

LOW COST CARBON FIBER FOR TRANSPORTATION APPLICATIONS

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ABSTRACT

The Department of Energy Freedom Car Program has shown that, by lowering overall weight, the use of carbon fiber composites could dramatically decrease domestic vehicle fuel consumption. For the automotive industry to benefit from carbon fiber technology, fiber production will need to be substantially increased and fiber price decreased to \$3 - \$5/lb. To achieve this cost objective, alternate precursors to pitch and polyacrylonitrile (PAN) are being investigated as possible carbon fiber feedstocks. High-volume, renewable or recycled materials, such as lignin, cellulosic fibers, routinely recycled petrochemical fibers, and blends of these components appear attractive because the cost of these materials is inherently both low and insensitive to changes in petroleum price. Current studies have shown that a number of recycled and renewable polymers can be incorporated into melt-spun fibers which are attractive as carbon fiber feedstocks. Highly-extrudable lignin blends have attractive yields and can be readily carbonized and graphitized. Examination of the physical structure and properties of carbonized and graphitized fibers indicates the feasibility of use in transportation composite applications. Initially, these studies were limited to single fibers. Recent studies, however, have demonstrated that tows of 20 micron drawable filament can be extruded with no sticking problems and with apparent improvements in filament properties.

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1. INTRODUCTION

Lightweight materials strategies are expected to play a major role in the FutureCAR initiative and are valuable components of passenger and heavy transport. New materials which meet the availability, cost, and performance requirements needed for transportation are under development in a variety of Department of Energy-supported programs. The Department of Energy, Office of Advanced Automotive Technologies, Lightweight Materials Program has been working with automobile manufacturing partners to develop technologies for the production of lower emissions, more energy efficient vehicles which use strong, lightweight materials, such as metals or fiber reinforced polymer-matrix composites, to replace vehicular steel. Adoption of lightweight materials could lower fuel use and emissions across a wide range of vehicles.

Cost and availability of carbon fiber reinforced composites remain the major barriers to use of carbon fiber resin composites in transportation applications. At costs below \$7/kg, carbon fiber could replace a significant portion of the steel now used in automobiles and light trucks. However, the large amounts of materials used in transportation - each automobile requires roughly a tonne of steel - mean that radically different technologies for producing carbon fiber are needed. Currently, the least expensive precursors are estimated to cost > \$3.00/kg when adjusted for yield. The intricate, painstaking processes required to produce polyacrylonitrile (PAN), rayon, and mesophase pitch precursor fibers increase the cost and inherent difficulty of bringing new carbon fiber production capacity on line. New technologies which could increase the 30,000 tonnes of carbon fiber capacity (1) by a hundred-fold (2) are needed to meet U. S. passenger transport needs.

If inherently simple processing technologies, such as direct melt-spinning, could be used to produce precursor fiber from high-volume renewables or routinely recycled polymers, it would be possible to produce significant quantities of carbon fiber precursor in sufficient quantities to support transportation industry use. The major requirements for this approach are: 1) selection of blendable polymers which produce a single-phase melt, 2) selection of fiber blends which melt at a high enough temperature to permit rapid stabilization, 3) development of low-cost methods for purifying starting materials, and 4) demonstration of proof-of-principle that acceptable, multifilament tows of feedstock for industrial grade carbon fibers can be produced from selected starting materials.

This paper reports progress in development of bench-scale methods for production of single and multiple melt-spun carbon fiber precursors from renewables, most notably Kraft lignin, blended with routinely recycled polyolefins and polyesters. Early evaluations of multifiber production have been encouraging and indicate the potential for production of melt-spun tow from high-volume, low-cost renewable and recycled materials.

2. MATERIAL CONSIDERATIONS

Carbon fibers have been used for applications which require high strength or stiffness, together with low weight, for more than three decades. Although a variety of different polymeric feedstocks have been demonstrated to produce carbon fibers, three feedstocks supply the bulk of current industrial use: PAN, pitch, and rayon. Each of these materials has been optimized for applications, such as aerospace, which stress performance over cost. The transportation industry requires carbon fibers optimized to provide acceptable performance at minimal cost.

During early carbon fiber research, the production of carbon fibers from lignins and other renewable polymers was demonstrated. For example, lignin fibers dry spun from minimally-modified acid sulfite or alkaline pulping liquors and regenerated cellulose were reported (3, 4). At pilot scale, Nippon Kayaku Company produced industrial grade carbon fibers from a lignosulfonate precursor spun from concentrated pulping liquors. Low furnacing temperatures and short stabilization periods were attributed to enhancement of crosslinking by functional radicals derived from the hydroxyl groups in lignin. However, defects (voids) created by volatilization of crystallized salts decreased fiber strength to industrial grades (5). Without a method for preparing feedstock low in void-forming chemicals, the dry-spun fibers were unsuitable for high performance uses.

Because of the ubiquity of lignin, which makes up around one-fourth of the dryweight of trees, several research groups have evaluated effects of modern processing techniques - demethylation (6), hydrogenation (7), and phenolysis (8, 9) - on downstream carbon fibers. All of these methods either require significant downstream chemical processing of the lignin or a fundamental change in the pulping process itself. Lignin from the Kraft pulping process, which makes up the bulk of U.S. chemical pulping (1) has received little attention as a carbon fiber feedstock. It is currently burned to provide mill steam and electric power and to recycle inorganic pulping chemicals.

Technology for the recovery and precipitation of Kraft lignin is well known, and Indulin AT, produced by MeadWestvaco, is a bulk commercial product. The softwood-derived Indulin AT has a relatively broad melting range but contains up to 10% inorganics. As reported by Schmidl (10), it is possible to melt extrude even softwood Kraft lignin. However, Kraft lignins derived from hardwoods have a more defined melting range and roughly 3% inorganic salts. The salt level in hardwood lignins can be reduced to 1,000 - 3,000 ppm by washing the powder with acidified distilled water.

The major difficulties in spinning lignin are caused by the friability of the lignin itself and by water absorption which affects downstream processing by lowering the glassy transition temperature to room temperature. Friability and water absorption of extruded lignin fibers were overcome by blending lignin powder with small amounts (1-25%) of other polymers, such as polyesters, polyolefins, or polyethylene oxides.

3. EXPERIMENTAL

The studies reported in this and earlier papers (11, 12) started with production and evaluation of single fibers using a small mixer-extruder. In a two step process, lignin was blended with a wide range of different polymers - polyolefins, polyesters, poly ethylene oxides - to produce small pellets. The pellets were then melt spun as single fibers.

After single fibers were spun, drawn down, and wound, they were stabilized and carbonized or graphitized. Raw fibers typically had sufficient strength to permit their handling and hot stretching during stabilization. As fibers became stabilized, carbonized, and graphitized, they increased in strength.

3.1 Fiber Blends A wide range of fiber blends have been prepared and successfully melt spun. Blending materials have included Kraft and organosolv lignins, polyesters, polyolefins, and polyethylene oxide. The blends are prepared by mixing finely divided solid polymers and melting them together. With the exception of lignin, whose preparation is described below, all of the polymers are standard commercial grades.

3.2 Lignin Preparation Because of its high production volume and low cost, a Kraft lignin, such as Westvaco Indulin AT #1369, was preferred as the major fiber component. Lignin powder was desalted by washing with acidified distilled water. When the desired salt concentration was reached, the lignin powder was freeze-dried or air dried. Non-melting contaminants, comprised primarily of cellulosic fibers and diatoms were removed by sieving.

3.3 Single Fiber Melt Spinning Fiber blends were prepared by mixing finely divided polymers and extruding pellets. The pellets were remelted and directly melt-spun using an Atlas Laboratory Mixing Extruder equipped with a tubular roll take-up system and single and multiple spinnerets. Temperatures at which successful fiber can be spun ranged between 130° and 260°C. Extrusion temperature varied with fiber blend and spinning additives.

3.4 Multiple Fiber Melt Spinning Fiber blends were prepared by mixing finely divided polymers and extruding pellets. The blends were then directly melt spun using a Leistritz ZSE-27 twin-screw extruder fitted with a multifilament die. The fibers were then taken up onto a spool. Extrusion temperature depended on the particular fiber blend.

3.5. Fiber Furnacing Computer control using the LabVIEW system in conjunction with mass flow controllers was used to provide precise control of furnacing atmospheres and furnace time/temperature profiles. Each furnace zone was controlled by a Eurotherm 2416 setpoint controller using Eurotherm ITOOLS software to communicate with the computer. Single fibers were stretched on quartz sheets during stabilization in an air or oxygen-enriched atmosphere within a 130 mm diameter quartz tube in a 3-zone Lindberg / Blue M furnace. In a typical experiment, temperature in the 50 cm. long furnace was stabilized at 60°C, gradually increased to 200°C, and held for 1 hr. During carbonization in a 3-zone Lindberg / Blue M furnace equipped with a 77 mm diameter tube, inlet nitrogen was maintained < 0.5 ppm O₂ using a heated zirconium sponge. Exit O₂ was < 3 ppm oxygen. The temperature was gradually

increased to 1200°C. In some experiments, batches of single fibers were graphitized to 1600°, 2000°, or 2400°C in a graphite resistance furnace under a nitrogen / argon atmosphere.

3.6 Powder X-Ray Diffraction Graphitized fiber specimens were prepared by making a slurry mixture of sample powder and methanol and spreading the slurry on a zero background plate. Room temperature x-ray powder diffraction measurements were conducted using a Scintag PAD V vertical $q/2q$ goniometer with $\text{CuK}\alpha$ radiation (45 kV and 40 mA) and a Si(Li) Peltier-cooled solid state detector. The data were collected as step scans, with a step size of $0.02^\circ 2q$ at a count time of 1 second/step between 10 and $70^\circ 2q$. The ambient temperature during data collection was 298 ± 1 K.

3.7 Scanning Electron Microscopy Fiber samples were placed on supports, gold coated (if needed), and analyzed using a Philips XL30 FEG scanning electron microscope. Particular attention was paid to examination of the fiber surface and the ends. Raw, carbonized, and graphitized fibers were evaluated.

3.8. Single-Filament Strength and Stiffness Tensile strength and Young's modulus of single fibers mounted on cardboard supports were determined using a single-fiber Instron, model MTS Alliance RT/5 operating at a test speed of 0.2 mm/min. Modulus calculations were based on strain from 0.3% to 0.6%. The tests followed ASTM D3379-75 procedure (13).

4. DISCUSSION

This paper reports the production of single and multiple Kraft lignin blend fibers by melt spinning. Based on current results, selected fiber blends provide high quality precursors for production of industrial grade carbon fiber. Single fiber properties indicate the likelihood that the fiber will be suitable for use in resin-fiber composites for transportation.

The graphite content of fibers fired at temperatures ranging at 1600° and 2400°C is shown in Figure 1. As with PAN, pitch, or rayon, the graphitic content rises with increasing temperature.

Lignin-blend fibers, as shown in Figure 2, were dense, smooth, and readily spooled. The major difficulties in production and handling of the fibers included water uptake if polyethylene oxide was used as the blending polymer and, where lignin and polyolefins were combined, production of fibers consisting of two phases. Figure 3 shows a carbonized fiber with a two phase structure.

The major difficulties with single fibers were inconsistent diameters among batches and a diameter higher than that appropriate for use in composites. However, the results from these stages of investigation indicated that the next step, production of melt-spun multifiber tow, was likely to be successful.

Using a conventional twin-screw extruder equipped with a multifilament die, it was possible to produce non-sticking, drawable multiple Kraft lignin blend fiber. The fiber was strong enough to permit drawing from a 600 μ die to a < 30 μ raw fiber. The Leistritz twin screw ZSE-27 extruder is a standard industrial extruder which can be readily scaled: the largest comparable Leistritz twin screw extruders can produce more than 100 tonnes of raw fiber, or enough for half the current worldwide carbon fiber production, per day.

This is believed to be the first successful melt-spinning of multiple Kraft lignin blend fibers.

The most significant difficulties encountered in melt-spinning the lignin blend fiber were due to an unforeseen (and unusual) contaminant in the hardwood Kraft lignin processed for this project. The primary constituent was a fibrous, non-melting cellulosic which blocked portions of the die. It appears to have been a residue from other types of processing performed in the same lignin production facility and was present at < 1%. The lignin manufacturer, MeadWestvaco, is preparing a fresh batch of hardwood lignin for this project.

Evaluations of the multiple fibers, which were first produced in late spring, are ongoing. However, as shown in Table 1, even 1200°C carbonized single fibers show significant strength and stiffness. It is expected that fibers carbonized at higher temperatures will show substantial increases in strength and stiffness. The variability of our early samples is the result of the residual contamination in the lignin feedstock. Fiber breaks during single fiber testing occurred at defects.

In the next year, experiments to evaluate the production and use of lignin-blend fibers as carbon fiber precursors are planned. In addition to spinning experiments to evaluate the production of multiple precision fibers, production of small tow for evaluation in a standard production facility is planned. Evaluations of best stabilization, carbonization, and graphitization conditions will be profiled. Methods for surface-treating and sizing the fibers to facilitate production of composites will also be evaluated. If possible, the processability of lignin-based fibers using the new ORNL microwave-assisted/plasma treatment process will be evaluated.

5. CONCLUSIONS

By lowering overall weight, the use of carbon fiber composites could dramatically decrease domestic vehicle fuel consumption. However, to permit economic use of carbon fiber composites in commercial production vehicles, fiber production will need to be substantially increased and fiber price decreased to \$7/kg. Although spinning and conversion to this point have been accomplished only at laboratory scale, it is believed that the process will be scaleable. Current studies demonstrated that multifilament fibers can be conventionally stabilized and carbonized. To our knowledge, this is the first time that a multifilament lignin-based blend precursor has been directly melt-spun. The combination of physical properties and yields available indicate that the desired cost range can be achieved. Such a fiber would meet the needs of a wide variety of transportation applications.

6. ACKNOWLEDGMENTS

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TABLE 1. PROPERTIES OF MULTIFILAMENT

LIGNIN-BLEND FIBERS CARBONIZED AT 1200°C

Fiber Diameter, μ	Modulus, GPa	Stress, MPa
15	127.6	949
20	77.9	572
25	60.0	467
28	42.7	315

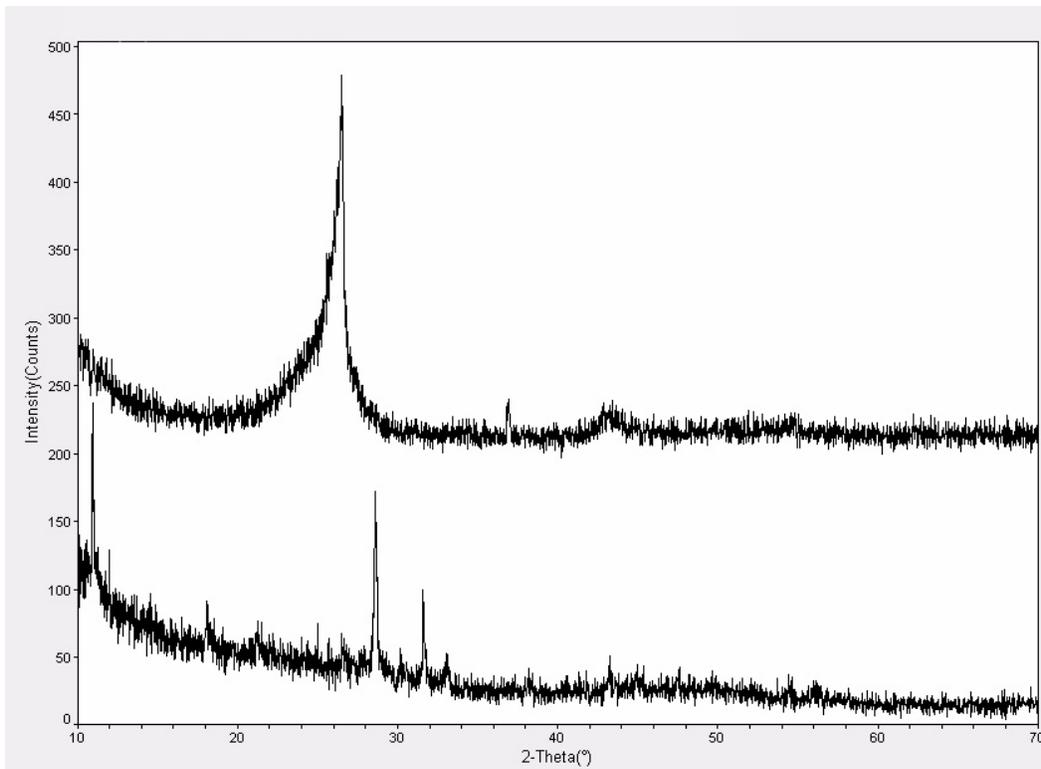


Figure 1. Comparative Graphite Content of Lignin Blend Fibers Fired at 1600° (lower curve) and 2400°C (upper curve). Height of dominant peak is a measure of graphitization.

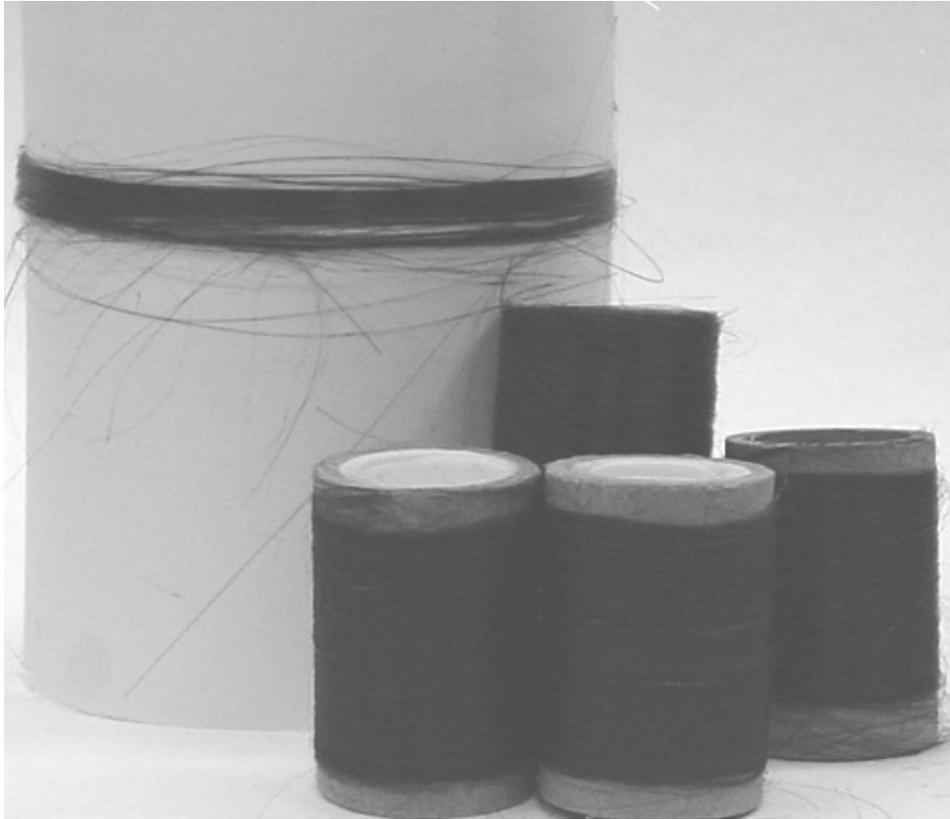


Figure 2. Spooled Raw Lignin-Blend Fiber.

Phillips XL30 FEG/00-12163

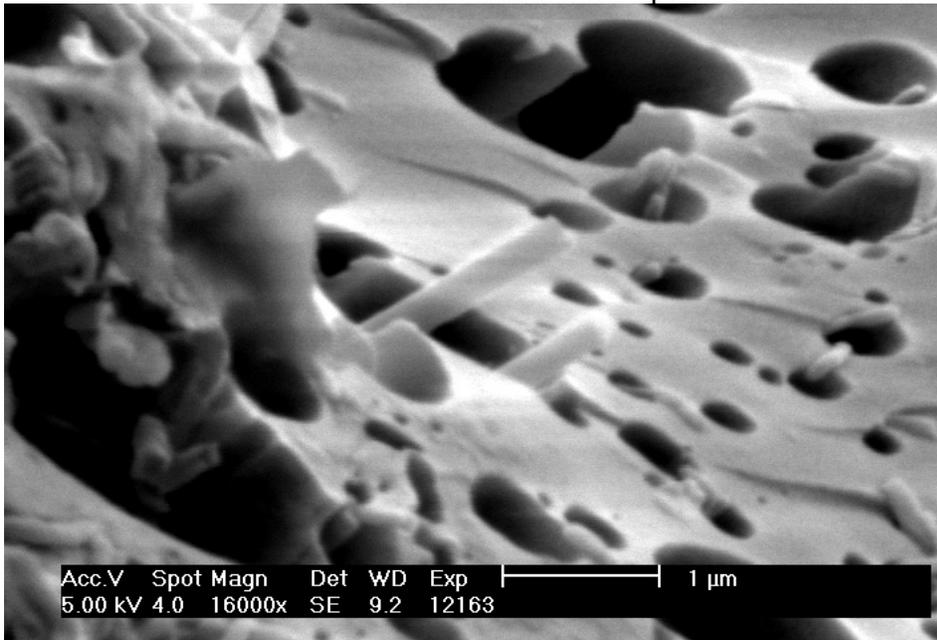


Figure 3. Scanning Electron Micrograph Showing Interior of Carbonized Lignin-Polyolefin Blend Fiber with Immiscible Phase Microfibers. Microfibers portrude from pores in larger fiber.