

Improving the Interlaminar Shear Strength of Carbon Fiber—Epoxy Composites Through Carbon Fiber Bromination

(NASA-TM-100248) IMPROVING THE INTERLAMINAR
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(NASA) 11 p

N88-15018

CSCL 11D

G3/24
Unclas
0118976

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December 1987

NASA

PROVING THE INTERLAMINAR SHEAR STRENGTH OF CARBON FIBER - EPOXY
COMPOSITES THROUGH CARBON FIBER BROMINATION

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SUMMARY

The use of bromine to improve the interlaminar shear strength of PAN-based carbon fibers was investigated. Composite test specimens fabricated from brominated T-300 fibers and a MY720 matrix exhibited, on average, a 30 percent improvement in ILSS over their pristine counterparts. Mass, electrical resistivity, density, contact angle, and scanning Auger microscopy results suggested a mechanism in which the bromine was covalently bonded to the surface of the fiber, and this resulted in an increased van der Waal's adhesion between fiber and matrix.

INTRODUCTION

The interlaminar shear strength (ILSS) of a composite is determined primarily by the interfacial bonding between the reinforcing fiber and matrix material (ref. 1). Hence surface chemistry and morphology of the carbon fibers play an important role in determining the mechanical characteristics of the composite. For example, small changes in the surface of the fiber can have a dramatic effect on ILSS. Several techniques are currently available for improving the ILSS of a composite, such as wet oxidation, dry oxidation, various surface coatings, and whiskerizing with silicon carbide (ref. 2). The halogenation treatment described here is a new alternative for improving the ILSS of certain composites.

Previous work with pitch-based carbon fiber-epoxy composites has shown that the ILSS was improved by reacting the fibers with bromine vapor prior to composite fabrication (ref. 3). To encourage widespread application, this technique of ILSS improvement must be useful on the more frequently used PAN-based fibers. As a result, ILSS testing of brominated T-300 and AS-4 fibers was initiated. Pristine and brominated fibers were subjected to a series of tests including resistivity, density, contact angle measurements, and differential scanning calorimetry. In addition to ILSS testing of uniaxial composites, selected composites were subjected to additional testing, such as density and scanning Auger microscopy. A possible mechanism is proposed to explain the improved ILSS, based on single fiber and composite test results. Finally, the bromination technique is compared to other techniques used to improve ILSS.

MATERIALS AND METHODS

Amoco T-300 carbon fibers and Hercules AS-4 carbon fibers were used throughout this study. These fibers were chosen because of their widespread acceptance and use in the aerospace community. The as-received T-300 fibers were free of sizing whereas the AS-4 fibers had a proprietary surface treatment. Bromination of these fibers was accomplished by winding approximately 100 g of fibers onto a glass mandrel and placing it in an all-glass reaction kettle. A small pool of bromine liquid at the bottom of the kettle was used as a source of bromine vapor. The fibers were kept in the bromine vapor for approximately three days. Upon removal, the fibers were allowed to degas for several days until bromine loss subsided.

Uniaxial composites were made from these fibers and three different matrixes, two epoxies (MY720 and 934 epoxies) and one polyimide (PMR-15). Thirty ILSS samples were cut from each composite test panel to yield a statistically large sample lot. The ILSS of each sample was calculated from breaking strength data obtained according to ASTM D 2344, using a three-point Instron testing machine (ref. 4). All tests were performed at room temperature.

Single fiber resistivity data were obtained on each fiber type using a four-point measurement. A Keithley model 225 constant current source was used to supply current to the outer two leads of the fiber while a Keithley model 181 nanovoltmeter was used to measure the voltage drop across the inner two leads of the fiber. The diameter of each fiber was obtained by scanning electron microscopy.

Single fiber density data were obtained on each fiber type using a density gradient column made from reagent grade bromoform and carbon tetrachloride. Glass density standards were used to calibrate each column, and a second degree polynomial curve fitting routine was used to generate a standard curve. Fiber density values were found through interpolation.

Single fiber contact angle data were obtained using a modification of the Wilhelmy plate technique (ref. 5). In the so-called micro-Wilhelmy method, a single fiber is mounted on one arm of an electrobalance and the fiber is dipped into and out of a liquid. Distilled water was used in this case. The force required to pull the fiber out of the liquid, the circumference of the fiber, and the surface tension of the liquid were used to calculate the contact angle.

Scanning Auger microscopy was used to determine the bromine concentration across the diameter of the fiber. Specifically, the concentration was measured at the edges and in the middle of a fiber embedded in a MY-720 epoxy matrix (ref. 6). Care was taken to polish one end of the composite specimen normal to the fiber axis by grinding with various silicon carbide abrasive papers as well as coarse and fine alumina slurries. The electron beam used for the analysis was approximately 0.5 μm in diameter (approx. 7 percent of the fiber diameter).

Composite densities were determined geometrically by cutting, measuring, and weighing small composite samples from the ends of those samples already

tested for ILSS. In this way, it was possible to compare specific composite density values with specific ILSS values.

RESULTS AND DISCUSSION

The interlaminar shear strength data from the T-300-MY720 system are summarized in the histograms shown in figure 1. As can be seen, the brominated samples exhibit a greater ILSS than their pristine counterparts, with an average improvement of about 30 percent (10.0 ± 1.4 ksi versus 7.6 ± 0.7 ksi, respectively). The ILSS of the T-300-934 system is summarized by the histograms in figure 2. In this case, bromination caused no significant change in the ILSS of the 934 epoxy system (13.8 ± 1.3 ksi versus 14.4 ± 1.9 ksi, respectively). The results from the polyimide samples, summarized in figure 3, show a marked decrease in ILSS (3.5 ± 0.3 ksi versus 17.2 ± 1.4 ksi). Apparently, the bromination technique described here is only useful on specific matrix materials and not universal in nature.

The large spread in the ILSS data for the brominated T-300 composite samples prompted further investigation. The density of these particular composite samples was measured to see if the spread in the ILSS data was due to inhomogeneity in the fiber fill fraction. The density of each sample was measured and plotted against ILSS, and the results are shown in figure 4. The composite density distribution was quite narrow compared to the ILSS distribution, and there was no apparent correlation between composite density and ILSS. Hence, the large spread in the ILSS data cannot be attributed to gross inhomogeneity in the composite samples.

Improvements in the interlaminar shear strength of carbon fiber-epoxy composites can be achieved through a number of mechanisms (ref. 5). The presence of oxides (such as $-OH$, $-COOH$, and $>C=O$) on the surface of the fiber results in increased hydrogen bonding with the amine hardener of the matrix. Likewise, the presence of polar groups on the surface of the fiber can increase the van der Waals adhesion between fiber and matrix, which can also improve ILSS. Another method to improve ILSS is through increasing the surface area of the fiber, which causes improved mechanical interlocking of fiber and matrix. In an effort to understand the mechanism responsible for the improved ILSS of the brominated T-300-MY720 epoxy system, several tests were performed on the brominated fibers used to make the composite. These included resistivity, density, and contact angle measurements on single fibers as well as scanning Auger microscopy on fibers embedded in the composite.

As shown in figure 5, the mass of bromine decreases slightly with time after the fibers are removed from the bromine environment. The amount of bromine is nearly 8.3 percent initially, but asymptotically approaches a value of about 7.7 percent after approximately 25 days. Although this indicates that some portion of the bromine reacts with the fibers, it does not reveal the type of reaction. The bromine may be either intercalated, covalently bonded, or adsorbed. One measure of intercalated bromine is the presence of an endothermic phase change at the two-dimensional melting point of 100°C , as observed by differential scanning calorimetry (ref. 7). However, no such phase change was observed in the brominated T-300 fiber system. The possibility of bromine intercalation can be ruled out based on this observation and the resistivity data presented below.

If the bromine was intercalated there would be a reduction in the electrical resistivity of the fibers. However, the electrical resistivity data shown in figure 6 reveal that the brominated fibers have a slightly greater electrical resistivity than their pristine counterpart (2600 $\mu\text{ohm-cm}$ versus 1800 $\mu\text{ohm-cm}$, respectively), suggesting that the bromine in these fibers is covalently bonded to the carbon lattice. The same trend was observed in a different set of pristine and brominated T-300 fiber data. Such covalent bonding causes additional scattering of the charge carriers which increases the electrical resistivity.

The diameters of the fibers used to determine electrical resistivity are summarized in figure 7. The average fiber diameter increases from $7.2 \pm 0.5 \mu\text{m}$ to $7.6 \pm 0.6 \mu\text{m}$ after bromination. Although this shift is small compared to the reported standard deviation, a similar shift was observed in another set of pristine and brominated T-300 fiber data. Hence, the brominated fibers have a cross sectional area about 10 percent greater than their pristine counterpart.

The density data shown in figure 8 reveal that there is little change in the density of the brominated T-300 fibers compared to their pristine counterpart. This result is consistent with the mass data and the fiber diameter data presented above. Both mass and volume increase by about 10 percent leaving no change in the density.

The wetting behavior of three pristine and three brominated T-300 fibers was measured using the micro-Wilhelmy technique. Preliminary contact angle results indicate that the wetting behavior of the brominated fibers was similar to the pristine fibers ($42^\circ \pm 6^\circ$ versus $44^\circ \pm 3^\circ$, respectively) when using distilled water as the wetting agent.

Bromine concentration at the edge and in the center of a T-300 fiber embedded in a MY720 epoxy matrix was determined by scanning Auger microscopy. SAM analysis revealed that there was a bromine concentration of 5 at % at the surface of the fiber, diminishing to an undetectable amount inside the fiber. These measurements were taken normal to the fiber axis.

Combining all of this information, a possible mechanism may be proposed. The bromine reacts with the carbon fiber such that most of the bromine resides on the surface of the fiber. The bromine is covalently bonded to the carbon at or near the surface, and creates an increased van der Waal's adhesion between the T-300 fibers and the MY720 matrix.

A similar suite of data was collected for AS-4 fibers. However, the AS-4 fibers did not have much bromine mass uptake, did not indicate any significant change in resistivity after bromination, and did not impart a marked increase to composite ILSS. The AS-4 fibers did not exhibit similar results because they had been pretreated with a proprietary sizing by the manufacturer. Apparently, all of the surface active sites were already occupied by the manufacturer's proprietary sizing and very little bromine was able to react with the fiber surface.

Finally, it seems appropriate to compare this technique of improving ILSS with other techniques (ref. 5). Wet oxidation techniques, such as treatment in boiling nitric acid, yields an improvement in ILSS of between 25 to 200 percent. However, treated fibers suffer from weight loss and reduced tensile

strength. Dry oxidation techniques, such as oxidation in air at 400 to 500 °C, result in 45 to 65 percent improvement in ILSS. However, this particular technique often suffers from etch pit formation which weakens the fiber. Whiskerizing with silicon carbide increases the ILSS of composites by 200 to 400 percent, but this technique is prohibitively expensive. Hence, the bromination technique described in this paper falls short of other techniques for improving ILSS, but it may be useful in specific cases where other treatments are undesirable for price, processing, or other performance reasons. Other halogens such as chlorine and iodine chloride may have the potential for improving ILSS.

CONCLUSIONS

Halogenation of carbon fibers with bromine results in improved ILSS, depending on the type of fiber and matrix used. Of the fibers and matrixes tested, brominated T-300 fibers in a MY720 epoxy matrix offered the most favorable results, while brominated T-300 fibers in a 934 epoxy matrix or brominated T-300 fibers in a PMR-15 polyimide matrix offered little or no improvement to ILSS. The T-300 fibers used in the ILSS testing contained 7.7 percent bromine by weight and most of this bromine was covalently bonded to the surface of the fibers, as indicated by electrical resistivity and scanning Auger microscopy results. Likewise, the volume of the T-300 fibers increased by about 10 percent upon bromination leaving no change in their observed density. Micro-Wilhelmy contact angle measurements using water as a wetting agent revealed little change in the wetting behavior of the brominated fibers compared to their pristine counterpart. One explanation for the observed improvements in ILSS may be an increased van der Waal's adhesion between fiber and matrix as a result of bromine on the surface of the fiber.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Polymers Branch of NASA Lewis Research Center, and Fiberite Corporation of Winona, MN for their assistance in the fabrication and testing of the composite test specimens. The authors also thank M.E. Slabe of Cleveland State University for her assistance in the fiber density determinations.

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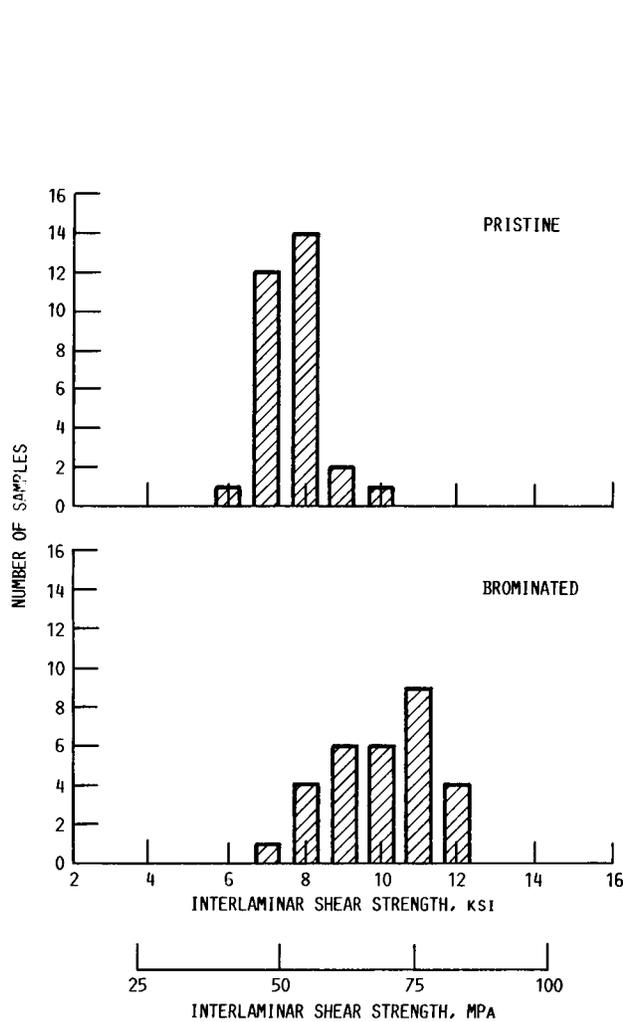


FIGURE 1. - ILSS OF PRISTINE AND BROMINATED T-300 FIBERS IN A MY720 EPOXY MATRIX.

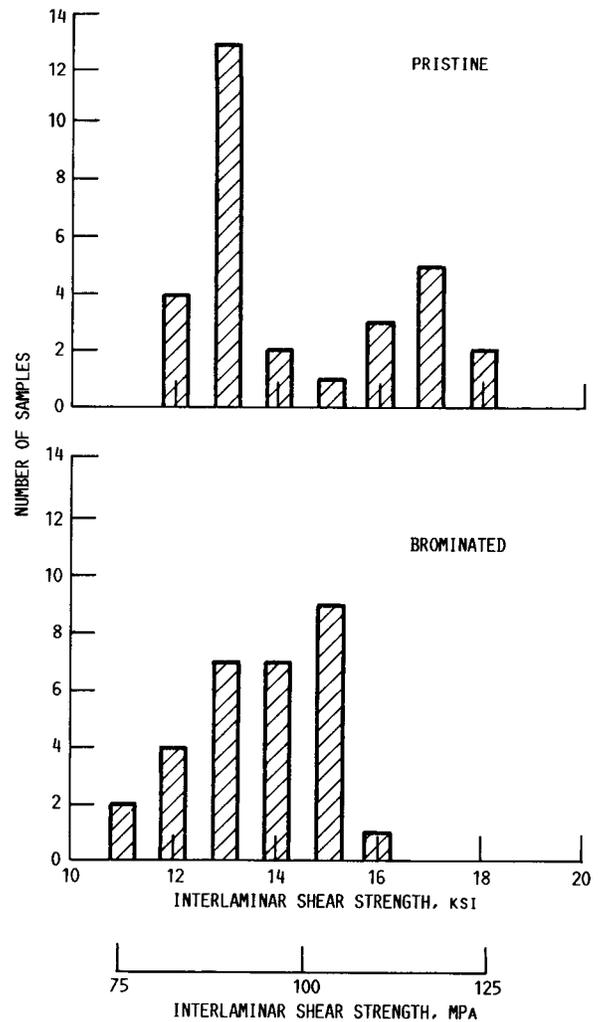


FIGURE 2. - ILSS OF PRISTINE AND BROMINATED T-300 FIBERS IN A 934 EPOXY MATRIX.

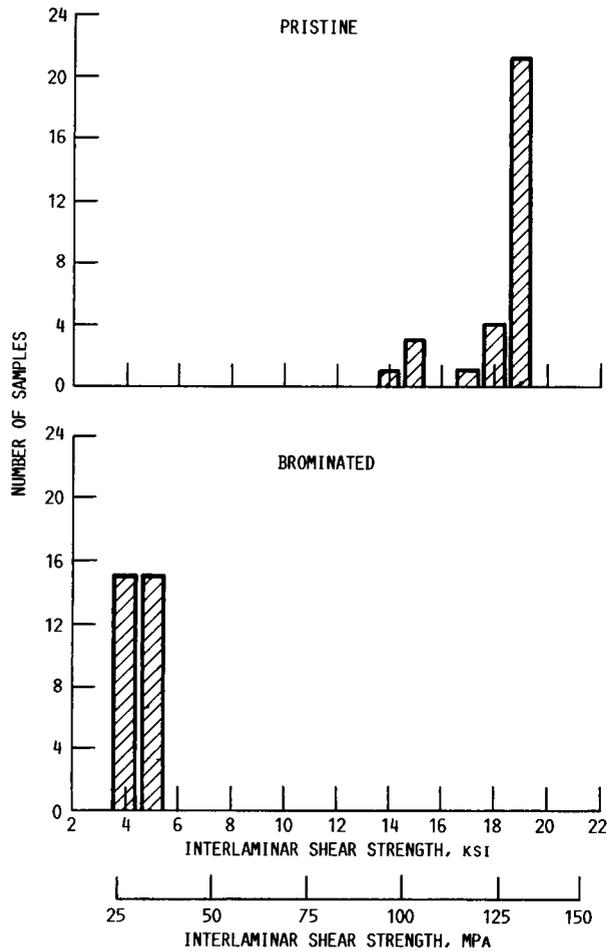


FIGURE 3. - ILSS OF PRISTINE AND BROMINATED T-300 FIBERS IN A PMR-15 POLYIMIDE MATRIX.

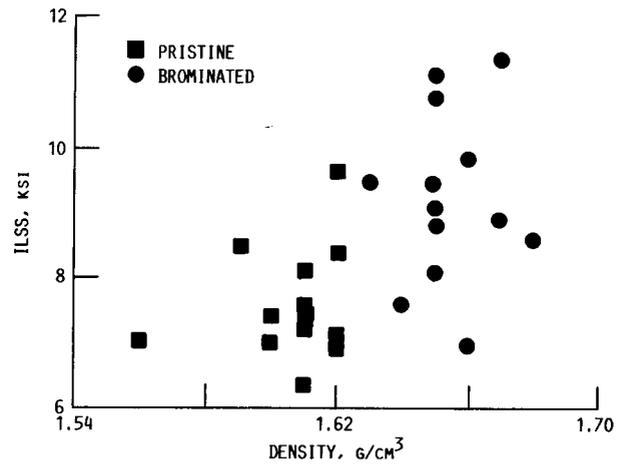


FIGURE 4. - COMPOSITE DENSITY VERSUS COMPOSITE ILSS FOR PRISTINE AND BROMINATED T-300 FIBERS IN A MY720 EPOXY MATRIX.

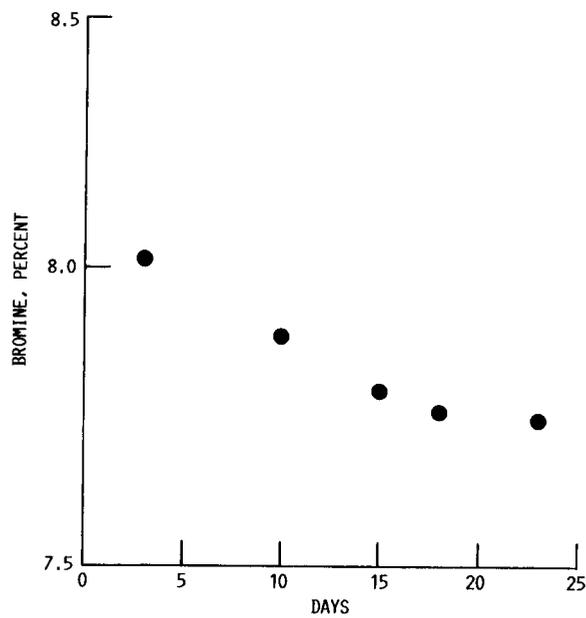


FIGURE 5. - BROMINE CONCENTRATION IN T-300 CARBON FIBERS AS A FUNCTION OF TIME, AFTER REMOVAL FROM THE BROMINE REACTION CHAMBER.

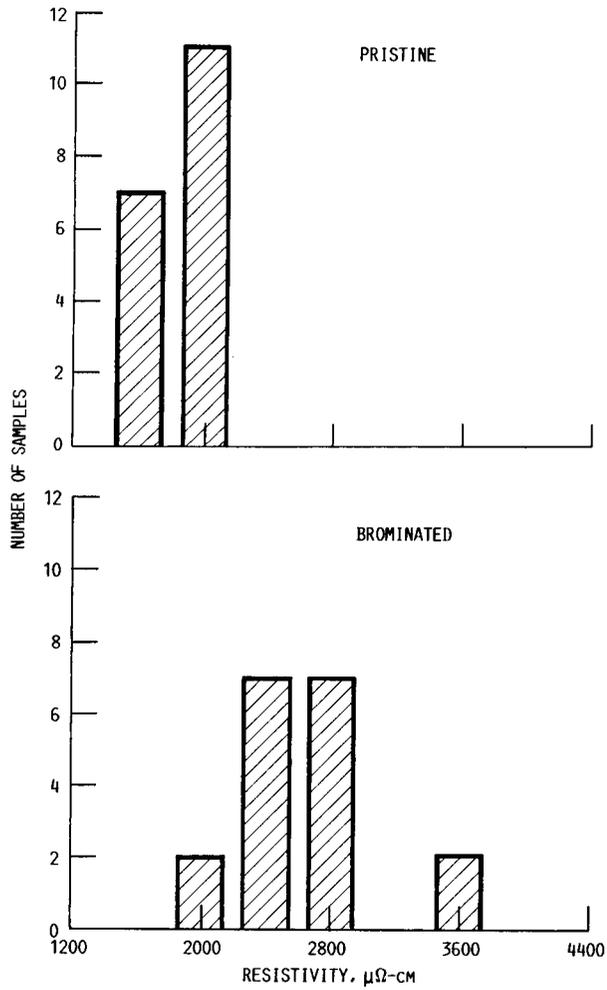


FIGURE 6. - ELECTRICAL RESISTIVITY OF PRISTINE AND BROMINATED T-300 CARBON FIBERS.

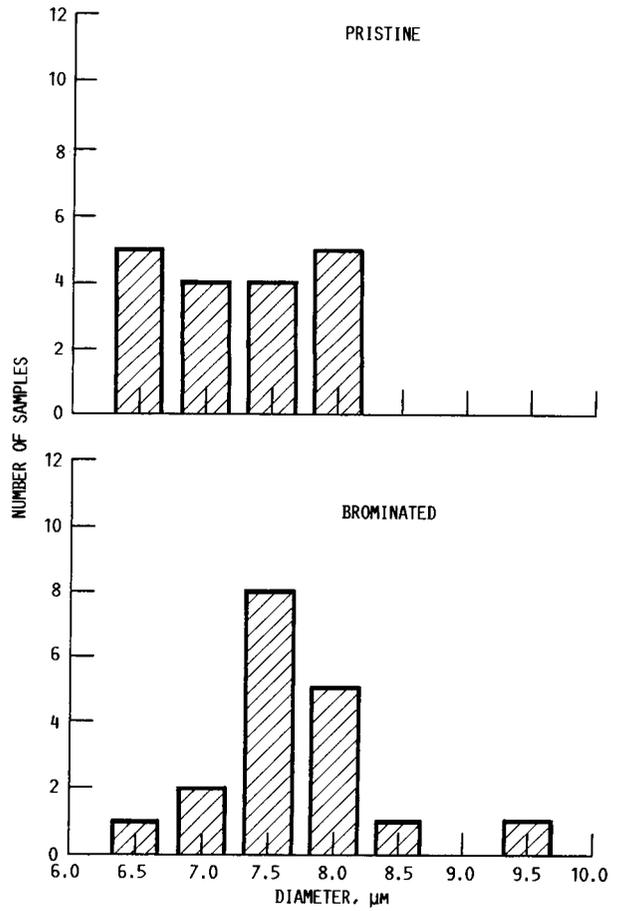


FIGURE 7. - DIAMETER OF PRISTINE AND BROMINATED T-300 CARBON FIBERS.

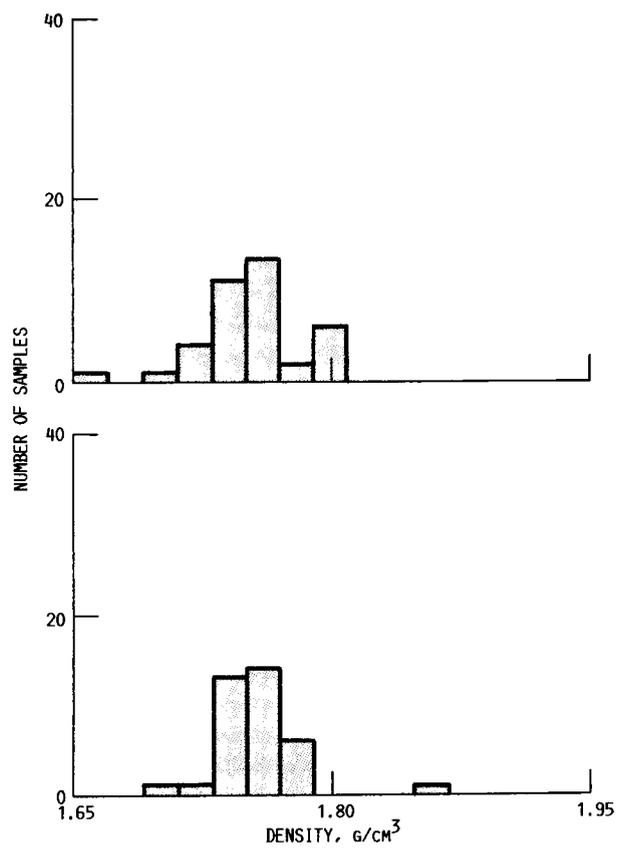


FIGURE 8. - DENSITY OF PRISTINE AND BROMINATED T-300 CARBON FIBERS.



National Aeronautics and
Space Administration

Report Documentation Page

1. Report No. NASA TM-100248		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Improving the Interlaminar Shear Strength of Carbon Fiber - Epoxy Composites Through Carbon Fiber Bromination				5. Report Date December 1987	
				6. Performing Organization Code	
7. Author(s) Donald A. Jaworske and Carolyn Maciag				8. Performing Organization Report No. E-3870	
				10. Work Unit No. 307-50-00	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001				14. Sponsoring Agency Code	
15. Supplementary Notes Donald A. Jaworske, NASA Lewis Research Center; Carolyn Maciag, Cleveland State University, Cleveland, Ohio 44115					
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17. Key Words (Suggested by Author(s)) Bromination Carbon fibers Interlaminar shear strength			18. Distribution Statement Unclassified - Unlimited Subject Category 24		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No of pages 10	22. Price* A02