

7. LOW-COST CARBON FIBER

A. Low-Cost Carbon Fiber from Renewable Resources

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Objective

- Carbon-fiber resin composite materials could substantially reduce the weight of passenger vehicles, increase vehicle fuel economy, and result in lower CO₂ emissions. Carbon fiber have the potential for substantial weight saving in vehicles because of their remarkable high strength, high modulus, and low density; each 10% reduction in vehicle weight would translate into an increase in vehicle fuel economy of about 6%, with concomitant reduction in emissions. To place the potential increase in fuel economy into perspective, body-in-white (BIW) modeling indicates that over 60% of the steel in a vehicle could be replaced with carbon-fiber composite materials without impacting vehicle crashworthiness. However, carbon-fiber is currently too expensive for large-scale automotive use, which necessitates a large reduction in cost of appropriate-strength fiber from about \$20/lb to about \$5/lb. 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. 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 range of \$3-5 per pound. In addition to precursor, cost savings will also be achieved through advanced processing techniques, including plasma oxidation (see 7.D), carbonization (see 7.E) and graphitization of the precursor fiber, to obtain more efficient utilization of energy resources.

Approach

- 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 database necessary to facilitate commercial production of lignin-based carbon fiber, including knowledge in the following respects:
 - Isolation and purification of lignin to obtain appropriate precursor properties for carbon-fiber production.
 - Melt-spinning technology, including extruder and spinneret configuration, spinning conditions, co-polymers, and plasticizing agents.
 - Thermal processing of precursor fiber into carbon fiber.
 - Advanced processing of lignin-based carbon fiber.
 - Mechanical properties of lignin-based carbon fibers.
 - Surface treatment and sizing technology for relevant resin systems.

- Economics of lignin purification and processing of precursor fiber into finished carbon fiber.
- Development of intellectual property for the production of lignin-based carbon fibers.

Accomplishments

- Proof-of-concept demonstration of the melt-spinning of lignin precursor fiber, utilizing lignin materials isolated from the Kraft chemical pulping of hardwood (for paper production) and the Organosolv pulping of hardwood (for lignin production), respectively.
- Proof-of-concept demonstration of the thermal processing of lignin-based precursor fiber into carbon fiber.
- Demonstration of melt-spinning of 28-filament lignin fiber tow from Kraft hardwood lignin (in collaboration with the University of Tennessee); melt-spinning not sustainable for any significant length of time because of impurities in the lignin.
- Development of a laboratory-scale procedure for purification of Kraft hardwood lignin to target specifications; production of 14 lb of purified lignin for melt-spinning studies through repetitive lab-scale runs.
- Proof-of-concept demonstration of melt-spinning of purified Kraft hardwood lignin fiber using polyethylene terephthalate (PET) as a copolymer to plasticize the purified lignin.
- Demonstration of the lab-scale production of (single) carbon fiber meeting 60% of the target engineering properties; thermal processing temperature limited to maximum 1200°C, too low for structure development.
- Development and demonstration of a scaleable procedure for purifying Kraft hardwood lignin to target specifications using an organic solvent-extraction approach; production of multi-kg batches of the purified lignin for melt-spinning studies.
- Construction, installation, and commissioning of custom-designed, multifilament melt-spinning equipment in ORNL research facility for low-cost carbon-fiber (LCCF) research.
- Demonstration of continuous melt-spinning and winding of 12-filament tow from the solvent-extracted lignin (SEL) over a sustained period of time (5 hours) without interruption; establishment of the relationship between winding speed (drawdown ratio) and filament diameter; demonstration of production of 10-micron-diameter, defect-free, lignin precursor fiber; spinning of target-diameter fiber at almost 70% of the preliminary target speed of 600 meters/minute.
- Proof-of-concept demonstration of cross-linking (stabilization) of SEL fiber through ultraviolet (UV)-irradiation at ambient temperature.

Future Direction

- Development of a technically- and economically-viable process for the commercial production of industrial-quality carbon fiber from lignin feedstock. Key tasks will include:
 - Identification of sources of lignin suitable for carbon-fiber production and establishment of conditions for purification of lignin to the desired specifications (as needed for specific sources of lignin).
 - Procurement of a large batch (100 lb +) of purified lignin from at least one source for carbon-fiber process development work.
 - Selection of appropriate copolymers and/or plasticizing agents as needed to facilitate melt-spinning of precursor fibers from specific sources of lignin.
 - Design of extruder and spinneret die to obtain high spinning speed of target-diameter fiber with good internal structure.
 - Development of techniques for spooling and rewinding of lignin-based precursor fiber tow.
 - Establishment of conditions for continuous melt-spinning of lignin fiber tow at speeds of at least twice the preliminary target of 600 meter/minute.
 - Establishment of conditions for batch-scale thermal processing of lignin-based precursor fiber into carbon fiber meeting target engineering properties

- Establishment of conditions for continuous thermal processing of lignin-based precursor fiber tow into carbon fiber.
- Identification of methods for surface treatment of lignin-based carbon fibers to enhance compatibility with relevant resin systems.
- Production of a suitable quantity of finished, lignin-based carbon fiber for composite testing by the Automotive Composites Consortium (ACC).
- Collaboration with industrial, government, and academic partners to:
 - Clearly establish sources of lignin suitable for carbon-fiber production, including lignin derived from the production of ethanol fuel from biomass resources; e.g., waste wood and switchgrass.
 - Resolve any outstanding issues regarding the isolation and purification of lignin from different sources.
 - Address knowledge gaps with respect to the use of recycled polymers as alloying agents for melt-spinning of lignin-based precursor fibers.
 - Complete identification of melt-spinning conditions and fiber-winding technology for continuous production of lignin-based precursor fiber tow.
 - Demonstrate carbon-fiber production from lignin-based, multifilament tow using a pilot-scale process line.
 - Achieve target engineering properties of lignin-based composite materials incorporating lignin-based carbon fibers (with the ACC).
 - License and transfer lignin-based carbon-fiber production technology to industry.

Introduction

The Department of Energy (DOE) FreedomCAR-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. The objective of the FreedomCAR project is to develop more energy-efficient, cost-effective processes for production of carbon fibers for use in composite materials for vehicles, which would substantially reduce vehicle weight, increase vehicle fuel economy, and result in lower CO₂ emissions. For example, each 10% reduction in vehicle weight would translate into an increase in vehicle fuel economy of about 6%, with concomitant reduction in emissions. 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, BIW modeling indicates that over 60% of the steel in a vehicle could be replaced with carbon-fiber composite materials without impacting vehicle crashworthiness. However, carbon fiber is currently too expensive for large-scale automotive use, which necessitates a large reduction in cost of appropriate-strength fiber

from about \$20/lb to about \$5/lb, and the supply 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; therefore, emphasis in the ORNL research work is being placed on the development of processes utilizing low-cost precursor materials, notably textile-grade PAN and lignin, a renewable resource material.

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 from the chemical pulping of wood for paper production (using either the Kraft or soda processes), the lignin by-product 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.

Currently, chemical pulping of wood is the only immediate 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 Organosolv pulping of wood, the first step in cellulosic ethanol production, has already 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.

Lignin is one of the main components of all vascular plants and the second most abundant polymer in nature (after cellulose). It is an amorphous, polyphenolic material arising from the enzymatic dehydrogenative polymerization of three phenyl propanoid monomers, namely, coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol. The biosynthesis process leads to the formation of a complex, three-dimensional polymer that lacks the ordered, repeating units found in other natural polymers such as cellulose and proteins. Lignin plays a significant role in the carbon cycle, sequestering atmospheric carbon into the living tissues of woody perennial plants. It fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components of wood. It is covalently bound to hemicellulose and thereby crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall and thereby to the plant as a whole.

An example of the complex structure of lignin is shown in Figure 1 for lignin isolated from beech hardwood. Hardwood lignin is composed of coniferyl alcohol and sinapyl alcohol units in varying ratios, whereas softwood lignin predominantly comprises coniferyl alcohol (> 90%) and a small proportion of *p*-coumaryl alcohol. Because it is almost impossible, certainly very difficult, to isolate lignin from wood without degradation, the true molecular weight of native lignin is a subject of debate. However, the weight-average molecular weight of softwood lignin isolated by mechanical milling of the wood (low-degradation process) is about 20,000. Milled hardwood lignin exhibits significantly lower molecular weights. These and other differences between the chemistries of hardwood and softwood lignins influence the utilization of lignin for carbon-fiber production.

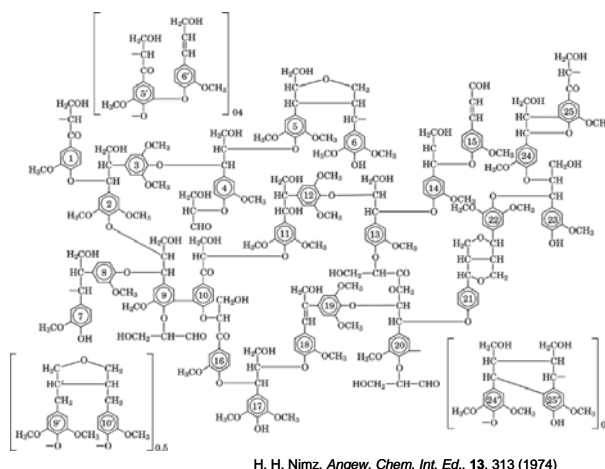


Figure 1. Chemical structure of hardwood lignin.

Depending on species, lignin comprises about 15-25 wt% of wood, compared to about 38-48 wt% cellulose (on a dry-wood basis); switchgrass has a similar content of lignin. Thus, wood and switchgrass contain significant amounts of lignin (about half of the proportion of cellulose), which if utilized for the production of value-added products, such as carbon-fiber, could effectively offset the high cost of producing cellulosic ethanol from biomass (a relatively small proportion of the lignin would be used as a fuel in the ethanol-production process). 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).

Worldwide, over 200 million metric tons of lignin passes through pulp mills annually, of which about 1.2 million tons are isolated for the production of lignin-based products. Lignin is not a waste product of the pulp-and-paper industry, but a co-product that is utilized in modern, highly-integrated pulping operations as a fuel (and reducing agent) in the pulping chemicals recovery process (it has about 70% of the calorific value of #2 fuel oil). In fact, many modern mills have co-generation facilities to produce electrical energy for sale to utility companies.

Lignin is already utilized in transportation applications on a large scale, for example, as

emulsifying agents for asphalt road surfaces. Similarly, it is used as a dispersing agent for cement and concrete mixes, much of which is utilized in the construction of roads. 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. Other large-scale uses include textile dye dispersants; oil-drilling muds; pesticide surfactants; sequestrants for micronutrients (agricultural and forestry uses); water treatment for boilers and cooling systems; and binders for plywood, particle board, fiberglass insulation, and animal feed.

Use of Lignin for LCCF Production

The majority (> 90%) of carbon fiber is currently produced from PAN precursor fiber, which is made using a wet (solvent-based) process. This first unit operation of carbon-fiber production is one of the most intensive operations of the overall process, involving many stages of washing to remove residual traces of solvent which would otherwise adversely impact carbon-fiber properties, especially of the high-end and expensive-grade fibers for aerospace applications (upwards of \$150/lb). The associated solvent-recovery and purification operations also add to the complexity and cost of PAN precursor fiber production. Melt-spinning of a precursor fiber is much preferred over the wet-spinning process, but currently is only utilized in the spinning of pitch-based carbon-fibers, which account for a relatively small proportion of worldwide carbon-fiber production. PAN cannot be melt spun, at least as formulated to achieve the engineering requirements of PAN-based carbon-fibers, because it rapidly decomposes close to its melting point.

Certain types of lignin, notably hardwood-derived, can be melt-spun providing that the contaminants in lignin isolated from the “black liquor” in chemical pulping operations can be substantially reduced to acceptable levels. Impurities include non-melting particulates (clays and sand, which block the very fine holes in the spinneret), inorganic salts (e.g., sodium sulfate), rosin, and residual carbohydrates (both in the form of fibers

and bound to the lignin). The contaminated hardwood lignin could be melt-spun in principle, but the spinning operation could not be maintained for any useful length of time to produce continuous fibers before the spinneret was blocked. Also, the contaminants in the spun fibers degrade the engineering properties of the carbon-fiber subsequently produced from the small quantities of lignin fiber. Nevertheless, the demonstration that even single carbon fibers could be produced from lignin was an encouraging development and represented a milestone achievement in the project.

A dedicated effort in earlier carbon-fiber project work at ORNL led to the development of laboratory-scale techniques to purify Kraft lignins to the targeted levels. Ironically, purification of the lignin, notably hardwood lignin, rendered the lignin non-melt-spinnable because the melting point of the lignin was raised above its decomposition temperature. Chemically-pulped lignin is a heterogeneous material that includes a wide range of molecular weights, etc., and it is the presence of some of the lowest molecular weight fractions that appears to impart melt-spinnability to the hardwood lignin as a whole. Unfortunately, the lower molecular weight lignin fractions, which in essence serve as plasticizing or alloying agents for the higher molecular weight fractions, were selectively removed during the purification process.

Thus, solutions to this unexpected challenge had to be found, which included the development of alternative methods of purifying the lignin to retain its desirable properties for melt-spinning. This was tackled on several fronts, including the funding of fundamental work at Pacific Northwest National Laboratory (PNNL) and the collaborative efforts of several large paper manufacturers, notably MeadWestvaco (MWV, Charleston, SC), the only current producer of Kraft lignin-based products worldwide. At the same time, work was also implemented to identify suitable plasticizing agents for purified lignins, including softwood lignin that, because of its chemistry, is not readily melt-spinnable. These efforts led to the development of a radically different process for purifying lignins, both hardwood and softwood and, more significantly, the first demonstration (in fiscal year [FY] 2007) of continuous and

uninterrupted spinning of multi-filament lignin fiber 'tow' over a period of many hours.

To support the efforts on the lignin-based carbon-fiber project, melt-spinning equipment was custom designed and built for the project, and installed at ORNL. The equipment, shown in Figure 2, is the main workhorse for establishing appropriate process conditions for melt-spinning of lignin fiber tows and for producing precursor fiber for thermal processing into carbon-fiber. The equipment includes a draw frame which permits fibers to be tensioned and hot-stretched through a series of rollers to both obtain the desired filament diameter and to help align the molecular structure of the precursor fiber to facilitate development of the desired engineering properties during the subsequent processing to carbon fiber.

Before attempts are made to melt-spin a lignin material on this equipment, however, it is characterized with respect to its rheological properties, most notably its viscosity and thermal stability at temperatures close to its melting point (above and below). Thermal-analysis measurements are carried out to determine the glass transition temperature (T_g) and melting point of the lignin, as well as the temperature range for carbonization of the lignin and yield of carbon, a very important factor with respect to the economics of carbon-fiber production. When an acceptable understanding of the fundamental properties of a candidate lignin material has been obtained, it is examined for melt-spinnability on small, single-fiber spinning equipment. If a candidate lignin shows promise for fiber spinning, it is examined on the larger and more effort-intensive, multi-filament spinning equipment. It is on this equipment that the process boundary limits will be defined for a given lignin and larger quantities of precursor fiber produced for processing into carbon fiber.

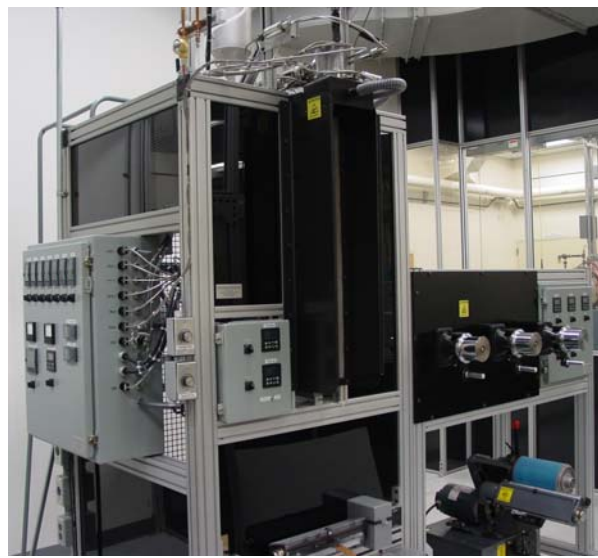


Figure 2. Multi-filament melt-spinning equipment

Lignin Purification and Fiber Spinning

As noted earlier, a laboratory-scale process was developed at ORNL to purify Kraft hardwood lignin to the required level. However, the laboratory process was not readily scaleable to either pilot-scale or commercial production and, therefore, a joint program of work was implemented by PNNL and MWV to develop an economically-viable process for lignin purification (based on the ORNL findings). As laid out in the timeline and tasks for the project, PNNL would focus on the use of combinatorial chemistry techniques to examine the key variables of the proposed process to establish appropriate processing conditions, MWV would scale-up the PNNL findings to produce larger samples of purified lignin for melt-spinning studies and perform the economic analysis of the proposed process, and ORNL would carry out the melt-spinning studies.

The first approach to lignin purification at PNNL using an aqueous method proved to be problematic, and MWV was unable to scale-up the process and furnish the purified lignin needed by ORNL to move its lignin-based carbon-fiber efforts forward. To overcome this hurdle in the short-term, MWV agreed to re-examine an alternative approach to the purification of Kraft lignin that had been investigated by the company (Westvaco) several years earlier, namely, extraction of the lignin with organic solvents to dissolve the lignin components away from the

insoluble salts, carbohydrates, and other impurities, which essentially is the opposite approach to the aqueous method.

Early in the fourth quarter of FY 2007, a small sample of the SEL was received from MWV. The rheometry measurements made on the material indicated that it exhibited the desired viscosity-temperature-time relationships and that it should be readily melt-spinnable. Examples of the rheometry test data are shown in Figure 3, in which the stability of the MWV SEL product is exemplified by the horizontal line for the plot (circular symbols) of transient viscosity as a function of holding time at a given temperature. In contrast, undesirable rheometry data are exemplified by the upper plot (square symbols) for the MWV hardwood lignin (“PC-1369”) as-received, which exhibits an unstable (rising) viscosity as a function of residence time; it was this hardwood lignin material that was solvent-extracted to produce the SEL product.

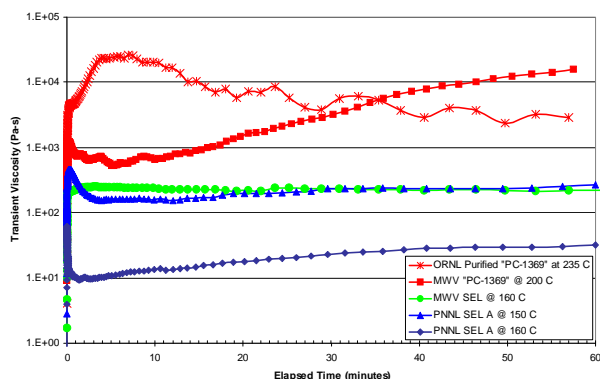


Figure 3. Viscosity of hardwood lignin as a function of time (at a given temperature).

The suitability of the MWV SEL product for melt-spinning was confirmed through single-fiber melt-spinning tests, during which lignin fiber was continually spun onto small spools; in fact, the lignin was the most readily melt-spinnable of all the lignin materials examined in the ORNL work to that date. On the basis of these positive findings, MWV committed to the production of kilogram quantities of the purified lignin for testing at ORNL on the multi-filament spinning equipment.

The first ‘large’ batch of MWV solvent-extracted (organic-purified) lignin was melt spun in early August 2007, with very positive results. Once

steady-state conditions were established in the extruder, metering pump, and spinneret, 12-filament fiber was continuously spun over several hours without interruption (other than to change take-up spools) and without the need for addition of alloying or plasticizing agents. An example of a spool of the lignin fiber is shown in Figure 4. Emphasis in this first run was placed on establishing the relationship between fiber winding speed and filament diameter, the results of which are summarized in Figure 5.

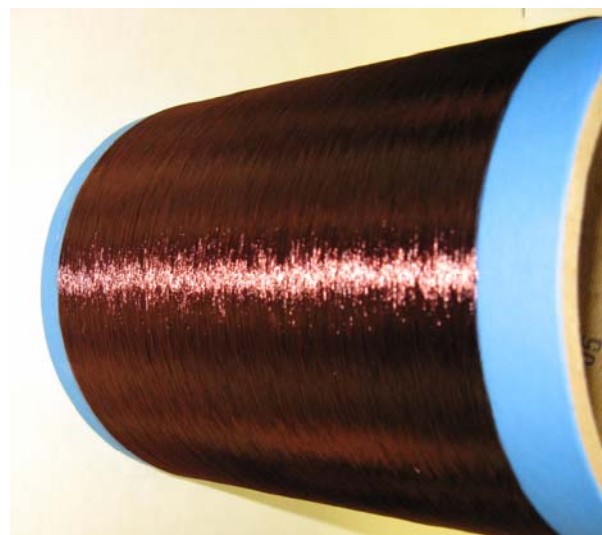


Figure 4. Lignin fiber tow comprising twelve filaments, each 11 micron in diameter.

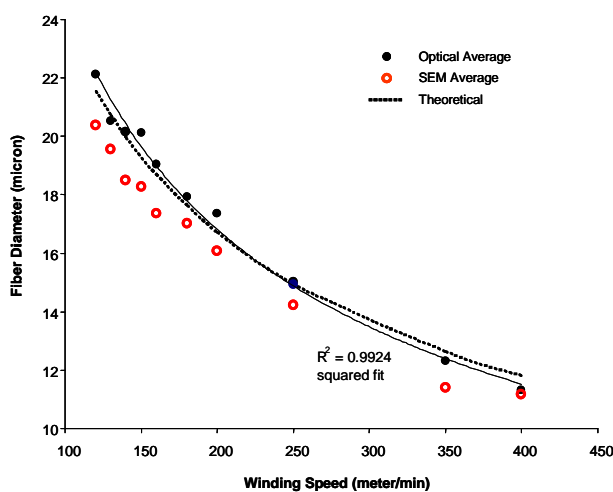


Figure 5. Lignin filament diameter as a function of winding speed.

The maximum fiber-winding speed achieved in this first multifilament spinning run was 400 meters/minute (m/min), i.e., 67% of the preliminary target speed of 600 m/min. This was a significant, first-time accomplishment. In fact, it was apparent that fiber-winding speed could have been increased to at least the preliminary target industrial rate of 600 m/min, but the subsequent increase in draw-down ratio would have resulted in filament diameters substantially below the target of 10 micron (μm), i.e., entering the upper end of the region of filament diameters that present a potential respiratory hazard. In the interest of safety, this particular study of spinning speed was terminated after five hours of continuous spinning when the lignin filament approached a visually-estimated diameter of 10 μm ; optical microscopy and scanning electron microscopy (SEM) measurements of filament diameter were made after the fact.

Representative SEM images of lignin filaments, about 15 μm in diameter, are shown in Figure 6. The SEM images revealed that, regardless of filament diameter, the filaments exhibited very uniform diameters, smooth outer surface, and a cross-section structure that was totally devoid of air-entrapment, impurity particles, or other observable defects that could impact the engineering properties of carbon fiber subsequently produced from the precursor fiber. SEM magnifications as high as 20,000x were made, confirming the structural uniformity of the lignin fibers.

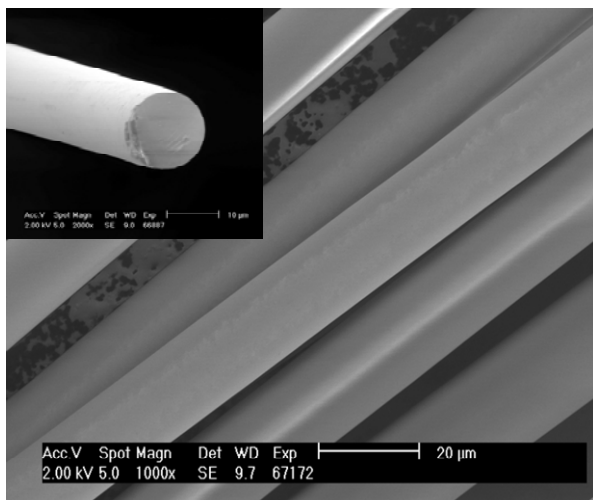


Figure 6. SEM Images of lignin precursor fibers.

The next study of spinning speed will target at least a two-fold increase in spinning speed (1000 m/min), increasing mass throughput in the melt extruder and spinneret such that the target filament diameter can be achieved at high spinning speed without exceeding the maximum draw-down ratio of 15:1 for the 12-filament die. Spinning of 24-filament lignin fiber tow will also be evaluated.

The first of the samples expected from the PNNL/MWV lignin-purification program arrived from PNNL in mid-September, too late to make a significant impact on our efforts in FY 2007. Nevertheless, based on the initial evaluation of the first PNNL lignin, it proved to be readily melt-spinnable without an additive. In fact, its thermal and rheological characteristics were very similar to those of the MWV solvent-extracted lignin that melt-spun so well. The similarity of the MWV SEL product and the first PNNL material is exemplified by the rheometry data shown in Figure 3, in which the viscosity data for the PNNL lignin are represented by triangle symbols, which are almost directly superimposed on the plot for the MWV SEL product (circular symbols).

PNNL subsequently confirmed that its first sample of purified lignin was not only produced from the same “PC-1369” hardwood lignin (i.e., not from black liquor, *per se*), but also was purified by a solvent-extraction approach (not aqueous). Thus, given these commonalities, it is not surprising that the MWV and PNNL purified hardwood lignin samples exhibited similar viscosity characteristics and were each readily melt-spinnable without the need for a plasticizing additive. Apparently, PNNL has refined its solvent extraction procedure to produce a higher melting point material (a desirable feature), which will be sampled to ORNL in the near future for evaluation.

In the meantime, PNNL also scaled-up production of an aqueous-purified hardwood lignin, an approach that, as mentioned earlier, had been problematic through most of the year. A (1 lb) sample of the aqueous-purified lignin, produced from the same “PC-1369” batch of hardwood lignin, was received in the first quarter of FY 2008 (11/9/07). The initial tests indicate that its melting point is approximately 220°C. However, the rheometer tests indicate that it is not sufficiently

stable at this temperature and begins to decompose within a short time span.

Single-fiber tests confirmed that the first sample of the PNNL aqueous-purified lignin was not melt-spinnable without the aid of a plasticizing agent. Further testes indicated that it may be melt-spinnable when blended with a solvent-extracted lignin, e.g., either the MWV or PNNL SEL products. These preliminary findings on the PNNL sample of aqueous-purified lignin are consistent with earlier findings on the same batch of hardwood lignin purified by ORNL using a similar aqueous approach.

The aqueous approach yields a clean lignin that more than meets the purity specifications and also exhibits a melting point (at least a “softening point”) at a desirable temperature (around 230°C). However, the purified hardwood lignins produced to date through use of an aqueous procedure are not melt-spinnable without a plasticizing agent. Nevertheless, it is a positive development that hardwood lignin purified through an aqueous procedure can be melt spun by inclusion of a minor proportion of a readily-spinnable, solvent-extracted lignin. The positive attributes of each are reinforced and the negative aspects essentially eliminated.

Apart from its good purity, a positive attribute of the aqueous-purified hardwood lignin is high carbon yield. This is highlighted in Figure 7 (A), in which thermogravimetric analysis (TGA) data are shown for ORNL aqueous-purified hardwood lignin together with the corresponding data for the unpurified lignin as-received. TGA data for an unpurified softwood lignin are included for the purpose of comparison. In this figure, carbon yields obtained at 950°C are compared on a dry basis (adjusted for the initial moisture content of the starting material). The beneficial effect of purifying the hardwood lignin using an aqueous procedure is discerned from the fact that carbon yield increased from 40.9% to 48.2%. The theoretical carbon content of hardwood lignin is about 55-60% (Table 1). For comparison, the yield of carbon obtained from carbon-fiber (CF) grade PAN under the same TGA conditions was 45.2% (Figure 7 B). The negative attribute of the aqueous-purified lignin is that it is not melt-spinnable without the addition of a plasticizing agent.

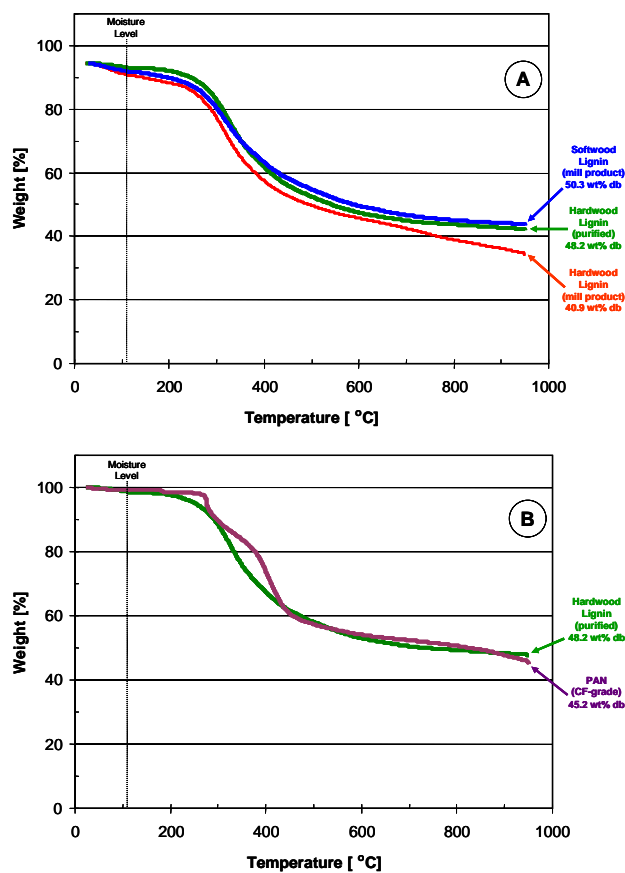
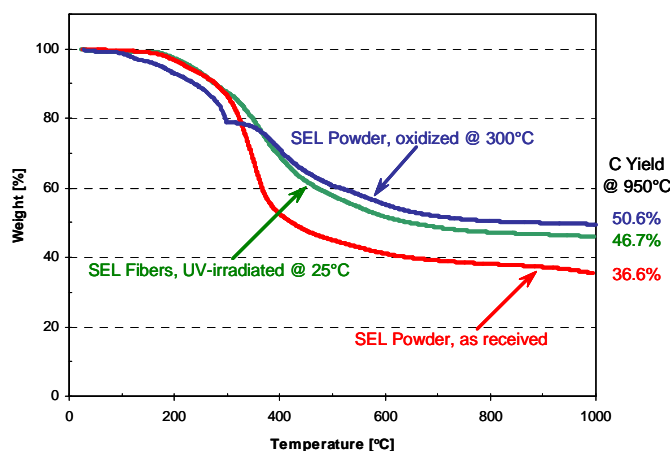


Figure 7. TGA data for lignins (A) and PAN (B).

Conversely, the positive attribute (in addition to high purity) of the organic-purified, solvent-extracted lignin is the fact that it is very readily melt-spinnable, and can also be used as a plasticizing agent for non-melt-spinnable lignins. The negative aspect of the SEL is relatively low carbon yield. This is apparent from the TGA data shown in Figure 8 for SEL samples. As-received, the SEL powder exhibited a carbon yield of 36.6% at 950°C. Encouragingly, though, when the SEL powder was oxidized with air, *in situ* at 300°C in the TGA instrument, the carbon yield increased to a respectable 50.6%. This demonstrated that the SEL material is cross-linkable, i.e., there is no thermodynamic barrier to stabilizing the solvent-extracted lignin or to achieving high carbon yield from the material. However, the temperature (300°C) at which the SEL powder was oxidized to obtain a meaningful rate of cross-linking was about twice that of the melting point of the lignin (about 140°C), and therefore impractical with respect to the production of carbon-fibers from the SEL material.

Table 1. Carbon Contents of Lignin and PAN

Precursor Material	Theoretical C-content	ORNL TGA Measurement
Hardwood Lignin Mill product	50-55	40.9
Hardwood Lignin Aqueous-purified	55-60	48.2
Softwood Lignin Mill product	55-60	50.3
Softwood Lignin Aqueous-purified	60-65	55 ?
PAN CF-grade	68	45.2

**Figure 8.** TGA data for fibers produced from MWV solvent-extracted hardwood lignin (SEL).

Thus, for solvent-extracted lignins to be of practical use with respect to the production of carbon fibers, a viable, alternative approach to stabilization of SEL materials must be identified. Very recent preliminary data in this context are summarized in Figure 8, in which the TGA data for SEL fibers irradiated with ultraviolet (UV) light at ambient temperature (25°C) in air are shown. Melt-spun fibers obtained from the multi-filament spinning run discussed above were UV-irradiated for different lengths of time; the data shown in Figure 8 are those for SEL fibers irradiated for 16 minutes. The carbon yield at the reference temperature of 950°C was 46.7%, indicating that the SEL lignin had cross-linked (oxidized) under the treatment conditions.

Although this is a very preliminary finding and must be confirmed through more detailed work, it nevertheless is encouraging that a relatively simple UV treatment of a lignin material will facilitate stabilization of the material in fiber form.

Based on the data obtained to date with respect to the purification and subsequent melt-spinnability of Kraft hardwood lignin, general conclusions can be drawn, namely, aqueous purification procedures are based on the separation of water-soluble contaminants and lignin (alike) at high pH and the subsequent separation of the contaminants and lignin through selective precipitation of the different species upon careful reduction of solution pH. The purified lignin so obtained is a higher molecular-weight material in which the lower molecular-weight lignin fractions are retained in solution with the salt and other mineral impurities. The lower molecular-weight lignin fractions appear to be the “plasticizing” agent for the lignin as a whole, and their elimination from the hardwood lignin renders the purified lignin non-melt-spinnable.

In marked contrast, organic solvent extraction of lignin purifies the lignin by dissolving the lignin away from the contaminants (mineral and carbohydrate). However, lower molecular weight lignin fractions are preferentially dissolved over higher molecular-weight fractions, at least under the organic solvents and process conditions examined to date. Thus, the organic-purified lignin contains a large proportion of the low molecular-weight lignin fractions that are plasticizing agents for the lignin as a whole, thereby retaining the melt-spinnability characteristics in the purified lignin. However, because of their lower molecular weight, these fractions depress the average molecular weight of the purified lignin, which is reflected by a melting point too low to permit stabilization of the subsequent fiber at an acceptable rate through conventional thermal-processing techniques alone.

Summary of Progress on the Lignin Project in FY 2007

Progress made on the lignin project over the past year (FY 2007) included:

- For the first time, multi-filament lignin tow was successfully melt-spun continuously

(without disruption) over an extended period of time (5-hours). The fiber exhibited excellent structural characteristics.

- The relationship between fiber winding speed and filament diameter was established (for a given set of melt-extrusion conditions).
- Target-diameter fiber (10 μm) was produced at 67% of the initial goal for spinning speed (600 m/minute), with indications that spinning speed can be readily increased several-fold.
- Preliminary data obtained indicate that melt-spun lignin fibers can be quickly stabilized through UV irradiation in air at 25°C.
- Demonstration that hardwood lignin purified using organic solvent-extraction procedures are readily melt-spinnable into the target-diameter filaments. Also, that they be used as plasticizing agents for hardwood lignin purified using aqueous procedures, the products from which are not melt-spinnable.
- Derivation of a better understanding of the factors that influence the melt-spinnability of lignin materials, what must be done to purify lignin to the target level and, at the same time, retain the melt-spinnability characteristic of hardwood lignin as produced in a pulp mill.
- Identification of commercial sources of lignin materials other than MeadWestvaco.

Lignin Sources for Continued Development Work

Following the merger of Mead and Westvaco in 2002, the business direction of the new corporation has been towards packaging and land development and away from the production of paper and specialty chemicals. Many of the new corporation's pulp-and-paper operations have been sold, and divestiture of its specialty-chemicals business, which is largely based on the isolation of tall oil, fatty acid, and lignin by-products from pulping operations (in Charleston, SC), is possibly part of MWV's long-term business strategy. Thus, even before the company's decision towards the end of FY 2007 to terminate all its long-term research efforts, including its support of the low-cost carbon-fiber project (LCCF), it was clear that an alternative industrial partner would need to be found.

Kruger Wayagamack, Inc., Quebec, Canada, is a large Canadian-based pulp-and-paper producer

that also utilizes the Kraft process for the pulping of wood (predominantly softwood in Canada). Almost two years ago, Kruger made it clear that it was interested in isolating lignin to debottle its recovery-constrained mills and increase pulp production. To increase small profit margins and stave off competition from China, many pulp-and-paper companies wish to increase pulp production and throughput of paper in their mills, but are largely unable to do so because the mills concerned are not able to also increase recovery of the pulping chemicals (new recovery boilers are very capital-intensive). Thus, some mills are seeking to isolate lignin from the black liquor, largely for the purpose of using it as a fuel in other operations but also a potential source of valued-added products. Kruger, for example, is initially targeting the production of fire logs, an application that has a value of about 20¢/lb of lignin. At a potential price of 50¢/lb, sale of lignin for low-cost carbon-fiber production is of substantial interest to Kruger.

Kruger has licensed the "LignoBoost" lignin-isolation technology from STFI-Packforsk, a Swedish research company. As a point of information, the LignoBoost process was developed to produce a lignin-based biofuel.

Kruger senior management has recently given the formal go-ahead for mill trials, a significant financial commitment. As part of this effort, the company is constructing a pilot-scale lignin-isolation plant with a capacity of 100 kg/day, which is expected to be on-stream within 4-6 months. Thus, we have another pulp-and-paper manufacturer on-board that is willing to take over from MeadWestvaco and furnish ORNL with Kraft lignin for the LCCF efforts. Needless to say, this will not be without its own challenges, not the least of which is that we must demonstrate melt-spinning of multi-filament tow from the lignin, which is softwood based. However, we have learned a great deal about spinning lignin materials over the past year, which will help us to move forward with the new source of lignin as a precursor material for carbon-fiber production.

We have already demonstrated that the first Kruger lignin material is melt-spinnable with a plasticizing additive, namely, the solvent-extracted hardwood lignin discussed above. Furthermore,

based on an analysis of the first lab-scale sample received from the company, the purity of the Kruger lignin is close to the desired specifications and certainly much better than that of the commercial Kraft lignin products from MWV with which we have worked to date. Refinement of the isolation procedure (e.g., through incorporation of additional washing stages) could result in a lignin material meeting the purity specifications *without* the need for subsequent purification.

Weyerhaeuser Company, WA

Weyerhaeuser has recently indicated that it is willing to provide its lignin to the FreedomCAR program for multi-filament melt-spinning evaluation and carbon-fiber production. Access by the FreedomCAR program to Weyerhaeuser lignin is considered to be an important element of future efforts on the FreedomCAR LCCF program.

Lignol Innovations Ltd., British Columbia, Canada

Lignol Innovations, a wholly owned subsidiary of the Lignol Energy Corporation, is building biorefineries in Canada for the production of ethanol fuel and other products from lignocellulosic biomass, notably waste wood. Lignol has improved on the process originally developed by General Electric (GE) and further refined by Repap Enterprises, Inc., from which the "Allcell" lignin product was produced. It has been known since the earliest days of the LCCF project at ORNL that the Allcell lignin product (derived from hardwood) is relatively pure as-isolated and is readily melt-spinnable. However, the Allcell product was unable to compete with commercial lignin products produced from conventional chemical pulping, and Repap consequently ceased business operations. With the greatly increased emphasis on the production of cellulosic ethanol, however, there is renewed interest in finding markets for the lignin by-products from cellulosic ethanol operations, and Lignol Innovations regards LCCF production as an attractive potential market for its lignin product.

Other Biomass-Derived Lignins

Biomass-derived lignins will become increasingly available from other cellulosic ethanol programs around the world, most notably from the joint venture by the University of Tennessee (UT) Knoxville and ORNL. We anticipate getting in on

the ground floor of the new UT/ORNL program with respect to evaluating the lignin produced in this particular biomass-to-ethanol research work. The economics of any biomass-to-ethanol process will partially depend on what one does with the lignin "by-product" from the process, which could account for upwards of 35% of the mass input of the biomass. Certainly, it will not be acceptable either environmentally or economically to landfill the lignin, and burning it for energy is worth only about 5¢/lb, even based on today's oil prices.

Solvent-Extracted Lignins

Recapping, both the MWV and PNNL solvent-extracted hardwood lignin materials exhibited excellent melt-spinnability characteristics, especially the former. The downside to these particular solvent-extracted lignin materials is their low melting point of about 140°C, which is fine from a melt-spinning standpoint but is too low to stabilize spun fiber at an acceptable rate using conventional thermal-processing techniques. Nevertheless, it was demonstrated that the MWV solvent-extracted lignin will readily cross-link at temperatures above its melting point, resulting in a substantial increase in carbon yield from 37 to 51%. It was also demonstrated that UV irradiation of the MWV solvent-extracted lignin fiber at ambient temperature (25°C) over a short period of time (16 minutes) resulted in a similar, substantial increase in carbon yield, indicating the potential for UV stabilization of fibers produced from such lignins. Furthermore, both the MWV and PNNL solvent-extracted lignins were useful plasticizing agents for other, non-melt-spinnable lignins, including those purified using an aqueous procedure.

Thus, some efforts will be continued to exploit the beneficial characteristics of lignins purified using a solvent-extraction process, particularly if it is demonstrated that, through refinement of the procedure, the melting point of such lignins can be raised to near the desired level of about 250°C. However, efforts at ORNL in this respect will be limited to evaluation of solvent-extracted lignins, i.e., the work will not encompass lignin purification, *per se*.

Approximately 5 tons of the "PC-1369" hardwood lignin produced by MWV in support of the LCCF project at ORNL is available for sale. If new

findings are developed that indicate that the molecular-weight and melting-point properties of a solvent-extracted lignin could be enhanced through refinement of the solvent extraction procedure (e.g., choice of solvents), then it would be appropriate to consider funding a solvent-extraction purification run by the toll processor identified by MWV for this purpose. Furthermore, it would be advantageous to have solvent-extracted lignin on-hand for use as a plasticizing agent for other purified lignins that are not readily melt-spinnable (about 2 kg of SEL is currently on-hand for this purpose).

Kraft lignin exhibits antioxidant properties because it is a radical scavenger (e.g., has been tested for the treatment of certain cancers). It readily absorbs UV radiation and, as noted above, UV irradiation may be a viable route to stabilizing solvent-extracted lignins as currently produced. In addition, though, an evaluation should be made of whether the SEL material could be satisfactorily stabilized using other advanced processing techniques, including plasma treatment or incorporation of a catalyst to promote oxidative stabilization of the spun fibers at temperatures below their melting point of about 140°C.

PNNL-Produced Lignin Materials

PNNL has overcome the difficulties encountered in the early part of the PNNL/MWV program to purify hardwood lignin using an aqueous procedure and has produced purified material for evaluation. Similarly, PNNL has refined its organic solvent-extraction procedure to produce a purified hardwood lignin of higher molecular weight and melting point. Both of these hardwood-lignin materials should be evaluated for melt-spinnability and production of multi-filament tow. However, PNNL is not in a position to furnish the kg-quantities of purified lignin required for multifilament melt-spinning; someone else must scale-up the PNNL process.

Project Deliverables

By the end of this multi-year program, production of carbon fibers suitable for transportation use, from one or more economically-feasible, renewable resource materials, will have been demonstrated and the transfer of production

technologies and related intellectual property to industry implemented.

Presentations/Publications/Patents (FY 2007)

1. Frederick S. Baker*, Nidia C. Gallego, Felix L. Paulauskas, and Amit K. Naskar, "Lignin-based Carbon-fibers: A Route to Energy Independence in the USA," Invited Keynote Lecture, *CARBON 2007 Conference*, Seattle, WA, July 15-20, 2007.
2. Frederick S. Baker*, Nidia C. Gallego, Felix L. Paulauskas, and Amit K. Naskar, "Production of Low-cost Carbon-fibers from Renewable Resource Materials for More Energy-efficient Vehicles and Reduced Environmental Pollution," Invited Lecture, *Carbons for Energy Storage and Environment Protection, CESEP'07 Conference*, Krakow, Poland, September 2-6, 2007.
3. C. Dave Warren*, C. Cliff Eberle, Felix L. Paulauskas, Fred S. Baker, Amit Naskar, and Alan Wheatley, "FreedomCAR and Low-cost Carbon-fiber for Automotive Applications," *7th International Congress on Materials for Lean Weight Vehicles*, University of Warwick, Warwick, England, September 26-27, 2007.

* = Presenter

B. Improved Lignin Purification/Recovery Process for Carbon-Fiber Applications

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Contract No.: DE-AC06-76RL01830

Objective

- The project objective is to develop an economically-viable and technically-sound process for the purification of lignin to make it acceptable as a raw material for the manufacture of low-cost carbon fiber (CF).
- Lightweighting the USA car and light-truck fleet for better fuel efficiency is a current DOE objective. The substitution of stamped steel panels and other body and interior parts with strong, yet lightweight and resilient carbon-fiber-reinforced plastic (FRP) parts can contribute significantly to this objective. Unfortunately, current processes for manufacture of CF are costly and produce CF at well above the established target cost of under \$5.00/lb needed for vehicle lightweighting.
- A considerable portion of the cost of current CF is borne by the expensive synthetic polymers that are the normal raw materials. Lignin, as a byproduct of the pulp-and-paper industry, is an attractive alternate and potentially low-cost raw material for CF. Unfortunately, today's standard means of recovering lignin from paper-mill streams is not able to yield lignin with the levels of acceptable purity and physical properties for fast and economically-viable melt-spinning and eventual conversion to CF.
- This project is tasked with developing and demonstrating at the lab-scale effective means to isolate, recover and purify pulp-mill-derived lignin with properties acceptable for its use as a raw material for CF. Initially, this effort is focused on hardwood lignin from Kraft black liquor and eventually will be extended to softwood lignin from Kraft black liquor. The purity targets that have been set for lignin by prior CF work at ORNL (see 7.A) serve as a guideline. However, we will also use a preliminary test for melt-spinnability (via a fiber-draw test) as a guideline for determining early-success potential. We will also examine other physical properties including melt index (MI) and dynamic viscosity. These physical properties are also expected to be a key to a material's ability to be processed economically into CF whose properties are acceptable for use in CF-reinforced car and truck parts.
- The focus in fiscal year (FY) 2007 was on hardwood lignin from Kraft black liquor. Eventually, the focus will extend to softwood lignin from Kraft black liquor. We are using a dynamic mechanical analyzer (DMA), and thermogravimetric analysis, differential scanning calorimetric (TGA-DSC) analysis for preliminary physical property evaluations.

Approach

- Evaluate the MeadWestvaco (MWV) concept of differential removal of impurities and lignin precipitation as a process route to achieving the desired level of lignin purity and properties for CF application.
- Evaluate post-pulping processes to remove carbohydrate from lignin using appropriate, representative Kraft black liquor(s).
- Screen and determine optimal process variables for the selected process.
- Scale selected process and the optimized conditions to 300 cc and/or to 1-liter batch levels or larger as appropriate, to verify process and determine overall material balance and perform preliminary assessment of adaptability to a continuous process.

Accomplishments

- Purchased MI instrument for lignin product characterization. Set up instrument and accomplished operator training and baselining with commercial polymers.
- Successfully addressed environmental, health and safety (EH&S) issues. This included standard operating procedures and safety reviews of instrumentation and autoclave equipment and approved procedures for disposal of waste and recycle materials.
- Developed approved material-handling, characterization and processing procedures.
- Developed procedures for TGA, differential thermal analysis (DTA) and DSC of samples to determine moisture, ash and melting-range behavior.
- Samples, which appear via these preliminary tests to represent potential candidate purification technologies, were scaled and sent to Clemson University and/or Oak Ridge National Laboratory (ORNL) for melt-spinning trials.
- Established and validated a preliminary “fiber-draw” test to assess the ability of lignin samples to be successfully melt-spun.
- Determined that existing PNNL DMA instrumentation can adequately measure lignin sample melt viscosity under shear, another property that is deemed key to predicting its ability to be melt-spun into fiber.
- Begun combinatorial, high-throughput experiments with well-per-plate format to assess post-pulping processes. Selected several leads for further evaluation.
- Performed a preliminary evaluation of the MWV differential process for lignin clean-up.
- Performed an evaluation of % loading and methods of incorporation for one recommended type of plasticizer / rheology control agent, to aid in lignin melt-spinning. Selected an appropriate loading and incorporation method. (Prior efforts by others have suggested that lignin must be plasticized in order to be effectively melt-spun.)
- Via the cooperative research and development agreement (CRADA) partner, established a technical-service type arrangement with a USA university to perform single-fiber melt-spin tests on samples that appear successful in preliminary testing.

Future Direction

- Development of technology capable of delivering hardwood lignin to the desired purity level.
 - Selection of one of three best-apparent technologies for hardwood-lignin recovery and scaling these to a level suitable for validation and to provide sufficient material for single-fiber melt-spin tests at a university.
 - Extension of hardwood-lignin recovery methods to the development of technology capable of delivering softwood lignin to the desired purity level.
 - Selection of one of three best-apparent technologies for softwood-lignin recovery and scaling these to a level suitable for validation and to provide sufficient material for single-fiber melt-spin tests at a university.
 - Delivery of 5 kilograms of the desired purified lignin for melt-spinning evaluations.
-

Introduction

CF derived from lignin-based feedstock offers the potential for meeting the aggressive cost goals established by FreedomCAR for structural applications CF. However, the critical requirement for successful development of a lignin-based CF is the ability to purify the lignin feedstock effectively so that it can be melt-spun and processed at attractive rates into a viable CF having the required physical and mechanical properties. Effective purification of lignin requires the removal of insoluble particulates, salts and undesirable carbohydrate fragments, which adversely affect the melt-spinning and overall fiber processing. In order to meet current cost targets it is essential that a practical purification process be compatible with current Kraft pulping operations as Kraft lignin is the largest practical source of lignin for the near future. It is also essential that the general lignin purification scheme be easily adaptable to both hardwood and softwood lignin. Longer term, the process must also be able to handle lignin from other renewable sources and processes other than those based on Kraft-type technology.

MWV, the project's cost-sharing CRADA partner, has developed a relatively untested and unrefined concept for lignin purification/recovery that has potential to meet the required purity levels in a cost-effective, environmentally-suitable manner. In addition, the MWV process concept is compatible with existing pulp-plant layout and function, which is a key requirement for early implementation of high-purity lignin for CF.

The most deleterious lignin components are perceived to be easily volatilized, lignin-bound carbohydrate fragments, along with inorganic salts, insoluble and non-melting materials. MWV's conceptual process is expected to remove these undesirable components very early in the lignin-recovery process and also can be retrofitted into a conventional pulp-mill design. Early experimental evidence suggests that this concept, although simple, is likely to be more complex and difficult to accomplish successfully than initially believed.

Approach

The overall project approach is multifold, including use of high-throughput, combinatorial methods at PNNL for fast screening and discovery. Bench-scale experiments at 300 cc to 1-liter levels to validate, verify and refine leads, found via high-throughput methods, are also planned. Scale-up to pilot-size and beyond as appropriate will also be conducted to provide confidence in the process and to provide material for single- and multiple-fiber melt-spinning evaluation and also carbonization tests. Initially, the project plan involved various tasks properly described as preparatory, including acquisitions, personnel training and items related to EH&S. This was followed by experimental recovery of lignin via various physical means and also experimental evaluations of a variety of chemical treatments. Ultrafiltration of the black liquor (BL) was also briefly examined.

Fundamentally, we are starting with lignin at the black-liquor stage, that is, when it is closest to the form in which it is first removed from the wood. Prior CF development work with lignin has used material that had already been recovered, isolated, subjected to some degree of purification and dried. Since lignin can have significant reactivity before and during drying, we think that beginning at the BL stage allows us to intercept lignin and process it more effectively before undesirable and irreversible changes take place.

Results

Early accomplishments include the acquisition, set-up, personnel training, a safety review and standard operating procedures (SOP) approvals of a Tinius-Olsen Melt Index testing machine. We have evaluated and validated this instrument with several commercial polymers with known ability to be melt-spun and blown into films.

We have also set-up and validated a preliminary test to very simply evaluate a new material's potential ability for melt-spinning. This preliminary test, known as the "fiber-draw" test is modeled closely after a test designed and successfully used by some staff at Clemson University for determining if a given sample is likely to be suitable for melt-spinning. The "fiber-draw" test apparatus is contained inside a nitrogen

(N)-filled glove box as lignin is often perceived to be reactive with air. The test is quite simple in concept. A sample is placed in a small aluminum pan on a hot plate whose surface temperature may be accurately controlled and changed. As the sample temperature is raised by increasing the hot plate's surface temperature, a visual indication of possible melting or softening can be observed. When melting or softening behavior is seen, a sharp-pointed pin is touched to the sample and slowly removed. If a long, uniform, thin fiber can be drawn from the sample as the pin is removed while the sample transitions through a melting or softening stage, then the sample is considered to have good potential for melt-spinning. Figure 1 shows the "fiber draw" behavior of M-50 pitch, a material known to have good melt-spinning behavior. Note the relatively nice looking, long fibers drawn from the melted pitch contained in the pan.

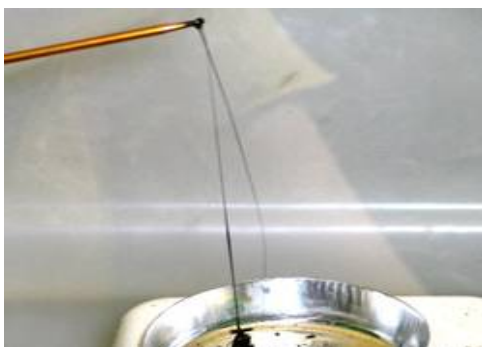


Figure 1. M-50 pitch fiber-draw test.

Other early activities included staff training on a TGA-DSC apparatus used to determine melting points or melting ranges and also weight loss vs. temperature in inert or air atmosphere.

Experimental work for recovering lignin from hardwood BL is using a commercial BL obtained from the MWV Kraft pulp mill in Charleston, SC. We found that most particulate matter and the tall oils could be removed in a single centrifuging step after appropriate pH adjustments. The liquid remaining after this treatment contained about 14% lignin along with dissolved inorganic salts and other organics. Simple precipitation of this lignin followed by washing to remove the inorganic salts and soluble organics followed by vacuum drying, did not yield a particularly good fiber draw test (see Figure 2). The "clumps" and "nodules" on the drawn fibers are indicative of

poor melt-spin behavior and are consistent with earlier work which established the need to plasticize the lignin prior to melt-spinning, regardless of its purity.



Figure 2.
Precipitated lignin.

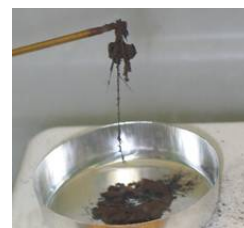


Figure 3.
PC-1369 lignin.

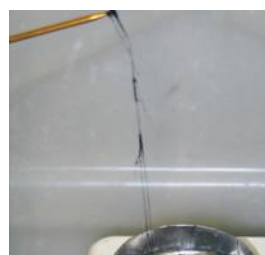


Figure 4. Fiber draw test.
Experimental combi lignin.

As a comparison, Figure 3 shows the fiber-draw test result with unprocessed PC-1369, which is a commercial grade of hardwood lignin shown in past ORNL studies not to be suitable for melt-spinning. The PC-1369 and also the lignins shown in Figures 2 and 4 contain the preferred plasticizer/rheology control agent; but, note the very severe degree of clumping and poor fiber formation in Figure 3 which suggests quite poor melt-spin behavior for PC-1369.

However, Figure 4 shows a fiber-draw test that appears positive for a lignin sample that was obtained from high-throughput screens to evaluate various other BL pretreatments before precipitation, washing and vacuum drying. An approach such as this in combination with a suitable plasticizer is expected to ultimately produce the desired result, an easily melt-spinnable, lignin-based precursor to CF.

These results appear to be worth following up. Thus, a series of follow-up tests is planned for next quarter at both the 20 mls combi level and at a larger bench-scale. Note that high-throughput combinatorial screens are performed in the PNNL

combi system using a 6-well plate. The capacity of each well is about 20 mls. Only a few grams of lignin can be recovered from these screens, about enough to do only TGA-DSC and a fiber draw test.

Conclusions

Experimental results suggest that the conceptual MWV differential recovery / purification process is not acceptable for hardwood-black-liquor-derived lignin.

PNNL combinatorial, bench-level scaling studies and corresponding fiber draw tests have suggested that both organic and completely aqueous post-pulping process schemes, may provide alternatives that have promise for leading to a lignin product acceptable for melt-spinning. Currently, however, only organic-based processes are able to yield a melt-spinnable lignin. Further evaluation is required to validate all-aqueous schemes. All schemes contemplated thus far should be easily integrated into a typical Kraft pulp mill.

Presentations/Publications/Patents

None in FY 2007.

C. Advanced Stabilization of PAN Fiber Precursor

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Contractor: ORNL

Contract No.: DE-AC05-00OR22725

Objectives

- Develop an improved technique for stabilizing carbon-fiber (CF) precursor with increased line speed and reduced CF cost.
- Verify that finished fiber properties satisfy automotive and heavy-vehicle manufacturers' requirements.
- Conduct a preliminary evaluation of the cost impact of the new stabilization technique.
- Integrate the stabilization module into an advanced technology pilot-line.

Approach

- Investigate thermochemical, ultraviolet (UV), and electron-beam (EB) processing stabilization routes.
- Select one of the aforementioned stabilization routes for detailed equipment and process development.
- Conduct parametric studies to correlate processing parameters and fiber properties.
- Determine process parameters that minimize residence time.
- Characterize fibers to confirm that they satisfy program requirements.

Accomplishments

- Discovered how to stabilize virgin precursor fibers via plasma-assisted thermochemical route.
- Thermochemically stabilized virgin precursor fibers in less than half of conventional stabilization residence time.
- UV-stabilized virgin precursor fibers in less than half of conventional stabilization residence time.
- Investigated various EB-stabilization irradiation parametric effects on plasma oxidation.
- Plasma-oxidized precursor fibers after they were UV-stabilized.
- Selected plasma stabilization as the primary route for implementation at a conversion factory and EB stabilization as the primary route for implementation at a precursor factory.

Future Direction

- Develop advanced thermochemical stabilization for implementation at a conversion factory.
- Develop e-beam stabilization for implementation at a precursor factory.
- Conduct parametric studies and fiber characterization to better understand process effects and to quantify fiber properties.
- Commence scaling the advanced-stabilization equipment and process.

Introduction

The purpose of this project is to investigate and develop a technique to rapidly and inexpensively stabilize a polyacrylonitrile (PAN) precursor. New processing techniques are being developed for the purpose of reducing the cost of CF conversion. Previous and ongoing research at ORNL has demonstrated that plasma processing shows great promise for inexpensively and rapidly oxidizing, carbonizing, and graphitizing polymer precursors to convert them to CFs. The precursor needs to be lightly stabilized, or cross-linked, before it can be subjected to plasma oxidation. Stabilization and oxidation together are estimated to represent ~ 18% of the cost of commercial grade carbon fiber.¹ A rapid, inexpensive and robust stabilization technique is needed to complement the aforementioned advanced-process modules and enable the development of an integrated, advanced-technology conversion line that converts polymer precursor fibers into CFs at significantly lower cost than conventional conversion technology.

This project, therefore, intends to develop an advanced-stabilization module that integrates with other advanced fiber processing modules to produce inexpensive CF with properties suitable for use by the automotive industry. Critical technical criteria include: 1) ≥ 25 Msi tensile modulus and

$\geq 1.0\%$ ultimate strain in the finished fiber; 2) uniform properties along the length of the fiber tow; 3) repeatable and controllable processing; and 4) significant unit cost reduction compared with conventional processing.

Project Deliverable

At the end of this project, the project team will have demonstrated satisfactory PAN precursor fiber stabilization with residence time well below that typical of conventional CF conversion lines. The project deliverable is a process specification that will enable the commencement of scaling experiments aimed at development of a subscale, multiple large-tow, advanced-technology pilot-line.

Technical Approach

The researchers are investigating three prospective PAN precursor fiber stabilization routes: electron beam processing, thermochemical processing, and UV processing. All three routes are based on discoveries previously made in other carbon-fiber projects, and each appears to offer certain advantages. After experimental concept investigation, the researchers will select the most promising route for detailed process development, with the principal criteria for selection being mechanical properties and finished fiber cost. The preferred

route will then undergo detailed parametric studies to characterize the process and develop the processing recipe.

Progress

Detailed design and process data are not disclosed in this report due to export-control restrictions. They are periodically reported to the program managers and partners in compliance with the export-control restrictions. Material properties and residence times can be disclosed, and example data are shown in Table 1.

EB Processing

EB stabilization was demonstrated in fiscal year (FY) 2006, showing very high throughput (line-speed) potential. The electron irradiation step is completed in seconds, but early experiments have required a few-minute thermal post-treatment to render the precursor fibers stable in the plasma-generated, oxidative environment. Current efforts are focused on understanding and resolving the cause of the unstable behavior when exposed to the plasma-generated, reactive, oxidative species. Electron spin resonance data indicate that irradiation generates free radicals, which are thought to cause the unstable behavior. Efforts to resolve the free radical problem are underway. FY 2007 irradiation experiments were conducted to study the effect of various irradiation parameters.

EB-stabilized precursor has been converted to finished fibers by a range of process combinations. The results, which are compared in Figure 1, include both previously-reported and new data. All of the conversions, even by fully-conventional means, were conducted at low carbonization temperature and without the benefit of fiber tensioning, tow spreading, or controlled stretching in any of the conversion stages; hence, the fiber mechanicals are expected to be low compared to those of corresponding commercial fibers. Most specimens exhibit a tensile modulus exceeding the 25 Msi requirement. The strain is generally somewhat below the 1% requirement. It is noteworthy that the EB-stabilized samples, even those that were subsequently plasma oxidized, exhibit mechanicals that are not far below those of the thermally-converted fibers. This gives us confidence that the property targets are well within reach.

New equipment for carbonizing fiber quantities at correct temperature and tension recently became operational and will be utilized in future testing.

Thermochemical Processing

Stabilization was originally found to be needed before plasma oxidation, because virgin precursor could not withstand the reactive oxidative species generated by plasma. When virgin precursor was exposed to the plasma-generated chemistry, significant exothermic heating occurred fairly rapidly, resulting in interfilamentary adhesion and tow rigidity. While it was necessary to investigate other stabilization routes, the quest to discover a way to stabilize the precursor fibers using plasma chemistry has continued. One obvious advantage of this route is that it would integrate seamlessly with the plasma-oxidation module (see 7.D), becoming essentially a single module for both stabilization and oxidation, and being directly analogous to the conventional conversion modules.

A non-plasma, thermochemical stabilization processing concept was developed in FY 2006, but the residence time was still longer than desired. Investigation of plasma-based thermochemical stabilization has continued. In FY 2007, *the research team was finally able to demonstrate plasma-based stabilization*. Serendipitously, this discovery was prompted by observations made on the results of EB and UV stabilization. In its current development status, plasma stabilization seamlessly integrates with plasma oxidation and requires less than one-third of the conventional stabilization residence time.

UV Processing

UV processing potentially offers the combination of high line speeds with low capital cost. The chemistry is generally similar to that of EB, but very often UV requires a photoinitiator that would not be needed for EB cross-linking. One of the major challenges is whether UV radiation can deliver uniform cross-linking throughout the bulk volume of individual filaments as well as throughout the tow, with acceptable residence time. The UV processing development is being conducted at Clemson University with ORNL providing technical consultation and direction.

Table 1. Example data from various stabilization routes with Hexcel 3k PAN precursor. For multiple-step experiments, steps are tabulated in the order of completion.

Experiment	Process	Density, g/cc		Residence time, min	
		Before	After	Pass	Total
Thermal Stabilization, Thermal Oxidation	Thermal 1st Pass	1.19	1.33 - 1.34	26	53
	Thermal 2nd Pass	1.33 - 1.34	1.37 - 1.38	27	
Thermal Stabilization, Plasma Oxidation	Thermal stabilization	1.19	1.22 - 1.23	23	49
	Plasma oxidation	1.22 - 1.23	1.35 - 1.36	26	
UV Stabilization, Plasma Oxidation	UV stabilization	1.19	~ 1.20	2.25	28
	Plasma oxidation	~ 1.20	1.34 - 1.35	26	
	UV stabilization	1.19	~ 1.20	4.5	31
	Plasma oxidation	~ 1.20	1.35 - 1.36	26	
	UV stabilization	1.19	~ 1.20	6.75	33
	Plasma oxidation	~ 1.20	1.33 - 1.34	26	
	UV stabilization	1.19	~ 1.20	10	36
	Plasma oxidation	~ 1.20	1.33 - 1.34	26	
EB Stabilization, Plasma Oxidation	EB Protocol 1	1.19	~ 1.19	0.1	53
	Thermal anneal	~ 1.19	1.23 - 1.24	26	
	Plasma oxidation	1.23 - 1.24	1.36 - 1.37	27	
	EB Protocol 2	1.19	~ 1.19	0.3	53
	Thermal anneal	~ 1.19	1.27 - 1.28	26	
	Plasma oxidation	1.27 - 1.28	1.36 - 1.37	27	
	EB Protocol 3	1.19	~ 1.19	0.3	53
	Thermal anneal	~ 1.19	1.28 - 1.29	26	
Plasma oxidation	1.28 - 1.29	1.37 - 1.38	27		
Plasma Stabilization, Plasma Oxidation	Plasma single pass	1.19	1.33- 1.34	26	26
	Plasma 1st pass	1.19	1.33- 1.34	26	53
	Plasma 2nd pass	1.33- 1.34	1.37 - 1.38	27	
	Plasma 1st pass	1.19	1.33- 1.34	26	106
	Plasma 2nd pass	1.33- 1.34	1.37 - 1.38	27	
	Plasma 3rd pass	1.37 - 1.38	> 1.40*	26	
	Plasma 4th pass	> 1.40*	> 1.40*	27	

* 1.40 g/cc is the maximum measurable density by the instrument used for these experiments

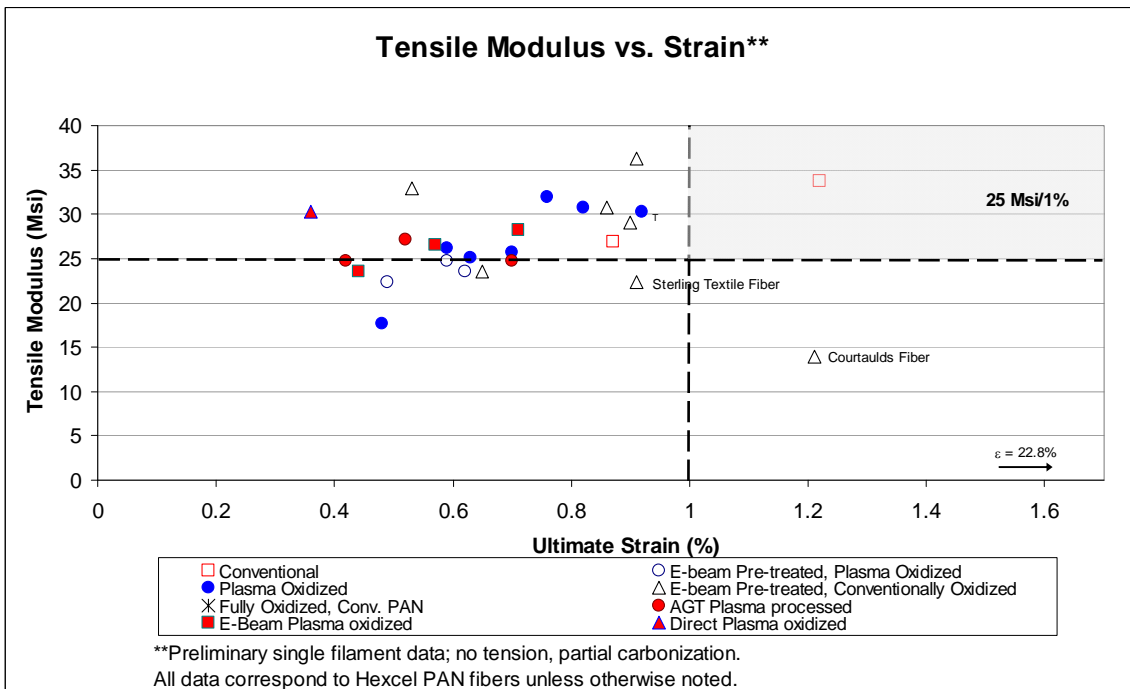
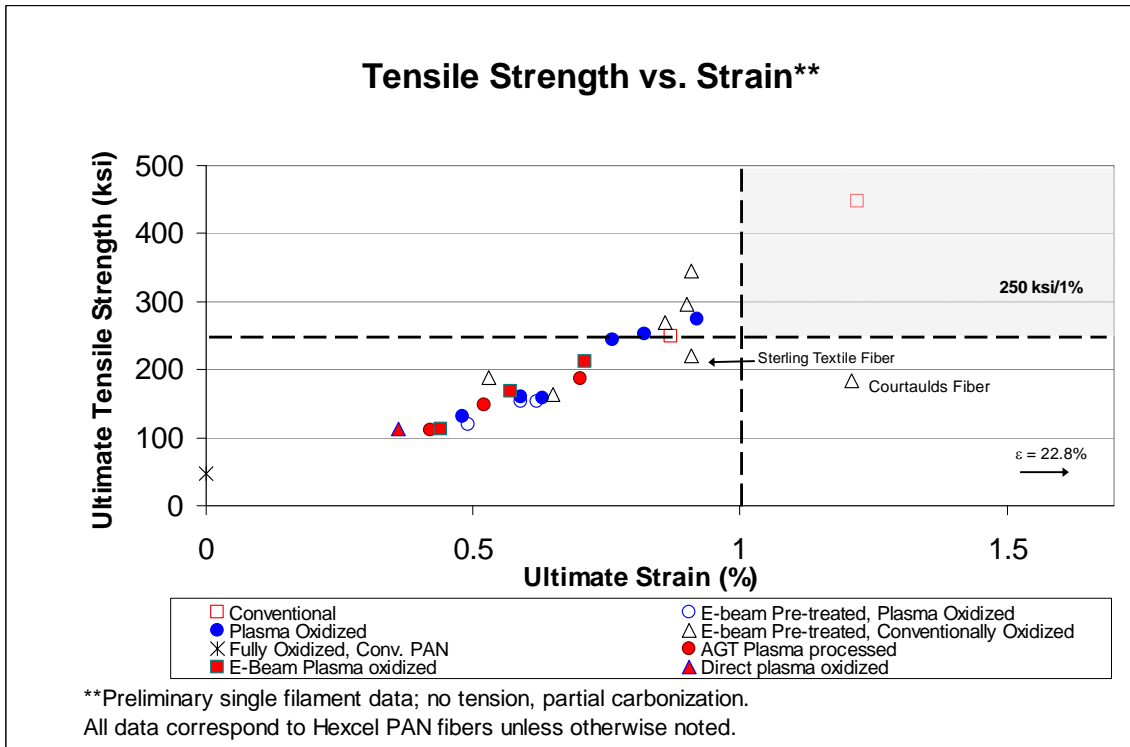


Figure 1. Mechanical properties of fiber specimens (tested by single-filament tensile strength method) converted by various routes. Conventional data points were thermally shocked and thermally ramped, respectively.

During FY 2007, effects of UV exposure were investigated in greater detail. As expected, increasing UV exposure produces increased cross-linking. The differential scanning calorimeter (DSC) thermogram is shown in Figure 2. In the latter half of FY 2007, continuous UV processing capability was developed. Uniform treatment throughout the tow is a problem, as illustrated in Figure 3, which shows DSC thermograms for UV-stabilized fibers taken from different parts of the same tow. The uniformity challenge has not been resolved to date, and we have not yet conceived a satisfactory approach to achieve uniform tow treatment with UV.

Stabilization Route Selection

A major FY 2007 milestone was to select one stabilization route for continued development.

The advanced stabilization project was started in late FY 2005 because we were then unable to achieve plasma stabilization, and at least light cross-linking was needed before plasma oxidation. In FY 2007, we finally discovered a plasma-stabilization recipe that delivers the necessary cross-linking without damaging the precursor fibers. Plasma stabilization seamlessly integrates with plasma oxidation and offers the same advantages as plasma oxidation. It is prudent to minimize the number of distinct technologies employed in the conversion line. Plasma stabilization was therefore selected as the primary stabilization route for further development.

EB stabilization offers, by far, the highest throughput per unit area of footprint. EB economies of scale are problematic in a conversion factory, but are well matched to implementation at a precursor factory, which typically runs at line speeds of order 100 m/min with factory capacities of order 100M lb/yr. There are scenarios where the precursor may be at least partially cross-linked in the precursor factory or a toll processing facility before shipment to the conversion factory. We are confident that with further development, we can resolve the free-radical problem and perhaps even learn to use it to advantage. E-beam stabilization was selected as the stabilization route for this scenario.

UV stabilization offers the potential for high line speeds at low capital cost. However, UV is fundamentally a surface phenomenon. We have observed that it cross-links the tow surface, but must depend on thermal or other means to cross-link the tow's interior. This can be readily overcome in laboratory experiments by tow spreading or other means to ensure that all fibers are irradiated. However, we think this is a fundamental limitation that is unlikely to be resolved at the production-scale within the program schedule. We are also concerned about the size and performance stability (UV lamp performance degrades significantly with time) of a UV-stabilization module. For these reasons, we have elected to discontinue the development of the UV-stabilization route.

Future Direction

We will focus our primary efforts on the development of plasma stabilization, its integration with plasma oxidation, and scaling of the plasma stabilization/oxidation technique. We will also continue development of EB stabilization as an option that can be implemented at the precursor factory or a toll-processing facility upstream of the conversion factory.

Patents and Publications

There was no new patent or publication activity during this period.

Education

Educational institutions participating in this project include Clemson University and the University of Tennessee. Clemson chemical engineering graduate students are conducting UV-processing studies under the direction of Professor Amod Ogale. UT materials science graduate students are providing characterization support to the project under the guidance of Professor Roberto Benson.

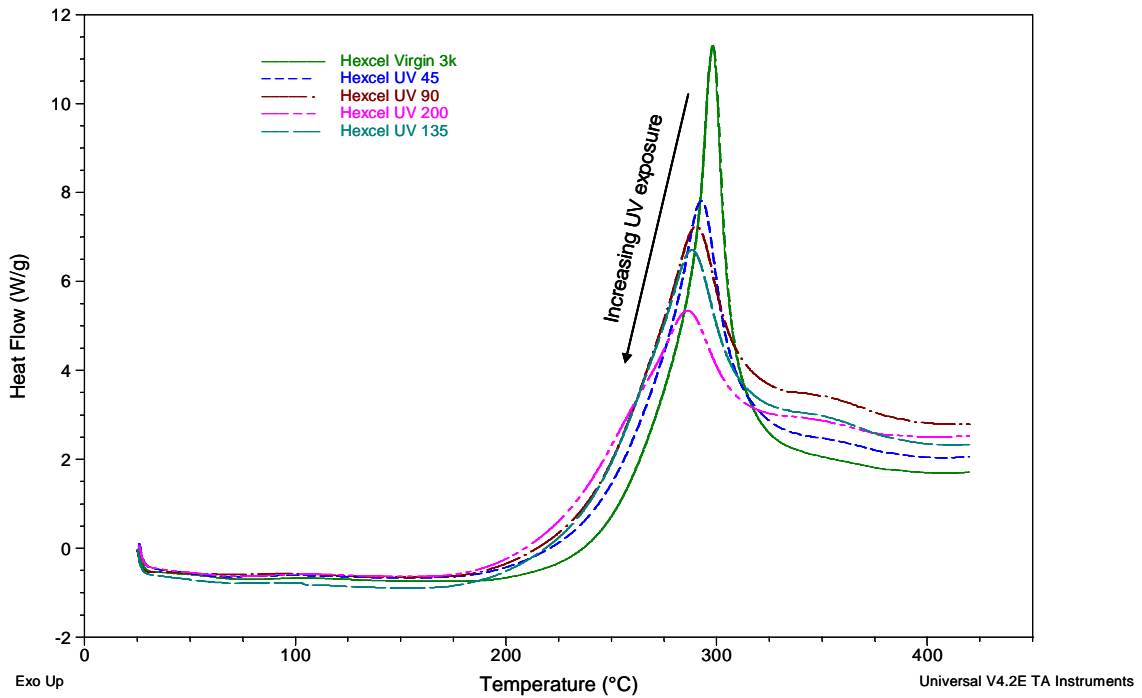


Figure 2. DSC thermogram of UV stabilized fibers showing the effect of increasing UV exposure.

UV Irradiation Uniformity

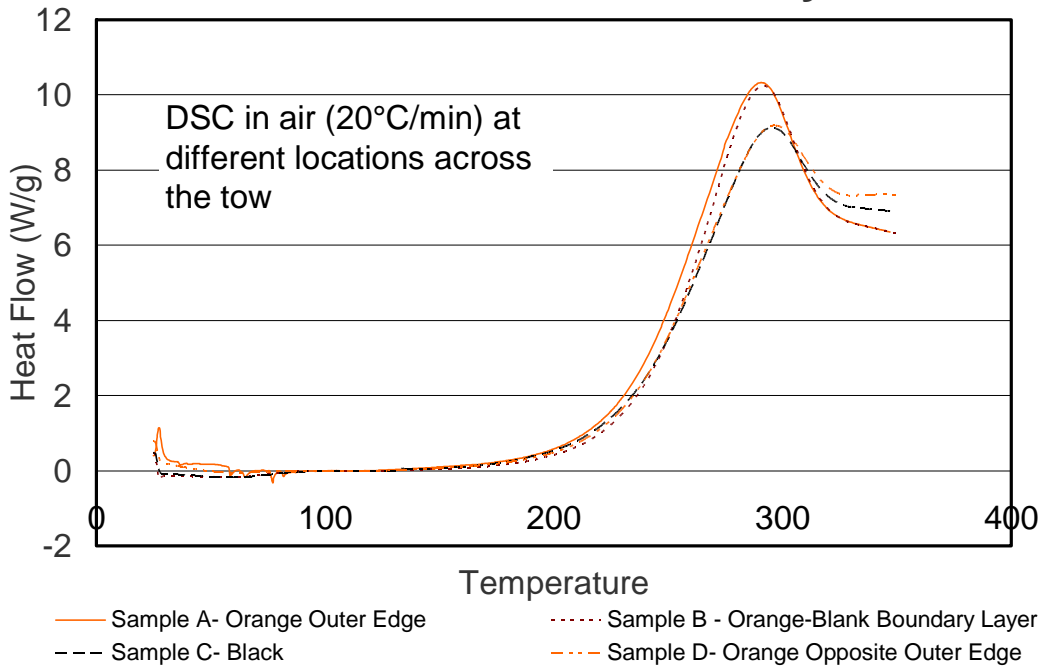


Figure 3. DSC thermograms from different parts of the same UV-stabilized tow sample.

Partners

ORNL gratefully acknowledges the following partners that have made valuable contributions to this project:

- Atmospheric Glow Technologies – plasma equipment design and processing (subcontract)
- Automotive Composites Consortium – programmatic and technical direction (complimentary)
- Clemson University – UV process development (subcontract)
- Hexcel Corporation – raw materials and technical consultation (complimentary)
- Radiation Dynamics Inc. – irradiation analysis, protocols, and beam time (complimentary)
- Toho Tenax America – raw materials and technical consultation (complimentary)
- University of Tennessee – characterization (subcontract)

Conclusions

Three prospective processing routes to lightly stabilize polymer precursors in an advanced carbon-fiber conversion line have been investigated. They are thermochemical, ultraviolet, and electron-beam processing. Thermochemical (plasma) stabilization has been selected as the stabilization route for use in a conversion factory. Electron-beam stabilization will be carried as an option for high throughput cross-linking upstream of the conversion factory.

ⁱ S. M. Cohn and S. Das, “A Cost Assessment of Conventional PAN Carbon Fiber Production Technology.” Energy Division, Oak Ridge National Laboratory, TN (1998).

D. Advanced Oxidation of PAN Fiber Precursor

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Daniel Sherman, Truman Bonds, Atmospheric Glow Technologies

Contractor: 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

- Developed stable protocol for stabilization and oxidation of 3k virgin PAN precursor tow with atmospheric-pressure plasma in < 1/3 of conventional residence time.
- Demonstrated 0.3 m/min plasma-stabilization/oxidation line-speed using a continuous, single-pass process.
- Demonstrated 4-hour continuous reactor operating time.
- Demonstrated the capability to plasma oxidize 100+ m continuous length of 3k tow. Delivered 100 m of plasma oxidized, spooled 3k tow to each Automotive Composites Consortium (ACC) original equipment manufacturer (OEM).

- Carbonized fibers after plasma oxidation and measured mechanical properties.
- Upgraded the six-tube reactor with improved flow control, process monitoring, and data acquisition.
- Instrumented the six-tube reactor with gas monitors and analyzed gas composition at various locations as a function of process parameters.
- Commenced construction of a next-generation, single-cavity (multiple-pass), multiple-tow reactor that was ~ 60% complete at fiscal year end.
- Successfully oxidized fibers that were stabilized by different routes.

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.
- Integrate plasma stabilization and plasma oxidation into a single conversion module.
- 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 (MAP) carbonization process and integrate into an advanced-technology pilot-line.

Introduction

The purpose of this project is to investigate and develop a plasma processing technique to rapidly and inexpensively oxidize polyacrylonitrile (PAN) precursor fibers. Conventional oxidation is a slow thermal process that typically consumes over 80% of the processing time in a conventional 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 greatly increasing line speed in the carbonization and graphitization stages and rapid stabilization techniques are being developed, but the oxidation time must be greatly reduced to effect fast conversion. This project intends to develop 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) ≥ 25 Msi tensile modulus and $\geq 1.0\%$ ultimate strain in the finished fiber; 2) uniform properties over the length of the fiber tow; 3) repeatable and controllable processing; 4) and significant unit cost reduction compared with conventional processing.

Project Deliverable

At the end of this project, the researchers will have developed an advanced oxidation process with residence time much less than that typical of conventional CF conversion lines. The advanced oxidation process will be sufficiently well understood and documented that the team can commence scaling it 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 non-equilibrium, non-thermal plasma at atmospheric pressure. Plasma processing is thought to enhance oxygen diffusion and chemistry in the PAN oxidation process. Atmospheric-pressure plasma provides better control over the thermal environment and reaction rates than evacuated plasma, in addition to eliminating the sealing problems accompanying 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.

Atmospheric-Pressure Plasma Processing Results

Exposure to plasma products at or near atmospheric pressure provides superior thermal control because the gas flow convectively heats or cools the fibers. This is deemed particularly important to avoid fiber melting from exothermic reactions. However, the short mean-free-path and lifespan of the chemically-reactive species at atmospheric pressure presents another set of challenges principally associated with finding a process recipe that delivers high process stability and short residence times.

In ORNL's conventional pilot-line, which represents the baseline process, PAN stabilization and oxidation occur in four successive furnaces in air, at temperatures increasing from about 200 to 250°C. Although there is not a precise transition from stabilization to oxidation, in general, one can consider stabilization to occur in the first furnace and (chemical) oxidation in the last three. So, in this project the researchers are working to reproduce the conversion advancement from the last three furnaces. The advancement from the first furnace is being addressed in the parallel advanced stabilization project. (See 7.C.)

At the end of fiscal year (FY) 2007, ~3X reduction in oxidation residence time and 0.3 m/min, single-pass line-speed was achieved in a six-zone reactor. Thus, the current tow speed in atmospheric plasma oxidation processing is more than twice the speed that was achieved at the end of FY 2006. Initial single-fiber mechanical data were generated, with results that fall short of property requirements but are encouraging at this stage of the development program.

During the first half of FY 2007, single fibers were carbonized after various combinations of stabilization and plasma oxidation and their mechanical properties measured. The results are shown in Figure 1, and do not differ substantially from previously reported results except that there are data from new combinations of stabilization and oxidation parameters. Despite the lack of fiber tension, tow-spreading, or controlled stretching during conversion and the low-temperature carbonization, plasma-oxidized fibers were generally about 25 Msi tensile modulus (25 Msi require-

ment) and $\geq 0.5\%$ ultimate tensile strain (1.0% requirement). These values exceed expectations at this stage of the investigation and inspire confidence that the required properties will be exceeded.

PAN fiber tows with different stabilization histories were plasma oxidized and subsequently carbonized. Based on the mechanical properties of the final carbonized fibers, researchers were able to evaluate effectiveness of different stabilization routes. It was observed that under similar oxidation protocols, ultraviolet (UV)-stabilization resulted in weaker CFs with significant variation in the properties. It is thought that poor penetration of UV radiation through the bundle of filaments (masking effect) caused such variation. However, untreated PAN and electron-beam (EB) pretreated fibers after plasma oxidation and subsequent carbonization produced carbonized filaments with moderate properties.

Significant equipment and process modifications were made during this reporting period. The reactor system was redesigned and reconfigured with additional gas-flow control ports and process monitoring ports. Additionally, new process-monitoring equipment, specifically for monitoring concentrations of certain critical gas species, was purchased and installed. The data acquisition system was upgraded. Also, the fiber-transport system was upgraded to enable multi-pass operation for achieving higher line speeds, as well as single- or multi-pass processing of long tows. At the end of the reporting period, the researchers had demonstrated plasma oxidation in ~ 1/3 of conventional residence time (unchanged from the previous reporting period), with a multi-pass line speed of 0.3 m/min (up from 0.15 m/min previously), and four hours of continuous reactor operation (up from approximately one hour). The length of fibers processed was extended to continuous lengths which were terminal only to the required sample size. Semi-continuous, multi-pass oxidation was conducted to obtain spools of continuous tow > 100 m length. 100+ m of plasma-oxidized, spooled 3k tow was delivered to each ACC OEM.

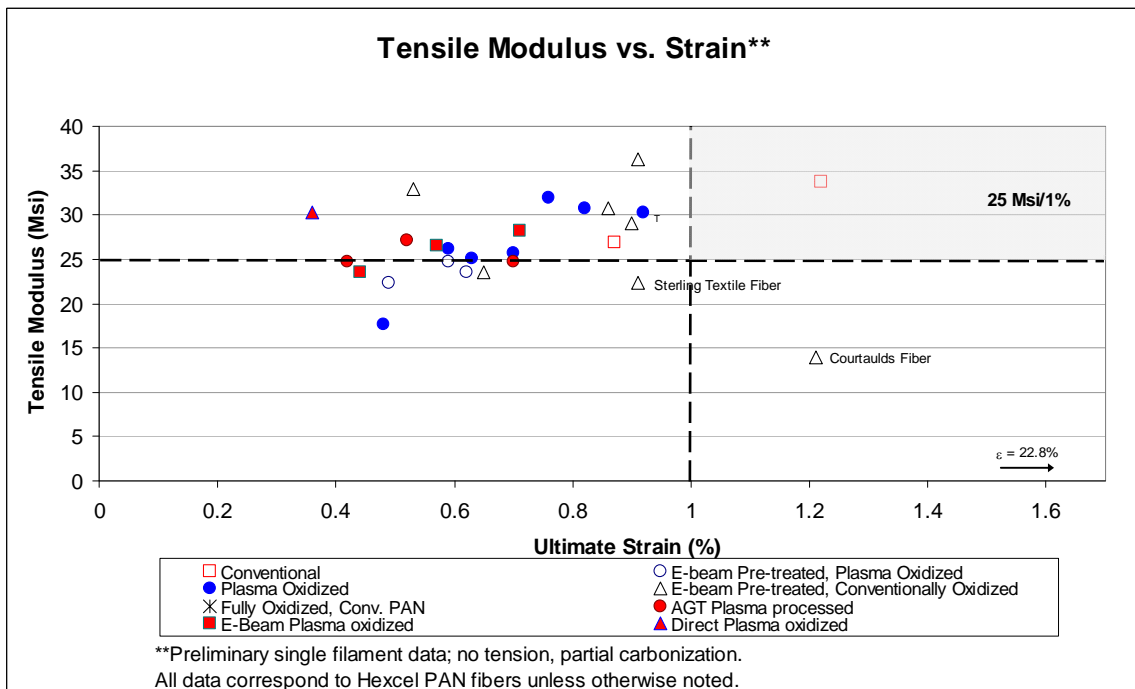
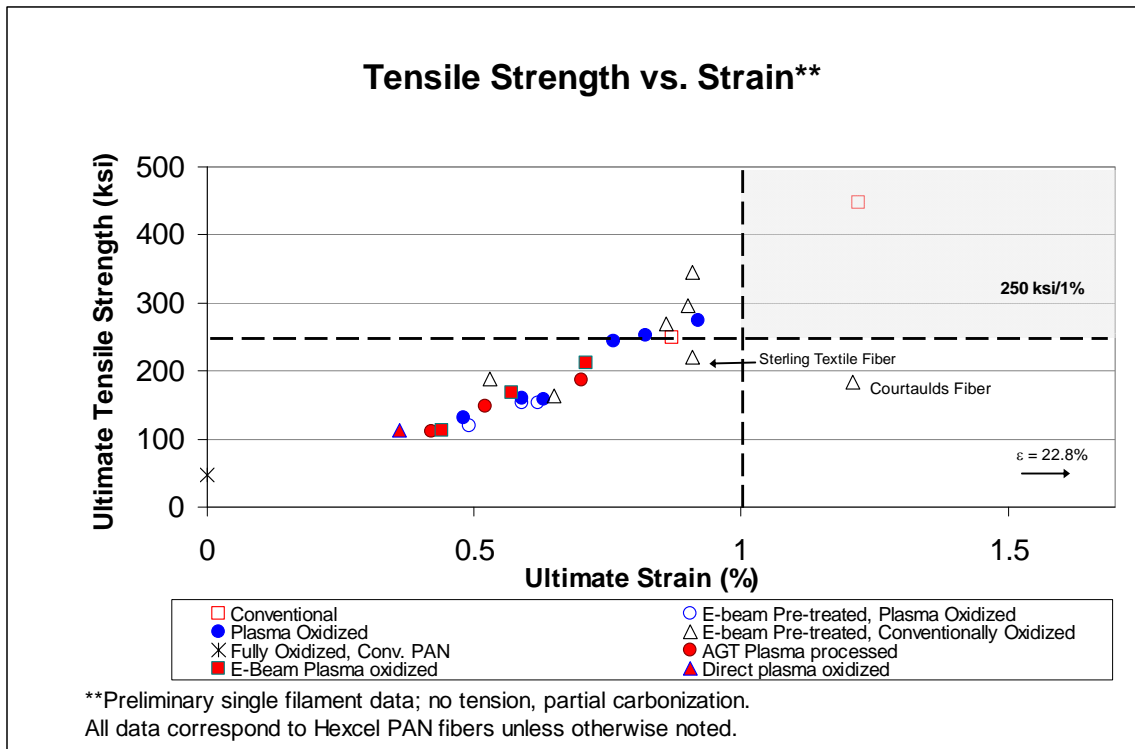


Figure 1. Mechanical properties of carbon fibers stabilized and oxidized by various routes, then conventionally carbonized at low temperature. There was no tensioning, controlled stretching, or tow-spreading during conversion. Conventional data points are for thermally-shocked and thermally-ramped heating protocols.

For the evaluation of composition, stability and consistency of the resulting atmospheric plasma, feed-gas analysis on heated tubes without fibers or reactive species (plasma) was conducted at several weekly intervals in the last half of FY 2007. The gas composition was found to be consistent throughout the temperature conditions tested.

A next-generation, single-cavity (multiple pass), multiple-tow reactor module was designed and partially constructed to ~ 60% completion at FY end. This reactor will be completed and used for scaling investigations starting in FY 2008.

For patent protection and export control reasons, equipment and process parameters are not published, but they are periodically disclosed to the relevant program managers in oral briefings.

Future Direction

During FY 2008, the project focus will shift from parametric studies with improved diagnostics to scaling to large multiple tows. The researchers will also carbonize plasma-oxidized fiber under more rigorous conditions (tension and temperature) using the new precursor evaluation system to validate its mechanical properties. We plan to complete the basic process development to the point that we can commence plasma-oxidation process and equipment-scaling investigations in FY 2008.

Patents and Publications

One invention disclosure was submitted on the development of PAN composition for accelerated stabilization and plasma oxidation.

Education

The 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, tech-

nical and programmatic consultation has been provided by the ACC.

Conclusions

Plasma oxidation of PAN fibers continues to progress toward the goal of reducing the cost of carbon-fiber manufacture. To date, the researchers have reduced oxidation residence time by ~ 3X compared to conventional oxidation, achieved 0.3 m/min line speed in a six-zone, multi-pass reactor configuration, and demonstrated four hours of continuous reactor operation. Plasma-oxidized fibers were carbonized and the mechanical properties checked, with good results considering the level of rigor applied and the current stage of process development. Continuous PAN 3k tow of >100 m length were plasma-oxidized in the reactor and 100 m spools of plasma oxidized 3k tow were delivered to each ACC OEM. Reactor system upgrades and new diagnostic capabilities made during this reporting period have enabled continued discovery and process improvements. Significant scaling experiments will commence in FY 2008.

E. Carbon-Fiber Systems Integration

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Contractor: ORNL

Contract No.: DE-AC05-00OR22725

Objectives

- Develop a sub-scale, modular test facility for demonstrating advanced carbon-fiber (CF) conversion technology.
- Integrate advanced-technology conversion modules into a functional and reliable system.
- Validate system process models and system inputs into cost analyses.
- Provide a capability for developing and testing conversion protocols for new polymer precursors.
- Provide the capability to produce small quantities of finished CF.
- Demonstrate advanced conversion technology to prospective commercialization partners.

Approach

- Procure and install a sub-scale, conventional CF pilot-line.
- Construct a prototypical, advanced-technology CF line using equipment and process specifications developed in other CF-conversion projects.
- Locate the advanced-technology and conventional lines adjacent to each other, highly instrument them for process characterization, and equip them with versatile fiber-transport equipment.
- Develop a small tube-furnace system for developing and evaluating conversion processes for prospective precursor fibers available in quantities of a few grams or less.

Accomplishments

- Continued making upgrades and performance improvements to the conventional pilot-line. Completed installation of carbon-proofing enclosures and modification of gas-supply and exhaust ducting to enable continuous operation. Implemented fully-programmable, automatic control. Partially completed implementation of a web-interfaced monitoring capability.
- Completed and approved safety basis for permanent, continuous operation of conventional pilot-line (previously approved on a run-by-run basis) and precursor-evaluation system.
- Initiated work on full-scale development of textile polyacrylonitrile (PAN) precursor.
- Completed a technical evaluation of the pilot-line and laboratory capabilities of Portuguese textile-PAN-fiber manufacturer FISIFE SA and entered into a partnership with them to scale-up and commercialize textile-PAN precursor technology.
- Down-selected a preferred textile-PAN/vinyl acetate (VA) chemical composition from among numerous candidate chemical compositions.
- Procured, installed, commissioned, and commenced operating a precursor-evaluation system.

Future Direction

- Defer further funding of the integration project until stabilization and oxidation modules are scaled sufficiently to construct and operate laboratory-scale pilot equipment.
- Redirect integration funding to new projects to support full-scale development of textile PAN precursor, maintenance and operation of equipment for delivering material samples to the Automotive Composites Consortium (ACC), and performing proof-of-concept investigations.
- Resume integration project when the various conversion technologies are more mature and sufficiently scaled to plug into a laboratory-scale, advanced-technology pilot-line.

Introduction

The purpose of this project is to integrate advanced CF technology developed in the Low-Cost Carbon Fiber (LCCF) initiative under Lightweighting Materials. The project encompasses the acquisition and operation of conventional conversion technology for benchmarking and validation; integration of advanced-technology conversion modules into a functional system; and developing and/or evaluating conversion protocols for prospective precursors.

A small pilot facility will be designed specifically for processing tows of commercial-grade (large-tow) fiber but will be sufficiently versatile that it can potentially process some higher-strength fibers. It will be designed to process a variety of polymer precursors. It may be adaptable to pitch precursors (this would require equipment and process modifications), but that is not a project requirement.

The heart of the pilot-scale conversion facility will be two adjacent, sub-scale, CF-conversion lines.

One line will be based on conventional pre-treatment, conversion, and post-treatment processes and the other will embody advanced-technology processes. The facility will be highly instrumented for characterizing fiber properties and process parameters. It will also be highly modular and be equipped with versatile tow-transport equipment so that tows can be routed through any combination of conventional and advanced-technology conversion, pre-treatment, or post-treatment modules. The systems-integration line will be capable of running a single tow or any number of tows up to its maximum capacity which will be at least five 50k tows. The integration line may eventually be mated with upstream or downstream processes. The facility is shown schematically in Figure 1. Essential advanced-technology modules are stabilization, oxidation, and carbonization. Optional advanced-technology modules include graphitization, surface treatment, advanced instrumentation and control, and downstream processing. The integration line will use conventional pre-treatment, sizing, and fiber-transport equipment.

New precursor development projects initially produce much smaller quantities of precursor fibers than are required by the aforementioned pilot-lines. Therefore, a precursor-evaluation system has been assembled for evaluating small quantities of prospective precursors and developing their conversion protocols.

It has become apparent that it will be multiple years before advanced stabilization and oxidation technologies are ready for integration. Therefore, the integration project will be temporarily halted after fiscal year (FY) 2007, to be resumed when those technologies are ready for integration. Beginning in FY 2008, the integration funding will be redirected to commercialization of textile-PAN precursor and operational support for the precursor-evaluation system. The commercialization of textile-PAN precursor received very significant effort this year and that progress is reported herein.

Project Deliverables

At the end of this project, advanced-technology modules will have been assembled into a functional, prototypical CF-conversion line with 5 – 10 large-tow capacity and alternative precursor-conversion protocols will have been developed and/or evaluated. The following tasks will have been completed:

- Confirm that advanced-technology conversion modules work together as a functional system.
- Determine interfaces to optimize system cost and performance.
- Determine and/or characterize system processing envelope, utility requirements, effluent streams, etc.
- Demonstrate system process control, stability, repeatability, scalability, safety, and reliability/availability/maintainability.
- Investigate system fault tolerance and response.
- Evaluate alternative precursor fibers and develop conversion protocols for selected precursors.
- Scale alternative precursor tow sizes and validate their conversion at the pilot-scale.
- Validate that program cost and technical targets were achieved.

Completion of these tasks should sufficiently demonstrate the advanced technology's value, robustness, and scalability to convince an industrial partner to commercialize it.

Current Status

Conventional Pilot-Line

In FY 2007, we completed critical upgrades to the conventional pilot-line. The most important of these were the addition of carbon-proofing enclosures around the take-up winders and sizing module to prevent the generation of airborne carbon particulate that might compromise the operation of nearby high-voltage equipment. Also, the gas supply was changed from compressed-gas bottles, requiring frequent bottle changes, to a large dewar that will support many days of continuous operation. Figure 2 shows the conventional pilot line installed at ORNL.

The previous owner of the pilot-line did not find it necessary to automate its operation. They run a 24/7 production facility, so it is quite simple for production operators to make manual adjustments to the pilot-line during its startup, operation, and shutdown. By contrast, ORNL research is a single-shift operation. Therefore, automation is necessary to enable safe and effective, single-shift operation. In FY 2007, we developed fully-programmable, automatic-control capabilities that will enable safe, unattended system warm-up and standby, enabling us to conduct experiments in a single-shift operation. We also partially completed the implementation of a web-interfaced monitoring system that will allow us to monitor warm-up and cool-down from our office or home computers via a web interface.

Advanced-Technology Pilot-Line

The microwave-assisted plasma (MAP) carbonization module is the base module for the advanced-technology integration line. Other modules will later be added to it. It is now in place and operational.

During this period, MAP-carbonized tow and plaques were made and delivered to the ACC for independent evaluation of mechanical properties. High-speed winders and tensioners are needed to support operation at the bandwidth (number of tows) and range of speeds targeted for the conventional and advanced-technology lines.

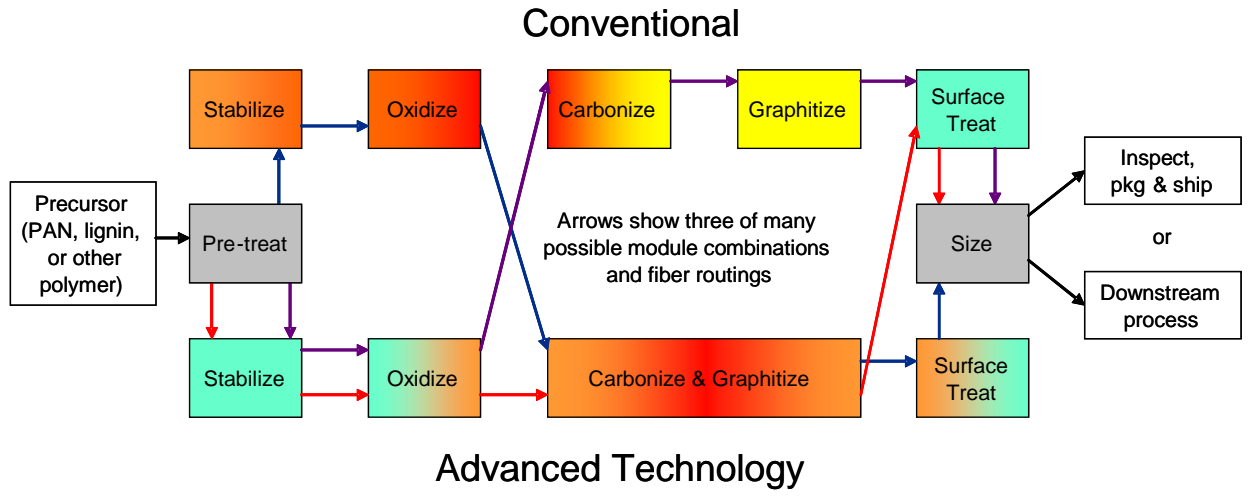


Figure 1. Schematic of carbon-fiber pilot-lines.



Figure 2. Conventional pilot-line installation at ORNL.

Acquisition was planned to commence in FY 2006; however, budget reprioritization delayed acquisition by a year. Winder specifications were developed in FY

2006 and reviewed in early FY 2007. The winder package procurement was released in the third quarter of FY 2007, satisfying a project milestone. The winder package should be received in FY 2008, quarter 2. We also commenced fabrication and installation of an improved MAP cooling system in FY 2007.

Because the stabilization and oxidation modules still require significant development before they are ready to integrate to the MAP carbonization module, advanced-technology integration will be deferred indefinitely and its budget will be redirected to other low-cost CF activities.

Precursor-Evaluation System

Due to its size, the aforementioned pilot facility requires $\geq 1\text{k}$ tows at least 50-m long. The tensioning system is designed for large tows and is, therefore, not sufficiently precise to accurately tension small tows and is likely to break tows smaller than about 1k. Startup time for the conventional pilot-line graphitization furnace is at least 10 hours, so

restringing and restarting after tow breakage requires many hours. This is incompatible with the need for inexpensive, fast- turnaround precursor evaluations. New precursor-development projects need many intermittent trials on very small tows, as they usually extrude one or a few filaments in short lengths for initial testing. The conventional pilot-line is not amenable to this kind of operation; therefore, a precursor-evaluation system based on compact tube furnaces and precision tensioners was commissioned for evaluating prospective precursors and developing their conversion protocols. The precursor-evaluation system has rapid start-up/shutdown capabilities and is capable of heat-treating short lengths of single filaments or a single tow from a few filaments up to large tow size. Controlled tension can be applied to tows larger than approximately 10 - 20 filaments. Tows too small for controlled tensioning can be "restrained" to provide some tension. Short fiber lengths can be readily transported through the system on trays or similar compact carriers.

The precursor-evaluation system design commenced in FY 2006. In FY 2007, we completed the design, procured and installed the furnaces and transport equipment, commissioned the system, and began operations. Figure 3 shows some of the tube furnaces awaiting installation.



Figure 3. Continuous stabilization/oxidation (in furnace at right) and low-temperature carbonization (in furnace at left) of conventional 3k PAN precursor tow in precursor-evaluation system.

Textile-PAN Precursor Scale-Up

Our evolving understanding of the probable costs and risks of various candidate precursors, coupled with the emergence of new partnership opportunities and the continued capacity constraints in the CF market, prompted us to revisit the textile-PAN technology that was mothballed in 2004. Therefore, in the first half of FY 2007, we began preliminary planning to scale-up the textile-PAN precursor technology that was originally developed by Hexcel under the LCCF initiative, and in the last half of FY 2007 we worked aggressively toward textile-PAN scale-up. We have established a highly-interactive and mutually-beneficial partnership with Portuguese textile fiber manufacturer FISIFE SA, and are in serious discussions with two other prospective commercialization partners.

FISIFE has installed a chemical-treatment unit in their pilot-line. ORNL has conducted extensive characterization of precursor chemical composition and extruded filaments generated by FISIFE, as well as conversion trials on filaments and tows generated by FISIFE from selected precursor chemical compositions. An example differential scanning calorimeter (DSC) characterization is shown in Figure 4. We have selected a preferred chemical composition that is the baseline for future work. At FY's end, FISIFE was making multiple spools of chemically-treated 26k tow at 1 – 2 kg of fiber per spool. This fiber will then be used for conversion trials on ORNL's precursor-evaluation system and pilot-line.

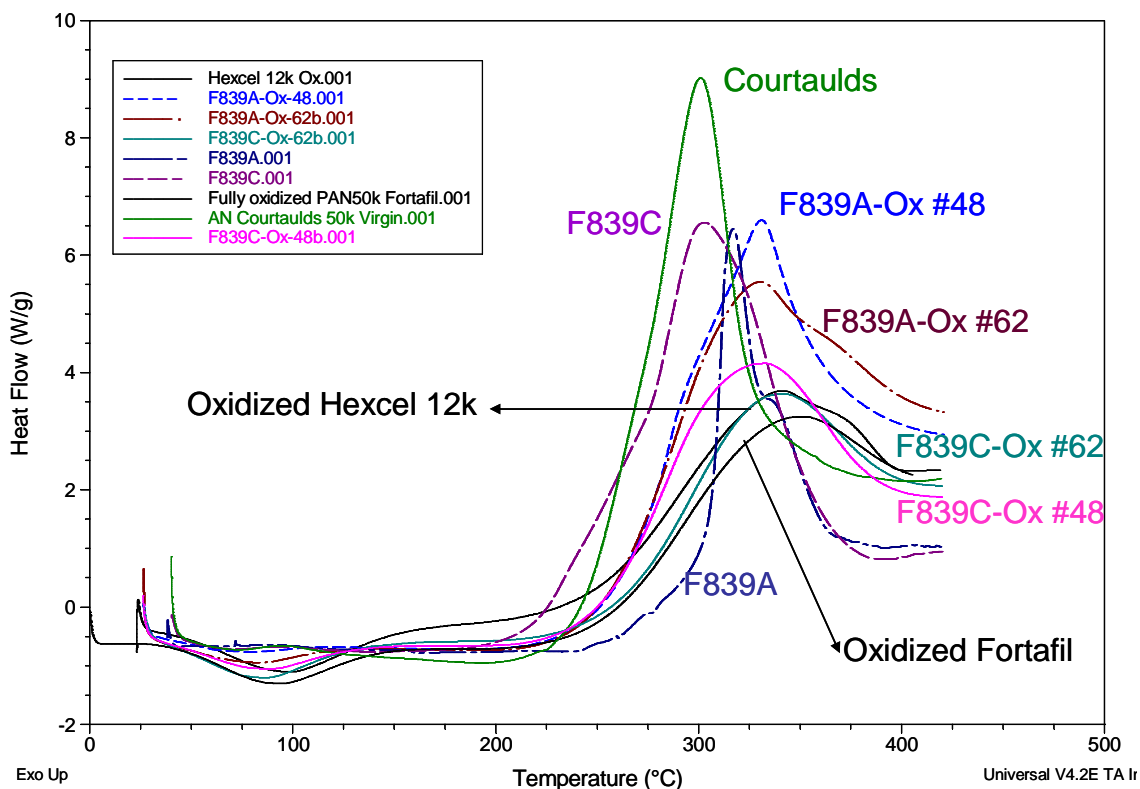


Figure 4. DSC characterization of various oxidized textile-PAN precursor compositions and comparison to oxidized commercial precursors.

Future Direction

The integration project will be deferred until stabilization and/or oxidation modules are ready to integrate into an advanced-technology pilot-line.

The integration budget will be reallocated to support textile PAN-precursor scale-up, materials sampling, proof-of-concept investigations, and/or other LCCF work.

Conclusions

Several pilot-line modifications were completed, and the development of a web-based monitoring capability is almost complete. A precursor-evaluation system was installed and commissioned, and is already being gainfully utilized.

Further integration of an advanced-technology pilot-line will be deferred until stabilization and oxidation modules are more mature. Full-scale development of textile-PAN precursor was initiated and is now well underway.

Presentations/Patents/Publications

None.