NON-FLAMMABLE GLASS REINFORCED PLASTIC MATERIAL FOR STRUCTURAL APPLICATIONS

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Charles L. Segal

Final Report

Contract Number NAS 9-9273

WHITTAKER CORPORATION
Research and Development Division
3540 Aero Court
San Diego, California 92123

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Supporting Development Branch
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NASA CR 108441

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FOREWORD

This report was prepared by Whittaker Corporation, Research and Development Division, under Contract No. NAS 9-9273, entitled "Non-flammable Glass Reinforced Plastic Material for Structural Applications". The work was administered under the direction of the Crew Systems Division, with Dale Sauers acting as project officer. The research work was conducted in Whittaker's R&D laboratory by Charles L. Segal, Senior Research Specialist, who served as program manager and principal investigator. Major contributions were made by Gene Fox and Charles Gifford, Senior Laboratory Technicians. This report covers the period from 17 February 1969 - 17 February 1970.

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ABSTRACT

Non-flammable reinforced structural composites were prepared from polyquinoxaline resin and glass fabric. A most important finding of this study was that even thin, i.e. 1/32", laminates of this composition were self-extinguishing when tested in high pressure oxygen environments. Independent reports had shown that thicker, e.g. 1/16", laminates made with PQ or other aromatic heterocyclic polymers were also self-extinguishing. While laminates with low void and excellent mechanical performance could be prepared by press curing at 200 psi and 750°F, laminates with acceptable mechanical strength could be prepared under vacuum bag conditions of 15 psi and 500°F. The later procedure led to higher voids, but still yielded a self-extinguishing laminate. Exposure to environmental extremes did not affect the composite.

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INTRODUCTION

OBJECTIVE

The primary objective of this program was to develop a non-flammable glass reinforced structural material based on polyquinoxaline resin. Non-flammability was defined in this case as being self-extinguishing, under the conditions of Test No. 1, MSC-P-A-D-67-13. A set of target mechanical property values was established. The resulting composite was also required to resist exposure to several different environmental extremes. Since weight saving was critical in the application for which this material was intended, thin laminates (i.e., 1/32") were desirable. And finally, fabrication procedures which were consistent with conventional shop practice were sought.

CONCLUSIONS

1. Polyquinoxaline/glass fabric laminates are self-extinguishing under the conditions of the present test if the resin content is low (24-30 o/w) even if the void content is high (15-20 o/v).

2. Excellent mechanical strength is exhibited by polyquinoxaline/glass fabric laminates prepared at 200 psi pressure. Vacuum bag techniques lead to higher voids and lower strengths, but the composites retain the self-extinguishing characteristic.

3. Environmental extremes, as witnessed in the Apollo spacecraft, do not effect the performance of these composites.

TECHNICAL DISCUSSION

The critical need for non-flammable, non-metallic materials in the high-pressure oxygen environment of the Apollo Spacecraft has been established. More specifically, this program has been directed toward the development of glass reinforced plastic structural composites which would replace certain Category A materials presently being used. In addition to the prime requirement of non-flammability, the composite should have sufficient strength to act as a structural member and also resist the other environmental extremes common to this spacecraft. While the development of a "shop-ready" materials system was not specified in this research contract, the amenability to fabrication under normal shop conditions was considered in the experimental study. Each of the three major areas of investigation --non-flammability, structural strength, and resistance to environmental extremes--will be covered in the discussion which follows.

NON-FLAMMABILITY

Non-flammability in this case has been defined as self-extinguishing according to Test No. 1, MSC-PA-D-67-13. The specific conditions used by MSC in testing candidate composites were: bottom ignition, a silicone rubber ignitor, and either 6.2 psia 100% oxygen or 16.5 psia 60% oxygen/40% nitrogen. Since weight saving is important in the present applications, it was considered desirable that the resulting composite be non-flammable in thin sections: 0.032 inch, or thinner, if possible.

There is no well-defined theory which relates polymer structure or composition to flammability in high pressure oxygen. Halogenated polymers (e.g. Teflon) or formulations containing inorganic halogen or phosphorous compounds, which are non-flammable in air, are flammable in high pressure oxygen. It has been postulated that certain aromatic heterocyclic polymers, which have a low yield of gaseous byproduct and a high char yield upon pyrolysis, would be non-flammable. Several glass composites containing such polymers were tested prior to this program (polyimide, polybenzimidazole, and polyquinoxaline) and were found to be self-extinguishing when tested in thicknesses of 0.060 inch or greater. The polyimide, however, was not self-extinguishing in sections as thin as 0.032 inch. Of the two other candidates, polybenzimidazole and polyquinoxaline (PQ), the later was chosen by MSC and Whittaker as being most promising to meet the requirements of this program.

The initial phase of this study centered on the preparation of glass fabric (1581 HTS 994) laminates with polyquinoxaline resin. Parameters investigated included: inherent viscosity (molecular weight) of resin, resin pickup, prepreg solvent content, laminating pressure, laminating temperatures, and number of plies (thickness). Physical characteristics of the resulting laminates were measured (resin content, specific gravity, and void content) and duplicate samples of selected laminates (2½ inches by 5 inches) were forwarded to MSC for flammability tests. Prepreg and laminate characteristics are given in Tables I - III.

TABLE I

CHARACTERISTICS OF PREPREG AND LAMINATES PREPARED WITH POLYQUINOXALINE RESIN WITH INHERENT VISCOSITY OF 1.22 dl/g

	Laminate Number					
	1	2	7	8	9	10
Prepreg Characteristics						
Resin Pickup, %	40.3	40.3	41.8	41.8	41.8	41.8
Volatile Content, %	12.5	12.5	12.9	12.9	10.8	10.8
Flow: Temp, °F	500	500	500	500	500	500
Pressure, psi	200	200	200	200	200	200
in^2/g	8.8	8.8	8.3	8.3	9.0	9.0
Laminate Characteristic						
Number of Plies	3	6	3	3	3	3
Lam. Pressure, psi	200[c]	200[c]	500[d]	200	200	800
Resin Content, %[a]	35.0	36.3	27.8	33.2	34.0	33.1
Sp. Gr., g/cm^3 [b]	1.78	1.84	1.81	1.77	1.76	1.75
Thickness, mil/ply	10.8	10.6	10.6	11.3	11.4	10.2
Void Content, %	5.8	2.1	8.6	7.3	7.4	8.4

(a) Resin content by weight, burnout

(b) Water immersion

(c) Final laminating pressure was approximately 500 psi

(d) Final laminating pressure was approximately 1000 psi

TABLE II

CHARACTERISTICS OF PREPREG AND LAMINATES PREPARED WITH POLYQUINOXALINE RESIN WITH INHERENT VISCOSITY OF 0.67 dl/g

	Laminate Number			
	13	14	15	16
Prepreg Characteristics				
Resin Pickup, %	40.8	36.0	36.0	36.0
Volatile Content, %	15.7	11.5	11.5	11.5
Flow: Temp, °F	400	400	400	400
Pressure, psi	200	200	200	200
in^2/g	12.2	13.5	13.5	13.5
Laminate Characteristics				
Number of Plies	3	6	3	6
Laminate Pressure, psi	200	200	200	200
Resin Content, % [(a)]	30.1	26.8	28.2	25.2
Sp. Gr., g/cm^3 [(b)]	1.85	1.93	1.90	1.83
Thickness, mil/ply	10.4	8.8	10.3	9.0
Void Content, %	6.65	3.5	4.0	9.4

(a) Resin content by weight, burnout

(b) Water immersion

TABLE III

CHARACTERISTICS OF PREPREG AND LAMINATES PREPARED WITH POLYQUINOXALINE RESIN WITH INHERENT VISCOSITY OF 0.78 dl/g.

	Laminate Number										
	19	20	21	22	23	24	27	28	29	30	31
Prepreg Characteristics											
Resin Pickup, %	≈ 30	≈ 30	≈ 30	≈ 25	≈ 25	≈ 25	≈ 25	~ 25	≈ 25	~ 25	~ 20
Volatile Content, %	18.5	18.5	18.5	11	20	20	~ 20	≈ 20	≈ 20	≈ 20	≈ 20
Flow: Temp, °F	500	500	500	500	500	500	500	500	500	500	500
Pressure, psi	15	15	15	15	15	15	15	15	15	15	15
in^2/g	11.9	11.9	11.9	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8
Laminate Characteristic											
Number of Plies	3	3	6	6	3	6	6	6	3	6	6
Laminate Pressure, psi	15	15	15	15	15	15	100	50	100	100	100
Laminating Temp, °F	500	500	500	600	600	750	750	750	750	750	600
Resin Content, % (a)	27.0	26.8	28.6	25.0	25.0	24.2	28.0	28.0	25.6	27.8	28.6
Sp. Gr., g/cm^3 (b)	1.60	1.60	1.62	1.67	1.69	1.63	1.80	1.75	1.75	1.85	1.85
Thickness, mil/ply	10.8	11.0	10.4	9.9	10.3	10.0	9.4	9.7	9.5	9.1	9.3
Void Content, %	20.0	20.0	18.2	17.4	16.3	20.0	9.1	11.6	13.7	7.5	6.6

(a) Calculated on #27-29, burnout on 30, 31

(b) Water immersion

The first set of laminates, 1-10, Table I, were prepared from a PQ resin with an inherent viscosity of 1.22 dl/g. This was the highest viscosity (highest molecular weight) used and as a result had the lowest flow and greatest thickness per ply of the different resins used. Also, the resin content in the prepreg was higher than used in subsequent prepregs. Laminating pressures in this series ranged from 200 psi to 1000 psi. Resin contents were nominally 35 o/w and voids ranged from 6-8 o/v. Exceptions were the laminate prepared at 1000 psi, which had lower resin content and higher void, and one six-ply laminate (No. 2) which had only 2.1 o/v void.

Of these laminates only two were tested for their flammability characteristics:

No. 1 (0.031", 35 o/w RC, 5.8 o/v void) - burned
No. 2 (0.064", 36 o/w RC, 2.1 o/v void) - self-extinguishing

On the basis of these test results it was concluded that the resin content should be lowered while maintaining the void content at the lowest possible level. A second series of laminates were prepared under similar conditions using a PQ resin with lower i.v. and, therefore, greater flow (13-16, Table II). Resin contents of 27-28 o/w and voids of approximately 4 o/v were achieved:

No. 14 (0.053", 27 o/w RC, 3.5 o/v void) - self-extinguishing
No. 15 (0.031", 28 o/w RC, 4.0 o/v void) - self-extinguishing

The final series of laminates (19-24, 27-31) were prepared with a PQ of i.v. of 0.78 dl/g, pressures ranging from 15 psi to 100 psi, and initial laminating temperatures of 500°F to 750°F, Table III. Resulting resin contents were in the range 24-28 o/w while voids ranged from 9-20 o/v. Half of each laminate was postcured to 750°F over a postcure period of approximately 65 hours. Samples of the as-cured and postcured laminates were submitted to MSC for flammability test. Results are given in Table IV. An unexpected result was observed: despite the high void content, all of the postcured laminates, regardless of thickness, were self-extinguishing in both conditions of test. Also unexpected was the self-extinguishing characteristic of the 0.060" laminates even without postcure and when cured initially at temperatures as low as 500°F. Most encouraging was that a three-ply laminate (No. 20, 0.033") was self-extinguishing without postcure even under the mild conditions of cure (15 psi, 500°F).

An important conclusion of this phase of the study would then be: thin PQ/glass laminates are self-extinguishing under these conditions of test if the resin content is low (i.e. 25-30 o/w) and if the void content is high (15-20 o/v).

TABLE IV

FLAMMABILITY TESTS ON POLYQUINOXALINE LAMINATES DESCRIBED IN TABLE III

Sample No.[a]	Approximate Thickness	Test Atmosphere (b)	
		6.2 psia (100% O_2)	16.5 psia (60% O_2/40% N_2)
20 (3-ply)	0.030"	S.E. 2 1/4	
20 (3-ply)	0.030"		S.E. 2"
20A (3-ply)	0.032"	S.E. 2 1/8"	
20A (3-ply)	0.032"		S.E. 1 3/4"
21 (6-ply)	0.064"	S.E. 2"	
21 (6-ply)	0.064"		S.E. 2 1/8"
21A (6-ply)	0.065"	S.E. 3/4"	
21A (6-ply)	0.065"		S.E. 7/8"
22 (6-ply)	0.060"	S.E. 3/4"	
22 (6-ply)	0.060"		S.E. 5/8"
22 (6-ply)	0.063"	S.E. 7/8"	
22A (6-ply)	0.063"		S.E. 7/8"
23 (3-ply)	0.032"	0.075 in/sec	
23 (3-ply)	0.032"		S.E. 1 3/8"
23A (3-ply)	0.031"	S.E. 1 3/8"	
23A (3-ply)	0.031"		S.E. 1 3/8"
24 (6-ply)	0.062"	S.E. 1"	
24 (6-ply)	0.062"		S.E. 1 1/4"
24A (6-ply)	0.060"	S.E. 7/8"	
24A (6-ply)	0.060"		S.E. 1"
27 (6-ply)	0.057"	S.E. 15/16"	
27 (6-ply)	0.057"		S.E. 1"

TABLE IV (continued)

Sample No.[a]	Approximate Thickness	Test Atmosphere (b)	
		6.2 psia(100% O_2)	16.5 psia(60% O_2/40% N_2)
27A (6-ply)	0.056"	S.E. 3/4"	
27A (6-ply)	0.056"		S.E. 15/16"
28 (6-ply)	0.058"	S.E. 1"	
28 (6-ply)	0.058"		S.E. 1 1/8"
28A (6-ply)	0.059"	S.E. 7/8"	
28A (6-ply)	0.059"		S.E. 1"
29 (3-ply)	0.029"	0.073 in/sec	
29 (3-ply)	0.029"		0.072 in/sec
29A (3-ply)	0.029"	S.E. 1 5/8"	
29A (3-ply)	0.029"		S.E. 2"
30 (6-ply)	0.056"	S.E. 3/4"	
30 (6-ply)	0.056"		S.E. 1"
30A (6-ply)	0.056"	S.E. 1"	
30A (6-ply)	0.056"		S.E. 7/8"
31 (6-ply)	0.056"	S.E. 3/4"	
31 (6-ply)	0.056"		S.E. 1½"
31A (6-ply)	0.057"	S.E. 7/8"	
31A (6-ply)	0.057"		S.E. 1"

(a) "A" designation behind sample number indicates postcured.

(b) A Silicone ignitor was used on all tests. All tests were ignited from the bottom. S.E. - Self extinguished, followed by length in which self-extinguishment occurred.

STRUCTURAL PROPERTIES

Three-ply (approx. 0.030") and six-ply (approx. 0.060") laminates were prepared under two different conditions of temperature and pressure:

Autoclave: 15 psi, initial cure temperature of 500°F, 2 hours; postcured to 750°F, Appendix A

Press Cure: 200 psi, initial cure temperature of 750°F, 4 hours; postcured to 750°F

Characteristics of these laminates and results of mechanical tests are given in Table V.

Test results for the 200 psi laminates of two different thicknesses exceeded the target values for most properties. Relationships between ultimate properties and thickness were as expected. The thicker specimen gave a more reliable value for compression strength (57,000 psi) than did the thinner specimen, which had a tendency to bend. An appropriate span/depth for the shear test could only be obtained with the thicker specimen. The actual shear strength of the composite is probably higher than the observed 2790 psi, since the failure was in compression and not in shear.

As expected, the lower pressure cure led to higher voids and lower mechanical properties, especially in the case of the six-ply laminate which had the lowest specific gravity and highest voids of all the laminates. Quite respectable flexural and tensile values were obtained for the three-ply laminate (approximately 70,000 psi) despite the high void content of this laminate (16%). It was observed in a separate set of tests that the postcure increased flexural and reduced tensile as compared to the as-cured laminate.

The mechanical test results lead to the conclusion that a sound structural (and non-flammable) PQ laminate as thin as 1/32 inch can be prepared at pressures as low as 15 psi (autoclave) and temperatures as low as 500°F. Optimum properties for laminates thicker than 1/32 inch would require laminating pressures greater than 15 psi and as high as 200 psi.

RESISTANCE TO ENVIRONMENTAL EXTREMES

Four laminates (1/16" x 5 3/4" x 12") were submitted to MSC for odor and outgassing tests. MSC-A-D-66.3, Test. No. 6, Odor Test requires a minimum rating of 2.5 and lists 1 as "barely detectable". The undiluted odor of the PQ/glass composite was found to be 1.3.

The maximum allowable total organic materials and carbon monoxide, per MSC-A-D-66-3, Test No. 7, Determination of Carbon Monoxide and Total Organics, are 100 microgram/gram and 25 micrograms/gram, respectively. Total organic found was 0.5 μgm/gm and total carbon monoxide was 4.3 μgm/gm.

TABLE V

MECHANICAL CHARACTERISTICS OF LAMINATES BASED ON POLYQUINOXALINE RESIN AND 1581-HTS 994 GLASS FABRIC

	Laminated at 15 psi		Laminated at 200 psi		Target Value
	3-Ply	6-Ply	3-Ply	6-Ply	
Laminate Characteristics					
Resin Content, o/w	28.9	27.5	35.0	36.3	-
Sp. Gravity, g/cm^3	1.65	1.49	1.78	1.84	2.2
Void Content, o/v	16.0	25.0	5.8	2.1	-
Mechanical Properties					
Flexural Strength, 10^3 psi	70.8	38.4	84.6	104.9	80.0
Flexural Modulus, 10^6 psi	3.11	2.48	2.82	3.17	2.0
Tensile Strength, 10^3 psi	69.1	55.6	75.0	71.4	80.0
Tensile Modulus, 10^6 psi	3.83	2.49	3.54	3.60	2.0
Compressive Strength, 10^3 psi	-	(a)	32.4	57.0	50.0
Compressive Modulus, 10^6 psi	-	(a)	3.53	3.56	2.0
Interlaminar Shear, 10^3 psi	-	(a)	-	2.79(b)	3.0
Hardness, Barcol	-	35-40	-	60-65	50

(a) Specimen warped during postcure; not suitable for compression or shear test.

(b) Specimen failed in compression.

Separate laminates were exposed to (1) 24 hours of hard vacuum, (2) 24 hours of ultra-violet radiation, (3) repeated cycling between -300°F and +300°F, and (4) 12 hours of 100% relative humidity. In all cases there was no sign of deterioration or change of mechanical property.

The conclusion drawn from this phase of the study was that PQ/glass laminates will withstand the environmental extremes of the Apollo spacecraft.

DELIVERABLE END ITEMS

A. Evaluation Specimens

A total of 20 laminates were prepared using the 15 psi/500°F vacuum bag technique described in Appendix A.

1. 10 each - 1/16" x 6" x 12", average resin content 24.3 o/w. Average specific gravity 1.41 g/cm^3. Two of these laminates were retained by Whittaker per agreement with MSC program manager and used for additional mechanical test (Table V).

2. 10 each - 1/32" x 6" x 12", average resin content 27.2 o/w, average specific gravity 1.44 g/cm^3.

B. One gallon of PQ resin: Batch No. TT3137-15, inherent viscosity 0.70 dl/g, 15.3 o/w solids.

C. Ten yards of glass fabric:

1. Three yards of fabric provided by MSC.

2. Seven yards of 1581-HTS-994 glass fabric, 19 sheets, each 13" (warp) by 39.5". Average total pickup was approximately 52 o/w. Average solvent (m-cresol) volatiles was approximately 20%.

RECOMMENDED FUTURE WORK

The success in achieving a non-flammable structural composite of polyquinoxaline/glass fabric points to the need for two future tasks:

1. A development program aimed at reducing the price of polyquinoxaline resin.

2. A program to fabricate significant items of hardware.

APPENDIX A

PROCEDURE FOR PREPARING POLYQUINOXALINE GLASS FABRIC PREPREG AND LAMINATES

Prepreg

1. Cut glass fabric (1581 HTS-994) to desired dimensions.
2. Place end of fabric under blade of dip tank coater set at 0.020" gap.
3. Place 1/2 of desired amount of resin solution (15% solids in m-cresol) behind blade.
4. Pull fabric forward at rate so as to distribute resin evenly over desired area.
5. Dry prepreg at 200°F for 10 minutes.
6. Repeat steps 2-5 with remaining 1/2 of resin solution with gap of 0.025".
7. Dry additional 10 minutes at 225°F (total pickup should be approximately 50 o/w, resin solids approximately 30 o/w).
8. Store prepreg in sealed polyethylene bag to avoid loss of volatiles.

Layup (six-ply, 13" x 13" laminate)

1. Spray aluminum caul sheet with release agent, Frekote.
2. One-ply 3A-108 Teflon fabric, 15" x 15".
3. Place 6-ply of prepreg on top of release fabric.
4. Next 2-ply of 3A-108 release breather fabric, 15" x 15".
5. Install thermocouple wire on prepreg.
6. One-ply 181 glass fabric bleeder to cover entire layup.
7. Caul plate, 13" x 13".
8. One-ply 181 bleeder to cover entire layup.
9. Bag layup with 3 mil Kapton using hi-temperature Prestite sealer.
10. Pull vacuum and check for leaks.
11. Clamp picture frame assembly in place.

Cure

1. Place picture frame autoclave in oven preheated to 300°F.
2. Apply vacuum of 29 inches mercury (approximately 15 psi).
3. Raise temperature to 500°F, approximately one hour.
4. Hold at 500°F under pressure for two hours.
5. Cool under pressure to room temperature.
6. Postcure, if required, under nitrogen from R.T. to 750°F at 8.5°F/hour. Hold at 750°F for twelve hours. Cool to R.T. under nitrogen.