

# **LOW COST CARBON FIBER FROM RENEWABLE RESOURCES**

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## **ABSTRACT**

The Department of Energy Partnership for a New Generation of Vehicles 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 \$7/kg. To achieve this cost objective, alternate precursors to pitch and polyacrylonitrile (PAN) are being investigated as possible carbon fiber feedstocks. Additionally, sufficient fiber to provide 10 to 100 kg for each of the 13 million cars and light trucks produced annually in the U.S. will require an increase of 5 to 50-fold in worldwide carbon fiber production. High-volume, renewable or recycled materials, including 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 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.

**KEY WORDS:** Carbon Fiber Precursor, Lignin, Cellulosic, Recycled

## 1. INTRODUCTION

The Department of Energy, under the Partnership for a New Generation of Vehicles, has been working with automobile manufacturing partners to develop technologies for the production of more energy efficient, lower emissions vehicles. Reduction in the weight of vehicles could contribute significantly to energy efficiency. Lightweight composites could dramatically reduce the weight, and thereby, the fuel consumption of an automobile and would also decrease emissions.

The major barriers to deployment of advanced carbon fiber composites in the automotive industry are the current high cost of carbon fiber and the high material requirements of the industry. The industry, as a part of the Partnership for a New Generation of Vehicles, has estimated that a carbon fiber price of \$7/kg would make use in passenger vehicles attractive. This would require significant reductions in both feedstock and production costs. Use of only 10 kg of carbon fiber in each of the 13 million automobiles and light trucks produced in the U.S. each year would require roughly 5 times the estimated current worldwide production (1). Use of only 100 kg of carbon fiber per domestic passenger vehicle would require a 50-fold increase in world production. It is particularly difficult and expensive to increase carbon fiber production because a producer must concurrently increase production of the virgin precursor fiber.

This study focuses on evaluation of the use of abundant renewable polymers, such as lignin or cellulose, and routinely recycled polymers, including polyolefins and polyesters, as feedstocks for carbon fiber precursors.

## 2. MATERIAL CONSIDERATIONS

Renewable and routinely recycled polymers have several advantages as carbon fiber precursors. They are typically low in cost and available in volumes sufficient to meet the needs of the automotive industry. Lignin, for example, is the second most common polymer on earth and is found in all plants. It typically constitutes 20-30% of the dry weight of wood and woody biomass. Lignin is a random polymer containing three aromatic subunits, each with a short alkane tail group, connected by ether linkages. In most developed countries, lignin and lignin derivatives are high-volume byproducts of wood pulping to produce paper, cardboard, and a variety of wood-based products. Detailed estimates place the volume of lignin produced and burned, by the domestic pulp and paper industry at around 1000 times worldwide carbon fiber production (2). Although lignin and lignin byproducts are recovered at a limited number of domestic mills, the pulp and paper industry is presently involved in development of high-temperature gasification processes to increase net electric energy generation. Gasification processes would facilitate production of carbon fiber precursors from lignin and, in some cases, might make the recovery and storage of large amounts of lignin commercially attractive. Additionally, the availability of high temperature process heat and electricity could decrease carbon fiber process costs.

Early research on production of carbon fiber from alkali lignins, thiolignins, and lignosulphonates during the last thirty years, were reported as successful carbon fiber feedstocks by

several research groups (3,4). Pilot scale production of lignosulfonate-based carbon fibers, called Kayacarbon, was demonstrated by Nippon Kayaku Co. in the early 1970s. The fibers were dry-spun from an aqueous alkaline solution. Based on pilot data, lignin-based carbon fibers could be produced at lower temperature with shorter stabilization periods than other feedstocks because functional radicals derived from the polymer's own hydroxyls and ether linkages facilitate crosslinking (5). Although the high sodium content of the lignins used to prepare Kayacarbon fibers created voids as the sodium burned off, the fibers were still in the mid-performance range.

In addition to feedstocks derived from renewables, recycled polymers can be used as feedstocks for industrial-grade carbon fiber production. Table 1 illustrates the range of feedstocks that have been evaluated and reported as feedstocks for industrial-grade carbon fibers. High volumes of many of these materials, and related materials, are available from recycled streams, and many of them are available at prices that could support production of low-cost carbon fiber. With present improvements in manufacturing quality and practice, many of these materials have the potential to be used as feedstocks for industrial grade carbon fiber.

Although proof-of-concept studies showed renewable and recycled materials to be feasible as carbon fiber precursors, often with good carbon fiber properties, these materials were gradually abandoned in the high-performance aerospace market. Polyacrylonitrile (PAN), pitch, and for some uses, rayon, came to dominate carbon fiber production. The automotive industry, however, requires a low-cost, high-volume, mid-range-performance material. For this high-volume use, renewable and recycled fiber feedstocks may be more appropriate.

**TABLE 1. CARBON FIBER FEEDSTOCKS**

<b>Polymer</b>	<b>Reference</b>
Kevlar coated with polyimide	6
Nylon	7
Poly (phenyleneoxadiazole)	8
Poly(methyl vinyl ketone)	9
Polyacetylene	10
Polyacetylene copolymer blends	11
Polyarylacetylene	12
Polybenzimidazole	13, 14
Polybutadiene	15
Polyethylene	16, 17
Polyimide	6
Polymerizable naphthalene derivatives	18
Polystyrene and pitch blends	19
Rayon	20, 21
Syndiotactic 1,2-polybutadiene	22

Changes in industrial production of polymers and in the ways in which carbon fiber precursors are produced which have occurred since the 1960s could significantly improve the quality and strength of carbon fibers from alternative sources. For example, sodium content of ligno-sulfonate fibers, which resulted in void formation, can be significantly reduced by modern precipitation and desalting techniques. The quality of industrial polyolefin and polyester fibers has improved, with significant increases in purity and consistency. Orientation and stretching, controlled temperature processing profiles, and controlled atmospheres, developed for pitch and PAN fibers, could substantially improve strength and stiffness gains of recycled and renewable fibers during the oxidation/carbonization processes. In addition, processing cost can be further reduced by recently developed Oak Ridge National Laboratory (ORNL) microwave processing technology.

Environmental and human safety requirements are also encouraging development of fibers and fiber blends which can be produced using melt-spinning. Use of melt-spinning also decreases production cost by eliminating solvent use (and recycle). The use of polymers, such as lignin or polyolefins, which contain little or no nitrogen, both eliminates a human hazard, cyanide production, and decreases the expenses associated with its destruction prior to off-gas release.

Because of inherent low cost, wide availability, and melt-spinnability, lignin-blend polymers were chosen for early investigation.

### 3. EXPERIMENTAL

**3.1 Fiber Blends** A wide range of lignin blends have been successfully spun. Blending materials have included polyethylene, polypropylene, poly (ethylene terephthalate), and polyethylene oxide. Olefins and polyesters are available as both virgin and recycled material. Successful fibers which included softening agents have also been successfully prepared.

**3.2. Fiber Melt Spinning** Lignins were 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°C and 260°C. Extrusion temperature depends on the fiber blend and spinning additives.

**3.3 Lignin Preparation** Because of its high production volume and low cost, a Kraft lignin, such as Westvaco Indulin AT #1369, was preferred. Lignin is desalted by washing with acidified distilled water. When the desired salt concentration is reached, the lignin powder is then air dried (or, in rare cases, freeze dried). This technique will typically reduce the concentration of soluble salts in the lignin to less than 1,000 ppm salts, as measured by ashing at 550°C for one hour in air.

**3.4 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  $\theta/2\theta$  goniometer with 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° 2 $\theta$  at a count time of 1 second/step between 10 and 70° 2 $\theta$ . The ambient temperature during data collection was 298 ± 1 K.

**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. This microscope is a part of the Shared Research Equipment Collaborative Research Center at ORNL.

Melt-spun polymer blends of lignin, which is commercially available as a byproduct of the Kraft pulping process, were used in these studies. Earlier Japanese research, performed in the 1970s to evaluate liginosulfonates, illustrated the feasibility of using lignin compounds. Our studies, however, have used Kraft lignin because ~¾ of virgin domestic pulp is produced by this process. A scanning electron micrograph (SEM) of raw lignin-blend fiber is shown in Figure 1.

Using the controlled atmosphere, controlled temperature furnaces developed for this project, satisfactorily stabilized melt-spun lignin fibers have been produced. Scanning electron micrographs indicate that dense, compact lignin-blend fibers can be produced. Stabilization conditions which provide an effective control of fiber adhesion and permit hot-stretching have also been developed for some lignin fiber blends.

Phillips XL30 FEG/00-10303

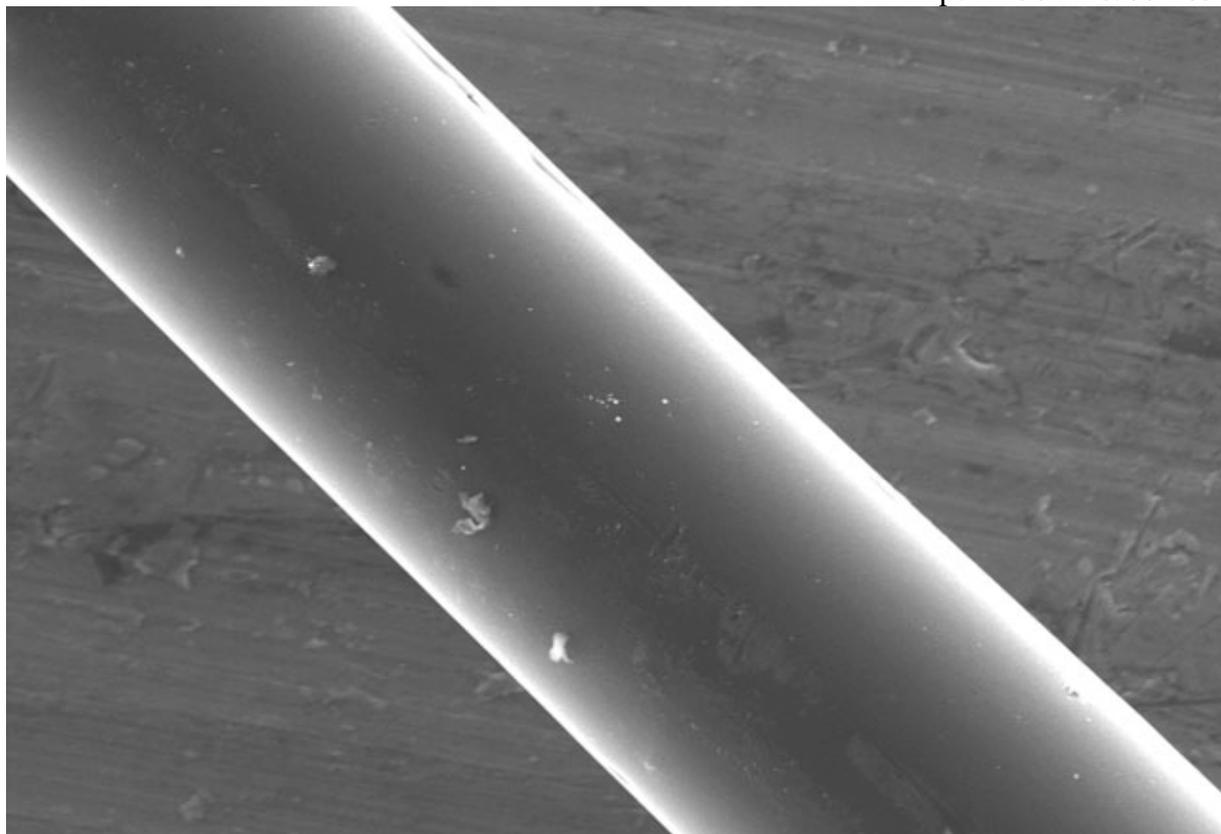


Figure 1. Scanning Electron Micrograph Showing End of As-Spun Lignin-Blend Fiber.

After stabilization, the fibers are typically carbonized in a reducing atmosphere, again with hot stretching. The resulting lignin-blend single fibers are dense and compact with relatively few visible defects, as shown in Figure 2. Yields of carbonized fiber are ~ 50% for most blends, although there is some variation due to the changes in composition introduced by alloying ingredients.

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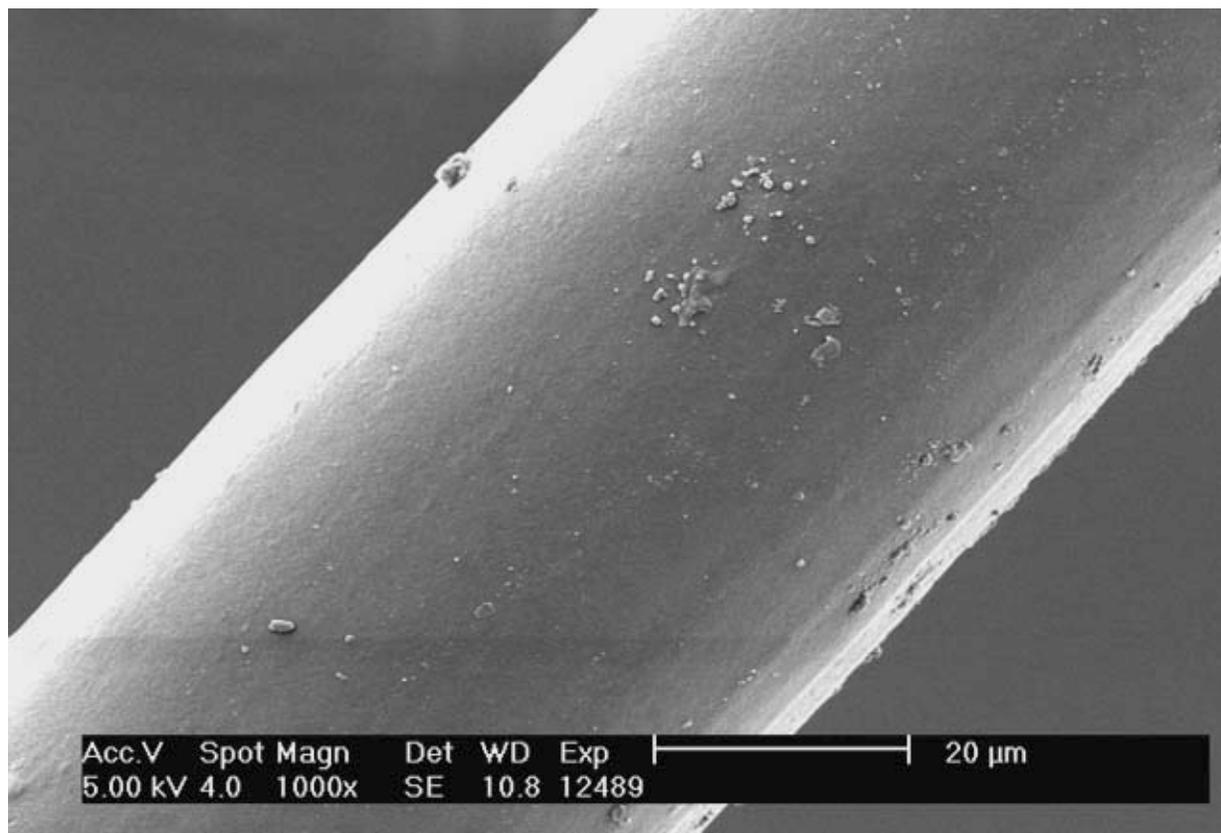


Figure 2. Scanning Electron Micrograph Showing Carbonized Lignin Blend Fiber

To demonstrate that graphitic fiber could be produced from Kraft lignin, carbonized lignin-polyester blend fibers were heated to 2400°C in a reducing atmosphere. Figure 3 shows a graphitized lignin-polyester fiber. This fiber, which is typical of the fibers obtained, is dense, compact, and has no visible defects.

Powder x-ray diffraction, shown in Figure 4, performed on the fiber indicates that the predominant structure is graphitic.

#### 4. DISCUSSION

The spinning of a range of lignin-blend fibers which can be oxidized, carbonized, and graphitized has been demonstrated using equipment and techniques developed during this project. Preliminary evaluations indicate that production of carbon fiber precursor from renewable and recycled materials is feasible. The yield of fiber appears to be approximately 50%. Further

studies are under way to extend the range of fibers and to evaluate and improve processing conditions.

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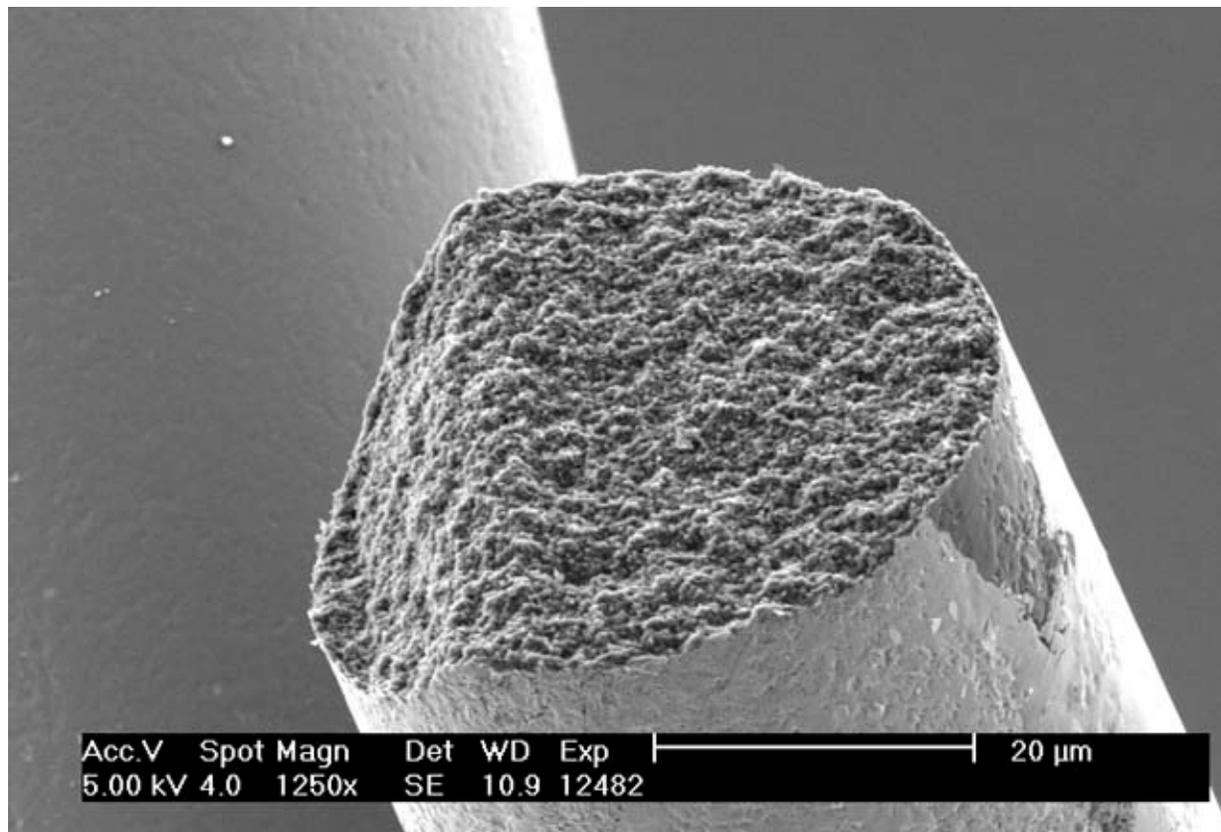


Figure 3. Scanning Electron Micrograph Showing Carbonized Lignin Blend Fiber.

## 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. To achieve this cost objective, high-volume, renewable or recycled materials such as lignin, cellulosic fibers, routinely recycled polyolefin and polyester 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 for production of 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 that the fibers are dense,

smooth, and have a highly graphitic content. The combination of physical properties, yield, feedstock availability, and cost indicates the feasibility of producing low-cost carbon fibers for use in transportation composite applications.

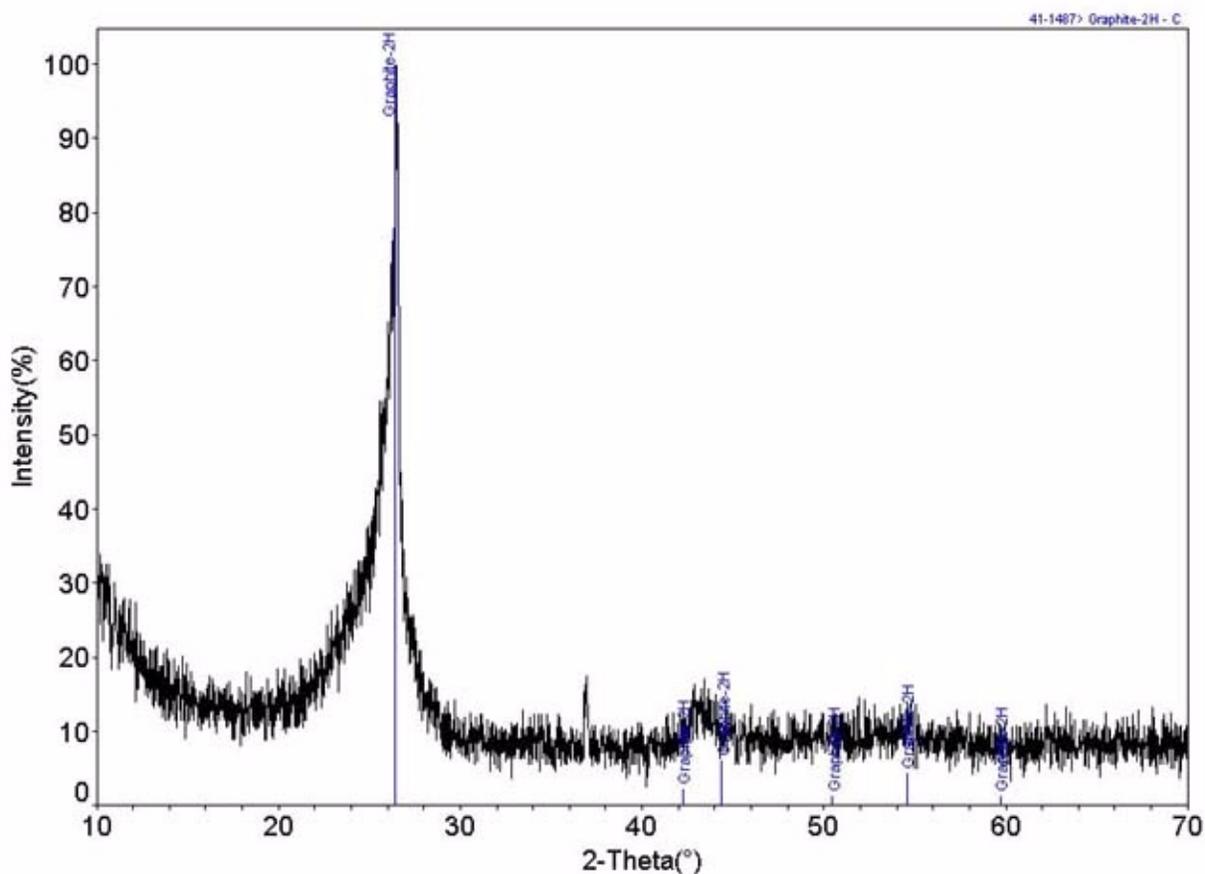


Figure 4. Powder Diffraction Data for Graphitized Lignin-Blend Fiber

## 6. ACKNOWLEDGMENTS

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## 7. REFERENCES

1. T.F. Lemire, Proceedings of the Carbon Fibers '99 Conference, Intertech, Orono, Maine, (1999).
2. Dyer, H., ed. in chief, Lockwood-Post's Directory of the Pulp, Paper, and Allied Trades for 1998, Miller Freeman, New York, 1997.
3. U.S. patent 3,461,082 (1969) S. Otani and Y. Fukuoka.
4. U.S. patent 3,723,609 (1973) M. Mannsmann, G. Winter, G. Pampus, H. Schnoring and N. Schon.
5. D. J. Johnson, I. Tomizuka and O. Watanbe, Carbon, **13**, 321 (1975).
6. H. Hatori; Y. Yamada, M. Shiraishi and Y. Takahashi, Shigento Kankyo, **2(3)**, 245 (1993).
7. French patent 2,062,005 (1971) Minister of Technology, London.
8. European patent 203,581 (1986) M. Murakami.
9. German patent 2,024,063 (1970) T. Araki, H. Takita and K. Asano.
10. U.S. patent 3,928,516 (1975) D.E. Sliva and W.G. Selley.
11. U.S. patent 3,852,235 (1976) C.M. Krutchen.
12. U.S. patent 5,288,438 (1994) R.W. Kobayashi and R. Zaldivar.
13. U.S. patent 3,528,774 (1970) H.M. Ezekiel and R.G. Spain.
14. D.E. Stuetz in Papers, Amer. Chem. Soc., Div. Org. Coatings Plast, American Chemical Society **31(1)**: 389 (1971).
15. U.S. patent 4,131,644 (1978) A. Nagasaka, H. Ashitaka, Y. Kusuki, D. Oda and T. Yoshinaga.
16. International patent 9,203,601 (1992) J.J. Dunbar, G.C. Weedon and T.Y.T. Tam
17. U.S. patent 4,070,446 (1978) S. Horiki, J. Iseki and M. Minobe.
18. European patent 381,493 (1990) I. Seo, T. Oono and Y. Murakami.

19. Japanese patent 1,282,349 (1989) M. Shiokawa and T. Matsumoto.
20. A.A. Konkin in W. Watt and B.V. Perov, ed., Strong Fibers, Elsevier Science Publishers, B.V., New York, 1985, pp. 275-325.
21. D.W. McKee and V.J. Mimeault in P.L. Walker, Jr., and P.A. Throver, Chemistry and Physics of Carbon, Marcel Dekker, Inc., New York, 1973, pp. 151-245.
22. H. Ashitaka, Y. Kusuki, S. Yamamoto, Y. Ogata and A. Nagasaka, Journal of Applied Polymer Science **29** (9), 2763 (1984).