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Homogeneity of Pristine and Bromine Intercalated Graphite Fibers

J.R. Gaier and D. Marino
Lewis Research Center
Cleveland, Ohio

NASA

HOMOGENEITY OF PRISTINE AND BROMINE INTERCALATED GRAPHITE FIBERS

J.R. Gaier and D. Marino
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

There are reports in the literature of wide variations in the resistivity of intercalated graphite fibers. To use these materials for electrical applications, their bulk properties must be established. The homogeneity of the diameter, the resistivity, and the mass density of 50 graphite fibers, before and after bromine intercalation was measured. Upon intercalation the diameter was found to expand by about 5 percent (from 9.14 ± 0.68 μm to $9.5?\pm0.79$ μm), the resistivity to decrease by a factor of five (from 253 ± 16 $\mu\Omega$-cm to 52.0 ± 5.3 $\mu\Omega$-cm), and the density to increase by about 6 percent (from 1.99 ± 0.13 g/cm^3 to 2.10 ± 0.10 g/cm^3). Additionally, each individual fiber was found to have uniform diameter (±1.4 percent) and resistivity (±5 percent) over macroscopic regions for lengths as long as 7 cm. The ratio of pristine to intercalated resistivity increased as the pristine fiber diameter increased at a rate of 0.16 μm^{-1}, but decreased with increasing ratio of intercalated diameter to pristine diameter at a rate of 0.08.

INTRODUCTION

Intercalated graphite fibers are becoming ever more attractive for practical application within the aerospace community. The first applications will probably involve the use of conductive composites for electro-magnetic interference shielding, ground busses, and improved lightning-strike resistant aircraft structures. One of the major technological hurdles, stability under a variety of environmental conditions, appears to have been overcome for bromine intercalated P-100 fibers (ref. 1).

This paper addresses another technological question, the degree of homogeneity of intercalated graphite fibers. There are many applications where the homogeneity of intercalated graphite fibers is of major importance. If, for instance, there is a section of an electrical grounding bus or power cable that has a significantly higher resistance than the average there will be local heating which could damage other components. Also, the power requirements for a circuit would vary from installation to installation presenting difficult design and replacement requirements.

Most of the experimental research on the intercalation of graphite fibers has been performed with single fibers. While this is a useful approach for characterizing the fibers, in actual applications they will be used as bulk materials. Wide variations have been reported in the properties of single graphite fibers even within the same experiments (see, for example refs. 2 to 5). It was thus thought useful to look at a single type of fiber, and to quantify the distribution of its properties, before and after intercalation. If sources of inhomogeneity could be identified, then processing steps might be modified to minimize them.

A systematic study was carried out on 50 fibers. The diameter, electrical resistivity, and mass density of individual fibers were measured before and after intercalation, and the results were compared, and correlated. The resistivity and diameter along macroscopic lengths of the fiber were also measured.

METHODS AND MATERIALS

Pitch based Union Carbide P-100 fibers were chosen for this study for several reasons. First, they are commercially available and possess attractive mechanical and electrical properties (ref. 6). Second, they are as uniform in diameter as present graphite fiber technology allows, and are available in arbitrary lengths because they are an extruded fiber. Further, these fibers have been shown to be a stable host for bromine intercalation compounds (ref. 1).

Before the fibers were intercalated they were first heated to 350 °C in air for 24 hr to remove the polyvinyl alcohol sizing which is added during their manufacture. Then the fibers were sealed in a quartz tube with a bromine reservoir, and allowed to react in room temperature by the vapor phase transport of bromine in the presence of air for about 24 hr. Our studies show that the reaction goes to completion in about 4 hr.

Individual fibers approximately 3 cm long were mounted on sample holders which contained four-point contacts. These were fabricated from microscope slides with contacts made from colloidal carbon paint. The fibers were also attached with carbon paint. Approximately 1 cm was broken off of the ends for the density and diameter determinations. The resistance measurements were made by using a Keithley model 225 constant current source which supplied a constant dc current along the fiber through the outer contacts, while a Keithley model 181 nanovoltmeter measured the voltage drop between the inner contacts. The polarity of the current was then reversed and the voltage again measured. The absolute values of the two voltage readings were the averaged to negate electrochemical and thermoelectric effects. Although studies showed the resistance of the fibers to be ohmic, all samples were measured with a current of 100 μA. Voltages were measured to the nearest 0.01 mV (about 0.2 percent). The fiber lengths were measured to the nearest 0.1 mm using a reticule within a Bausch and Lomb microscope. By using fibers approximately 1 cm in length, the error in the length measurement was reduced to about 1 percent.

Fiber diameters were measured by attaching the fibers to scanning electron microscope sample holders using silver paint contacts at either end of the fiber. Polaroid photographs of the center section of the fibers at 3000 and 5000x were measured with vernier calipers, and compared to polaroid photographs of a silicon calibration chip (Structure Probe, Inc.) made up of 10 μm squares which was also magnified 3000 and 5000x. Using this procedure it was found that the magnification of the electron microscope drifted from one session to the next. The magnification was also found to be a function of angle. The maximum and minimum true magnification and the nominal magnification is shown in table I. When the variation in magnification and angle were corrected for, 0.1 μm diameter differences were readily discernable.

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The resistance per unit length of P-100 fibers from 5 to 10 cm long was measured by the following procedure. Fibers were mounted on microscope slides with carbon paint contacts painted on about every 5 mm along the length of the fiber. Current was applied down the length of the fiber, and the voltage was measured at each 5 mm interval. These fibers were then intercalated with bromine and the measurements repeated.

Density measurements were made using a calibrated density gradient column made from carbon tetrachloride and bromoform. There was some concern that the bromine might be drawn out of the fibers and dissolve in the density gradient medium. As a test, six bromine intercalated fibers were soaked in a 50 percent bromoform in carbon tetrachloride solution and their resistance was checked periodically. After 6 days the resistance of the fibers was unchanged. It was concluded that the density gradient solution did not remove significant amounts of bromine from the fibers, at least within the time scale (a few hours) of the density measuring experiment.

RESULTS AND DISCUSSION

The distribution of the diameters of pristine and bromine intercalated fiber is shown in figure 1. The mean pristine fiber diameter was 9.14 μm and the standard deviation of the distribution of pristine fiber diameters was 0.68 μm (henceforth reported as 9.14±0.68 μm). The mean diameter of the bromine intercalated fibers was 9.52±0.79 μm. Thus the expansion brought about by bromine intercalation, while not large, was much larger than the resolution of the measurement (about 0.1 μm). As figure 2 shows, every fiber expanded by a measurable amount. The mean expansion for the fibers was 5±3 percent for the 34 fibers for which reliable data could be measured. Ignoring negligable expansion in the fiber length (the "a" direction) implies a volume increase of about 10 percent.

The distributions of resistivities of the pristine and intercalated fibers are shown in figure 3. The mean resistivity for 32 pristine fibers was 253±28 $\mu\Omega$-cm. This is in excellent agreement with the 250 $\mu\Omega$-cm resistivity reported by Union Carbide in their specifications (ref. 6). The standard deviation of the distribution of fiber resistivities was again considerably larger than the error in the measurement (about 2 percent). The mean resistivity of the bromine intercalated fibers was 52.0±5.2 $\mu\Omega$-cm. This implies a mean resistivity ratio (pristine fiber resistivity/bromine intercalated fiber resistivity) of 4.87±0.32. It should be noted that the corrections in the electron microscope magnification, and hence in the diameter measurements, resulted in more homogenious resistivity values. Figure 4 shows that fibers whose pristine resistivies are lower, give rise to intercalated fibers whose resistivities are lower, as might be expected.

It has been shown that graphite with more crystalline order will have lower resistivity (ref. 7), and will intercalate more easily and to a higher concentration (ref. 8). Thus, if their are macroscopic regions along the fiber with higher crystalline order, the resistivity of the fiber will vary along the length. Because intercalation of those regions with higher crystalline order results in higher intercalant concentrations, these regions will also have a greater percentage drop in resistivity than those regions with low crystalline order. A hypothetical plot of resistance per unit length as a function of distance down the fiber is shown in figure 5(a) for a fiber

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of arbitrarily varying crystalline order. Those places where the crystalline order is better than average should (as shown qualitatively) produce intercalated resistivites lower than the average and vice versa. Thus the effect of intercalation would be to exaggerate the deviations from the mean. Figures 5(b) through 5(d) show data from actual fibers. The variation of the resistance per unit length from the mean along the length of the fibers is not consistant with the proposed model. In fact, the variation from the mean of the resistance per unit length along the fiber is less than 5 percent, which is comparable to the probable error of the length measurement. Thus, the resistance of the fibers does not vary macroscopically more than 5 percent along the length of the fibers.

Diameter measurements along the length both pristine and bromine intercalater fibers were also performed with a scanning electron microscope. Pieces about 5 mm in length were cut from both ends of fibers which were from 5 to 7 cm in length. The diameters were measured in a scanning electron microscope at 5000x and compared. The results indicate that both the pristine and bromine intercalated fiber diameters were constant to within 1.4 percent along their lengths. Thus, taken along with the resistance measurements, it can be stated that within 5 percent the resisitivity of a single fiber is constant over at least 7 cm lengths. This suggests that both pristine and bromine intercalated P-100 fibers are homogeneous on a macroscopic scale, an important consideration for bulk fiber usage, though it does not shed light on possible microscopic inhomogeneities.

The distribution of the mass densities of pristine and bromine intercalated fibers is shown in figure 6. The mean mass density of the pristine fibers is 1.99 ± 0.13 g/cm^3, and upon bromine intercalation that increases to 2.10 ± 0.10 g/cm^3. The error in the density measurement is less than 0.05 g/cm^3. This implies a bromine intercalated fiber density of 1.06 times the pristine fiber density. Taken with the diameter expansion data, bromine makes up about 13 percent by weight, and 2 percent by stoichiometric composition of the intercalated fiber. Gravimetric experiments where gram quantities of P-100 fibers were intercalated with bromine were consistant with these results (ref. 9).

Both pristine fiber density and pristine fiber diameter were also examined as predictors of bromine intercalated fiber resistivity values. If pristine density correlates with the drop of the resistivity upon bromine intercalation, then those fibers with anomalous densities may be weeded out before the intercalation process begins. If pristine fiber diameter correlates with the drop resistivity upon bromine intercalation, then fibers of a diameter greater or less than the 10 μm fibers used in this study might have a considerable advantage.

The plot showing the influence of pristine fiber density on resistivity ratio is shown in figure 7. There is no meaningful correlation between these two variables (correlation coefficient = 0.03). There is also no correlation between pristine fiber density and either pristine or bromine intercalated fiber resisitivity. Nor is there correlation between intercalated fiber density and pristine or intercalated fiber resistivity.

The plot of pristine fiber resistivity versus pristine fiber diameter (fig. 8) shows only very weak correlation, (correlation coefficient = 0.20). However, there is a stronger correlation (coefficient = 0.34, or to a

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98 percent confidence level) between bromine intercalated fiber diameter and bromine intercalated fiber resistivity (fig. 9). The slope of the least squares line is -2.79 $\mu\Omega$-cm/μm, implying that the fiber resistivity will decrease by 1 $\mu\Omega$-cm for every increase of 0.36 μm in fiber diameter. Figure 10 shows the restivity ratio as a function of pristine fiber diameter. The least squares line has a slope of 0.16 μm^{-1} with correlation coefficient of 0.31. The correlation implies that the decrease of resistivity with increasing fiber diameter is a result of the intercalation process itself, and not merely a consequence of the increasing fiber diameter.

When the fiber expansion (diameter bromine intercalated/diameter pristine) is plotted against resistivity ratio, the trend is towards increasing resistivity ratio with decreasing expansion (fig. 11). The least squares line has a slope of -0.08 with a correlation coefficient of -0.83. This is the opposite of what might first be expected. The suspicion is that fibers which expanded more did not do so because they contain more intercalant, but because they contain more structural disruptions.

There are at least two reports in the literature of a diameter dependance in graphite fibers. Tahar et. al. (ref. 10) report seeing a diameter dependance on the resistivity of pristine benzene derived fibers. They found that the resisitivity decreases with fiber diameter for fiber diameters less than 6 μm, but did not show data for intercalated fibers. Hambourger et al. (ref. 11), showed no diameter dependance on resistivity with pristine natural gas derived fibers, but the smallest fibers used had a diameter of 20 μm. Upon intercalation, those fibers with smaller diameters were found to have lower resistivities, contrary to the results reported herein.

These results can be explained in terms of the structure of the fiber. Both Tahar et al. and Hambourger et al. used vapor grown fibers that have the carbon planes arranged in concentric circles, like the growth rings of a tree (fig. 12). The result is larger crystallite sizes in the regions of larger diameter. Thus, larger fibers are made up of larger crystallites, and so are better conductors. When these fibers are intercalated, the intercalant must diffuse through the layers to the center, hence the middle of the fiber may not be fully intercalated. Alternately, when current is applied to the skin of the fiber, because of the poor conduction in the "c" plane, which is emphasized upon intercalation with acceptor compounds, the charge may not travel through the center portion of the fiber. This would also result in a reduction of the resistivity with increasing diameter.

The P-100 fibers, however, have the planes arranged like the spokes of wheel (fig. 13). Neither of the above effects would be present because conduction to the middle of the fiber would be facilitated by the geometry of the planes. Intercalation of bromine to the center of these fibers has been shown to be com- plete (ref. 12) with some depletion from the edges, similar to HOPG (ref. 13). If the depletion zone is independent of fiber size (about 2 to 3 μm from the outer wall of the fiber), then there would be a smaller percentage decrease for larger fibers, and that could account for the decrease in resistivity with increasing fiber size.

CONCLUSIONS

The homogeneity of the diameter, resistivity, and mass density of graphite fibers were measured before and after bromine intercalation. The

results are simmarized in table II. Both the pristine and the bromine inter-calated fibers were found to be homogeneous to within 10 percent for all the measured properties. The process of bromine intercalation did not appear to affect the degree of homogeneity of the fibers. It is suspected that while much of the resistivity variation reported in the literature is due to errors in diameter and length measurements, there are still real inhomogeneities between f bers on the order of 10 percent. The homogeneity is probably also a function of both the intercalant and the host fiber, so it is not clear how far these results may be generalized. Although the resistivity of pristine P-100 fibers is independant of fiber diameter, the resistivity ratio of the intercalated fibers decreased as their diameter increased at a rate of 0.16 μm-1. While this behavior is different from that exhibited by vapor grown fibers, it can be explained in terms of the structure of the P-100 fibers. The ratio of pristine to bromine intercalated fiber diameter decrease with increasing ratio of intercalated diameter to pristine diameter at a rate of 0.08. This can be explained if the increased expansion of the bromine intercalated fibers
is being caused by increased lattice disruption.

REFERENCES

1. J.R. Gaier, Stability of Bromine Intercalated Graphite Fibers, NASA TM-86859 (1984).

2. V. Natarajan, and J.A. Woollam, In Intercalated Graphite, (Edited by M.S. Dresselhaus, and G. Dresselhaus), pp. 45-50, North Holland, New York, (1984).

3. H.A. Goldberg, I.L. Kalnin, I.L. Spain, and K.J. Volin, Ext. Abstr. 16th Bienn. Conf. on Carbon, pp. 281-282, (1983).

4. P. Kwizera, M.S. Dresselhaus, D.R. Uhlmann, J.S. Perkins, and C.R. Desper, Carbon, 20, 387 (1982).

5. H. Oshima, J.A. Woollam, and A. Yavrouian, J. Appl. Phys., 53, 9220 (1982).

6. "Thornel" R-100 Carbon Fiber Grade VS-0054, Technical Information Bulletin No. 465-246, Union Carbine Corp.

7. A.A. Bright and L.S. Singer, Carbon, 17, 59 (1979).

8. A. Herold, In Intercalated Layered Materials, (Edited by F. Levy), pp. 323-421, D. Reidel Publishing Co., New York (1979).

9. C-C. Hung, (1985). "A Micrographic and Gravimetric Study of Intercalation and Deintercalation of Graphite Fibers", TM-87026.

10. M.Z. Tahar, O.C. de Hodgins, M.S. Dresselhaus, and M. Endo, In Graphite Intercalation Compounds, (Edited by P.C. Eklund, M.S. Dresselhaus, and G. Dresselhaus), pp. 217-220, Materials Research Society, Pittsburgh, (1984).

11. P.D. Hambourger, D.A. Jaworske, and J.R. Gaier, In Graphite Intercalation Compounds, (Edited by P.C. Eklund, M.S. Dresselhaus, and G. Dresselhaus) pp. 208-210, Materials Research Society, Pittsburgh, (1984) (and unpub-lished data).

12. D.A. Jaworske and R. Zinolabedini, Graphite Fiber Intercalation Dynamics of the Bromine Intercalation Process, NASA TM-87015 (1985).

13. L.E. McNeil, J. Steinbeck, L. Salamanca-Riba and G. Dresselhaus, Bull. Am. Phys. Soc., 29, 253 (1984).

TABLE I. - VARIATION OF ELECTRON
MICROSCOPE MAGNIFICATION

Date	Nominal	Minimum	Maximum
9-17	3000x	3070x	3260x
10-1	5000x	4870x	5070x
10-10	2000x	2130x	2320x
	5000x	4900x	5460x
10-24	2000x	2130x	2390x
	5000x	4970x	5410x
11-6	5000x	4630x	5150x
1-10	5000x	4540x	4910x

TABLE II. - SUMMARY OF PRISTINE AND BROMINE INTERCALATED
GRAPHITE FIBER PROPERTIES

Property	Pristine value	Intercalated value
Diameter	9.14 ± 0.68 μm (7%)	9.52 ± 0.79 μm (8%)
Resistivity	2.53 ± 28 μΩ-cm (11%)	52.0 ± 5.2 μΩ-cm (10%)
Mass density	1.99 ± 0.13 g/cm^3 (7%)	2.10 ± 0.10 g/cm^3 (5%)
Resistivity variation along fiber length	<5%	<5%
Diameter variation along fiber length	<1.4%	<1.4%
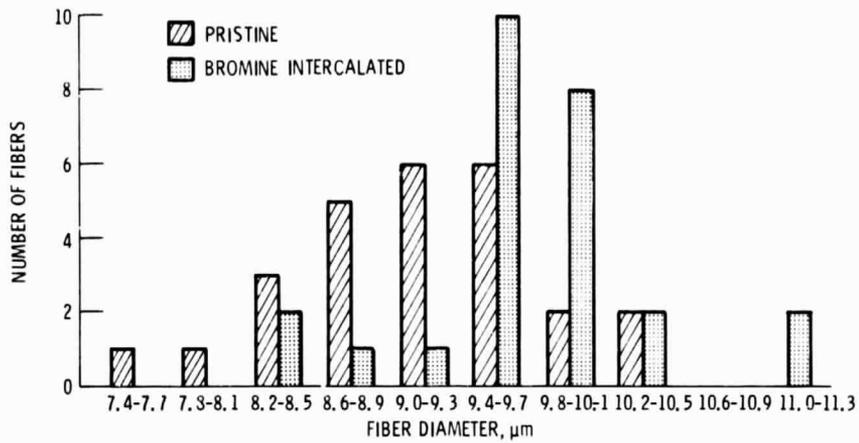
Figure 1. - The distribution of Pristine and Bromine intercalated P-100 fiber diameters.
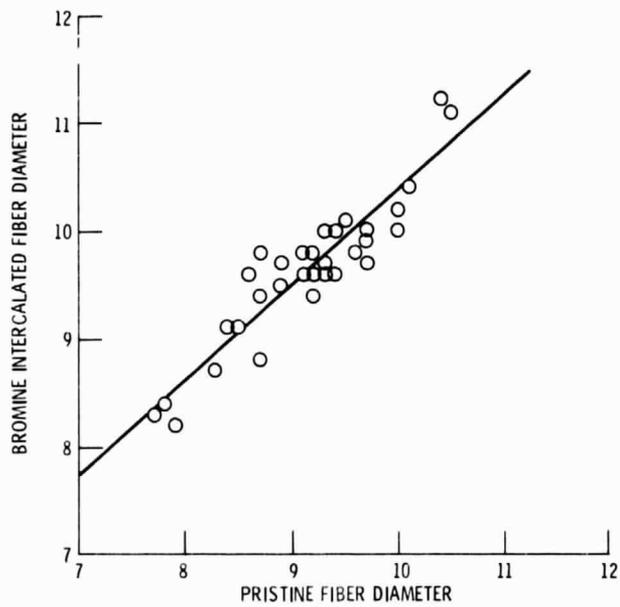
Figure 2. - Bromine intercalated fiber diameter as a function of
Pristine fiber diameter.
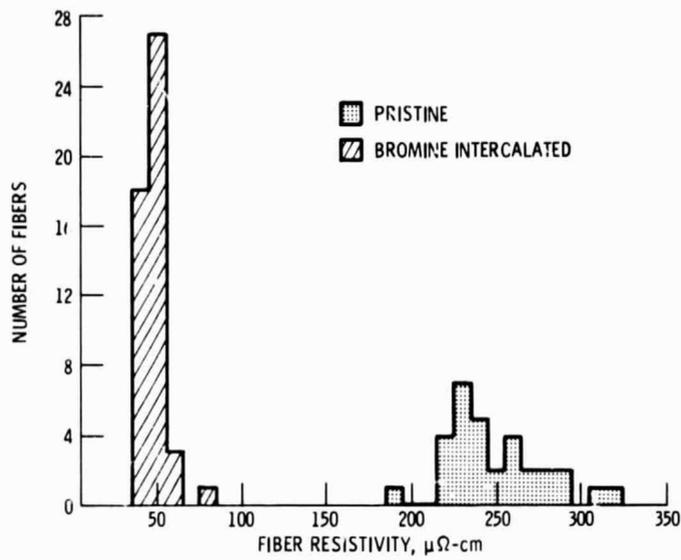
Figure 3. - The distribution of Pristine and Bromine intercalated P-100 fiber resistivities.
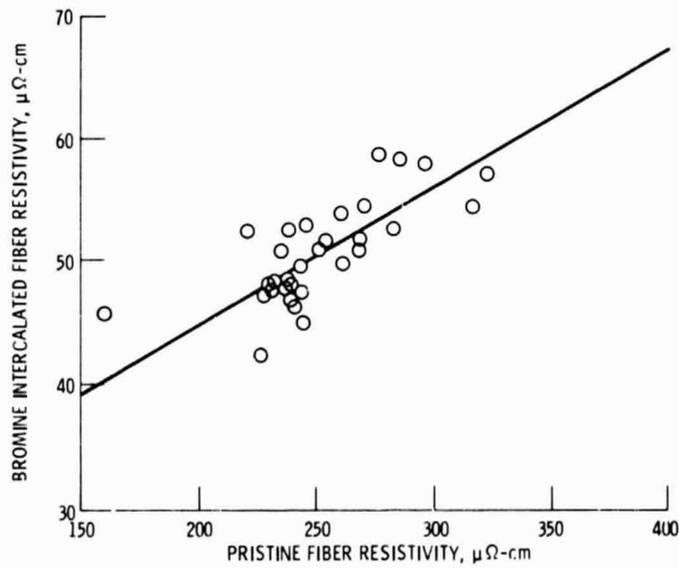
Figure 4. - Resistivity of Bromine intercalated fiber as a function of Pristine fiber resistivity.
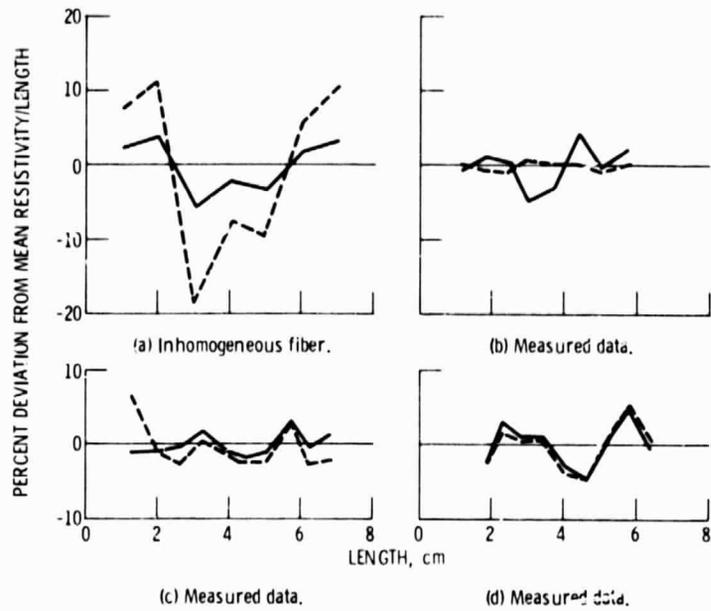
Figure 5. - Expected resistivity/length distribution for an inhomogeneous fiber and measured data. Intercalated fiber is shown by dashed line.
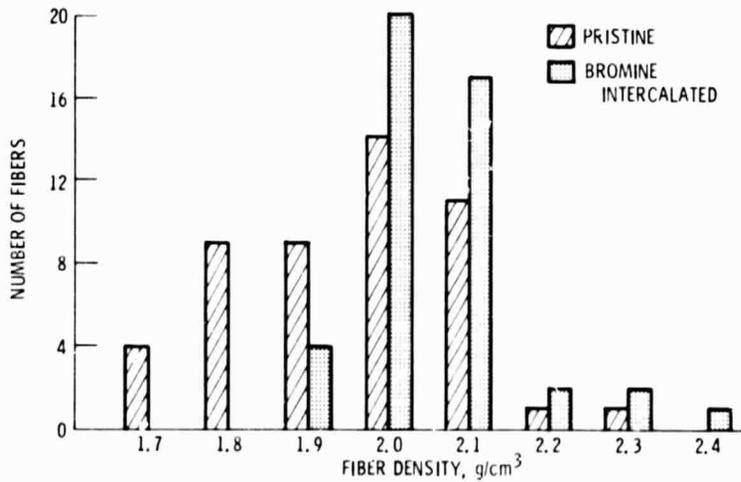
Figure 6. - The distribution of Pristine and Bromine intercalated P-100 fiber mass densities.
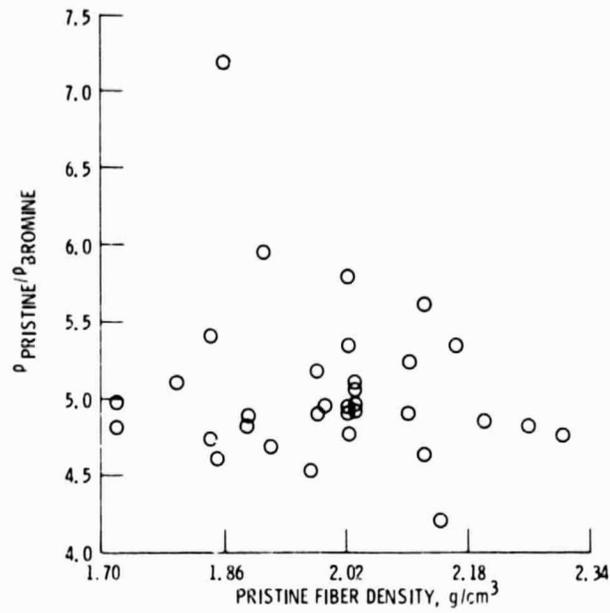
Figure 7. - The resistivity ratio (φ pristine/ρ bromine inter-calated) of P-100 fibers as a function of Pristine fiber mass density.
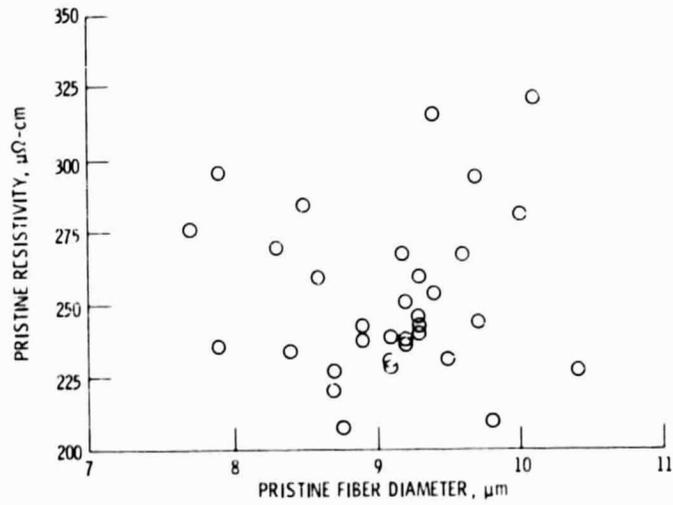
Figure 8. - Resistivity as a function of diameter for Pristine P-100 fibers.
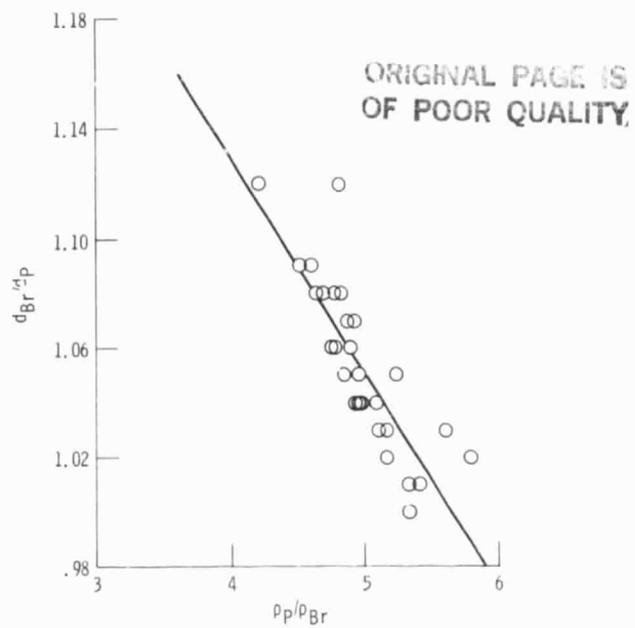
Figure 11. - The expansion of the fiber upon intercalation ($d_{bromine\ intercalated}/d_{pristine}$) as a function of resistivity ratio ($\rho_{pristine}/\rho_{bromine\ intercalated}$).
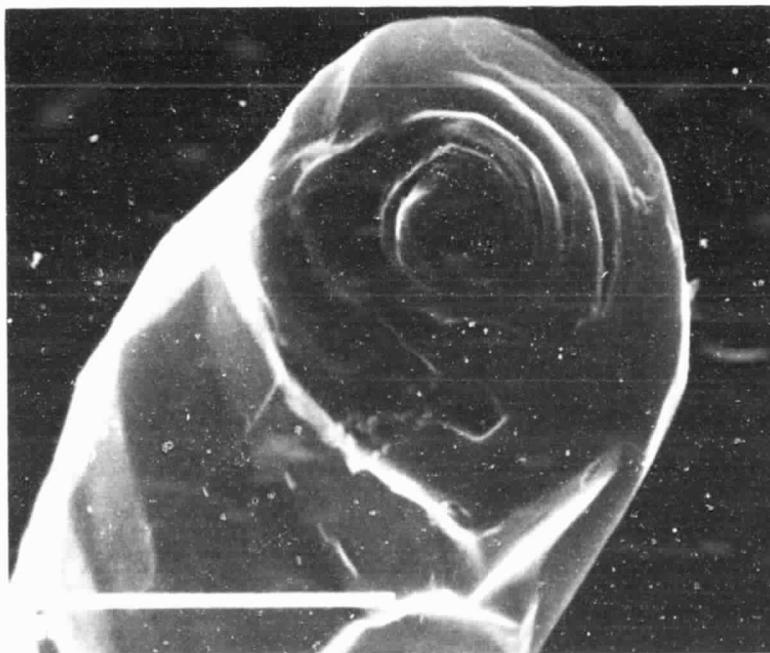

Figure 12. - Scanning electron micrograph of an organic vapor grown graphite fiber.
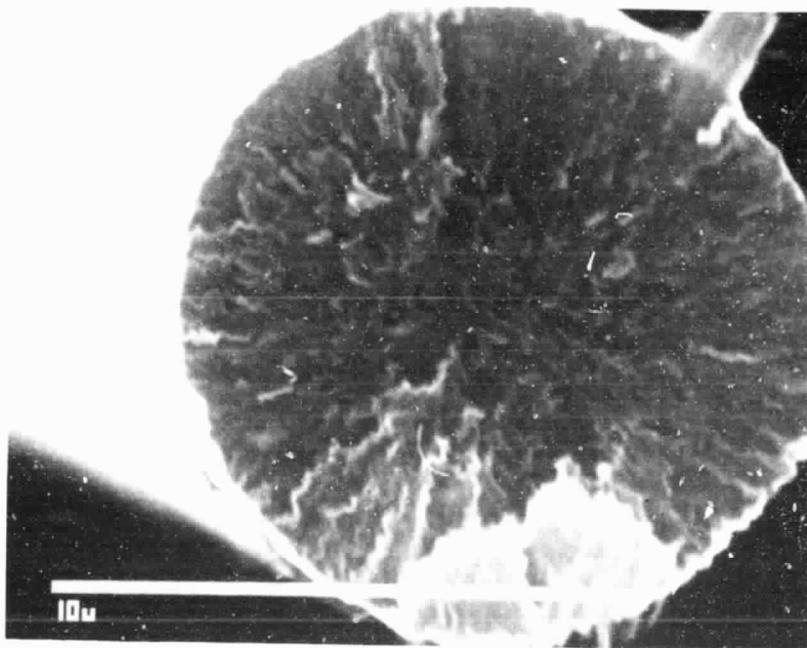
Figure 13. - Scanning electron micrograph of a P-100 graphite fiber.

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15. Supplementary Notes

16. Abstract

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