Homogeneity of Pristine and Bromine Intercalated Graphite Fibers

by

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Intercalated graphite fibers are becoming ever more attractive for practical application (EMI shielding, conductive control surface, etc.)within the aerospace community. One of the major technological hurdles, demonstrating 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 hurdle, the homogeniety of graphite fibers which have been intercalated with bromine. Most of the experimental research on the intercalation of graphite fibers has been done with single fibers. While this is a sensible approach for characterizing the fibers, in application they will be used as bulk materials. Wide variation in the properties of single graphite fibers have been reported even within the same experiments (see, for example refs. 2 and 3). It was thus thought useful to look at a relatively large number of very similar fibers, and to try to quantify the distribution of some of their properties, before and after intercalation. A systematic study was carried out on 50 fibers. Their electrical resistivity, diameter, and mass density before and after intercalation, were measured and compared. Resistivity and diameter along macroscopic lengths of the fiber were also measured.

METHODS AND MATERIALS

Fibers used in this study were Union Carbide pitch based P-100. These were chosen for a variety of reasons. First, they are commercially available and possess good mechanical and electrical properties (ref. 4). 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 shown to be a stable host for bromine intercalation compounds (ref. 1).

The fibers were intercalated by the vapor phase transport method at room temperature for 24 hours. The fibers were mounted on four point probe sample holders (ref. 1) which were used for the resistivity measurements. Diameters were measured using a scanning electron microscope at 3000-5000x.

The resistance per unit length of P-100 fibers from 5 to 10 cm long were measured by mounting them 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, 6 bromine intercalated fibers were soaked in a 50% 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 of the density measuring experiment (a few hours).

RESULTS AND DISCUSSION

The distribution of the pristine and intercalated fiber diameters is shown in figure 1. The mean pristine diameter was 9.14 ± 0.13 μm (where the latter number is the observed standard deviation of the distribution of diameters). The mean bromine intercalated diameter was 9.53 ± 0.79 μm. Every fiber expanded by a measureable amount. The mean expansion was 5 ± 3% in diameter for the 34 fibers for which reliable data could be measured. This implies a volume increase of about 10%.

The distribution of pristine and intercalated fiber resistivities is shown in figure 2. The mean pristine resistivity (for 32 fibers) was 253 ± 28 μΩ-cm. This is in good agreement with the resistivity reported by Union Carbide in their specifications of 250 μΩ-cm (ref. 4). The mean resistivity of the bromine intercalated fibers was 52.0 ± 5.22 μΩ-cm. This implies a mean resistivity drop (ρ_o/ρ) of 4.87 ± 0.32.

The resistance per unit length measurements were designed to look for macroscopic regions along the fiber where intercalation may not have been uniform. The observed variation along the fiber was less than 5% for both pristine and intercalated fibers which was within the error in the length measurements.

Diameter measurements along the length of the fiber were also performed with the electron microscope. These results indicate that the fiber diameter is constant to within 1.4% along a 5 cm length for both the intercalated and pristine fibers. Taken along with the resistance measurements, it can be stated that within 5% the resistivity of a single fiber is constant.

The distribution of pristine and bromine intercalated fiber mass densities is shown in figure 3. 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 ± 0.09/cm^3. This implies an intercalated density of 1.06 times the pristine density. Taken with the expansion data, the bromine makes up about 13% by weight, and 2% by composition of the fiber. Gravimetric experiments where gram quantities of P-100 fibers were intercalated with bromine were consistent with these results (ref. 5).

No meaningful correlation was found between the density of the fibers and either the diameter or the resistivity for either pristine or bromine intercalated fibers.

No correlation was found between pristine fiber diameter and pristine fiber resistivity, but there is a strong correlation between bromine intercalated fiber diameter and intercalated fiber resistivity. This is illustrated in figure 4 which shows the resistivity ratio (ρ_o/ρ) as a function of fiber diameter. The slope of the least squares line is 0.16 μm^{-1}, and the correlation coefficient is 0.31 (to a certainity of 0.91). This shows

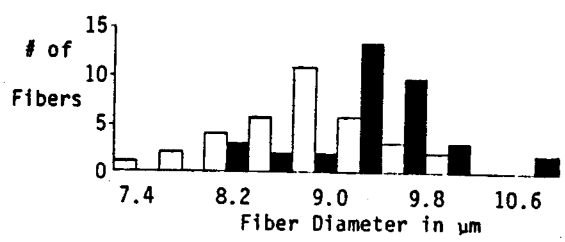

Fig. 1. The Distribution of Pristine and Bromine Intercalated (Shaded) P-100 Fiber Diameters.

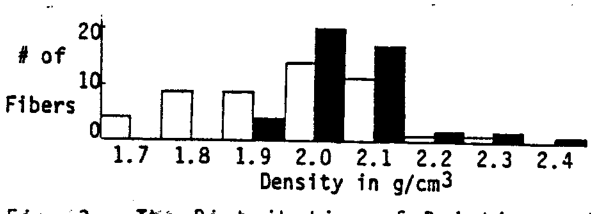

Fig. 3. The Distribution of Pristine and Bromine Intercalated (Shaded) P-100 Fiber Mass Densities.

that the intercalation process, and not the fiber diameter is responsible for the diameter dependance of the resistivity.

There are at least two reports in the literature of a diameter dependance in graphite fibers. Tahar et. al. (ref. 6) report seeing a diameter dependance on the resistivity of pristine benzene derived fibers. They found that the resistivity decreases as fiber diameter increases for fiber diameters less than 6 µm, but did not have data for intercalated fibers. Hambourger et. al. (ref.7), found no diameter dependance on resistivity with pristine natural gas derived fibers, but the smallest fibers used had a diameter 20 µm. Upon intercalation, those fibers with larger diameters were found to have higher resistivities, contrary to the results reported herein, but it should be noted that both the benzene derived and the natural gas derived fibers have a "tree ring" geometric arrangement of carbon planes, whereas the P-100 fibers have a "radial spoked" geometry.

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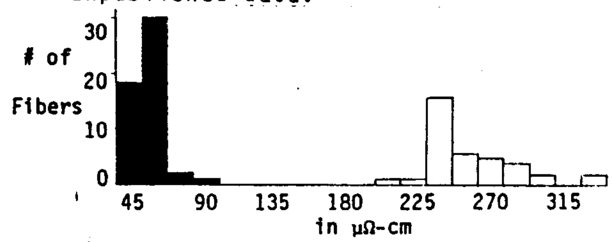

Fig. 2. The Distribution of Pristine and Bromine Intercalated (Shaded) P-100 Fiber Resistivities.

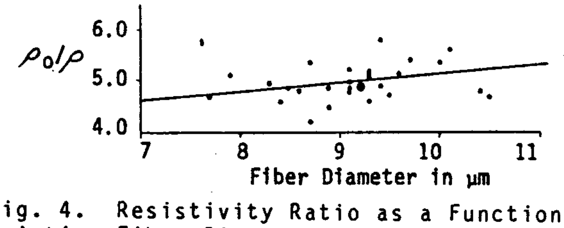

Fig. 4. Resistivity Ratio as a Function of Pristine Fiber Diameter