5. LOW-COST CARBON FIBER

A. Low-Cost Carbon Fibers from Renewable Resources

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Objective

- Demonstrate the use of new precursor materials that decrease the cost and increase the availability of carbon fiber, which meets the performance and price needs of the automotive market.
- Demonstrate that one or more renewable/recycled precursor formulations can be expected to produce industrial-grade carbon fibers at a cost of $3.00–$5.00/lb.

Approach

- Provide the data needed to scale processing up to industrial levels and to consistently achieve desired fiber properties at larger scale.
- Systematically develop the technical base needed to produce lignin-blend carbon fiber feedstocks at industrial scale:
  - Lignin production to obtain best molecular weight, low-volatile, low-salt material;
  - Spinning, oiling, and sizing technology;
  - Spinning technology, including production die structure, plasticizers, and nucleating agents;
  - Plasma treatment and sizing technology to make the fiber compatible with selected resin systems;
  - Selection of appropriate polyesters; and
  - Evaluation of properties and economics of fiber and composite systems.
- Work with industrial partners to scale and transfer the technology for the production of carbon fiber precursors from lignin-blend feedstock.
  - Evaluate melt-extrusion properties of lignin-based feedstock at increasing scale using near-industrial equipment that can be readily obtained by fiber manufacturers.
  - Evaluate production of carbon fiber using a research production line at an industrial facility.
  - Evaluate mechanical and composite compatibility properties of graphitized melt-spun lignin-blend fibers.
  - Work with partners to evaluate and develop process metrics and standards.
  - Work with partners to better define process economics.
- Transfer technology, including intellectual property, for the production of carbon fibers from lignin to industrial partners.

Accomplishments

- Demonstrated proof-of-concept of the melt extrusion of 28 filament tow of lignin-based fibers. This validated selected compositions, processing methods, and testing technologies. It also provided a basis for understanding the process improvements required for larger scale manufacture of lignin-based carbon fiber feedstocks.
- Showed from preliminary data that yields of 50%, consistent with those obtained commercially for lignin-based activated carbon, are feasible.
- Spun significant amounts of 28 filament tow successfully at the University of Tennessee (UT) using a two-step process. No sticking problems were apparent, and fiber diameter was reduced from ~45 μm to ~15 μm, with an apparent increase in mechanical properties.
- Discussed that preliminary evaluations of a plasma surface treatment + silanation for lignin-based fibers indicated a significant improvement in fiber-resin bonding over conventional carbon fibers.
- Made small epoxy resin composites using carbon fibers produced from UT 28 filament tow that showed composite mechanical properties.
- Determined sources of volatiles within lignin and developed purification methods that remove or mitigate volatiles.
- Developed of initial process control technologies.

Future Direction

- Develop methods for production of industrial-quality carbon fibers from lignin-blend feedstocks. Studies will include the following:
  - Optimization of lignin preprocessing to minimize contaminants (salts and particulates) and provide the best molecular weight.
  - Development of conditioning and spinning processes that remove water and volatiles prior to fiber production.
  - Selection and design of spinning dies that provide the best internal structure.
  - Selection of plasticizers and nucleating agents for lignin-polyester fiber blends.
  - Selection and development of techniques for spooling and oiling lignin blend fiber at each step.
  - Development of methods for surface treating and sizing the surface of carbon fibers to improve compatibility with proposed resin systems. This is particularly critical for chopped fiber–resin composites.
- Work with project partners to
  - address raw fiber production issues (lignin, preconsumer recycled polyesters, spinning and winding technologies); and
  - evaluate carbon fiber production from lignin-based multifilament tow using an industrial research process line.
- Transfer technology to industry.

Introduction

This project is developing methods for production carbon fibers from high-volume, low-cost, renewable and recycled feedstocks to reduce precursor and processing costs. Use of these materials also decreases sensitivity of carbon fiber cost to changes in petroleum production and in energy cost.

Proof-of-concept production of single fibers from a variety of high-volume natural, renewable, and recycled materials was demonstrated first. Single fibers melt spun from blends of Kraft lignin, an inexpensive, high-volume wood pulping by-product, with small amounts of routinely recycled polyolefins and polyesters could be processed using conventional stabilization (oxidizing atmosphere), carbonization, and graphitization (inert atmosphere) furnacing to yield carbon fibers. Fiber properties improved if the fibers were stretched during furnacing. Graphite content, measured with X-ray diffraction, increased with increasing graphitization temperature. Carbon fiber yield from this lignin-blend feedstocks was ~50%, and the fibers were dense, smooth-surfaced, and round.

Larger amounts of a lignin-recycled polyester feedstock were melt extruded as a multifilament (4 to 28 fiber) tow using the University of Tennessee (UT) twin-screw Leistritz extruder to meet a September 2003 composite preparation and testing milestone. The U.T. Leistritz is the smallest member of a line of commercial melt extruders. Meeting this milestone showed that (1) lignin-blend fiber can be melt-extruded as a small tow using near-commercial spinning equipment, (2) composites made from graphitized lignin-blend fibers can be used in resin-fiber composites that have normal fracture patterns, and (3) although very smooth, lignin-blend fibers can be plasma treated and silanated to provide good fiber/resin adhesion.

Analysis of the samples obtained indicated that bubbles and inclusions were the major flaws in lignin-blend fibers. Flaws are known to decrease the strength of carbon fibers and are typically the initiation point for fiber breakage. The source of the bubbles was found to be volatiles from the lignin, and this year, methods were developed to mitigate these problems. Additionally, methods for controlling salt content in the fibers and for prefiltering black liquor prior to lignin production have been developed.

Project Deliverables

Goal: By the end of this multiyear program, production of one or more environmentally friendly, economically feasible carbon fiber precursors will be demonstrated and transfer of production technologies and any related intellectual property to industry initiated.

In FY 2004, major milestones, including the initial tests of the effect of lignin molecular weight on fiber properties (6/30/04) were completed on time.

FY 2005 milestones include development of a lignin feedstock specification to facilitate industrial production of carbon fibers meeting program goals (5/2005) and establishment of basic rheology for extruding and winding lignin bundles with improved handling characteristics (9/2005).

Planned Approach

Production of industrial-grade carbon fibers from a radically new type of feedstock requires the simultaneous development of methods for feedstock recovery, preparation, blending, spinning, handling, and spooling in addition to the furnacing, stretching/orientation, oiling, and sizing technologies required for conventional fibers. These are combined with evaluations of fiber quality and suitability for use in composites.

Because of high levels of emissions and costs typically associated with spinning of fiber from liquids, first priority was placed on development of melt-spinning techniques for fiber. Use of lignin and other non-nitrogenous feedstocks was preferred because it would eliminate cyanide emissions during furnacing. Use of modern furnacing techniques, such as hot-stretching and controlled atmosphere processing, are being evaluated to improve properties and yield of carbon fiber precursors from feedstock.

Industrial partners are increasingly involved in the development of process technologies. They have been working with project staff on the selection of blending polymers for lignin, purification of lignin, strategies for production of cleaner lignin, and spinning of fiber. In the later stages of the project, industrial partners will also assist in production of lignin-based carbon fiber using a research industrial production line.

Transfer of project technology, including any intellectual property, is planned.

Lignin Feedstock Quality

Lignin is an inexpensive, high-volume by-product of paper production. Although the bulk of Kraft lignin is burned to provide process energy, a fraction is recovered from black liquors. At acid pH, Kraft lignin forms a loose gel that is recovered, washed, dried, and marketed as a free-flowing powder. Softwood Kraft lignin forms the bulk of commercial materials, although hardwood lignin is also available. The current one-step precipitation process leaves several materials (e.g., particulates, cellulosics, water, volatile, and inorganic pulping chemicals) within the lignin gel. Although these are acceptable in the current product, which is marketed for applications such as cold-rolled asphalt, they interfere with the production of satisfactory carbon fibers.

Developing cost-effective, industrially feasible methods for improving the quality of lignin as a carbon fiber feedstock has remained a major focus of this project. Removal of salts, particulates, and carbohydrates from lignin will be discussed below.

Control of Ash Levels in Lignin

To improve the strength of carbon fibers, it is desirable to minimize defects, such as inclusions. A typical alkaline pulping liquor contains ~10% salts, which can coprecipitate with lignin gel. When lignin is dried, extruded, and fired, these salts will create inclusions or, for fibers fired at temperatures in excess of 2000°C, voids. To minimize salts, lignins have been desalted by washing with slightly acidified water.

To develop an understanding of desalting, data on the salt concentrations of lignin and lignin wash waters were evaluated. As shown in Figure 1, there appears to be a good correction between the salt concentrations in the wash water and dried lignin across the likely range of process values. The ability to estimate salt concentration in lignin from that in wash waters will facilitate production of low salt lignins.

The major difficulty in desalting lignin was estimating the ash content of the resulting lignin. As shown in Figure 1, there is good correlation between the ash contents of lignin and wash water. A number of industrial technologies for measuring the dissolved inorganic solids, or ash, in water are available to industrial lignin producers, and the correlation should facilitate real-time process control.

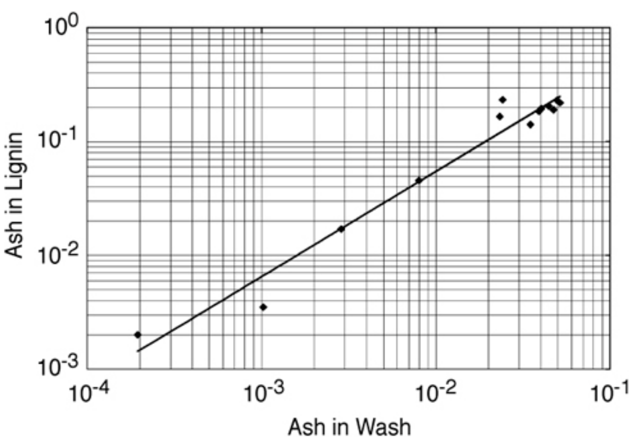

Figure 1. Ash (salts) content of dried lignin and water used to wash.

Black Liquor Filtration

Particulate contaminants, such as sand grains, diatoms, or bits of wood and paper, coprecipitated in the lignin gel cause difficulties in spinning. Although the black liquor from which lignin is precipitated is typically coarse-screened to recover wood and pulp, screens do not provide adequate removal of particulates in the 0.5- to 100-μm range, which could block spinning dies.

As the project scales up lignin production for use in fiber spinning, a filtration step could be inserted to decrease inclusions. Because the pulp and paper industry does not generally filter black liquor, a series of tests was performed to determine whether it would be feasible to use conventional submicron filtration prior to lignin precipitation. These tests were performed by obtaining black liquors made from several starting chemical concentrations and filtering them through 1-in. diameter, 0.45- or 0.2-μm filters, and measuring the flow rates or fluxes.

As shown in Table 1, the initial fluxes, or flow rates, of Kraft black liquor through various media were in an industrially feasible range. However, filtration rate was sensitive to both initial pulping chemical concentration, and to the type of filter used.

The most effective filter type was hydrophilic polypropylene. This material is particularly suited to use in carbon fiber precursor feedstock for two reasons. First, industrial polypropylene filters and filter cloths are readily available, inexpensive, and alkali resistant. Second, any residual filter material that became combined with the lignin would likely

Table 1. Filtration rate (cm/min) of Kraft black liquors

Filter material	Pore size (μm)	Pulping chemicals (% AA)		
		8	12	16
Polypropylene	0.45	9.2	12.2	18.3
Polysulfone	0.45	3.7	4.1	9.2
PVDF	0.45	4.3	6.1	7.3
Nylon	0.45	4.3	2.4	7.3
Alumina	0.20	6.9	7.6	4.4
PTFE	0.45	0.1	1.2	1.2

melt under the fiber extrusion conditions used. This would minimize blinding of spinning dies.

As the data indicated, use of submicron polypropylene cartridge filters and micron polypropylene filter felts has proven effective on high-volume black liquor samples processed to recover both high- and low-sulfur lignins from alkaline pulping.

Polypropylene filter felts can be used in a wide variety of industrial-scale filter configurations, such as belt filters or plate and frame filters. Although polypropylene filter felts are currently produced in the 1-µm and higher range, discussions with manufacturers indicated that felts capable of removing submicron particles are planned.

Purification to Decrease Volatiles

Bubbles in multifilament fibers could be produced in a number of ways: by release of sorbed water, by overpressurization of nitrogen during extrusion, by release of small volatiles in the feedstock, or by chemical breakdown of feedstock constituents. Some of these factors are best controlled during lignin preparation, others by modification of lignin purification and prespinning processing. For example, overpressurization during extrusion is likely due to the residual amount of particulate matter in the feedstock and will be controlled by the use of a feedstock that has been filtered prior to precipitation.

The color variation in as-spun raw fiber provided a valuable clue in understanding a major reason for die plugging and for volatile materials, including water, released during extrusion. Consideration of the spinning temperature, coupled with increased fiber darkening and carbon deposits noted on extruder cleanup, suggested that a material in commercial lignin was charring during long periods at processing temperatures of >225°C. Nuclear magnetic resonance profiles of desalted commercial lignin showed the presence of a significant amount of carbohydrate. Carbohydrate gels are hydrophilic, and additionally, carbohydrates may be carboxylated during the pulping process. Most of the carbohydrate occurs as beta-linked polysaccharides, and many carbohydrates are known to char.

Efficient separation of lignin-bound carbohydrates presents a significant technical challenge. The first method evaluated was enzyme hydrolysis of carbohydrates at pHs ranging from 3 to 8. However, enzyme treatments did not significantly reduce the amount of carbohydrate in commercial lignin samples.

The project staff were able to obtain experimental Kraft black liquors with varying pulping chemical levels from another Oak Ridge National Laboratory (ORNL) project. These liquors were to be used to prepare lignins. In conventional industrial lignin preparation, pH is dropped from ~13 to 3.5–4.5 in a single step. The lignin precipitates as a gel, which is washed and dried prior to use. However, this technique coprecipitates carbohydrates, such as short chain cellulosics, with the lignin.

An ORNL consultant suggested use of a modified version of a fractional precipitation technique used to separate Kraft lignin from black liquor for analysis. This technique takes advantage of the selective precipitation of cellulosic carbohydrates at pH 9–10.5. The cellulosic precipitate can be removed, and the liquid acidified to pH 3.5 to 4.5 to precipitate the lignin.

Figure 2 shows thermogravimetric analyses of three different types of lignins and the carbohydrate removed from a Kraft lignin. The cellulosic carbohydrate fraction has a significantly higher weight loss than do the lignins. Within the lignins, lignins from alkaline and organosolv pulping (Lignol Innovations) have the lowest weight loss. The alkaline pulping lignin was prepared using a two-step process in which the carbohydrate was first precipitated and removed, and then the lignin was precipitated.

Figure 3 shows a solid state nuclear magnetic resonance pattern (NMR) for carbohydrate removed in step precipitation. Carbohydrate removed in the first step was estimated to contain ~9% chemically bound lignin. Additionally, the carbohydrate contains a small amount of carboxylate. This is most probably due to changes that normally occur in wood carbohydrate during pulping.

Figure 4 shows the solid state NMR pattern of precipitated lignin that has been stripped of a portion of its carbohydate by fractional precipitation. This material has been reduced from 20–30% carbohydrate to estimated 12% carbohydrate.

At present, the bench-scale data discussed above have been evaluated during the processing of significant amounts of lignin from alkaline pulping black liquors. Although commercial lignins are relatively impure, having as much as 20–30% carbohydrate content, highly pure lignins, up to 97% as

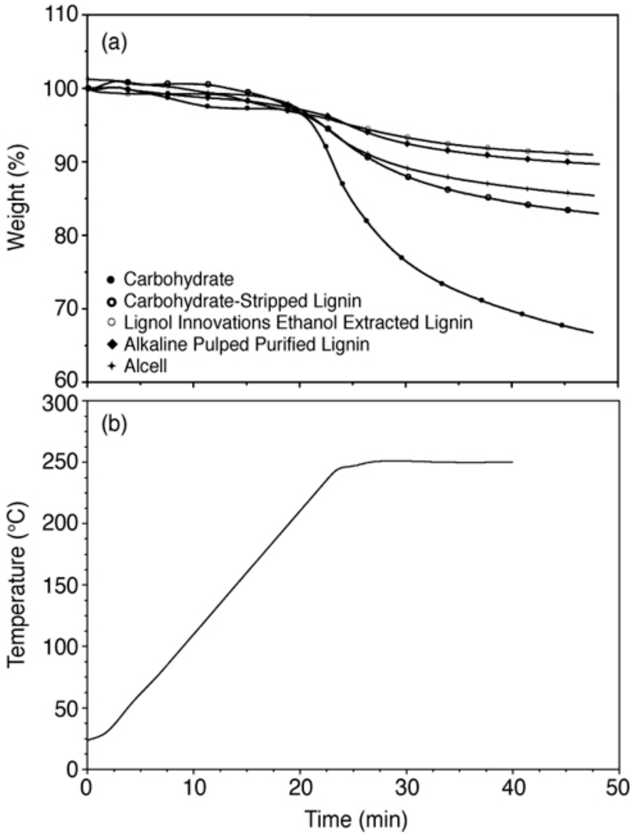

Figure 2. Thermogravimetric analysis of selected lignins and a lignin-derived carbohydrate: (*a*) weight loss curves and (*b*) temperature–time curve for the analysis.

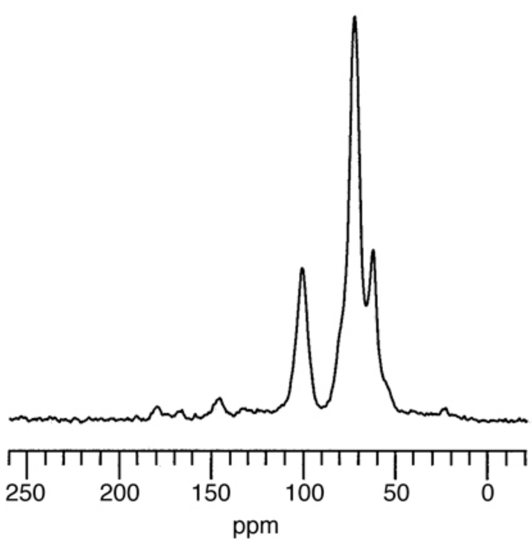

Figure 3. NMR analyses of celluloselike polymer removed from lignin by fractional precipitation.

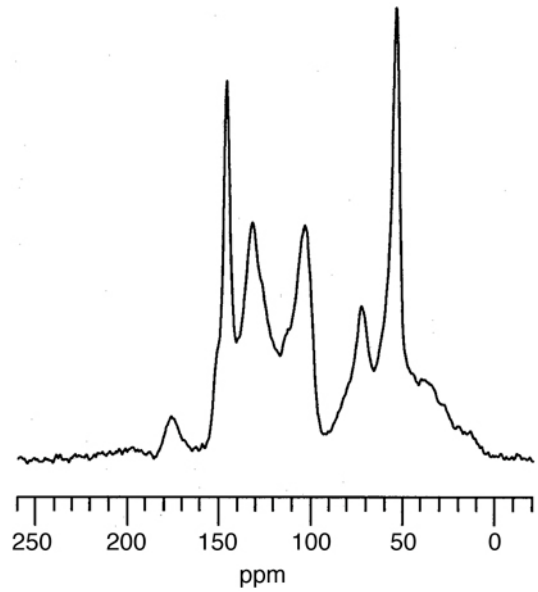

Figure 4. NMR analyses of Kraft lignins with reduced amounts of celluloselike carbohydrate after fractional precipitation.

measured by solution NMR, can be produced from black liquors.

The critical factor in recovering highly pure lignin appears to be effective removal of the carbohydrate. In early experiments, lignin and carbohydrate were separated by centrifugation. High-purity lignin required several purification steps, and the precipitates from both steps were both very small (around a micron) and quite gelatinous.

It was thought that this could be improved through the use of flocculants. The question was finding effective flocculants whose recycle would be acceptable to pulp and paper mills. Discussions with industrial partners, as well as industrial experience, indicated appropriate the levels and classes of flocculants.

Currently, two flocculants, applied at 10 ppm, are providing effective carbohydrate particulate aggregation. This permits use of a single filtration step for carbohydrate removal.

A combination of flocculants, applied at 10 ppm each, has also been used to improve the filterability of lignin aggregates.

Addition of small amounts of selected industrial enzymes to the lignin increases removal of residual carbohydrate from precipitated lignin during desalting.

The combination of coagulation and filtration is used effectively at industrial scale and the materials and the enzymes used are standard commercial materials used by the forest products and food industries in other applications.

Removal of the carbohydrate, salt, and particulates changes the final lignin product. Commercial lignin with its associated carbohydrate functions as a liquid crystal surfactant. Carbohydrate-stripped lignin is significantly more hydrophobic. This will likely have the benefit of decreasing water sorption, but requires reformulation of the alloying polymers and plasticizers used in the lignin blend.

To minimize use of materials, fiber blends are currently being evaluated using a bench-scale melt extruder and winder.

Fiber Graphitization

As shown by wide-angle X-ray scattering, lignin-based fibers form graphene crystallites at temperatures as low as 1200°C. Figure 5 shows a typical wide-angle scattering pattern from a small bundle of carbonized lignin-blend fibers mounted across a pinhole. These data were obtained at the University of Tennessee Central X-ray Diffraction Facility Molecular Metrology Pinhole SAXS System equipped with a 120X, two-dimensional (2-D) detector.

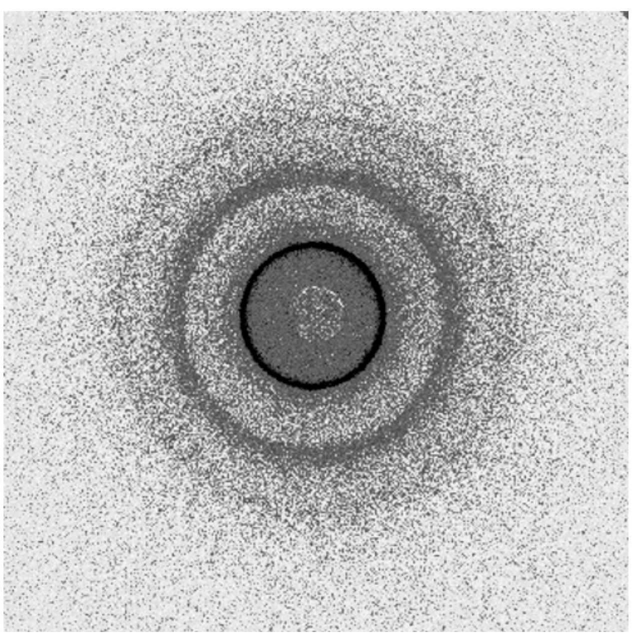

Figure 5. Wide-angle X-ray diffraction pattern showing the presence of graphene crystallites in lignin-based carbon fibers fired to 1200°C.

Future Directions

Significant production of lignin-based multi-filament (28 strand) tow and successful use of this material in small resin-fiber composites was demonstrated in FY 2003. This project was re-proposed and extended to permit evaluation of methods for producing high-quality lignin-based feedstocks for low-cost production of automotive carbon-fiber resin composites.

Having established proof-of-concept, the project staff is systematically addressing the technical issues required to produce industrial-grade, lignin-based carbon fiber at prices and properties meeting automotive need. Because the bulk feedstock used in this process is derived from alkaline (Kraft and soda) pulping, a major concern is developing methods for consistently recovering clean, high-quality lignin low in volatiles, water, particulates, and salts. Additionally, an understanding of the effect of pulping conditions on the molecular weight of lignin will be required to consistently produce industrial-grade carbon fiber and will be evaluated.

The purification and precipitation of carbohydrate and lignin is expected to evolve and improve. The goal is an industrially practicable method that permits one-step carbohydrate stripping and produces a material that can be directly reused in paper manufacture. If only small amounts of flocculants are used and if carbohydrate structure can be preserved, it is likely that the carbohydrate (and associated inorganics) can be directly recycled back to the pulp mill. The carbohydrate, which is primarily hemicellulose, can be used in several ways. First, it can be directly burned for mill energy. Second, it can be incorporated into the pulp produced by its original mill, by mills pulping a different furnish, or by mills pulping recycled fiber. This would be particularly advantageous because it would (1) significantly increase pulp yield and (2) significantly increase the tear and burst strength of papers and boards in which it is incorporated. It would also likely decrease the production cost for purified lignin because it would provide a second revenue stream, minimize waste production, and improve chemical return to the mill.

In addition to techniques for the production of lignin, fiber blends appropriate to the more hydrophobic purified lignin will be evaluated at bench and larger scales.

Spinning die designs for production of lignin-based fibers will be evaluated. Initial tests indicated that dies, similar to those use for spinning pitch-based feedstocks, which provide high shear, create a more uniform internal structure in the raw fiber. Spinning parameters, including rheology, of the blend will be optimized for multifilament production.

Production techniques that provide high-quality, handleable, spoolable, raw lignin-based fiber will be required and are being evaluated. These techniques include selection and evaluation of plasticizers and nucleating agents, as well as raw fiber coatings and oils. Spooling techniques will also be evaluated.

After lignin-based fiber is carbonized, it must be surface treated and sized to increase compatibility with the resin system. Fiber-resin compatibility is particularly critical in automotive applications because the current program plan calls for use of chopped, rather than woven or wound, fiber.

Throughout the period, a variety of analytical techniques, including physical property evaluations of fiber and resin, as well as X-ray diffraction and electron microscopic examination, will be used to assess fiber quality.

As studies proceed, project partners expect to become increasingly involved in research activities. These will include tests of the fiber on a research furnacing line of an industrial partner. In 2006, formal transfer of technology for production of carbon fiber from Kraft lignin-blend feedstocks will be initiated.

Partnerships

A number of different entities have been instrumental in development of this technology. North Carolina State University earlier spun a variety of lignin-blend polymers as single fibers. These were used in initial feasibility evaluations. At present, UT is working to prepare significant quantities of multi-filament tow for project use.

Since its inception, this project has benefitted from participation of MeadWestvaco, the dominant domestic lignin producer, which has provided hundreds of pounds of softwood and hardwood lignins, including a wide variety of research lignins, for project use.

In FY 2004, this project attracted interest and participation from three other pulp and paper companies: Weyerhaeuser; Granit, S.A.; and Lignol Innovations. Their participation is broadening the variety of lignins available to the project. As was shown in Figure 2, this facilitates selection of lignins that have better melt spinning properties. Lignins from alkaline (sulfur-free) pulping and the ethanol extracted low-carbohydrate lignin (Lignol Innovations) have the lowest gas evolution. The participation of several lignin producers is welcomed because it improves feedstock selection and will likely increase the amount of carbon fiber feedstock.

Conclusions

In FY 2003, the project was reproposed and in FY 2004, retasked, to focus on larger scale production of carbon fiber precursor feedstocks. Relationships with MeadWestvaco and Eastman Chemical Company were formalized, and two additional pulp and paper companies have joined the project. A third paper company has informally sent significant samples of various black liquors from which lignins can be prepared.

During preparation of small lignin fiber tow, the project staff found that a combination of particulates in lignin and evolution of gas from lignin during spinning were significant problems. During this period, methods for addressing both of these concerns with technologies that can be used at industrial scale were developed. Carbohydrate, in the form of cellulosic polysaccharides that coprecipitate with lignin, was determined to contribute significantly to evolution of gas during spinning and also to produce char if held for long periods above 200°C. Carbohydrate-stripped lignins show significantly reduced volatile evolution between 150 and 250°C.

Methods for removal of carbohydrate from black liquor were developed and have been shown to be successful at increasing scale. These methods are industrially tractable. Filter materials that permit the removal of submicron particulates from black liquor were evaluated at bench scale and shown, at larger scale, to be effective in black liquor filtration. The most successful material is polypropylene, which has the additional advantages of acid and alkali resistance and melting below the temperatures at which lignin blends are typically spun.