

LOW-COST, LIGNIN-BASED 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 \$7/kg. To achieve this cost objective, alternate precursors to pitch and polyacrylonitrile (PAN) are being investigated as possible carbon fiber feedstocks. From many high-volume, renewable or recycled materials, lignin and lignin blends were selected based on low cost, high-volume, and ability to melt-spin fiber. Current studies have focused on the use of high-lignin blends which can be melt-spun to produce small tows of 10-20 micron non-sticking, drawable filaments. The fibers have attractive yields and can be readily stabilized, carbonized, and graphitized. Additionally, lignin could be produced in quantities sufficient for extensive use in transportation applications. Examination of the physical structure and properties of carbonized and graphitized fibers indicates the feasibility of use in transportation composite applications. Current studies are focusing on detailed examination of methods to improve lignin purification and devolatilization during multifiber spinning.

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

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

*Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

programs. Within the Department of Energy, FreedomCAR and Vehicles Technology Program Office, the Automotive Lightweighting Materials Program has been working with automobile manufacturing partners to develop technologies which replace ferrous metals with aluminum, magnesium, and fiber-reinforced resin composites. Integration of lightweight metals and composites into vehicles has the potential to reduce the weight of structural steels used in vehicles by nearly 2/3 (1). Weight reduction in vehicles has the potential to increase fuel efficiency and decrease emissions without sacrificing passenger comfort or safety.

Cost, availability, and manufacturability remain major barriers to use of carbon fiber-reinforced resin composites in transportation applications. The Automotive Lightweighting Materials (ALM) Program has been working with the U.S. Council for Automotive Research (USCAR), the U.S. Automotive Materials Partnership (USAMP), and the Automotive Composites Consortium to systematically develop a technical base for use of cost-effective advanced lightweight materials in production vehicles. 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 preforming, for glass fiber composites.

As aluminum is rapidly becoming a major component material in standard production vehicles, the DOE ALM program has moved toward developing a technology base to support use of carbon fiber reinforced resin composites, together with advanced metals, such as magnesium, in production transportation applications. In order to accomplish this goal, new methods for: 1) carbon fiber production which incorporate a combination of high materials availability with reduced cost; 2) modern manufacturability, including rapid, repeatable forming and environmentally-conscious manufacturing, are needed; 3) engineering support, including development of a design database, test and analysis methods, and analysis of durability and safety issues; 4) new technologies for joining composites; and 5) plans and technologies for recycling and repairing automotive composites.

A number of the studies required to establish a technology base for use of carbon fiber resin composites in production automobiles and light trucks have been initiated. A technology for high-speed, low-capital cost carbonization of carbon fiber from polyacrylonitrile (PAN) feedstock using microwave / plasma processing of carbon fibers has moved toward pilot scale with good fiber properties (2). Manufacturability (3) and extended durability (4) of carbon fiber composites have been evaluated and found satisfactory. Models of carbon fiber composite performance during crash have also been evaluated and found satisfactory (5). Studies evaluating recycling of critical resin-fiber components have also been initiated.

The development of high-volume, low-cost sources of carbon fiber feedstocks is a key requirement for use of these materials in automotive applications because replacement of ferrous metals in light transportation - automobiles, pickup trucks, and sports-utility vehicles - will require an increase of almost two orders of magnitude in carbon fiber production (1). Two approaches to carbon fiber feedstock production are being evaluated: use of chemically-treated split textile tows and melt spinning of Kraft lignin-blend fibers.

This 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 pulping uses a combination of sodium hydroxide and sodium sulfide to free cellulose from wood. In the U.S., approximately 160,000 air-dried Mg of Kraft pulp is produced a day. Approximately 85,000 Mg/day of lignin, a wood constituent removed during pulp digestion, is available in a liquid stream called black liquor. In most pulp mills, lignin is burned with other wood extractives and inorganic process chemicals to provide steam and electricity (6). MeadWestvaco recovers Kraft lignin as a basis for a variety of polymeric chemicals (7). 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 (8).

For several years, the pulp and paper industry is considering implementation of black liquor gasification technology,

in combination with advanced electric generations systems (turbines or fuel cells) to replace the recovery boiler systems in existing mills. Early tests of various process configurations have been successful and the technology is being evaluated in large pilot studies (9, 10, 11). Successful implementation of gasification would greatly improve the efficiency of energy production from Kraft pulp mills and also has the potential to decrease emissions.

Carbon fiber production from Kraft lignin could be readily integrated into a mill using gasification with several advantages over conventional carbon fiber processing: 1) a fuel gas stream to supply energy for furnacing; 2) significant amounts of lignin, a likely carbon fiber feedstock, which will be recovered and dried to smooth feed rates and load; 3) in some configurations, available process heat up to 900°-1000°C; and low-cost in-mill electric power. These features have the potential to greatly reduce the overall cost of carbon fiber furnacing and handling operations.

3. EXPERIMENTAL

The studies reported in earlier papers (12-15) 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, polyethylene oxides - to produce small pellets. The pellets were then melt spun as single fibers. This paper reports studies of multiple 10 to 30 micron fibers extruded in small tow using a twin screw extruder. 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.

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 fiber blends are typically prepared by a two-step process which involves blending of finely divided polymers, melt-spinning the blends to pellets, and using the pellets as feedstock for spinning of multifiber tow. 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. 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.

3.4. Multiple Fiber Melt Spinning Fiber blends were prepared by mixing finely divided polymers 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.

3.5. 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 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 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 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.

3.7. 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 (16).

3.8. Surface Modification to Increase Resin Compatibility To improve compatibility between lignin-based fiber and resins, the surface of the fibers can be modified by use of conventional agents, such as A1100 silane (Dow), using the manufacturer's recommended procedure.

4. DISCUSSION

This paper reports the production 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 suitable for use in automotive and industrial composites. Single fiber measurements of mechanical properties indicate the likelihood that the fiber will be suitable for use in fiber reinforced composites for transportation. Additionally, the fibers respond to conventional surface treatments which improve resin-fiber compatibility.

Small bundles of multiple lignin-polyester blend fibers have been spun at the University of Tennessee using a Leistritz ZSE-27 twin screw extruder. 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 Mg of raw lignin-blend fiber, or enough to supply approximately half the current worldwide carbon fiber production, per day. The major modification to the equipment was addition of a sandpack unit to remove non-melting lignin contaminants particular to the batch of Kraft lignin being processed. (It contained a small amount of residue from filtration operations.) As described under "Experimental," lignin and polyester were preblended and prepared as pellets. The pellets were fed to the extruder to produce raw lignin-blend fiber.

As shown in Figure 1, raw fibers produced using a multifilament die with 28 holes of 225 microns diameter were readily spooled. No interfiber sticking was apparent during the spinning and spooling process. Scanning electron micrographs of the raw fiber showed them to be relatively dense, smooth, round, and consistent in size, as shown in Figure 2.

During stabilization and carbonization no interfiber sticking was evident. The only apparent problem was the development of voids, due to expansion of volatile components (gases, small amounts of water) in fibers during stabilization. Carbonized lignin blend fibers are shown in Figure 3, and a detail micrograph of the end of a carbonized fiber, in Figure 4.

Untreated carbonized lignin blend fibers have a smooth, difficult-to-wet surface. Carbonized fibers which have not been surface treated slip out of the resin in broomstraw specimens. However, carbonized fibers which have received conventional surface treatment with A1100 silane form strong bonds with conventional epoxy resins. Figure 5 shows a micrograph of a resin impregnated and cured carbon fiber tow specimen and figure 6, the EDS measurement of the surface composition along a bondline. The silica peak indicates silanation of the fiber. Other surface treatments will be required to make the fibers compatible with the thermoplastic resins preferred for use in transportation applications.

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. In conjunction with studies of fiber surface modification and fiber-resin compatibility studies, this will provide valuable data which will indicate how best to use lignin blend fibers as an industrial carbon fiber feedstock. 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 through a combination of new feedstocks and new processing technologies. 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, carbonized, and silanated. Present single and multifilament data 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

Sponsorship of this research by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the Automotive Lightweighting Materials Program, under contract DE-AC05-00OR22725 UT-Battelle, LLC., is gratefully acknowledged. A Mead-Westvaco researcher, F. S. Baker, kindly supplied substantial quantities of Westvaco Indulin lignin and has provided information on handling procedures for this material. The assistance of P. A. Menchhofer, who performed scanning electron micrography, was very much appreciated. The scanning electron micrograph used in these studies was supported by the Shared Research Equipment (SHaRE) Collaborative Research Center at Oak Ridge National Laboratory. Under subcontract, University of Tennessee research staff members J. R. Collier, S. Petrovan, and D. Fielden prepared multiple fiber tows using a Leistritz twin-screw extruder. Properties evaluations of single fibers were performed by R. D. Lomax, whose skill and patience is gratefully acknowledged.

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Figure 1. Spool of lignin-blend fiber spun through 28 filament die using UT Leistritz twin-screw extruder.

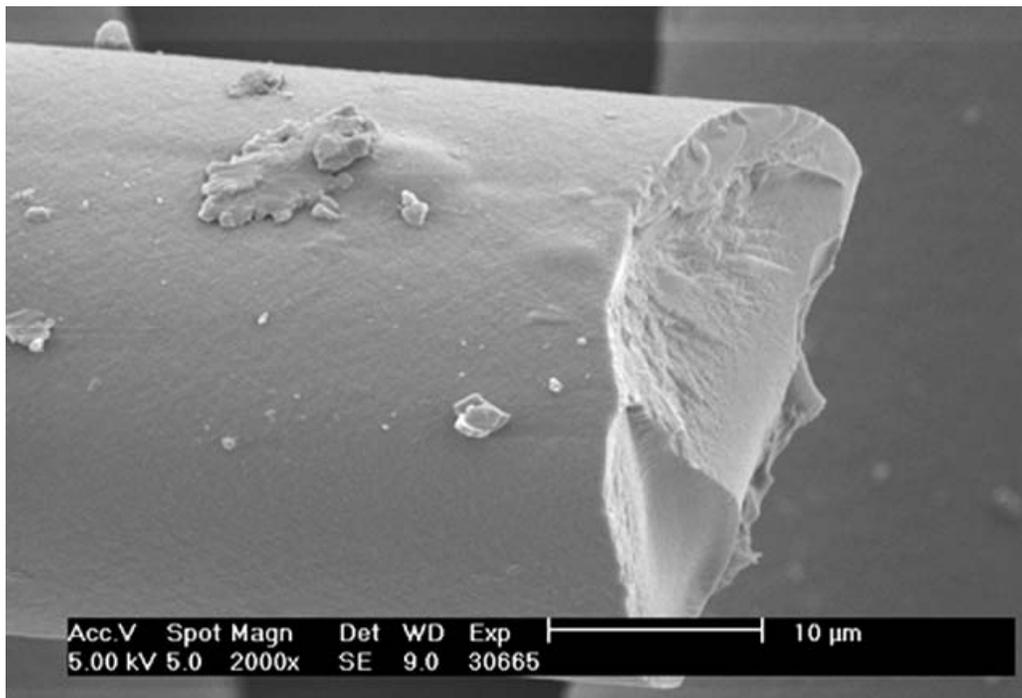


Figure 2. Scanning electron micrograph of raw lignin blend fiber produced during multifilament spinning.

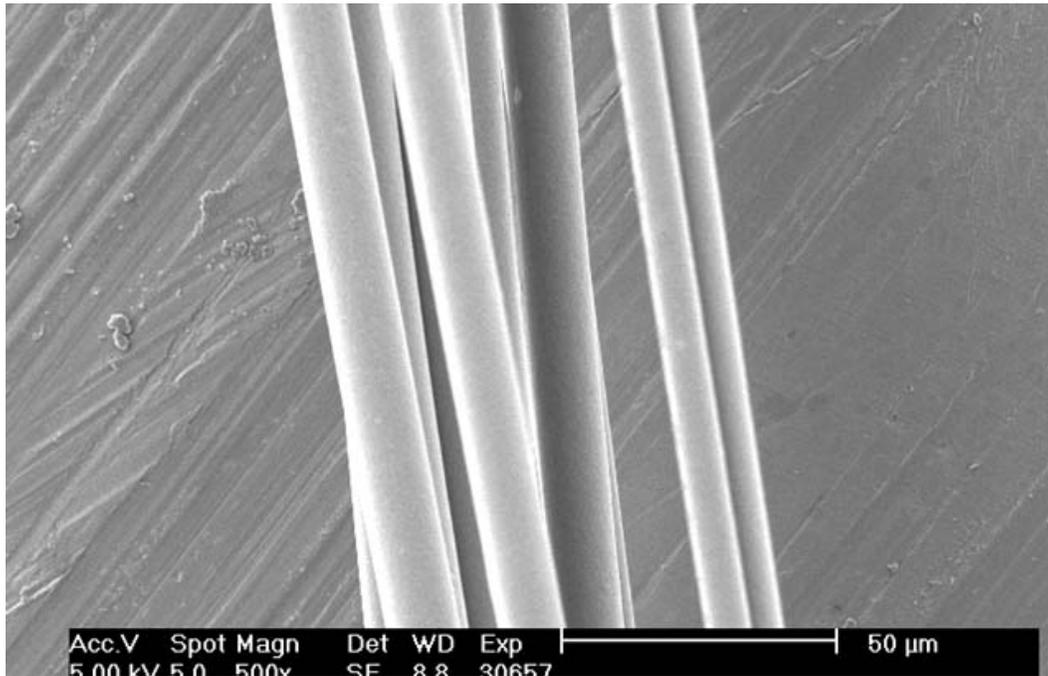


Figure 3. Scanning electron micrograph of carbonized lignin blend fibers produced during multifilament spinning.

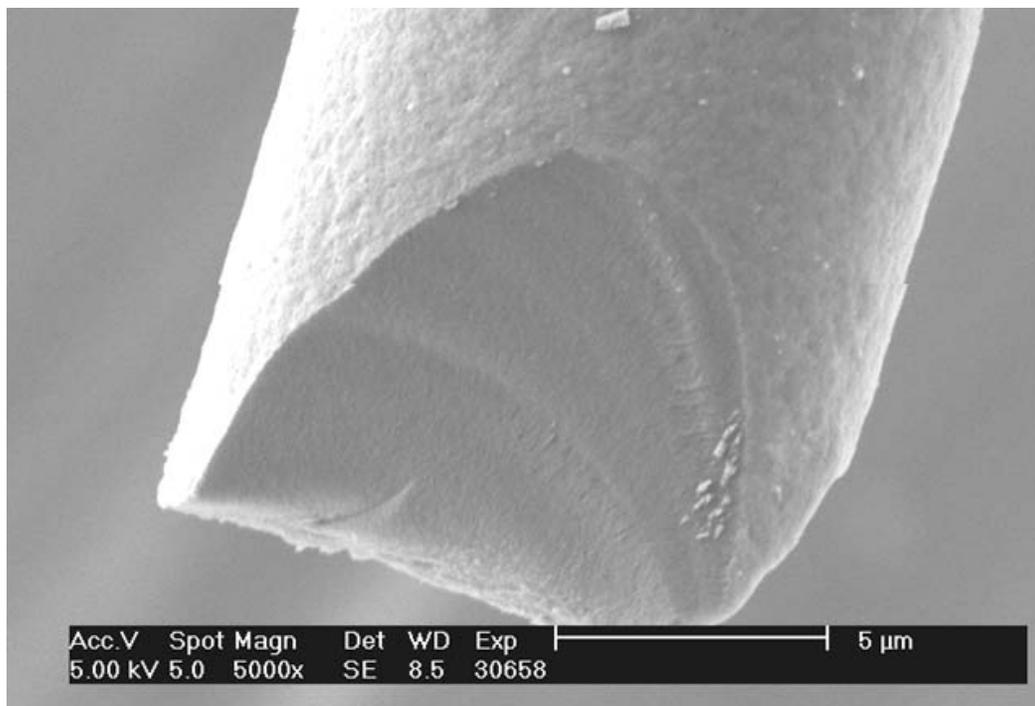


Figure 4. Carbonized fiber from 28 filament die with dense structure and smooth surface.

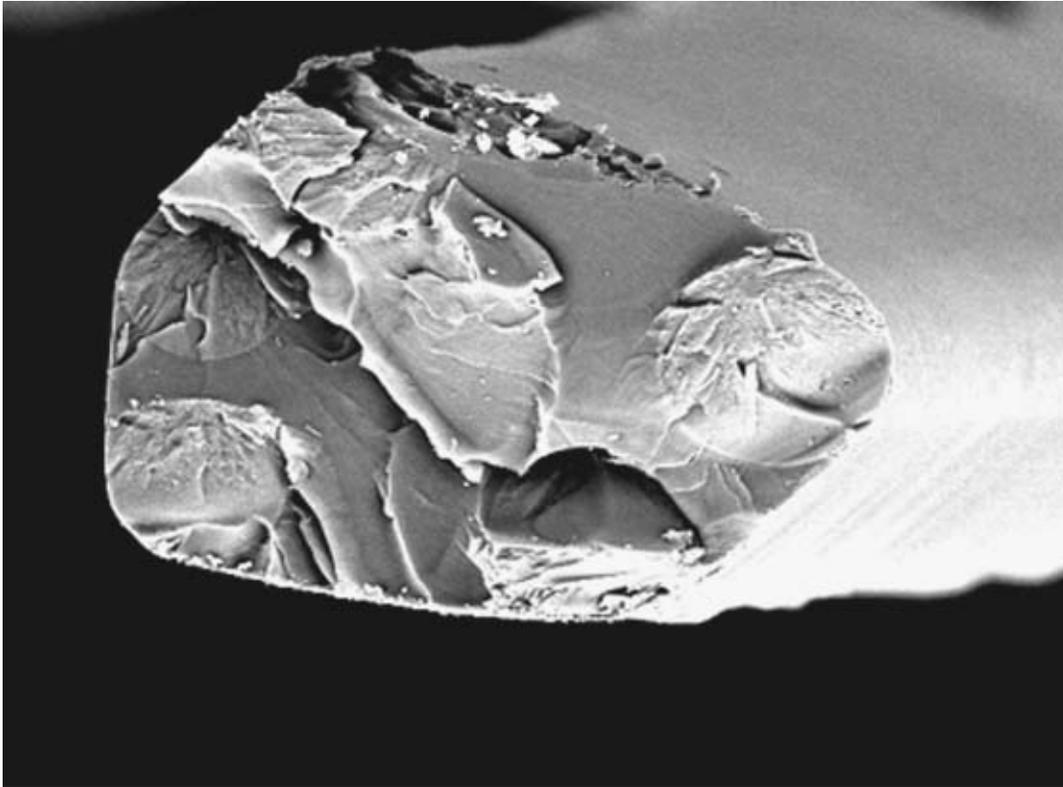


Figure 5. Resin impregnated and cured carbon fiber tow showing lignin blend fiber treated with A1100 silane in epoxy resin. Fiber and resin show good compatibility.

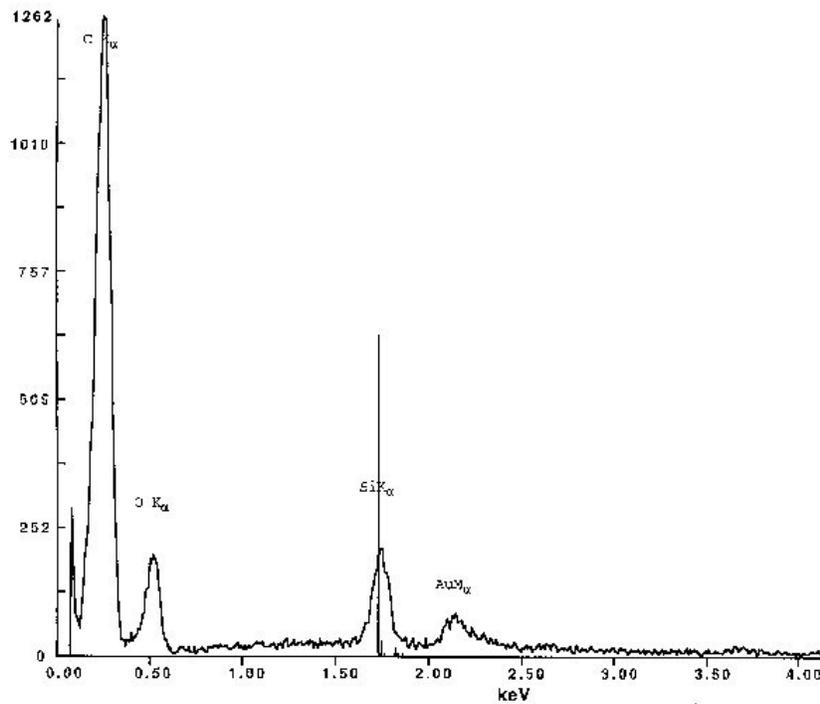


Figure 6. Composition of surface of silanated fiber.