

UTILIZATION OF SUSTAINABLE RESOURCE MATERIALS FOR PRODUCTION OF CARBON FIBER MATERIALS FOR STRUCTURAL AND ENERGY EFFICIENCY APPLICATIONS

Frederick S. Baker, Nidia C. Gallego, and Darren A. Baker

Oak Ridge National Laboratory, Materials Science and
Technology Division, One Bethel Valley Road, Oak Ridge,
TN 37831-6087

Introduction

U.S. DOE Vehicle Technologies-funded work at Oak Ridge National Laboratory (ORNL) is directed to the development of more energy-efficient, cost-effective processes for production of carbon fiber for use in lightweight composite materials for vehicles. Body-in-white modeling indicates that over 60% of the steel in a vehicle could be replaced with carbon fiber-reinforced composite materials without impacting vehicle crash worthiness; each 10% reduction in vehicle weight increases fuel economy by 6-8% as well as lowering greenhouse gas emissions. However, carbon fiber is currently too expensive for large scale automotive use, which necessitates a substantial reduction in the cost of industrial grade fiber from about \$20/lb to \$5-7/lb (\$10-15/kg). Here we report on the utilization of lignin as a precursor material for the low cost production of carbon fiber for automotive use. In addition, new work on the utilization of lignin-based carbon fiber for production of high surface area electrode materials for electrical energy storage (supercapacitors) and high energy efficiency systems for capture of greenhouse gases and volatile organic compounds (VOCs) is introduced.

Carbon fiber composite materials are currently used to great advantage in a few vehicles, but the use is confined to high end (expensive) vehicles such as the Aston Martin Vanquish, Corvette ZR1, Dodge Viper, and Ford GT, for which the high cost of carbon fiber is justified by increased performance. Furthermore, the current supply of carbon fiber is far too limited to meet the projected demand for large scale automotive use. The work at ORNL includes the evaluation of advanced processing techniques such as plasma oxidation, carbonization, and 'graphitization' of the fiber. Each stage of the manufacturing process is being closely scrutinized to determine how to reduce both processing time and energy consumption, and thereby reduce manufacturing cost.

Experimental

Kraft-pulped and organosolv-pulped hardwood lignins used for the present study were furnished by MeadWestvaco Corporation (Charleston, SC, USA) and Lignol Innovations (Burnaby, BC, Canada), respectively. Kraft hardwood lignin, designated as "HWL", was isolated in powder form (by MeadWestvaco) from the black liquor obtained during the Kraft pulping of mixed hardwood (predominantly red and

white oaks) for the production of paper. This lignin was subjected to two distinct and proprietary procedures of purification, described here simply as "aqueous" (producing the "HWL-A" lignin material) and "organic" (producing the "HWL-O" lignin material). The "Alcell™" organosolv-pulped hardwood lignin was furnished by Lignol Innovations, and was isolated from the production of cellulosic ethanol fuel. The lignins were subjected to elemental analysis to identify the main elements (and salts) in the materials.

Melt-spinnability of the lignin materials was initially evaluated using a single filament, Dynisco Laboratory Mixing Extruder (LME) with winding unit. Multi-filament spinning trials were conducted using a pilot scale melt-spinning unit, custom built by Alex James and Associates (Greenville, SC). To obtain a suitable feedstock material, the lignin was pelletized using the pilot-scale melt-spinning unit equipped with a 2-hole strand die (each hole of 3 mm in diameter) in place of the spinneret. Pellets were then melt spun into fibers using the pilot-scale unit equipped with a 12-hole spinneret (each hole 150 μm in diameter). Once suitable melt-spinning conditions were established, the take up (winding) speed was varied in order to change the drawdown ratio and thereby obtain fibers of various diameters, including the target diameter of 10 μm . Under favorable melt-spinning conditions, fiber spinning speeds of 1500 meter/minute, the maximum physical limit of the winder, were readily maintained.

Stabilization and carbonization of the lignin precursor fibers were carried out in a Lindberg tube furnace, 6" in diameter, 9' long, with a nitrogen flow rate of 40 L/min during precursor fiber stabilization and 20 L/min during fiber carbonization. To comply with Export Control regulations, specific details of the heating rates, residence times, and other process conditions associated with the conversion of lignin precursor fiber to carbon fiber are not provided in this paper; only qualitative information in this respect can be discussed.

At each stage of processing, the lignin and carbon fibers were examined for flaws in their morphology using scanning electron microscope (SEM). Fiber diameters were estimated from the SEM images. The mechanical properties of carbonized fibers were measured by single-filament testing using an Instron tensile testing machine model 3342 with 5 N load cell in accordance with ASTM procedure D3379-75. X-ray diffraction analyses on carbon fiber samples were conducted using a PANalytical X'pert Pro diffractometer. The carbon fiber was ground to a fine powder and placed on a zero background holder. 2 θ scans between 16 and 90° were collected.

Results and Discussion

The complex rheological behavior of lignin materials is illustrated in Figure 1. Repetitive runs on Alcell hardwood lignin were made in atmospheres of nitrogen (Figure 1A) and air (Figure 1B), respectively. The first scan in each atmosphere was made on a disk of the lignin (Run 1). The sample was cooled back to room temperature and the scan repeated (Run 2). This procedure was performed for a total of six runs on the Alcell lignin sample for each atmosphere.

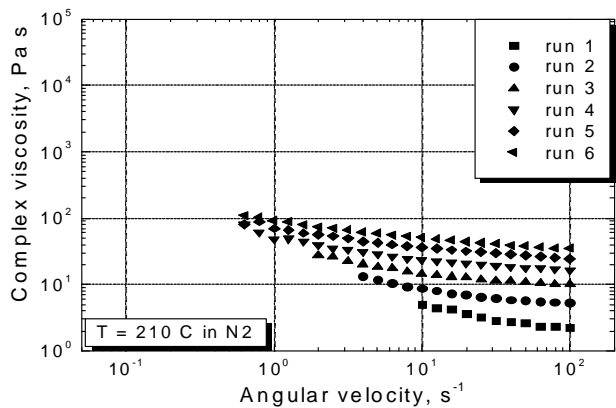


Figure 1A - Viscosity of Alcell lignin (at 210°C, in N₂)

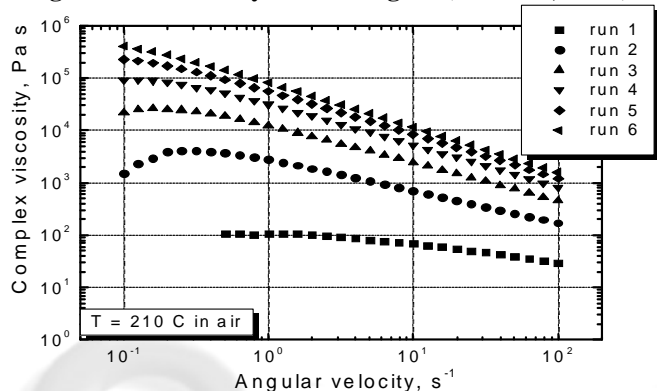


Figure 1B - Viscosity of Alcell lignin (at 210°C, in air)

From the data obtained in a nitrogen atmosphere at 210°C (Figure 1A), it is apparent that the viscosity of the lignin progressively increased with each subsequent run on the sample, increasing by a little over an order of magnitude from the 1st to the 6th run. A similar trend was observed under an atmosphere of air at 210°C (Figure 1B), but much more markedly. From the 1st to the 6th run, viscosity of the material increased by almost four orders of magnitude and in a more complex fashion. Under an atmosphere of air, lignin crosslinks to higher molecular weight material, which increases its T_g and melting point, and thereby its viscosity at a given temperature. This complex rheological behavior must be considered during melt spinning of lignin materials.

Although the Alcell lignin (as received) and the organic-purified Kraft hardwood lignin (HWL-O) exhibited excellent spinability and yielded structurally sound fibers, these lignin fibers required excessively long stabilization times of several days duration before they could be carbonized. However, with the addition of a relatively simple, proprietary pre-treatment step before melt spinning, stabilization times were reduced from 4-5 days to < 15 minutes, a very significant step forward with respect to carbon fiber production. Furthermore, upon carbonization of the rapidly stabilized precursor fibers, notably higher yields of carbon fiber were obtained. These findings are exemplified by the data shown in Figure 2, in which carbon fiber yield is expressed as a function of rate of heating of the precursor fiber to the stabilization temperature.

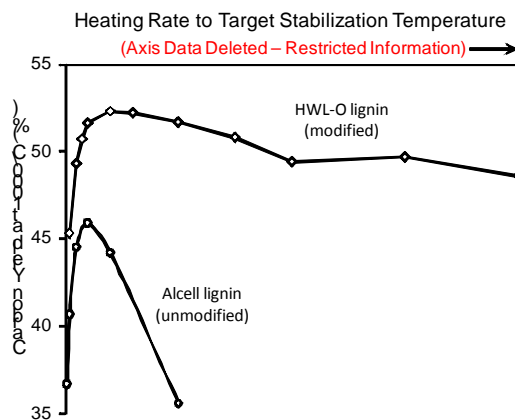


Figure 2 - Relationship between stabilization heating rate and carbon fiber yield at 1000°C

The X-ray diffraction data shown in Figure 3 demonstrate the development of “graphitic” structure in lignin-based carbon fiber as a function of increasing heat treatment temperature, as exemplified by the 002 peak. Data for a commercial PAN-based carbon fiber (Thornel T300) are shown for comparison.

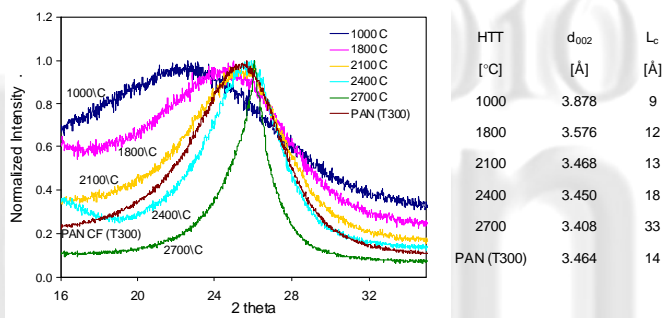


Figure 3 - Development of graphitic structure in lignin-based carbon fiber upon heat treatment

Conclusions

Lignin meeting specifications for melt spinning and conversion into carbon fiber can be isolated from the black liquor of either Kraft or Organosolv pulping of wood; i.e., expensive purification processes are not necessary. The chemistry of hardwood lignin favors fiber melt spinning, but not the rate of fiber stabilization (unless the lignin is appropriately modified); the converse is the case for softwood lignin. Carbon fiber derived from lignin is “graphitizable” through high temperature treatment, which has the potential for use of the carbon fibers for Li-ion batteries. Alternatively, low cost, high surface area nanoporous carbon fibers can be produced for other applications, including supercapacitors.

Acknowledgment

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, as part of the Lightweight Materials Program, under contract DE-AC05-00OR22725 UT-Battelle, LLC. D.A. Baker acknowledges additional support from ORAU/ORISE.