NASA Technical Memorandum 100236

The Effect of Bromination of Carbon Fibers on the Coefficient of Thermal Expansion of Graphite Fiber—Epoxy Composites

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November 1987

NASA

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E-3665-1

SUMMARY

To examine the effect of bromination of carbon fibers on the coefficient of thermal expansion (CTE) of carbon fiber epoxy composites, several pristine and brominated carbon fiber - epoxy composite samples were subjected to thermomechanical analysis. The CTE's of these samples were measured in the uniaxial and transverse directions. The CTE was dominated by the fibers in the uniaxial direction, while it was dominated by the matrix in the transverse directions. Bromination had no effect on the CTE of any of the composites. In addition, the CTE of fiber tow was measured in the absence of a polymer matrix, using an extension probe. The results from this technique were inconclusive.

INTRODUCTION

As an engineering parameter, the coefficient of thermal expansion plays an important role in position sensitive structural components that are exposed to temperature extremes, such as orbiting satellite antenna dishes and solar dynamic power systems. In order to limit the influence of temperature extremes, much of the proposed space station will be composed of graphite epoxy composites designed to yield near-zero CTE's. In composite materials, the overall CTE of the product is influenced by the CTE's of its constituents. Hence, it is important to understand the thermal properties of any new material being considered for composite applications. One such material that is being considered for conductive cofunctional space structures is brominated pitch-based carbon fibers (ref. 1).

This paper addresses the effect of bromination of carbon fibers on the CTE of their composites. In addition, the CTE of the fibers alone was measured.

MATERIALS AND METHODS

The unidirectional composite samples were fabricated using either PAN-based T-300 fibers, pitch-based P-75, or pitch-based P-100 fibers manufactured by Amoco. Pristine fibers were used as-received. Details of the bromination process may be found elsewhere (ref. 1). The T-300 fibers were approximately 7 percent Br_2 by weight, while the P-75 and P-100 fibers were approximately 15 percent Br_2 by weight. The MY720 epoxy was used with DDS hardener (ref. 2).

After the composite was fabricated, four sample cubes were cut from each laminate using a diamond saw, and their dimensions were measured to the nearest 0.01 mm with digital callipers. Care was taken to cut the samples as orthogonally as possible.

Linear expansion data were collected on a Perkin-Elmer TMS-2 thermomechanical analyzer in the temperature range of 30 to 130 °C, at a scan rate of 20 °C/min. The CTE was calculated over this range using a two point method. Although there was curvature in some of the data, this method yielded an average expansion over this temperature range. The instrument was calibrated using an aluminum standard. On the first sample, triplicate measurements of the CTE in the a-direction were obtained, followed by triplicate measurements in the b-direction and the c-direction (fig. 1). This provided a measure of the variation within the technique. On the next three samples, the CTE was measured once in each direction. This provided a measure of sample to sample variation. Since the variation within the technique was smaller than the variation within the samples, the results reported for each composite are the average of the four samples.

A special extension probe was used to measure the CTE of several carbon fiber tows (ref. 3). This was accomplished by clamping the carbon fiber tow between two copper clips and mounting the clips between the quartz sample probes. A small drop of epoxy was used to secure each copper-to-carbon joint. In addition to the suite of carbon fibers, several materials of known CTE were prepared in a similar fashion, and these data were used to generate a standard curve for comparison.

RESULTS AND DISCUSSION

Of the two methods chosen to study CTE, the use of composite cubes was much more reliable than the use of fiber tows. The fiber tow work suffered from a large spread in the data, as indicated by the nonuniform results obtained from metal wire standards. This was attributed to nonuniform preparation of the fiber tow or wire samples, compared to the composite cubes. Hence, only the composite data will be presented.

There was little difference in the observed values of CTE before and after bromination in the uniaxial a-direction, as shown in table I. For example, the pristine P-75 composite had a value of -1.5 ± 0.1 ppm/K while the brominated composite had a value of -1.7 ± 0.5 ppm/K. Likewise, there was little difference in the transverse b- and c-directions. The pristine and brominated P-75 composites had CTE values in the b-direction of 32 ± 2 and 34 ± 2 ppm/K, respectively; while they had values in the c-direction of 30 ± 5 and 36 ± 4 ppm/K, respectively. This result is not surprising when one considers that the CTE in the a-direction is controlled by the a-axis expansion of the graphite lattice within the fiber, while the CTE's in the transverse directions are controlled by both the c-axis expansion of the graphite lattice within the fibers and the expansion of the matrix.

Whether the bromination reaction is adsorption or intercalation, bromination does not seem to alter the graphite lattice significantly. Although bromination does alter the surface characteristics of the fiber to an extent measurable by interlaminar shear strength (ref. 1), this alteration goes unnoticed in terms of CTE.

The observed CTE values in the uniaxial direction were of the same order of magnitude as values of pyrolytic graphite, and showed a trend with increasing graphitization similar to the trend indicated by the manufacturer. Pyrolytic graphite has a CTE value of -0.6 ppm/K parallel to the plane of deposition, and Amoco indicates that the CTE values of the pristine T-300, P-75, and P-100 fibers are -0.5, -1.3, and -1.6 ppm/K, respectively (refs. 4 and 5). The CTE values in the transverse directions were less than the 52 ppm/K of the neat resin and more than the 23 ppm/K of pyrolytic graphite measured perpendicular to the plane of deposition, indicating that the the c-axis expansion of the composite has contributions from both fibers and matrix (refs. 2 and 4).

The somewhat larger variation in the transverse direction CTE results can probably be attributed to a nonhomogeneous fiber distribution within each composite as well as differences in fiber loading from composite to composite. The estimated fiber volume percent, as determined from mass, volume, and fiber density data, varied from 51 to 76 percent. No estimate of void content was made.

It is interesting to note that the fibers have a negative CTE in the a-axis direction, which becomes more negative with an increasing degree of graphitization. This unusual property, combined with the positive CTE of the matrix, makes these fibers useful in tailoring a near-zero CTE for orbiting space structures. The fact that bromination does not alter this property paves the way for cofunctional structures made from highly electrically conductive brominated pitch-based fibers.

CONCLUSIONS

The bromination of carbon fibers has little effect on the coefficient of thermal expansion of carbon fiber - epoxy composites. The CTE in the uniaxial direction is dominated by the a-axis expansion of the carbon fibers while the CTE's in the transverse directions are dominated by both the c-axis expansion of the carbon fibers and the matrix. The negative CTE of the brominated fibers combined with the positive CTE of the matrix make these materials suitable for tailoring cofunctional composite space structures with near-zero thermal expansion.

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TABLE I. - COEFFICIENT OF THERMAL EXPANSION (in ppm/K) OF PRISTINE AND BROMINATED CARBON FIBER - EPOXY COMPOSITES, AS MEASURED IN THE TEMPERATURE RANGE OF 30 to 130 °C

	Coefficient of thermal expansion (in ppm/K)		
	a-Direction	b-Direction	c-Direction
Pristine T-300	-1.6±0.4	25±3	25±1
Brominated T-300	-1.1±1.2	32±1	29±1
Pristine P-75	-1.5±0.1	32±2	30±5
Brominated P-75	-1.7±0.5	34±2	36±4
Pristine P-100	-2.1±0.8	52±2	41±2
Brominated P-100	-1.8±0.3	42±2	41±1

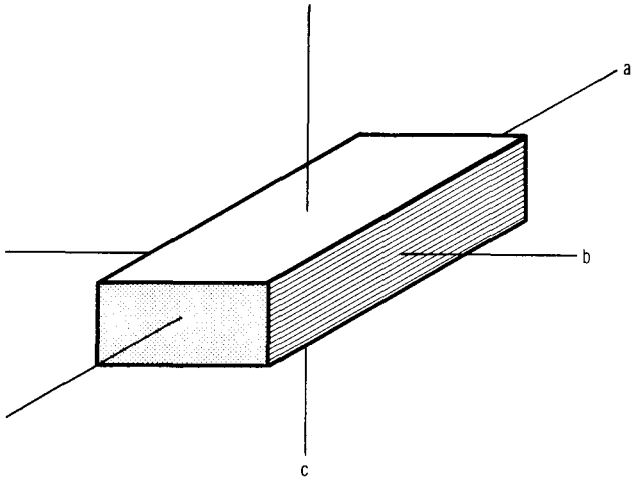

FIGURE 1. - SCHEMATIC DIAGRAM OF A UNIAXIAL CARBON FIBER - EPOXY COMPOSITE SHOWING THE A-, B-, AND C- DIRECTIONS.

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Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-100236		

4. Title and Subtitle	5. Report Date
The Effect of Bromination of Carbon Fibers on the Coefficient of Thermal Expansion of Graphite Fiber - Epoxy Composites	November 1987
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
D.A. Jaworske and C. Maciag	E-3665-1
	10. Work Unit No. 506-41-46

9. Performing Organization Name and Address	11. Contract or Grant No.
National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191	
	13. Type of Report and Period Covered: Technical Memorandum
12. Sponsoring Agency Name and Address	14. Sponsoring Agency Code
National Aeronautics and Space Administration Washington, D.C. 20546-0001	

15. Supplementary Notes

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16. Abstract

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17. Key Words (Suggested by Author(s))	18. Distribution Statement
Graphite fibers Coefficient of thermal expansion Graphite fiber - epoxy composites	Unclassified - Unlimited Subject Category 24

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No of pages	22. Price*
Unclassified	Unclassified	5	A02

*For sale by the National Technical Information Service, Springfield, Virginia 22161