DEVELOPMENT OF LIGHTWEIGHT GRAPHITE/POLYIMIDE HONEYCOMB PHASE I - MATERIALS SELECTION

H400-12-1-8

July 1971

NASA Contract NAS 9-11368

HERCULES

CHEMICAL PROPULSION DIVISION
HERCULES POWDER COMPANY
INCORPORATED
BACCHUS WORKS MAGNA, UTAH

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Prepared for

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DEVELOPMENT OF LIGHTWEIGHT
GRAPHITE/POLYIMIDE HONEYCOMB
PHASE I - MATERIALS SELECTION

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FOREWORD

This report covers the work performed in Phase I of National Aeronautics and Space Administration (NASA) Contract NAS 9-11368 during the period of 1 January through 30 May 1971. The work was performed under the sponsorship of the NASA Manned Spacecraft Center R&D Procurement Branch. The program is administred under the direction of Mr. T. J. Dunn, Technical Monitor.

The work is being performed by the Composite Materials Development Department, Hercules Incorporated, Bacchus Works, Magna, Utah.

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ABSTRACT

The work reported herein was accomplished during the materials selection phase (Phase I) on NASA Contract NAS 9-11368. This report is submitted in compliance with Article I, requesting reports at the end of each phase of the contract.

This being the first report under Contract NAS 9-11368, an outline of the total program is presented under paragraph A, Introduction. Basic requirements of the materials selected and the rationale for these requirements are discussed in paragraph B.1.

The selected resin for the first core and face sheet fabrication is Monsanto RS6234 polyimide. Later cores may use another resin. The selected fiber for core manufacture is Hercules HT-S, and the selected fiber for face sheets is Hercules HM-S; these selections are discussed in paragraphs B.2 and B.3, respectively. Bonding adhesives for face sheet-to-core bonding are to be made in Phase III of the program; however, screening of candidates is discussed in paragraph B.4.

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DEVELOPMENT OF LIGHTWEIGHT GRAPHITE/POLYIMIDE HONEYCOMB

A. INTRODUCTION

The objective of this program is to develop the tools and techniques necessary to produce extremely lightweight honeycomb sandwich panels, to fabricate and test these panels, and to develop design data. Carbon fibers are to be used with a resin suitable for a 200-hour, 600° F, exposure. The target core weight is 2.0 lb/cu ft, requiring 0.001 to 0.002 in. per ply thicknesses. Honeycomb core in various weights and cell sizes and candidate face sheet orientations will be made and tested. Sandwich panels will then be made from the lightest workable gauges until a minimum feasible weight configuration is established. Structural tests will be performed to establish design parameters, allowable strengths, and resultant deflections. Test results for the graphite panels will be compared with results to be expected from glass fiber panels of comparable weight and configuration.

The program is being conducted in five phases as follows:

Phase I - Materials Selection

Phase II - Thin Gauge Material Manufacture

Phase III - Fabrication Development

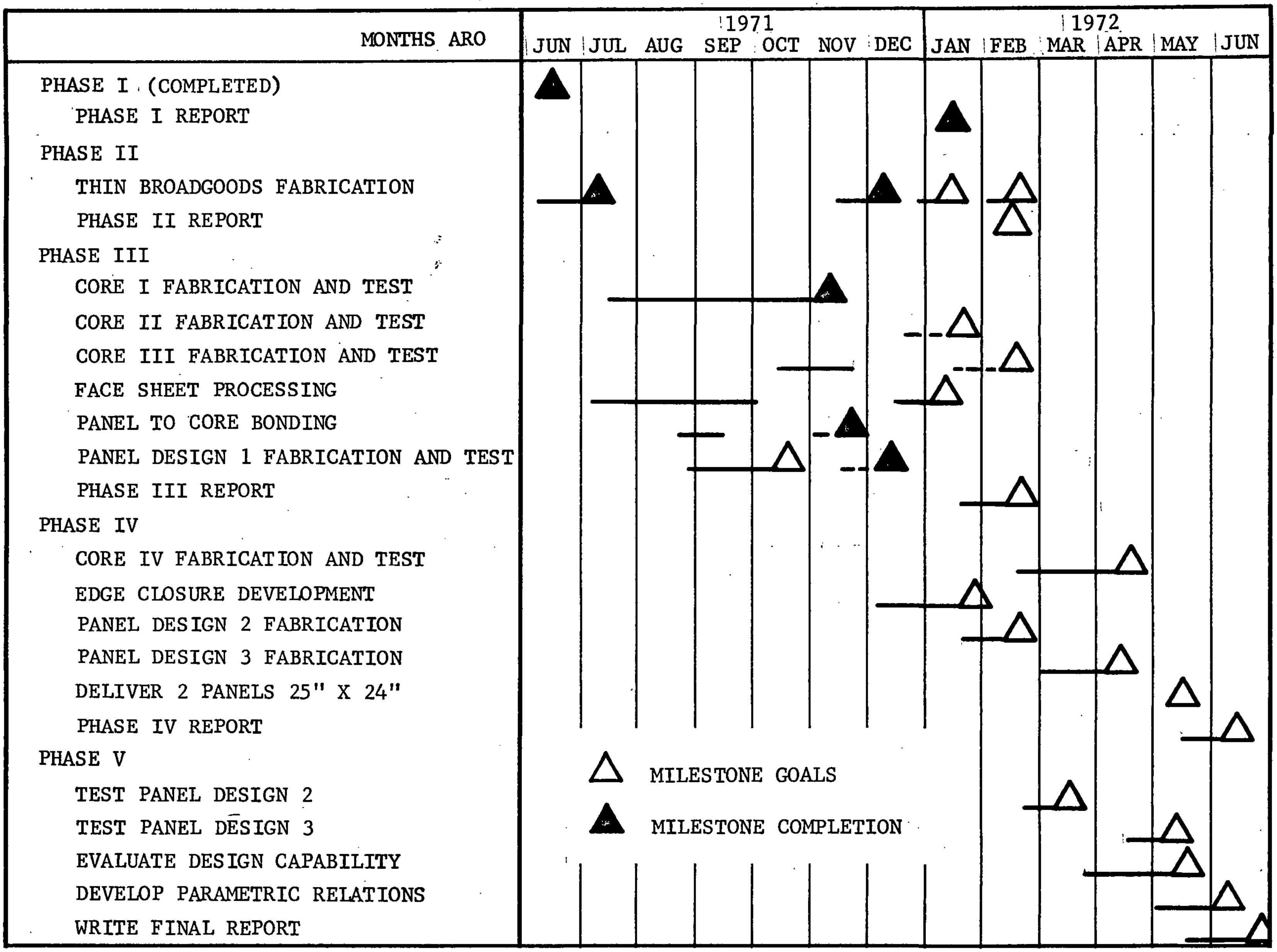
Phase IV - Design and Manufacture of Panels

Phase V - Panel Testing and Design Allowables Determination

The program will be conducted in an 18-month time span with reports written at the end of each phase. The program milestone schedule is presented in Table I.

TABLE I

PROGRAM MILESTONE SCHEDULE



B. PHASE I EFFORT - MATERIALS SELECTION

High temperature resin systems were evaluated through both literature review and materials testing. Recommendations for potential materials were made on the basis of analysis work under Phase I and Phase IV materials studies.

Five fibers known to have the capability of achieving the desired thin gauge composite thickness with no fiber manufacturing changes were considered: Hercules (Courtaulds) HM, HT, and A; and Morganite I and II. Processibility, cost, availability, and sandwich panel design requirements were used to reduce this to two fibers. Tested properties were evaluated on these two fibers prior to final selection.

Face sheet-to-core bonding adhesive candidates were selected on the basis of resin filleting tests, resin handling, processing characteristics, and high temperature bond strength. Final bonding adhesive selection will occur in Phase III of the program.

The following subparagraphs give the results of the materials selection effort.

1. Material Requirements

The materials selection is controlled by the intended use of the lightweight honeycomb sandwich panels which are to be delivered at the end of the program. The intended use is to be the structural support panel for a thermal protection system. The general configuration is shown in Figure 1. The panel is 24-in. wide and is to be simply supported at a distance of 25 in. The load is distributed uniformly over the panel at a maximum value of 8 psi. The insulation system which the sandwich panel supports has an elongation capability of 0.4 percent (4,000μ in./in.). The minimum temperature the panel is to be designed to meet is 500° F with a goal of 600° F and an exposure duration of 200 hours.

The effects of these design requirements on the materials to be selected (core, face sheet, and face sheet-to-core bonding adhesive) are discussed in the following subparagraphs.

a. Core Material Requirements

The material from which the core is to be manufactured must enable the core to meet the following specific requirements:

(1) The core must have sufficient shear strength to withstand the design induced shear stresses through the relation

$$F_s = \frac{2V}{b(d + t_c)} \qquad (1)$$

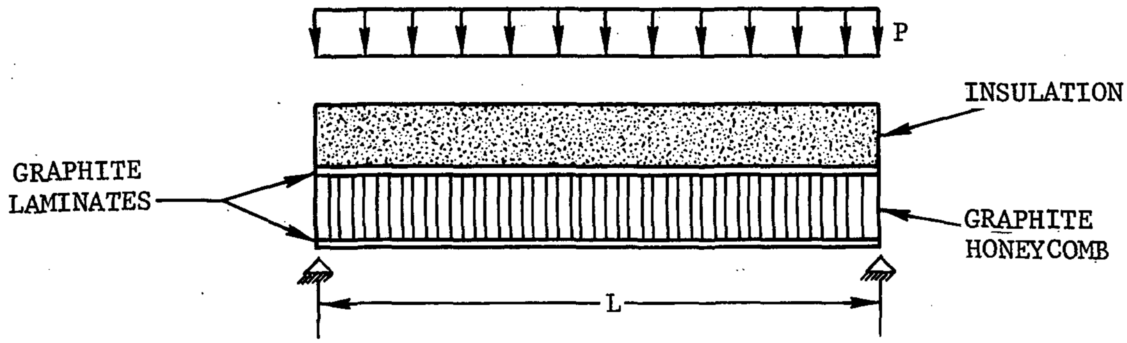


Figure 1. Panel Configuration

where:

F_s = core shear stress

V = applied shear load

b = panel width

d = panel height

t_c = core thickness

(2) The core bending and shear modulus must be of sufficient magnitude to prevent excessive deflection of the core, and to prevent face sheet wrinkling through the relation

$$F_{fs\ wrinkling} = 0.5\ (G_c\ E_c\ E_f)^{1/3} \qquad (2)$$

where:

G_c = core shear modulus

E_c = core Young's modulus

E_f = face sheet Young's modulus

(3) The core must have the compressive strength to resist crushing by both the design loads acting normal to the panel facings and by flexure-induced core compressive stresses.

The most important of these three requirements is core shear strength. If the shear requirements can be met, the core compressive strength and modulus will normally exceed design requirements.

Continuous unidirectional graphite in a resin matrix represents a possibly optimum material system for maximizing strength and modulus to weight. The major advantage of graphite would be reduced weight; however, for very stringent deflection limits, the higher stiffness of graphite core also results in thinner gauge skins and a further weight saving.

Core cell size is another variable of great importance. For a given base material, cell size will determine ultimate density and associated honeycomb properties. Further, it has a significant influence on core-to-face sheet bonding efficiency, and on face sheet thickness and weight. The latter influence on the face sheet results from intercell buckling which is inversely proportional to cell size through the relation

$$F_{cr\ buckling} = \frac{2}{(1 - \mu_f^2)} E_f \left(\frac{t_f}{s}\right)^2 \qquad (3)$$

where:

$F_{cr\ buckling}$ = critical intercell buckling stress

E_f = modulus of facing

t_f = thickness of facing

μ_f = Poisson's ratio of facing

s = cell size

It is this relation which prevents the reduction of core weight through the use of larger and larger cell sizes. The design of a minimum weight panel requires a balance between core shear strength, face sheet bending stress, face sheet wrinkling stress, and the intercell buckling stress. Preliminary calculations,[1] using assumed values for composite properties and core properties, have shown a cell size between 1/4 and 3/8 in. should produce the minimum weight sandwich panel for this application.

[1]Refer to List of References

In order to obtain the target core density of less than 2.0 lb/cu ft, a tradeoff between extremely thin web thickness and cell size is required. Table II gives core density versus foil thickness and cell size for a graphite composite of 95 lb/cu ft density (0.055 lb/cu in.). Table II is based upon the relation from Reference 2 for hexagon cell

$$W_c = \frac{8\ to}{3s} W_o \qquad (4)$$

where:

W_c = core density

W_o = density of web or ribbon material

to = web thickness

s = cell size

It can be seen that at a cell size of 0.500 in., the web thickness must be less than 0.004 in., and at a cell size of 0.250 in., the web thickness must be less than 0.002 in. Further, the more efficient laminates for combined shear and compressive stress will require more than one ply, such as ±45 or 0 ± 45. These orientations require 2 and 3 plies, respectively, ignoring the possible need for a balanced layup which would require 4 and 6 plies, respectively. The fiber selected, and its form (random mat, oriented mat, cloth, or broadgoods) must, therefore, be capable of achieving less than 0.002 in. per ply.

b. Core Manufacturing Requirements

Honeycomb core manufacturing techniques must also be considered in the selection of the fiber/matrix core material. There are two principle methods for manufacturing honeycomb core: The corrugation process, and the expansion process. In the corrugation process, the web stock material is just corrugated and, subsequently, bonded at the node points to form the honeycomb. In the expansion process, the web stock is first bonded at the node points and then the stacked sheets pulled or expanded to the desired cell configuration. The expansion process could use either cured or uncured sheets; however, it is limited to web stock which is sufficiently pliable to withstand expansion. High stiffness-low elongation materials are very difficult to expand successfully; therefore, it is expected that uncured web stock would be required with graphite fiber. The development of a graphite prepreg system, with a high temperature matrix which could be expanded, was considered to be of too high a risk to this program; therefore, the corrugated process was selected. The two fabrication procedures are illustrated in Figures 2 and 3.

[2] Refer to List of References

TABLE II

CALCULATED CORE DENSITY (POUNDS PER CUBIC FOOT)

Designated Foil Thickness (in.)	Cell Size (in.)					
	1/8	5/32	3/16	1/4	3/8	1/2
0.001	2.0*	1.6	1.3	1.0	0.7	0.5
0.0015	3.0	2.4	2.0	1.5	1.0	0.7
0.0020	4.0	3.2	2.6	2.0	1.3	1.0
0.0025	--	4.0	3.3	2.5	1.7	1.3
0.0030	--	--	4.0	3.0	2.0	1.5
0.0035	--	--	--	3.5	2.4	1.8
0.0040	--	--	--	4.0	2.7	2.0
0.0045	--	--	--	--	3.0	2.3
0.0050	--	--	--	--	3.4	2.6
0.0055	--	--	--	--	3.7	2.8
0.0060	--	--	--	--	--	3.0

Graphite Composite V_f = 59%, ρ_c = 95 lb/ft^3

*lb/ft^3

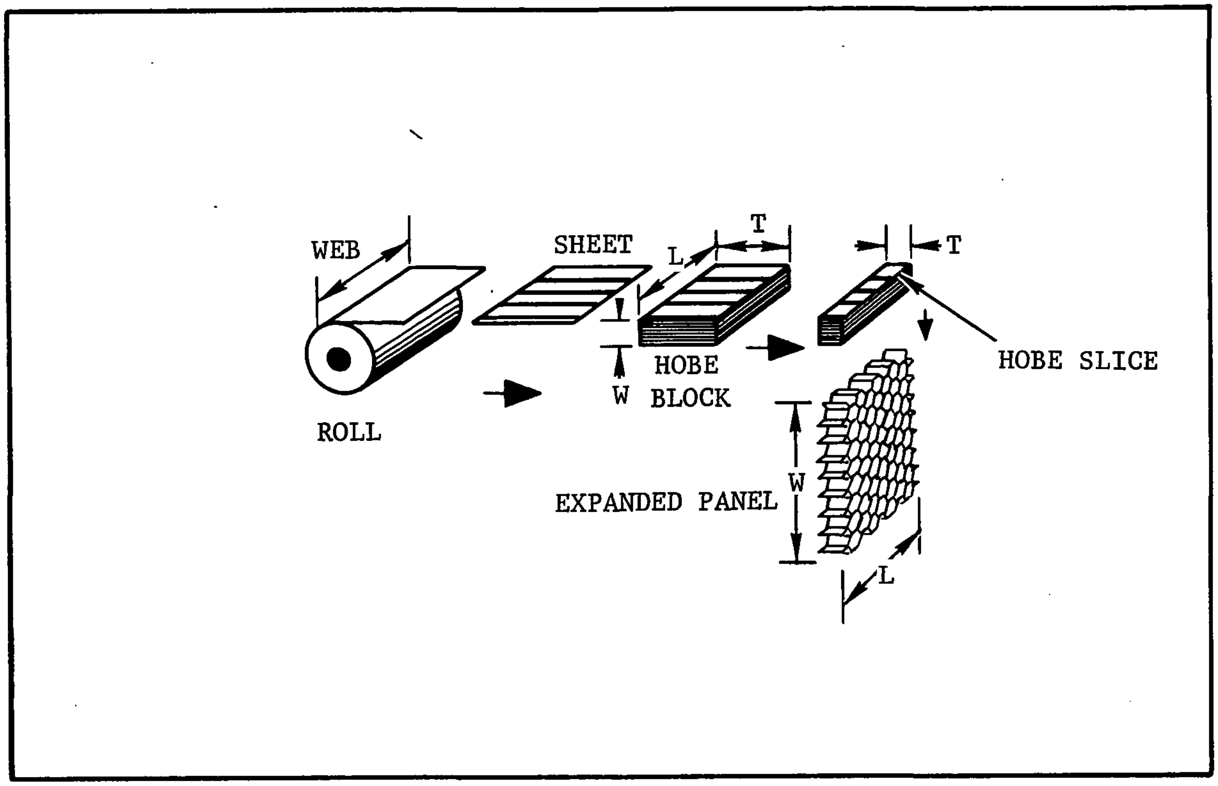


Figure 2. Expansion Process of Honeycomb Manufacture

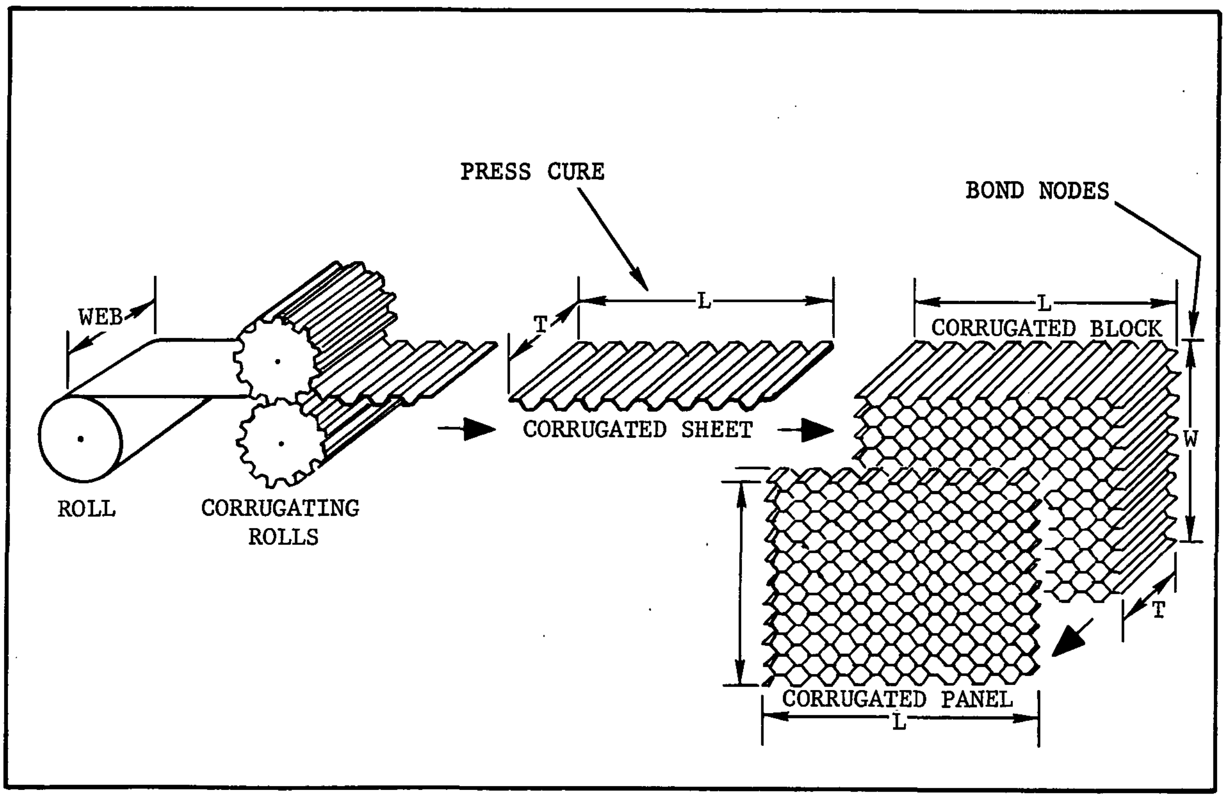


Figure 3. Corrugation Process of Honeycomb Manufacture

In the corrugation process, the web stock is corrugated while it is still pliable, then the corrugated sheets are cured in metal molds which have been carefully designed to produce the configuration desired. Since it is a press-cure procedure, the use of high pressures and temperatures is possible. Vacuum can also be used; however, higher production rates and lower cost would be attainable without vacuum.

c. Face Sheet Material Requirements

In a sandwich panel with symmetrical facings, uniformly loaded as a simple-supported beam, the optimum panel design is controlled by the face sheet allowable stress, allowable panel deflection, and minimum weight. Since the insulation the sandwich panel is to support has a limited elongation capability (0.4 percent), small panel deflections are required. It has also been pointed out in Equations (2) and (3) in subparagraph a. that a high face sheet modulus produces an advantage and would lead to a lighter panel. Studies run in Reference 2 have indicated that face sheet thicknesses in the order of 0.007 to 0.015 in. produce the minimum weight panels with presently available cores of glass and nomex. These face sheets were mostly unidirectional with 10 to 20 percent of the fibers in the transverse direction to permit handling and to carry stresses resulting from the Poisson effect.

Thus, high modulus graphite with an ultimate elongation, around 0.4 percent and ply thicknesses of 0.005 in., are required for the spanwise direction of the face sheet while very thin plies of material, 0.001 to 0.003 in., are required for the transverse direction.

2. Fiber Selection

As discussed in paragraph 1, the fiber stock material selected for the core must have high shear strength and shear modulus while the fiber stock material selected for the face sheet must have high tensile modulus. The face sheet material must be capable of achieving less than 0.003 in. per ply while the core material must be less than 0.002 in. per ply.

A study was performed to evaluate available prepreg forms including random mat, unidirectional mat, woven cloth, and unidirectional fiber. The evaluation included cost and mechanical properties, but was primarily based upon thickness. The results presented in Table III show that the only one of these capable of achieving the desired thickness was unidirectional fiber, and that unidirectional fiber also gives superior properties. The cost to achieve the thickness is high, however, and, if it were not for the low weight at a small cell size requirement, the more conventional thickness would be more desirable.

TABLE III

COMPARISON OF AVAILABLE GRAPHITE FIBER PREPREG FORMS

Material	Minimum Thickness Per Ply (in.)	Modulus* (psi x 10^6)	Strength* (psi x 10^3)	Approximate Cost/lb** ($)
Random mat	0.005	12.0	35.0	180
Oriented mat	0.005	15.6	53.0	180
Woven cloth	0.006	8.0	60.0	145
Unidirectional	0.005	20.0	180.0	130
Unidirectional	0.0016	16.0	130.0	450

*High strength fiber

**Based upon $150/lb fiber cost

There were three distinct fiber types considered: High strength, high modulus, and an intermediate strength and modulus fiber. To meet the thickness requirement, the fiber had to either be available in 0.002 in. thickness or be amenable to spreading to such a thickness. Listed in Table IV are the fibers considered. Thornel 400 was not available at the time of fiber selection. Clearly, only Morganite and Courtaulds fibers have demonstrated thickness/ply values in the range required.

Composite properties obtained with these fibers in epoxy matrices are presented in Table V. Properties given were obtained from the literature. Consistently higher tensile and shear strengths are given by the HT-S and Morganite II fibers while the highest modulii are found with Thornel 75S and GY-70 followed by Morganite I, HM-S, HMG-50, Fortafil 5 and Thornel 50 grouped together.

Hercules chose the HM-S material for the face sheet material based upon its high modulus and demonstrated thin gauge capability. Neither the GY-70 nor the Thornel 75S could be processed to produce ply thicknesses less than 5 and 7 mils, respectively. The HT-S fiber was selected for the core material based upon its high shear strength and demonstrated thin ply capability. Morganite I and II are also acceptable materials and have been treated as equivalent to HM-S and HT-S, respectively, by several companies. Lower cost and processing familiarity with the Courtaulds fibers further dictated their use.

TABLE IV

TYPICAL GRAPHITE FIBER PROPERTIES

Graphite Filament	Precursor	Modulus (10^6 psi)	Strength (10^3 psi)	Density (lb/in.^{3})	Standard Form	Minimum Thickness (mil/ply)	Manuracturer
HMG-50	Rayon	50	310	0.062	2 ply yarn 4 twist/in.	7.5	Hitco
Fortafil 6T	Pan	59	420	0.069	38,000 filament tow	5.0*	Great Lakes
Fortafil 5T	Acrylic yarn	50	250	0.069	1 ply yarn 2 twist/in.	4	Great Lakes
Thornel 50S	Rayon	50	285	0.059	2 ply yarn 1.5 twist/in.	7.5	Union Carbide
Thornel 75S	Rayon	75	350	0.067	2 ply yarn 1.5 twist/in.	7.5	Union Carbide
GY-70	Pan	70	300	0.067	2 ply yarn 1/2 twist/in.	5	Celanese
HT-S	Pan	36	350	0.0635	10,000 filament tow	1.6	Courtaulds
HM-S	Pan	52	300	0.069	10,000 filament tow	1.8	Courtaulds
A	Pan	29	300	0.065	10,000 filament tow	1.6	Courtaulds
Morganite I	Pan	58	250	0.072	10,000 filament tow	1.8	Morgan
Morganite II	Pan	40	350	0.063	10,000 filament tow	1.6	Morgan

*At 1 two per in.

TABLE V

COMPARISON OF COMPOSITE PROPERTIES AT 77° F GRAPHITE/EPOXY

Graphite Filament	Matrix Resin	Prepreg By	Tested By	0° Flexure Strength (10^3 psi)	0° Flexure Modulus (10^6 psi)	Horizontal Shear (10^3 psi)
HMG-50	X-05	Fiberite	Fiberite	125.0	26.0	9.0
HMG-50	4617	Hitco	Hitco	135.2	21.4	7.1
Thornel 50S	4617	Fiberite	Northrop	118.6	26.3	7.3
Thornel 75S	4617	Union Carbide	GD/Convair	116.8	38.9	--
Thornel 75S	4617	Union Carbide	Union Carbide	115.0	41.0	6.0
GY-70	R-350-A	Celanese	Celanese	110.0	39.0	9.0
Fortafil 5T	F-293	Cordo	Northrop	137.4	24.6	9.0
Morganite I	4617	Fiberite	Northrop	140.7	22.8	8.6
HM-S	X904	Fiberite	Fiberite	135.0	27.0	10.5
HT-S	3002	Hercules	GD/Fort Worth	243.0	20.1	16.7
Morganite II	1004	Whittaker	NAR	268.0	19.2	14.1
A	BP-907	Hercules	Hercules	223.0	16.0	13.0
Fortafil 6T	4617	GLCC*	GLCC	170	30.0	9.0

*Great Lakes Carbon Company

3. Matrix Selection

Matrix evaluation encompassed literature review, the manufacturing of prepregs and plates, and testing for composite properties.

The evaluation was made on the basis of mechanical properties (flexural strength and modulus and interlaminar shear), void content, processing variables (handling of resin, preparation of prepreg, and fabrication of composite structure), and cost. The handling of resin was further divided into (1) the uniformity of the resin film or the ease of applying a uniform liquid resin coat, and (2) the necessity of modifying the resins either by solvent dilution or by adding chemicals to give the resin films tack. Prepreg preparation included B-staging time and temperature, ease of solvent removal, tack and drape. The following procedures were included under composite structure fabrication: Precure treatment, cure conditions (time, temperature, and pressure), and postcure schedule.

a. Literature Review

Since 1968, Hercules has had a continuing company-funded program in the use of high temperature resins with graphite fibers. Extensive literature surveys and screening tests of potentially useful resin systems have developed a comprehensive background in polyimide chemistry and a general knowledge of the suitability of commercially available resins. Tables VI and VII summarize some of the resin data compiled through early 1971. The five general classes of commercially available resins considered in these tables are polyimides (PI), polybenzimidazoles (PBI), polysulfones, polyamideimide, and polyquinoxalines. Numerous other classes of resins currently generating considerable interest including pyrrones, poly-as-triazines, polyimidazoquinazolines, and polyquinazolotriazoles were not considered to be far enough along in their stage of development to be considered for this program.

1) Polybenzimidazoles

Although polybenzimidazoles offer good initial strengths and very good high temperature strength retention for short times, long exposure (100 hours and up) at elevated temperature (500° F and up) in air causes rapid polymer degradation. Resin weight losses of 50 percent in glass laminates after 50 hours exposure at 700° F

TABLE VI

HERCULES EVALUATED RESIN DATA SUMMARY

Resin	Data Source	Laminate	Test Temp (°F)	Tensile (psi) Strength	Tensile (psi) Modulus	Flexural (psi) Strength	Flexural (psi) Modulus	B-Stage Cycle Temp (°F)	B-Stage Cycle Time	Cure Cycle Temp (°F)	Cure Cycle Time	Cure Cycle Pressure	Post Cure Temp (°F)	Post Cure Time	Comments
P13N	HI/ABL[3]	Graphite Hercules HM	77 600			$138 - 156 \times 10^3$ $66 - 99 \times 10^3$	$23 - 28 \times 10^6$ $23 - 28 \times 10^6$	150 then 300	30 min 16 hr	550 600	1 hr 2 hr	300 psi 300 psi	None		Optimum cure and layup technique used
		Graphite Hercules HT	77 600			225×10^3 110×10^3	23×10^6 22×10^6	150 then 300	30 min 16 hr	550 600	1 hr 2 hr	300 psi 300 psi	None		Same as above
		Graphite Hercules HM 0.086 thick	77 600			108.7×10^3 130.7×10^3	21.4×10^6 21.8×10^6	150 then 300	30 min 16 hr	550 600	1 hr 2 hr	300 psi 300 psi	None		Same as above
	TRW[4]	Graphite Morganite	77 600			260×10^3 200×10^3	20×10^6 13×10^6	150	30 min	550 (then 550° at pressure, time and pressure not stated)	4 min	0	None		
	TRW[5]	Glass - 181E 13 plies	RT			$89 - 95 \times 10^3$	$3.4 - 3.6 \times 10^6$			600	60 min	200 psi	None		
	Monsanto[6]	Graphite HMG-50	RT 600			128×10^3 78×10^3	19×10^6 14×10^6								No cure information
	AFML[6]	Graphite Morgenite II	RT 600			241.9×10^3 101.3×10^3	15.3×10^6								No cure information
		Graphite Thornel-50	RT 600			107.1×10^3 85×10^3	14.9×10^6								No cure information
Pyralin 4707	HI/ABL[3]	Graphite Hercules HM	77 600			40.5×10^3 32.7×10^3	23.9×10^6 21.2×10^6	180 220 250	1 hr 0.5 hr 1 hr	400 400 500 500	1 min 2 hr 2 hr 2 hr	Contact 500 psi 500 psi 500 psi	600 650	4 hr 4 hr	Not optimum cure
QX-13	HI/ABL[3]	Graphite Hercules HM	77 600			129.1×10^3 97.9×10^3	28.4×10^6 27.7×10^6	392	3 hr	572 572	20-25 min 15 min	Contact 900 psi	302-572 572 572-662	5 hr 16 hr 2 hr	Good high properties. Relatively easy cure
Skybond 703	HI/ABL[3]	Graphite Hercules HM	77 600			81.4×10^3 33.7×10^3	21.7×10^6 12.3×10^6	250	1 hr	Pre-heat 400 400	40-60 sec 30 min	Contact 300 psi	400 500 600 650	4 hr 4 hr 4 hr 4 hr	Panel blistered during post cure. Cure cycle not optimized
	Convair[7]	Graphite Modmor II	RT 550	158.4×10^3 104.1×10^3*				Precompacted at 130°-150°, 25-50 psig for 10-15 min		Heated to 350 in stages (intermediate temp and time not given)		Vacuum bag	None		

*All failures in test grips

3 through 7 Refer to List of References

TABLE VI (Cont)

HERCULES EVALUATED RESIN DATA SUMMARY

Resin	Data Source	Laminate	Test Temp (°F)	Tensile (psi)		Flexural (psi)		B-Stage Cycle		Cure Cycle			Post Cure		Comments
				Strength	Modulus	Strength	Modulus	Temp (°F)	Time	Temp (°F)	Time	Pressure	Temp (°F)	Time	
Skybond 703 (Cont)	Convair[7]	Graphite Modmor II	RT	175.2×10^3	19.0×10^6			Precompacted at 130°-150°, 15-25 psig for 10-15 min		Heated to 350 in stages (intermediate temp and time not given)		Vacuum bag + 75 psig			
	Whittaker	Graphite Modmor II	RT	148×10^3	19×10^6	161×10^3	17×10^6								No cure information given
	Monsanto[6]	Graphite HMG-50	RT 600			104×10^3 66×10^3	17×10^6 14×10^6								No cure information
	Monsanto[8]	Glass - 181E 12 plies 0.125 thick	75 600			$71 - 79 \times 10^3$ 62×10^3		250-300	No time stated	Pre-heat 400 400	40-60 sec 30 min	25 psi 250 psi	400 500 600 650	4 hr 4 hr 4 hr 4 hr	
		Glass - 181E 12 plies 0.125 thick	75 550			$65 - 75 \times 10^3$ 37×10^3		250-300		Heat up to 350 350	 1 hr	Vacuum Apply 100 psi at 250° Maintain above	400 500 600 650	4 hr 4 hr 4 hr 4 hr	
AI-1137	HI/ABL[3]	Graphite Hercules HT	77 600			33.8×10^3 21.1×10^3	12.1×10^6 9.2×10^6	300	30 min	Pre-heat 600 600	2-4 min 30 min	Contact 500-1200 psi	400 450 500 550 600	2 hr 2 hr 2 hr 2 hr 2 hr	Very viscous, difficult to use. Cure cycle not optimized (Intermediate temperature resin)
	AMOCO[9]	Glass - 181E	75 550	56×10^3	3.5×10^6	$70 - 75 \times 10^3$ 47×10^3	$3.2 - 3.5 \times 10^6$ 3.5×10^6	275	10 min	Same					
		Glass - 181E	75	54×10^3	3×10^6	$50 - 60 \times 10^3$	$2.8 - 3.1 \times 10^6$	Same		Raise to 350 350	2 hr	Full vacuum 50-200 psi	Same		

8 through 9 Refer to List of References

TABLE VII

LITERATURE SURVEY DATA SUMMARY

Resin	Data Source	Laminate	Test Temp (°F)	Tensile (psi) Strength	Tensile (psi) Modulus	Flexural (psi) Strength	Flexural (psi) Modulus	B-Stage Cycle Temp (°F)	B-Stage Cycle Time	Cure Cycle Temp (°F)	Cure Cycle Time	Cure Cycle Pressure	Post Cure Temp (°F)	Post Cure Time	Comments
Skybond 700	Monsanto[10]	Glass - 181E 12 plies 0.125 thick	75	57,000	3.12×10^6	75 - 85,000		250-300	Not stated	Pre-heat 600	1.5-2.5 min	10-25 psi	392	2 hr	
			700			45 - 60,000				600	30 min	250 psi	Inc by 45° incre Final 700	2 hr each step 4 hr	
			75	50,300		76 - 83,500		Same		Raise to 350	30 min	25-29 in. Hg	Same		
			700			22 - 32,000				350	30 min	100 psi			
	AFML[12]	Graphite Thornel 50	RT 600			113,800 113,800	14.6×10^6								
Skybond 709	Monsanto[11]	Glass - 181E 12 plies 0.125 thick	75	61,500 - 66,000				Not stated		Raise to 275	2°-3° per min	5 in. Hg	450 550 650 700	2 hr 2 hr 2 hr 2 hr	
			700			20,000				Raise to 350	2°-3° per min	26-29 in. Hg			
										350	30 min	100 psi + vac			
Skybond RS-6234	Monsanto[12]	Same	75			48,000		Not stated		Same as 709			Same as 709		
			700			26,000									
	Convair[7]	Graphite Modmor II	RT	156,400	20×10^6			Precompacted at 130°-150° 25-/50psig for 10-15 min		350 Staged (Intermediate time and temp not given)		Vacuum bag	None		
			550	91,600*											
			RT	192,300	21×10^6			Same as above		Same as above except 75 psig in addition to vacuum bag			None		
			550	127,000*											
	Convair[7]	Graphite Courtaulds HTS	RT	96,000	32×10^6			Same as above		Same as above			350 400 450 500 550 600	2 hr 2 hr 2.5 hr 4.5 hr 4 hr 4 hr	
			600	100,000											
	Convair[13]	Graphite Courtaulds HTS	320 75 500 600 650	 173.2 160.9 151.1		198.5 207.9 182.9 146.6 99.4				175 260 260 350	30 min 30 min 2 hr	Vacuum Vacuum Vacuum + 100 psi Vacuum + 100 psi	350 400 450 500 550 600 650 700	1 hr 1 hr 1 hr 1 hr 2 hr 2 hr 4 hr 8 hr	

*All test grip failures

10 through 13 Refer to List of References

TABLE VII (Cont)

LITERATURE SURVEY DATA SUMMARY

Resin	Data Source	Laminate	Test Temp (^oF)	Tensile (psi) Strength	Tensile (psi) Modulus	Flexural (psi) Strength	Flexural (psi) Modulus	B-Stage Cycle Temp (^oF)	B-Stage Cycle Time	Cure Cycle Temp (^oF)	Cure Cycle Time	Cure Cycle Pressure	Post Cure Temp (^oF)	Post Cure Time	Comments
Gemon	Ref 6	Graphite Courtaulds HMX	RT 500			93,000 107,000	21.5×10^6 21.3×10^6								
		Graphite Morganite I	RT 500			104,000 125,000	20.6×10^6 19.2×10^6								
		Graphite Morganite II	RT			170,000	15.3×10^6								
F174	Hexcel[14]	Glass - 181E	RT 500	60,300	4×10^6	79,200 55,900	3.65×10^6 3.07×10^6	Not stated		270 350	30 min 2 hr	Vacuum Autoclave not stated	400 450 500 550 600	2-3 hr 2-3 hr 4-5 hr 4-5 hr 4-5 hr	
Astrel 360 Polyarysulfone	3M[15]	No	75	13,000		17,200									Molded specimens. Injection molded, 725°, 20,000 psi
Polyquinoxaline	Whittaker[16]	Glass 1581 HTS-994 7 plies	RT	71.4×10^3	3.6×10^6	104.9×10^3	3.17×10^6	Not stated		450-750	No time stated	50 psi	750	No time stated	
		Graphite Morganite II 14 plies	RT 600			106,600 99,700	15.5×10^6 15.1×10^6	Not stated		450 750	10 min 4 hr	200 psi 200 psi	RT 300 750	During 1 hr 12 hr	Post cure in nitrogen
		Graphite Morganite I	RH 600			82,800 49,800	32.6×10^6 19.8×10^6	Not stated		Same as above			RH 300 750	During 2 hr 12 hr	Post cure in nitrogen
	Boeing[17]	No	RT 350	18,000 14,000	400,000 280,000			158	15 hr	Heat to 392 392 572	2 hr 4 hr 1 hr	Vacuum Vacuum Vacuum	None		Monoether film
		Glass - 1581 AF-994 HTS 4 plies	RT 700			96,000 61,600	3.64×10^6 2.44×10^6	266	1 hr	450 765	10 min 4 hr	200 psi 200 psi	400 450 500 550 600 650 700 750 700	4 hr 4 hr 10 hr 8 hr 4 hr 4 hr 4 hr 4 hr 8 hr	Cured in nitrogen. Some thermoplastic failure noted
		Graphite Modmor II	RT			122,100	15.5×10^6	266	1 hr	Heat to 450	Hold 10 min	250 psi	Same as above thru 700 then 740	4 hr	

14 through 17 Refer to List of References

TABLE VII (Cont)

LITERATURE SURVEY DATA SUMMARY

Resin	Data Source	Laminate	Test Temp (°F)	Tensile (psi) Strength	Tensile (psi) Modulus	Flexural (psi) Strength	Flexural (psi) Modulus	B-Stage Cycle Temp (°F)	B-Stage Cycle Time	Cure Cycle Temp (°F)	Cure Cycle Time	Cure Cycle Pressure	Post Cure Temp (°F)	Post Cure Time	Comments
Polyphenyl-quinoxaline	Whittaker[16]	Glass - 1581 HTS 994 7 plies	RT			118,300	3.97×10^6	Not stated		Not stated			800		Diether PPQ
			600			35,050	2.73×10^6								
			700			8,180	0.98×10^6								
	Boeing[17]	No	RT	17,000	300,000										
			350	12,000	240,000										
Pyrrone	NASA[18]	No	RT	15 - 22,000	0.6 - 1.0 x 10^6			255 435	1 hr 1 hr	615	3 hr	None			
Polyphenyl-astriazines	Boeing[19]	Graphite Morganite I	RT			85,000	32×10^6	350 in vacuum		550	1 hr	200 psi	550	2 hr	Limited to below 500° F
			500			81,000	29×10^6								
Kerimid 601	Rhone-Poulenc[20]	Glass - 181E	RT	49,000		78,000	4.1×10^6			Cure cycles not clearly defined					Limited to below 500° F
Polybenzi-midazole	Whittaker[21]	Glass - 1581 HTS-994	RT	86,000	5.1×10^6	109,000	5.3×10^6	Not stated		250		Contact to 200 psi	600 650 700 750 800 700	24 hr 24 hr 24 hr 24 hr 8 hr 3 hr	600-800 in nitrogen, then final 3 hr in air
			500	77,000	4.3×10^6	86,000	5.2×10^6			700	3 hr				
			600	62,000	3.9×10^6	57,000	3.6×10^6								
Skybond 703	McDonnell[22] Aircraft Company	Graphite Morganite II	RT			105 - 189,000				200 250 350	1 hr Heat to 2 hr	Vacuum Apply 100 psi	400 500 600	2 hr 2 hr 2 hr	
			550			25.8 - 103,000									

18 through 22 Refer to List of References

have been reported.[23] Also, PBI processing is difficult, requiring long postcure cycles in nitrogen or vacuum at temperatures up to 800° F. Volatile removal during cure is particularly difficult and leaves the resin matrix somewhat porous. This porosity is part of the reason for the PBI's poor performance with long, high temperature exposure. Increasing cure pressure to prevent porosity is not a solution to the problem since the trapped volatiles disturb the equilibrium reaction which results in lower molecular weight polymer and poorer performance. Incorporation of antioxidants in the resin or sealing the laminate with other resins improve the high temperature performance but do not correct the fundamental weakness of the material. For these reasons, PBI is not generally considered as a desirable laminating resin in the industry at present and was dropped from consideration.

2) Polyquinoxalines

Whittaker Research and Development has been working on polyquinoxalines (PQ) and polyphenylquinoxalines (PPQ)[16] and is marketing polymer solutions in pilot quantities at approximately $750 per gallon. The quinoxalines are storable at room temperature, stable to oxidation to 700° F, laminates retain 95 percent of room temperature strength at 600° F and 62 percent at 700° F (based on preliminary data[17]), and have better physical properties than P13N which appears to be the strongest polyimide evaluated to date. Their major disadvantages (besides cost) are low solubility and the requirement for carefully controlled cure at high pressures and temperatures up to 750° F. The PPQ shows greater solubility and easier processing that the PQ; however, this material is not as far along in its development as the PQ. Both the PQ and PPQ typically show some thermoplastic failure behavior when tested to failure. Carefully prepared samples, however, in which all solvent has been removed do not show this behavior. Although these matrices show promise, the cost was prohibitive; and both PQ and PPQ were dropped from consideration.

3) Pyrrones

The pyrrones are being evaluated by several investigators on a laboratory basis, but no one as yet is offering the materials as salable items. These materials (depending on the precursor) can have a complete ladder structure and are stable in air at 750 to 800° F. Reported values of tensile strength, elongation, and Young's modulus are in the range of 15,000 to 22,000 psi, 3 to 7 percent, and 600,000 to 1,000,000 psi, respectively.[24] These are film property values; no laminate data is currently available. Disadvantages of the material are: Low solubility, sensitive cure cycle, and availability.

[23,24] Refer to List of References

4) Resin Candidate Selection

As a result of the literature survey, polyimide resins were judged to be the more reliable resin system for use in the program from the standpoint of cost, availability, processibility, and experience. Three of the polyimide systems were selected for further screening tests, TRW's P13N, Hexcel's F174, and Monstanto's RS6234. P13N was selected because of its excellent high temperature stability and low void processing; F174, a modified Monsanto Skybond 709, was selected since it is being used by Hexcel in glass polyimide core at the present time. RS6234 was selected since it has been selected for characterization by General Dynamics/Convair for space shuttle applications under NASA Contract NAS 8-26198.

P13N is basically a polyamic acid solution of low molecular weight with the polymer chain terminated by reactive end groups (nadic anhydride is used) which can further react at high temperatures by an addition mechanism to form high molecular weight crosslinked polymers without evolution of volatile material. The polyimide ring is formed at temperatures much below the cure temperature under conditions which permit easy removal of the water formed. Very low void composites can be made with this resin system.

Monsanto's resin variations are solutions of monomers. Because the resin solution is made up of monomeric reactants, the precursor polyamic acid must be formed during resin cure. With the entire reaction performed during cure, these resin systems are somewhat more sensitive to cure variations and require more stringent control of the cure cycle.

b. Screening Test Results

Prepregs were fabricated with all three resin candidates using the same spool of HT-S fiber (2CT 10A/26AR). The tow was spread to 1.0 in. width and wound onto a drum (10-ft circumference, 40 in. wide) at 3.5 tows/in. to produce prepreg that would mold to 0.005 in./ply. Resin was metered onto the release film just ahead of the fiber by a low pressure pump. All three materials were staged on the drum for 1 hour at 77° F. The prepregs of RS6234 and F174 were low in resin content and had poor resin penetration of the fiber tow. The P13N prepreg was within expected values. The prepreg values are summarized in Table VIII.

TABLE VIII

INITIAL PREPREG FABRICATION DATA

Resin	Resin Content	Volatiles Content	B-Stage
RS6234	32.7	22.4	1 hr at 77° F
F174	31.1	24.11	1 hr at 77° F
P13N	42.8	27.1	1½ hr at 77° F

Fifteen ply, 4 by 5 in. plates were fabricated from each material using vendor recommended cure cycles for F174 and RS6234 and Hercules developed imidization and cure cycle for P13N as follows:

<u>P13N</u>

Imidization:

(1) Place each ply separately between two wire screens and arrange in oven

(2) Heat to 150° F for 1 hr

(3) Raise temperature to 300° F and hold for 16 hr

Cure:

(1) Preheat press to 600° F

(2) Place ply stack in mold and mold in press. Apply 300 to 1200 psi

(3) Establish part temperature at 550° F and hold for 1 hr

(4) Raise temperature to 600° F and hold for 3 hr

<u>Hexcel F174</u>

Cure:

(1) Raise temperature to 350° F at 2° F per minute under vacuum

(2) Apply 100 psi after reaching 350° F

(3) Hold 2 hr at 350° F

Post Cure:

(1) 1/2 hr at 350° F

(2) 1/2 hr at 400° F

(3) 1/2 hr at 450° F

(4) 1/2 hr at 500° F

(5) 2 hr at 550° F

(6) 2 hr at 600° F

(7) 2 hr at 650° F

<u>RS 6234</u>

Cure:

(1) Bag and pull a partial vacuum

(2) Heat to 350° F at 3° F per minute, pulling a full vacuum after 60 minutes

(3) Apply 100 psi after reaching 350° F

(4) Hold 2 hours at 350° F

Post Cure:

(1) 1/2 hr at 350° F

(2) 1/2 hr at 400° F

(3) 1/2 hr at 450° F

(4) 1/2 hr at 500° F

(5) 2 hr at 550° F

(6) 2 hr at 600° F

(7) 2 hr at 650° F

The resulting plate with P13N had good visual appearance. The F174 plate was thick and dry in appearance, while the RS6234 plate was well compacted but light brown in color. Samples for flexure and shear tests were cut from the plates. The properties are summarized in Table IX.

The low resin contents of the F174 and RS6234 resulted from the low resin content prepreg and poor resin penetration of the tow. Two additional prepreg batches of both F174 and RS6234 were manufactured. One batch was manufactured at 5 tows/in. (0.008 in./ply) and the other at 0.76 tow/in. ($<$0.002 in./ply). The resins were diluted to a viscosity of 300 cps with Ethanol, one-half of the required resin was sprayed onto the release film prior to fiber winding and one-half onto the fiber after winding. All prepregs contained between 40 and 45 percent resin content with 15 to 20 percent volatiles. Staging was performed in a press at 200° F and 200 psi for 5 min. A series of plates was fabricated from both thicknesses of prepreg as described in Table X. The cure cycles follow:

<u>RS6234</u>

Cure:

(1) Bag and pull vacuum

(2) Heat to 175° F and hold 1/2 hr

(3) Heat to 250° F and hold 1/2 hr

(4) Apply 100 psi

(5) Raise to 350° F and hold 1 hr

Post Cure:

(1) 2 hr at 400° F

(2) 2 hr at 450° F

(3) 2 hr at 500° F

(4) 2 hr at 550° F

(5) 2 hr at 600° F

(6) 2 hr at 650° F

TABLE IX

INITIAL COMPOSITE PLATE DATA RESIN SCREENING

Property	HT-S/P13N	HT-S/6234	HT-S/F174
Flexural Strength (psi)			
70° F	174,430	100,325	102,360
600° F	128,007	114,360	79,124
Flexural Modulus (psi x 10^6)			
77° F	14.02	17.0	13.8
600° F	13.92	20.0	17.7
Interlaminar Shear (psi)			
77° F	13,955	6,650	--
600° F	6,772	4,646	--
Resin Content (Wt %)	42.7	23.8	29.0
Density (lb/in.^{3})	1.55	1.411	1.45

F174

Cure:

(1) Bag and pull vacuum

(2) Heat to 270° F and hold 1/2 hr

(3) Raise to 350° F and apply 100 psi

(4) Hold 350° F for 2 hr

Post Cure:

(1) 2 hr at 400° F

(2) 2 hr at 450° F

(3) 2 hr at 500° F

(4) 2 hr at 550° F

(5) 2 hr at 600° F

(6) 2 hr at 650° F

TABLE X

COMPOSITE PLATE FABRICATION SUMMARY

Plate	Material	Lay Up	Thick (in.)	Density (lb/in.^{3})	Resin Content (% by Wt)	Viber Volume (%)	Void Content (%)
X 188-109	HT-S/6234	4 x 5 in. (0^o) 10 ply	0.086	0.055	38	53.6	2.76
X 188-111	HT-S/F174	4 x 5 in. (0^o) 10 ply	0.097	0.0506	31	54.7	13.9
X 188-119	HT-S/6234	4 x 5 in. (0^o) 9 ply	--	--	--	--	--
X 188-120	HT-S/6234	4 x 5 in. (0, 90) 2 ply	0.005	--	--	--	--
X 188-121	HT-S/6234	4 x 5 in. (0, 90) 2 ply	0.0055 to 0.0071	--	--	--	--
X 188-122	HT-S/6234	4 x 5 in. (0, 90, 90, 0) 4 ply	0.033	0.0524	27	60.0	11.9
X-188-123	HT-S/F174	4 x 5 in. (0^o) 10 ply	0.083	0.0520	30	57.3	12.0
X 188-124	HT-S/6234	4 x 5 in. (0, 90) 2 ply	0.004	--	--	--	--
X 188-125	HT-S/F174	4 x 5 in. (0, 90) 2 ply	0.004	--	--	--	--
X 188-126	HT-S/F174	4 x 5 in. (0, 90) 90, 0) 4 ply	0.008	--	--	--	--
X 188-127	HT-S/6234	4 x 5 in. (0^o) 9 ply	0.075	0.0556	25	65.7	5.3
X 188-128	HT-S/6234	4 x 5 in. (0^o) 9 ply	0.078	0.056	30	61.9	5.0

Plate quality was in general better for RS6234 although both resins yielded some plates that were poorly consolidated.

Flexure tests (4 pt at 32/1 span to thickness) and interlaminar shear tests (short beam at 4/1 span to thickness) were run at temperatures from -150 to 600° F after 30 min exposures on the better plates. Table XI summarizes the results. The results clearly show (Tables X and XI) that RS6234 gives better strengths than F174 at 600° F and somewhat lower void contents.

Of the three resins evaluated, P13N gave higher properties at both room temperature and 600° F; however, the system has several disadvantages in converting over to core fabrication. The fully imidized material is very dry and fragile, and is difficult to transfer to a corrugated mold without incurring damage, particularly in handling thin gauges. Thus, imidization should be done in the corrugated mold. A 16-hour imidization cycle for each sheet in a matched metal mold would be extremely expensive. P13N was, therefore, considered as a backup to RS6234, and the latter resin chosen for fabrication of the first core in the program.

4. Core to Skin Bonding

The adhesive system and the bonding techniques utilized to bond facings to honeycomb core are critical with very low density core for high temperature applications. It is undesirable to eliminate weight from the core and facings only to reintroduce it later with unnecessary adhesive. Thus, the development of an effective "cell edge" adhesive bonding system was indicated. To be considered as a bonding adhesive for the purpose of this program, the resin must be available as a spreadable fluid as opposed to a solid or a supported fiber. Further, the fluid must form a stable film which does not bead when applied at ambient temperature to a graphite/polyimide surface.

The candidate bonding adhesives were evaluated according to the following criteria:

(a) The cured bond must show satisfactory filleting.

(b) The resin must be curable at a temperature not exceeding 600° F, and at a minimum pressure to prevent damage to the face plate or core.

(c) The volatile by-products given off during cure must be minimal.

TABLE XI

COMPOSITE PLATE DATA SUMMARY

Plate	Flexure Strength x 10^3 psi			Flexure Modulus x 10^6 psi			Shear Strength (psi)		
	-150° F	77° F	600° F	-150° F	77° F	600° F	-150° F	77° F	600° F
X 188-109	--	108.4	65.0	--	19.5	11.6	6624	6303	4899
X 188-111	131.1	103.7	77.4	15.9	15.0	14.5	7357	5548	4256
X 188-119	135.9	86.9	49.1	14.1	14.4	13.0	--	--	--
X 188-123	83.0	73.3	51.8	15.2	14.7	15.1	3418	3236	3924*
X 188-127	150.8	162.3	91.6	17.5	15.7	15.0	9476	8798	5700
X 188-128	--	171.0	101.0	--	18.0	16.0	--	9120	5860

*2866 at 650° F

a. Literature Review

Literature reviewed[22,25,26] indicates that polyimide adhesives in core-to-face sheet flatwise tension can be expected to exhibit from 400 to 600 psi at room temperature, and 100 psi at 550° F. FM-34 (film version of BR-34) by Bloomingdale Rubber Division of American Cyanimide showed the highest strength. The polyimides were the only family of adhesives readily available and were generally meeting the requirements outlined above. Tables XII, XIII, and XIV, along with Figure 4, summarize the data leading to this conclusion.

Three polyimide adhesives were selected from the literature and from vendor data for screening tests. The three adhesives selected are Bloomingdale's BR-34, Hexcel's HX-971, and the new Hexcel's LR-3050A-1.

b. Screening Test Results

Filleting tests have been completed on the three resins. Process studies yielding optimum fillet formations were completed. These involved solvent addition to provide more uniform resin distribution (lower viscosity), pressure drying cycles, and cure studies.

Each of the three adhesives were found to form satisfactory fillets with BR-34 having slightly better fillet appearance. Therefore, each of these will be subjected to face-sheet-to-core bonding tests in Phase III of the program for final adhesive selection.

[25,26] Refer to List of References

TABLE XII

BASIC FAMILIES OF ADHESIVES*

Type	Basic Family	Typical Shear		Typical Peel Strength
		°F	psi	
A	Epoxy modified with polyamides, nylon, nitrile or unknown modifiers	-420 +450	5500 1500	Good to excellent
B	Vinyl phenolic	-67 +250	2500 1500	Fair to good
C	Epoxy phenolic	-420 +500	3500 2000	Poor
D	Nitrile phenolic	-67 +400	4000 1000	Good
E	Unmodified epoxy	-70 +500	3000 1000	Fair to good
F	Polyimide or polybenzimidazole	-110 +700	3000 1200	Poor
G	Urethane	-423 +200	4500 1600	Excellent
H	Epoxy Novolac	-65 +450	3000 1300	Excellent

*Refer to List of References, Reference 25

TABLE XIII

COMMON ADHESIVES IN CURRENT USE*

Type	Trade Designation	Manufacturer
A	350° F Cure	
	Metlbond 328	Narmco Materials Division, Whittaker
	AF 120	3M Company, Minneapolis
	FM 1000	Bloomingdale Rubber Division, American Cyanimide
	250° F Cure	
	Metlbond 252	Narmco Materials Division, Whittaker
	AF 126	3M Company, Minneapolis
	FM 123	Bloomingdale Rubber Division, American Cyanimide
B	FM 47	Bloomingdale Rubber Division, American Cyanimide
	AF 31	3M Company, Minneapolis
	Metlbond 105	Narmco Materials Division, Whittaker
C	Aerobond 422	Adhesive Engineering
	HT 424	Bloomingdale Rubber
	Epon 422	Shell Chemical Corp.
D	AF 30, AF 33	3M Company
E	Epon VI, VIII	Shell Chemical Corp.
	EC-1386	3M Company
	Narmco 574	Narmco
F	Imidite 850, 840	Narmco
	FM 34	Bloomingdale Rubber
G	XA-3512	3M Company
	Narmco 7343	Narmco
H	Plastilock 677	B. F. Goodrich
	Metlbond 329	Narmco

*Refer to List of References, Reference 25

TABLE XIV

POLYIMIDE ADHESIVE FLATWISE TENSION RESULTS*

Polyimide Adhesive	Flatwise Tension Strength (psi)	
	@ 75° F	@ 550° F (30 min)
Bloomingdale FM-34	640	105
MCAIR SB703 (No. 1)	525	94
MCAIR SB703 (No. 2)	390	--
WRD SB703	In test	In test

*Refer to List of References, Reference 22

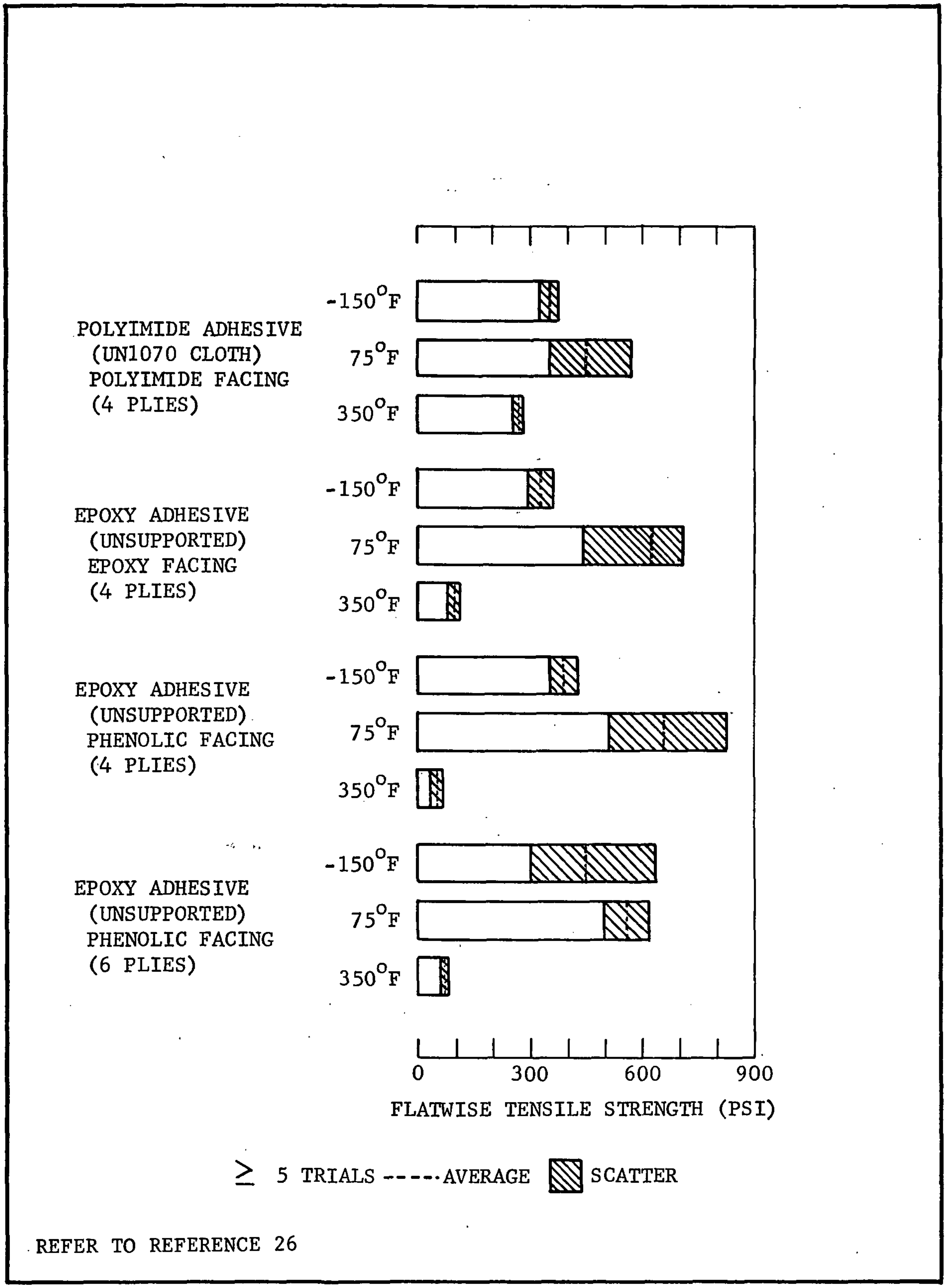


Figure 4. Effect of Temperature on Adhesive Strength

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