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FURTHER DEVELOPMENT OF HIGH TEMPERATURE-RESISTANT GRAPHITE FIBER COUPLING AGENTS

Prepared for

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William B. Alston, Project Manager

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by

R. N. Griffin

General Electric Company
Space Sciences Laboratory
P. O. Box 8555
Philadelphia, Pennsylvania 19101

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16 Abstract

Seven potential coupling agents for graphite fibers were screened by their effect on the weight losses of Thornel 300, HMS, and HTS fibers at 588K for 200 and 400 hours.

Unidirectional laminates were made from HMS and HTS fibers, untreated, and treated with each of the seven coupling agents. The matrix of all laminates was PMR polyimide (PMR-PI). On the basis of the best overall retention of elevated temperature interlaminar shear strength after 200 hours at 588K, composite weight after 200 hours at 588K, and fiber weight after 400 hours at 588K, Ventromer T-1 applied from aqueous solution and pyrolyzed PPQ were selected for further evaluation as coupling agents for HTS fiber while Ventromer T-2 and pyrolyzed PPQ were selected as coupling agents for HMS fiber.

Laminates made with the untreated fibers and with fibers treated with the selected coupling agents were then exposed in air and in nitrogen for periods up to 1000 hours at 588K. Composite wieght losses were measured, and interlaminar shear strengths measured at 297K and 588K.

Laminates made from HTS fiber with pyrolyzed PPQ as a coupling agent were subjected to further testing. Flexural strength and modulus, impact strength, and transverse tensile strength were determined at 297K and 588K for samples in air and in nitrogen at 588K for periods up to 1000 hours. The above properties plus interlaminar shear strength were also determined at 297K and 588K the day after exposure to boiling water for two hours.

It was shown that pyrolyzed PPQ as a coupling agent improves the oxidative stability of HTS/PMR-PI composites.

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Composites - Coupling Agent - Fiber - Graphite - Polyimide - Ventromer - Interface - Flexure - Pyrolyzed Polyphenylquinoxaline - Interlaminar Shear - Impact - Transverse Tensile - PMR

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FOREWORD

This document constitutes the final report of the work accomplished between 8 January 1975 and 7 October 1975, by the General Electric Company for the National Aeronautics and Space Administration, Lewis Research Center, under contract NAS 3-18931, on Further Development of High Temperature-Resistant Graphite Fiber Coupling Agents.

This work was performed under the technical direction of Dr. William B. Alston of the Lewis Research Center, Cleveland, Ohio.

The Space Processing Programs Section of the Space Sciences Laboratory was responsible for the work performed on this program. Mr. Louis R. McCreight, Manager, Space Processing Programs Section, provided overall program supervision and management. The principal investigator responsibilities for the program were performed by Dr. R. N. Griffin. Major technical contributions throughout the program were provided by Mr. E. F. Muziani and Mr. R. J. Grosso.

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SUMMARY

The objective of this program was to develop improved high temperature resistant coupling agents for polyimide/graphite fiber composites. Seven potential coupling agents were investigated on Thornel 300, HMS, and HTS graphite fibers. Weight losses of the three fibers with the seven coupling agents were determined at 588K 600°F in a circulating air oven for 200 and 400 hours. Composites were made from HMS and HTS fibers and polyimide made by polymerization of monomeric reactants (PMR) using the monomethyl ester of 5 norbornene-2, 3 dicarboxylic acid, 4, 4'-methylenedianiline, and the dimethyl ester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid in a molar ratio of 2:3.087:2.087. Interlaminar shear strength of the composites was measured at 297K and 588K, and at 588K after 200 hours exposure at 588K.

On the basis of these tests the best coupling agent/fiber combinations were determined to be HMS fiber treated with Ventromer T-2, HMS fiber treated with pyrolyzed PPQ, HTS fiber treated with Ventromer T-1, and HTS fiber treated with pyrolyzed PPQ. The interlaminar shear strengths of these composites were determined at room temperature and 588K before and after aging in air and nitrogen at 588K for times up to 1000 hours.

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Laminates of PMR/PI and HTS graphite fiber treated with pyrolyzed PPQ were also tested for flexural strength and modulus, transverse tensile strength, and impact strength before and after aging at 588K in air and in nitrogen for exposure times up to 1000 hours. The coupling agent appeared to improve the retention of flexural strength and modulus, interlaminar shear and impact strength of the HTS composites, but did not appear to have any beneficial effect on the retention of transverse tensile strength after prolonged exposure at 588K.

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I. INTRODUCTION

One of the chief problems in the development of high-modulus carbon fiber reinforced composites is the fact that under multiaxial stress conditions, many of these composites appear to fail within the matrix or at the filament-matrix interface rather than by rupture of the filaments.

The surface treatments that are used for graphite/epoxy systems are not adequate for use with high temperature resins. The short time elevated temperature interlaminar shear and transverse tensile strength of polyimide/graphite composites are significantly lower than the room temperature values. Composites exposed in air to elevated temperatures exhibit excessive further decreases in these strength values. In earlier work we developed two coupling agents which were shown to increase the room temperature and elevated temperature interlaminar shear strength of polyimide/graphite composites (1), and to improve the stability of these properties when the composites are exposed in air to elevated temperatures. The purpose of this program was to optimize the previously-developed coupling agents, and to extend their use to other commercially available carbon fibers. One of the coupling agents developed previously was a reaction product of titanium tetrachloride and trimethylborane.

Optimum conditions for applying this material to the carbon fiber were found, and the use of other closely related products as coupling agents was investigated.

II. MATERIALS

A. Polyimide Matrix

The polyimide used throughout this study was formed from the monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid (NE), 4, 4'-methylenedianiline (MDA), and the dimethyl ester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid (BTDE) in the molar ratio of 2:3.09:2.09, giving a "formulated molecular weight" of 1500.

5-Norbornene-2, 3, -dicarboxylic anhydride (NA) was made from cyclopentadiene and maleic anhydride according to the literature procedure. A 95% yield of material, m.p. 431-433K (158-160C) (Lit. 164-5C (2) was obtained. The monomethyl ester was prepared according to Walton. After two washes with isopropyl ether and two washed with ligroin the product was obtained in 79% yield, m.p. 374-375K (101-102C) (Lit. 375-376K) (102-103C). (3)

The dimethyl ester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid was prepared by heating benzophenonetetracarboxylic dianhydride (BTDA) with methanol according to the method of Serafini, Delvigs, and Lightsey. (4) A fresh ester solution was prepared and immediately used for each polyimide formulation. The proper amount of anhydride was heated in refluxing methanol, and the solution used directly in the polymer formulation without isolation of the BTDE.

Eastman 4,4'-methylenedianiline, 500 g, was dissolved in 2.5 liters of boiling isopropanol containing decolorizing carbon. The mixture was filtered hot through a filter-aid cake and allowed to crystallize. Recovery was 80%, m.p. 365-366K (92-93C).

A 40 weight percent solution of the three monomers in methanol was applied to drum wound tapes of graphite fibers. The prepreg was heated at 323K (50C) for two hours on the drum to reduce the solvent content to less than 10 percent.

B. Graphite Fiber

For the selection and preliminary evaluation of coupling agents, three types of graphite fiber were used. Union Carbide's Thornel 300 graphite yarn, grade WYP 30 1/0 was used for comparison with our earlier work(1) along with Hercules HTS and HMS graphite fibers. Composites were prepared from the polyimide and HMS and HTS fibers for evaluation of composite density, fiber volume, resin content, void content, and interlaminar shear strength at room temperature and 588K. Finally, HTS graphite fiber was used to prepare laminates for flexural strength and modulus, impact strength and transverse tensile strength measurements.

C. Coupling Agents or Surface Treatments

Seven methods for improving the elevated temperature stability of graphite/polyimide composites were selected for evaluation. The seven treatments and the code thereof are listed in Table 1.

Table 1

Fiber Treatment Code

0	Control, no treatment
11	Ventromer T-1 applied from aqueous solution
12	Ventromer A-1 applied from aqueous solution
13	Ventromer T-1 in methanol
14	Ventromer A-1 in methanol
15	Ventromer T-2 in methanol
16	Ventromer A-2 in methanol
17	Pyrolyzed PPQ

Treatment #11, Ventromer T-1 applied from aqueous solution, is similar to one of the treatments used in last year's work. The Ventromer was applied to the graphite surface either as a 0.33% solution dissolved in water containing 0.33% sodium tripolyphosphate and neutralized to pH 7 with ammonium hydroxide, or alternatively as a 0.33% solution which had been treated gradually to form a prepolymer. No differences were found between the two methods of application.

Treatment #12 was analogous, using the Ventromer A-1. In this case, however, neutralization was unnecessary since the solution of Ventromer A-1 and sodium tripolyphosphate is essentially neutral.

Treatment #13 involved a 0.33% solution of Ventromer T-1 in methanol.

Treatment #14 involved a 0.33% solution of Ventromer A-1 in methanol.

Treatments #15 and #16 were analogous to treatments #13 and #14 except with the Ventromers T-2 and A-2 respectively.

Treatment #17 was carried out with a 0.1% solution of PPQ in N-methyl pyrrolidone, B staging of the PPQ, and pyrolysis at 1050°C in nitrogen for 3 minutes.

Ventromer T-2 and Ventromer A-2 were made according to the procedure of Wade (5).

III. COUPLING AGENTS SELECTION AND PRELIMINARY EVALUATION

A. Fiber Weight Loss Tests

The seven coupling agents were applied to Thornel 300, HTS, and HMS fibers as described above. Treated fibers were exposed in a circulating air oven at 588K for 200 and 400 hours. The complete set of fiber weight loss data is shown in Table 2. The only coupling agent which appeared to diminish the rate of fiber weight loss was pyrolyzed PPQ (Treatment #17). Among the other coupling agents there was relatively little difference, although Ventromer T-1 (Treatment #11) applied from aqueous solution appeared to be slightly better than the remainder. Subsequently, fiber weight loss data were extended to 1000 hours exposure at 588K for the following selected graphite fiber/coupling agent combinations: Thornel 300 fiber, no surface treatment, Ventromer T-1, pyrolyzed PPQ, and Ventromer A-2; HTS fiber, no surface treatment, Ventromer T-1. and pyrolyzed PPQ; HMS fiber, no surface treatment, Ventromer T-2, pyrolyzed PPQ, and Ventromer A-2. It is shown clearly in Table 3 that the HMS fiber is far more stable than either the HTS or the Thornel 300 at 588K. It is also evident that neither of the Ventromer treatments has an appreciably beneficial effect on the oxidative stability of Thornel 300 or HTS; but pyrolyzed PPQ coupling agent appears to improve significantly the oxidation resistance of both these fibers.

TABLE 2

FIBER WEIGHT LOSSES UP TO 400 HOURS IN AIR

Fiber	Treatment	Percentage Weight Loss 200 hours	 400 hours
Thornel 300	0	12.96	30.06
	11	21.19	44.44
	12	21.32	47.05
	13	20.97	46.64
	14	21.86	48.15
	15	25.76	54.47
	16	23.94	54.16
	17	5.27	19.28
HTS	0	19.65	28.38
	11	18.74	29.48
	12	20.26	35.67
	13	31.31	44.88
	14	32.05	47.05
	15	31.61	51.43
	16	34.64	51.74
	17	6.79	10.10
HMS	0	0.94	0.50
	11	0.28	0.23
	12	0.28	0.30
	13	0.50	0.36
	14	0.40	0.48
	15	0.31	0.30
	16	-	0.07
	17	0.56	0.22

TABLE 3

FIBER WEIGHT LOSSES UP TO 1000 HOURS AT 588K IN AIR

		Percentage Weight Loss				
Fiber	Treatment	200 hrs.	400 hrs.	600 hrs.	800 hrs.	1000 hrs.
Thornel 300	None	12.96	30.06	42.50	57.26	64.77
	Ventromer T-1	21.19	44.44	67.50	81.09	86.89
	Pyrolyzed PPQ	5.27	19.28	27.62	43.21	50.10
	Ventromer A-2	23.94	54.16	67.93	77.56	82.85
HTS	None	19.65	28.38	34.42	36.94	39.31
	Ventromer T-1	18.74	29.48	36.08	38.73	42.20
	Pyrolyzed PPQ	6.79	10.10	9.88	13.36	14.09
HMS	None	0.94	0.50	1.00	0.66	0.64
	Ventromer T-2	0.28	0.23	0.39	0.39	0.35
	Pyrolyzed PPQ	0.56	0.22	0.36	0.56	0.32
	Ventromer A-2	-	0.07	0.05	0.07	-

B. Composites Fabrication and Testing

Sixteen PMR polyimide/graphite laminates were prepared from HTS and HMS fibers, and the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid, 4,4'-methylenedianiline, and the freshly prepared dimethylester of 3,3',4,4'-benzophenonetetracarboxylic acid. Ultrasonic C-scans of these 16 laminates showed that they were generally free of voids with the notable exception of the laminate made with HMS fiber treated with Ventromer A-2. This particular laminate had so little void-free area that *there was barely enough material for the preparation of interlaminar shear* and resin content specimens. The properties of the sixteen laminates are summarized in Table 4. The laminates were prepared by winding the graphite fiber on a mandrel, impregnating with the calculated amount of a 40% methanol solution of the monomer mixture, and drying under heat lamps. After the pre-preg was dry, it was removed from the mandrel, stacked between Teflon-coated glass and aluminum foil, and imidized for 2 hours at 400°F 477K in an oven. It was transferred to a pre-heated (477K) mold, and placed in a press at ~~505K~~ 450°F for 10 minutes under contact pressure. Pressure of 3.45 MPa (500 psi) was applied and maintained while heating to ~~588K~~ 600°F and holding for 1 hour. The composite was cooled slowly to 477K, then rapidly to room temperature. Post-curing was accomplished according to the following schedule:

TABLE 4 - COMPOSITE PANELS MADE FROM PMR-POLYIMIDE AND GRAPHITE FIBERS FOR TASK 1 TESTS

Fiber Type	Treat-Ment #	Treatment	Prepreg Weight, Grams	Weight Cured Panel, Grams	Weight Loss, Grams	Bulk Density Before Post-Cure	Density of Resin Content Samples	% Resin Content	Volume Fraction Resin, %	Volume Fraction Fibers, %	Volume Fraction Voids, %
HMS	0	None	58.7	50.7	8.0	1.64	1.65	28.75	36.71	62.49	0.79
HMS	11	Ventromer T-1, aqueous	60.6	50.0	9.1	1.65	1.65	28.13	36.26	61.37	2.36
HMS	12	Ventromer A-1, aqueous	59.4	53.3	6.1	1.62	1.63	31.33	38.50	60.52	0.90
HMS	13	Ventromer T-1, non-aqueous	58.9	52.1	6.8	1.59	1.64	29.09	37.93	60.92	1.15
HMS	14	Ventromer A-1, non-aqueous	66.7	53.9	12.6	1.64	1.63	29.92	36.73	62.12	1.15
HMS	15	Ventromer T-2	66.1	54.2	11.9	1.56	1.63	30.97	37.28	59.94	2.78
HMS	16	Ventromer A-2	59.9	53.3	6.6	1.58	1.63	31.06	38.70	58.76	2.54
HMS	17	PPQ pyrolyzed	64.6	53.2	11.4	1.62	1.64	29.81	38.73	60.36	0.91
HTS	0	None	61.5	53.6	7.9	1.52-	1.61	29.80	36.35	60.28	3.37
HTS	11	Ventromer T-1, aqueous	56.2	51.5	4.7	1.55	1.58	31.46	39.06	59.06	1.88
HTS	12	Ventromer A-1, aqueous	57.3	53.0	4.3	1.53	1.56	31.61	38.58	57.76	3.66
HTS	13	Ventromer T-1, non-aqueous	61.0	52.7	8.3	1.57	1.59	30.98	38.42	59.70	1.88
HTS	14	Ventromer A-1, non-aqueous	61.0	51.7	7.3	1.55	1.59	31.98	38.74	58.37	2.89
HTS	15	Ventromer T-2	60.2	53.5	6.7	1.57	1.59	32.19	37.94	60.42	1.64
HTS	16	Ventromer A-2	58.7	52.9	5.8	1.54	1.58	34.78	39.91	58.58	1.51
HTS	17	PPQ Pyrolyzed	60.0	52.3	7.7	1.54	1.58	28.13	35.64	61.15	3.20

Composite Weight Losses After 200 Hours at 588K in Air

Fiber	Treatment Number	% Wt. Loss of Three Samples	Avg.	Fiber	Treatment Number	% Wt. Loss of Three Samples	Avg.
HMS	0	1.15 1.22 1.27	1.21	HTS	0	2.13 1.79 1.90	1.94
	11	1.44 1.06 1.78	1.43		11	1.63 1.71 2.42	1.92
	12	1.99 1.55 1.58	1.71		12	1.83 2.05 1.98	1.95
	13	1.24 0.78 0.84	0.95		13	2.01 2.00 2.36	2.12
	14	1.88 1.92 1.63	1.81		14	2.08 1.81 1.71	1.87
	15	0.98 1.12 1.24	1.11		15	2.10 1.83 1.92	1.95
	16	0.99 0.79 0.78	0.85		16	2.25 2.20 2.16	2.20
	17	0.99 1.77 1.03	1.26		17	1.64 1.67 1.78	1.70

Room temperature to 505K in 8 hours
505K - hold for 16 hours
588K - hold for 24 hours
588K to room temperature overnight.

Weight losses of the 16 laminates were measured after 200 hours exposure in a circulating air oven at 600°F 588K. The weight losses of the composites made with HMS fiber were all quite low. In the worst case the weight loss amounted to 1.8% in the composite made with HMS fiber treated with Ventromer A-1 (Treatment #14). The smallest weight loss observed was 0.85%, in the laminate made with HMS fiber and Ventromer A-2 (Treatment #16). As might be expected, the weight losses of the HTS laminates were generally higher than those of the HMS laminates. The lowest weight loss observed with the HTS laminates was with the composite made from HTS fiber treated with pyrolyzed PPQ (Treatment #17). The highest weight loss observed was with HTS fiber treated with Ventromer A-2 (Treatment #16). These data are summarized in Table 5.

The interlaminar shear strengths of the 16 laminates were measured at room temperature, at 588K, and at 588K after 200 hours exposure in a circulating air oven at 588K. The data are summarized in Table 6.

On the basis of the interlaminar shear strength data and the composite and fiber weight loss data, two surface treatments were selected for further investigation with each of the two graphite fibers. The surface treatments

TABLE 6

INTERLAMINAR SHEAR STRENGTH OF POLYIMIDE COMPOSITES

Treatment	Fiber	ILSS at 298K MPa$_1$	ILSS at 588K MPa$_1$	ILS at 588K After 200 Hrs. at 588K MPa$_1$	% Increase
0	HMS	72.6	48.9	59.3	21.3
11		53.8	44.7	49.6	11.0
12		52.4	43.3	49.6	14.5
13		66.4	42.6	53.1	24.6
14		65.7	36.3	52.4	44.3
15		66.4	41.2	57.3	39.1
16		63.6	37.0	52.4	41.6
17	HMS	83.1	45.4	56.6	24.7
0	HTS	115.3	58.0	63.6	9.7
11		108.3	50.3	62.9	25.0
12		93.6	48.2	58.7	21.8
13		85.2	51.0	60.1	17.8
14		104.8	44.7	60.8	36.0
15		98.5	50.3	60.8	20.9
16		111.1	50.3	57.3	13.9
17	HTS	119.4	49.6	60.1	21.2

selected for further evaluation with HMS fiber were pyrolyzed PPQ and Ventromer T-2 (Treatments #17 and 15). For HTS fiber the surface treatments selected were pyrolyzed PPQ and Ventromer T-1 applied from aqueous solution (Treatments #17 and 11).

IV. PREPARATION AND EVALUATION OF COMPOSITES

The six laminates selected in the screening work were aged at 588K in air and in nitrogen for periods up to 1000 hours, and the weight losses and interlaminar shear strengths of the laminates were measured at 200, 500, and 1000 hours. The composites included those made with HMS fiber, untreated, treated with Ventromer T-2, and treated with pyrolyzed PPQ; composites made with HTS fiber,untreated, treated with Ventromer T-1, and treated with pyrolyzed PPQ.

Aging in nitrogen caused little loss of weight as is indicated clearly in Table 7. Exposure in air at 588K, however, caused considerably greater losses in weight of the laminates. As indicated in Table 8 the two coupling agents tested with each of the two fibers appeared to make little difference in the weight loss of HMS composites, while both seemed to improve the HTS composites. There was, however, at least a 3:1 ratio in the weight losses observed with the HTS composites and the HMS composites. This was to be expected in the light of the results of the fiber weight loss studies.

Interlaminar shear strength data obtained after exposures at 588K for 200, 500 and 1000 hours in air and in nitrogen are summarized in Table 9. The most noteworthy results was that after 1000 hours at 588K in air, the HTS laminate made without coupling agent was reduced to a pile of disconnected fibers. Figure 1 shows the difference between the HMS and HTS composites after aging. All the HTS samples had a number of loose fibers on the outside.

TABLE 7

COMPOSITE WEIGHT LOSSES AT 588K IN NITROGEN

Fiber	Treatment	Percent Weight Loss 200 hrs.	500 hrs.	1000 hrs.
HMS	None	0.34	0.55	0.65
	Ventromer T-2	0.59	0.63	1.10
	Pyrolyzed PPQ	0.55	0.57	0.77
HTS	None	0.77	1.01	1.21
	Ventromer T-1	0.87	1.17	1.33
	Pyrolyzed PPQ	0.90	0.86	1.17

TABLE 8

COMPOSITE WEIGHT LOSSES AT 588K IN AIR

Fiber	Treatment	Percent Weight Loss 200 hrs.	 500 hrs.	 1000 hrs.
HMS	None	1.21	2.14	6.39
	Ventromer T-2	1.14	1.77	5.32
	Pyrolyzed PPQ	1.26	2.11	5.47
HTS	None	1.94	5.03	25.43
	Ventromer T-1	1.92	4.55	15.32
	Pyrolyzed PPQ	1.70	4.34	18.66

TABLE 9

INTERLAMINAR SHEAR STRENGTH OF POLYIMIDE/GRAPHITE FIBER COMPOSITES, MPa

	Aged in Air Environment HTS Fibers Treatment No. *			Aged in Nitrogen Environment HTS Fibers Treatment No.			Aged in Air Environment HMS Fibers Treatment No.			Aged in Nitrogen Environment HMS Fibers Treatment No.		
Temp, K/Time Aged	0	11	17	0	11	17	0	15	17	0	15	17
Tested @ 297K/0 hours	91.0	104.8	117.2				73.8	65.5	79.3			
	124.1	108.9	118.6				71.0	66.2	82.1			
	126.2	107.6	117.2				71.0	64.1	84.5			
Tested @ 588 K/0 hrs.	58.6	47.6	49.0				49.0	38.6	44.8			
	56.5	48.3	48.3				48.3	33.1	44.1			
	56.5	53.8	50.3				47.6	49.6	46.2			
Tested @ 588 K/200 hrs. @ 588 K	62.1	63.4	60.0	59.3	57.9	54.5	52.4	56.5	56.5	50.3	51.7	53.8
	62.7	61.4	58.6	60.7	60.7	56.5	56.5	56.5	54.5	55.2	49.0	54.5
	63.4	61.4	58.6	60.0	57.2	55.2	66.9	57.2	55.8	56.5	46.2	53.1
Tested @ 297K/200 hrs. @ 588 K	82.0	100.0	99.3	129.6	108.3	115.1	66.9	65.5	83.4	66.2	64.1	86.9
	122.0	95.2	98.6	128.2	100.7	113.1	67.6	66.2	82.7	62.7	62.7	89.6
	122.7	108.3	108.9	93.8	103.4	109.6	68.9	65.5	85.5	66.9	79.8	89.6
Tested @ 588 K/500 hrs. @ 588 K	51.0	52.4	49.6	50.3	54.5	55.2	49.6	48.3	49.0	43.4	45.5	49.0
	52.4	55.2	48.3	60.7	54.5	55.8	47.6	46.9	49.6	42.7	46.2	48.3
	53.1	55.8	49.6	61.4	55.1	59.3	47.6	47.6	50.3	42.7	44.8	50.3
Tested @ 297K/500 hrs. @ 588 K	106.9	99.3	106.2	133.1	109.6	110.3	56.5	68.3	81.4	58.3	75.5	76.5
	108.9	104.8	103.4	95.8	107.6	109.6	58.6	65.5	79.3	57.9	71.7	76.5
	106.2	105.5	97.2	131.0	103.4	106.9	57.9	61.4	78.6	62.0	73.8	74.5
Tested @ 588 K/1000 hrs. @ 588 K	NA**	64.1	55.2	68.3	NA***	67.6	42.1	43.4	48.3	47.6	54.1	55.2
		61.4	59.3	68.3	66.2	65.5	42.1	37.9	48.3	54.5	53.0	51.7
		60.0	57.9	68.3	68.3	66.2	39.3	49.6	48.3	54.5	53.4	55.2
Tested @ 297K/1000 hrs. @ 588°K	NA**	106.2	104.8	137.2	114.5	118.6	60.7	63.4	57.9	68.9	72.4	83.3
		108.2	102.7	133.1	118.6	111.0	68.3	68.3	60.7	71.0	70.3	86.7
		107.6	92.7	139.3	117.2	112.4	59.3	64.8	60.7	71.0	71.7	82.4

** Degradation too severe to permit ILSS Test.
*** Test equipment failure.

* Treatment No.

0 - Untreated
11 - Ventromer T-1, Aqueous
15 - Ventromer T-2
17 - PPQ Pyrolyzed

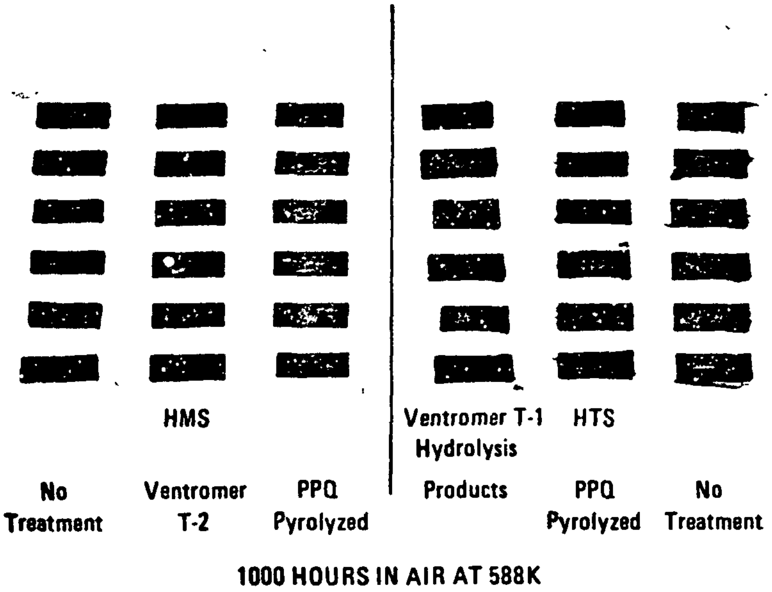

Figure 1. Graphite Fiber Composites After 1000 Hours at 588K in Air.

Although it is not evident from Figure 1, the HTS samples made with coupling agents still had good integrity with only surface damage, while the control samples were destroyed. The HMS laminates showed little evidence of damage after the 1000 hours exposure in air at 588K.

V. ADVANCED COMPOSITE EVALUATION

The laminates of HTS graphite fiber treated with pyrolyzed PPQ were selected by the NASA Project Manager as the material for complete evaluation. Laminates were prepared from PMR/PI and HTS fiber treated with pyrolyzed PPQ. Control panels were prepared from PMR/PI and HTS fiber without surface treatment. The laminates were examined by ultrasonic C-scans, and void-free areas were used for interlaminar shear strength tests after water boiling, flexural strength and modulus, transverse tensile strength, and impact strength. Tests were performed at 297K and 588K.

A. Interlaminar Shear Strength After Water Boiling

Interlaminar shear strengths were measured at 297K and 588K the day following a 2-hour exposure to boiling water. Comparison of the data in Tables 9 and 10 indicates clearly that the boiling water treatment had no significant effect on the laminates.

Table 10

Interlaminar Shear Strength After Boiling Water Exposure

Treatment	ILSS @ 297K, MPa	ILSS @ 588K, MPa
Pyrolyzed PPQ	124	50.3
	121	51.7
	120	49.6
Control	129	50.3
	128	48.9
	130	48.9

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Table 11. Flexural Strength and Modulus of Composites with Untreated HTS Fiber.

Temp.	Aged Hours	Atmos-phere	Tested at	Flexural Strength MPa x 10^{-2}	Flexural Modulus MPa x 10^{-4}	Temp.	Aged Hours	Atmos.	Tested at	Flexural Strength MPa x 10^{-2}	Flexural Modulus MPa x 10^{-4}
-	0	-	297K	16.2	11.3	588K	500	Air	588K	8.99	9.86
			"	16.6	11.2					10.3	10.2
			"	16.9	11.4					10.4	9.86
Water Boil			297K	15.7	10.8	588K	500	Air	297K	14.4	10.2
			"	15.7	11.1					11.4	9.52
			"	15.4	10.6					12.9	10.1
-	0	-	588K	11.0	11.4	588K	500	N_2	588K	9.84	10.7
			"	10.4	11.3					10.2	10.6
			"	10.4	10.3					11.1	11.0
Water Boil		-	588K	9.48	10.5	588K	500	N_2	297K	14.3	10.9
			"	9.52	10.6					14.0	10.7
			"	9.54	9.79					12.9	10.8
588K	200	Air	588K	11.9	10.5	588K	1000	Air	588K	6.75	6.05
			"	11.2	10.5					7.06	6.56
			"	10.7	10.5					6.94	6.44
588K	200	Air	297K	7.78	10.0	588K	1000	Air	297K	9.03	6.87
				8.72	10.3					7.84	6.11
				14.1	10.7					7.37	5.87
588K	200	N_2	588K	11.7	10.2	588K	1000	N_2	588K	10.2	11.5
				11.1	10.1					9.83	11.2
				11.0	11.4					10.5	11.0
588K	200	N_2	297K	16.2	10.9	588K	1000	N_2	297K	9.42	11.1
				15.0	11.1					9.49	11.0
				16.2	11.2					9.60	11.3

Table 12. Flexural Strength and Modulus of HTS Composites with *Pyrolyzed PPQ Coupling Agent*

Aged		Atmos-phere	Tested at	Flexural Strength MPa x 10^{-2}	Flexural Modulus MPa x 10^{-4}	Aged		Atmos.	Tested at	Flexural Strength MPa x 10^{-2}	Flexural Modulus MPa x 10^{-4}
Temp	Hours					Temp.	Hours				
-	0	-	297K	14.7	10.6	588K	500	Air	588K	10.4	11.7
				15.1	11.0					9.88	11.3
				16.2	11.6					9.66	11.0
Water Boil			297K	16.8	11.2	588K	500	Air	297K	12.5	15.4
				14.7	10.8					14.0	15.4
				14.3	10.8					13.7	15.6
-	0	-	588K	8.27	10.8	588K	500	N_2	588K	10.4	12.4
				9.54	11.0					11.2	11.0
				9.60	10.9					11.5	11.3
Water Boil			588K	6.42	9.24	588K	500	N_2	297K	11.6	11.0
				7.15	9.72					15.1	11.2
				6.81	10.2					15.8	11.8
588K	200	Air	588K	11.1	11.9	588K	1000	Air	588K	8.85	9.17
				9.37	11.5					8.97	9.38
				9.74	11.5					8.69	9.24
588K	200	Air	297K	14.3	11.9	588K	1000	Air	297K	9.76	9.58
				12.3	11.0					8.70	8.48
				13.2	11.1					9.23	8.76
588K	200	N_2	588K	8.72	11.9	588K	1000	N_2	588K	9.67	11.6
				9.74	12.6					10.4	11.9
				9.16	11.7					10.7	12.5
588K	200	N2	297K	15.6	10.9	588K	1000	N_2	297K	14.1	11.7
				16.3	11.8					15.2	11.9
				15.3	11.0					15.0	11.7

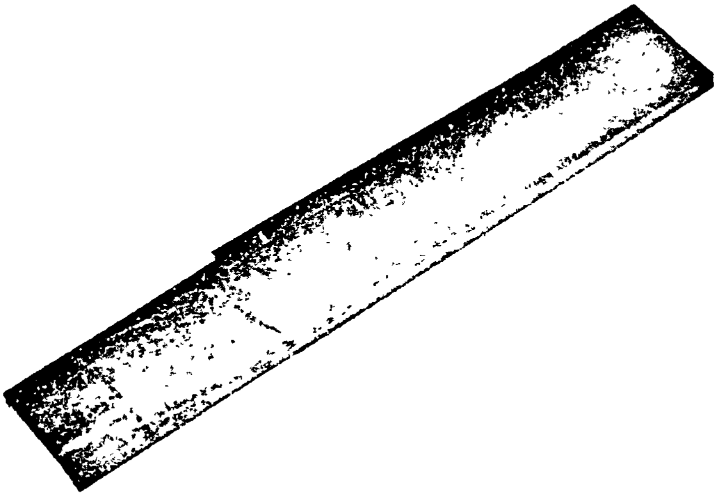

Figure 2. Typical Flexural Fracture of Unaged PI/HTS Specimen Without Coupling Agent

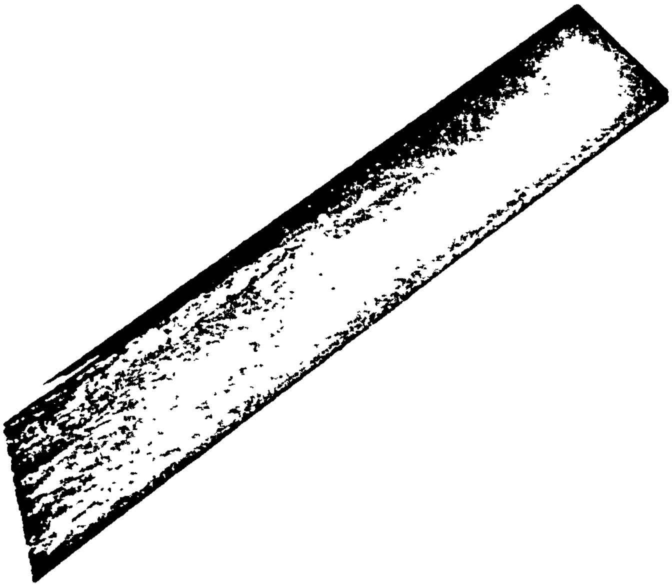

Figure 3. Typical Flexural Fracture of Unaged PI/HTS Specimen With Pyrolyzed PPQ Coupling Agent

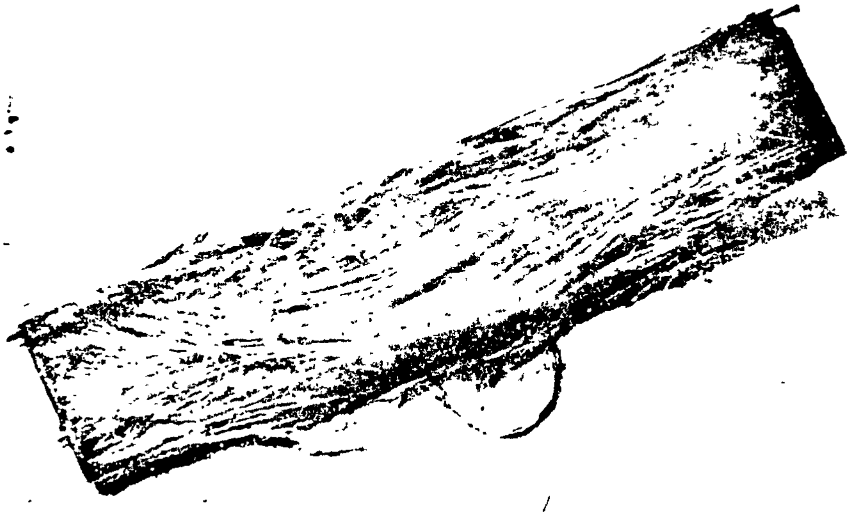

Figure 4. Flexural Strength Specimen Made Without Coupling Agent, Aged 1000 Hours at 588K in Air

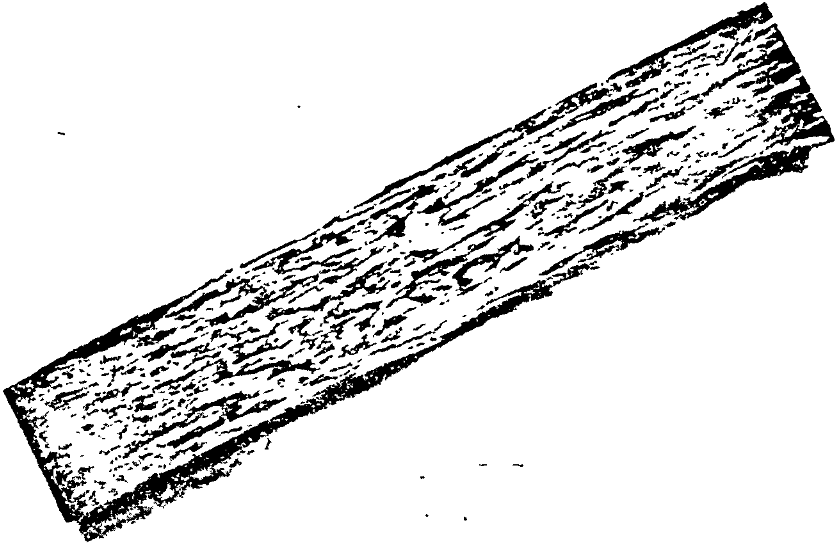

Figure 5. Flexural Strength Specimen Made with Pyrolyzed PPQ Coupling Agent, Aged 1000 Hours at 588K in Air.

samples shown in Figures 4 and 5 have both been fractured, but in both cases the fracture is hidden by the loose fibers on the surface.

C. Transverse Tensile Strength

The use of the pyrolyzed PPQ coupling agent did not have a beneficial effect on the transverse tensile strength of the laminates, nor on the thermo-oxidative stability of the transverse tensile strength on aging at 588K in air. The laminates made without coupling agent decreased in transverse tensile strength by about 61% after air aging at 588K for 1000 hours. During the same time the laminate made with pyrolyzed PPQ coupling agent lost 86% of its transverse tensile strength as measured at 297K. A two hour exposure to boiling water resulted in significant decreases in the transverse tensile strength in all cases except the 297K transverse tensile strength of the laminate made with pyrolyzed PPQ coupling agent. These data are summarized in Tables 13 and 14.

D. Impact Strength

The impact strength of laminates was assessed by a modified Izod impact test using specimens approximately 1.27 by 0.254 centimeters. The specimens were not notched. No toss correction was attempted, and data were used regardless whether or not a clean break was obtained. A typical cleanly broken specimen is shown in Figure 6, which is an unaged specimen made from HTS

Table 13. Transverse Tensile Strength of Composites with Untreated HTS Fiber

Aged Temp	Aged Hours	Aged Atmosphere	Tested at	Transverse Tensile Strength, MPa	Aged Temp	Aged Hours	Aged Atmosphere	Tested at	Transverse Tensile Strength, MPa
-	0	-	297K	54.5 53.8 53.8	588K	500	Air	588K	9.08 11.2 4.19
Water Boil			297K	38.4 39.8 44.7	588K	500	Air	297K	21.6 24.5 18.2
-	0	-	588K	12.6 32.1 32.1	588K	500	N_2	588K	25.1 15.4 26.5
Water Boil			588K	20.0 20.0 16.5	588K	500	N_2	297K	44.7 53.8 49.6
588K	200	Air	588K	9.78 11.9 13.3	588K	1000	Air	588K	6.89 10.5 9.78
588K	200	Air	297K	15.8 29.6 21.4	588K	1000	Air	297K	18.9 20.2 23.7
588K	200	N_2	588K	31.4 32.8 37.0	588K	1000	N_2	588K	18.2 21.6 17.5
588K	200	N_2	297K	48.9 41.2 52.4	588K	1000	N_2	297K	34.9 30.7 33.5

Table 14. Transverse Tensile Strength of HTS Composites with Pyrolyzed PPQ Coupling Agent

Aged Temp	Aged Hours	Aged Atmosphere	Tested at	Transverse Tensile Strength, MPa	Aged Temp	Aged Hours	Aged Atmos.	Tested at	Transverse Tensile Strength, MPa
-	0	-	297K	42.6	588K	500	Air	588K	8.38
				51.7					6.98
				46.1					5.59
Water Boil			297K	46.8	588K	500	Air	297K	11.2
				39.8					11.9
				51.0					12.6
-	0	-	588K	21.0	588K	500	N_2	588K	20.2
				21.6					21.6
				19.6					23.0
Water Boil			588K	13.1	588K	500	N_2	297K	45.4
				15.8					49.6
				15.8					47.5
588K	200	Air	588K	6.78	588K	1000	Air	588K	3.49
				11.9					3.84
				12.6					2.79
588K	200	Air	297K	20.7	588K	1000	Air	297K	6.28
				18.6					8.38
				22.8					4.89
588K	200	N_2	588K	25.1	588K	1000	N_2	588K	14.0
				26.5					25.8
				26.5					24.4
588K	200	N_2	297K	44.0	588K	1000	N_2	297K	44.7
				41.2					39.1
				46.8					43.3

fiber treated with pyrolyzed PPQ coupling agent. Imperfectly broken specimens are typified by Figure 7, which shows a control specimen broken at 588K after 200 hours exposure in air at 588K. The specimen broke cleanly at the edge of the vist, but in addition the free end delaminated into two approximately equal parts. Figure 8 shows an imperfect break that occurred in a sample made with coupling agent and tested at 297K after 1000 hours exposure at 588K in air.

Comparison of the data in Tables 15 and 16 shows that the PPQ coupling agent may have had a slight beneficial effect on impact strength, but that the improvement is probably marginal. Exposure of specimens to boiling water for 2 hours had no apparent deleterious effect. In fact, any small effect there may have been appears to have been beneficial. On the other hand, aging in air at 588K appeared to have no deleterious effect on the impact strength of any of the laminates.

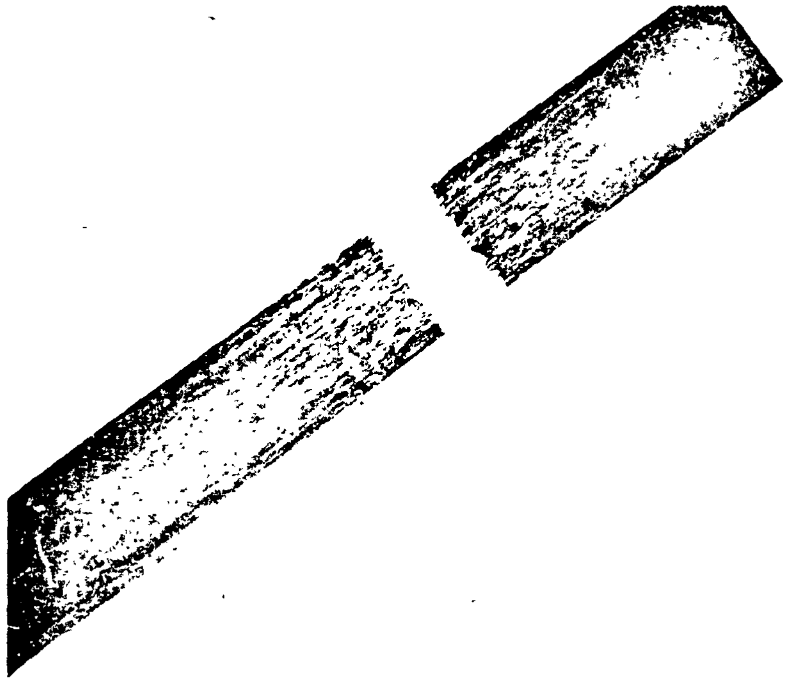

Figure 6. Izod Impact Fracture of Unaged HTS Laminate.

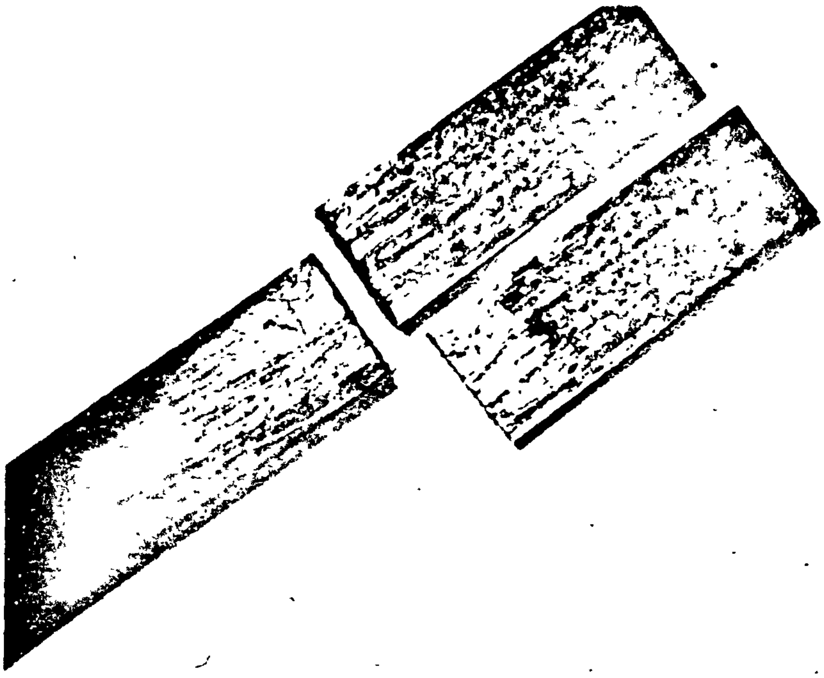

Figure 7. Izod Impact Fracture and Delamination of Control HTS Laminate Aged 200 Hours at 588K and Tested at 588K.

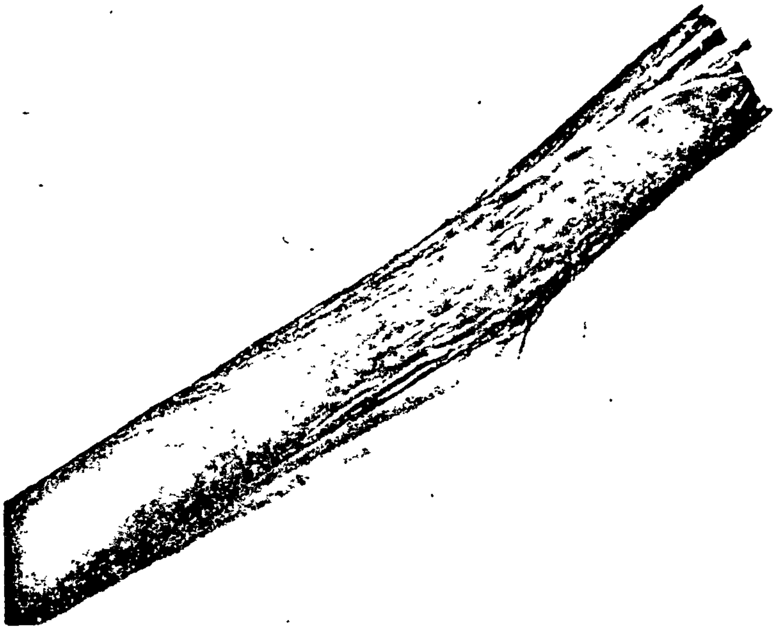

Figure 8. Imperfect Fracture of Izod Impact Specimen Tested at 297K After 1000 Hours Aging in Air at 588K.

Table 15. Impact Strength of Composites with Untreated HTS Fiber.

Temp	Aged Hours	Atmos-phere	Tested at	Impact Strength J/m^2 x 10^{-4}	Temp	Aged Hours	Atmos.	Tested at	Impact Strength J/m^2 x 10^{-4}
-	0	-	297K	5.51 5.26 4.71	588K	500	Air	588K	5.48 4.71 4.27
Water Boil			297K	5.08 3.75 4.60	588K	500	Air	297K	4.17* 4.17* 4.18*
-	0	-	588K	5.02 6.65* 7.79*	588K	500	N_2	588K	5.99 5.11 5.55
Water Boil			588K	8.88 8.18 8.02	588K	500	N_2	297K	4.54 4.08 3.69
588K	200	Air	588K	8.39 6.69* 5.53	588K	1000	Air	588K	5.92 6.16 7.86
588K	200	Air	297K	3.84 3.54 3.82	588K	1000	Air	297K	4.76 4.59 5.15
588K	200	N_2	588K	7.09 6.60 5.15	588K	1000	N_2	588K	5.88 6.50 4.48
588K	200	N_2	297K	3.98 4.78 4.43	588K	1000	N_2	297K	3.05 2.70 2.92

* Imperfect Break

Table 16. Impact Strength of HTS Composites with Pyrolyzed PPQ Coupling Agent

Aged					Aged				
Temp	Hours	Atmosphere	Tested at	Impact Strength $J/m^2 \times 10^{-4}$	Temp	Hours	Atmos.	Tested at	Impact Strength $J/m^2 \times 10^{-4}$
-	0	-	297K	4.57 4.69 4.88	588K	500	Air	588K	5.29 5.67 5.66
Water Boil			297K	4.31 4.69 4.87	588K	500	Air	297K	4.27* 5.24* 4.76*
-	0	-	588K	5.18 5.55 7.32	588K	500	N_2	588K	6.06 5.99 5.74
Water Boil			588K	8.46 9.04 9.60	588K	500	N_2	297K	4.41 4.71 4.73
588K	200	Air	588K	9.84 6.32 6.27	588K	1000	Air	588K	6.08 5.71 5.32
588K	200	Air	297K	4.71 4.20 4.55	588K	1000	Air	297K	6.00 6.99* 5.62
588K	200	N_2	588K	8.05 8.30 4.87	588K	1000	N_2	588K	4.82 5.13 5.27
588K	200	N_2	297K	4.10 4.46 4.13	588K	1000	N_2	297K	4.73 4.41 4.52

*Imperfect Break

Polymerization of Monomeric Reactants

VI. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this study to develop high temperature resistant graphite fiber coupling agents for use with PMR polyimide. Based on the conclusions, recommendations are given for further studies.

A. Conclusions

1. Pyrolyzed polyphenylquinoxaline as a coupling agent or surface treatment for HTS graphite fiber improves the oxidative stability of HTS/PMR-PI composites. During 1000 hours aging in air at 588K such composites suffer some loss in interlaminar shear strength, about 50% loss in flexural strength and flexural modulus, and loss of a major fraction of their transverse tensile strength. Little effect was noted on impact strength. The coupling agent reduces the rate of weight loss from such composites, and prevents the total oxidative destruction of small samples during 1000 hours exposure at 600°F 588K in air.

2. The pyrolyzed polyphenylquinoxaline coupling agent brought about a slight improvement in the interlaminar shear strength of HMS/PMR-PI composites. No particular effect was noted on the long term thermo-oxidative stability of HMS/PMR-PI composites.

B. Recommendations

It appears from the results of this study that the oxidative stability of the polyimide used depends to a large extent on the nature of the graphite fiber used in the composite. Therefore it is recommended that a more fruitful approach to understanding the oxidative stability of polymide/graphite fiber composites depends on determination of the chemical reactions involved in the oxidative degradation rather than on the measurement of the effect of the thermo-oxidative degradation on composite mechanical properties.

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