number of formal inquiries and numerous informal inquiries about licensing low cost carbon fiber composites intellectual property. Our interactions with many prospective partners suggest that successful commercialization will require us to deliver to the industrial partner(s) a competitive advantage based on intellectual property created in the research program. Thus we are carefully creating and managing the low cost carbon fiber composites intellectual property portfolio, which currently contains well over twenty distinct intellectual properties and continues to grow. This is one of ORNL's largest intellectual property portfolios. ORNL has commenced developing an integrated portfolio valuation and licensing strategy that is focused on achieving DOE's mission goals for this technology. ORNL's Technology Transfer Department is leading the intellectual property management, with extensive engagement by program and research staff.

Future Direction

ORNL will continue to execute the research program, engage prospective industrial partners, and develop the facilities necessary to successfully commercialize low cost carbon fiber composites. We anticipate the creation of multiple partnerships, probably with a high degree of vertical integration, as well as broadening the funding base to create an integrated low cost carbon fiber composites program with financial support spanning multiple offices or agencies. Partially as a result of the Workshop on Low Cost Carbon Fiber Composites in Energy Applications, DOE issued a solicitation for a low-cost carbon fiber composites technology demonstration facility at a DOE laboratory. In early FY10, it was announced that the facility will be located at ORNL. ORNL will use this facility as a major cornerstone of its transition strategy, leveraging it to create partnerships and to give those partners the technological and business confidence needed to foster technology commercialization.

Conclusions

Low cost carbon fiber composites are reaching a level of maturity that is beginning to attract significant industrial interest in their deployment and commercialization. Textile PAN Precursor is in its final stage of development and will soon be ready for commercial deployment. While considerable work remains to be done on other low cost carbon fiber composites technologies, they are now sufficiently mature to generate substantial industrial interest in their commercialization. ORNL hosted a government-industry Workshop on Low Cost Carbon Fiber Composites in Energy Applications, which has created significant momentum and opportunity for developing strategic partnerships. We are now engaged in discussions with several prospective partners and are developing an intellectual property management strategy to enable effective partnership and commercialization that meets DOE goals. ORNL is also identifying the additional equipment and facilities needed to enable successful commercialization, and working toward development of those capabilities.

Presentations/Patents/Publications

1. C. David Warren and Felix L. Paulauskas, “Investment in the Carbon Fiber Business for Commercial Grade Low Cost Composites,” Proceedings of the Carbon Fiber 2008 Conference, Hamburg, Germany, September 30–October 2, 2008.
2. Felix L. Paulauskas and C. David Warren, “Producing Low-Cost, High Volume Fibers for Commercial Applications,” Proceedings of the Carbon Fiber 2008 Conference, Hamburg, Germany, September 30–October 2, 2008.
3. C. David Warren, “Development of Lower Cost Carbon Fiber for High Volume Applications,” Proceedings of ICCM-17, 27-31 July 2009
4. Felix L. Paulauskas et al., “Novel Precursor Materials and Approaches for Producing Lower Cost Carbon Fiber for High Volume Industries,” Proceedings of the Composites + Polycon 2009 Conference, Tampa, Florida, January 15–17, 2009.

F. Carbon Fiber Precursors from Polyolefins

Principal Investigator: Amit K. Naskar
Oak Ridge National Laboratory
PO Box 2008; Oak Ridge, TN 37831-6053
(865) 576-0309; e-mail: naskarak@ornl.gov

Technology Area Development Manager: Dr. Carol Schutte
(202) 287-5371; e-mail: carol.schutte@ee.doe.gov

Field Technical Manager: C. David Warren
(865) 574-9693; e-mail: warrencd@ornl.gov

Team Members:
Christopher J. Janke, Rebecca H. Brown, Soydan Ozcan, Cliff Eberle, Felix L. Paulauskas, Frederick S. Baker, C. Dave Warren, Fue Xiong, Ronny D. Lomax, and Kenneth D. Yarborough - Oak Ridge National Laboratory

Contractor: Oak Ridge National Laboratory
Contract No.: DE-AC05-00OR22725

Objectives

- Develop polyolefin-based fiber that can be rendered infusible prior to carbonization.
- Demonstrate accelerated stabilization via an economic chemical route.
- Obtain carbonized fiber from the stabilized precursors by developing optimal conversion parameters.
- Characterize the carbon fiber and show that the mechanical properties are satisfactory for future product development in automotive applications.
- Estimate the cost of polyolefin-based carbon fibers and show that they are likely to satisfy program cost metrics.
- Demonstrate the technology at pilot scale and transition it to industry.

Approach including industrial partner/collaborator and path to technology transfer and commercialization

- Modify polyolefin resin without affecting the melt-rheology and generate fibers with appropriate diameter using conventional melt processing.
- Develop a fast stabilization method suitable for the produced precursor fiber. The stabilization method should chemically modify the precursor fiber and increase the softening point.
- Design, construct, and operate a reactor for stabilization of the precursors in ≤ 1 hour of residence time.
- Conduct carbonization runs under various operating conditions and optimize processing parameters.

- Characterize fibers to confirm that they satisfy program requirements.
- Commercialize the technology with different industrial partners that manufacture melt-spinning equipment and produce polyolefin resins.

Milestones, Metrics and Accomplishments

- Established partnership with a commercial melt-spinning equipment manufacturer for trial of required fiber spinning and optimization of design specifications for the equipment (FY'09).
- Produced precursor fibers of varied compositions and different diameter ranges (≤15 μm). (FY'09)
- Completed batch mode stabilization work. Commenced work on semi-continuous mode fiber stabilization. (FY'09)
- Demonstrated possibility of accelerated stabilization (significantly faster, ~ 5x, than the previously reported results). (FY'09)
- Tailored mechanical properties of the precursors (10-20 KSI tensile strength) and characterized batch stabilized fibers. (FY'09)
- Commenced partnership discussions with potential polyolefin suppliers. (FY'09)

Future Direction

- Obtain polyolefin fibers with diameters low enough (comparable to PAN fibers, 10-15 μm) to ensure faster stabilization (<1 h) and demonstrate accelerated stabilization.
- Set-up a precursor stabilization module, preferably in semi-continuous mode.
- Demonstrate carbonized fiber properties ≥250 KSI strength and ≥25 MSI modulus (by FY'12).
- Understand the carbonization process and optimize carbon yield (50-70 %).
- Explore non-traditional stabilization methods for the polyolefin precursors.
- Scale and transition the technology.

Introduction

The goal of this project is to develop the technology for production of low-cost carbon fiber from melt-spun polyolefin precursor fibers. Fuel-efficient, light-weight vehicles based on carbon-fiber reinforced composites are necessary to minimize global petroleum consumption and CO_2 emission. Currently, common commodity grade carbon fibers are produced from polyacrylonitrile (PAN) based precursors. PAN-based textile precursors are a potential candidate for low-cost carbon fibers with the projected costs savings being around $2.00 per pound for finished carbon fiber. Currently, however, there are no domestic producers of textile PAN, so supply and price stability may become an issue. Textile fibers are solution-spun and the manufacturing process deals with multiple unit operations such as coagulation, washing and stretching, drying, and solvent recovery to produce the precursors. Also, in solution spinning, the mass (solid) throughput rate is significantly less than that of the relatively simpler conventional melt-spinning process. Polyolefin-based fibers (polyethylenes and polypropylene) are industrially produced in United States and are very low-cost commodity plastic fibers ($0.50 - 0.75/lb). The cost of precursor

fibers from polyolefin is projected to be less than half of that of the PAN based precursor fibers. Since polyolefin fibers are melt-spun, a stabilization route needs to be developed to render the precursor fibers infusible prior to carbonization.

Lignin-based carbon fiber precursors are another potential option for low-cost carbon fiber. However, to date no commercial manufacturer of lignin precursor fiber is established globally. Lignin-based fiber suffers from handling issues. The most attractive feature for considering polyolefin as carbon fiber precursor is its very high carbon content (~86%) in comparison to that of the PAN based fibers (68%) or lignin based fibers (67%).

In the past, conversion of polyolefin precursors was attempted by a few research groups via chemical functionalization of the precursor fibers [1]. Although the reported practical carbon yield was very high (~78%) for the polyolefin fibers, in comparison to that of the PAN based fibers (~50%), the residence time requirement in the stabilization step was very high. Recently, ORNL researchers have developed a potentially patentable conversion technology for polyolefin precursors that requires less than one hour stabilization time and enables direct carbonization without any further oxidation step. Critical technical criteria of this technology includes: (1)≥ 25 MSI tensile modulus, > 250 KSI breaking strength and ≥ 1.0% ultimate strain in the finished fiber; (2) uniform properties along the length of the fiber tow; (3) repeatable and controllable processing; (4) and significant cost reduction compared with other precursor options.

Project Deliverable

At the end of this project (in FY'12), the project team will have developed a composition of polyolefin precursor that can be produced with small diameter filaments and will have characterized the rheological and melt-spinning conditions for modified polymers. The team will have identified parameters for efficient and accelerated stabilization of melt-spun polyolefin fibers and designed a stabilization module (reactor) for processing said precursors. The team will have produced spools of carbonized fiber with tensile properties at least 250 KSI ultimate strength and 25 MSI modulus.

Technical Approach

Novel conversion technology is being developed at ORNL for production of carbon fiber from low-cost, melt-processible polyolefin precursors. The details of the technical approach are shown in a flow-diagram below (Figure 1).

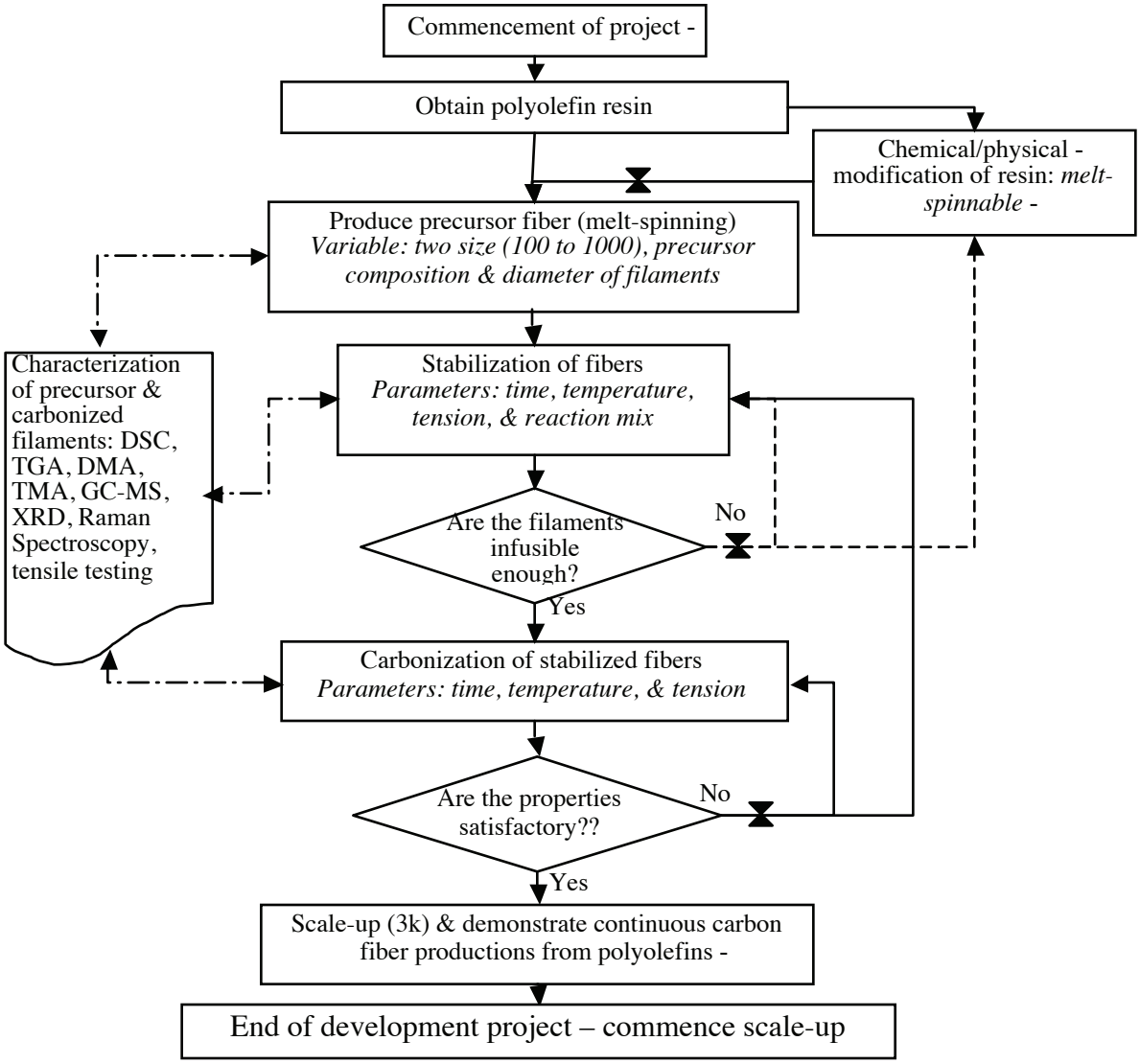


Figure 1. Flow-diagram of the proposed research on polyolefin-based carbon fibers.

Polyolefins are attractive alternative carbon precursors because of their low cost and high carbon yield.

During FY 2009 initial conversion conditions were explored. A route that is significantly faster than the previously reported stabilization routes for polyolefins has been developed at ORNL. The precursor fibers were melt-spun from neat and modified resin using standard melt-spinning equipment at a US-based melt-spinning equipment manufacturer's facility. Melt-spun precursor fibers with varied diameter (8-15 μm) and varied orientation parameters were produced.

Stabilization of the as-spun fibers was explored in a batch reactor with varied residence times. The stabilized fibers successfully produced carbon fiber. As shown in Figure 1, the optimization of conversion parameters for the polyolefin precursors required several iterations of stabilization and carbonization runs with varying conditions.

Progress

Due to proprietary reasons, the public nature of this report and export control regulations the detailed technical discussion is not included in this progress report. Those detailed information are periodically reported to the program managers, partners, and program monitors in compliance with the export control restrictions.

Precursor Generation

The extrusion studies revealed insignificant variation of melt-viscosity of the modified resins. Ten different spools of neat polyolefin and modified polyolefin fibers were produced using a commercial melt-processing device. Photograph of the representative spools is shown in Figure 2. In the preliminary series of samples, tensile properties of the representative filaments were determined. As expected, the fiber properties (tensile strength and modulus) improved with increase in draw ratio. The tensile stress-strain profiles of a few samples are displayed in Figure 3.

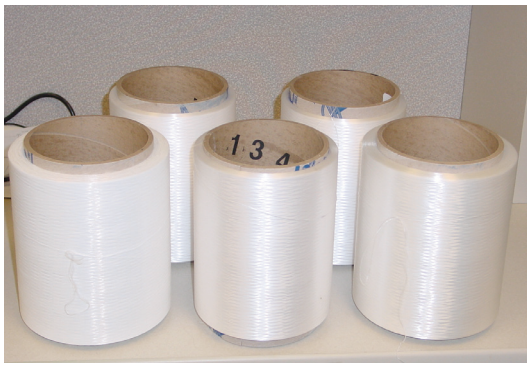


Figure 2. Spools of polyolefin fiber.

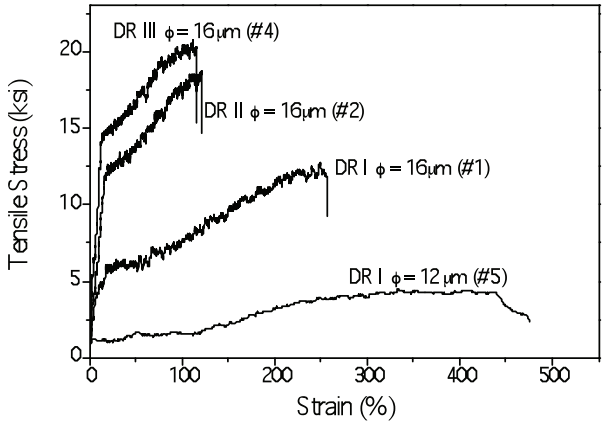


Figure 3. Tensile stress-strain profiles of different polyethylene fibers.

Stabilization and Carbonization

A stabilization reaction that was found in preliminary experiments and a method for chemical crosslinking of polyolefin was adopted for these fibers. The resulting stabilized fibers did not show a melting endotherm (i.e., crystallinity was completely eliminated for practical purpose). Representative

DSC scans of stabilized fibers under different conditions are displayed in Figure 4. Elimination of crystallinity in polyolefin was required to render the filaments infusible. The time requirement for such a stabilization method is significantly less than is required for PAN-based textile filaments. In a few early experiments with carbonization of the stabilized precursors, less than optimal carbonized fibers were obtained. Based on these experiments, im-proved-quality stabilized fibers were obtained that could be carbonized without filament breakage.

SEM micrographs of some of the early carbonized filaments are displayed in Figures 5a-b. Incomplete stabilization caused hollow carbon fiber. However, adequate stabilization (with stabilization time <1 h) eliminated hollow core formation during carbonization.

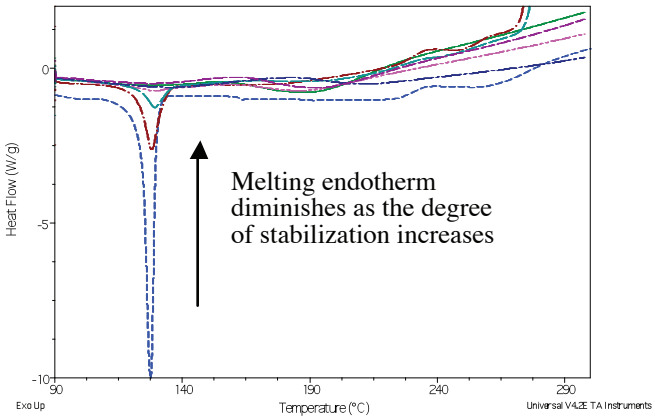
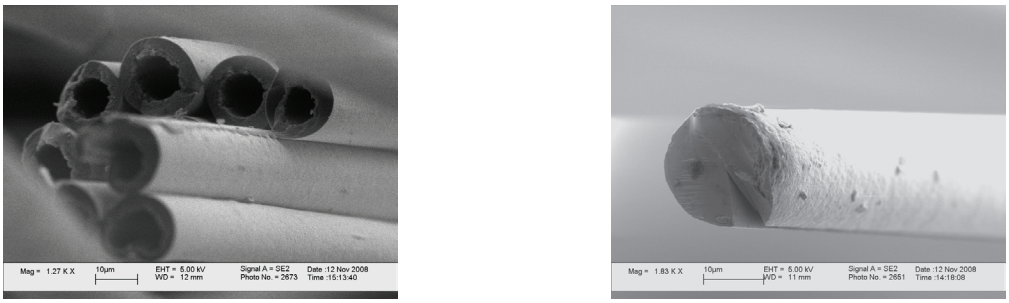


Figure 4. DSC scans of various stabilized filaments showing gradual elimination of melting endotherm.



(b) (a)

Figure 5. SEM micrographs of polyolefin-based carbon fibers.

Evolved gas analysis during pyrolysis of stabilized fibers was conducted to understand the stabilization and carbonization chemistry. Due to proprietary reasons those results are not reported here.

Future Direction

To date the researchers have demonstrated accelerated stabilization of polyolefin precursor fibers. Earlier work by other researchers produced carbonized fiber with moderate strength and modulus (380 KSI & 28 MSI); however it required prolonged stabilization (6-10 h). In this work it has been demonstrated that stabilization can be achieved within 1 h period. However mechanical properties were low (110 KSI & 8 MSI) and that could be either due to nature of the precursor fiber or lack of tension during stabilization and carbonization. A tension controlled stabilization protocol is being developed. During the FY10, the polyolefin research will primarily focus on obtaining 150 KSI strength and 15 MSI modulus property targets. The functionalization route that is being followed is a significantly modified version of the procedure followed by other researchers. The ORNL method is about 5 times faster than the other methods. During fast functionalization molecular relaxation happens, and the properties deteriorate if the relaxation is not controlled. In FY'10 the team's goal is to find out reasons of molecular relaxation and to demonstrate continuous processing. The team expects to produce carbonized fibers with 150 KSI strength and 15 MSI modulus. However, next year (FY2011) the goal is to increase the properties to 200 KSI and 20 MSI. It is anticipated that at the end of FY'12 researchers will be able to demonstrate target properties (250 KSI and 25 MSI). During this period attempts will also be made to demonstrate semi-continuous processing for the stabilization of the precursors.

Education

Six high school students (sponsored by Appalachian Regional Commission) were mentored by the team during last summer at ORNL for their exposure to high performance materials, especially carbon fibers. Students tested single filament properties of the precursor fibers.

Partners

ORNL gratefully acknowledges the partnership with Hills, Inc., Melbourne, FL on precursor fiber melt-spinning (subcontract).

Conclusions

Polyolefin precursor fibers (modified and unmodified) have been produced for stabilization and conversion studies. Tows (288 filaments) with different draw ratios and filament diameters (8-15 μm) were produced. Accelerated ($t < 60$ min) stabilization of polyolefin fiber has been demonstrated. Carbon yield as high as 70% were obtained from the stabilized fibers. Optimization of precursor processing parameters for production of low-cost carbon fiber is underway.

Presentations/Publications/Patents

Three invention disclosures have been made so far relevant to polyolefin precursors. ORNL intends to file a patent in the near future. No publication has been made. No presentations.

References

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)

G. Conventional Interfacial Optimization of Reinforcement Fibers for Polymeric Systems

Principal Investigator: Felix L. Paulauskas
Oak Ridge National Laboratory
PO Box 2008; Oak Ridge, TN 37831-6053
(865) 576-3785; e-mail: paulauskasfl@ornl.gov

Principal Investigator: Soydan Ozcan
Oak Ridge National Laboratory
PO Box 2008; Oak Ridge, TN 37831-6053
(865) 241-2158; e-mail: ozcans@ornl.gov

Principal Team Members:
Amit K. Naskar, Cliff Eberle, Chris Janke, Kenneth D. Yarborough, Ronny Lomax, and Fue Xing - Oak Ridge National Laboratory
Truman Bonds - Sentech
Professor Roberto Benson and Tiffany Flick - University of Tennessee

Technology Area Development Manager: Dr. Carol Schutte
(202) 287-5371; e-mail:carol.schutte@ee.doe.gov

Field Technical Manager: C. David Warren
Oak Ridge National Laboratory
(865) 574-9693; e-mail: warrencd@ornl.gov

Contractor: Oak Ridge National Laboratory
Contract No.: DE-AC05-00OR22725

Objectives

- Develop carbon fiber post treatment technique for low-cost carbon fibers making them compatible with automotive resin systems.
- Develop and optimize surface treatment methods on an industrial scale and do so with technologies that are readily implementable in current carbon fiber and composite production plants.
- Develop corresponding sizings which feature a suitable chemical affinity between carbon fibers surface treated using developed treatment technique and selected automotive matrix resins.
- Demonstrate the target interlaminar shear strength in composites (8.5 ksi or more) using the developed surface treatment techniques and sizing treatments.

Approach

- Develop in-line gas phase surface treatment for carbon fiber.
- Conduct parametric studies to correlate surface treatment parameters, fiber surface characteristics and manufactured composite properties.

- Determine the optimum surface treatment applicator design that minimizes the residence time and maximizes the load transfer efficiency at the lowest cost.
- Characterize fibers to confirm that they are not damaged by the after surface treatment.
- Determine and tailor the sizing chemistry to achieve optimal interaction between the carbon fibers and resins to promote the adhesion between fibers and the polymer matrix in composites.

Accomplishments

- Strategic research partnerships were established with automotive part manufacturers and a university (Magna International Inc. and General Motors Company and the University of Tennessee).
- Low cost carbon fiber sources have been secured (textile-based Fisipe S.A. and commodity-type Zoltek Companies, Inc.) and first set of fibers have been received.
- Continuous operation gas phase surface treatment applicator has been designed and built.
- Evaluation of as-received fibers has begun to establish the baseline data.

Future Direction

- Continue characterization effort and establish baseline data.
- Conduct parametric studies to correlate surface treatment parameters, fiber surface characteristics and manufactured composite properties.
- Establish partnership with industrial chemical company to engage for developing of corresponding sizing chemistry and following commercialization effort.

Introduction

The purpose of this project is to develop surface treatment techniques and sizings for textile-based and commodity-type carbon fibers that are amenable to the resin systems of interest to the automotive industry. These particular types of carbon fibers were chosen because they currently are the lowest cost carbon fibers available to the automotive industry and are projected to remain so for the foreseeable future. Via partnerships with current carbon fiber manufacturers and sizing producers, it is planned to develop technologies that can readily be incorporated in today's manufacturing lines with minimal disruption. The sizings are to be compatible with selected thermoset resin systems (i.e., different sizings) of interest to current automotive original equipment manufacturers using current or near-term commodity- and textile-based carbon fibers.

Carbon fiber is currently sized and surface treated for only a few aerospace resin systems. When automotive part designers try to use it in non-aerospace resin systems, the result is poor carbon-resin adhesion, poor load transfer and thus poor composite properties. There are new carbon fibers becoming commercially available from new, lower cost precursors and ultimately new processing technologies. These still will not yield good composite properties unless they are properly surface treated and sized. Post-treatment technology is highly proprietary to the few carbon fiber suppliers in the world and is usually targeted at epoxy resins. Development of non-epoxy surface treatments and sizings is critical to the incorporation of lower cost carbon fibers into automotive structural materials.

The ORNL effort is to develop standard post treatments for carbon fibers, with a specific focus on commercial, commodity-type and textile-based carbon fibers. Post treatments include surface treatments and sizings that are applied to carbon fibers after carbonization. These post treatments determine how well the fibers bond to matrices, which in turn control or significantly affect many mechanical composite properties. Surface treatment and sizing will affect the interfacial bonding between the fiber and the polymer matrix which will impact the following composites properties.

- Axial and transverse tensile strengths and stiffness
- Axial and transverse compression strengths and stiffness
- In-plane and interlaminar shear strength and stiffness
- Interlaminar fracture toughness for Modes I, II and III
- Delamination
- Impact
- Manufacturing residual stresses
- Creep and fatigue resistances
- Resistance to environmental effects on the reduction of the mechanical and physical properties.

Benefits

- Optimized interfacial bonding improves the mechanical properties and therefore reduces the quantity of carbon fiber required to meet designed targets.
- Improved adhesion at the carbon/fiber interface will enable the fabrication of thinner parts with comparatively higher mechanical performance results for weight reduction and cost savings.
- Development of post treatment technology addressing low cost carbon fiber will accelerate the utilization of low cost carbon fiber precursors and Lightweighting composite applications.
- Specialty post-treatment recipes targeting resin systems of interest to automotive and other emerging high volume industries will allow the incorporation of more carbon fiber composites and their associated Lightweighting benefits.

Technical Approach

Present common practice is to surface treat finished fibers (carbon or graphite, depending on degree of graphitization) in an electrochemical bath. After surface treatment, the fibers are sized with a water-borne polymer (usually epoxy) by immersion in a sizing bath. The current tendency in the manufacture of carbon fiber is to stay away from commonly used electrochemical surface activation due to the effluents generated. A secondary effluent post-treatment is needed to eliminate emissions before discharge to the environment. Additionally, the electrochemical method features a sequence of discrete processing steps making this process complicated, difficult, and more prone to process failure.

This projects focus is on developing ozone-based surface treatments which are clean and require minimal steps. The ozone surface treatment process requires only an ozone generator, a piping

system, and an ozone applicator where the ozone will interact with the carbon fiber and is easily implemented in the manufacturing plant. A simplified flow diagram of this project is shown in Figure 1.

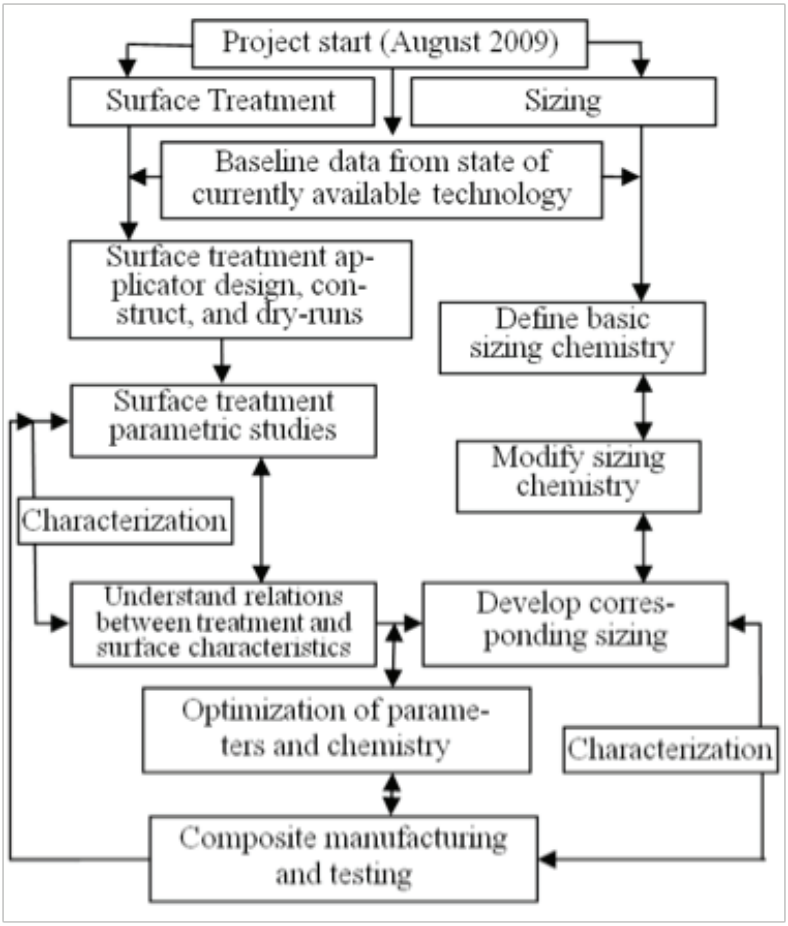


Figure 1. Flow-diagram of the technical research approach.

In the course of this project, scientists at ORNL will also investigate various polymer blends, catalysts, and additives as a means for improving the sizing strength, toughness, and reactivity between the fiber and matrix resin in a partnership with an experienced chemical company.

Progress

This project is a two-year effort divided into two project years spanning most of FY 2010 and FY 2011. Due to the high priority nature of the effort, initial work was began in the fourth quarter of FY 2009 and the progress during that time period is limited to formation of partnerships, selection of materials, procurement of test fixtures and finalization of the test matrix. The project team has started by establishing strategic partnerships with low-cost fiber manufacturers, automotive composite part manufacturers, polymeric resin matrix producers and a university. By the guidance of Materials Technology Team and the other project partners, vinyl ester based resin system has been chosen as a target polymeric matrix due to its widespread use and key constituent in sheet molding compound (SMC). Surface treated and sized low-cost commercial carbon fibers along with unsized, untreated carbon fibers were manufactured and delivered by Zoltek Companies, Inc. Fisipe S.A. manufactured low cost textile based PAN precursor fibers to be converted to carbon fiber at ORNL. A Master of Science (MS) student has been assigned to work for the project in the Department of Materials Engineering at University of Tennessee. The first characterization studies of fibers have been started.

Project Deliverable

At the end of this project, the project team will developed ozone-based surface treatment technology and corresponding sizing compositions that are optimized for the selected automotive resin systems. The team will identify the surface treatment parameters and demonstrate composite interlaminar shear strength of 8.5 ksi or more at the end of FY 2011.

Future Direction

The researchers will establish a strategic partnership with an expert chemical company to develop corresponding sizings. Baseline data will be collected and the interface properties between carbon fibers and matrix will be optimized to achieve optimum composite properties by following the systematic proposed research approach. The research effort will continue in close relationships with all project partners.

Presentations/Publications/Patents

Soydan Ozcan, Felix Paulauskas; “Surface Compatibility” Composite World Conferences; Carbon Fiber 2009; San Diego, CA; December 9-11, 2009

Education

The Department of Materials Engineering at University of Tennessee has been engaged in part of the project. A M.S. student has been assigned to work for the project and his M.S. thesis will be prepared under the supervision of Professor Roberto Benson.

Partners

ORNL gratefully acknowledges the partnership of Magna International Inc., General Motors Company, Sentech Inc., Zoltek Companies Inc., Fisipe AS., and University of Tennessee.

Conclusions

A development effort has begun to optimize the interfacial performance of carbon fiber composites for use in the manufacturing of automotive parts. With widespread industrial and university partnerships, this project will develop standard post treatments for carbon fibers with a specific focus on commercial commodity-type and textile-based carbon fibers. Post treatments include both surface treatments and sizings that are applied to carbon fibers after carbonization. Vinyl ester based resin systems were chosen to be the first target polymeric matrix which is interest of automotive part manufacturers.