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Manufacturing of Carbon Fibers Using Microwave-Assisted Plasma Technology

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ABSTRACT

The most significant obstacle to the widespread use of carbon-fiber-based composites by the automotive industry is the high cost of carbon fibers in comparison to other potential structural materials. Carbon fibers are currently produced by thermal pyrolysis of a polyacrylonitrile (PAN) precursor to obtain the desired properties. The most significant cost factors in the process are the high cost of precursors and the high capital equipment and energy costs in conversion to carbon fiber. The Department of Energy is supporting developmental efforts to reduce costs in both precursor production and conversion areas. This paper describes developments in the conversion process.

Because of the unsuccessful results of manufacturing carbon fibers through their direct heating with microwave radiation (variable frequency microwave [VFM] and single frequency microwave [SFM] energy), new avenues were explored for this processing.

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carbon fibers. These preliminary studies show that microwave energy may be able to enhance portions of the production line throughput speed by an approximate factor of 4, so the manufacturing cost may be reduced substantially. Fibers that are produced by this technology show equivalent properties to carbon fibers of moderate cost (e.g., Fortafil 3[c]) in the area of density, electrical resistivity, fiber diameter, and overall weight reduction during processing. This is a very good indication of the potential of this new technology. Nevertheless, more research and development are required to advance this technology. Experimental results indicated that the use of VFM to process PAN-precursor material was not viable. The lack of success in this effort led to the evaluation of another technological alternative. This alternative method had to provide sufficient energy in an intense and uniform electric field in order to process the fibers homogeneously. A properly controlled plasma presented an attractive alternative technology for evaluation. Furthermore, use of microwave technology to create and maintain the required plasma appears feasible.

EXPERIMENTS

FIBER CHARACTERIZATION

To evaluate the progression through the processing of the PAN-precursor in the microwave-based technological approach, it is necessary to develop a detailed baseline fiber characterization of important fingerprint fiber properties throughout all the single processing steps in the conventional manufacturing process. From this methodology, a logical comparison at any single step or point in the process sequence can be established between the conventional and microwave-plasma-assisted manufacturing process. The selected fingerprint characterization properties follow:

1. Density, which will indicate the progress in the conversion/stabilization/carbonization in the fibers. Two types of densities were determined: (1) intrinsic density, which indicates the density of the fiber constituents and was determined via volume displacement with a gas by means of ultra-pycnometry; and (2) bulk density, which indicates the fiber bulk density and was determined by the buoyancy method with water.
2. Electrical resistivity which is measured by the four-point probe method. Electrical resistivity will indicate the advancement in the graphitization in the fibers (with progressive graphitization, fibers increase their ability to conduct electricity). (See Table I.)
3. Fiber diameter, which approximately indicates the location in the process sequence in the conventional manufacturing process. Associated here is the total fiber tow area, which also was evaluated.
4. Mechanical evaluation, which consisted of the measurement of mechanical strength in completed tow specimens (broom-straw type test specimens) for ultimate tensile strength (UTS) (σ_B), elongation to break (ε_B), and Young's modulus (E). These mechanical values will indicate how well the fibers are processed and intrinsically indicate the condition, quality, orientation, density of the graphene planes in the fibers, fiber damage, and irregularities in the fibers.
5. Network analysis, which determines the microwave energy deposition in the fibers to be processed as a function of frequency. A detailed evaluation of the dielectric properties of these fibers was undertaken. Since the dielectric properties (dielectric constant, real and imaginary, loss tangent and scattering parameter) are temperature, frequency, and composition dependent, work was carried out to characterize these dependencies. Fibers taken from each single stage of the conventional process sequence were evaluated for their coupling characteristics. Examples of dielectric property data for different types of materials are indicated in Table II. The dielectric evaluation was performed with an HP8510C network analyzer, using both the coaxial and resonant cavity techniques. The coaxial method employed a 7-mm-diam., 10-cm-long air line, and frequency range from 0.5 to 15 GHz. One limitation of this evaluation is that the measurement was taken at room temperature or slightly higher than room temperature, but the fibers are subjected to higher temperature during the actual processing.
6. For further comparison of fibers produced by these two different technologies, additional qualitative evaluation was needed. These additional evaluation techniques consist of microscopy (optical and scanning electron microscopy [SEM]), x-ray diffractometry, and single-filament tensile strength.

FIBER EVALUATION AND PROCESSING

At various stages of fiber processing, material was examined using an HP8510C network analyzer.

exact reason for this variation in dielectric properties is not known, it is likely due to a local structural variation, resulting in local morphological variation. A factor that could explain the increase in tan δ as the fibers proceed along the process cycle is the conversion of carbon into graphite. While carbon is a good absorber of microwave radiation at 2.417 GHz, graphite is not. 2.417 GHz is the resonance frequency of the available dielectric measurement cavity.

Microwave Processing of PAN-Precursor and Oxidized Fibers

The processing of PAN-precursor via microwave energy was extensively evaluated. The PAN-precursor was evaluated "as delivered" for carbon fiber processing by the PAN-fiber manufacturer (Courtaulds). This PAN-precursor is unstretched, curly in texture, and nonuniform in fiber spatial density or distribution. These fibers are characterized by local areas of high spatial density (more congregation or conglomeration of fibers) and other areas of remarkably low fiber spatial density.

Extended studies on polymerization of PAN-fiber indicate a highly exothermic reaction during the oxidation/stabilization phase [1,2,3,4,5,6]. This effect is a very important factor to consider during the conventional or microwave process. In the conventional process, adequate time is provided for the fiber stabilization. This phase is a diffusion-controlled phase; the rate of oxidation is a function of the square of fiber diameter (one of the many parameters that affect this phase). During this processing time, the PAN-fibers undergo a dramatic change from a thermoplastic to a thermoset material. Fibers change from a highly molecular-oriented thermoplastic to a rigid three-dimensional network structure, which is non-meltable and can be subjected to high-temperature processing conditions.

After several intensive experimental trials using direct microwave heating (VFM and SFM) and considerable changes and alterations in this processing technique, no acceptable fiber processing was achieved. Several deficiencies were observed with this processing technique, such as localized heating/burning of fibers, runaway exothermic fiber heating during stabilization, and an inhomogeneous electric field in the fiber bundle in the cavity. Because of these deficiencies a more suitable fiber processing technology was explored.

Plasma Processing

Plasma technology was another alternative technology evaluated. Earlier experiments indicated a potential application of this technology for fiber manufacturing. To continue this work it was necessary to use microwave sources with much higher power levels. High-power SFM was needed to initiate and sustain a plasma (corona discharge of inert gasses) for fiber processing. Initial work was performed in a 2.45-GHz resonant cavity (2 ft. x 2 ft. x 2 ft.) with a maximum input power of 6 kW. This SFM applicator provided sufficient energy to carbonize and graphitize PAN-fibers. In this work the fibers were processed in a batch mode and were placed inside a pyrex container supplied with an inert gas (nitrogen or argon). Fibers were placed in various configurations within the glass container. Some were wrapped around a quartz tube then placed in the middle of the pyrex container; other fibers were loosely placed in the container.

Power was increased slowly up to the initiation of a visible light blue/reddish plasma; then power was reduced to the minimum power necessary to maintain the plasma. At times the plasma extinguished during the power reduction operation, which caused the overall process to have to be restarted. This proved to be cumbersome for the manufacture of fibers. To minimize the presence of oxygen in the fiber/batch container, an oxygen sensor was used to monitor oxygen content during the initial purge. When the purger indicated very little oxygen, the sensor was removed from the chamber, and then microwave power was applied. Although the sensor indicated a minimum of oxygen present, minute quantities of oxygen were still present. The oxygen present during the plasma processing caused a localized combustion in the fiber bundle many times, thus some segments in a sample were eliminated via combustion. Also, the plasma was degraded and, in some cases, extinguished because of the generation of large quantities of combustion gases. In some cases the container experienced localized melting, and also the core, around which the fibers were wrapped, experienced some melting. Note that two types of glass were used: pyrex and fused quartz glass. Pyrex in many cases melted completely, while quartz only experienced softening to the point of physical deformation. Another concern was plasma stability. In general, the use of a SFM resulted in an unstable plasma, and it also changed location within the processing chamber. This proved very impractical to produce adequate loose fiber of adequate length or quantity for subsequent mechanical testing and evaluation of fingerprint properties.

Through this approach only small fiber lengths were obtained (i.e., maximum 3 in. long with both ends burned). This was not acceptable as defined by the requirement of the project. A new method had to be explored to produce an adequate quantity of fiber with suitable lengths for testing.

The new design is shown in Figure 1. Here a microwave chamber was designed so that a quartz tube could be placed at an angle through the microwave applicator. This tube will contain the sample to be processed and will be supplied with inert gas at one end and vacuumed out of the other end. Based on the prior batch work and the known microwave coupling characteristics of quartz

(high-temperature stability, extremely low loss tangent), this tube was made of fused quartz glass. An “H”-frame made of fused quartz rod was designed and built to hold the fiber sample. The sample was wrapped along the main axis of the double-H frame and placed inside the quartz tube.

The quartz tube used to contain the fiber samples has a nominal outer diameter of 30 mm. Two different wall thicknesses were used: 2.1 mm and 1.5 mm. Similar to the H-frame sample holder, the intent of reducing physical dimensions was to reduce the mass to be heated by the microwave plasma. In some cases this reduction of wall thickness and/or diameter of the quartz rod of the H-frame resulted in structural deformations (bending, collapsing); these devices with smaller dimensions were not structurally stable enough for the subjected loads during processing.

The power supply of the system was a Cober S6 microwave generator (6 kW, 2.45 GHz). Due to the translation of the sample back and forth through the application (through 4 microwave electric fields), this process cannot be defined as either batch or a continuous process. For all practical purposes, it will be a quasi-batch process. The normal length of this fiber sample is between 12 and 24 in. The maximum possible length inside the applicator at any time is approximately 10 to 11 in. Thus only a portion of the fibers were exposed to the microwave/plasma at any time. For this reason, the effective processing (exposure time) time will be different than the overall process time.

In this new technique/system, some process-related issues arose. By wrapping a complete loop of 50K tow fiber bundle, the total fiber bundle cross-section became 100K filament tow. After plasma processing, it became evident that the plasma was not able to completely penetrate the interior of the fiber bundle. However, the exterior fiber exhibited advanced processing characteristics (higher density, lower electrical resistivity). This effort was more pronounced when higher input microwave power was used (with an intent to shorten processing time). For this reason, a closed loop was no longer used. A single 50K tow strand was used with the fiber tied at both ends of the H-frame, so that the cross-section remained 50K.

During the process, the fibers automatically will be under tension because of physical restraint and the natural shrinkage. This resulting tension will not be constant within our experimental arrangement. It was not possible to monitor or control this fiber tension in this setup. On some occasions when the sample frame was built using a small-diameter fused quartz rod (3 mm), the frame broke due to fiber shrinkage.

RESULTS

PLASMA PROCESSING OF OXIDIZED FIBER

Evaluation of initial fibers is shown in Figure 2. The initial fiber from this work was a fully oxidized Zoltek fiber. Two different inert gas environments were used. As indicated earlier, the microwave-plasma-processed (MPP) fiber was limited to small segments (3 to 4 in. in length). Indicated clearly in the figure is a dramatic reduction in the electrical resistivity from an initial value greater than 1000 Ω-cm to approximately 25 Ω-cm.

Similarly, the fiber bulk density increased from 1.39 g/cm^3 to values in the range of 1.6 g/cm^3. The trend of the evaluated properties indicated a movement toward manufacturing with this method. More samples were processed with similar repeatable results. This indicated the potential of this process but also the need for an improved system to produce processed fiber in larger quantities suitable for fiber characterization.

After the system depicted in Figure 1 was assembled and tested for proper functioning, samples were processed and characterized. Initial trials produced samples with moderately acceptable results. With the improvement in the processing conditions and parameters, much better samples were obtained. Approximately 25 suitable samples were fabricated by this technique with different lengths and different process conditions to evaluate their effect, as shown in the results obtained on sample 6 in Figure 3. Initial fiber was fully oxidized Fortafil Fibers material. This sample was attached to a long H-frame sample holder (24 in.) that was introduced into the fused quartz tube and placed in the microwave applicator (see Figure 1). Due to its length, it was possible to subject the fibers at one end of the sample to longer residence time inside the microwave applicator. A gradient in properties along the length of the fiber tow was expected, and in fact this was observed. This indicated a variation in the degree of processability along the tow length. These test results confirm a direct correlation between residence time (in the electric field/plasma) and degree of processing.

Results found in the processing of sample 6 (only 4 points were possible to evaluate) are shown in Figures 3–5. Figures 3 and 4 depict electrical resistivity as a function of the bulk density and instrinsic density, respectively. As shown here, as density increases, the electrical resistivity decreases. Figure 5 shows how electrical resistivity varied as a function of calculated tow area. Here the electrical resistivity decreases as the calculated tow area also decreases. Figure 6 indicates how weight per tow length (linear density) varies as a function of intrinsic density. Depicted is a general decreasing trend in weight per tow length with increasing pycnometer density. In general, with more processing, higher fiber density (bulk and pycnometer) is accompanied by a reduction in the electrical resistivity, calculated tow area, and weight per tow length. A similar result is indicated in Figure 7. Here sample 3 was processed using the same long H-frame sample

holder. This sample was processed in nitrogen plasma with a longer processing time at lower power. Here also a gradient in processability is clearly recognizable (electrical resistivity vs bulk density).

Figure 8 presents data from the microwave plasma processing. Incorporated are filament diameter data from samples processed with microwave plasma (samples 7, 14, 15, and 18). The fiber filament diameter values of MPP material clearly correlate well with the general tendency in conventionally processed fibers. Their value is equivalent to or smaller than the corresponding 50K tow commercial product of Fortafil Fibers and Zoltek. In some cases, the obtained filament diameters were seen with lower values than those of the commercial final product.

Figure 9 depicts data obtained for the tow area for a large number of MPP samples. These data match the data for the final commercial product. Figure 10 depicts pycnometer density for MPP obtained material and is compared with the Fortafil Fiber finished product. It is easily seen that the MPP material matches the density levels of conventionally processed material.

Figure 11 shows an exploded view of the data in the area of stage VIII, which represents the carbon fiber finished product in the conventional process. Figure 11 shows an assemblage of data points around 0.01 Ω-cm. The minimum value obtained for their MPP material was 0.006 Ω-cm, which is in the range of graphitized carbon fibers. The MPP samples were processed at different conditions; thus, some dispersion in the data is observed.

MECHANICAL CHARACTERIZATION

Table III represents data obtained from mechanical characterization of MPP fibers (MPP samples 8, 9, 10, 11, 12, 13, 16, 17, 19, 20). Sample 10 was disregarded due to its large deviation from the sample group (invalid point). For comparison, the corresponding values of conventionally processed samples were also incorporated in this table. Note that these data represent results on graphitized fibers prior to any surface treatment or sizing.

These data indicate an acceptable comparison between these two techniques. It is apparent that UTS of the MPP fibers is lower than the UTS for the conventional fibers. Many factors can explain this, such as testing, specimen preparation, and monitoring and control of the process parameters. The Young's moduli of elasticity (E) are approaching equivalent values. The elongation at failure for the MPP material indicates slightly lower values. Higher levels of UTS are obtainable by refining the sample preparation process. Consequently, higher values of the elongation at break are also expected because these properties are directly interrelated.

This SFM-assisted plasma processing technology not only provided acceptable comparison to the conventionally processed material, but also demonstrated consistency and repeatability under each specific fiber process condition and its evaluated properties.

CONCLUSION

PLASMA PROCESSING

These conclusions are based on quasi-batch processing in which the overall time for processing is considerably larger than the effective processing time. When microwave-assisted plasma processing is compared with conventional processing, a shorter (effective) microwave processing time was observed. The real effective time is when the fibers are inside the cavity and subjected to microwave energy. Only the carbonization, graphitization, and surface treatment steps of the processes are evaluated here. This is because the starting material for the plasma process was the fully oxidized (in some cases, partially oxidized) precursor material. A very good assumption is that the real effective time is one-quarter or smaller than the overall conventional processing time. This calculation is based on observations of the real residence time of the fiber sample inside the microwave applicator.

From the obtained results, the following conclusions can be made:

1. MPP fibers are comparable to final conventionally graphitized material. A comparison between all of the evaluated fingerprint properties of these two technologies (electrical resistivity, both densities, filament diameter, tow area) shows excellent correspondence between MPP material and conventionally processed material. The mechanical characterization indicates that discrepancies are found in some of the UTS values and the corresponding associated elongation at failure.

The slightly lower mechanical properties observed in the MPP fibers could be due to differences in sample preparation. The conventionally prepared sample fiber used for mechanical evaluation was prepared in a continuous process, which is the standard method used in mechanical characterization of carbon fiber tows. The MPP fiber test specimens were manufactured one by one in manual modes, which could have introduced error such as nonuniform resin infiltration between the fibers, nonhomogeneous external surface, and improper tension during sample preparation. This may be one of the reasons for the slightly lower observed mechanical properties. Another reason could be that the optimized process conditions for the MPP fibers are still to be discovered. Few preliminary studies have been carried out to characterize and to obtain baseline data on MPP fibers. No proper control of the real residence time in the application was possible in this feasibility study.

2. The processing path in this feasibility study with plasma was relatively simple and comparable with a similar conventional batch process. It is expected that transitioning this processing technology from a batch to a continuous mode may not be extremely difficult.

ACKNOWLEDGMENTS

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Table I. Electrical Resistivity

Conductors		
Silver	1.5E-6	Ω-cm
Copper	1.7E-6	Ω-cm
Aluminum	2.6E-6	Ω-cm
Iron	10.0E-6	Ω-cm
Stainless Steel	50.0E-6	Ω-cm
Insulators	>1E+10	Ω-cm
Semi-conductors	1E-2 to 1E+7	Ω-cm
Graphitized Carbon Fibers	2E-4 to 2E-3	Ω-cm
Oxidized PAN Precursor	>1000	Ω-cm

Table II. Dielectric Data

(at Room Temperature 22° - 25°C)

	3 GHz		**10 GHz**	
Materials	**$\varepsilon'/\varepsilon_0$**	**tanδ**	**$\varepsilon'/\varepsilon_0$**	**tanδ**
PTFE (TEFLON) **Polytetraflouroethylene**	2.1	0.00015	2.08	0.00037
PMMA **Polymethyl methacrylate**	2.75	0.0078	2.75	0.0083
PE **Polyethylene**	2.26	0.00031	2.26	0.00036
Fused Quartz Glass **SiO_2 (GE)**	3.78	0.00006	3.78	0.0001
Water	76.7	0.157	55	0.54

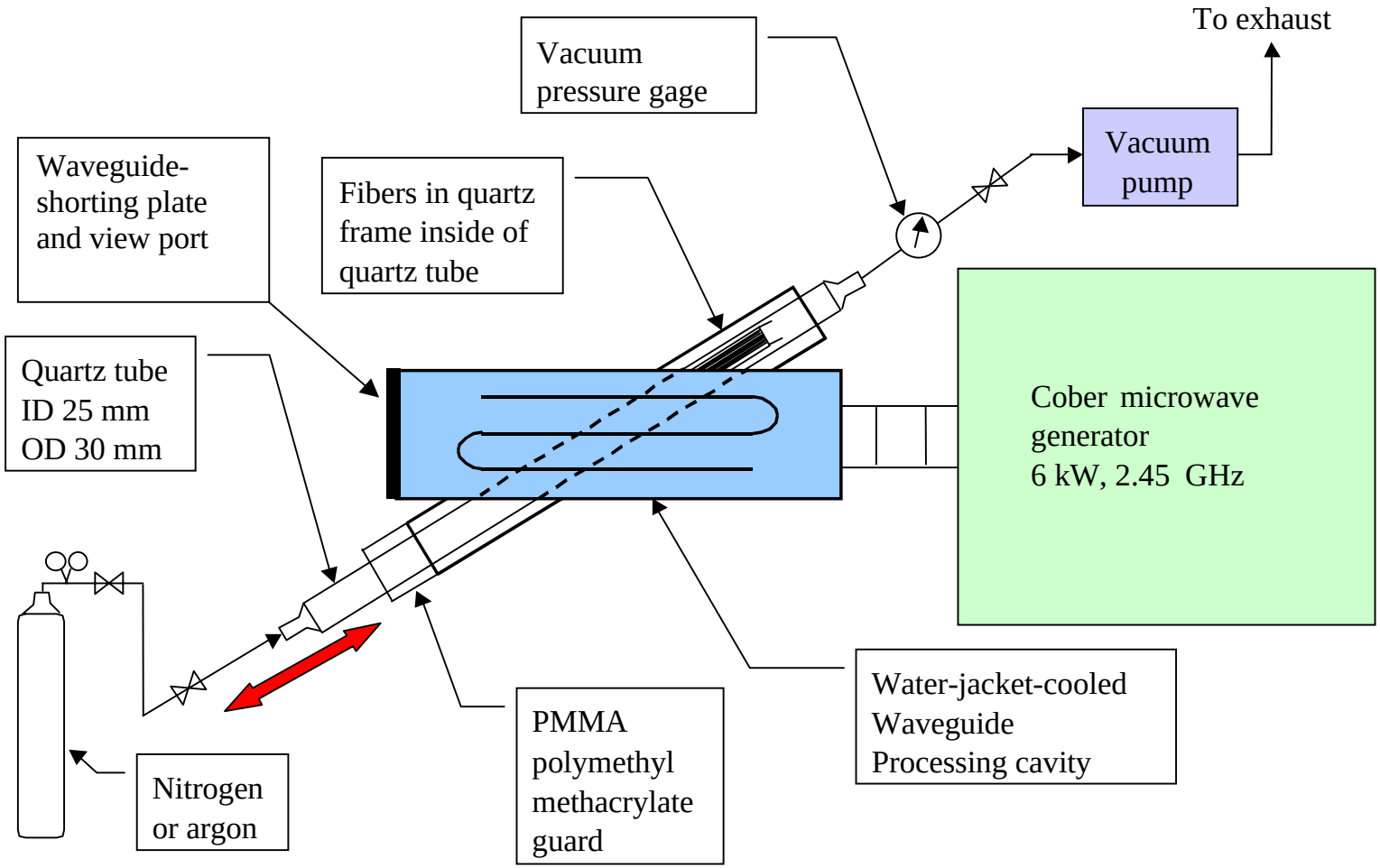

Figure 1. Demonstration of fiber processing via microwave plasma.

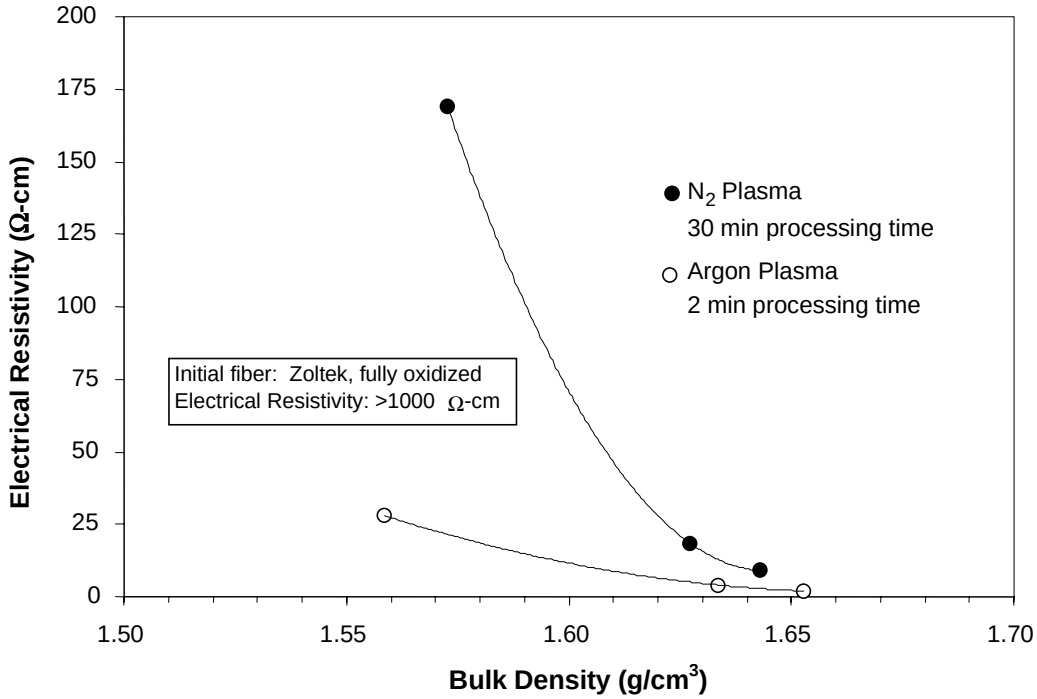

Figure 2. Electrical resistivity as a function of bulk density for plasma processing of several short samples.

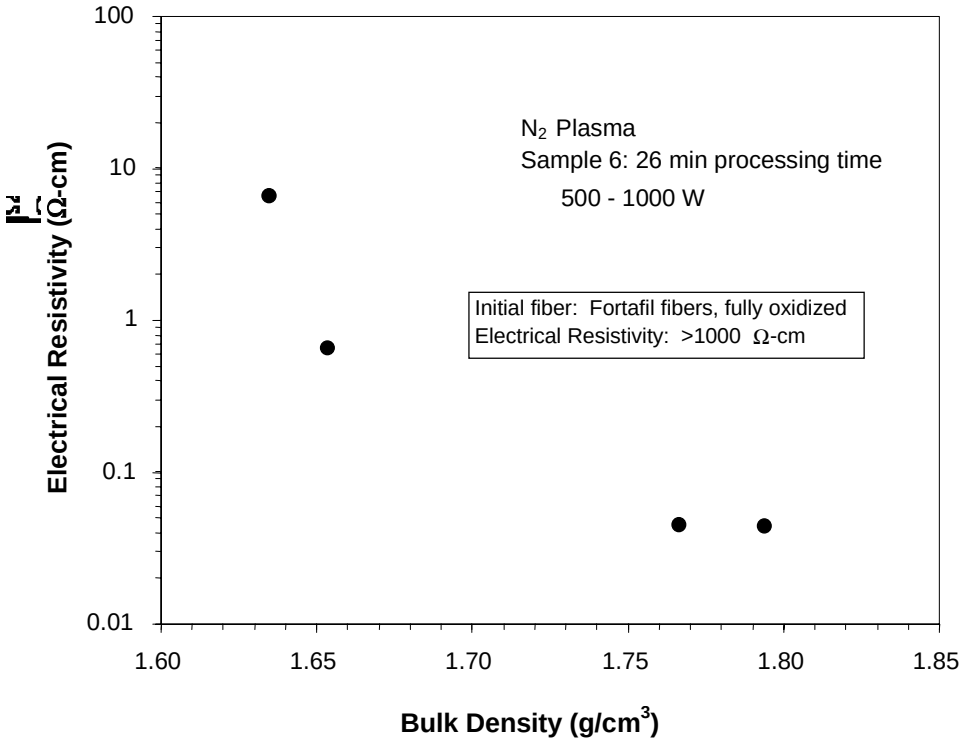

Figure 3. Electrical resistivity as a function of bulk density for plasma processing of sample 6.

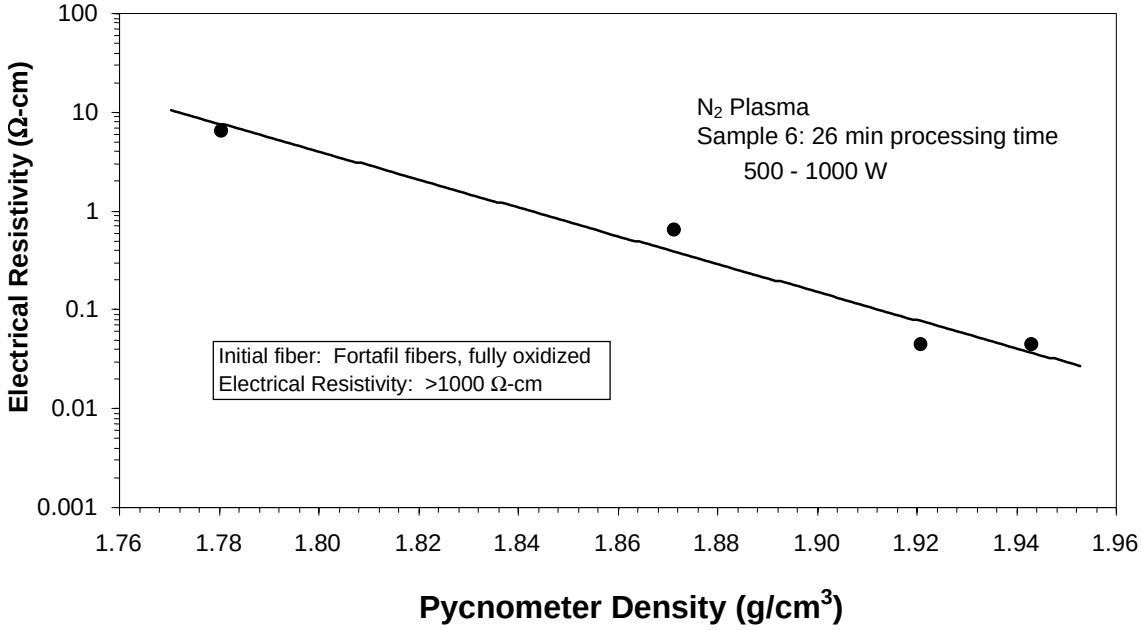

Figure 4. Electrical resistivity as a function of pycnometer density for plasma processing of sample 6.

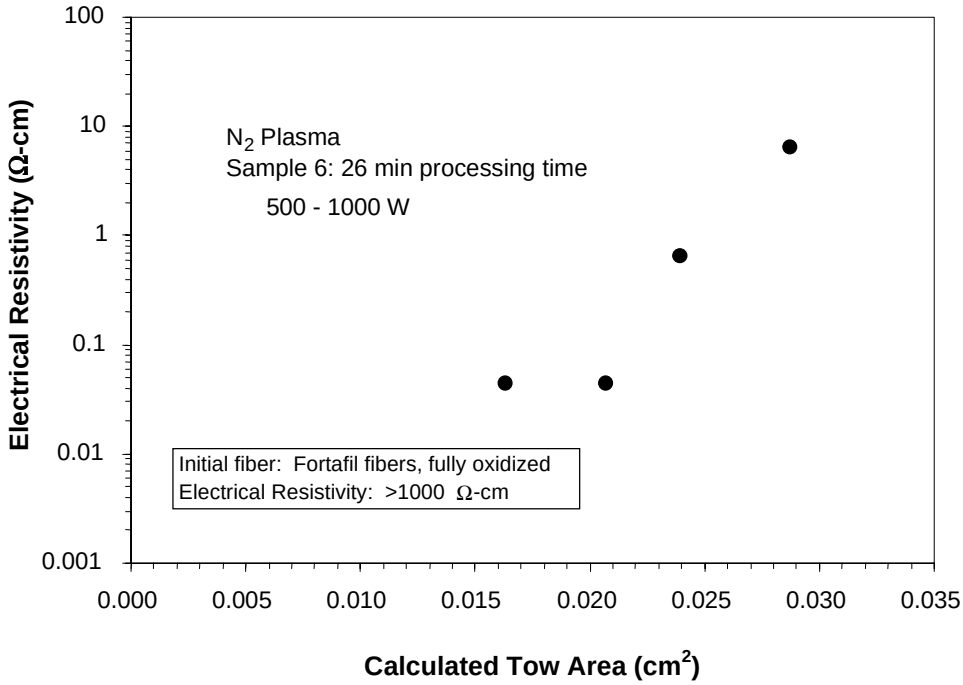

Figure 5. Electrical resistivity as a function of calculated tow area for plasma processing of sample 6.

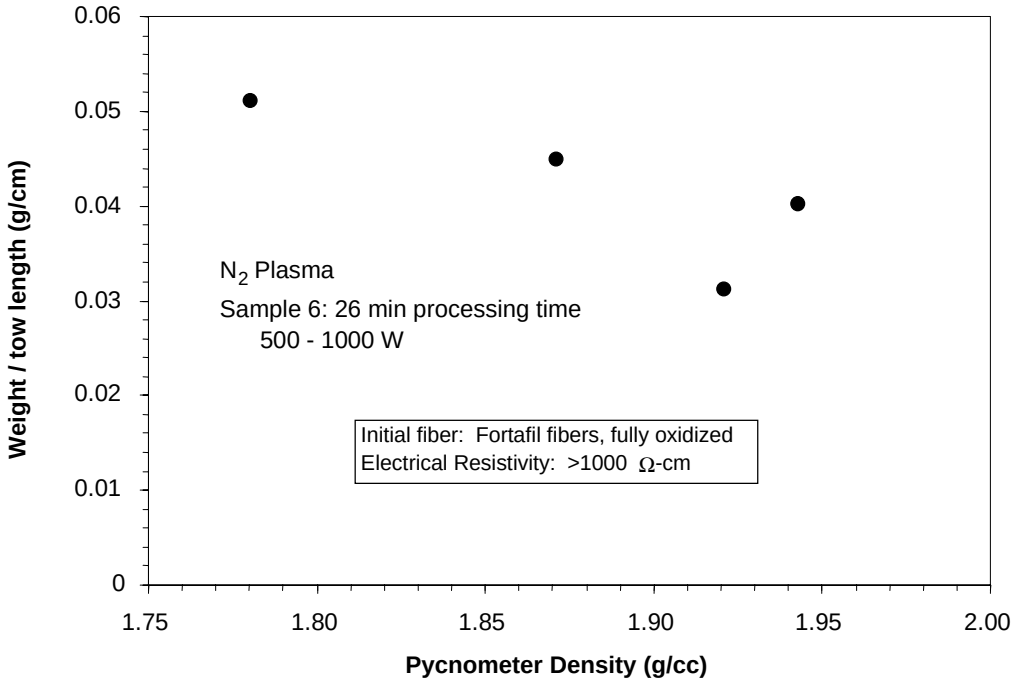

Figure 6. Weight/tow length as a function of pyconometer density for plasma processing of sample 6.

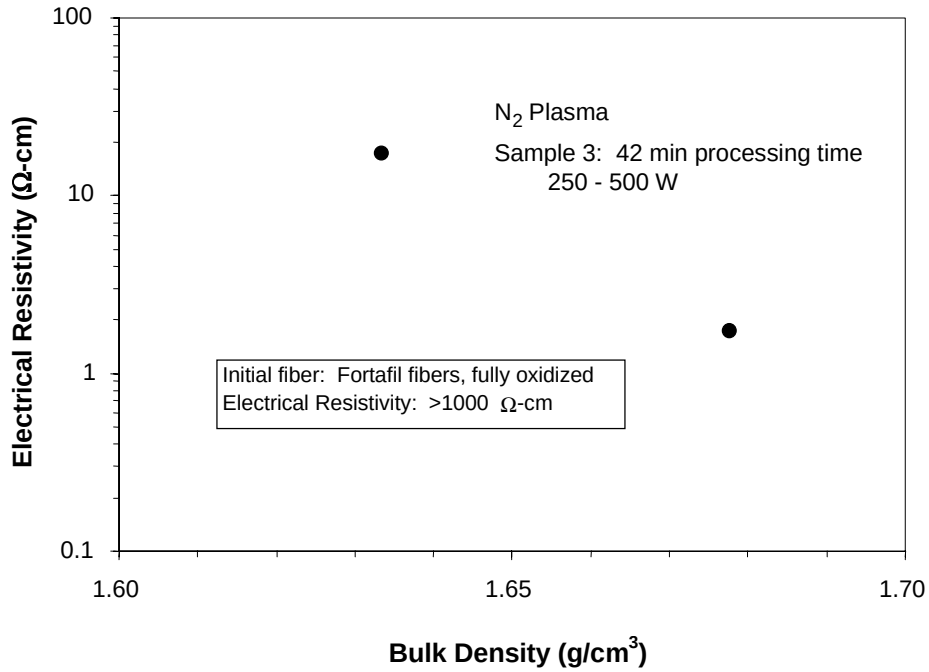

Figure 7. Electrical resistivity as a function of bulk density for plasma processing of sample 3.

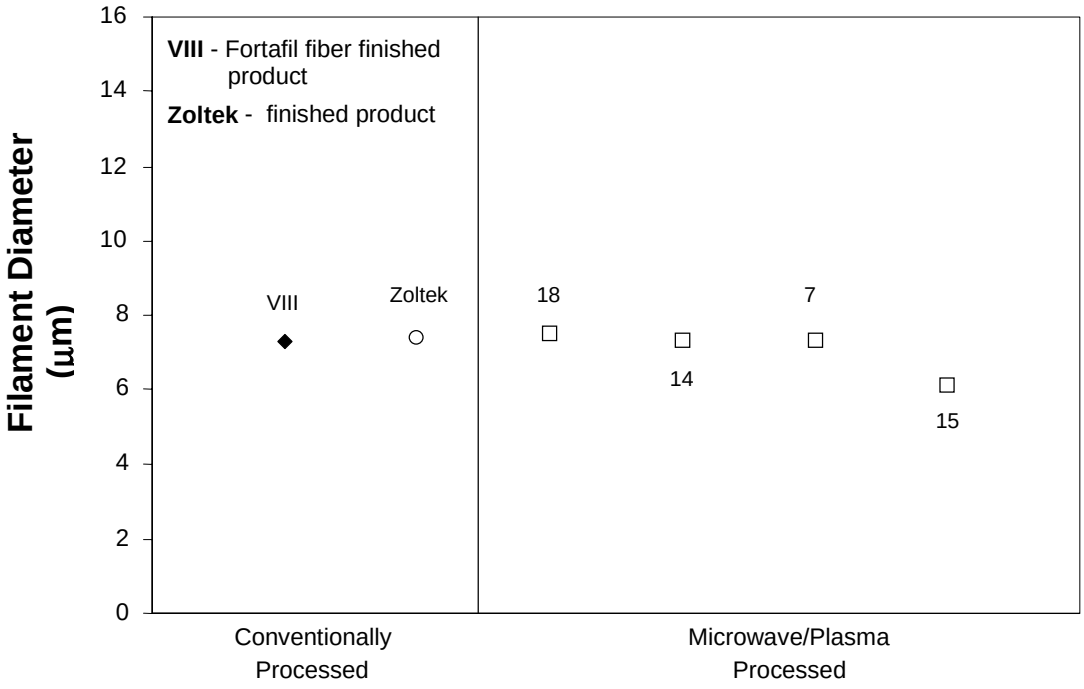

Figure 8. Comparison of fiber diameters of conventionally processed and plasma processed fibers

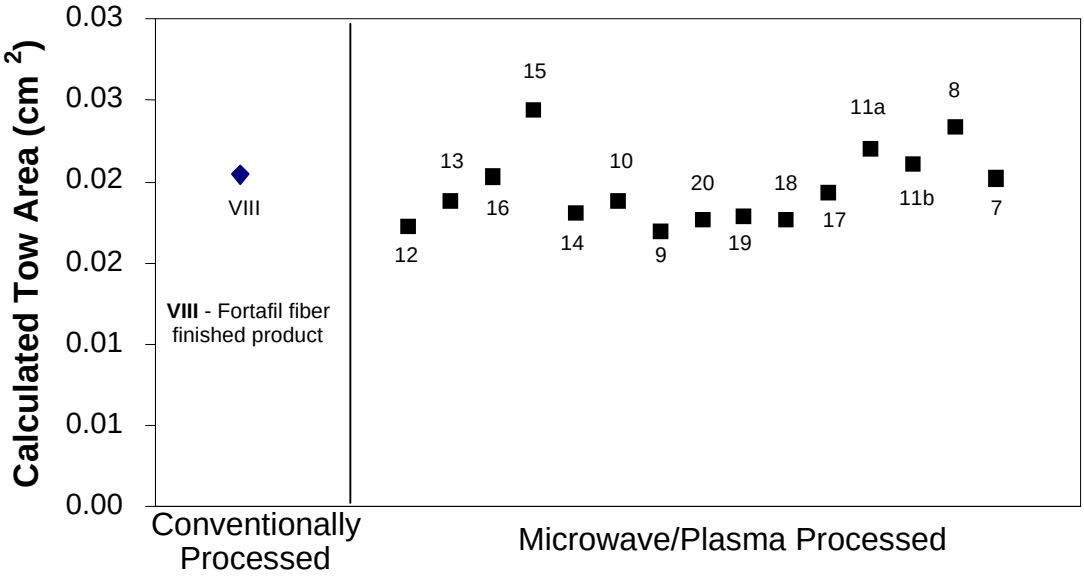

Figure 9. Comparison of the calculated fiber tow areas of conventionally processed and plasma processed fibers

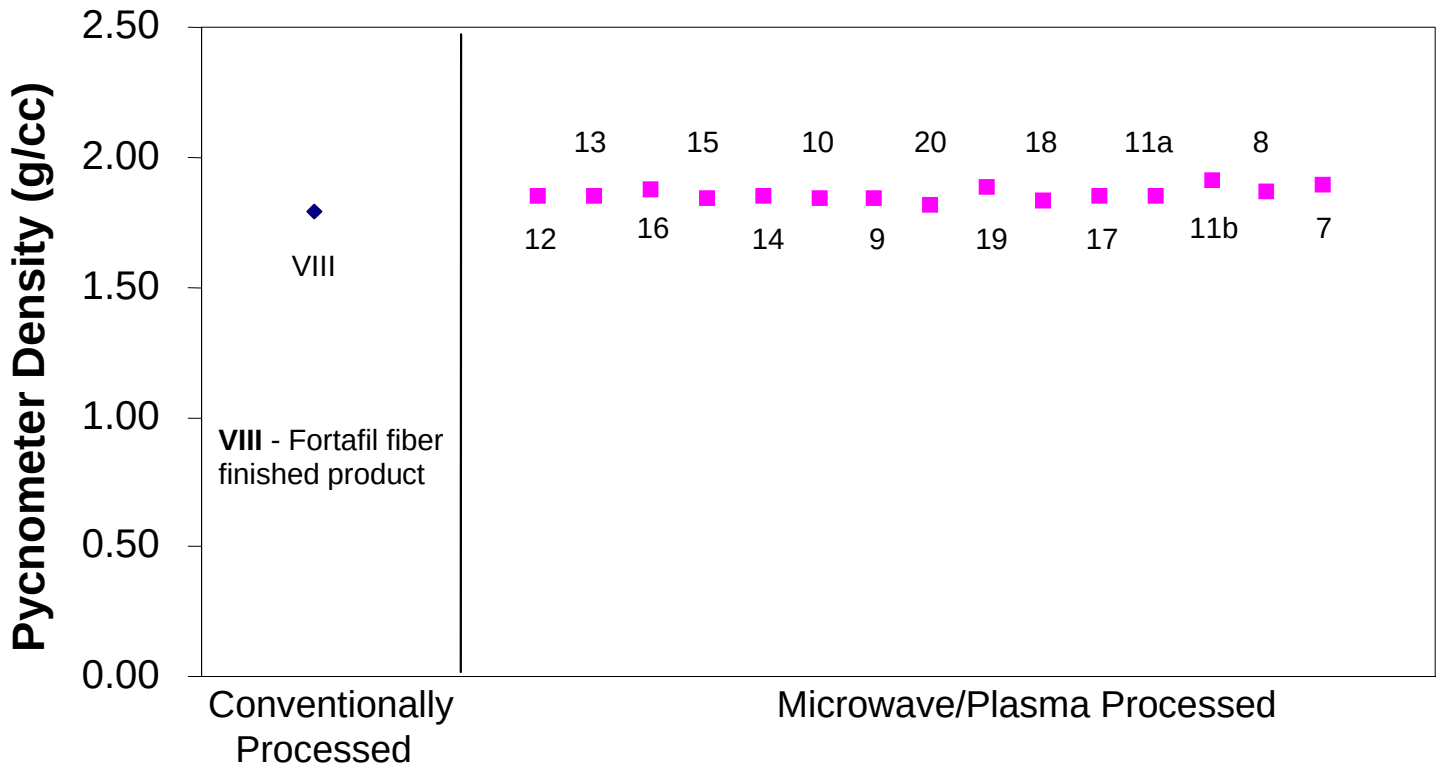

Figure 10. Comparison of pycnometer density of conventionally processed and plasma processed fibers

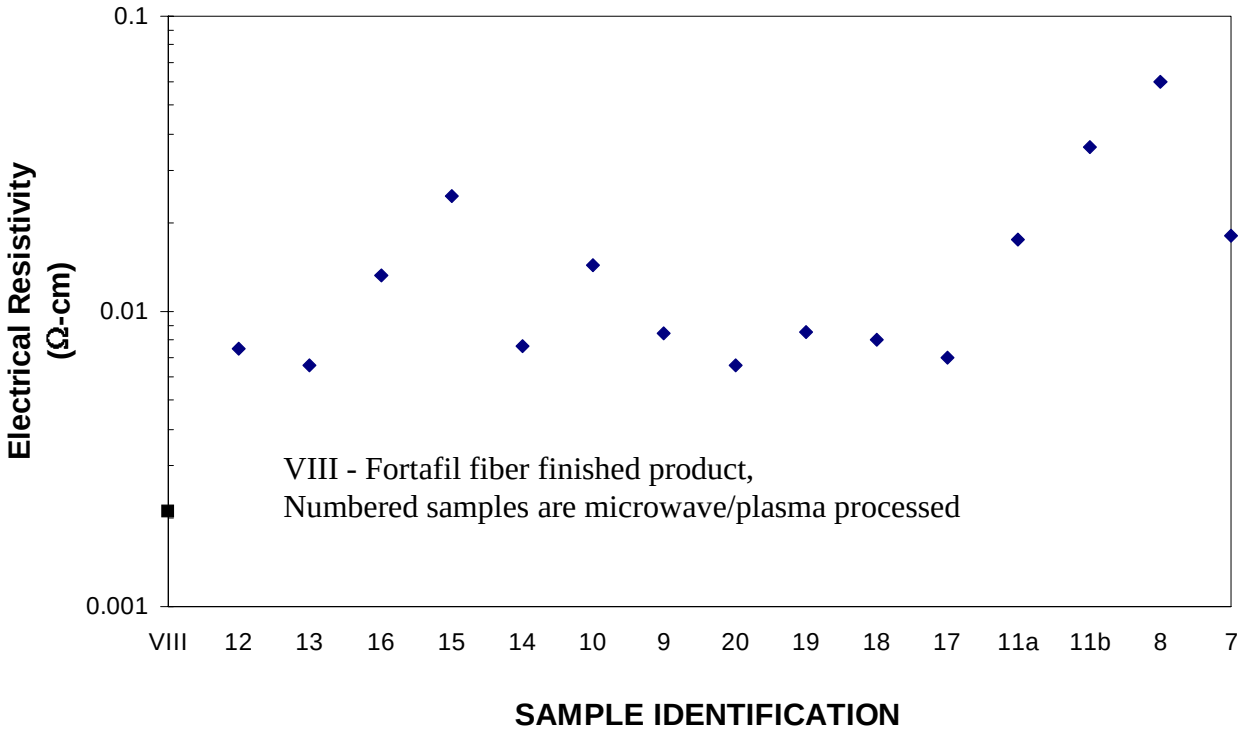

Figure 11. Comparison of electrical resistivity of conventionally processed and plasma processed fibers

Table III. Mechanical Testing Data

Fibers tested after graphitization without surface treatments or sizing.
PAN - precursor based fiber, 50K tows

	Conventionally graphitized	**Microwaved/ plasma processed**
Ultimate Tensile Strength, σ_B (ksi)	443.1	203 - 344
Young's Modulus, E (Msi)	29.16 - 30.0	16.3 - 27.91
Elongation at Failure, ε (%)	1.27	0.73 - 0.95