Lignin Carbon Fiber

ABSTRACT

The Department of Energy Freedom Car Program has shown that domestic vehicle fuel consumption can be dramatically decreased by reducing the overall weight of production vehicles. Carbon fiber composites provide an attractive route to this goal. Significant automotive use of carbon fiber technology will require substantial increases in fiber production coupled with decreases in fiber price to ~$7/kg. Based on low-cost, high-volume, carbon yield, and melt-spinnability, Kraft lignin blends were selected as an alternative carbon fiber feedstock. Current studies have established the ability to melt-spin small tows of 10-20 micron diameter fibers. These tows were subsequently stabilized, carbonized, and graphitized with properties approaching those needed for transportation applications and reasonable yields.With feasibility established, project focus has shifted to development of cost-effective, scaleable technology to process byproduct Kraft lignin to remove unwanted contaminants (ash, cellulosic fibers, particulates, organic volatiles, and water), improve as-spun structure of raw and carbonized fibers, and increase resin-fiber adhesion. This paper reports results of studies to improve the fundamental properties of lignin-based carbon fibers. Later studies focusing on methods for improvement of fiber handlability, plasticity, surface coatings to improve spoolability and decrease water sorption, and spinning process optimization are planned.

KEY WORDS: Carbon Fiber Precursor, Lignin, Polyester, Polyolefin, Recycled

1. INTRODUCTION : The U.S. Department of Energy FreedomCar Lightweighting Materials Program has worked with domestic automotive manufacturers, through the U.S. Council for Automotive Research (USCAR), the U.S. Automotive Materials Partnership (USAMP), and the Automotive Composites Consortium (ACC), to reduce overall weight of vehicles by systematic replacement of materials with lighter weight, cost-effective substitutes. Integration of lightweight metals and resin-fiber composites into vehicles has the potential to reduce the weight of structural steels used in vehicles by nearly 2/3 with significant increases in fuel efficiency and decreases in emissions (1). Earlier steps in the program have included selective replacement of nodular iron parts by aluminum structures and development of rapid, cost effective production technologies, such as P-4 performing, for glass fiber composites. As earlier technologies become established in production vehicles, newer technologies for weight reduction are investigated. The present program is supporting studies to develop feedstocks and technologies for the production of high volumes of carbon fiber at costs which encourage use in automotive applications. As with lightweight materials implemented earlier, the range of technologies and information needed to support industrial implementation is being developed. Studies supported by the program include: 1) novel low-cost carbon fiber feedstocks and production methods; 2) rapid, repeatable, environmentally conscious manufacturing, including materials reuse/recycle; 3) novel composite joining technologies; and 4) technology information development to support design, test, analysis, and safety/durability simulations. Current industrial feedstocks for carbon fiber include petroleum and coal base pitches, polyacrylonitrile (PAN), and, for a few aerospace applications, rayon. Carbon fiber production is roughly two orders of magnitude too low for significant use in domestic automotive applications. Two approaches for supplying large quantities of carbon fiber feedstock are being evaluated: 1) use of chemically-treated split PAN textile tows and 2) melt spinning of fibers composed primarily of lignin from Kraft paper pulping.

These paper reports studies of melt-spun, multifilament lignin-blend fibers produced from a desalted commercial Kraft lignin, Indulin, marketed by MeadWestvaco.

2. MATERIAL CONSIDERATIONS: Kraft lignin is a high-volume byproduct from the production of paper from wood. In wood, lignin is a long-chain molecule randomly polymerized from three aromatic subunits. Domestic papermills burn approximately 85,000 Mg/day of lignin in "black liquor" to provide process energy and inorganic chemical recycle (2). Lignin is also dried and sold as an industrial chemical and used as a feedstock for polymeric products. An earlier study which evaluated lignin production from renewable and recycled streams showed that diversion of 10% of U.S. lignin is sufficient to produce enough carbon fiber to replace half of the steel in all domestic passenger transport vehicles (3).The ability to use a bio-derived, high-volume byproduct as a melt spun carbon fiber feedstock improves availability, decreases sensitivity to petroleum cost, and decreases environmental impacts associated with carbon fiber production. Because Kraft lignin is a byproduct, it contains significant quantities of contaminants and processes for their management will be required to maintain fiber quality. Lignin contaminants come from a variety of sources. In wood, lignin exists as part of a lignin-carbohydrate complex, and short lengths of polysaccharide may remain attached to lignin after pulping. Kraft pulping liquors consist of solutions of sodium sulfide and sodium hydroxide, and commercial lignins are precipitated from those solutions. The salt content, molecular weight, and derivatization of the precipitated lignin is variable, and particulate contaminants, such as sand or clays, which came into the process as wood chip contaminants, may be coprecipitated. Dried lignin also contains water and other volatiles which can cause bubble formation during melt spinning. Lignin is a friable material but can be blended with a plasticizing polymer to improve fiber handlability. To provide a successful carbon fiber, the polymer blends and melt extrusion conditions need to be selected to provide a consistent, single phase system.The studies reported in earlier papers (4-7) started with production and evaluation of single fibers made from blends using a bench scale mixer-extruder. In a two step process, lignin was blended with a wide range of different polymers – polyolefins, polyesters, polyethylene oxides – to produce small pellets. The pellets were then melt spun as single fibers. Later studies of multiple 10 to 30 micron fibers spun as 4-28 filament tow using a twin screw extruder have also been reported (8). After extrusion and spooling, the fibers are stabilized, carbonized, and graphitized as described below. Raw fibers typically have sufficient strength to permit their handling and hot stretching as single fibers. As fibers became stabilized, carbonized, and graphitized, they increased in strength and modulus.

3. EXPERIMENTAL : 3.1 Fiber Blends Kraft lignin - polyester blends are typically prepared by a two-step process which involves mixing finely divided powders, melt-spinning to produce pellets, and using the pellets as feedstock for spinning of multifiber tow. The polyester used in these experiments is a preconsumer recycle material. 3.2 Lignin Preparation Because of its high production volume and low cost, a Kraft lignin, such as Westvaco Indulin AT #1369, was used as the major fiber component. Commercial lignin powder was desalted by washing with acidified distilled water. When the desired salt concentration was reached, the lignin powder was dried in a Refrigeration for Science #5006 lyophilizer and stored in a desiccant cabinet. Non-melting contaminants, comprised primarily of cellulosic fibers and diatoms, occurred in some batches of lignin. These were removed by 2 dimensional sieving. 3.3. Multiple Fiber Melt Spinning Fiber blends were prepared by mixing finely divided lignin and polyester powders and extruding pellets. The pellets were then directly melt spun using a Leistritz ZSE-27 twin-screw extruder fitted with 4 to 28 hole multifilament spinnerettes. Where lignin had significant quantities of non-melting materials, a pre-extrusion filter was used. After extrusion, the fibers were taken up onto a spool. Extrusion temperature depended on the particular fiber blend. 3.4. 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 section time/temperature profiles. Furnaces were controlled by a Eurotherm 2416 setpoint controller using Eurotherm ITOOLS computer software. 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 80°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 N2 was maintained < 0.5 ppm O2 by passage through a heated zirconium sponge. Exit O2 was < 3 ppm oxygen. The temperature was gradually increased to 1200°C. In so me experiments, batches of single fibers were also heated to 1600°C in a graphite resistance furnace u nder a nitrogen/argon atmosphere. 3.5. 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. The microscope was equipped with EDS for determination of elemental composition of selected sample areas. 3.6. Small and Wide Angle X-Ray Scattering Analyses X-ray diffraction spectra of raw and carbonized fiber bundles were made at the University of Tennessee Central X-ray Diffraction Facility Molecular Metrology Pinhole SAXS System equipped with a 120X, 2-D detector. Samples, comprised of a bundle of fibers, were mounted horizontally across pinholes. 3.7. Surface Modification to Increase Resin Compatibility To improve compatibility between lignin-based fiber and resins, the surface of the fibers were modified by plasma treatment followed by silanation with a conventional silane, using the manufacturer's recommended procedure. Dow A1100 was used as it is known to improve compatibility with the epoxy resin in small composite samples.

4. DISCUSSION : Carbon fiber properties are dependent on the quality, consistency, and purity of the feedstock because defects, such as voids, contaminants, or inclusions, can cause downstream breakage of carbon fibers (9). Commercial Kraft lignin is a fine, brown powder prepared as a byproduct by precipitation from pulping liquors followed by drying. Removal of contaminants, salts, and inclusions, as well as preparation of a consistent byproduct material, can present a

significant challenge. Development of cost effective methods for lignin purification are critical to improvement of fiber properties. The primary contaminants in as received Kraft lignin are inorganic salts (from pulping chemicals) and water. Although salts are expected to form inclusions in low temperature fibers, salt volatilization within high-fired fibers spun from lignosulfonates can produce voids (10). Better than 90% of the salts can be removed by washing lignin powder with slightly acidic distilled water, followed by re-drying of the lignin. Because lignin is melt spun above 150°C, removal of water and any volatile organics is critical to production of a high quality fiber. A two-step spinning process has been used to decrease bubbles formed in fibers by volatiles. The bulk of the volatiles are removed during a pellet spinning process. Pelletization also produces a storable, shippable intermediate lignin feedstock. Multifilament melt spinning uses the pellets as a feedstock. Although pre-spinning pellet production does greatly decrease volatiles which can form voids in fibers, sufficient volatiles remain to form residual microvoids in the fibers. Changes in the structure of spinning dies have improved the fracture patterns of lignin fibers spun using the University of Tennessee Leistritz twin screw ZSE-27 extruder. Figure 1 shows the ends of fracture test specimens produced using high-shear dies. The break patterns indicate anisotropic structure. Figure 2 shows carbonized fibers from a 28 filament tow. As shown in Figure 3, even 1200°C fibers have a significant content of graphene crystallites, although they do not have the highly crystalline structure characteristic of higher fired fibers. Production of 10-20 micron lignin fibers as 4 to 28 filament small tow requires the use of dies with small (380-600 micron) orifices. During early experiments, these dies became plugged. Contaminants were removed by sieving and evaluated using a combination of optical and scanning electron microscopy. As shown in Figure 4, common contaminants of the lignin include sand grains, diatoms, and cellulosic fibers. This has been controlled by two simple methods: 1) prior to spinning, dried lignin powder has been treated by two dimensional sieving to remove larger contaminants and 2) sandpack filters have been installed prior to the spinning die. Although these measures have been adequate to support limited scale production, a different production strategy will likely be required for industrial scale fiber production. In order to satisfactorily spin dense, solid fibers, it is necessary to have a single phase melt and, additionally, to provide good mixing immediately prior to extrusion. Like commercial carbon fibers, the smooth untreated lignin-based fibers, slip out of the resin in small composite test samples, as shown in Figure 5. A surface treatment to improve surface adhesion of carbon fiber and resin was developed. Preliminary studies using a combination of plasma treatment and conventional silanation with Dow A1100 significantly improved the adhesion between lignin-based carbon fiber and epoxy resins. Figure 6 shows both a conventional photograph of a small composite and a scanning electron micrograph of its surface after evaluation. The plasma treated and silanated fibers showed good adhesion to the resin during breakage. In the next year, a number of experiments focused on improvement in the quality of lignin feedstocks for carbon fiber are planned. Commercial Kraft lignin contains significant quantities of chemically bonded polysaccharides, as shown by nuclear magnetic resonance (NMR) spectra. Methods for the hydrolysis of lignin-bound polysaccharides are being evaluated for several reasons: 1) carbohydrate could contribute to plugging of spinning dies during extended processing runs by carbonizing, 2) polysaccharides will likely increase the amount of water bound within the lignin aggregate, and 3) polysaccharides have a low carbon yield. Filtration of black liquor prior to precipitation could greatly decrease the concentration of particulate material in precipitated lignin. Use of low-salt pulping processes could further decrease the concentration of salts in the lignin. Effect of lignin molecular weight on fiber properties will also 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 increased by orders of magnitude and fiber price decreased to $7/kg through a combination of new feedstocks and new processing technologies. Carbon fibers made from blends composed primarily of Kraft lignin have costs and properties approaching the program goal. The production of lignin as a pulping byproduct introduces a variety of contaminants. Methods for removing salts, sand,
fibers, moisture, and volatiles have been developed. However, studies to evaluate and develop processes suitable for use in the lignin production environment are continuing. In addition to removal of contaminants, techniques for modification of the fiber surface which provide good resin adhesion are needed. At bench scale, a combination of plasma treatment and silanation with a conventional agent has been shown to provide good fiber epoxy resin compatibility.
Development of this process technology through increasing scale and trials on a research production line are planned.
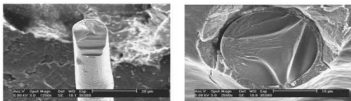
Figure 1. Ends of carbon fiber fracture test specimens showing improved fracture patterns resulting from better mixing of melt prior to spinning.
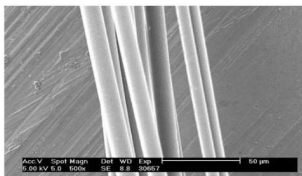
Figure 2. Scanning electron micrograph of carbonized lignin blend fibers produced during multifilament spinning.
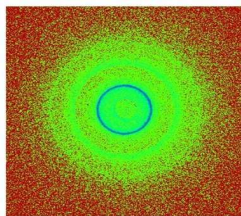
Figure 3. Wide angle x-ray diffraction pattern showing the presence of graphene crystallites in lignin-based carbon fibers fired to 1200°C.
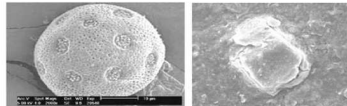
Figure 4. Common contaminants in commercial lignin (left) diatom and (right) sand grain.
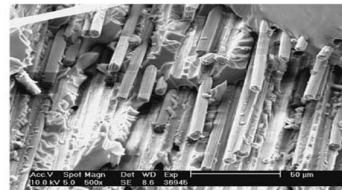
Figure 5. Commercial PAN fibers prepared by conventional surface treatment and sizing show poor adhesion to epoxy resin and slip out of the resin matrix in small composite fracture tests.
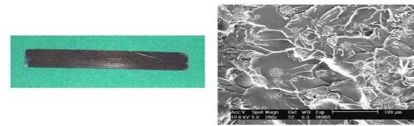
Figure 6. Small composite test specimen (left) made from lignin-based fibers showing good resin-fiber adhesion along fracture edge (right).

LINEAR PROGRAMMING

PRODUCT MIX (USING LINEAR PROGRAMMING):
Linear programming is a quantitative tool for optimal allocation of limited resources
amongst competing activities. It is perhaps the most popular amongst OPERATIONS RESEARCH techniques and has
found application in several functional areas of business- production, finance, marketing, distribution,
advertising and so forth.
Any resource allocation problem is characterised by specification of an objective such as minimising cost,
or maximising profit. The constraints can be of a financial, technological, marketing or anyother nature.

Linear programming involves formulating the problem in linear terms and solving it to provide a plan for deploying the resources in an optimal manner.

This technique is being used by many managements to maximise the profit or to minimise the cost.

In earlier days, fomulating a linear programming model and solving the same was a tedious process.

frontsys software company has developed a tool called solver which will be used with MICROSOFT EXCEL SPREADSHEETS to solve LINEAR PROGRAMMING MODELS.

This is a very simple tool which can be used by everyone who can use MICROSOFT EXCEL and understand little about formulating the constraints.

PRODUCT MIX USING LP FOR A SPINNING MILL

Let us assume C1,C2,C3 and C4 are quantities of four counts to be produced in cotton

TC1,TC2 and TC3 are quantities of three counts to be prodced in Poly/Cotton blend.

CX1,CX2,CX3 and CX4 are Contribution in US$/KG for four cotton counts. TCX1,TCX2 and TCX3 are contribution IN US$/KG for three POLY/COTTON counts correspondigly.

HOW TO FORMULATE A LP MODEL: EXAMPLE

TARGET FUNCTION: (TO MAXIMISE)

(C1*CX1)+(C2*CX2)+(C3*CX3)+(C4*CX4)+(TC1*TCX1)+(TC2*TCX2)+(TC3*TCX3) = CONTBN. MAXIMUM

BY CHANGING : (THE FOLLOWING QUANTITIES)

C1,C2,C3,C4,TC1,TC2,TC3

CONSTRAINTS:

· C1+C2+C3+C4 less than or equal to 180 tons
· TC1+TC2 less than or equal to 100 tons
· C1 should be 19.6 tons (committed to the customer)
· TC2 more than 19.6 tons (committed to the customer)
· C1+C2+C3+C4 no of m/cs allotted should not be more than 20 (m/c constraint)
· TC1+TC2+TC3 no of m/cs allotted should not be more than 10 (m/c constraint)
· C1 less than or equal to 20
· C2 less than or equal to 20
· C3 less than or equal to 20
· C4 less than or equal to 20
· TC1 less than or equal to 10
· TC2 less than or equal to 10
· TC3 less than or equal to 10

HOW TO SOLVE THIS:

MICROSOFT EXCELL Spreadsheet has a tool called SOLVER.

This can be used to solve any LINEAR AND NON-LINEAR EQUATIONS.

· OPEN an EXCEL SHEET
· FEED the PARAMETERS in the Excell Sheet
· SELECT SOLVER in the Tools Menu, Now Solver parameters are seen
· SET the TARGET cell and it should contain the target function
· FEED the range of cells to be changed
· FEED the constraints
· press SOLVE, THE RESULTS ARE ALREADY THERE

ISN'T IT SIMPLE?

PLEASE TRY THIS. LP IS THE RIGHT SOLUTION FOR PRODUCT MIX OF ANY INDUSTRY.