7. LOW-COST CARBON FIBER

A. Low-Cost Carbon Fibers 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 CO_2 emissions. Carbon fibers 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 modeling indicates that more than 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 will necessitate a large reduction in cost of appropriate strength fiber (from about $20/lb to about $5/lb) before we see significant use in the automotive industry. 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 using 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 $5–7/lb. In addition to precursor, cost savings will also be achieved through advanced processing techniques, including plasma oxidation, carbonization, and graphitization of the precursor fiber, to obtain more efficient use 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 of 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, copolymers, 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

- Demonstrated continuous melt spinning of multifilament fiber from a 50-50 blend of unpurified kraft softwood lignin (SWL)—a notable first—using a purified kraft hardwood lignin (HWL) as the plasticizer.

  — The SWL was produced by Kruger Wayagamack (Quebec, Canada) using the LignoBoost process (developed by STFI-Packforst in Sweden) to isolate the lignin from kraft black liquor under process conditions that were more carefully controlled than currently practiced for the production of commercial kraft lignin products. The lignin still contained a very small proportion of cellulose fibers, which impacted the structural integrity of the spun fiber (as revealed by scanning electron microscope imaging) and subsequent processing into carbon fiber. Nevertheless, this demonstrated that it is possible to isolate lignin from a kraft chemical pulping operation which is very much cleaner than current commercial kraft lignin, and that with refinement of the isolation process, kraft lignin meeting the target specifications for carbon fiber production could be produced <u>without</u> the need for an additional purification process. Such a development would enhance the economics of lignin-based carbon fiber production; a reduction of lignin cost from 50 to 30¢/lb would reduce carbon fiber cost by 60 to 80¢/lb.

- Demonstrated stabilization, carbonization, and graphitization of 50-50 softwood-hardwood lignin fibers.

  — The mechanical properties of the carbonized fibers (1,000°C treatment) were about 60% of the milestone target for fiscal year (FY) 2008, an encouraging result for the first successful melt spinning of blends incorporating an SWL and, furthermore, a lignin that had not been subjected to a purification procedure. Further heat treatment of the carbon fiber at 1,700°C decreased mechanical properties, a probable consequence of the defects created in the fiber through volatilization of the cellulose fiber contaminant in the SWL. Kruger Wayagamack is working to refine the lignin isolation procedure to produce a kraft lignin product meeting the target purity specifications.

  — On a related note, through a meeting at ORNL (October 10), contact was established with key personnel at STFI-Packforst, Swedish Research Institute, where the LignoBoost process for isolating lignin from kraft black liquor was developed. As a result, a preliminary agreement has been reached whereby STFI and ORNL will collaborate on further development work on the use of lignin for carbon-fiber production; specifically, STFI will provide kraft lignin meeting the purity specifications and, based on results obtained at ORNL, will modify the lignin chemistry as appropriate to enhance the properties of carbon fiber produced from the lignin. STFI-Packforst is the world's leading institution with respect to lignin materials, and bringing it onboard the project will help to accelerate progress on the development of lignin-based carbon fibers as well as promote the ORNL research effort to a larger and more diverse industry base of potential lignin suppliers.

- Implemented work on Alcell, a lignin material produced by the Organosolv process in which waste wood materials are pulped with solvents to produce cellulose (for ethanol fuel production) and lignin. The Alcell lignin (200 lb) was furnished by Lignol Innovations (Vancouver, Canada), the leading company with respect to the production of cellulosic ethanol (recently awarded a $30M Department of Energy [DOE] contract to build a biorefinery in Colorado). The Organosolv process produces a much cleaner lignin than current commercial kraft lignin products and more than meets the purity specifications for carbon-fiber production.

  — Conditions were established for devolatilization of the Alcell lignin to remove residual solvents, and rheological and thermal analysis measurements were made to help establish melt-spinning conditions. Fibers were readily melt spun on the multifilament equipment (without the need for a plasticizing additive), and conditions for processing the precursor fibers into carbon fibers were established. The mechanical properties of the Alcell lignin-based carbon fibers are currently falling well short of the target properties (approaching 50% of target), but each new spinning run on the Alcell material has resulted in a greater understanding of the properties of this very different but promising type of lignin. One important characteristic of the Alcell lignin is its higher glass transition temperature (T_g) and melt spinning temperature, which enable the fiber stabilization stage of processing to be carried out at a significantly higher temperature (i.e., faster rate) than

possible for the high-purity kraft HWL (solvent extracted) on which much of the process development efforts this fiscal year were focused.

- Melt-spinning speed trials confirmed that the spinning speed of lignin can be increased to at least 2 times the Kline economic model baseline speed of 600 meters/minute (m/min), the speed for commercial mesophase pitch-based fiber. Alcell lignin fibers of the target diameter of 10 microns (µm) were successfully spun and wound at a winding speed of 1,200 m/min. For this demonstration, a suitable spinning die was manufactured to accommodate the required increase in mass throughput of the lignin melt and to achieve the required fiber draw-down ratio of 25 : 1 (instead of 15 : 1). Spinning speed is one of the most important process parameters with respect to the economics of carbon-fiber production from lignin (precursor cost and carbon yield are the most important material considerations). Demonstration of further increases in spinning speed is dependent on upgrading the melt-spinning equipment, notably installation of a higher-speed winder.

- Demonstrated that ultraviolet (UV) irradiation of lignin fibers facilitates subsequent thermal stabilization of the fibers.

  — Thermal stabilization-differential scanning calorimetry (DSC) studies on high purity kraft HWL fibers confirmed that UV irradiation of the fibers greatly enhanced (20-fold) the rate of stabilization during subsequent thermal treatment of the fibers at about 130°C, a temperature dictated by the melting point of the lignin but too low to obtain an acceptable rate of stabilization through thermal treatment alone. The studies to date indicate that a short (<1 minute) UV irradiation of the HWL fibers increases the rate of stabilization of the fibers at 130°C to an acceptable level. As resources and higher priority work permit, further work will be carried out to determine whether other lignin fibers (e.g., Alcell) could be stabilized through UV irradiation alone.

- A comprehensive thermal analysis database was compiled to facilitate carbon-fiber conversion processing.

  — Thermal analysis (DSC, thermogravimetric analysis [TGA]), rheometry, and molecular weight characterizations were made on selected lignin materials representing different species of wood (hardwood and softwood), different methods of pulping (kraft, soda, and Organosolv), and different methods of purification (aqueous, organic, none). The extensive database provides insight into the relationships between lignin chemistry, method of isolation/purification, purity, and melt spinnability, and facilitates more efficient evaluation of a lignin material for suitability for carbon-fiber production. Similarly, to facilitate conversion of lignin fiber into carbon fiber, the thermal analysis data provide information on T_g and melting points; volatiles content; rates of stabilization at selected temperatures; and the influence of atmosphere and UV-irradiation treatment, temperature range of carbonization, carbon yield (at 1,000°C), and ash content of the carbon (relates to initial salt content of the lignin). Ultimately, the database will help correlate the engineering properties of lignin-based carbon fibers with the fundamental properties of the lignin precursor material and conversion conditions.

- A research paper on the use of lignin as a precursor material for carbon fiber production was written.

  — This particular paper covers only the production of melt-spun fibers, not details of conversion into carbon fiber. When the manuscript has passed through the ORNL approval process, the paper will be submitted for publication in a major materials journal, possibly the *Journal of Materials Science*. Similarly, a section on lignin-based carbon fibers was written for a paper on the low-cost carbon fiber (LCCF) project as a whole ("Multitask Research Program to Develop Commodity Grade, Lower Cost Carbon Fiber") to be presented by Dave Warren at the SAMPE Fall Technical Conference 2008 in Memphis, Tennessee (September 8–11).

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 the following.

  — Down-selection of key sources of lignin (upwards of three) suitable for carbon-fiber production without purification and procurement of large batches for 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.

— Installation and commissioning of an extrusion compounding-pelletizing line to facilitate production of lignin feedstock pellets for melt spinning into precursor fibers (with or without copolymers and plasticizers).
— Design of extruder and spinneret die to obtain high spinning speeds of target diameter fiber with good structural characteristics.
— Establishment of conditions for continuous melt spinning of lignin fiber tow at speeds of at least 1,200 m/min (i.e., twice the Kline economic model baseline spinning speed of 600 m/min).
— Development of techniques for spooling and rewinding of lignin-based precursor fiber tow.
— 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) and other entities.

• Collaboration with industrial, government, and academic partners to do the following.

— 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 DOE FreedomCAR-funded work at ORNL is directed toward 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 (see reports 7.B and 7.C). 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 CO_2 emissions (e.g., 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, body-in-white modeling indicates that more than 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, and the supply is far too limited to meet the projected demand. Thus, a large reduction in the cost of appropriate strength fiber (from about \$40/kg to about \$10/kg) and an increase in supply must take place before we will see substantial increases in carbon fiber use in the automotive industry. 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 using 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 LCCF 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, essentially being based on its fuel value of about 5¢/lb. On the downside, however, relatively little is known about how to transform lignin into 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, although not prohibitively.

Currently, chemical pulping of wood is the only immediate source of lignin in the United States, but as biomass refineries come onstream, 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 cross links different plant polysaccharides, conferring mechanical strength to the cell wall and thus 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. HWL is composed of coniferyl alcohol and sinapyl alcohol units in varying ratios, whereas SWL predominantly comprises coniferyl alcohol (>90%) and a small proportion of *p*-coumaryl alcohol.
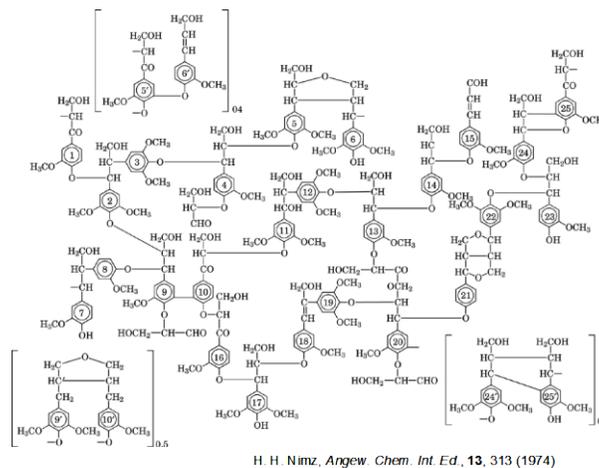

H. H. Nimz, *Angew. Chem. Int. Ed.*, **13**, 313 (1974)

Figure 1. Chemical structure of HWL.

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 SWL isolated by mechanical milling of the wood (low degradation process) is about 20,000. Milled HWL exhibits significantly lower molecular weights. These and other differences between the chemistries of HWLs and SWLs influence the use of lignin for carbon-fiber production.

Depending on species, wood is about 15-25 wt % lignin, 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 50% of the proportion of cellulose), which if used 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, use 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 enhanced national security (e.g., reducing dependence on imported fossil fuels).

Worldwide, more than 200 million metric tons of lignin pass 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 coproduct that is used 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 number 2 fuel oil). In fact, many modern mills have cogeneration facilities to produce electrical energy for sale to utility companies.

Lignin is already used on a large scale in transportation applications (e.g., as an emulsifying agent for asphalt road surfaces and as a dispersing agent for cement and concrete mixes, used 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 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

Most (>90%) 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 used 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 reduced to acceptable levels. Impurities include nonmelting 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 HWL 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, we found that the contaminants in the spun fibers degraded 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, because the melting point of the purified lignins, notably HWLs, was above their decomposition temperatures, they could not be melt spun. Chemically-pulped lignin is a heterogeneous material that includes a wide range of molecular weights, and it is the presence of some of the lowest molecular weight fractions that appears to impart melt spinnability to the HWL 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. As so often happens in

research, progress was made in one area at the expense of another.

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 collaborative efforts with several large paper manufacturers, notably MeadWestvaco Corporation (MWV) of Charleston, South Carolina, 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 SWL, which, 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 FY 2007) of continuous and uninterrupted spinning of multifilament 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 help align the molecular structure of the precursor fiber to facilitate development of the desired engineering properties in the subsequent 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 T_g and melting point of the lignin and the temperature range for carbonization and the carbon yield, 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 multifilament 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 for processing into carbon fiber will be produced.
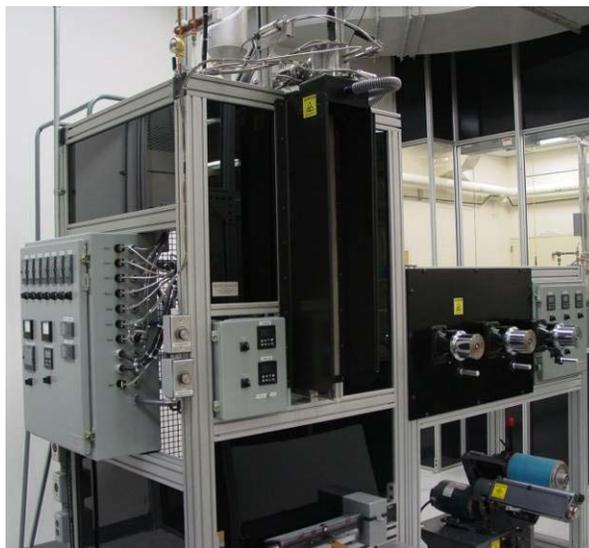

Figure 2. Multifilament melt-spinning equipment.

Lignin Purification and Fiber Spinning

As noted previously, a laboratory-scale process was developed at ORNL to purify kraft HWL to the required level. However, the laboratory process was not readily scalable 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 reexamine an alternative approach to the purification of kraft lignin that it had investigated 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—essentially the opposite approach to the aqueous method.

Early in the fourth quarter of FY 2007, a small sample of the solvent-extracted lignin (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.
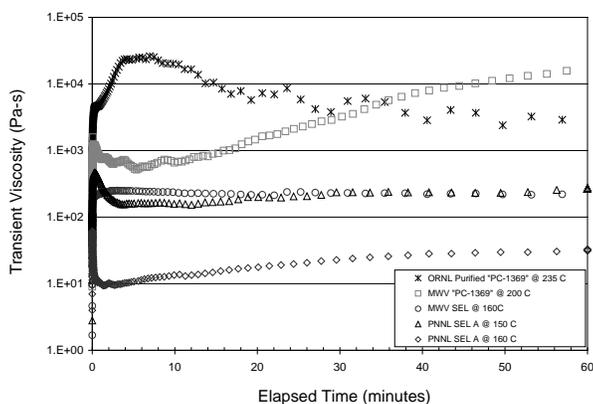
of residence time. It was this HWL material that was solvent extracted to produce the SEL product.

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 multifilament spinning equipment.

The first "large" batch of MWV solvent-extracted (organic-purified) lignin was melt spun in late FY 2007 (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 <u>without</u> 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.
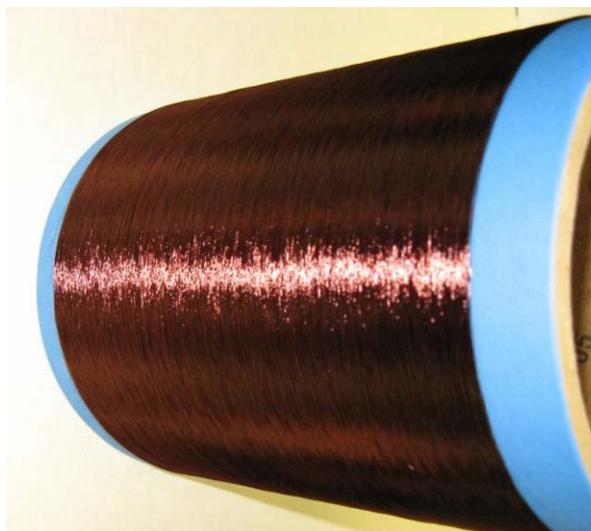

Figure 3. Viscosity of HWL as a function of time (at a given temperature).

In contrast, undesirable rheometry data are exemplified by the upper plot (square symbols) for the MWV HWL (PC-1369) as received, which exhibits an unstable (rising) viscosity as a function

Figure 4. Lignin fiber tow comprising 12 filaments, each 11 μm in diameter.
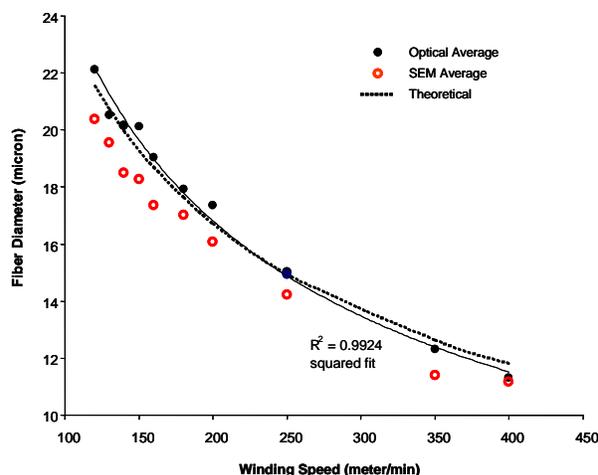
Figure 5. Lignin filament diameter as a function of winding speed.

The maximum fiber winding speed achieved in this first multifilament spinning run was 400 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 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 5 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 20,000× were

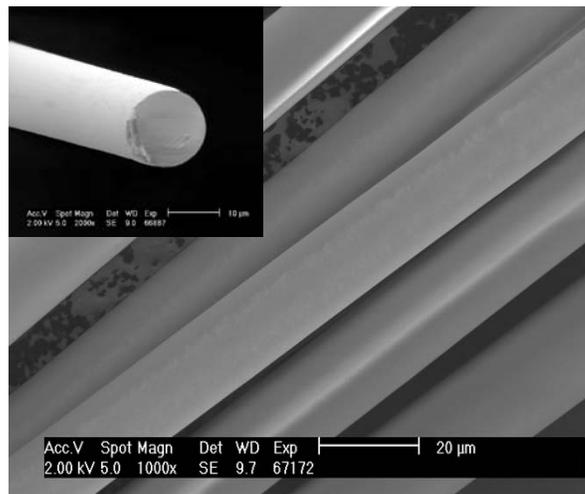made, confirming the structural uniformity of the lignin fibers.

Figure 6. SEM images of lignin precursor fibers.

Subsequent studies of spinning speed targeted a twofold increase in spinning speed over the baseline speed assumed in the Kline economic model (i.e., 1,200 m/min instead of 600 m/min, the spinning speed of commercial mesophase pitch-based fiber). The target speed was achieved using (unpurified) Alcell lignin (q.v.) as the feedstock. This necessitated increasing the mass throughput in the melt extruder and spinneret and increasing the fiber draw-down ratio from 15 : 1 to 25 : 1 so that the target filament diameter of 10 µm could be achieved at the much higher winding speed. Further studies of spinning speed will target yet higher winding speeds and also spinning of 24-filament tow at high rates.

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. However, the initial evaluation indicated that it was readily melt spinnable without an additive. In fact, its thermal and rheological characteristics were very similar to those of the MWV SEL that was so readily melt spinnable. 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 HWL (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 HWL 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) that will be sent to ORNL in the near future for evaluation.

In the meantime, PNNL also scaled up production of an aqueous-purified HWL, an approach that, as mentioned previously, 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 HWL, was received in the first quarter of FY 2008 (11/9/07). The initial tests indicate that its melting point is in the desired ballpark, namely, around 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 tests indicated that it may be melt spinnable when blended with an SEL (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 HWL purified by ORNL using a similar aqueous approach.

The aqueous approach yields a clean lignin that 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 HWLs produced to date through use of an aqueous procedure are not melt spinnable without a plasticizing agent. Nevertheless, it is a positive development that HWL purified through an aqueous procedure can be melt spun by

inclusion of a minor proportion of a readily spinnable SEL. 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 HWL is high carbon yield. This is highlighted in Figure 7(a), in which TGA data are shown for ORNL aqueous-purified HWL together with the corresponding data for the unpurified lignin as received. TGA data for an unpurified SWL are included for the purpose of comparison.
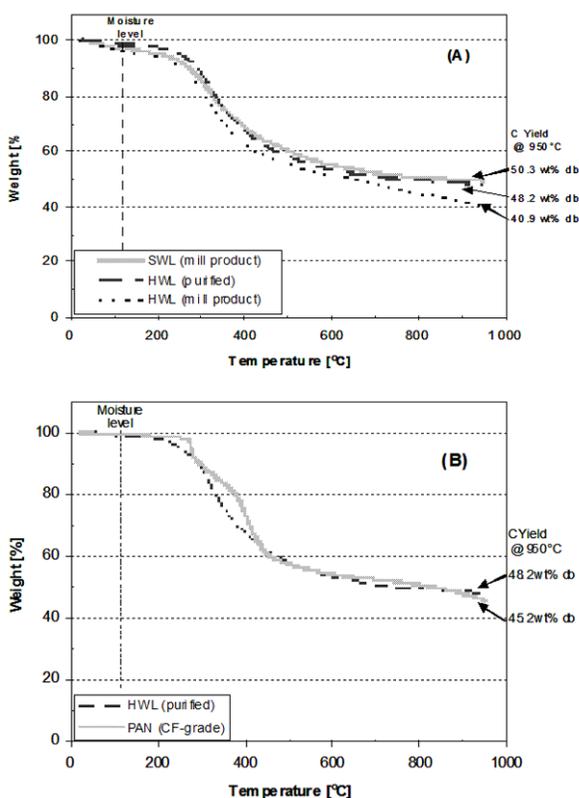

Figure 7. TGA data for lignins (a) and PAN (b).

In Figure 7, 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 HWL using an aqueous procedure is discerned from the fact that carbon yield increased from 40.9% to 48.2%. The theoretical carbon content of HWL is about 55–60% (Table 1). For comparison, the yield of carbon obtained from carbon-fiber-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.

Table 1. Carbon contents of lignin and PAN

Precursor Material	Theoretical Carbon 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 (carbon-fiber grade)	68	45.2

Conversely, the positive attribute (in addition to high purity) of the organic-purified SEL is the fact that it is very readily melt spinnable and can also be used as a plasticizing agent for lignins that are not melt spinnable. 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.
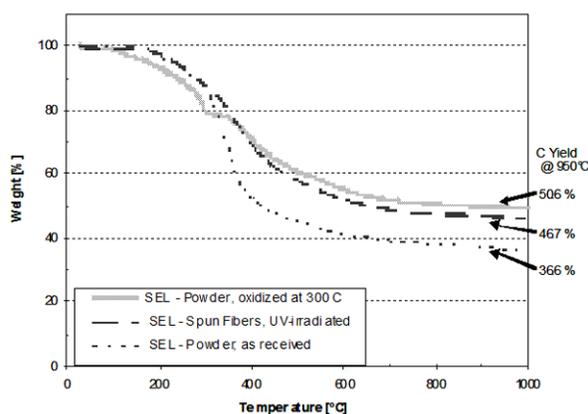

Figure 8. TGA data for fibers produced from MWV SEL.

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 SEL or to achieving high carbon yield from the material). However, the temperature at which the SEL powder was oxidized to obtain a meaningful rate of cross-linking (300°C) 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.

Thus, for SELs 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, which shows the TGA data for SEL fibers irradiated with UV light at ambient temperature (25°C) in air. Melt-spun fibers obtained from the multifilament 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 HWL, the following general conclusion can be drawn. 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 HWL negatively impacts the melt spinnability of the purified lignin.

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 through 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.

Melt Spinning and Production of Carbon Fiber from Unpurified Lignin Materials

The recent commercialization of the LignoBoost process for isolating lignin from kraft black liquor has resulted in much cleaner unmodified kraft lignin material becoming available (i.e., compared to current commercial, unmodified lignin products). The process was developed by STFI-Packforst (Swedish Research Institute) and its partner companies in the project over a 4-year period. The process was developed primarily for the production of lignin fuel pellets, thereby helping to increase paper mill productivity, but is also attracting increasing interest as a means of isolating lignin for production of chemicals and related materials, including carbon fiber. Several large pulp and paper companies around the world are evaluating the process for both purposes. One of these companies, Kruger Wayagamack in Ontario, Canada, has furnished kraft SWL for evaluation for carbon-fiber production.

The work carried out on the Kruger lignin to date has demonstrated that the quality of the SWL is close to the target specification for carbon-fiber production and that the material can be melt spun

as-received, at least with the aid of a plasticizing agent (a prerequisite for all unmodified, kraft SWL materials). In the initial work, a 50–50 blend of the Kruger lignin with the solvent-extracted kraft HWL (produced by MWV) as the plasticizing agent was readily melt spun on the multifilament equipment. The carbon fiber produced from the lignin precursor fiber exhibited mechanical properties approaching 50% of target. This was the first time that an unpurified kraft lignin, and more notably an SWL material, had been successfully spun on the multifilament equipment, albeit with the addition of a high proportion of a purified lignin to serve as the plasticizing agent. This represented a significant development with respect to the economics of carbon-fiber production from lignin materials, with the potential for reducing the cost of a lignin-based carbon fiber by 60-80¢/lb. Further work on this lignin material to greatly reduce the proportion of plasticizing agent was placed on hold to permit evaluation of a second source of unpurified lignin materials; namely, the Alcell lignin by-product of the production of cellulosic ethanol fuel.

So-called biomass-derived lignins will become increasingly available from cellulosic ethanol manufacturers as biorefinery programs ramp up to produce ethanol fuel from lignocellulosic materials, such as wood and switchgrass, instead of corn. As mentioned in more detail below, Lignol Innovations is a leading company in this respect and was recently awarded a $30M DOE contract to build a demonstration biorefinery in Colorado. Lignol Innovations uses the Organosolv pulping process to separate cellulose and lignin in lignocellulosic materials; this process uses a small proportion of the ethanol that is subsequently produced from the cellulose through enzymatic hydrolysis as the pulping solvent. Lignol Innovations was contacted, and the company furnished 200 lbs of its Alcell lignin product to the FreedomCAR program for evaluation for carbon-fiber production.

Conditions were established to remove traces of residual solvents from the Alcell lignin, and rheology and thermal analysis measurements were made to establish melt-spinning conditions. Fibers were readily melt spun on the multifilament

equipment, from the lignin as-received and without the need for a plasticizing additive, and conditions were established for processing the precursor fibers into carbon fibers. The mechanical properties of the Alcell lignin-based carbon fibers are currently falling well short of the target properties (approaching 50% of target), but each new spinning run on the Alcell material has resulted in a greater understanding of the properties of this very different but promising type of lignin. One important characteristic of the Alcell lignin is its higher T_g and melt-spinning temperature, which enable the fiber stabilization stage of processing to be carried out at a significantly higher temperature (i.e., faster rate) than possible for the high-purity kraft HWL (solvent extracted) on which much of the process development efforts this fiscal year were focused.

Pending further improvements in the quality of the Kruger SWL, the efforts in the second half of FY 2008 were focused on the Alcell lignin, the quality of which more than met the specifications for carbon-fiber production. These efforts included melt-spinning speed trials in which it was demonstrated that the melt-spinning speed of lignin can be increased to at least twice the baseline speed assumed in the Kline economic model [i.e., 1,200 m/min vs the baseline speed of 600 m/minute (the spinning speed of commercial mesophase pitch-based fibers)]. Thus, in addition to the advantage of being able to use a lignin material without the need for (relatively expensive) purification, increases in the spinning speed of this magnitude will also have a beneficial impact on the economics of carbon fiber from lignin materials. Demonstration of spinning speeds greater than 1,200 m/min is dependent on upgrading the winder on the multifilament spinning equipment.

Finally, to place into perspective the quality of the key lignin materials examined in the work during FY 2008, some of the elemental analysis data obtained on each of the relevant lignin materials are summarized in Table 2.

The elemental analysis and ash data in Table 2 clearly demonstrate the superiority of the Alcell (Organosolv) lignin, as-received, with respect to purity, most notably in contrast with the

commercial kraft HWL product. When discussing lignin quality, however, it should be noted that the commercial kraft lignin product in question is an unmodified lignin (i.e., in the form as isolated from black liquor). Relatively little of the lignin is sold in this form, and that which is sold for commercial applications meets the quality needs of the customers. The majority of kraft lignin products are chemically modified forms of the lignin isolated from black liquor (e.g., sulfonated derivatives for use as dispersants). The processes of modification result in very much higher quality kraft lignin products with much lower residual salt contents. From both chemistry and cost standpoints, however, the modified kraft lignins are not suitable for carbon-fiber production.

Table 2. Elemental analysis of lignins

Lignin Material	C (%)	S (%)	Na (ppm)	K (ppm)	Ca (ppm)	Ash (%)
HWL	59	2.45	19,000	1770	650	2.8
HWL-Aq	65	1.48	73	70	255	0.05
HWL-SE	65	1.40	1,160	104	76	0.01
SWL-K2	67	1.18	2,390	100	78	0.2
Alcell	66	0.05	17	44	163	0.001

HWL = MWV hardwood lignin as received
HWL–Aq = Hardwood lignin aqueous purified by ORNL
HWL–SE = Hardwood lignin solvent extracted by MWV
SWL-K2 = Kruger softwood lignin as received (2nd sample)
Alcell = Lignol Innovations (Organosolv) lignin as received

Summary of Progress on the Lignin Project in FY 2008

Progress made on the lignin project over the past year included the following.

- For the first time, multifilament lignin fiber tow was successfully melt spun, continuously and for extended periods of time, from unpurified lignin materials, including SWL and Organosolv lignin (i.e., from lignin materials which, as isolated from biomass, were either close to or exceeded the purity specifications for melt spinning and carbon fiber production).
- Target diameter fiber (10 µm) was produced at the Kline economic model baseline speed of 600 m/min. Melt-spinning speed was successfully increased to 1,200 m/min, the limit of the winding equipment, producing a fiber diameter less than 10 µm.

- Preliminary data obtained indicate that melt-spun lignin fibers can be quickly stabilized through UV irradiation in air at 25°C.
- It was demonstrated that kraft HWL purified using an organic solvent-extraction procedure is not only readily melt spinnable but can also be used as a plasticizing agent for other lignins that are not inherently melt spinnable.
- A sounder understanding of the factors that influence the melt spinnability of lignin materials was achieved.
- Thermally-processed precursor fibers melt spun from different types (and sources) of lignin were processed into carbon fiber. Mechanical properties of the carbon fibers currently fall in the range of 45–60% of target, but several possible causes have been identified, including inadequate compounding of powder lignin into the pellets required as the feedstock for the spinning operation.
- Additional sources of lignin materials were identified, including kraft SWL from Kruger Wayagamack and STFI-Packforst (Sweden), and Organosolv lignin from Lignol Innovations (a by-product of cellulosic ethanol production).

Lignin Sources for Continued Development Work

Following the merger of Mead and Westvaco in 2002, the business direction of the new corporation has been toward 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 (including the Charleston, South Carolina mill that is the company's sole source of kraft lignin), and divestiture of its specialty chemicals business is possibly part of MWV's long-term business strategy. Thus, even before the company's decision toward the end of FY 2007 to terminate all its long-term research efforts, including its support of the LCCF project, it was clear that an alternative industrial partner would need to be found.

Kruger Wayagamack, Inc., Quebec, Canada

Kruger Wayagamack is a large Canadian-based pulp and paper producer that also uses the kraft process for the pulping of wood (predominantly softwood in Canada). Almost 2 years ago, Kruger made it clear that it was interested in isolating lignin for much the same reason as Weyerhaeuser; namely, 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 use as a fuel in other operations but also as 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 LCCF production is of substantial interest to Kruger. Kruger is evaluating the LignoBoost lignin isolation technology from STFI-Packforsk, the Swedish Research Institute. As a point of information, the LignoBoost process was developed to produce a lignin-based biofuel, and Weyerhaeuser is one of the industrial stakeholders in LignoBoost process development efforts under a 4-year (2005–2008) research and development program titled, "Future Resource Adapted Pulp Mill—step 2" ("FRAM 2"). Thus, both Weyerhaeuser and Kruger may well be producing lignin from kraft black liquor using the same lignin isolation technology.

Kruger senior management gave the formal go-ahead for mill trials this year, 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 onstream in 2009. Thus, we have another pulp and paper manufacturer on-board that is willing to 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 the lignin is softwood-based (as is Weyerhaeuser's lignin) and thus is not melt spinnable without the aid of a plasticizing agent (or chemical modification). However, we have learned a great deal about spinning lignin materials over the past year, which will help us to

continue to move forward with new sources of lignin as a precursor material for carbon-fiber production, notably those lignins that do not require purification for this purpose.

We have already demonstrated that the first two samples of Kruger's lignin (the solvent-extracted HWL discussed above) are melt spinnable with a plasticizing additive. Furthermore, based on an analysis of the second sample received from the company (5 kg), the purity of the Kruger lignin is approaching the desired specifications and is certainly much better than that of the commercial, unmodified kraft lignin product from MWV with which we have worked to date. Refinement of the isolation procedure (e.g., through incorporation of additional washing stages) is expected to result in a lignin material meeting the purity specifications <u>without</u> the need for subsequent purification. This would represent a very distinct economic benefit with respect to LCCF production.

Weyerhaeuser Company, Washington

Under a Cooperative Research and Development Agreement for a separate project, Weyerhaeuser has sent sample kraft SWL to ORNL for evaluation for LCCF production. Apparently, it has been demonstrated that the Weyerhaeuser SWL is melt spinnable with the addition of a plasticizing agent, at least on a single fiber scale, and that carbon fibers can be produced from the precursor lignin fiber. This is consistent with the preliminary evaluation of the Kruger SWL under the FreedomCAR program, a kraft lignin believed to have been isolated using the same LignoBoost technology. Weyerhaeuser has indicated that it is willing to provide samples of its lignin to the FreedomCAR program for multifilament melt-spinning evaluation and carbon-fiber production but has yet to furnish the material. Access by the FreedomCAR program to Weyerhaeuser lignin is considered to be an important element of future efforts on the FreedomCAR LCCF program.

STFI-Packforst (Swedish Research Institute)

STFI-Packforst developed the LignoBoost process for isolating lignin from kraft black liquor for the primary purpose of producing fuel pellets and for enhancing the productivity of kraft pulp mills.

However, increasing attention is being given by several pulp and paper companies to use of the kraft lignin for production of value-added chemicals, including carbon fiber. STFI-Packforst has carried out preliminary work on the melt spinning of lignin fibers and conversion into carbon fibers. As a result, STFI is interested in collaborating with ORNL on the use of kraft lignin for LCCF production. STFI is the leading research institute with respect to the science and technology of lignin materials and will bring to the table considerable expertise in this area. This, in turn, will allow ORNL to focus on the development of processes for converting lignin into carbon fiber.

Following a recent visit to ORNL by STFI (October 10), STFI has to date identified five pulp and paper companies interested in collaborating on the project, initially through furnishing kraft lignin products (meeting the purity specification) for evaluation. STFI will carry out the detailed characterizations of the lignin materials, which will add to our current database and help to better correlate lignin properties, notably chemistry, with melt spinnability and carbon-fiber quality. Further discussions with STFI-Packforst regarding collaboration will be held during the DOE workshop on carbon fiber at ORNL, tentatively proposed for January 21–22, 2009.

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 and further refined by Repap Enterprises, Inc., from which the Alcell lignin product was produced. It has been known since the earliest days of the LCCF project at ORNL that the Alcell lignin product (derived from hardwood) is relatively pure as isolated and is readily melt spinnable. However, the Alcell 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 University of Tennessee (UT), Knoxville joint venture with 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 is done 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 price of nearly $70/barrel.

Purification of Lignin Materials

The need to purify lignin materials to make them suitable for melt spinning and carbon-fiber production has been superseded as a result of the project findings this year. Elimination of a purification step will significantly reduce the cost of lignin-based carbon fiber by an estimated 60-80¢/lb.

It was clearly demonstrated in FY 2008 that it is possible, under appropriate process conditions, to isolate lignin with the required state of purity from the black liquor of commercial kraft pulping of softwood for the production of pulp and paper. Furthermore, even cleaner and more readily melt-spinnable lignins are becoming available from the production of cellulosic ethanol fuel from lignocellulosic materials, such as wood and switchgrass. Thus, the following discussion of the lignin purification processes evaluated is largely included for the record.

Solvent-Extracted Lignins

Both the MWV and PNNL solvent-extracted HWL materials exhibited excellent melt-spinnability characteristics, especially the former. The downside to these particular SEL 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 SEL will readily crosslink 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 SEL 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 SELs were useful plasticizing agents for other, non-melt-spinnable lignins, including those purified using an aqueous procedure.

Thus, some efforts to exploit the beneficial characteristics of lignins purified using a solvent-extraction process will be continued, 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 SELs (i.e., the work will not encompass lignin purification per se). PNNL is considering extending its work in this respect, and other entities may be interested in picking up the MWV work.

About 5 tons of the PC-1369 HWL, produced by MWV in support of the LCCF project at ORNL, are available for sale. If new findings are developed that indicate that the molecular weight and melting point properties of an SEL could be enhanced through refinement of the solvent-extraction procedure (e.g., choice of solvents), then it would be appropriate to consider funding of a solvent-extraction purification run by the toll processor identified by MWV for this purpose. Furthermore, it would be advantageous to have SEL 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., it 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 SELs as currently produced. In addition, 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

Apparently, PNNL may have overcome the difficulties encountered in the early part of the PNNL-MWV program to purify HWL using an aqueous procedure, and has produced purified material for evaluation. Similarly, PNNL may have refined its organic solvent-extraction procedure to produce a purified HWL of higher molecular weight and melting point. If so, both of these HWL materials should be evaluated for melt spinnability and production of multifilament tow. Needless to say, though, PNNL is not in a position to furnish the quantities of purified lignin required for multifilament melt spinning; someone else must scale up the PNNL process.

Project Deliverables

By the end of this multiyear 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.

Awards/Presentations/Publications/Patents

Awards

American Carbon Society Graffin Lecturer for 2008/2009

The American Carbon Society's Graffin Lectureship is endowed by Asbury Carbons in honor of George D. Graffin, a pioneer in the natural graphite industry. Each year, the American Carbon Society selects a lecturer who has made distinguished contributions to carbon science and engineering. The lecture is made available to North American universities, companies, and government agencies by arrangement with the lecturer, and all travel expenses for the lecture tour are picked up by the American Carbon Society. The Graffin Lecture for the 2008/2009 period is "*Nanoporous Carbon Materials—How They Benefit Our Lives and the Environment.*"

Presentations

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

2. C. David Warren et al., "Multitask Research Program to Develop Commodity Grade, Lower Cost Carbon Fiber," SAMPE Conference, Memphis, Tennessee, September 8–11, 2008.

3. Frederick S. Baker and Nidia C. Gallego, "Lignin-based, Low-cost Carbon Fiber," Invited Paper, Boeing Fiber Workshop, Seattle, Washington, July 23–25, 2008.

4. Frederick S. Baker, "A Carbon Cycle: Use of Biomass-based Carbon Fiber Materials for Reduction of Carbon Emissions to the Environment," Invited Plenary Lecture, CARBON 2008 Conference, Nagano, Japan, July 13-18, 2008.

5. Frederick S. Baker, "Production of Carbon Fibers from Renewable Resource Materials," Invited Seminar (3-hour) at Buckeye Technologies, Inc., Memphis, Tennessee, June 20, 2008.

Publications

1. Trishelle Copeland-Johnson (student intern) et al., "Viscoelastic Properties of Alcell Lignin for Carbon Fiber Production," submitted to DOE for consideration for publication in the *Journal of Undergraduate Research*, August 2008. (Trishelle received the 2nd place award

in the SERch competition for her poster on her project at ORNL.)

United States Patents (those patents involving carbon fibers)

1. "Lightweight, Durable Lead-Acid Batteries," Edgar Lara-Curzio, Ke An, Jim Kiggans, Nancy J. Dudney, Cristian I. Contescu, Frederick S. Baker, and Beth L. Armstrong, Application filed May 2008 (UT-Battelle).

2. "Rotary Adsorbers for Continuous Bulk Separations," Baker, Frederick Stanley; US-2008-0047436, Application published February 28, 2008 (UT-Battelle).

3. "Activated Carbon Fibers and Engineered Forms from Renewable Resources," Baker, Frederick Stanley; US-2007-0142225, Application published June 21, 2007 (UT-Battelle).

B. Advanced Stabilization of Polyacrylonitrile Fiber Precursor

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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

- Develop plasma processing as the primary stabilization route for the conversion factory.

- Develop electron-beam (E-beam) processing as the preferred stabilization route for implementation at a precursor factory.

- Integrate plasma stabilization and plasma oxidation into a single process module.

- 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

- Initiated integration of plasma stabilization and plasma oxidation into a single experimental reactor module.

- Constructed and commissioned a multi-tow plasma reactor for stabilization and oxidation.

- Commenced operation and obtained first experimental results from multi-tow plasma reactor.

- Initiated discussions with a precursor manufacturing partner regarding in-line E-beam stabilization at the precursor factory.

- Conducted experiments to characterize free radical concentration in E-beam stabilized precursor.

- Successfully developed and executed a plan for recovering from the loss of a key partner, resuming experimental operations within two fiscal quarters.

Future Direction

- Complete integration of stabilization and oxidation into one module.

- Scale the integrated plasma stabilization/oxidation process to achieve high speed, multiple large tow, semicontinuous (multiple pass) plasma stabilization-oxidation process.

- Conduct parametric studies and fiber characterization to better understand process effects and the processing window and to quantify fiber properties.

- Investigate stabilization of alternative precursors.

- Integrate plasma stabilization into an advanced technology pilot conversion line.

- Develop E-beam stabilization for implementation at a precursor factory.

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 demonstrated that plasma processing shows great promise for inexpensively and rapidly oxidizing, carbonizing, and graphitizing polymer precursors to convert them to CFs. Initial results indicated that the precursor needed to be lightly stabilized, or cross-linked, before it could be subjected to plasma oxidation. Stabilization and oxidation together are estimated to represent ~18% of the cost of commercial grade CF [1]. A rapid, inexpensive, and robust stabilization technique is needed to complement the aforementioned advanced processing 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

At the start of the project, a successful plasma-based stabilization process had not been discovered, so researchers investigated three other prospective PAN precursor fiber stabilization routes, E-beam processing, thermochemical processing, and ultraviolet (UV) processing, while simultaneously continuing to work on developing a plasma-based process. In fiscal year (FY) 2007, the project team finally discovered a plasma-based recipe that rapidly and effectively stabilized the virgin precursor fibers. At the end of FY 2007, plasma stabilization was selected as the preferred stabilization route, and E-beam stabilization was kept as a backup option for implementation at the precursor factory.

The selected stabilization processes must be effectively integrated with the plasma oxidation process. As shown in Figure 1, the stabilization-oxidation interface may not be precise. It can be affected by the process routes and parameters. Ideally, stabilization will require minimum residence time with the interface moved as far to the left (Figure 1) as possible to minimize the total residence time for both processes combined.
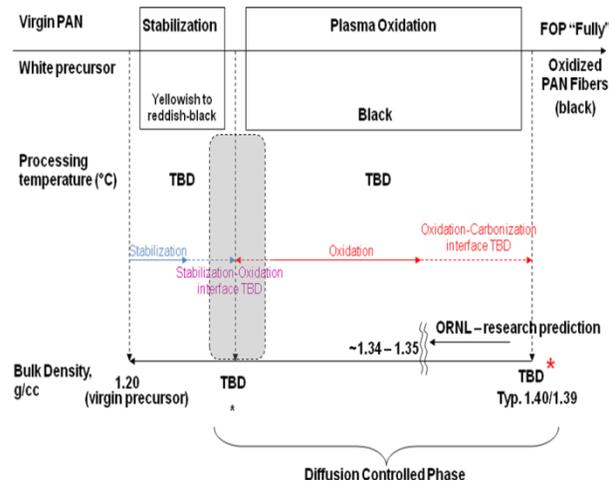

Figure 1. Stabilization-oxidation diagram showing the uncertain interface position.

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. Table 1 shows abbreviated data on the experiments with UV, E-beam, and thermochemical stabilization processes.

Table 1. Selected data from experiments with various stabilization routes

Precursor type	Density (g/cc)		Residence time (min)
	Initial	**Final**	
Virgin Hexcel	1.19	1.33–1.34	26
	1.33–1.34	1.37–1.38	27 (total 53 min)
Lightly prestabilized (conventionally processed) (residence time 23 min)	1.22–1.23	1.35–1.36	26 (total 49 min)
UV pretreated	~1.19	1.34–1.35	26
	~1.19	1.35–1.36	26
	~1.19	1.33–1.34	26
	~1.19	1.33–1.34	26
E-beam pretreated	~1.19	1.23–1.24	26
	1.27–1.28	1.36–1.37	27 (total 53 min)
	~1.19	1.27–1.28	26
	1.23–1.24	1.36–1.37	27 (total 53 min)
	~1.19	1.28–1.29	26
	1.28–1.29	1.37–1.38	27 (total 53 min)

Plasma Stabilization

The discovery of an effective plasma stabilization process and its selection as the baseline stabilization route enabled the seamless integration of stabilization and oxidation into a single process module. Figure 2 shows selected differential scanning calorimetry (DSC) thermograms for plasma stabilization (labeled "direct oxidized" in the figure). Based on these data, plasma stabilization was selected as the preferred stabilization route. Therefore, the major stabilization accomplishment during this reporting
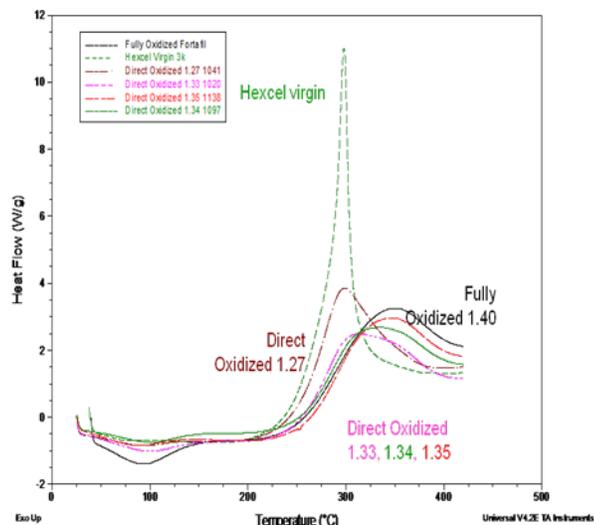
Figure 2. Selected DSC thermograms from plasma stabilization experiments.

period was the commencement of integration of the plasma stabilization and oxidation processes and equipment. Plasma stabilization seamlessly integrates with plasma oxidation and each requires less than one-third of the conventional process residence time. The researchers completed construction and initial operation of the first multi-tow reactor for the integrated plasma stabilization-oxidation module. Reactor construction was completed in early February, immediately followed by operational tests and "sweetening." By the end of March, the project team had achieved single-tow line speed in the multi-tow reactor roughly equivalent to that previously demonstrated in the single-tow reactor. Multi-tow operation has not yet been attempted.

In the preliminary series of experiments, plasma stabilized fibers were successfully oxidized at higher level in a simultaneous operation using the new reactor.

Electron Beam Stabilization

E-beam stabilization delivers very high throughput (line speed) potential, with the electron irradiation step completed in seconds. It can potentially be implemented in-line in a precursor factory. Electron spin resonance (ESR) data (Figure 3) indicate that electron irradiation generates free radicals, which are the probable source of thermal runaway when E-beam stabilized fibers are
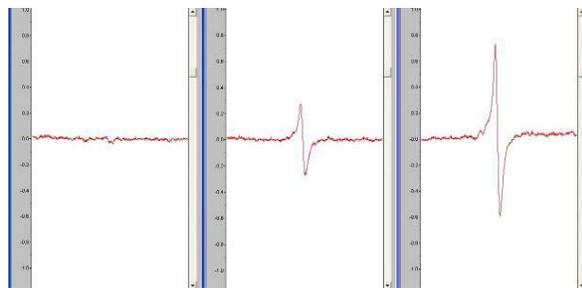

Figure 3. ESR traces, with dose increasing from left (unirradiated) to right. Higher peak indicates higher free radical concentration.

exposed to atmospheric pressure plasma or its chemically reactive exhaust. The project team is working to develop an approach to resolve, or perhaps even exploit, the free radical generation. Irradiation experiments were conducted with in situ ESR at the University of Notre Dame's Department of Energy-funded radiation laboratory to better characterize the free radical generation and test potential approaches to control it. The test results are tabulated in Table 2. Initial results based on the data obtained at the University of Notre Dame (Figure 4) indicate that the population of free radicals in E-beam irradiated PAN fiber gradually decreases with exposure of the irradiated fibers in a slightly elevated temperature environment. This supports our initial finding of a fiber annealing requirement prior to oxidation of irradiated PAN tow.

Table 2. ESR spectroscopy test matrix

Run No.	Sample ID	Irradiation	ESR scan Temperature ($^{\circ}$C)	Environment
1	Hexcel PAN	Yes	25	Air
2	Alanine	Yes (dose calibration)	25	Air
3	Hexcel PAN	Yes	100	N_2 then Air
4	Hexcel PAN	No	100	N_2 then Air
5	PAN (homopolymer)	No	25	Air
6	Hexcel PAN	Yes	150	Air
7	Hexcel PAN	No	150	Air
8	Textile PAN	No	25	Air

Initial results were obtained on evolved gas analysis from a thermogravimetric analyzer (TGA) during aerial oxidation of neat PAN fibers and those pretreated with E-beam and UV radiation. An abrupt evolution of gases like CO_2 and NH_3 in the cases of neat PAN and UV treated PAN was observed. On the other hand, E-beam treated PAN
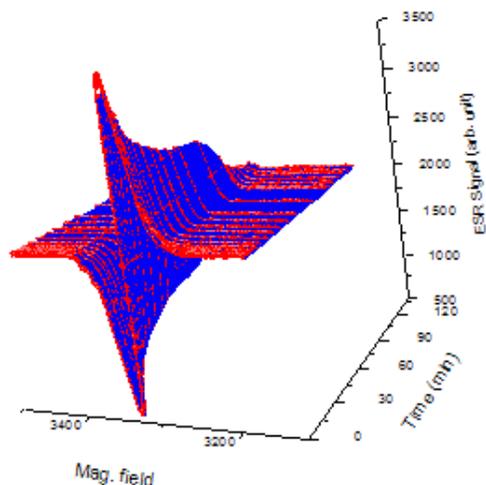
Figure 4. ESR spectra of irradiated PAN fibers during annealing at a temperature below that of oxidation.

did not show any abrupt release of gases. This result was also supported by TGA weight loss rate during the initial part of oxidation. This study proved E-beam irradiation actually stabilized the PAN molecular structure. However, E-beam caused generation of macro-free radicals which accelerated oxidation at elevated temperature. This suggests controlling the reaction by reducing dosage and using suitable additives in PAN composition. At a lower temperature than that at which vigorous oxidation takes place, the level of free radicals generated by E-beam undergoes time dependent decay. Therefore, well controlled oxidation of E-beam treated PAN will be a potential route for rapid oxidation of CF precursors.

At least one prospective precursor manufacturing partner has indicated interest in using E-beam stabilization in the precursor factory. ORNL, its irradiation partner IBA Industrial, Inc., and the precursor manufacturer met at IBA's U.S. headquarters and have begun initial discussions to assess equipment parameters and investment scenarios.

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 E-beam

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

University of Tennessee materials science graduate students are providing characterization and evaluative support to this project (mainly on oxidized fiber samples) under the guidance of Professor Roberto Benson.

Partners

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

- Atmospheric Glow Technologies (AGT)—plasma equipment design and processing (subcontract).
- Automotive Composites Consortium—programmatic and technical direction (complimentary).
- Hexcel Corporation—raw materials and technical consultation (complimentary).
- IBA Industrial, Inc. (formerly Radiation Dynamics Inc.)—irradiation analysis, protocols, and beam time (complimentary).
- Sentech—plasma equipment design and processing (subcontract).
- TohoTenax America—raw materials and technical consultation (complimentary).
- University of Tennessee—characterization (subcontract).

About midyear it became apparent that our key plasma processing partner, AGT, was in a state of acute financial distress. We had previously considered courses of action in case of such an event, and it became necessary to plan and execute an alternative project approach that did not depend on AGT as a partner. Extensive inventories and documentation of assets and experimental data were completed. We investigated the following options: (1) finding another partner with atmospheric pressure plasma processing expertise,

(2) acquiring the key employees and assets to make all of the plasma oxidation research internal to ORNL, and (3) acquisition of key AGT employees and assets by another private entity that would assume AGT's former role. The second and third options were pursued in parallel, with the final solution being that Sentech, Inc., hired the key AGT employees, acquired AGT's relevant assets, and subcontracted with ORNL to assume AGT's former role. A contract with Sentech was signed at the end of FY 2008, and experimental operations were resumed at the former AGT premises. Those premises are currently shared with another company that acquired other portions of AGT's business, assets, and employees, and there are some problems with the arrangement that have to be resolved before we are able to restore fully effective experimental operations. We are currently able to conduct experimental operations, but with some inconveniences and limitations that we expect to resolve in the first half of FY 2009.

Conclusions

The plasma stabilization process has been integrated with plasma oxidation. A multi-tow reactor was constructed and commissioned, and we initiated scale-up of the integrated plasma stabilization-oxidation process. E-beam stabilization is being developed as an option for high throughput cross-linking in the precursor factory.

Reference

1. S. M. Cohn and S. Das, "A Cost Assessment of Conventional PAN Carbon Fiber Production Technology," Energy Division, Oak Ridge National Laboratory (unpublished draft, 1998).

C. Advanced Oxidation of Polyacrylonitrile Fiber Precursor

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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

- Characterized decomposition profiles of the key reactive oxidative species.

- Constructed and commissioned first multi-tow plasma oxidation reactor.

- Commenced operation and obtained initial experimental results from multi-tow plasma oxidation reactor.

- Commenced integrating stabilization and oxidation into a single plasma-based conversion module.

- Successfully developed and executed a plan for recovering from the loss of a key partner, resuming experimental operations within two fiscal quarters.

Future Direction

- Continue refining and scaling the reactor design and processing protocols to achieve high speed, multiple large tow, semicontinuous (multiple pass) plasma oxidation process.

- Complete integration of 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 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 PAN precursor fibers. Conventional oxidation is a slow thermal process that typically consumes more than 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 will develop a plasma oxidation technology that integrates with other advanced fiber conversion processes to produce inexpensive CF with properties suitable for use by the automotive industry. Critical technical criteria include: (1) ≥25 Msi tensile modulus and ≥1.0% ultimate strain in the finished fiber, (2) uniform properties over the length of the fiber tow, (3) repeatable and controllable processing, and (4) significant unit cost reduction compared with conventional processing.

Project Deliverable

At the end of this project, the researchers will have developed an advanced oxidation process with residence time much shorter than that typical of conventional CF conversion lines. The advanced oxidation process will be sufficiently well understood and documented that the team can commence scaling it up to develop a multiple, large-tow oxidation module for an advanced technology pilot line.

Technical Approach

The researchers are investigating PAN precursor fiber oxidation using nonequilibrium, nonthermal plasma at atmospheric pressure. 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.

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.

Experimental Results

At the end of fiscal year (FY) 2007, a reduction in oxidation residence time of about two-thirds and 0.3 m/min single-pass line speed had been achieved in a six-zone, single-tow reactor. Initial single-fiber mechanical data were generated (Figure 1). The results fall short of property requirements but are encouraging at this stage of the development program. After the encouraging single-filament data were produced, we started oxidizing 3k tows for tow testing, following conventional carbonization. These tows were oxidized in a six-zone, single-tow reactor configuration.
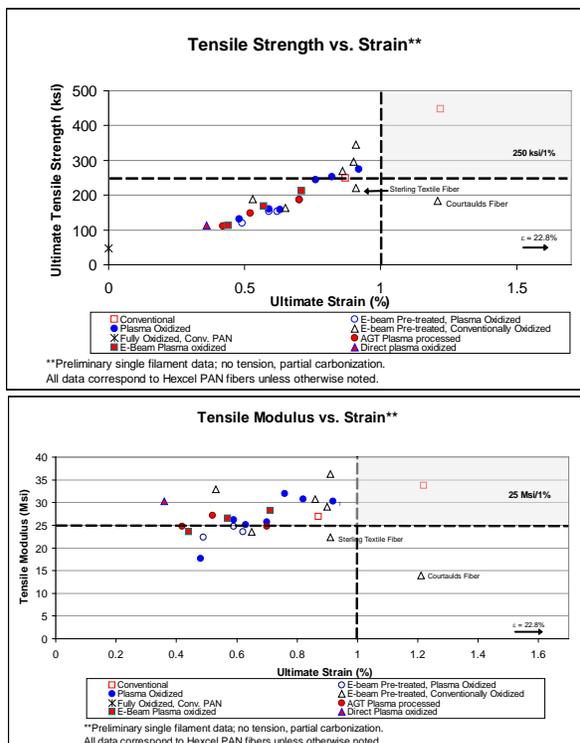

Figure 1. Mechanical properties of CFs stabilized and oxidized by various routes then conventionally carbonized at low temperature. There was no tensioning, controlled stretching, or tow spreading during conversion. Conventional data points are for thermally shocked and thermally ramped heating protocols.

There were problems with the tow tensioning system, so it was upgraded during construction of the multi-tow reactor, described later in this report. The tow production and testing were not completed during FY 2008 because of a key partner's bankruptcy (described in further detail below).The initial tow oxidation is tabulated in Table 1 and will be completed after resumption of experimental operations in FY 2009.

Table 1. Plasma oxidized 3k tow samples produced for carbonization

Sample #	Length (m)	Density (g/cc)	Tow tension during oxidation
1486	67	>1.40	No
1543	90	1.34–1.35	No
1637	53	1.36–1.37	No
1531	72	1.36–1.37	Yes
1532	66	1.37–1.38	Yes
1410	25	1.33–1.34	No
1411	21	1.34–1.35	No
1361	38	1.36–1.37	No

During FY 2008, technical efforts were primarily focused on characterizing the concentration of reactive oxidative species (ROS); better understanding the parameters that control concentration; and construction, commissioning, and initial operation of a multi-tow plasma oxidation reactor.

ROS concentration is extremely important for initiating and controlling the oxidation process. Recently acquired instrumentation and reactor modifications have enabled characterization with significantly improved spatial resolution and measurement precision. Figure 2 shows the normalized results of one set of ROS measurements for various reactor configurations and thermal conditions. Figures 3(a) and 3(b), representing data from two sets of samples run on different dates (three- or four-digit numbers given in the legend of the figures indicate sample IDs), show that the current plasma oxidation process is comparable to or better than conventional oxidation in terms of completing the exothermic oxidation reactions. Differential scanning calorimetry (DSC) thermograms are shown for a number of different samples and/or processing

protocols, and in all cases the plasma oxidation thermogram lies below the conventional oxidation thermogram.
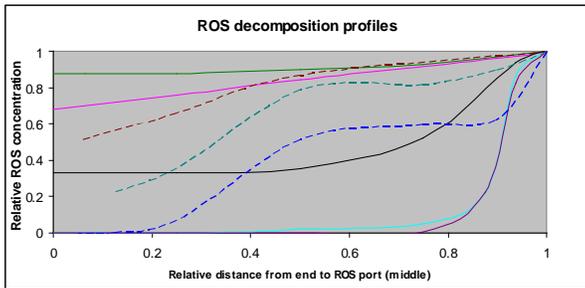

Figure 2. Normalized ROS decomposition profiles for various plasma oxidation reactor configurations and thermal conditions.
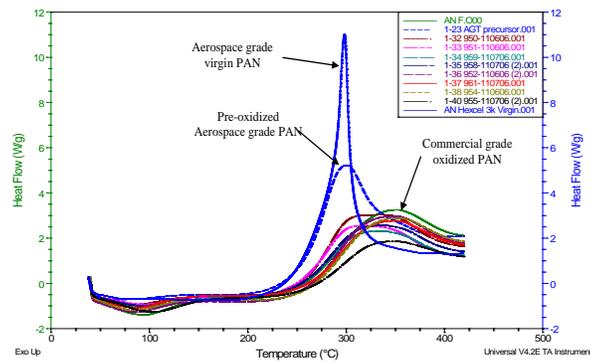

Figure 3(a). DSC thermograms of PAN tow, conventionally oxidized in a commercial factory or plasma oxidized in ORNL's multi-zone, single-tow reactor.
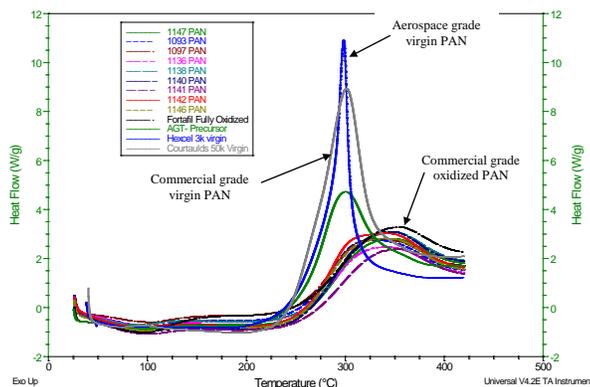

Figure 3(b). DSC thermograms of PAN tow, conventionally oxidized in a commercial factory or plasma oxidized in ORNL's multi-zone, single-tow reactor.

The project team began scaling to multiple tows with the commencement of construction of a multi-tow reactor in late FY 2007. Scaling is now a major part of this project's focus. The multi-tow reactor construction was completed, followed by initial testing and "sweetening," during this reporting period. Initial operations yielded surprisingly good results. Figure 4 shows similar data for the multi-tow reactor; again the DSC thermogram of plasma oxidized PAN fibers lies below that of conventionally oxidized PAN precursor, thus indicating that complete chemical oxidation was achieved. Figure 5 shows that, depending on the reactive species concentration and operating parameters, plasma oxidized fibers show controllable residual heat of reaction. Processing time versus density enhancement during conventional and advanced oxidation processes is presented in Figure 6. It is apparent that the rate of oxidation in plasma oxidation is significantly faster than the conventional route.
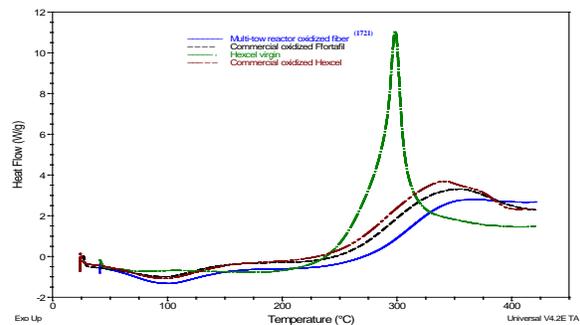

Figure 4. Representative DSC thermogram of multi-tow reactor processed oxidized precursor in comparison to those of virgin PAN and commercial oxidized precursors.
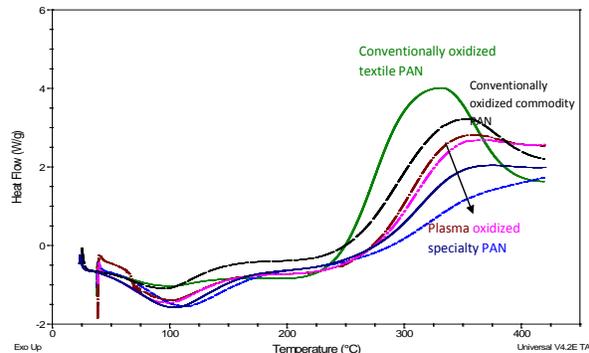

Figure 5. DSC thermograms of different PAN fibers oxidized conventionally or by plasma oxidation.
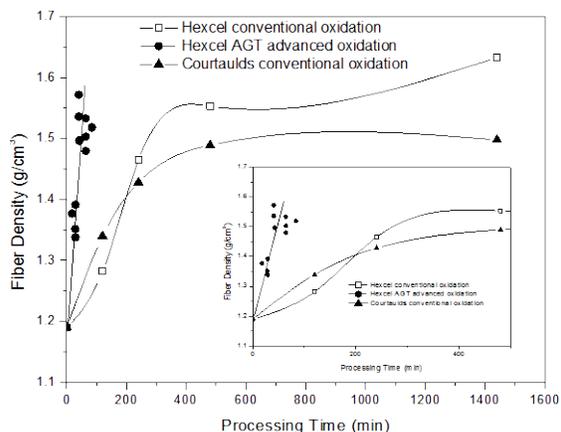
Figure 6. Processing time vs density profiles for fibers in conventional and ORNL proprietary oxidation process.

By the end of this reporting period, the project team had achieved single-tow line speed in the multi-tow reactor roughly equivalent to that previously demonstrated in the single-tow reactor. Multi-tow operation has not yet been attempted. For patent protection and export control reasons, detailed equipment design and process parameters are not published, but they are periodically disclosed to the relevant program managers in oral briefings.

Future Direction

In early FY 2009 we will restore fully effective experimental operations, possibly by moving to another facility. The future project direction will focus on scaling, achieving improved properties of carbonized fibers, oxidation of alternative precursors, process and equipment reliability, integration with other conversion process modules, and commercialization with an industrial partner.

Patents and Publications

There were no new invention disclosures, patent activities, or publications arising from this project during this reporting period.

Education

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

Partners

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

About midyear it became apparent that our key plasma processing partner, Atmospheric Glow Technologies (AGT), was in a state of acute financial distress. We had previously discussed potential courses of action in case of such an event. It became necessary to plan and execute an alternative project approach that did not depend on AGT as a partner. Extensive inventories and documentation of assets and experimental data were completed. We investigated the following options: (1) finding another partner with atmospheric pressure plasma processing expertise, (2) acquiring the key employees and assets to make all of the plasma oxidation research internal to ORNL, and (3) acquisition of key AGT employees and assets by another private entity that would assume AGT's former role. The second and third options were pursued in parallel with the final solution being that Sentech, Inc., hired the key AGT employees, acquired AGT's relevant assets, and subcontracted with ORNL to assume AGT's former role. A contract with Sentech was signed at the end of FY 2008, and experimental operations were resumed at the former AGT premises. Those premises are currently shared with another company that acquired other portions of AGT's business, assets, and employees, and there are some problems with the arrangement that have to be resolved before we are able to restore fully effective experimental operations. We are currently able to conduct experimental operations, but with some inconveniences and limitations that we expect to resolve in the first half of FY 2009.

Conclusions

Plasma oxidation of PAN fibers continues to progress toward the goal of reducing the cost of CF manufacture. To date, researchers have reduced oxidation residence time by about two-thirds compared to conventional oxidation.

Critical process characterization was conducted during this period, and scale-up began to receive significant attention with the completion and initial operation of the first multi-tow plasma oxidation reactor.

D. Precursor and Fiber Evaluation

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Objectives

- Provide capability for production of small quantities of fiber or composite material samples.

- Provide capability to test the convertibility of alternate precursors into carbon fiber (CF), and develop their conversion protocols.

- Provide capability to test new concepts that can potentially lower CF cost.

Approach

- Maintain and operate ORNL's conventional pilot line for production of fiber or composite material samples.

- Maintain, upgrade, and operate ORNL's precursor evaluation system.

- Use the aforementioned facilities to test new concepts that can potentially lower CF cost.

Accomplishments

- Evaluated textile polyacrylonitrile (PAN), polyolefin, and proprietary precursors in the precursor evaluation system.

- Ordered equipment for independently tensioning up to three tows on conventional pilot line.

- Ordered 2,500ºC furnace for precursor evaluation system.

Future Direction

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

Introduction

The purpose of this project is to perform the general evaluations that support the LCCF initiative. The key aspect of this project is maintenance, intelligent upgrading, and wise use of the critical facilities that have been developed in previous projects. The "wise use" of these

facilities includes evaluation of alternate precursor convertibility, production of fibers and/or composite specimens for evaluation by the Automotive Composites Consortium and other interested parties, and new concept evaluations. The primary facilities supported by this project are the precursor evaluation system; the 1 : 20 scale, conventional, CF pilot line; and the microwave-assisted plasma (MAP) carbonization unit.

ORNL's conventional pilot line enables production on the order of 1 pound/day of 50,000 (50k) filament tow. Therefore, it is useful for making small quantities of fiber for tow and composite evaluations. It can also be used to conventionally oxidize or carbonize tows that are partially converted by advanced processes. Minimum material requirements for evaluation on the pilot line are hundreds of feet of ≥1k tow, and startup time for the high-temperature furnaces is ≥10 hours.

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

The MAP carbonization unit was developed in the advanced carbonization project and continues to be maintained and operated for demonstration purposes. It is expected that at some point in the future the current MAP carbonization unit will be the starting point for development of an advanced technology demonstration line.

Project Deliverables

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

Current Status

The conventional pilot line and the precursor evaluation system are currently operational. The precursor evaluation system was used to evaluate textile PAN, polyolefin, and proprietary precursors in fiscal year (FY) 2008. A 2,500°C furnace has been ordered to replace the aging high-temperature furnace and increase the system's maximum temperature capability. The conventional pilot line was used extensively for processing textile PAN precursor obtained from Fibras Sinteticas Portugal, S.A. (Lisbon, Portugal). A tow tensioning system to independently tension three tows was ordered for the pilot line. The MAP carbonization cooling system was upgraded for improved safety. The MAP system operation was frequently demonstrated for guests, including the assistant secretary for the Department of Energy's Office of Energy Efficiency and Renewable Energy. These facilities are pictured in Figures 1–3.

Figure 1. Operation of oxidation and low-temperature carbonization furnaces in precursor evaluation system.

Figure 2. Conventional pilot-line installation at ORNL.

Figure 3. MAP carbonization unit in operation.

Future Direction

New equipment has been ordered to upgrade the precursor evaluation system's high-temperature capability and the pilot line's creeling and fiber transport/tensioning system. This equipment will be installed and commissioned in FY 2009, and these facilities will continue to be maintained and operated as needed to continue the development of low-cost CF.

Conclusions

The precursor evaluation system, conventional pilot line, and MAP carbonization unit have been upgraded, maintained, and operated to continue the development of low-cost CF.

Presentations/Patents/Publications

None.

E.　Commercialization of Textile and Lignin Precursors

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Objectives

- Develop textile-based polyacrylonitrile (PAN) precursors for conversion into carbon fiber (CF).

- Develop all processing parameters needed for use of textile-based PAN and lignin-based precursors.

- Help current and future CF producers incorporate the new precursors into manufacturing plants.

- Assist with plant design and equipment specifications.

- Transfer time-temperature-tension (T3) profiles to users of the alternate precursors. Assist in optimization of the manufacturing parameters.

- Develop any needed surface treatment and sizing technologies for CFs made from alternative precursors as project times allow (may be handled under a separate effort).

- Provide the capability to develop and test conversion protocols for new polymer precursors.

- Produce small quantities of finished CF using the new precursors.

Approach

- Work with potential precursor manufacturers to develop alternative, lower cost precursors.

- Determine the T3 conversion profiles for converting alternative precursors into CF.

- Work with potential CF manufacturers to incorporate the alternative precursors into current or future CF production facilities.

- Assist potential CF manufacturers with specifying and designing CF plants and lines that allow the use of alternative, lower cost precursors.

- Develop sizing technologies, tow splitting technologies, and alternate final material formats to make the products from lower cost CF lines amenable to high volume industries.

Accomplishments

- Initiated work on full-scale development of a textile PAN precursor.

- Completed a technical evaluation of the pilot precursor line and laboratory capabilities of Portuguese textile PAN fiber manufacturer FISIPE, S.A., 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.

- Began developing the conversion protocols for converting the textile precursor into CF.

- Delivered spools of fully carbonized textile-precursor-based CF to Ford, General Motors, and Chrysler.

- Achieved current best fiber properties for strength of 350 ksi (kips or kilopounds per square inch) on 26,600 filament tows. Program requirement is 250 ksi.

- Achieved current best fiber properties for modulus of 31.7 Msi on 26,600 filament tows. Program requirement is 25 Msi.

- Met with and evaluated the potential for partnering with Bluestar Fibres Company Ltd. to develop a methyl-acrylate-based (MA-based) PAN textile precursor.

- Met with Owens Corning, Zoltek, Hysoung, SGL, DuPont, Great Lakes Carbon Fiber, and others protected by secrecy agreements to scope out possible collaborative efforts to commercialize textile- and lignin-based precursors.

Future Direction

- Continue to optimize the FISIPE precursor processing conditions. Will require adding differential tensioning to the pilot line to yield more precise fiber stretching during stabilization and oxidation.

- Defer any further developments with Bluestar and Owens Corning.

- Pursue commercialization of lower cost precursors with one current research partner, protected by a secrecy agreement.

- Pursue commercialization of lower cost precursors with other current industrial CF suppliers.

- Evaluate potential collaboration with new entrants into the CF market.

- Upgrade the CF pilot line to allow for more precise tensioning during oxidation and the production of larger volumes of fiber.

- Scale up textile precursor technology from pilot line scale to production line scale at the FISIPE plant in Portugal.

Introduction

During the past several years, the Lightweighting Materials (LM) thrust has been developing technologies for the production of lower cost CF for use in body and chassis applications in automobiles. Program requirements target materials that have tensile strengths in excess of 250 ksi and moduli of at least 25 Msi. Past work included the development of alternate, lower cost precursors and alternate, lower cost methods for manufacturing precursors into finished CF. The purpose of these projects was to take two

precursor technologies, textile-based and lignin-based, from the technical feasibility stage and scale up to a manufacturability demonstration. The technology being pursued for the textile-based precursor is the chemical modification of textile PAN containing either MA or VA using a proprietary solution bath while the fiber is still in the uncollapsed state. This project will result in determination of the best concentration-temperature-exposure profiles to render the fiber carbonizable by conventional processes and also readily and inexpensively manufacturable in existing textile PAN plants. Successful completion of this project will result in (1) ORNL providing project partners with specific instructions for precursor conversion, subject to export control limitations, and (2) a selected manufacturer being ready to sell products based on the new technologies to producers. The technology being pursued for the lignin precursors is the conventional conversion of melt-spun lignin fibers from other LM projects and from non-Department of Energy (DOE) projects. Deliverables include spools of fully carbonized and sized CF and composites made from that CF.

The project also includes collaborative efforts with current and potential CF manufacturers to enable them to incorporate these new precursors into their manufacturing facilities. T3 profiles for each precursor will be developed. The program researchers will then work with current CF manufacturers to modify their equipment and facilities to use these lower cost precursors. The program researchers will also work with future CF manufacturers to design factories and specify equipment for future CF lines.

Three separate efforts are described in this report: (1) work with FISIPE, S.A. (Lisbon, Portugal) to develop PAN-VA textile-based precursors, (2) potential work with Bluestar Fibres (Grimsby, United Kingdom [UK]) to develop PAN-MA precursors, and (3) work with other companies to incorporate new precursors into their current and future manufacturing facilities.

Background

Previously under a separate contract as part of the LM program, Hexcel Corporation (Connecticut,

U.S.A.) developed the basic science necessary to render textile-based PAN polymers carbonizable. That science included subjecting the textile precursor to a chemical pretreatment bath while the fiber was still in the uncollapsed state. That work was conducted offline from the textile fiber manufacturing. Fiber samples were split off from the line by hand, packaged, and shipped to Hexcel's Decatur, Alabama, plant for processing. Hexcel obtained satisfactory samples but under only one set of processing conditions and with one specific textile fiber. Certain issues needed to incorporate the technology into manufacturing plants were not addressed but will be addressed for VA- and MA-containing precursors in this project. They include the following.

1. Determination of how and when in the production line to split the precursor into manageable sizes for use by the automotive industry. A specific "standard" tow size of approximately 24,000 filaments is the current program goal.
2. Determination of the necessary chemical absorption required to create a sufficient shift in the differential scanning calorimetry (DSC) curves to indicate that the precursor is stabilizable in an acceptable amount of time. The shift in the DSC curves is tied to both the absorption of the pretreatment chemical by the fiber and the diffusion of the elements into the fiber.
3. Acceleration of the chemical pretreatment to make the chemical treatment readily amenable to textile fiber production processes without slowing down the production processes and thus adding cost to the precursor.
4. Design of the chemical treatment equipment.
5. Determination of the required processing conditions for converting the precursor into finished CF. Early samples are being processed using ORNL's precursor evaluation equipment. Later materials are being processed using ORNL's 1/20th scale CF line and the precursor evaluation system (Figure 1).
6. Evaluation of conventional processing, sizing, and surface treatment technologies to ensure the finished CF will have the properties needed by the automotive industry and that those properties will translate into finished

composites. ORNL, with Automotive Composites Consortium (ACC) guidance, is testing tow samples, making composites from the finished fiber, and delivering the samples to ACC for evaluation.

7. Development of a thorough understanding of the processing temperatures, tensions, and conversion protocols for each new precursor material.

8. Provision of assistance to current and future users of the alternative precursors to help them specify equipment and design CF lines that will most efficiently convert the precursors into CF. The main goal is to reduce the risks from incorporating alternative precursors into manufacturing processes.

Figure 1. Conventional pilot line installation at ORNL.

Project Deliverables

At the end of this project, lower cost precursors will have been made from textile grade PAN in textile mills. The technologies for chemically pretreating, and converting the precursors into CF will have been fully developed integrated into commercial manufacturing facilities. Conversion protocols for lignin will be developed in a sister project in which the tasks necessary to commercialize lignin-based precursors will be accomplished in collaboration with industrial partners. To accomplish the goal of commercialization, the following tasks will have to be completed. Tasks that have been completed are indicated by (C), and those in-process are indicated by (I).

- (C) Development of suitable formulations of textile PAN.
- (C) Development of chemical pretreatment methods for textile PAN.
- (I) Design and incorporation of chemical pretreatments in textile plants.
- (C) Determination of T^3 processing profiles for textile PAN.
- (I) Determination of T^3 processing profiles for lignin precursors.
- (I) Determination of methods of splitting and/or maintaining splits in textile-based precursors during the spinning process.
- (I) Development of surface treatment technologies for CFs made from textile PAN and lignin precursors.
- (I) Development of sizing technologies for CFs made from textile PAN and lignin precursors.
- (I) Development (if necessary) of alternate material formats that may be required by higher volume industries.
- Assistance given to current CF manufacturers to incorporate alternative precursors into their manufacturing facilities.
- Assistance given to future CF manufacturers to utilize alternative, lower cost precursors in their manufacturing facilities.
- (I) Upgrade of ORNL pilot line to allow for more optimization of final CF properties from alternative precursors.
- (I) Upgrade of ORNL pilot line to allow for production of larger amounts of laboratory-scale produced fiber from alternative precursors.

Completion of these tasks should allow for the lowest risk commercialization and incorporation of alternative precursors into conventional CF manufacturing facilities.

Current Status

The efforts to commercialize alternative precursors are separated into three distinct but interrelated areas that are budgeted as three separate entities: (1) development of PAN-VA precursors, (2) development of PAN-MA precursors, and (3) commercialization of alternative precursors.

Development of PAN-VA Precursors

ORNL has established a highly interactive and mutually beneficial partnership with Portuguese textile fiber manufacturer FISIPE, S.A., which produces VA-comonomered PAN for textile applications. FISIPE is a high volume manufacturer that produces a commodity fiber that is roughly one-half the cost of conventional acrylic CF precursors. Our efforts are aimed at developing a chemical pretreatment for the FISIPE manufacturing line that will render one of its textile formulations oxidizable and carbonizable and thus satisfactory as a CF precursor.

The first step in development of the precursor was to evaluate the DSC curves of more than 30 potential formulations that FISIPE made with a variety of proprietary additives. The onset of the exotherms, seen in the DSC curves, is indicative of the onset of stabilization, and the steepness of the curves is indicative of the severity of the exotherm during oxidative stabilization. Less steep curves indicate a less severe exotherm that correspondingly could result in more rapid stabilization.

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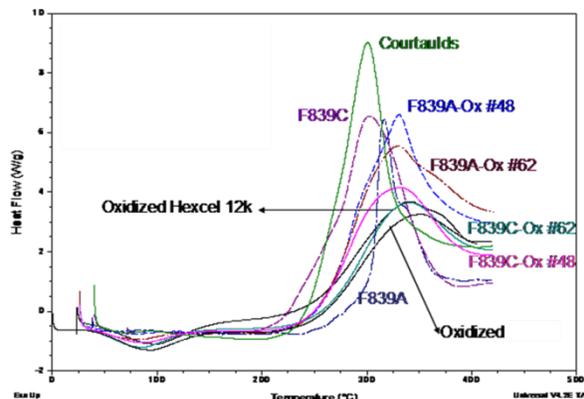

Figure 2. DSC characterization of various oxidized textile PAN precursor compositions and comparison to oxidized commercial precursors.

The next step at ORNL was to determine oxidation temperatures to obtain optimal processing conditions. This was done using the precursor evaluation line and measuring the oxidation density while targeting values that would be close to conventional CF precursors that were fully oxidized. Evolution of the oxidation profile is shown in Figure 3 with standard CF precursors used as a baseline. Oxidized densities slightly higher than industrial grade precursors and slightly lower than aerospace grade precursors have been obtained.
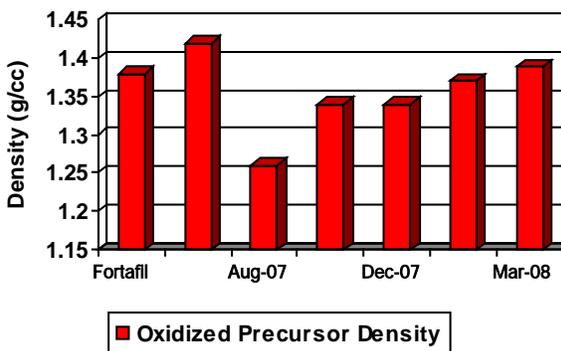

Figure 3. Oxidized density of FISIPE precursor over time when compared to conventional precursors.

For the period covered by this report, ORNL has been using both the precursor evaluation line and the pilot line to determine T^3 processing profiles for the FISIPE precursor. Program requirements are to develop fibers with strength values of at least 250 ksi and modulus values of at least 25 Msi. Figures 4 and 5, respectively, show the evolution of the strength and modulus during development of processing conditions over time. We have currently reached strength values of 363 ksi, exceeding program goals, and are also well above program goals on modulus, with a current value of 31.7 Msi. The addition of
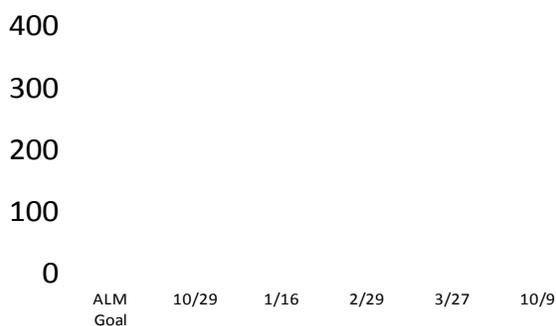

Figure 4. Obtained strength (ksi) of CF produced from FISIPE precursor during development of the processing protocol as a function of time.
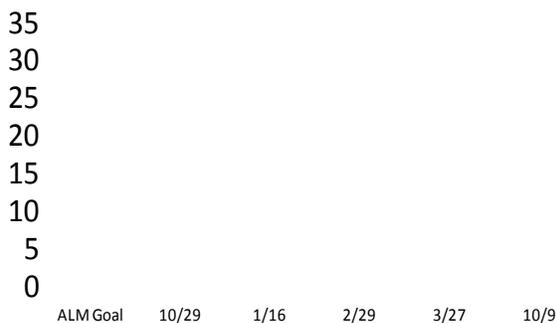

Figure 5. Obtained modulus (Msi) of CF produced from FISIPE precursor during development of the processing protocol as a function of time.

differential tensioning during upgrade of the pilot line should yield significant improvement in the ability to align grapheme planes and increase modulus. Figures 6 and 7, respectively, show manufacturing of the CF on the precursor evaluation line and the resultant carbonized fiber tows.

At the end of FY 2008, ORNL delivered spools of fully carbonized textile-precursor-based CF to Ford, General Motors, and Chrysler, meeting the program milestone and property requirements.

Development of PAN-MA Precursors

At the outset of the program, ORNL approached Fibres Worldwide in Grimsby, UK, as a potential development partner. The Grimsby plant had produced CF precursors for a wide variety of CF manufacturers worldwide, and two lines for producing textile PAN at textile costs had been installed in recent years. The textile lines were based upon an MA comonomer.

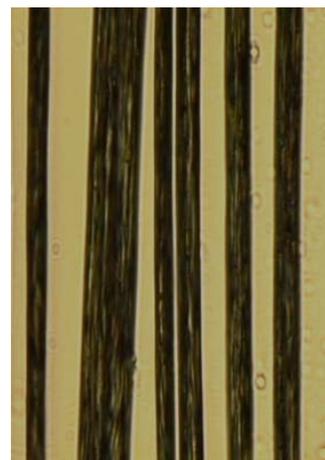**Figure 6.** Processing of FISIPE precursor using ORNL's precursor evaluation line.

Figure 7. Carbon fibers produced from FISIPE precursor.

While personnel at the plant have remained essentially unchanged (mostly UK citizens), Fibres Worldwide was acquired by a large multinational Chinese corporation, Blue Star, in late 2006 and renamed Bluestar Fibres Company

Ltd. The Grimsby plant was visited by ORNL program management in February to assess the feasibility of continuing to develop a partnership.

During that trip it was learned that Bluestar's textile lines had been decommissioned and that its CF precursor lines were undergoing major renovations. The purpose of the renovations is to produce precursor for a CF plant being built in China. Targeted uses for the CF are reported to be windmills, power cables, and other industrial applications.

Because of the decommissioning of the textile lines, which provided the opportunity for producing lower cost precursors; U.S. competitiveness issues related to potentially enabling a foreign company to more competitively enter the market; and export control issues related to CF manufacture, Fibres Worldwide/Bluestar Fibres is no longer considered a likely partner.

We attempted to identify other likely partners in both the U.S. and the U.K.; however, this part of the project has since been terminated and funding diverted to other efforts.

Commercialization of Advanced Precursors

This portion of the project was initiated during the period covered by this report. At the start of the current fiscal year, Owens Corning and ORNL were negotiating a Cooperative Research and Development Agreement (CRADA) for the commercialization of conventionally processed textile precursor. The original plan was to develop two factories, a smaller one in the United States and a larger one in a yet to be determined location. However, as a result of a merger with Vetrotex and the associated refocusing of efforts, Owens Corning decided not to pursue the joint effort.

Subsequently, DOE and ORNL were approached by another large U.S. company to collaborate on commercializing advanced precursors by developing the technology necessary to build a large factory in the United States. ORNL and this partner are currently in discussions with DOE program management about a cost-shared CRADA. Identity of the company and specific plans are confidential at this time.

ORNL continues to field frequent inquiries about the CF technology under development. Over the past year, we have hosted about a dozen prospective industrial partners at ORNL, who were making site visits to tour our facilities and inquire about potentially licensing and commercializing CF technology. We have responded to numerous other inquiries that did not result or have not yet resulted in site visits. At this time, we are in very active discussions with multiple potential partners and are maintaining some degree of continued discussion with several other partners.

The technological advances in the program, combined with recent growth in the CF industry, are responsible for much of this interest by prospective industrial partners. Additionally, ORNL staff members routinely participate in industry conferences, including the cochairmanship at the 2008 Global Outlook for Carbon Fibers Conference, and numerous contacts have been made at these events. ORNL staff will continue to engage prospective industrial partners and work to develop partnerships that will lead to successful commercialization and deployment of the advanced CF technology.

The commercialization plans under discussion will require the capability to produce a sufficient quantity of advanced CFs for prospective end users to sample and to support downstream part manufacturing process development. Therefore, immediate upgrades to ORNL's facilities are being implemented, including a higher temperature furnace, improved tow transport and stretching/tensioning, and increased line speed for ORNL's conventional pilot line.

Future Direction

The future plans for each of the three subprojects are described below.

Development of PAN-VA Precursors

During the next few months, ORNL will refine the processing parameters for converting the FISIPE precursor into CF with the goal of increasing both the modulus and the strength of the fiber. FISIPE is in the process of developing an improved precursor formulation which should yield a better

product. Work to date has been focused on developing processing conditions using material from the FISIPE pilot line. Currently FISIPE is installing equipment in its production facility to produce textile-based precursor. Once that equipment is in place, material will be processed at ORNL to confirm that the scale-up to full industrial scale has been successfully completed. If time remains in the project, efforts will then be turned toward developing the best surface treatment and sizing technologies to allow good load transfer from the fiber to the resin systems, which is critical to making good composites with excellent properties. Once these steps are completed, fiber and composite samples will be made and supplied to ACC for composite testing. In addition, we have begun tow splitting studies with the object of making one precursor into a variety of finished CF tow sizes.

This project will be followed by an intense effort to introduce current and future CF manufacturers to the project goals and results so that the technology will be integrated into future CF production facilities.

Development of PAN-MA Precursors

No further activities are planned.

Commercialization of Advanced Precursors

Equipment capabilities will be upgraded to enable the production of sufficient quantities of advanced CFs to support property testing and process development material needs. ORNL will continue to engage prospective industrial partners and pursue CRADAs with CF manufacturers to commercialize advanced precursors. Meetings have been held and are being planned with a variety of current CF manufacturers, potential future CF manufacturers, and fiber production equipment manufacturers to develop more than one commercialization route.

Conclusions

The development of PAN-VA textile precursors is well ahead of schedule. Strength values (363 ksi) exceed program requirements (250 ksi), and modulus values (31.7 Msi) are above program requirements (25 Msi). A more refined version of

the precursor is being developed, and commercialization plans are being developed.

No future efforts to develop PAN-MA precursors are planned.

A major effort to commercialize alternative precursors is being developing, and related activities are being planned.

Presentations/Patents/Publications

1. Joseph A. Carpenter et al., **"**FreedomCAR and Low Cost Carbon Fiber for Automotive Applications," Low Carbon Generation, 3M innovation Centre, London, UK, February 9, 2008.

2. C. David Warren, "The Development of Lower Cost Carbon Fiber Technologies for Automotive Applications," Proceedings of *The Global Outlook for Carbon Fiber 2007*, San Diego, California, October 23–25, 2007.

3. C. David Warren, "A Comprehensive Research Program to Develop Commodity Grade, Lower Cost Carbon Fiber," to be published in the proceedings of the *ACMA Breaking New Ground: Structural Composites Applications in Defense, Infrastructure, Transportation and Corrosion-Prevention*, University of Alabama-Birmingham, March 4–6, 2008.

4. C. David Warren et al., "Multi-Task Research Program to Develop Commodity Grade, Lower Cost Carbon Fiber," proceedings of the *2008 SAMPE Fall Technical Conference*, Memphis, Tennessee, September 8–11, 2008.

5. C. David Warren et al., "Future Lower Cost Carbon Fiber for Autos: International Scale-up & What is Needed," Proceedings of the *2008 SPE Composites Conference*, Detroit, Michigan, September 16, 2008.

6. C. David Warren and Felix L. Paulauskas, "Investment in the Carbon Fibre Business for Commercial Grade Low Cost Composites," Proceedings of the *Carbon Fibre 2008 Conference*, Hamburg, Germany, September 30–October 2, 2008.

7. Felix L. Paulauskas and C. David Warren, "Producing Low-Cost, High Volume Fibres for Commercial Applications," Proceedings of the *Carbon Fibre 2008 Conference*, Hamburg, Germany, September 30–October 2, 2008.

8. C. David Warren, "Development of Lower Cost Carbon Fiber for High Volume Applications," Proceedings of the *Composites + Polycon 2009 Conference*, Tampa, Florida, January 15–17, 2009.