COMPOSITES FOR EXTREME ENVIRONMENTS

A symposium
sponsored by ASTM
Committee D-30 on
High Modulus Fibers and
Their Composites
Bal Harbour, Fla., 11 Nov. 1980

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Foreword

The symposium on Composites for Extreme Environments was held on 11 Nov. 1980 in Bal Harbour, Fla. ASTM Committee D-30 on High Modulus Fibers and Their Composites sponsored this symposium. N. R. Adsit of General Dynamics/Convair Division served as symposium chairman and edited this publication.

Related ASTM Publications

Joining of Composite Materials, STP 749 (1981), 04–749000–33

Methods and Models for Predicting Fatigue Crack Growth Under Random Loading, STP 748 (1981), 04–748000–30

Test Methods and Design Allowables for Fibrous Composites, STP 734 (1981), 04–734000–33

Fractography and Materials Science, STP 733 (1981), 04–733000–30

Fatigue of Fibrous Composite Materials, STP 723 (1981), 04–723000–33

Nondestructive Evaluation and Flaw Criticality for Composite Materials, STP 696 (1979), 04–696000–33

Composite Materials: Testing and Design (Fifth Conference), STP 674 (1979), 04–674000–33

A Note of Appreciation to Reviewers

This publication is made possible by the authors and, also, the unheralded efforts of the reviewers. This body of technical experts whose dedication, sacrifice of time and effort, and collective wisdom in reviewing the papers must be acknowledged. The quality level of ASTM publications is a direct function of their respected opinions. On behalf of ASTM we acknowledge with appreciation their contribution.

ASTM Committee on Publications

Editorial Staff

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SUMMARY

Introduction

This volume presents a state-of-the-art review of "Composites for Extreme Environments" by publishing the papers presented at a symposium by the same name held at Bal Harbour, Fla. on 11 Nov. 1980. The papers represent the latest data and applications of polyimide with use temperatures up to 316°C. Metal matrix composites which would be useful at extreme environments have been excluded from this volume as a result of government restrictions on publication of information for these materials.

Although the authors have made considerable progress in generating the data needed for designing with composites in extreme environments, the papers also point up the need for more complete studies. Results presented here can do much to guide future studies on composites.

The first of the three groups of papers covers recent work on polyimide matrix composites. They present an excellent review of the state-of-the-art for these materials and other information useful to all composite investigators.

The second set of papers addresses applications of epoxy matrix composites and is more limited in scope, but clearly shows that composite matrix can be used in some harsh environments. The conditions considered (for the space shuttle and for military aircraft) are real and represent areas where the breakthroughs on composites will be made.

The third set of papers continues the saga of what moisture does to epoxy-matrix composites. This area is one of great concern and has been covered in previous ASTM publications. Undoubtedly, it will be the topic of future symposiums.

N. R. Adsit

General Dynamics/Convair Division, San Diego, Calif. 92138; symposium chairman and editor.

Polyimides—Materials for High-Temperature Environments

T. T. Serafini[1] *and M. P. Hanson*[1]

Environmental Effects on Graphite Fiber Reinforced PMR-15 Polyimide

REFERENCE: Serafini, T. T. and Hanson, M. P., **"Environmental Effects on Graphite Fiber Reinforced PMR-15 Polyimide,"** *Composites for Extreme Environments, ASTM STP 768,* N. R. Adsit, Ed., American Society for Testing and Materials, 1982, pp. 5–19.

ABSTRACT: Studies were conducted to establish the effects of thermo-oxidative and hydrothermal exposure on the mechanical properties of T300 graphite fabric reinforced PMR-15 composites. The effects of hydrothermal exposure on the mechanical properties of HTS-2 continuous graphite fiber composites were also investigated. The thermo-oxidative stability characteristics of T300 fabric and T300 fabric/PMR-15 composites were determined. Flexural strengths of specimens from composites in the as-fabricated and environmentally exposed conditions were determined. The useful lifetime of T300 fabric/PMR-15 composites in air at 316°C was found to be about 100 h. The useful lifetimes in air at 228 and 260°C were determined to be 500 and 1000 h, respectively. Absorbed moisture was found to reduce the elevated temperature properties of both the T300 fabric and HTS-2 continuous fiber composites. The moisture effect was found to be reversible.

KEY WORDS: PMR-15 polyimide composites, graphite fabric, thermo-oxidative exposure, hydrothermal exposure, mechanical properties, composite materials

Fiber reinforced polymer matrix composites, particularly those based on epoxies, are achieving considerable acceptance as engineering materials for the fabrication of aerospace structural components. However, the maximum use temperature of fiber reinforced epoxies is limited to about 177°C. Until the development of PMR polyimides,[2] attempts to increase the use temperature of fiber reinforced composites by utilizing high temperature resistant polymers as matrix materials invariably met with little success. The commercial availability of prepreg materials based on the PMR polyimide, designated as PMR-15, now has made it possible to design and fabricate fiber reinforced polymer matrix composites for use at temperatures up to 316°C, or nearly twice the use temperature of epoxy-based composites.

[1] Head, Polymer Matrix Composites and materials engineer, respectively, National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio 44135.

[2] Serafini, T. T., Delvigs, P., and Lightsey, G. R., "Thermally Stable Polyimides from Solutions of Monomeric Reactants," *Journal of Applied Polymer Science*, Vol. 16, No. 905, 1972.

The effects of long-term exposure in air at elevated temperatures (thermo-oxidative exposure) and the combined effects of absorbed moisture and elevated temperatures (hydrothermal exposure) on composite properties are two areas of vital concern to the designers of composite structures. Many studies have been performed to determine the effects of thermo-oxidative exposure on the properties of PMR-15 reinforced with continuous graphite fibers. In contrast, studies to determine the effects of thermo-oxidative exposure on the properties of graphite fabric reinforced PMR-15 composites have not been reported. The area of hydrothermal effects on PMR-15 composites has not been extensively studied. Although the effects of hydrothermal exposure on the properties of PMR-15 reinforced with continuous Celion 6000 graphite fibers have been investigated,[3] the effects of hydrothermal exposure on T300 graphite fabric reinforced PMR-15 have not been reported.

The purpose of this investigation was to determine the effects of thermo-oxidative and hydrothermal environments on the properties of T300 graphite fabric/PMR-15 composites. The effects of hydrothermal exposure on the properties of HTS-2 continuous graphite fiber composites were also determined. The effects of the thermo-oxidative and hydrothermal environments on composite properties were established on the basis of changes to the room temperature and elevated temperature composite flexural strengths and moduli and interlaminar shear strengths after environmental exposure. The thermo-oxidative stability characteristics of T300 graphite fabric and T300 graphite fabric/PMR-15 composites also were determined.

Experimental Procedure

Materials

Style 182 fabric woven from Union Carbide T300 graphite fibers and Hercules HTS-2 graphite fiber tows were used as reinforcing materials. The T300 fibers consisted of 3000 filaments in a one-ply construction and were sized with an epoxy compatible sizing. The HTS-2 fibers consisted of 12 000 filaments per tow.

The polyimide resin used in this investigation was the high-temperature polyimide designated as PMR-15. The monomers used to formulate PMR-15 are shown in Fig. 1. The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) and 4,4′-methylenedianiline (MDA) were obtained from commercial sources. The dimethyl ester of 3,3′, 4,4′-benzophenonetetracarboxylic acid (BTDE) was prepared as a 50 weight percent solution by refluxing a suspension of the corresponding dianhydride in anhydrous methanol for approximately 2.75 h. The monomer stoichiometry for the PMR-15 solution

[3] Davis, J. G., Jr., "High Temperature Resin Matrix Composites for Aerospace Structures," *Selected NASA Research in Composite Materials and Structures*, NASA CP 2142, National Aeronautics and Space Administration, 1980, pp. 143–182.

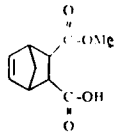
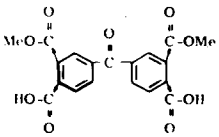
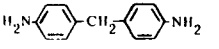
STRUCTURE	NAME	ABBREVIATION
	MONOMETHYL ESTER OF 5-NORBORNENE-2,3-DICARBOXYLIC ACID	NE
	DIMETHYL ESTER OF 3,3',4,4'-BENZOPHENONETETRACARBOXYLIC ACID	BTDE
	4,4'-METHYLENEDIANILINE	MDA

FIG. 1—*Monomers used for PMR-15 polyimide.*

was 2NE/3.087MDA/2.087BTDE. The PMR-15 solution was prepared by dissolving the monomers in a calculated amount of anhydrous methanol to yield a 50 weight percent solution.

Composite Fabrication and Specimen Preparation

To prepare the unidirectional fiber prepreg tape, the HTS-2 tows were wound on a drum at approximately 3 turns per centimeter, and impregnated with a predetermined quantity of resin to provide cured laminates having a fiber content of 55 to 60 volume percent. The prepregs were air dried to reduce the solvent content to approximately 10 percent prior to removal from the drum. HTS-2 laminates having a thickness of 0.20 cm were prepared by cutting 7.6 by 20.3 cm plies from the prepreg tape and unidirectionally stacking ten plies between porous Armalon fabric in a preforming mold. The stacked layup was imidized at 204°C for 1 h under a pressure of approximately 0.07N/cm^2. Compression molding was accomplished by placing the preform into a matched metal die that had been preheated to 232°C. Following a dwell time of 5 min at essentially zero pressure, a mold pressure of 345N/cm^2 was applied, and the mold temperature was increased to 288°C at the rate of 5.6°C/min. Pressure and temperature were maintained for 2 h, followed by cooling to 204°C before releasing the pressure and removing the laminate from the die. The cured laminates were postcured in an air circulating oven in which the temperature was raised from ambient temperature to 288°C at a rate of 2.2°C/min and held at 288°C for 16 h.

The T300 graphite fabric/PMR-15 prepreg was obtained from a commercial source with a resin content of approximately 40 percent by weight. Laminates having thicknesses of 0.14 and 0.28 cm were fabricated using the same procedure that was employed for the unidirectional HTS-2/PMR-15 lami-

nates. All plies for the fabric laminates were stacked with their warp yarns in the 0-deg direction.

Composite Environmental Exposure

Coupons (approximately one third of a 7.6 by 20.3 cm laminate) were subjected to either thermo-oxidative or hydrothermal exposure. All of the coupons were cut from essentially void-free laminates as assessed by ultrasonic C scan. The thermo-oxidative environments were provided by air circulating ovens. Bleed air was metered into the ovens at a rate of 100 cm^3/min. Coupons were periodically removed from the ovens, and allowed to cool to room temperature in a desiccator before reweighing to determine weight losses. The hydrothermal environment was accomplished by supporting the laminate coupons in a closed chamber above a water bath held at 82°C so that condensate formed on the laminate surfaces. The coupons were periodically removed from the chamber, blotted dry, and then weighed. After saturation had been attained (no significant increase in coupon weight with increased exposure time), the coupons were removed from the chamber and sealed in a vapor-proof container. The conditioned coupons were cut into flexural and short beam shear specimens using a diamond cutting blade. Flexural specimens were 1.27 cm wide by 6.67 cm long. The short beam shear specimens were 0.64 cm wide; the lengths of the specimens were selected so as to result in a shear test span-to-thickness ratio of 4.

Composite Testing

Flexural tests conformed essentially to the ASTM Tests for Flexural Properties of Plastics and Electrical Insulating Materials [D 790-71 (1978)]. Tests were made on a 3-point loading fixture with a variable span. Tests were performed using a span-to-thickness ratio of approximately 32. The rate of center loading for flexural testing was 0.127 cm/min. Interlaminar shear strength tests were conducted in accordance with the ASTM Test for Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short Beam Method (D 2344-76) using a constant span-to-thickness ratio of 4. For the elevated temperature tests, the load was applied to the specimens after the chamber had equilibrated at the test temperature for 10 min. A limited number of temperature spike tests were performed on moisture-saturated specimens. For these tests, the load was applied to the specimen immediately after the specimen was installed in the preheated test fixture.

Results and Discussion

Fiber and Composite Thermo-Oxidative Stability

Figure 2 shows the weight loss characteristics of T300 and HTS-2 graphite fibers after isothermal exposure in air at 316°C. The data for the HTS-2 fi-

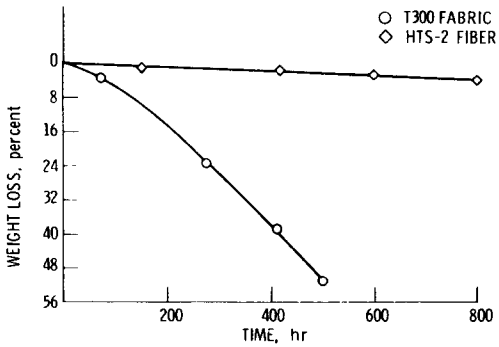


FIG. 2—*Weight loss of graphite fibers exposed in air at 316°C.*

bers were taken from Delvigs, Alston, and Vannucci.[4] The superior thermo-oxidative stability of the HTS-2 fibers is clearly evident. After 800 h of exposure in air at 316°C, the weight loss of the HTS-2 fibers was only 4.2 percent, compared to the 50 percent weight loss exhibited by the T300 fibers after 500 h in air at 316°C. The comparatively poor elevated temperature thermo-oxidative stability of T300 fibers very likely would be manifested in inferior composite performance at temperatures approaching 316°C.

The weight loss behavior of T300 graphite fabric/PMR-15 composites as a function of exposure time is shown in Fig. 3 for composites exposed in air at 260, 288, and 316°C. In contrast to the behavior of the bare unprotected T300 fibers, which exhibited a weight loss of 50 percent after 500 h of exposure at 316°C, the weight loss of the T300/PMR-15 composites was only 4.8 percent after 500 h at 316°C. The significant increase in the rate of composite weight loss after about 400 h at 316°C is clearly evident. Similar weight loss behavior has not been reported previously for graphite fiber reinforced PMR-15 composites exposed at 316°C. The significantly increased weight loss rate found in this study for the T300/PMR-15 composites is undoubtedly due to the limited thermo-oxidative stability of the T300 fibers at 316°C. As expected, the T300/PMR-15 composites exhibited improved oxidative stability at 260 and 288°C. After 1000 h at 288°C and 500 h at 260°C, the composite weight losses were only 4.2 and 0.8 percent, respectively. The results of these composite weight loss studies indicate that the useful life of T300/PMR-15 composites at 316°C is likely less than 400 h and is at least 1000 h at 260 and 288°C.

Figure 4 shows the flexural and interlaminar shear properties retention characteristics of 0.14-cm-thick laminates and the flexural properties retention characteristics of 0.28-cm-thick laminates. Specimens of both thicknesses were exposed at 316°C for various time intervals, and then tested at

[4] Delvigs, P., Alston, W. B., and Vannucci, R. D., "Effects of Graphite Fiber Stability on the Properties of PMR Polyimide Composites," NASA TM 79062 and AVRADCOM TR 78-62, National Aeronautics and Space Administration, May 1979.