NASA CR-134900

DEVELOPMENT OF AUTOCLAVE MOLDABLE ADDITION-TYPE POLYIMIDES

By R. W. Vaughan, R. J. Jones, M. K. O'Rell

and G. A. Zakrzewski

Prepared under

Contract No. NAS 3-17824

TRW
SYSTEMS GROUP

for

National Aeronautics and Space Administration

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16. Abstract

Chemistry and processing modifications of the poly(Diels Alder) polyimide (PDA) resin were performed to obtain structural composites suitable for 589K (600°F) service. This work demonstrated that the PDA resin formulation developed under Contract NAS 3-17770 is suitable for service at 589K (600°F) for up to 125 hours when used in combination with Hercules HTS graphite fiber. Sandwich panels were autoclave molded using PDA/HTS skins and polyimide/glass honeycomb core. Excellent adhesion between honeycomb core and the facing skins was demonstrated. Fabrication ease was demonstrated by autoclave molding three-quarter scale YF-12 wing panels.

17. Key Words (Suggested by Author(s))

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Cocured polyimide sandwich panels
Polyimide core-fill
Syntactic foam

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SUMMARY

The objective of this program was to improve the PDA polyimide chemistry and processing to provide composites suitable for long-term service at 589K (600°F). The technical approach included 1) evaluating polymer modifications to the PDA resin, 2) optimizing fabrication procedures, 3) testing composite and honeycomb sandwich panels, and 4) fabricating three-quarter scale YF-12 wing panels.

The work performed during this program demonstrated that the current PDA resin formulation is suitable for 125 hours service at 589K (600°F). Also, fabrication ease was demonstrated by autoclave molding five three-quarter scale YF-12 wing panels.

These sandwich panels consisted of PDA/HTS skins cocured to polyimide/glass honeycomb core, *i.e.*, the PDA matrix resin was used to bond to the honeycomb core. A core-fill material was developed and used to reinforce the honeycomb core in the beveled area. Attempts to improve the PDA chemistry were unsuccessful.

Based on the results of this work, it was concluded that the PDA resin is suitable for use in composites intended for short service mission at 589K (600°F).

1. INTRODUCTION

This final report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS 3-17824 during the period 12 June 1974 through 30 September 1975. The objective of this program was to improve the PDA polyimide chemistry developed previously under Contract NAS 3-17770 (Reference 1) and to optimize processing to fabricate low void content graphite fiber reinforced composites suitable for long-term (∿1000 hours) use at 589K (600°F).

The work described in this document was a continuation of that previously reported (Reference 1) during which it was demonstrated that polyimide resin matrix composites could be prepared by a poly(Diels Alder) reaction at ∿477K (400°F) to yield low void content composites. The most promising poly(Diels Alder) polyimide (PDA) resin identified during that work consisted of benzophenone tetracarboxylic imide (BFBI) and *bis*(4-maleimidophenyl) methane (BMPM). Composite panels were autoclave molded from prepreg tape consisting of Hercules AS graphite fiber impregnated with the PDA resin. The prepreg tapes were prepared from a solution of the PDA resin in a methanol, acetone and dioxane mixture. Evaluation of the resultant composites demonstrated the suitability of the PDA resin for long-term use (>1000 hours) at 533K (500°F) and shorter term use at 561K (550°F).

During the work reported in this document, additional chemistry and processing development studies were performed to obtain 589K (600°F) service with the PDA resin. Short-term service at 589K (600°F) was obtained using the original BFBI/BMPM PDA resin formulation in combination with Hercules HTS graphite fiber. Attempts to obtain long-term service at 589K (600°F) by polymer modification were unsuccessful. Both solid composite panels and cocured honeycomb sandwich panels were autoclave molded between 0.35 to 0.7 MN/m^2 (50 to 100 psig) pressure and cured at 472K (390°F). Further demonstration of the PDA resin's fabrication ease was made by autoclave molding five three-quarter scale YF-12 wing panels.

The work performed under this contract was accomplished in three tasks as follows:

TASK I - Polymer Synthesis and Evaluation - Attempts to prepare new monomers for the synthesis of improved PDA polymers were unsuccessful. Consequently, the PDA resin used in Contract NAS 3-17770, which is derived from *bis*(4-maleimidophenyl) methane (BMPM) and *bis*-(2-furfuryl) benzo phenone tetracarboxylic imide (BFBI) was selected for use in Task II and Task III.

TASK II - Autoclave Process Development - A satisfactory autoclave molding cycle was developed for fabricating prototype three-quarter scale YF-12 wing panels with the BMPM/BFBI PDA resin.

TASK III- Fabrication and Evaluation of Prototype Component - The resin and process selected from Tasks I and II was employed to fabricate five three-quarter scale YF-12 wing panels.

This document is divided into sections covering each of the key activity areas:

- Resin Development
- Process Development
- Prototype Component Fabrication and Evaluation

The significant conclusions reached and assessments of the results are listed together with recommendations for activities that warrant further investigations. The information given in the main body of this document is supplemented by appendices covering detailed descriptions of procedures used in material preparation and processing.

2. RESIN DEVELOPMENT

Experimental studies were conducted to synthesize new monomers for use in a modified PDA approach to addition-type polyimides. The new monomers were sought as replacements for the monomers used in the previous PDA resins (Reference 1), namely benzophenone tetracarboylic imide (BFBI) and *bis*(4-maleimidophenyl) methane (BMPM). The new monomer structures were selected primarily to increase the thermo-oxidative stability of the PDA resin and to reduce the amount of water evolved during *in situ* aromatization.

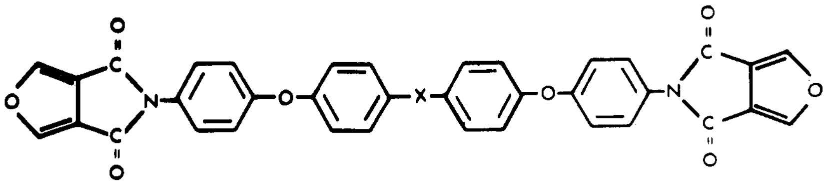
The experimental studies resulted in the successful synthesis of two new aromatic diamines. One of the diamines, *bis*[4-(4-aminophenoxyphenyl)] sulfone then was converted to the corresponding *bis*(maleimide) by conventional synthetic procedures. However, difficulties were encountered in the attempted preparation of *bis*(furan-3,4-carboimide) compounds from diethyl 3,4-furandicarboxylate and aromatic diamines. This resulted in the decision to discontinue the investigation of new PDA monomers. Studies also were conducted to assess the possibility of using PDA/A-type polyimide copolymers. However, the expected improvements in 589K (600°F) performance was not achieved and this approach also was considered unsuccessful. An improved procedure for recrystallizing BMPM was established that provided higher purity monomer for use in the standard BFBI/BMPM PDA resin. The PDA resin prepared for use throughout the process development and demonstration component fabrication work (see Sections 3 and 4) used BMPM recrystallized by this procedure.

2.1 NEW PDA RESIN STUDIES

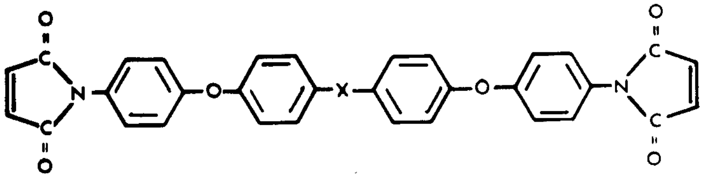
One of the two approaches that were investigated in an attempt to develop an autoclave moldable resin that would provide long-term service in a 589K (600°F) aerobic environment was modification of the PDA resin developed under Contract NAS 3-17770 (Reference 1). During this previous program, PDA/AS graphite composites were shown to be limited to 561K (550°F) service. Another concern with this resin was the water formed during post-cure by the *in situ* aromatization reaction. Modification studies were performed on the PDA resin in an attempt to minimize the quantity of water formed and to increase the upper use temperature of the PDA resin. To accomplish these objectives, new monomer structures were selected for study (structures 1 and 2) for the following reasons:

- To reduce the water evolved during *in situ* aromatization of the PDA reaction to ∿2% w/w (compared to 4.5% w/w for the BFBI/BMPM couple), and
- To eliminate the unstable furfuryl α-methylene group in the BFBI reactant, thus raising the thermo-oxidative stability of the resultant polymer.

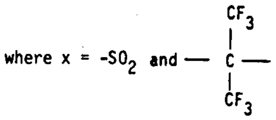
Details of the experimental procedure used to prepare the desired monomers are given below.



(1)

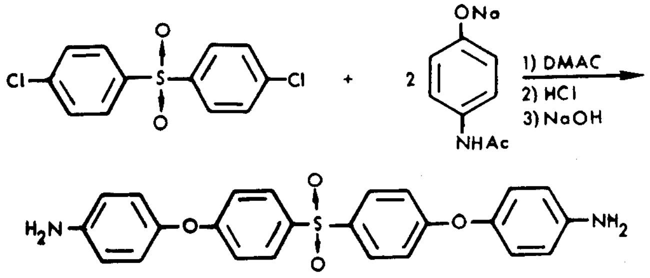


(2) .



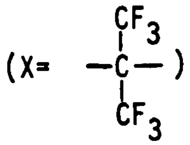
$$\text{where } x = -SO_2 \text{ and } -\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{\overset{|}{\underset{|}{C}}}}-$$

The first monomer to be prepared successfully was *bis*[4-4-aminophenoxyphenyl) sulfone] (BDAS). The entire synthesis route is outlined in Equation 1. The route is based upon an aromatic nucleophilic displacement reaction of a halogen (chloride) by a phenoxide. Hydrolysis of the resulting *bis*(acetanilide) with methanolic hydrogen chloride followed by neutralization of the amine hydrochloride with aqueous sodium hydroxide gave the desired diamine. The diamine then was converted to its corresponding *bis*(maleimide) by reacting the diamine with maleic anhydride. The experiemntal details are given in Appendix A.



Equation 1

A different synthesis scheme was utilized to prepare the perfluoro isopropylidene analogue (see structure 3) because the desired starting material, 2,2-*bis*(4-chlorophenyl)hexafluoropropane, was not commercially



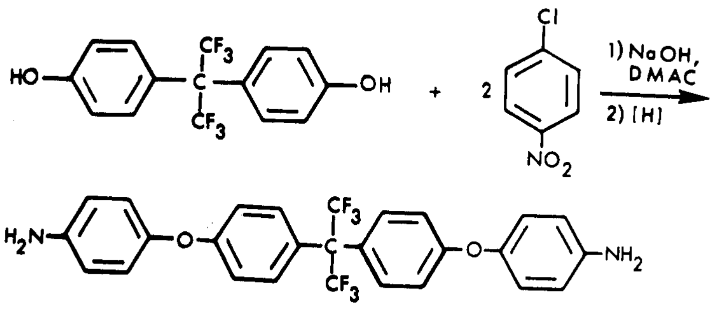
$$(X= -\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{C}}-) \qquad (3)$$

available. However, 2,2-*bis*(4-hydroxyphenyl)hexafluoropropane was available and was used to prepare the diamine.

The first approach to prepare the diamine employed 4-chloroacetanilide (prepared from *p*-chloroaniline) and the disodium salt of 2,2-*bis*(4-hydroxyphenyl)hexafluoropropane in dimethylacetamide (DMAC). However, this approach yielded no coupling product after 150 hours of heating at 423K. Apparently, the acetamido group does not sufficiently activate the chloro group for the nucleophilic reaction to occur. Based on previous experience at TRW with aromatic nucleophilic substitution reactions, the phthalimide derivative of *p*-chloroaniline then was selected as a possible candidate for the nucleophilic reaction. The imide was prepared from the substituted aniline and phthalic anhydride in toluene. However, it was determined that this coupling reaction again afforded only starting materials.

These results suggested that a highly electron withdrawing group was necessary to successfully promote the coupling. As a result, *p*-chloronitrobenzene was employed in the coupling reaction. The coupling reaction did yield the desired dinitro product in 93% yield.

This dinitro compound was successfully reduced to the diamine with iron and hydrochloric acid. The infrared spectrum (see Appendix A, Figure A-2) for the compound was consistent for the structure and elemental analysis also confirmed that the diamine had been synthesized. The entire route to the diamine is outlined in Equation 2.



Equation 2.

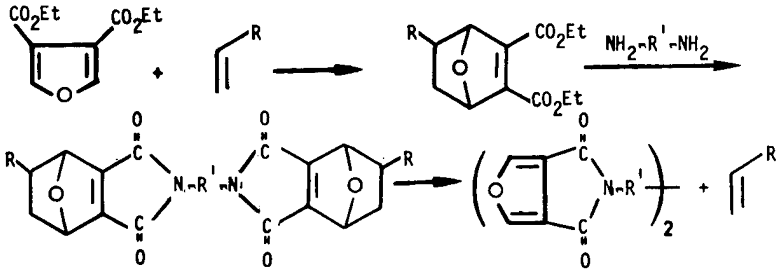
Concurrent with the above studies, experimental work was conducted in order to find a synthesis route to the desired imide structures (see structure 2) from diethyl 3,4-furandicarboxylate and the diamines. For this preliminary study, oxydianiline (ODA) was substituted initially while the desired diamines were being prepared. Several attempts were made to prepare *bis*[4-(furan-3,4-carboximide)phenyl]oxide from ODA and the diester. The first attempts were run in toluene or xylene employing catalysts such as *p*-toluene sulfonic acid, sulfuric acid, and sodium methoxide. None of these attempts showed any promise of producing the desired imide or amide ester.

Additional experiments employing toluene as the solvent and 0.5% to 1% (w/w) ammonium chloride as the catalyst, did show some promise for preparing the amide ester. After 16 hours at reflux, thin layer chromatography (tlc) analysis indicated the formation of a new product. The presence of an amide linkage was confirmed by infrared spectroscopy. However, continued reaction time failed to yield significant amounts of additional amide-ester.

At this point, it was decided that the diester should be converted to the anhydride to facilitate preparation of the desired imides. Consequently, the diester was first hydrolyzed in methanolic potassium hydroxide. Subsequent treatment of the 3,4-dicarboxyfuran with acetic anhydride failed to yield the desired anhydride. Additional dehydration attempts were performed with acetyl chloride but again none of the desired anhydride was detected.

Another attempt to dehydrate the diacid was performed using phosphorus pentoxide in xylene. Various reflux times were examined but none were successful in producing the anhydride. An examination of the structure employing molecular models indicates that the bond angles of the carboxy groups on the furan ring are such that formation of the anhydride is not favored. As a result, new synthetic routes to the N-substituted 3,4-furancarboximide were investigated.

The first route selected for study was based on converting diethyl 3,4-furandicarboxylate to an "oxynadic-like" structure via Diels Alder reaction. Based on previous work at TRW, the oxynadic derivative was expected to undergo the sought after condensation reaction with the diamines to yield the imide structures. A subsequent reverse Diels Alder reaction would yield the imide monomers needed for the PDA modification studies (see Equation 3).



Equation 3.

For the initial studies, cyclohexene was the first dieneophile selected for use in preparing the "oxynadic-like" adduct. The reaction first was attempted employing toluene as the solvent. Refluxing the mixture for a period of 48 hours failed to yield any adduct. Because cyclohexene is not a highly reactive dienophile, higher temperature reaction conditions then were employed. Heating the mixture of the reactants in xylene at 453K (356°F) for 36 hours in a sealed tube failed to yield the desired adduct. It was concluded from these results that either cyclohexene or the diester is not sufficiently reactive to yield the desired Diels Alder adduct. Consequently, styrene, a more highly reactive dieneophile, was employed in an attempt to prepare the "oxynadic-like" compound. A mixture of the two reactants in xylene was refluxed for 72 hours but none of the adduct was detected. More drastic conditions then were employed in which the reactants were subjected to 433K (320°F) for 36 hours. Thin layer chromatography (tlc) indicated that a small amount of a new component was present in the mixture after the heating period. An increase in reaction time or reaction temperature did not significantly increase the amount of new component.

Because the attempted synthesis described above were unsuccessful, it was decided to discontinue development of new PDA monomers. Instead, blending A-type polyimide resins with PDA resin was investigated as an alternative approach to meeting the program objectives (see Section 2.2).

2.2 COPOLYMER STUDIES

The other approach that was investigated as a route to develop an autoclave moldable laminating resin suitable for 589K (600°F) aerobic service was the use of A-type/PDA polyimide copolymers. In this approach, various mixtures of BFBI/BMPM:1500 FMW NA/MDA/BTDA prepolymer were combined, cured and then postcured. This combination of ingredients was investigated because it was postulated that the PDA resin portion of the mixture would cure the resin at low temperatures and the A-type component would result in improved thermo-oxidative stability.

Three different formulations were prepared (Table I) and cured for 2 hours at 505K (450°F). The resins obtained appeared to be homogeneous but were not found to be fully consolidated. The resins were post-cured employing a 3.5 hour linear heat-up from 505K (450°F) to 589K (600°F) followed by 2 hours at 589K (600°F). The neat, postcured resin samples then were assessed for initial thermo-oxidative stability by TGA. The resins were found to possess increased initial thermo-oxidative stabilities over the neat PDA resins prepared from BFBI/BMPM. The three copolymer samples then were isothermally aged in a forced-air oven at 561K (550°F) to assess their long-term thermo-oxidative stability (see Table I). Measured weight losses for all of the samples were significantly larger than those observed for the neat BFBI/BMPM resin, *e.g.*, at 300 hours, the weight loss for the BFBI/BMPM resin was ∿3.5% (Reference 1). In view of these results, no additional work was performed on the PDA/A-type copolymer approach.

2.3 PDA RESIN PREPARATION

The BMPM used throughout this program was prepared from methylenedianiline and maleic anhydride, as described in Appendix A. However, it became clear that each lot of BMPM was of varying quality (*i.e.*, as assessed by melting point) after one or more recrystallizations from toluene and/or methanol. Consequently, a study was undertaken to find an improved

TABLE I.

SUMMARY OF RESULTS ON A-TYPE/PDA COPOLYMERS

Formulation, (by weight)	Temp of Initial Wt. Loss in TGA(K/°F)[(a)]	**Weight Percent Loss During** Isothermal Aging at 561 K		
	Postcured Resin (b)	100 Hr.	168 Hr.	300 Hr.
70 PDA/30 1500FMW	633/680	8.4	10.5	12.7
50 PDA/50 1500FMW	653/716	10.7	13.2	16.2
40 PDA/60 1500FMW	663/734	5.6	7.0	8.77

a. Scan rate 3K/min. and air flow 100 ml/min.

b. Cured for 2 hours at 505 K (450°F) under vacuum, postcure cycle consisted of 3.5 hour linear heatup from 505 K (450°F) to 589 K (600°F) followed by isothermal cycle of 2 hours at 589 K (600°F).

method for preparing and/or purifying the BMPM before preparing large amounts of monomer.

The procedure employed during the previous program (Reference 1) to prepare BMPM was the dehydration of the methylene dianiline/maleic anhydride amide acid adduct in DMF with acetic anhydride at 323-333K. The crude material obtained from this procedure displayed a wide melting point range (413-421K) which was considerably lower than the literature value (429-431K). Repeated recrystallization from toluene or methanol was necessary to improve the melting point of the monomer to >423K. Consequently, another method for preparing BMPM was investigated. In this procedure, the amide acid was prepared in chloroform, isolated and dried before being dehydrated in acetic anhydride at 363K. BMPM prepared by this procedure did possess an improved melting point (420-425K), but a minimum of two recrystallizations from the aforementioned solvents were necessary before acceptable material was obtained.

At this point, a study was undertaken to find an alternative solvent (or solvent system) to recrystallize the BMPM. It was determined that aqueous dioxane is an attractive recrystallization solvent. One recrystallization of crude BMPM (prepared by either procedure) from the solvent yielded nearly colorless material possessing a melting point of 424-427K. A second recrystallization raised the melting point to 426-429K. Consequently, this solvent was selected as the recrystallization solvent for BMPM.

The PDA laminating resin (see Table II) then was prepared by dissolving BTDA in the tersolvent (acetone, methanol and dioxane) and then adding furfurylamine dropwise to the solution. This solution was stirred for one hour under a nitrogen atmosphere while cooling the mixture with an ice bath. The recrystallized BMPM then was added to the solution and stirred for 24-36 hours.

TABLE II.

PDA RESIN FORMULATION

PBW	CONSTITUENT
51.6[a)]	*bis*(furfuryl) benzophenone tetracarboxylic imide (BFBI) [b)]
35.8[a)]	*bis*(4-maleimidophenyl) methane (BMPM)
61.2[c)]	methanol
61.2[c)]	acetone
81.2[c)]	dioxane

[a)] 1 : 1 mol ratio

[b)] amide acid formed *in situ* from benzophenone tetracarboxylic acid dianhydride (BTDA) and furfurylamine

[c)] 3 : 3 : 4 pbw solvent mixture

3. PROCESS DEVELOPMENT

Process development studies were performed to develop a procedure for manufacture of cocured honeycomb sandwich panels with the PDA resin. The autoclave molding process was based on the procedure developed under the previous contract (Reference 1). It also was necessary to develop honeycomb core preparation procedures and to develop a honeycomb corefill material. All of this work was directed toward fabrication of a prototype component, *i.e.*, a three-quarter scale YF-12 wing panel.

3.1 PDA/HTS COMPOSITE PANEL FABRICATION

A PDA/HTS unidirectional composite panel was fabricated to determine if the autoclave process developed under Contract NAS 3-17770 (Reference 1) for PDA/AS composites would yield acceptable PDA/HTS composites. Hercules type HTS graphite fiber tow was dip-coated in the PDA resin to give ∿40% w/w resin content and then the resultant prepreg tape was dried to ∿17% volatile content and a 12-ply by 15.2-cm by 15.2-cm (6-inch by 6-inch) unidirectional lay-up was made and processed using the following cycle:

- 120 minutes at 377K (220°F) at 50.8 kN/m^2 (7 psia) vacuum bag pressure
- Heat to 436K (325°F) and dwell for 30 minutes
- Apply full vacuum bag pressure and 0.7 MN/m^2 (100 psig) pressure dwell at 436K (325°F) for 30 minutes
- Heat to 472K (390°F) and dwell for 180 minutes
- Cool to room temperature under pressure
- Postcure, Hours/K(°F)

1/477(400)
1/491(425)
1/505(450)
1/519(475)
1/533(500)
1/547(525)
16/561(550)
4/589(600)

The flexural strength values of the resultant unidirectional panel (see Table I) were comparable to the values obtained for PDA/AS composites on Contract NAS 3-17770, although the shear strength values were slightly lower. Consequently, a second unidirectional composite was fabricated in an attempt to optimize processing conditions for the PDA/HTS system. In this experiment, the prepreg volatile content was adjusted to 13% at the time of the vacuum bag lay-up. A 12-ply unidirectional composite was prepared using the following process cycle.

- 120 minutes at 377K (220°F) at 50.8 kN/m^2 (7 psia) vacuum bag pressure
- Heat to 436K (325°F) and dwell for 30 minutes
- Heat to 450K (350°F) and apply full vacuum bag pressure and 0.7 MN/m^2 (100 psig) pressure, and dwell for 30 minutes
- Heat to 472K (400°F) and dwell for 180 minutes
- Cool to room temperature under pressure
- Postcure Hours/K(°F)
  - 1/477(400)
  - 1/491(425)
  - 2/505(450)
  - 3/475(475)
  - 16/533(500)
  - 10/547(525)
  - 16/561(550)
  - 4/589(600)

Although the panel did have one small blister, significant property improvements were obtained from the resultant panel (see Table I). The high retention of flexural and shear strengths (70% and 66%, respectively) at 561K (550°F) indicated that the modified processing cycle was more suitable to fabrication of PDA/HTS composites. However, during a cooperative IR&D effort with Rockwell International Corporation (Reference 2), difficulty was experienced during fabrication of larger, *i.e.*, ∿30-cm by 30-cm, unidirectional panels. Small longitudinal cracks and blisters were observed in these panels. Consequently, the processing cycle was modified further by extending the postcure time at 505K (450°F) to three hours. The values obtained by Rockwell International Corporation (reference 2) on panels molded by this process were higher (see Table III) and there were no visible defects in these panels. These evaluations also demonstrated useful properties of the PDA/HTS composites after 125 hours in a 589 K (600°F) aerobic atmosphere.

TABLE III.

PROPERTIES OF UNIDIRECTIONAL PDA/HTS COMPOSITE PANELS

Property	Value		
	Panel A[a]	Panel B[a]	Panel C[a]
Flexural Strength, Pascals (Ksi)			
at R.T.	1670(242)	1588(230)	1861(270)
at 561K(550°F)	1007(146)	1131(164)	-
at 589K(600°F)	- -	- -	1034(150)
Strength Retention, %	60	72	54
Flexural Modulus, giga Pascals (Msi)			
at R.T.	-	-	148.2(21.5)
at 561K (550°F)	-	-	-
at 589K (600°F)	-	-	131.7(19.1)
Shear Strength, Pascals (Ksi)			
at R.T.	62.8(9.1)	108(15.6)	77.0(17.0)
at 561K(550°F)	42.8(6.2)	10.2(10.2)	-
at 589K (600°F)	-	-	43.4(6.3)
Strength Retention, %	68	66	37
Iso-Thermal Aging, 125 Hours 589K (600°F)			
Flexural Strength at R.T., Pascals (Ksi)	-	-	1379 (200)
Strength Retention, %	-	-	74
Shear Strength at R.T., Pascals (Ksi)	-	-	12.2 (17.7)
Strength Retention, %	-	-	104

[a] Panel A fabricated by process developed under Contract NAS 3-17770 (Reference 1).

Panel B fabricated by process using extended postcure.

Panel C fabricated and tested by Rockwell International (Reference 2) using the final molding cycle (see Section 3.2).

Based on these results, a 12-ply, 10-cm by 10-cm (4-inch by 4-inch) ± 45° composite panel was fabricated using the modified process. Visual inspection of the resultant multidirectional panel revealed it to be blister-free. This panel was tested for room temperature and 561K (550°F) flexural and shear strengths in the 0° direction (see Table IV). At 561K (550°F) test temperature the flexural and shear strength values indicated 61% and 69% strength retention respectively. It was concluded that these values met the program's objectives and therefore the same process was evaluated for fabricating honeycomb sandwich panels (see Section 3.2).

TABLE IV.

PROPERTIES OF 12-PLY ± 45° MULTIDIRECTIONAL PDA/HTS GRAPHITE COMPOSITE

Property	Value	
Flexural Strength, Pascals (Ksi)		
at 293K (R.T.)	181	(26.3)
at 561K (550°F)	110	(16.0)
Property Retention, %	61	
Shear Strength, Pascals (Ksi)		
at 293K (R.T.)	32.4	(4.7)
at 561K (550°F)	22.1	(3.2)
Property Retention, %	69	
Density, g/cc	1.59	
Fiber Volume, % v/v	58	
Void Content, % v/v	1.2	

3.2 HONEYCOMB SANDWICH PANEL FABRICATION

Process studies were performed to fabricate honeycomb sandwich panels consisting of PDA/HTS multidirectional skins and polyimide glass honeycomb core. The honeycomb core used throughout this program was Hexcell HRH 327 one-inch thick. A two-step autoclave molding process was evaluated in which an outer skin and honeycomb core subassembly was cocured first, after which the inner skin was molded over the honeycomb core and outer skin subassembly. Seven honeycomb sandwich panels were made during this study (see Table V). In each fabrication, the honeycomb was brush coated with PDA resin varnish prior to skin lay-up to promote fillet formation. The first panel was made using 0.7 MN/m^2 (100 psig) pressure, and the same cure cycle as the composite panels (see Section 3.1), while the second was made using 0.35 MN/m^2 (50 psig) pressure. In the first panel fabrication cycle, the 0.7 MN/m^2 (100 psig) molding pressure resulted in significant penetration of the honeycomb into the skins (see Figure 1).

TABLE V.

FLATWISE TENSILE STRENGTH OF HONEYCOMB PANELS

Molding Pressure MN/m^2 (psig)	Process Variable	Flatwise Tensile Strength Pascals (psi)	Failure Mode
0.7 (100)	Pressure	1.7 (250)	Skin to core
0.35 (50)	Pressure	1.37 (200)	Skin to core
0.35 (50)	Pressure	1.36 (197)	Skin to core
0.35 (50)	Thixotropic Core Coating	1.04 (150)	Skin to core
0.35 (50)	Resin Coated Scrim Interface (Lay-up to core)	0.88 (129)	Skin to core
0.35 (50)	Core[a] Impregnated	2.05 (307)	Skin to core
0.35 (50)	Core Etched[b] & Impregnated	1.95 (293)	Skin to core

[a] Impregnated with dilute PDA resin

[b] Etched with sulfuric acid/sodium dichromate and impregnated with dilute PDA resin

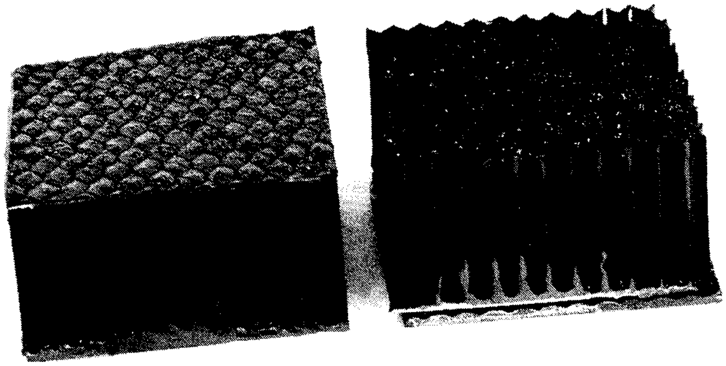


Figure 1. Dimpled Panel Skin Resulting From High Molding Pressure

The second panel provided satisfactory skins and a third panel then was fabricated using 0.35 MN/m^2 (50 psig) pressure. This panel also had satisfactory skins although all three of these panels provided lower than the anticipated 2 Pascals (300 psi) flatwise tensile strength values. Four approaches were evaluated in an attempt to improve the flatwise tensile strength values. These approaches consisted of a) adding a thixotropic agent to the honeycomb core coating resin, b) using a resin film with a glass scrim carrier between the core and skin prepreg, c) impregnation of the honeycomb core with low viscosity PDA resin solution, and d) surface treatment of the honeycomb core, followed by PDA resin solution soak.

The first approach of adding a thixotropic agent (Cab-O-Sil) decreased the flatwise tensile strength value (see Table V). Also use of a resin rich bonding layer (approach b) appeared to degrade the bond strength. Because both of these approaches were aimed at increasing the resin fillet size and both approaches were unsuccessful, it was apparent that methods for improving adhesion to the core were required. Consequently, approaches (c) and (d) then were evaluated. In approach (c) the honeycomb core was soaked for twelve hours in a 5% w/w PDA tersolvent solution and air dried. The other approach consisted of treating the core with concentrated

$H_2SO_4/Na_2Cr_2O_7$ at 330K (135°F) for 10 minutes, then washed with water, dried and allowed to soak 12 hours in a 5% w/w PDA/tersolvent solution in the same manner as approach (c). It was the objective of this treatment to oxidize the polyimide surface resin on the honeycomb cell walls, in order to provide improved adhesion. The results of this study (see Table V) indicated that the PDA resin soak did improve adhesion, although no additional improvement was provided by the etch treatment. Consequently, a twelve-hour soak of the honeycomb core in a 5% w/w PDA tersolvent solution was used throughout the rest of this program.

3.3 CORE-FILL MATERIAL DEVELOPMENT

In order to facilitate fabrication of sandwich panels with an edge close-out configuration using a two-step cocure molding process, development of a core-fill material was performed. These studies indicated that a PDA resin and glass microspheres mixture provides a satisfactory material (see Table VI). The core-fill material was prepared by mixing the PDA resin and glass microspheres together and then drying the resultant slurry for 16 hours at room temperature to remove the solvent. An 8-ply prepreg lay-up then was prepared and honeycomb core was located on top of the lay-up. The core-fill material was packed into the peripheral cells of the honeycomb core and a vacuum bag was installed over the assembly using angle iron to protect the honeycomb core edges (see Figure 2). This assembly then was autoclave molded after which the inner 4-ply lay-up was placed over the top of the cured first stage. The molding sequence for the second stage was the same as the first, except angle iron edge protectors were not used. It was demonstrated during this study that the PDA glass microspheres core-fill material is satisfactory for reinforcing the edges of honeycomb core (see Figures 3 and 4). Compressive strength determinations were made on core-fill materials samples (see Table VII).

TABLE VI.

PDA/GLASS MICROSPHERES CORE FILL MATERIAL FORMULATION

CONSTITUENT	PARTS BY WEIGHT
PDA RESIN SOLIDS	30
GLASS MICROSPHERES	63
METHANOL/ACETONE/DIOXANE SOLVENT[a)]	70

[a)] 3 : 3 : 4 pbw SOLVENT MIXTURE

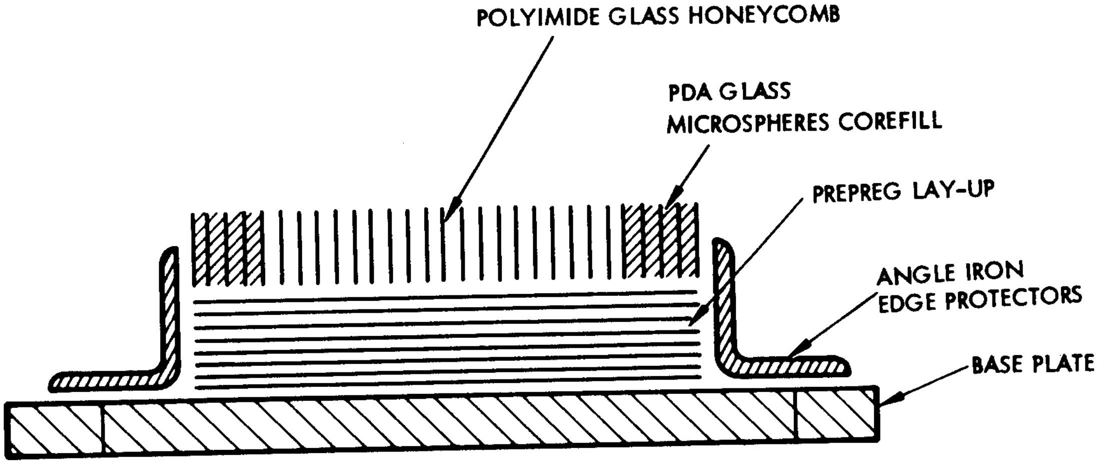


Figure 2. Honeycomb Sandwich Panel Lay-up Schematic

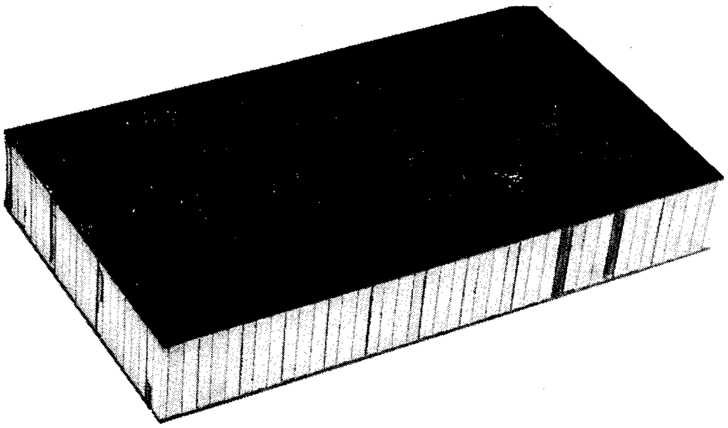


Figure 3. Autoclave Molded Cocured Honeycomb Sandwich Panel With Core-Filled Edges

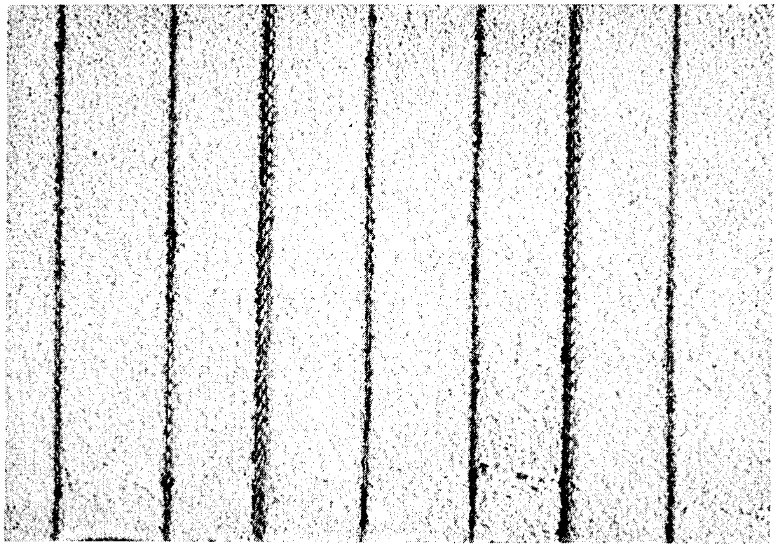


Figure 4. PDA Glass Microspheres Core-Filled Honeycomb Sandwich Panel

TABLE VII.

COMPRESSIVE STRENGTH OF CORE-FILL SAMPLES

Test Temperature, K(°F)	Compressive Strength, Pascals (psi)
R.T.	1.28 (186)
561(550)	1.17 (170)
589(600)	1.03 (149)

3.4 SANDWICH PANEL EVALUATION

Honeycomb sandwich panels were fabricated using 8-ply ±45° PDA/HTS skins and Hexcell HRH 327 polyimide glass honeycomb core. The fabrication was performed in two steps consisting of curing one skin with the honeycomb core as the first step (see Figure 2) followed by lay-up and cure of the second skin. Postcure was performed after the second skin had been cured. The complete molding cycle for these panels consisted of the following steps 1 through 5 for the first skin followed by steps 1 through 6 for the second skin:

1. Heat 120 minutes at 377K (220°F) at 50.8 kN/m^2 (7 psia) vacuum bag pressure
2. Heat to 436K (325°F) and dwell for 30 minutes
3. Heat to 450K (350°F), apply full vacuum bag pressure and 0.35 MN/m^2 (50 psig) and dwell for 30 minutes
4. Heat to 472K (400°F) and dwell for 180 minutes
5. Cool to room temperature under pressure
6. Postcure, hours/K(°F)
    1/477(400)
    1/491(425)
    3/505(450)
    3/475(475)
    16/533(500)
    10/547(525)
    16/561(550)
    4/589(600)

The resultant panels were machined into flexural test beams 2.54-cm by 20.32-cm (1-in by 8-in) and tested in accordance with Table VIII.

TABLE VIII.
HONEYCOMB SANDWICH PANEL FLEXURAL TESTS

Thermal Aging Cycle, Hrs/K (°F)	Test Temperature, K (°F)	Flexural Strength Pascals (Ksi)	Failure Mode
None	R.T.	120 (17.4)	Compressive
None	533 (500)	120 (17.4)	Compressive
1000/533 (500)	533 (500)	30 (4.4)	Flatwise
None	589 (600)	68 (9.8)	Flatwise
1000/589 (600)	589 (600)	Unsuitable for test	Oxidation

These results show that the current PDA resin formulation is suitable for long-term service at 533K (500°F) but will not survive a 1000-hour use cycle at 589K (600°F).

4. PROTOTYPE COMPONENT FABRICATION AND EVALUATION

To demonstrate the suitability of the PDA resin for use in flight hardware, five prototype components were fabricated. The component design selected for this effort was a three-quarter scale version of the YF-12 wing panel currently being developed at NASA Langley Research Center. (Reference 3). Details of the fabrication procedure and component evaluation performed under this contract are provided below.

4.1 MANUFACTURE OF THREE-QUARTER SCALE YF-12 WING PANEL

The three-quarter scale YF-12 wing panel design was similar to the full scale design, except the length and width were scaled down to 0.75 (see Figure 5). Also, the chamfered section of the honeycomb core was filled with PDA core-fill material (see Section 3.3) and metal foil edge reinforcements were not interleaved with the prepreg plies, as required for the full scale design.

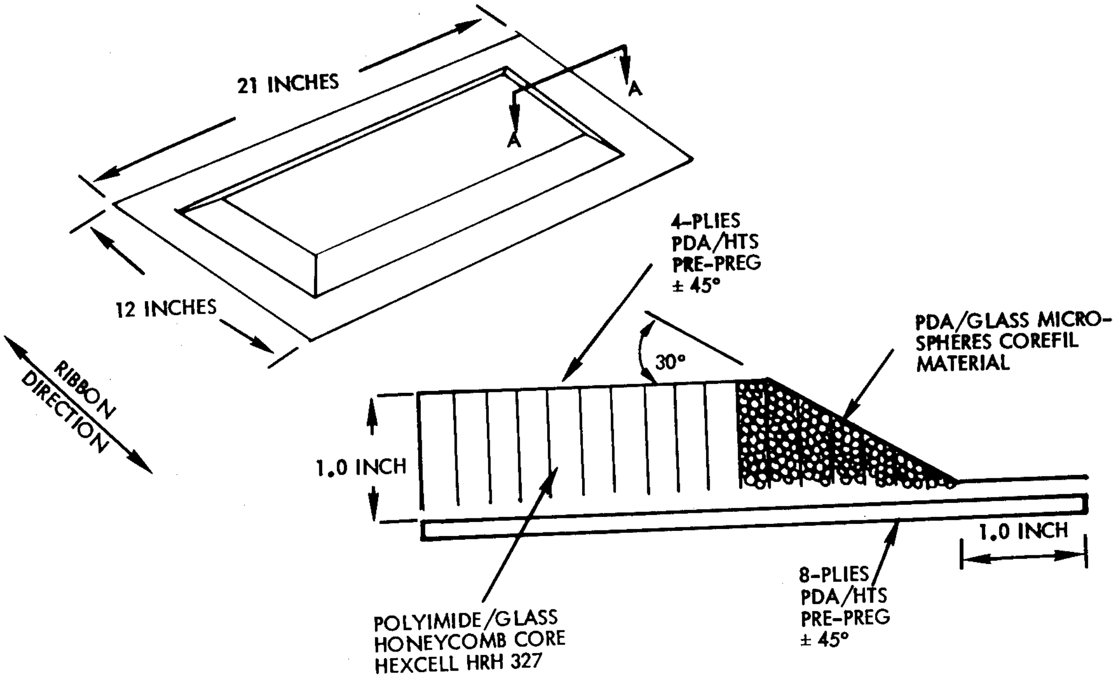


Figure 5. Three-Quarter Scale YF-12 Wing Panel

Fabrication of these panels proceeded by first filling the peripheral honeycomb cells in a 5-cm (2-in) wide area with the PDA core-fill material (see Table VI). The PDA core-fill material was cured in the honeycomb core under vacuum bag pressure for 4 hours at 377K (220°F), 1 hour at 450K (350°F) and 4 hours at 472K (400°F). A 30° chamfer then was machined along all four edges of the honeycomb core (see Figure 6). Finally, the bottom half of the honeycomb core was soaked for 16 hours in a 5% w/w solution of the PDA resin, followed by drying for 2 hours in air at 311K (100°F).

PDA/HTS prepreg tape was drum wound at 6 tows per inch and dried to a 14 - 18% w/w volatile content. This higher volatile matter content provided prepreg tape with greater tack and drape than previously used for flat panels in order to facilitate tailoring of the prepreg over the chamfered core. The outer skin of the wing panel was laid-up eight-ply

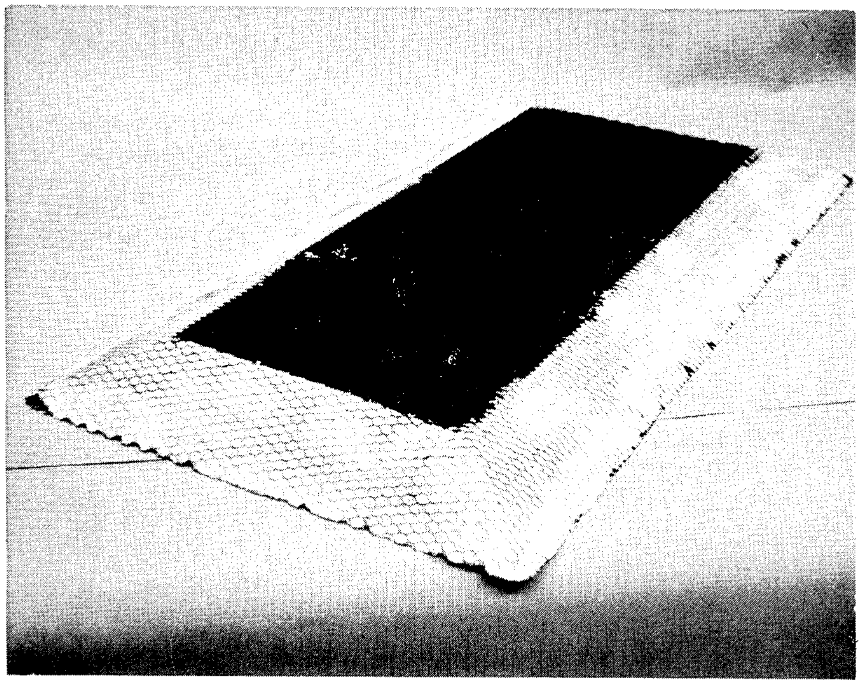


Figure 6. Chamfered Honeycomb Core

thick in a ± 45° configuration on top of three layers of style 181 glass fabric and one layer of porous glass reinforced Teflon coated fabric (see Figure 7). A flat aluminum alloy caul plate was used as the mold for this part. The lay-up was covered with one layer of porous glass reinforced Teflon coated fabric and a thin (1.6mm) aluminum alloy caul plate was laid over the flat area of the honeycomb core. An additional two layers of glass fabric then were laid on top of the caul plate.

The complete assembly was sealed in a vacuum bag and cured in an autoclave as follows:

- 16 Hours at 366K (200°F) at 50.8 kN/m^2 vacuum bag pressure
- Heat to 436K (325°F) and dwell for 30 minutes
- Heat to 450K (350°F) and apply full vacuum bag pressure and 0.7 MN/m^2 (50 psig) pressure, and dwell for 30 minutes

- Heat to 472K (400°F) and dwell for 180 minutes
- Cool to room temperature at 25°F/hour under pressure.

After cooling to room temperature, the cured outer skin and honeycomb core assembly was prepared for the outer skin installation by lightly abrading all molded surfaces and soaking the top of the core in the PDA resin solution. The four-ply ± 45° outer skin then was laid-up and autoclave molded in the same manner as the outer skin. After removal from the autoclave the finished part (see Figure 8) was postcured as follows:

Hours/K(°F)
1/477(400)
1/491(425)
3/505(450)
3/475(475)
16/533(500)
10/547(525)
16/561(550)
4/589(600)

The part was finally cooled to R.T. at a rate of 25°F/hour.

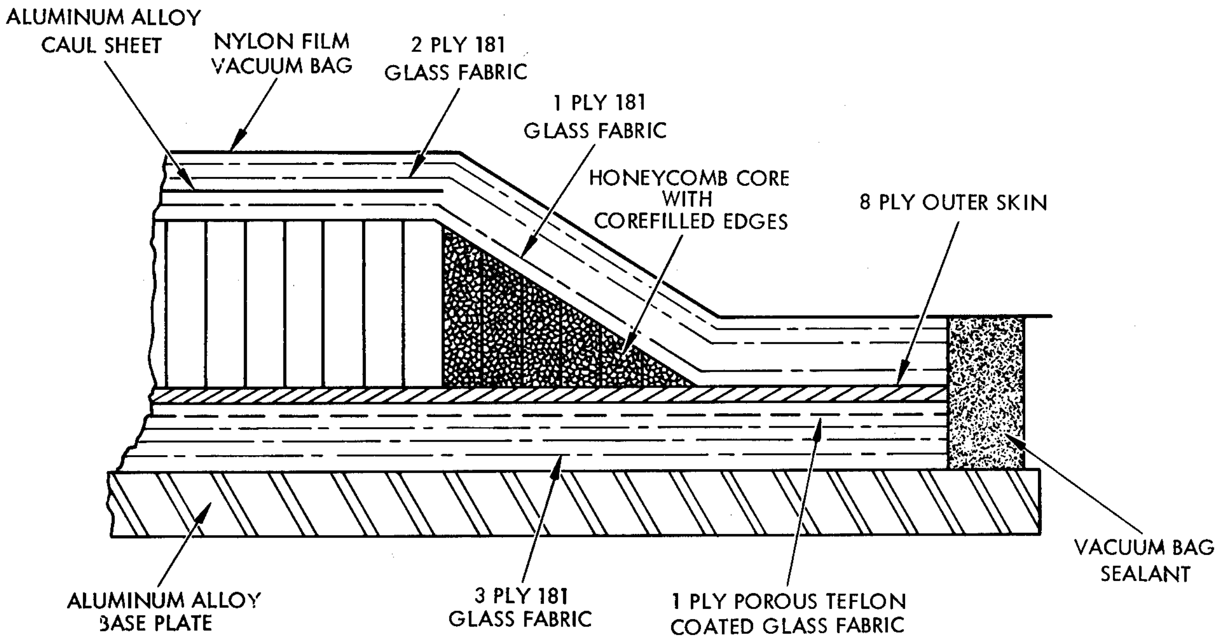


Figure 7. Outer Skin Lay-up

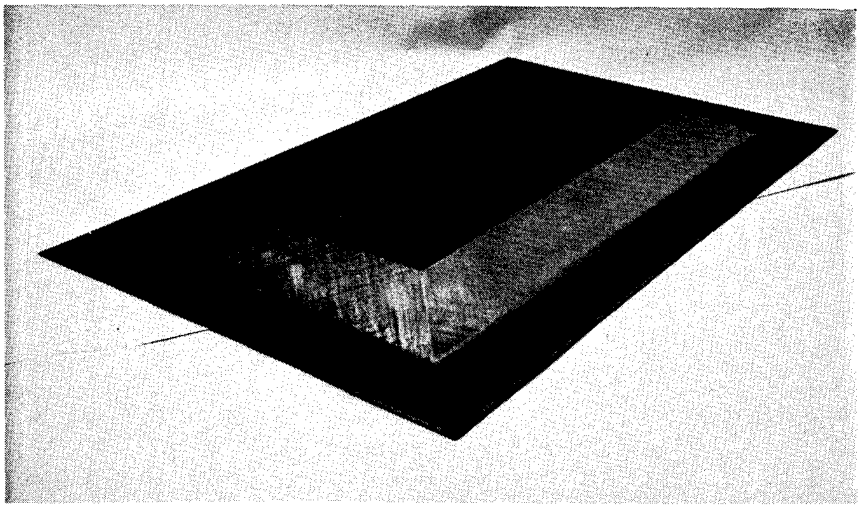


Figure 8. Three-Quarter Scale YF-12 Wing Panel

4.2 EVALUATION OF THREE-QUARTER SCALE YF-12 WING PANELS

Flexural strength measurements were made on two of the three-quarter scale YF-12 wing panels. The necessary test beams were machined out of the flat area of the panels (see Figure 9) to the same dimensions as the beams used previously (see Section 3.4). Close examination of the dissected wing panels indicated no visible voids in the composite cross section, good filleting between honeycomb core and skin and no severe dimpling of the skins into the core cells (see Figure 10).

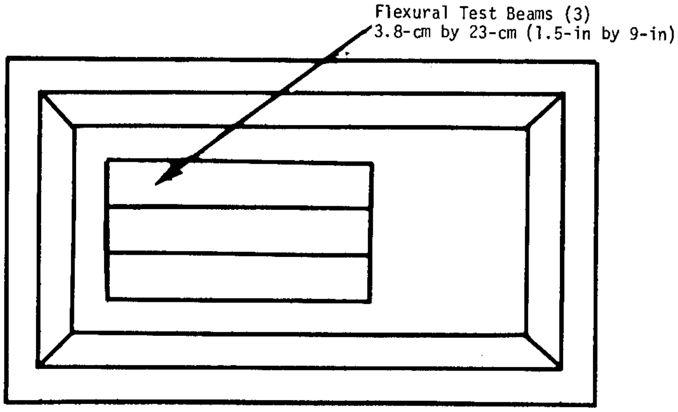


Figure 9. Wing Panel Test Pattern

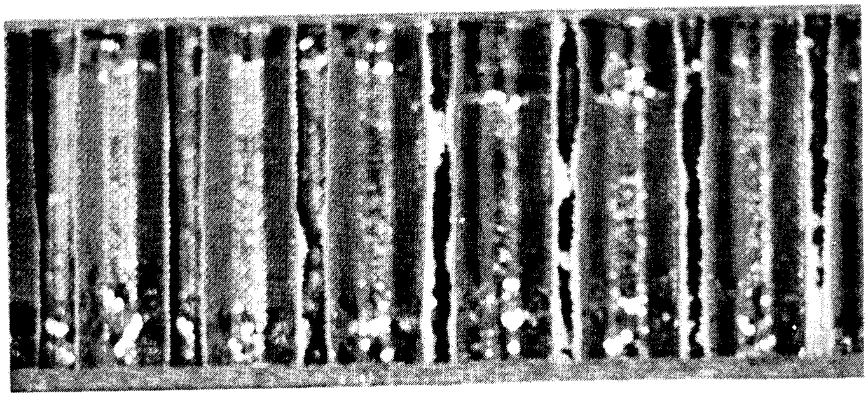


Figure 10. Wing Panel Cross Section

The test values obtained from these prototype units (see Table IX) provided good correlation with those obtained for the previous test panels (see Table VIII). Failure mode for all of the beams was in compression as anticipated (the four-ply top skin was loaded in compression). Because of the chamfered edge close-out configuration it was not possible to test the core-filled honeycomb core. However, visual examination of a cross section indicated that a uniform, void-free syntactic foam was produced (see Figure 11).

TABLE IX.
PROPERTIES OF DISSECTED WING PANELS

Property	Value$^{a)}$	Failure Mode
Flexural Strength, Pascals (Ksi)		
at R.T.	113 (16.4)	Compressive
at 533K (500°F)	96 (13.9)	Compressive
at 589K (600°F)	72 (10.4)	Compressive
Flatwise Tensile Strength, Pascals (psi)		
at R.T.	1.14 (165)	Adhesive
Resin Content, % w/w	25.3	-
Density, g/cc	1.57	-
Void Content, % v.v	3.9	-
Fiber Volume, % v.v	66	-

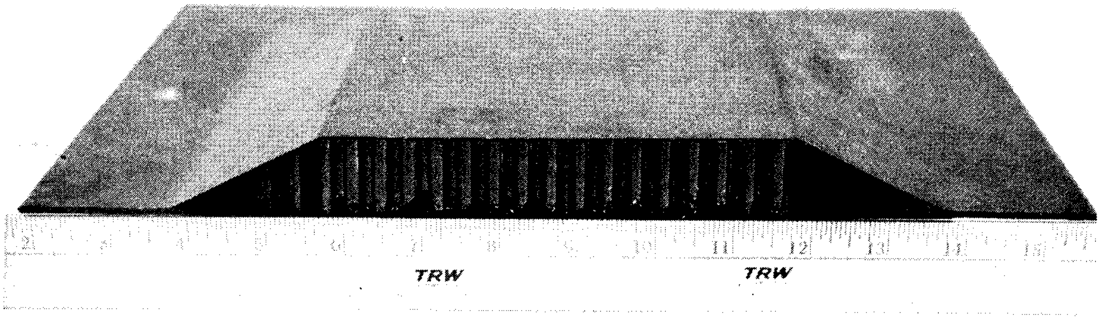


Figure 11. Wing Panel Close-Out Section

5. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this effort to improve the PDA polyimide chemistry and processing to provide composites suitable for long-term service at 589K (600°F). Based on these findings, recommendations are given for further developmental activities.

5.1 CONCLUSIONS

- A process was developed for autoclave molding PDA/HTS composites suitable for short-term service at 589K (600°F). The autoclave molding process used to fabricate these composites required a maximum cure temperature of 472K (400°F) and a maximum molding pressure of 0.7 MN/m^2 (100 psig).
- A process was developed for autoclave molding co-cured polyimide sandwich panels consisting of PDA/HTS skins and polyimide/glass honeycomb core. The panels were autoclave molded under a pressure of 0.35 MN/m^2 (50 psig) and cured at 472K (400°F).
- A syntactic foam core-fill material was developed for reinforcing honeycomb core close-out sections. The syntactic foam consisted of PDA resin and glass microspheres.
- Fabrication ease was demonstrated by manufacturing five three-quarter scale YF-12 wing panels using the PDA resin. It was concluded from the successful evaluation of these prototype units that the PDA resin is suitable for fabrication of components using commercial equipment.

5.2 RECOMMENDATIONS FOR FURTHER WORK

- Reproducibility Studies

  Establish reproducibility of PDA resin from scale-up batches (∿10 kg) and determine affects of storage on resin. Optimize prepreg preparation procedure including drying cycles, solvent content level and resin content level. Modify solvent system to provide controlled tack. Determine storage stability of prepreg and open time for prepreg. Optimize molding process and postcure cycle.

- Hot-Melt Prepreg

  Develop technology for preparing graphite fiber prepreg tapes by hot-melt impregnation from solid PDA resin. Perform resin modification and process development to facilitate fabrication of solvent-free, tacky prepreg tapes. Characterize prepregs, develop molding procedures and test composites.

- Improved PDA Resin

  Develop improved PDA resin suitable for long-term 600°F service using alternative monomers. Perform processing studies and determine composite panel properties.

APPENDIX A.
MONOMER AND POLYMER SYNTHESIS

A.1 Preparation of *Bis* [4-(4-aminophenoxy)phenyl] sulfone

To a solution of 166.3 g (1.10 mole) *p*-hydroxyacetanilide in 600 ml of DMF were added 56.1 g (1.05 mole) sodium methoxide under a nitrogen atmosphere. The reaction mixture was warmed until a solution was obtained and then 143.5 g (0.50 mole) *bis*-*p*-chlorophenyl sulfone were added. The resulting reaction mixture was heated to 373°K (212°F) and maintained at that temperature for 48 hours. After allowing the reaction mixture to cool, the coupling product was precipitated by adding the mixture to 4000 ml water. The precipitate was collected by filtration and washed with two 500 ml portions of water. The coupling product then was hydrolyzed by refluxing it for 24 hours in a mixture of 500 ml concentrated hydrochloric acid and 500 ml methanol. The resultant amine hydrochloride was collected by filtration and then dissolved in 3000 ml of water. The desired diamine was precipitated by making the aqueous solution basic by adding 10% w/w NaOH The diamine was collected by filtration, washed with two 1000 ml portions of water and dried *in vacuo*. Recrystallization (twice) from ethanol afforded colorless diamine, mp 464-466°K.

A.2 Preparation of *Bis* [4-(4-maleimidophenoxy)phenyl] sulfone

To a solution of 108.1 g (0.25 mole) *bis* [4-(4-aminophenoxy)phenyl] sulfone in 100 ml of DMF were added dropwise a solution of 49 g (0.50 mole) of maleic anhydride in 50 ml DMF with cooling (ice-bath). After the addition was completed, the mixture was stirred for 1 hour at room temperature. To the mixture then were added 56.1 g (0.55 mole) acetic anhydride and 4.92 g (0.06 mole) sodium acetate and the mixture was heated to 333°K and maintained at that temperature for 3 hours. The reaction mixture then was poured into 3500 ml water and the resulting precipitate was collected by filtration and washed well with water. The crude bismaleimide was air dried and then recrystallized from benzene/hexane (charcoal) to afford 86 g yellow product; mp 468-469°K. The infrared spectrum of this compound is shown in Figure A.1.

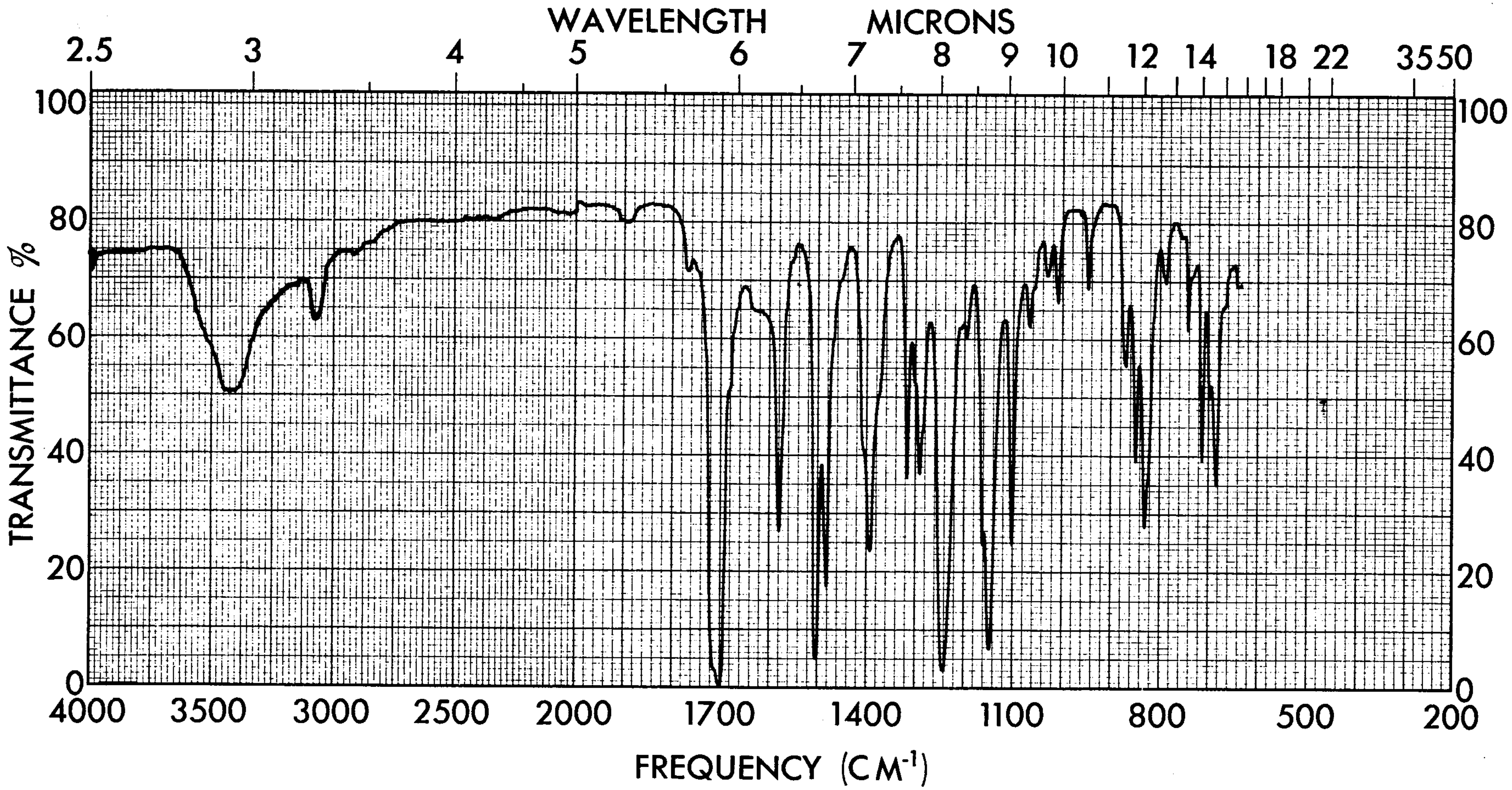


Figure A.1. Infrared Spectrum of *Bis*[4-(4-maleimidophenoxy) phenyl] sulfone.
Concentration: 3.3 mg/g KBr.

A.3 Preparation of 2,2-*Bis* [4-(4-aminophenoxy)phenyl] hexafluoropropane

The following sections describe the various synthesis routes investigated for the preparation of this compound from 2,2-*bis*(4-hydroxyphenyl) hexafluoropropane.

A.3.1 From 4-Chloroacetanilide

To a 76.5 g portion of *p*-chloroaniline were added 67.4 g (0.66 mole) acetic anhydride, 80 g acetic acid and 0.6 g sodium acetate. The mixture was cooled by an ice-bath during the initial exothermic reaction. The mixture then was heated until a clear solution was obtained (ca. 333°K). After heating 30 minutes at 333°K, the mixture was added to 2000 ml water and the resulting white precipitate was collected by filtration and washed thoroughly with water. The product was dried *in vacuo* to yield 94.5 g (92%) of amide; mp 451-453°K.

To a solution of 50.4 g (0.15 mole) 2,2-*bis*(4-hydroxyphenyl)hexafluoropropane in a mixture 240 g of DMAC and 125 ml toluene were added 13.2 g (0.33 mole) sodium hydroxide and 5 ml water. The mixture was heated to reflux and the water was removed by means of a Dean-Stark trap. After all of the water was removed, the toluene was removed by distillation until the pot temperature reach 425°K. To the disodium salt was added 51.1 g (0.33 mole) of 4-chloroacetanilide and the mixture was heated at 423°K for 150 hours. The reaction then was poured into 1500 ml of water. The product isolated was found to be 4-chloroacetanilide, indicating that no coupling reaction occurred.

A.3.2 From N-4-Chlorophenylphthalimide

To 29.62 g (0.2 mole) phthalic anhydride in 150 ml of toluene were added 25.52 g (0.2 mole) *p*-chloroaniline. The mixture was refluxed for 8 hours and the water formed was removed with a Dean-Stark trap. Upon cooling, the phthalimide precipitated and then was collected by filtration, and dried to give 38.6 g (74%) of colorless product; mp 473-475°K. Using the same reaction conditions as were employed for the 4-chloroacetanilide coupling reaction the phthalimide was treated with the disodium salt in DMAC at 423°K.

After 72 hours of heating, no reaction could be detected by thin layer chromatography (tlc) and only starting material was isolated upon workup of the reaction mixture.

A.3.3 From 4-Chloronitrobenzene

The disodium salt of 2,2-*bis*(4-hydroxyphenyl)hexafluoropropane was prepared as reported in A.3.1 and treated with 4-chloronitrobenzene as described below.

To 30.25 g (0.08 mole) disodium salt in 154 g DMAC were added 31.51 g (0.2 mole)4-chloronitrobenzene. The reaction mixture was heated at 423°K for 48 hours and then poured into 1000 ml water. The yellow precipitate was collected by filtration and washed well with water. Recrystallization from ethanol afforded 43 g (93%) of 2,2-*bis*[4-(4-nitrophenoxy)phenyl] hexafluoropropane; mp 431-433°K. A mixture of 11.56 g (0.02 mole) 2,2-bis [4-(4-nitrophenoxy) phenyl] hexafluoropropane, 8.96 g (0.16 mole) powdered iron, and 20 ml of ethanol were added to a 100 ml three necked flask. The mixture was heated to reflux and then 0.14 ml (6 mmole) of hydrochloric acid in 5 ml of ethanol was added dropwise with vigorous stirring. The mixture was refluxed for two hours, then made alkaline to litmus by adding alcoholic potassium hydroxide. The mixture was filtered hot and the filter cake was boiled twice with fresh ethanol to remove all of the amine. The filtrate was cooled and 300 ml of conc. hydrochloric acid were added. The resulting amine hydrochloride was collected by filtration and washed with ethanol. The dihydrochloride was dissolved in water (150 ml) and then 5% (w/v) sodium hydroxide was added until the mixture was alkaline to litmus. The insoluble diamine was collected by filtration and then recrystallized from ethanol to give 6.3 g of nearly colorless needles; mp 423-425°K. The infrared spectrum for the compound is shown in Figure A.2.

Anal. Calcd for $C_{27}H_{20}N_2O_2F_6$:C, 62.55; H, 3.89; N, 5.40. Found: C, 62.43; H, 3.94; N, 5.27.

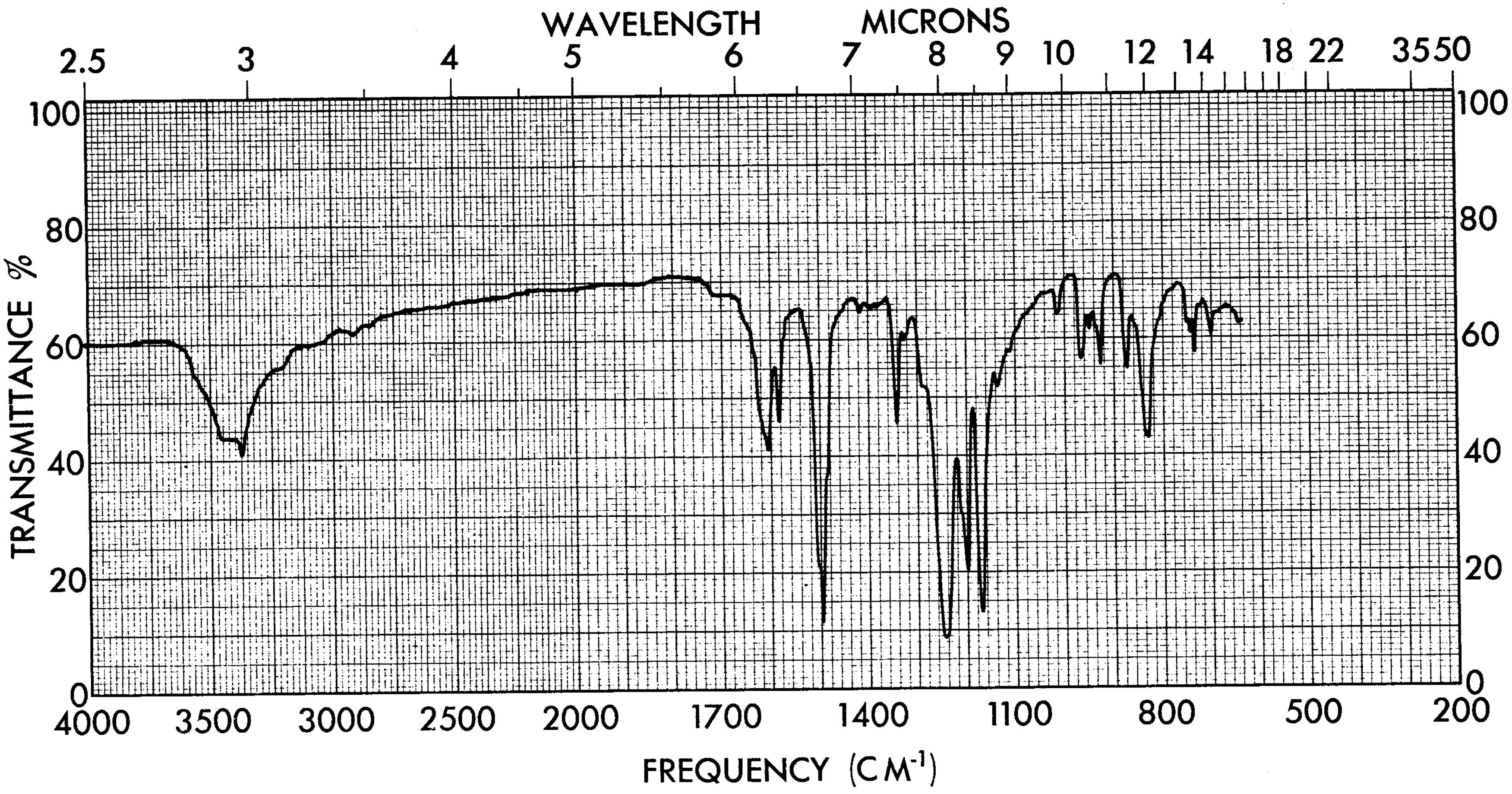


Figure A.2. Infrared Spectrum (KBr) of 2,2-*Bis*[4-(4-aminophenoxy) phenyl]hexafluoropropane. Concentration: 3.1 mg/g KBr.

A.4 Preparation of Furan-3,4-Dicarboxylic Acid

A mixture of 10.6 g (0.05 mole) 3,4-diethyl furandicarboxylate, 20 ml of 5N potassium hydroxide and 40 ml of methanol was refluxed for 2 hours. The solvent then was removed at reduced pressure and the resulting residue was dissolved in 50 ml water. Acidification of the aqueous solution to pH3 with hydrochloric acid precipitated the dicarboxylic acid. The diacid was collected by filtration, air dried and then recrystallized from water (charcoal) to afford 4.1 g (52%) of the desired product; mp 489-491°K.

A.5 Attempted Preparation of Furan-3,4-dicarboxylic Anhydride

A 2.0 g portion of furan-3,4-dicarboxylic acid was refluxed in 30 g acetic anhydride for 2 hours. The diacid was not readily soluble in this solvent and to increase solubility, 20 g of acetic acid were added After refluxing the mixture for 18 hours, the mixture was filtered and the filtrate was cooled. The resulting precipitate (from the filtrate) was collected and dried (0.6 g). However, infrared spectroscopy indicated both the precipitate and insoluble portion in the reaction mixture were starting material.

A second attempt to prepare the anhydride was made using acetyl chloride as the dehydrating agent. A 1.0 g portion of diacid was refluxed in 10 g acetyl chloride for 18 hours and then the acetylchloride was removed at reduced pressure. Again, no anhydride was detected by infrared spectroscopy. In a similar fashion the diacid was refluxed with phosphorus pentoxide in xylene but this reaction also was unsuccessful.

A.6 Synthesis of *Bis*(4-Maleimidophenyl) Methane (BMPM)

To a solution of 158 g (0.8 mole) of methylenedianiline in 480 ml of dimethyl formamide was added a solution of 157 g (1.6 moles) of maleic anhydride in 240 ml of dimethyl formamide at such a rate as to keep the temperatures below 343K (70°C). After stirring the mixture for an additional 15 minutes, it was cooled to room temperature and 204 g (2 moles) of acetic anhydride followed by 16 g (0.2 moles) of sodium acetate were added. The resulting mixture was heated to 323K (50°C) and maintained there for three hours. The crude product was precipitated by pouring the reaction mixture into 4000 ml portions of water. The precipitate was collected by filtration, washed twice with 4000 ml portions of water and dried. Crystallization from methanol afforded 203 g (71%) of *bis*imide, mp 429-432K (156-159°C). The infrared and nuclear magnetic resonance spectra are presented in Figure B.1 and Figure B.2, respectively.

A.7 Preparation of PDA Varnish in the Tersolvent

To 83.77 g (0.26 mole) of benzophenone tetracarboxylic acid dianhydride in 531 g of a solvent mixture containing 212 g dioxane (passed through a column of alumina to remove peroxides) 159 g acetone and 159 g methanol were added 50.5 g (0.52 mole) furfurylamine during a 30 minute period under a nitrogen atmosphere while cooling the mixture with an ice bath. The resulting light brown solution was stirred for one hour and then 93.16 g (0.26 mole) of *bis*(4-maleimidophenyl) methane (BMPM) was added. The mixture was stirred for 24 hours before being used to prepare the graphite prepreg.

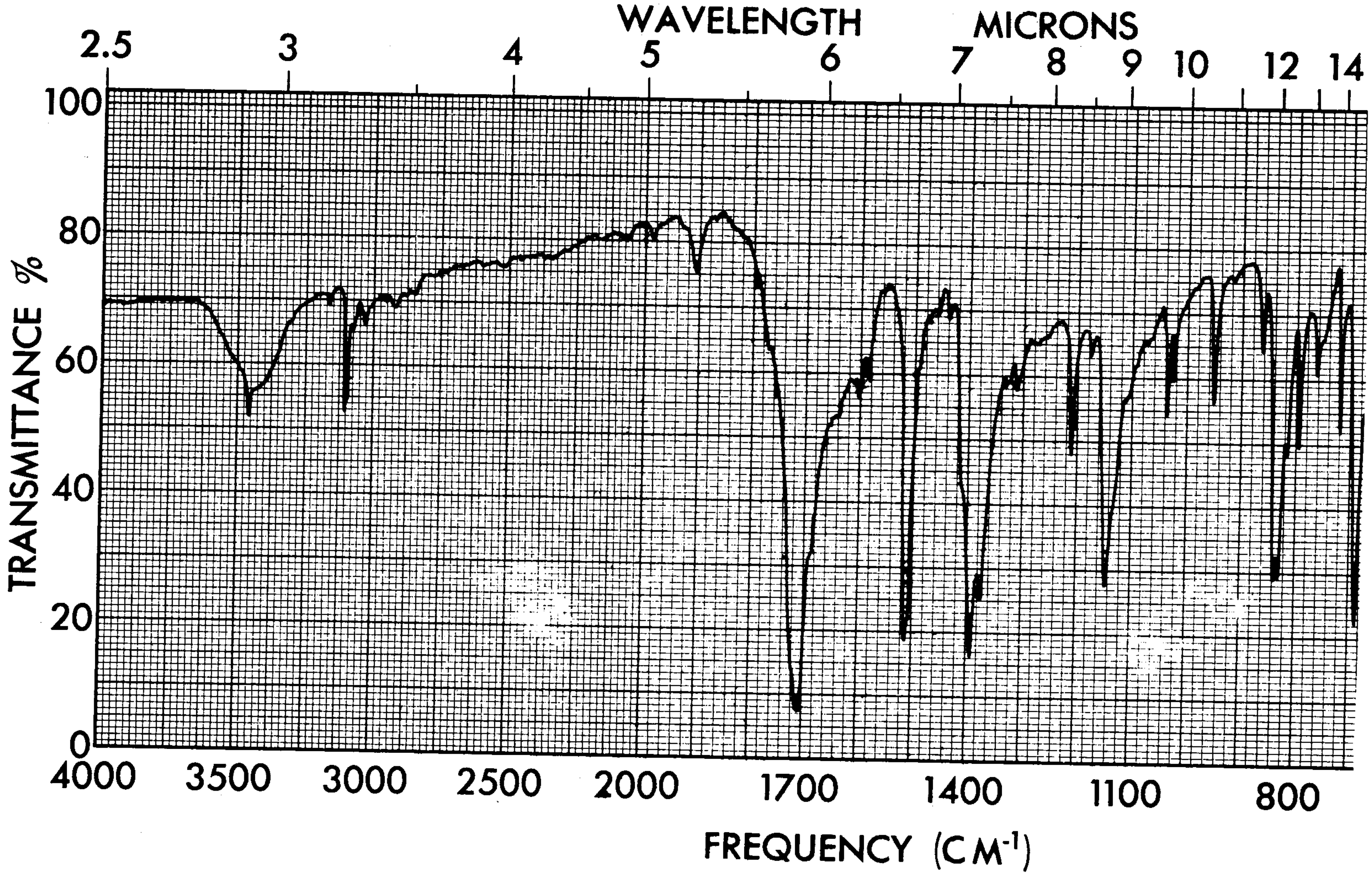


Figure B.1. Infrared Spectrum of *Bis*(4-maleimidophenyl) methane (KBr)
Concentration: 3.1 mg/g (KBr)

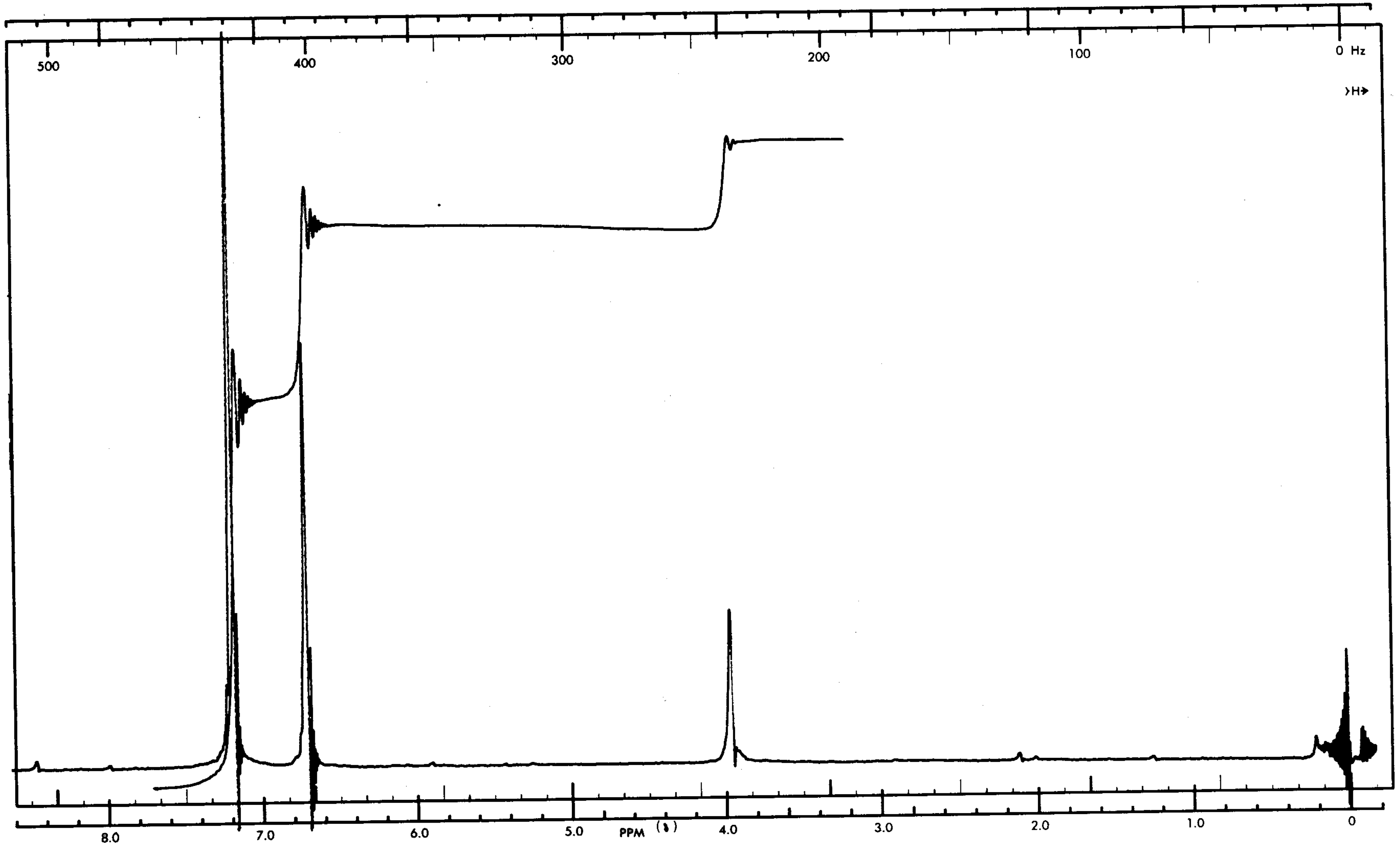


Figure B.2. Nuclear Magnetic Resonance Spectrum of *Bis*(4-maleimidophenyl) Methane
Solvent: DMSOd_6

APPENDIX B.
TEST PROCEDURES

B.1 Graphite Tape Characterization

B.1.1 Volatile Matter

Volatile content of graphite prepreg was determined by thermally treating a tarred sample for 30 minutes at 561 K (550°F). After cooling to R. T., the specimen was reweighed and the volatile content was calculated by the following formula:

$$\text{Volatile Content} = \frac{W_1 - W_2}{W_1} \times 100$$

Where:

W_1 = Weight Sample

W_2 = Weight Sample After Heat Aging

B.1.2 Resin Content

Resin content was determined by soxhlet extraction using DMF as the solvent. A weighed sample was placed in the soxhlet extraction apparatus and the solvent was heated to reflux until the solvent surrounding the extraction thimble became clear. The sample then was reweighed and the resin content was calculated by the following formula:

$$W_{wr} = \frac{W_2}{W_1} \times 100$$

$$W_{dr} = \frac{W_2 - VW_2}{W_1 - VW_2}$$

Where:

W_{wr} = Wet Resin Content
W_{dr} = Dry Resin Content
W_1 = Weight Sample

W_2 = Weight Sample Lost
W_3 = Weight Graphite in Sample
V = Volatile Matter Content of Graphite Tape, Fraction

B.2 Composite Characterization

B.2.1 Graphite Composite Resin Content

The resin was digested from the cured sample by pouring acid (concentrated H_2SO_4) onto the sample in a glass beaker and then heating the acid until it turned black. At this point, 30% hydrogen peroxide solution was added dropwise to the acid until it turned clear again. The acid was reheated for a minimum of one hour. During this period, further drops of hydrogen peroxide solution were added to clear the acid whenever the acid turned black. Upon completion of this cycle, the acid was cooled to room temperature and an additional 2 ml of hydrogen peroxide solution was added. The solution was heated again until white fumes appeared after which it was cooled to room temperature. The acid was decanted from the filaments using a fritted glass filter, washed first in distilled water and then in acetone, after which the filaments were dried for 15 minutes in a 450 K (350°F) air circulating oven. Resin solids contents were calculated:

$$W_r = \frac{(W_1 - W_2)}{W_1} \times 100$$

Where:

W_r = Weight Content of Resin Solids, % w/w
W_1 = Weight of Cured Composite Sample
W_2 = Weight of Filaments after Acid Digestion of the Resin Matrix

B.2.2 Density of Composites

Specific gravity of composites was determined by weighing specimen in air and in water. Specific gravity was calculated by the formula:

$$\text{Specific Gravity} = \frac{W_A}{W_A - W_W} \times 100$$

Where:

W_A = Weight Sample in Air
W_W = Weight Sample in Water

B.2.3 Composite Fiber Volume

Fiber volume percent of the composites was calculated by the formula:

$$V_f = 100\ (1\text{-}K)\ \frac{D_C}{D_f}$$

Where:

V_f = Volume Percent Fiber, %
D_C = Measured Density of Composite, g/cm^3
D_f = Density of Fiber, g/cm^3
K = Weight Fraction, Resin

The specific gravity of the Hercules A-S fiber is 1.76.

B.2.4 Composite Void Content

Void contents of the composites were calculated using the formula:

$$V_v = 100 - D_C \left[\frac{W_r}{D_r} + \frac{W_f}{D_f} \right]$$

Where:

V_v = Volume of Voids, % v/v
D_C = Measured Density of Composite, g/cm^3
D_r = Density of Resin, g/cm^3
D_f = Density of Fiber, g/cm^3
W_r = Weight Content of Resin, %
W_f = Weight Content of Fiber, %

B.2.5 Shear Strength of Composites

The cured composites were machined into short beam shear specimens 0.63 cm wide x 6 times the specimen depth in length and tested in flexure loading point using a 4:1 span to depth ratio. Loading rate was 1.3 mm/minute.

Shear strengths were calculated using the simple formula:

$$S_u = \frac{0.75V}{tb}$$

Where:

S_u = Ultimate Shear Strength, MN/m^2
V = Load at Failure, N
t = Specimen Thickness, mm
b = Specimen Width, mm

B.2.6 Flexural Properties of Composites

The cured composites were machined into flexural specimens 0.63 cm wide by 10 cm long and tested in flexure at a single point loading at mid-span point using a 32:1 span-to-depth ratio. Loading rate was 1.33 mm/minute.

Flexural strengths and moduli were calculated using the formulae:

$$F_u = \frac{3PL}{2Bd^2}$$

and

$$E_b = \frac{L^3m}{4bd^3}$$

Where:

F_u = Stress in the Outer Fiber at Mid-span, MN/m^2
E_b = Modulus of Elasticity in Bending, GN/m^2
P = Load at Failure, N
L = Span, mm

b = Width of Specimen, mm
d = Thickness of Specimen, mm
m = Slope of the Tangent to the Initial Straightline Portion of the Load Deflection Curve, N/mm

B.3 Honeycomb Sandwich Panel Characterization

B.3.1 Flatwise Tensile Strength of Sandwich Panels

Flatwise tensile strength was determined according to the method described in MIL-STD-401B using 5.08-cm by 5.08-cm (2-inch by 2-inch) specimens. These were machined from a cocured honeycomb sandwich panel which had 4-ply 0°, 90°, 90°, 0° skins with the ribbon direction of the honeycomb in the 0° direction.

B.3.2 Sandwich Flexure Testing

Flexure testing was performed on the sandwich panels according to MIL-STD-401B using 27.94-cm (11-inch) long (honeycomb ribbon direction and 0° skin direction) by 4.45-cm (1.75-inch) wide specimens. The average facing stress was determined using the formula:

$$F = \frac{P_B \ a_B}{4 \ t(d + t_c)b}$$

where F = facing stress
P_B = total force, applied at 2 points located at a distance of $a_B/4$ from each reaction
a_B = span length
t = facing thickness
d = total sandwich thickness
t_c = core thickness
b = sandwich width

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