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PPQ ADHESIVES FOR LARGE AREA BONDING OF TITANIUM ALLOYS

TRW SYSTEMS GROUP
REDONDO BEACH, CALIFORNIA

AUGUST 1975

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AIR FORCE MATERIALS LABORATORY
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Wright-Patterson Air Force Base, Ohio 45433

NOTICE

This technical report has been reviewed and is approved for publication.

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A Diels-Alder reaction was investigated as a means to crosslink polyphenylquinoxalines (PPQ) which were intended for use as adhesives in large area bonding of titanium alloys. Two promising candidate polymers were identified for process development studies. Double lap-shear specimens were press cure fabricated from the adhesives and Ti-6Al-4V adherends which demonstrated room temperature strengths of 4000 psi and elevated temperature strengths of 2800 psi and 2000 psi at 450°F and 550°F, respectively. Detailed evaluation studies were conducted which included stress durability determinations, crack →

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extension measurements, peel strength measurements and blister detection tests which demonstrated applicability for preparing large area bonded specimens. The results of the detailed testing indicated that the crosslinked PPQ adhesive possessed toughness and that large area bonded specimens can be press cure fabricated.

FOREWORD

This report was prepared by TRW Systems Group, Redondo Beach, California, under Contract F33615-74-C-5017. This contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734003, "Structural Plastics and Composites". It was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. L. G. Picklesimer (AFML/MBC) as Project Engineer.

The report covers work conducted during the period 1 March 1974 through 31 May 1975.

Dr. E. A. Burns, Manager, Applied Chemistry Department and Dr. R. J. Jones, Assistant Manager, Applied Chemistry Department, TRW Systems, provided overall program supervision. Mr. M. K. O'Rell was Program Manager and Mr. C. H. Sheppard was Principal Investigator. Significant technical contributions and guidance were made by Mr. R. W. Vaughan. Additional participants were Mr. R. A. Buyny, Mr. J. L. Bell and Mr. J. N. Kennedy.

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I. SUMMARY

The objective of this program was to develop a tough adhesive for large area bonding of titanium alloys for use at 450°F to 550°F. The objective was accomplished by sequential program tasks which included 1) monomer and polymer synthesis studies, 2) process development studies and 3) detailed testing.

The first phase of the work involved the synthesis and characterization of eight linear polyphenylquinoxalines (PPQ). Characterization of the linear PPQ's included inherent viscosity determination, polymer melt temperature, TGA and solubility. The polymers were crosslinked with two different crosslinking agents using a Diels-Alder reaction. Both crosslinking agents gave crosslinked PPQ's which showed high promise for meeting program objectives. A preliminary process screening study was conducted to enable selection of the two most promising polymers for adhesive studies. Lap-shear specimens were press cure fabricated from Ti-6Al-4V substrate and the adhesive candidates. It was determined that the high molecular weight versions of the polymers did not process well and that one of the crosslinking agents caused too rapid a cure during the fabrication procedure. Bonding procedures were developed for two adhesive formulations and both single and double lap-shear specimens were fabricated. Isothermal aging studies at 450°F and 550°F showed acceptable strength retention for one adhesive formulation while the other formulation debonded from the Ti-6Al-4V substrate.

As part of a detailed testing study, wedge opening specimens were prepared from the two adhesive candidates and exposed to 95-100% relative humidity environment at 160°F. The results of this test demonstrated that both adhesive formulations were tough. Stress durability also was determined using stressed lap-shear specimens and peel strength was measured. The ability to manufacture large area bonded specimens was demonstrated by the fabrication of blister detection panels.

II. INTRODUCTION

At the inception of this program a need existed for organic resins to serve as high performance adhesives for fabrication of titanium to titanium and titanium to composite large area bonded structures for use in high temperature (>600°F) applications. Although several types of aromatic/heterocyclic polymers were potential adhesive candidates, most of them fell considerably short of meeting the one or more of the following high performance adhesive requirements:

- Long-term property retention in air at temperatures greater than 600°F
- Long-term titanium compatability at high temperatures
- Long-term high humidity resistance
- Processability characteristics suitable for fabrication of large area bonded structures.

The initial objective of the technical effort described in this report was the development of a polyphenylquinoxaline (PPQ) adhesive that would meet the above requirements. However, during the course of this program, Air Force mission objectives were altered and as a result the emphasis of the program was shifted to the development of a "tough" adhesive system for 450°F to 550°F use from that of development of high temperature adhesive. Fortunately, the PPQ resin can be tailored to either end-use application.

The PPQ's are ideally suited for use on this program because of their outstanding thermo-oxidative properties and toughness. In addition, the polymer backbone is fully formed and consequently does not evolve large amounts of volatile matter during processing thus making it possible to prepare large area bonded specimens. However, the linear PPQ suffers from one severe problem, namely that of thermoplasticity at elevated temperature (>500°F). Consequently, the real potential of the PPQ's can be realized only if the system is crosslinked by a suitable mechanism.

During this program, a promising approach based on the Diels-Alder reaction was investigated for crosslinking PPQ resins. The crosslinked PPQ's then were evaluated as adhesives for large area bonding of Ti-6Al-4V. The experimental work was planned and conducted according to three tasks:

Task I - Resin Studies

Task I was concerned with 1) synthesis of the required monomers [e.g., *p-bis*(phenylglyoxalyl)benzene], 2) preparation of linear polymers, 3) crosslinking studies, and 4) evaluation of the cured resins.

Task II - Preliminary Adhesive Development and Evaluation Studies

Task II was concerned with process development for bonding Ti-6Al-4V with the crosslinked PPQ's. The work included evaluation of process variables such as cure time, cure temperature, cure pressure, tape preparation and surface preparation. The processing and methodology developed in this task was used in Task III to prepare test specimens for detailed evaluation of the most promising adhesive candidate.

Task III - Detailed Evaluation

Task III was devoted to a detailed property evaluation of the most promising PPQ adhesive system. The studies included stress durability determinations by wedge opening and lap-shear specimens, peel strength and applicability to preparing large area bonded specimens by fabrication of blister detection panels.

The results of these studies are discussed in the following sections of this report.

III. TECHNICAL DISCUSSION

The experimental effort described in this document was conducted to develop a polyphenylquinoxaline (PPQ) adhesive and a process for large area bonding of titanium alloys. It was initially intended that the adhesive system be developed for high temperature (>600°F) applications, but as a result of changes in long-term mission objectives, program emphasis was shifted to development of a tough adhesive for 450°F to 550°F applications. The following sections describe studies conducted to prepare the crosslinked PPQ adhesive candidates, process development and detailed evaluation of the most promising adhesive candidate.

3.1 TASK I - RESIN SYNTHESIS AND EVALUATION

It was the objective of this task to prepare crosslinked PPQ's (CPPQ's) and to evaluate the promising cured resins for potential to meet the program objectives. This work included 1) the synthesis of the required monomers, 2) synthesis of the linear PPQ's, 3) crosslinking studies and 4) evaluation of the crosslinked polymers. Descriptions of the work conducted on this task are presented in the following sections.

3.1.1 Monomer Synthesis

Three different *bis*(1,2-diketones) compounds were synthesized for use in this program. Two of the *bis*(1,2-diketones), *p,p'*-oxydibenzil (ODB) and *p-bis*(phenylglyoxalyl)benzene (BPGB), were prepared by the normal selenium dioxide oxidation method previously reported (Reference 1). The synthesis scheme employed for the preparation of BPGB is shown in Figure 1 and experimental details are given in Appendix A. The second monomer, ODB, was synthesized using a similar route from diphenyl ether and phenylacetyl chloride. Both compounds were obtained in polymer grade purity by recrystallization.

The third *bis*(1,2-diketone), *p-bis*(2-furylglyoxalyl) benzene (BFGB) was prepared by a different synthesis route. The BFGB monomer was used in this program to introduce the crosslinking sites (furan ring) into the polymer backbone. (The chemistry of the crosslinking reaction is described in section 3.1.3). BFGB was prepared from furfural and tere-

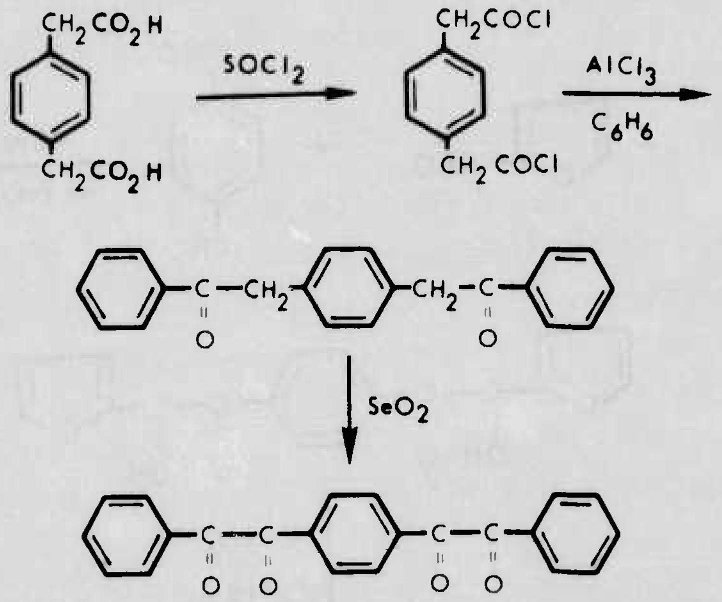


Figure 1. Synthesis Route to *p*-Bis(phenylglyoxalyl) Benzene (BPGB).

phthalaldehyde by the simple two-step route employing a benzoin condensation reaction as shown in Figure 2. It should be noted that this synthesis scheme does not require the usual seleium dioxide oxidation used in preparation of BPGB and ODB. The crude benzoin condensation product was obtained in high yield (>90%). However, during purification of the product by recrystallization, nearly half of the material was lost. Two recrystallization solvent systems were investigated (DMF/ethanol and pyridine), but both resulted in relatively low yields (35-40%) of purified adduct. As a result, it was decided to first oxidize the crude benzoin condensation product and then purify the oxidation product, BFGB, because it is easily purified by recrystallization from acetone. Using this preferred approach, BFGB was obtained in an overall yield of 56%. The experimental details are given in Appendix A.

The tetraamines, 3,3'-diaminobenzidine (DAB) and 3,3',4,4'-tetraaminodiphenyl oxide (TADPO), were acquired commercially. Sufficient amounts of both were purified to an acceptable level by recrystallization from water.

Two different crosslinking agents were used in the crosslinking studies described in Section 3.1.3. The *bis*maleimide, 1,3-dimaleimidobenzene (DMB), was prepared from *m*-phenylene diamine and maleic anhydride

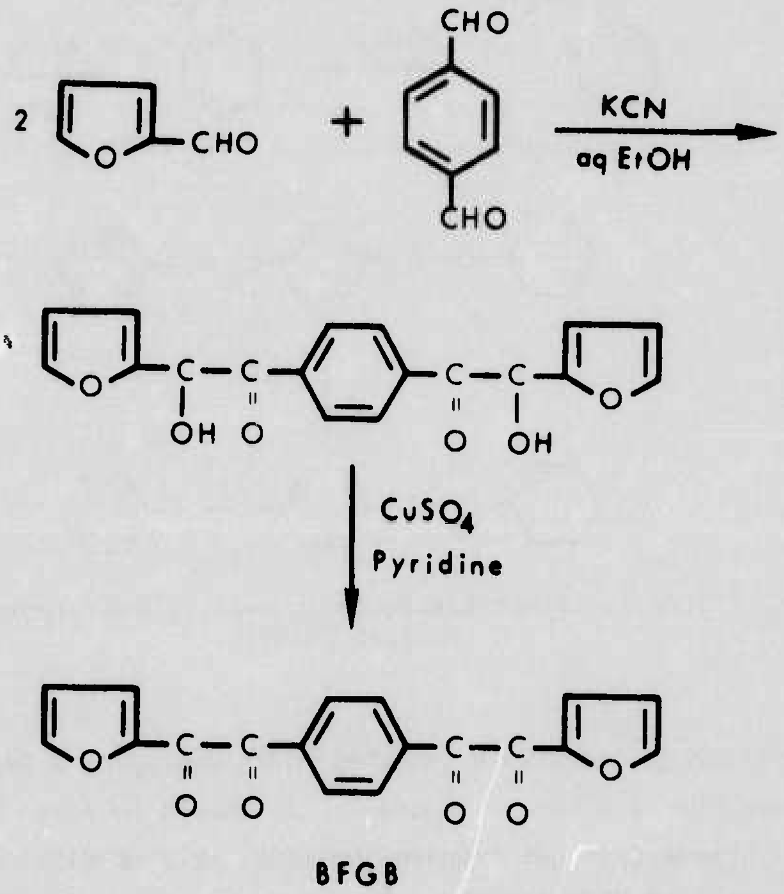


Figure 2. Synthesis Route to *p*-Bis(2-furylglyoxalyl)Benzene (BFGB).

using a reported procedure (Reference 2). The other crosslinking agent, 1,4-divinylbenzene, was obtained commercially and purified by distillation at reduced pressure.

3.1.2 Polymer Synthesis

The eight candidate resin formulations selected for study in this program are given in Table I. These specific formulations were selected to provide linear PPQ's demonstrating a range of glass transition temperatures (T_g) from high temperatures of ∿ 700°F down to fairly low temperatures of ∿ 550°F. The eight resins were prepared by reported methodology (Reference 1). Specifically, the polymers were prepared by adding

TABLE I

HIGH MOLECULAR WEIGHT AND CONVENTIONALLY POLYMERIZED, LINEAR PPQ RESINS STUDIED

Tetramine Ingredient	Co-Bis(benzil) Ingredients	Probable Linear PPQ T_g[a]	Mole Percent of Crosslink Agent (BFGB)		Attributes
			Level 1	Level 2	
DAB	ODB/BFGB	Medium[b]	15 ①[c]	20 ②[c]	Provides baseline data for 15% w/w, plus allows study of higher level which may provide higher properties judged on previous work.
	BPGB/BFGB	High[b]	10 ③[c]	15 ④[c]	Provides comparison of high T_g at a crosslink level with medium T_g, plus will allow determination if a lower crosslink level is sufficient with this system.
TADPO	ODB/BFGB	Low[b]	20 ⑤[c]	25 ⑥[c]	Provides higher crosslink levels to see if it is possible to elevate useful temperatures to ~700°F; these formulations should require the mildest processing temperatures.
	BPGB/BFGB	Medium[b]	15 ⑦[c]	20 ⑧[c]	Provides a sort of "reverse case" of DAB-ODB/BFGB to investigate whether this medium T_g ingredient combination will approach an optimum combination of properties and processability.

a. Values based on literature results of PPQ's containing no BFGB

b. Code: High = >700°F; Medium = ~650°F; Low = ~550°F

c. Polymer sample number

a mixture of the *bis*(1,2-diketone) compounds to a slurry of the tetraamine in a 1:1(w/w) mixture of *m*-cresol:xylene at ∿ 8% w/w solids loading. The polymer solutions obtained were viscous to extremely viscous and in some cases, gelatinous. The gelling phenomenon of PPQ's has been observed by other workers, particularly when a stoichiometric amounts of tetraamine and *bis*(1,2-diketone) is employed. One suggested approach for alleviating gel formation is to upset the stoichiometry, preferably in favor of the tetroketone (Reference 1). When the stoichiometry was upset by 2% (on molar basis) in favor of the tetraketone, polymers were obtained that displayed relatively high viscosities (e.g., ∿ 1.8 dl/g).

The linear polymers were isolated by precipitation into methanol using a Waring blender. The vibrous yellow solid obtained for each run was boiled twice in methanol and then dried *in vacuo* at 250°F for 6 hours. The inherent viscosity of each polymer was determined in *m*-cresol at 86°F (see Table II). In this preliminary screening of linear candidates, a goal value of at least 1.5 dl/g was established as the lower minimum of acceptability. As can be seen in Table II, all of the candidates, initially synthesized in Task I were found to be acceptable.

The major technical difficulty encountered in this work was that of gel formation. The gelling phenomenon was prevalent when one or more of the monomers contained an ether linkage (i.e., TADPO or ODB). The problem was particularly acute when attempts were made to redissolve the linear resins in the *m*-cresol/xylene solvent mixture, even at low solids loading (e.g., <5% w/w).

The polymer softening temperature (PST) of each linear PPQ candidate was determined by applying spatula pressure to a polymer sample placed between glass cover slips which had been placed onto a preheated Fisher Johns Melting Point Apparatus. The temperature range where the sample softened and became almost completely transparent was taken as the PST. This was intended to be a rough screening test to aid in structuring processing conditions in Task II. The results of this characterization test confirmed that the PST is dependent on molecular composition. That is, the PPQ polymers containing ether linkages displayed PST of ∿ 550°F to 570°F and the PPQ's without ether linkages (i.e., samples 3 and 4) displayed a PST of 600°F or above.

TABLE II

CHARACTERIZATION OF LINEAR POLYPHENYLQUINOXALINE RESINS

Polymer Sample Number	Composition (mole %)	Inherent Viscosity[a] (dl/g)	Polymer Softening Temperature[b] (°F)	Temp. of Init. Weight Loss in TGA (°F)[c]	Solubility in 50/50 v/v *m*-cresol/ xylene % w/w
1	50DAB/42.50DB:7.5BFGB	Gel			
1a	50DAB/42.50DB:7.5BFGB[d]	1.64	590-603	842	9
2	50DAB/40ODB:10BFGB	2.12	574-585	833	6
3	50DAB/45BPGB:5BFGB	1.92	599-608	860	7
4	50DAB/42.5BPGB:7.5BFGB	1.94	604-617	842	7
5	50TADPO/40ODB:10BFGB	2.23	554-563	824	6
6	50TADPO/37.50DB:12.5BFGB	2.16	549-567	815	6
7	50TADPO/42.5BPGB:7.5BFGB	3.03	572-583	833	5
8	50TADPO/40BPGB:10BFGB	2.43	579-594	827	7

[a] 0.5% in *m*-cresol at 86°F.

[b] Determined on Fisher Johns Melting Point Apparatus.

[c] Scan rate 5.4°F/min and a flow 100 ml/min.

[d] 2% molar excess of *bis*(1,2-diketone) used.

[e] Average of three specimens.

The linear polymer samples also were subjected to thermogravimetric analysis (TGA) to determine the temperature at which each sample exhibits an initial weight loss. The results obtained from this experimentation also are given in Table II. The TGA results correspond well with what would be expected for the basic polymer structures. That is, the more highly aromatic polymer structures (e.g., sample 3) are more thermo-oxidatively stable than the structures containing ether linkages (e.g., sample 5). However, the temperature range observed for onset of decomposition for the samples is not large. This was attributed to the presence of the thermally unstable furan rings in the linear samples which undergo decomposition at lower temperatures than do the backbones.

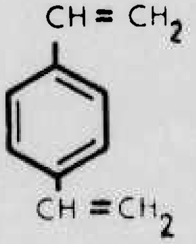
The solubility of each linear candidate in a 50/50 w/w *m*-cresol/xylene mixture also was determined. A powdered sample of the polymer was slowly added, portionwise, to the solvent mixture at 104-122°F (40-50°C), with stirring at such a rate that each portion was allowed to dissolve before the next portion was added. Addition was continued until the mixture was judged to be no longer useful in adhesive applications (i.e., of such a viscosity that the solution could no longer be used to prepare a useful adhesive formulation). The concentration of the solution was determined and the results obtained are given in Table II. All samples displayed a lower level of solubility than expected, implying that low concentration solutions will have to be used in the adhesive work.

The solutions prepared in the solubility studies then were used to prepare film samples. The films were prepared by doctoring the polymer solution on a glass plate followed by initial drying at 80°F for 24 hours, then *in vacuo* at 176°F (80°C) for three hours, and finally, at 284°F (140°C) for four hours. The film samples obtained were tough, flexible and transparent. All of the films were varying shades of yellow. The use of BFGB as a co-tetraketone monomer did not appear to alter the physical appearance of the PPQ's.

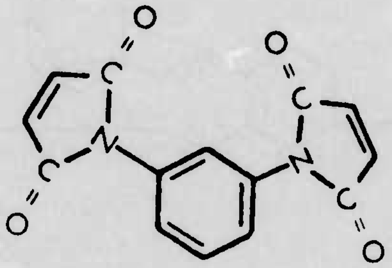
3.1.3 Crosslinking Studies

The linear PPQ candidates prepared above were subjected to crosslinking studies using a Diels-Alder reaction to accomplish cure. The basic cure chemistry was reduced to practice on Contract NAS3-15824 (Reference 3). Basically, it was shown that a maleimide adds to a furan ring to form an oxygen bridged intermediate. Upon heating to >450°F, the bridged intermediate splits out a molecule of water to give a thermally stable phenyl ring. Employing this Diels-Alder reaction, polyimides have been prepared from difunctional monomers and used to fabricate graphite reinforced composites which show excellent 550°F stability.

The same Diels-Alder reaction was used in this program to produce crosslinked PPQ's. The idealized crosslinking reaction is shown in Figure 3 on the next page. For this illustration, *p*-divinylbenzene (DVB) was used as the crosslinking agent. Similarly, when 1,3-dimaleimidobenzene (DMB) is used as the crosslinking agent, a crosslinked PPQ is obtained that has imide linkages in the crosslink. Thus, for high temperature applications, DVB is the more desirable crosslinking agent.



DVB



DMB

The crosslinking studies were conducted using thin film methodology. Basically, the stoichiometric amount of crosslinking agent was added to a solution (∿ 6% w/w) of the polymer in a *m*-cresol/xylene solvent mixture. The mixture was heated to 302°F (150°C) over a 1-hour period and then allowed to cool. Thin films (∿ 8-10 mils) were prepared from the varnish by doctoring the polymer solution on a glass plate followed by drying at 150°F for 12 hours and then *in vacuo* at 176°F for three hours followed by four hours at 284°F. The resultant yellow film for each candidate was postcured in a forced-air oven employing a linear heat-up rate from 450°F

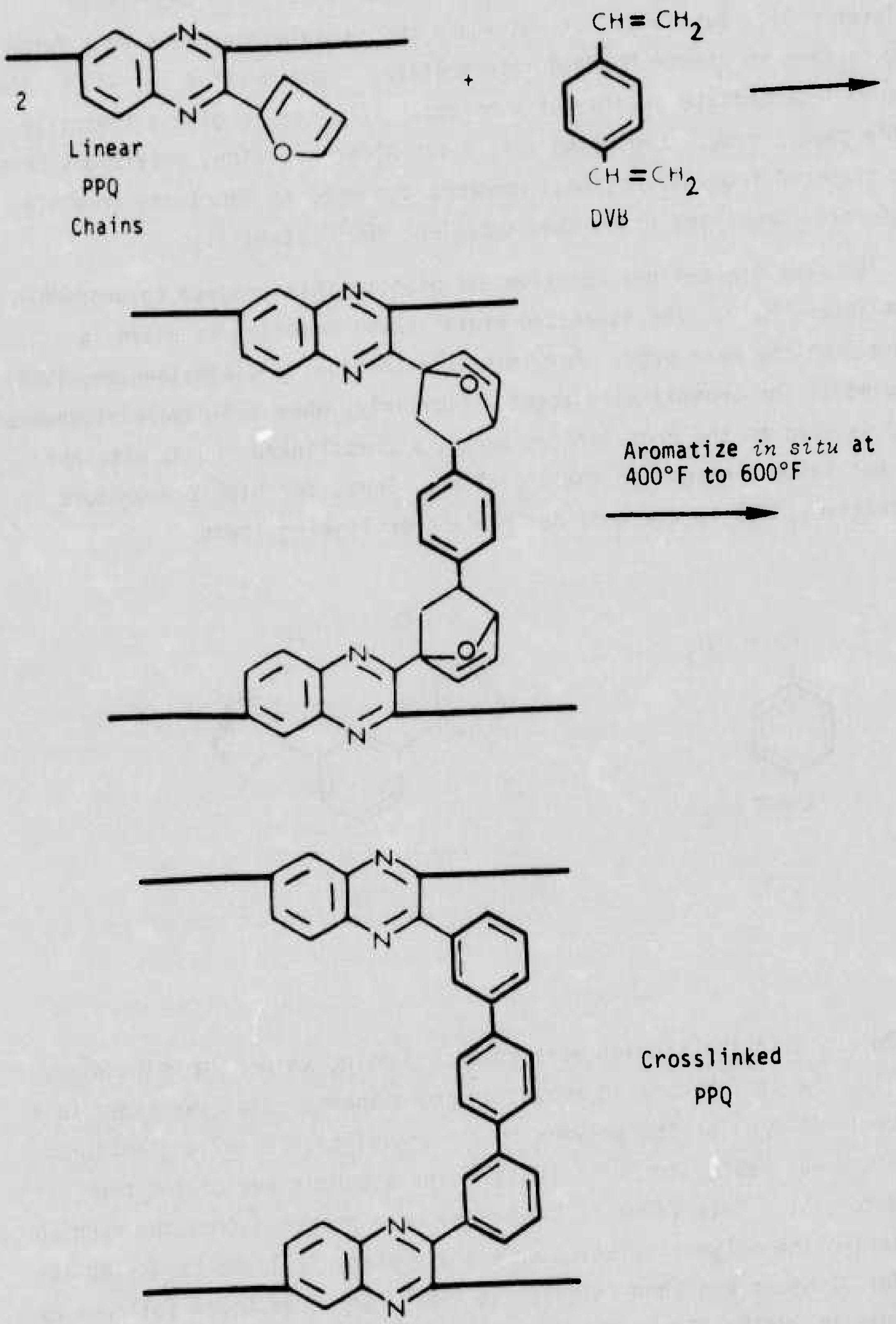


Figure 3. Idealized Crosslinking Reaction

to 600°F over a two-hour period, followed by an isothermal treatment at 600°F for one hour. The dark amber crosslinked samples were found to be tough and flexible. Film tensile properties were obtained on selected CPPQ samples. The samples displayed high tensile strengths and relatively high elongations at break indicating that crosslink formation did not result in an overly brittle material. For example, polymer sample 2 crosslinked with DMB had a tensile strength of 15 ksi and 20% elongation at break and polymer sample 4 crosslinked with DVB had a tensile strength of 17.5 ksi and 17% elongation at break. There were no detectable physical differences between samples cured with either crosslinking agent (i.e., DMB or DVB). The results of the characterization study on the CPPQ's are given in Table III.

Confirmation of cure was accomplished by boiling each sample (thin film) in a 50/50 w/w *m*-cresol/xylene mixture for 2 hours at a 5% w/w polymer solids loading level. The mixture then was filtered and the polymer sample was dried *in vacuo* at 302°F (150°C) for 12 hours. The samples were found to be <5% soluble, indicating a high degree of cure was obtained. The crosslinked samples also were characterized by TGA. It was found that the crosslinked samples exhibited an initial weight loss at higher temperatures than those of the linear resins. This result was expected because crosslink formation removes the thermo-oxidatively unstable furan ring from the polymer backbone.

It was near completion of this task that emphasis of the program was shifted to development of a tough adhesive for 450°F applications. It also was important that the adhesive developed display no creep under use conditions which required that the quinoxaline backbone be crosslinked. It was felt that any of the candidate resins studied on Task I would meet the new program objectives. Therefore, Task II studies were initiated to screen processability of these resins as adhesives. The results of the studies conducted on Task II are given in the following paragraphs.

TABLE III

CHARACTERIZATION OF CROSSLINKED POLYPHENYLQUINOXALINE RESINS

Polymer Number[a]	DVB Crosslinked		DMB Crosslinked	
	Percent Insoluble in Solvent[b], % w/w	Temp. of Initial Wt. Loss in TGA[c] (°F)	Percent Insoluble in Solvent[b], % w/w	Temp. of Initial Wt. Loss in TGA[c] (°F)
1	98	941	97	950
2	97	932	97	959
3	98	950	98	968
4	97	941	99	968
5	96	914	96	896
6	95	907	97	903
7	d	d	d	d
8	97	932	95	932

a) See Table I for composition

b) After 2 hours of boiling in 1:1 w/w *m*-cresol/xylene mixture

c) Scan rate 5.4°F/min and air flow rate 100 ml/min

d) Not obtained due to gelation problems

3.2 TASK II - PRELIMINARY ADHESIVE DEVELOPMENT AND EVALUATION STUDIES

It was the objective of this task to conduct screening evaluations on process variables with the ultimate goal of developing bonding procedures for the most promising CPPQ adhesive. These studies included 1) an initial screening of processability for the CPPQ's and 2) evaluation of processing conditions such as cure time, cure temperature, cure pressure, effect of postcure, etc.

3.2.1 Initial Process Screening of PPQ Candidates

The initial screening study was performed to determine the processability of each type of PPQ formulation prepared in Task I. The four major resin types (i.e., polymers 1,2; 3,4; 5,6; 7,8 in Table I) were found to have a wide range of polymer melt temperatures in Task I and as a result, were expected to vary considerably in ease of processability. The initial adhesive screening study was conducted by preparing Ti-6Al-4V lap-shear panels from a candidate of each formulation. The resultant lap-shear specimen from each resin was evaluated by measuring lap-shear strength and by a visual examination of the bondline (i.e., type of failure, resin flow, etc.). The lap-shear specimens were prepared by a procedure consisting of coating the cleaned (Turco 5578 Method) faying surfaces of the lap-shear panels with a primer solution (2-5% w/w) of the PPQ polymer in *m*-cresol/xylene (50/50 w/w). After drying the primer for 4 hours at 180°F, the adhesive paste (5-10% w/w) was applied and dried for 16 hours at 180°F. In this initial study, a light weight Style 112, A-1100 finished glass scrim was employed as a carrier. The lap-shear panels then were loaded in a preheated bonding jig at 700°F and a bonding pressure of 100 psig was applied. The part was cured for 60 minutes at 700°F, then cooled to 400°F or less before releasing the bonding pressure. The results of the initial processability screening study are given in Table IV and

TABLE IV

RESULTS OF INITIAL PROCESSABILITY SCREENING STUDY

Polymer Number[1]	Crosslinking Agent[2]	Filter	Lap Shear Strength, psi	Comments
1	DMB	Al Powder	2020 at R.T. 1810 at 450°F 1060 at 550°F	Failure to glass, limited flow
4	DVB	Al Powder	1000 at R.T.	No flow
4	DMB	Al Powder	2820 at R.T. 2700 at 450°F 450 at 550°F	Limited flow
5	DMB	Al Powder	1650 at R.T.	Limited flow
8	DMB		ND[3]	

1) See Table I for polymer structure

2) DMB = 1,3-dimaleimidobenzene; DVB = 1,4-divinylbenzene

3) ND = Not determined, a satisfactory adhesive could not be prepared because of gelation.

show that some of the resin candidates, as formulated at that time, were very difficult to process at 700°F. In addition, it was impossible to make a useful adhesive paste from polymer sample 8 because of gelation. At first, it was thought that the gelling phenomenon resulted from cross-link formation upon standing prior to adhesive formulation. However, a freshly prepared varnish sample of each linear polymer without a cross-linking agent also gelled upon standing. On the basis of the results obtained from this preliminary processability screening study, polymer sample 4 was initially selected for use in a short processing study to define conditions that would give bonded specimens truly representative of the resin. The results obtained on the processing study are given below.

3.2.2 Preliminary Process Screening Study

As was discussed in the preceeding section, polymer sample 4 (formulation DAB/85 BPGB:15 BFGB) was selected for a preliminary process screening study. Two crosslinking agents, 1,4-divinylbenzene (DVB) and 1,3-dimaleimidobenzene (DMB), were used to crosslink the linear resin. Other processing variables investigated included cure temperature, cure pressure effect of carrier and effect of postcure, The results obtained in this study are given in Table V. The data indicated that the DVB crosslinked PPQ cured very rapidly and no flow was obtained from this resin system (panel 3). It also was evident that longer drying cycles (>6 hours at 180°F) were required to remove the *m*-cresol/xylene solvent from the bondline. The residual solvent in these specimens drastically reduced the elevated temperature properties (panel 4) compared to the values (i.e., 1800 psi at 600°F) previously observed for this system. It also was observed that the failure mode in the specimens using the glass carrier was to the glass. The last set of results (panel 5) clearly indicated that processing temperatures in excess of 700°F adversely effect the adhesive properties of this particular resin formulation.

3.2.3 Process Development Studies

At the conclusion of the initial processability studies and the preliminary process screening studies, two of the polymer candidates were

TABLE V

RESULTS OF PRELIMINARY PROCESS SCREENING STUDY

Polymer Sample No.	Panel No.	Cross-linking Agent	Filler/ Carrier	Cure Conditions °F/psi	Lap Shear Properties			
					Coverage of lap area, %	Test Temp. °F	Shear Strength, psi	Failure Mode
4	1	DMB	Al Powder/112 Glass	700/200	85-90	R.T.	2820	Cohesive
						450	2700	Cohesive
						550	450	Cohesive
4	2	DMB	Al Powder/112 Glass	600/200	90	R.T.	1700	Cohesive
						450	2100	Cohesive
						550	830	Cohesive
4	3	DVB	Al Powder/112 Glass	700/200	(1)	(1)	(1)	-
			Al Powder/112 Glass	600/200	(1)	(1)	(1)	-
			Al Powder/112 Glass	600/500	80-90	R.T.	1990	Adhesive
					70-80	450	1570	Adhesive
					70-80	550	490	Adhesive
				(2)	70-80	550	900	
4	4	DMB	Al Powder	600/200 (3)	90	R.T.	2370	Cohesive
						450	590	Cohesive
4	5	DMB	Al Powder	600/200	90-100	R.T.	570	Cohesive
				700/200				
				800/200				

(1) Panels delaminated on machining
(2) Additional postcure of 16 hours at 650°F
(3) B stage of lap coupons before press bonding was 2 hours @ 180°F after application of adhesive paste

selected for additional study. The first resin studied was polymer 1 (DAB/85 ODB:15 BFGB) with DMB as the crosslinking agent. This resin formulation showed the greatest potential for processability at temperatures near 600°F. The second resin selected for Task II studies, DAB/85 BPGB:15 BFGB, required higher processing temperatures but offered potentially higher elevated temperature properties. Both of the linear polymers were prepared for these studies in a 1:1 w/w *m*-cresol/xylene mixture at 12% solids. The crosslinking agent was added to the varnish and then used as described below.

The following critical processing elements were screened:

- Cure temperature and pressure
- Postcure temperature and time
- Adhesive primer coating procedure.

The lap-shear specimens were prepared by a procedure consisting of coating the cleaned (Turco 5578 Method) faying surfaces of the Ti-6Al-4V lap-shear panels with a primer solution (5% w/w) of PPQ polymer in *m*-cresol/xylene (50/50 w/w) and drying in an air circulating oven (for conditions, see Table VI). After drying the primer an adhesive paste (1 part PPQ resin solids and 1.7 parts aluminum powder, Alcoa 101) was applied in successive coats until the desired thickness was obtained, i.e., ∿ 9-10 mil cured bondline. Using this technique, suitable lap-shear specimens were fabricated, although it was difficult to obtain good reproducibility. The most prevalent problem associated with processing this resin system was the application of a low resin solids content adhesive and/or primer to the faying surface. This procedure caused problems because as each new adhesive coating was applied, the solvent dissolved the primer and/or previous coatings. As a result, during this procedure a film was formed which lifted away from the cleaned faying surface exposing the cleaned Ti-6Al-4V adherend. This behavior ultimately resulted in adhesive failures in the final lap-shear specimens. The second major problem encountered in processing these PPQ polymers was lack of flow resulting in the lack of contact pressure over the complete surface of the bondline. Consequently, the breaking loads obtained in testing the lap-shear specimens were adjusted to reflect the less than 100% bondline in order to

TABLE VI

RESULTS OF PROCESS DEVELOPMENT STUDIES ON DAB/ODB:BFGB ADHESIVE

			Lap Shear Properties			
Panel Number	B Staging Conditions °F/Hours	Cure Conditions °F/psi/hrs	Coverage of Lap Area, % (4)	Test Temp °F	Shear Strength, psi	Failure Mode
1	Primer 180/4	600/500/1	55	RT	4150	Cohesive
	1st Adhesive 180/2	650/0/16	80	450	2770	Cohesive
	2nd Adhesive 180/6		> 10	550	2500	Cohesive
2	Primer 180/4	600/500/1	70	RT	3970	Cohesive
	1st Adhesive 180/2	650/0/16	25	450	3510	Cohesive
	2nd Adhesive 180/8		15	550	2400	Cohesive
2A		600/500	75	RT	3330	Cohesive
	"	650/0/16	20	450	2980	Cohesive
			30	550	1830	Cohesive
3	Primer 180/4	600/500/1	25	RT	3150	90-100 Cohesive
	1st Adhesive 180/2	650/0/16	65	450	2510	90-100 Cohesive
	2nd Adhesive 180/4		100	550	1540	90-100 Cohesive
4		600/500/1	> 90	RT	2110	70% Cohesive
	"	650/0/8	> 90	450	1790	70% Cohesive
			> 90	550	700	70% Cohesive
5		600/200/1	> 90	RT	2370	Cohesive
	"		> 90	450	590	Cohesive
			> 90	550	390	Cohesive
6	"	600/500/1		RT	1990	Adhesive
				450	1570	Adhesive
7(1)	"	700/500/1	> 90	RT	2580	Adhesive
			> 90	450	1490	Adhesive
			> 90	550	1140	Adhesive
8	"	650/500/1	(2)	(2)	(2)	(2)
		650/0/16				
9(3)	"	600/500/1	20	RT	2800	Cohesive
		650/0/16	50	550	1230	Cohesive

1) PPQ resin DAB/85 BPGB:15 BFGB

2) Panels delaminated on machining

3) PPQ resin DAB/75ODB:25 BFGB

4) Percent coverage of lap areas was determined by the following formula

$$\text{Percent Coverage} = \frac{\text{Contact area of adhesive} \times 100}{\text{Total Bondline Area}}$$

5) Calculated: Bonded Area x Load

obtain more representative values than those obtained using the lap joint area.

The test data for the lap-shear specimens (Table VI) prepared from the DAB/85 ODB:15 BFGB system gave some indication of the critical processing parameters. For example, the results showed that 1) postcure improves the shear strength of the test specimens (i.e., panels 3 and 4), 2) increased drying time at 180°F after application of the final adhesive coat reduced coverage of lap area (panels 1,2 and 3) increased bonding pressure gave higher elevated temperature shear strengths (panels 5 and 6).

The results obtained from this screening study were somewhat disappointing, particularly the 550°F values. As a result, another resin was prepared from the same monomers which contained a higher crosslink density to determine if this approach would improve the elevated temperature lap-shear properties (panel 9). The results showed that this approach did not significantly improve the elevated temperature properties, but rather, the higher crosslink density decreased the total bondline coverage.

A process screening study also was conducted employing the DAB/85 BPGB:15 BFGB resin. This resin system offers potentially higher elevated temperature properties as a result of its higher T_g. However, the higher T_g necessitated higher processing temperatures. To improve the resin's processability, a lower molecular weight version of the polymer was prepared by offsetting the stoichiometry in favor of the tetraketones (inherent viscosity of 1.16 dl/g). It was determined that a minimum of 700°F and 500 psi were required in order to successfully fabricate lap-shear panels. However, the initial results obtained for this non-ether containing system were not dramatically higher than for the ether containing resin studied above. However, the failure mode of the specimens was primarily adhesive giving indication that potentially higher lap-shear values could be obtained with improved processing techniques.

3.2.4 Additional Process Development Studies

The results of the process development studies discussed in the previous section indicated that additional improvements in the process were necessary for both PPQ formulations prior to fabrication of isothermal aging specimens. Consequently, studies were conducted to investigate 1) the reduction in the number of coatings placed on the cleaned faying surfaces, 2) the use of a glass scrim carrier 3) the use of resins with different crosslink densities and 4) the effect of employing excess crosslinking agent (i.e., DMB).

The lap-shear panels used in this study were prepared for bonding by the procedure outlined in Section 3.2.3 which consisted of coating the cleaned faying surfaces of Ti-6Al-4V substrate with a primer solution (6% w/w) of PPQ polymer in 1:1 w/w *m*-cresol/xylene mixture and drying in a 180°F air circulating oven. An adhesive film of each polymer formulation was prepared using an A1100 finish 112 glass scrim. The varnish used was a 12% w/w solids of PPQ polymer in *m*-cresol/xylene and was painted onto the glass scrim. After one hour drying in a 180°F air circulating oven, an adhesive paste (1 part PPQ resin solids and 1.7 parts aluminum powder, Alcoa 101) was applied in successive coats to the glass scrim until the desired quantity of PPQ solids was obtained. Both the primed lap-shear panels and the adhesive film were then dried for 16 hours at 180°F prior to the press curing operation. The volative content of the adhesive tape was ∿ 8% (w/w) after the drying cycle for each of the adhesive candidates.

Lap-shear panels using the two different DAB/ODB:BFGB resins (different crosslink densities) were processed in a 600°F bonding fixture and pressure was applied within a 30-second time period. The panels were cured for 60 minutes and then removed from the press and postcured for 16 hours at 650°F in an air circulating oven. The lap-shear panels using the DAB/BPGB:BFGB resin were processed in a 700°F press employing the conditions described above. These panels were not subjected to any additional postcuring operation prior to testing.

The test data for the lap-shear specimens fabricated above are reported in Table VII. The results in Table VII indicate that 1) complete coverage of lap area was obtained, 2) cohesive failure of bondline was predominate, 3) panels prepared from the higher crosslink density resin possess lower room temperature properties and only slightly higher properties at 550°F and 4) panels prepared from the PPQ with the higher T*g* (i.e., DAB/85 BPGB:15 BFGB) possess superior strength retention at

TABLE VII

SUMMARY LAP-SHEAR DATA OBTAINED FROM OPTIMIZED PROCESSING PROCEDURE

Panel Number/ Resin Formulation	Cure Conditions °F/psi/Hrs	Coverage of Lap Area(1) (%)	Bondline Thickness(1) (Mils)	Lap Shear Properties		
				Temp Test °F	Shear Strength psi(2)	Failure Mode / Number of Specimens
1	600/500/1	100	16	RT	3480	100% Cohesive/3
DAB/85 ODB:	650/0/16	100	16	450	2620	100% Cohesive/3
15 BFGB			16	550	1600	100% Cohesive/5
2	600/500/1	100	13	RT	2460	60-70% Cohesive/3
DAB/75 ODB:	650/0/16	100	13	450	2490	100% Cohesive/3
25 BFGB		100	13	550	1720	100% Cohesive/5
3	700/500/1	100	16-17	RT	2610	65-75% Cohesive/3
DAB/85 BPGB:		100	16-17	450	2320	100% Cohesive/4
15 BFGB		100	16-17	550	2180	100% Cohesive/4

(1) Percent coverage of lap areas was determined by the following formula

$$\text{Percent Coverage} = \frac{\text{Contact area of adhesive x 100}}{\text{Total Bondline Area}}$$

(2) Calculated: Bonded area x load

elevated temperature. Based on these results, the DAB/85 ODB:15 BFGB formulation and the DAB/85 BOGB:15 BFGB were selected for isothermal aging studies as described below.

3.2.5 Isothermal Thermal Aging of Lap-Shear Specimens

The Ti-6Al-4V lap-shear test specimens were prepared from the two CPPQ adhesive candidates using the procedure described in Section 3.2.4 and were subjected to isothermal aging at 450°F and 550°F. The test specimens were aged in air circulating ovens with an air velocity of approximately 250 ft/minute and an air exchange rate of approximately 400 ft^3/minute. Specimens were withdrawn from the ovens after aging durations of 100, 500 and 1000 hours and their lap-shear strengths determined at the aging temperature. The results of the isothermal aging study are given in Table VIII. Plots of strength retention versus aging duration at each test temperature for the two PPQ adhesives are shown in Figure 4 and Figure 5. The results clearly indicated higher strength retention for the DAB/85 ODB:15 BFGB adhesive at both aging temperatures. However, it was observed that the DAB/85 BOGB:15 BFGB adhesive system debonded from the Ti-6Al-4V substrate. This behavior was tentatively attributed to the surface preparation procedure. This was the first long-term isothermal aging data obtained for PPQ/Ti-6Al-4V specimens using the Turco 5578 cleaning method. In addition, the original Turco cleaning method being used in the program was later modified to include a dilute nitric acid wash. This modification was not used on samples prepared up to this point in the program, and may have been the cause of the debonding. From this point on in the program, the modified cleaning procedure was used.

3.2.6 Double Lap-Shear Specimens

The results obtained on lap-shear strength determinations strongly indicated that the CPPQ resin systems were somewhat brittle at room temperature. To confirm this conclusion, the adhesives were tested using double lap-shear specimens (Figure 6). The double lap-shear configuration minimizes the peel stress which is significant in a single lap-shear configuration.

TABLE VIII

RESULTS OF ISOTHERMAL AGING STUDY ON TI-6Al-4V LAP SHEAR SPECIMENS

CPPQ Resin	Aging Temp, °F	Aging Time, Hours	Test Temp, °F	Lap Shear Properties		
				Ultimate Strength(1) (psi)	Failure Mode / No. of Specimens	% Strength Retention
DAB/850D8:		0.0	R.T.	2550	Cohesive/8	
15BFG8	450	0.0	450	2040	Cohesive/5	80(2)
	550	0.0	550	1930	Cohesive/5	76(2)
	450	100.0	450	2580	Cohesive/5	126(3)
	550	100.0	550	1900	Cohesive/5	99(3)
	450	500.0	450	2110	93% Cohesive/5	103(3)
	550	500.0	550	1420	75% Cohesive/5	74(3)
	450	1000.0	450	2060	80% Cohesive/5	101(3)
	550	1000.0	550	990	45% Cohesive/5	51(3)
OAB/858PGB:		0.0	R.T.	2500	Cohesive/5	
158FGB	450	0.0	450	2210	Cohesive/5	88(2)
	550	0.0	550	2050	Cohesive/5	82(2)
	450	100.0	450	2072	85% Cohesive/5	94(3)
	550	100.0	550	1350	65% Cohesive/5	66(3)
	450	500.0	450	1700	65% Cohesive/5	77(3)
	550	500.0	550	640	30% Cohesive/4(4)	29(3)
	450	1000.0	450	900	10% Cohesive/4(4)	41(3)
	550	1000.0	550	280	100% Cohesive/1(4)	14(3)

(1) Calculated: Load : Bonded Area

(2) Calculated: $\frac{\text{Lap Shear Strength at Test Temperature}}{\text{Lap Shear Strength of Control at R.T.}} \times 100$

(3) Calculated: $\frac{\text{Lap Shear Strength at Test Temperature}}{\text{Lap Shear Strength of Control at Test Temperature}} \times 100$

(4) Remaining specimens debonded during isothermal aging. Primer resin still in place on specimens

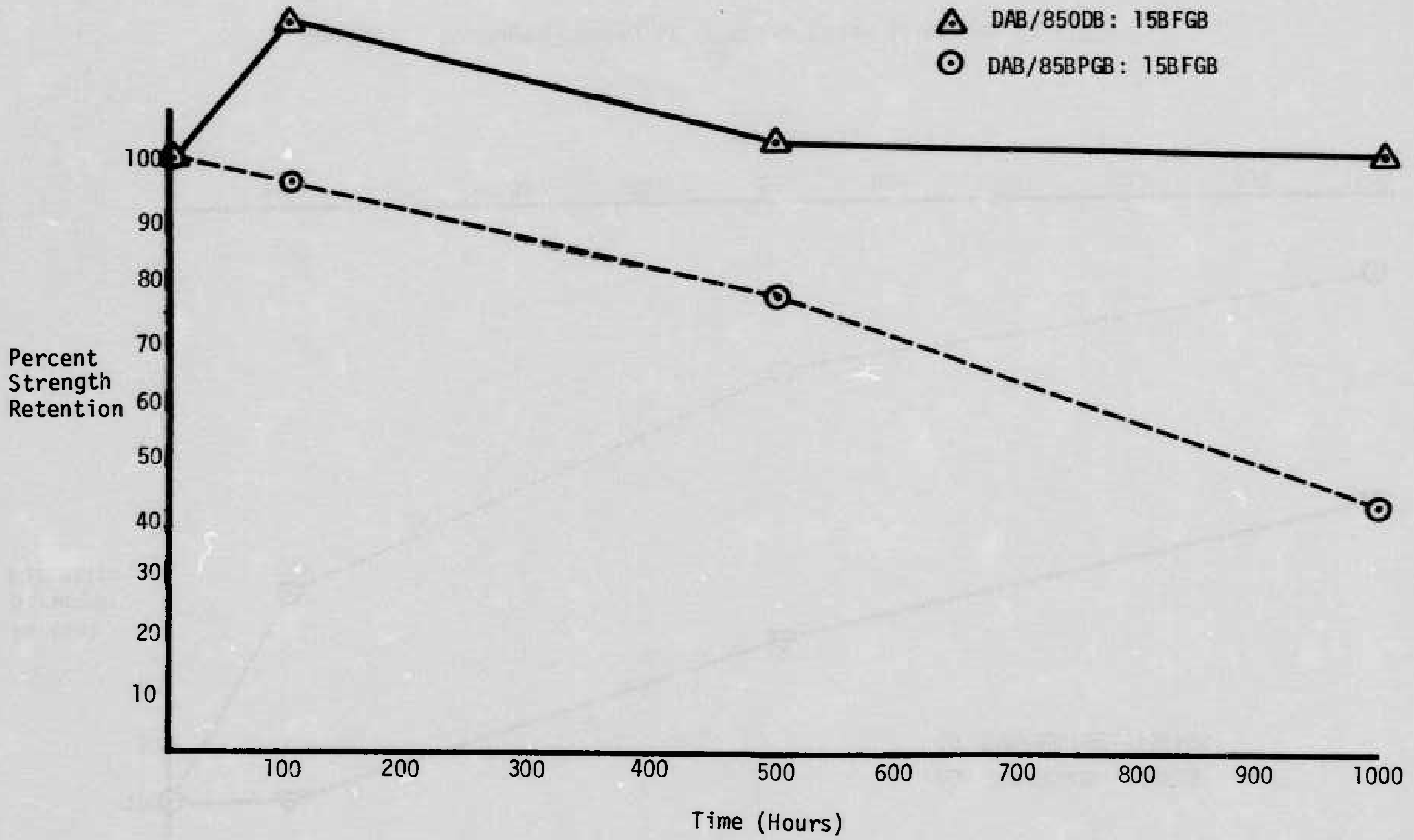


Figure 4. Isothermal Aging of CPPQ Lap Shear Specimens at 450°F

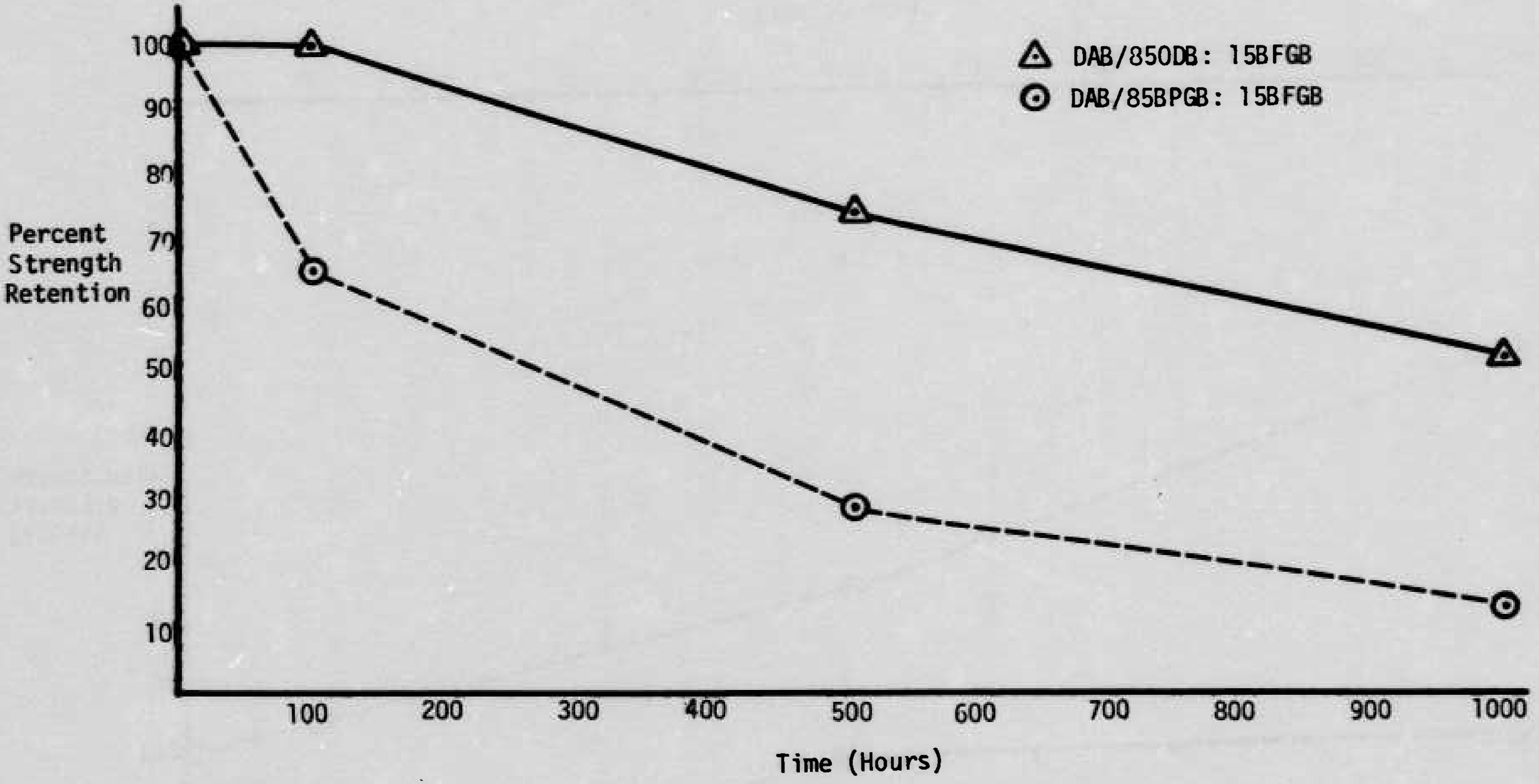


Figure 5. Isothermal Aging of CPPQ Lap Shear Specimens at 550°F

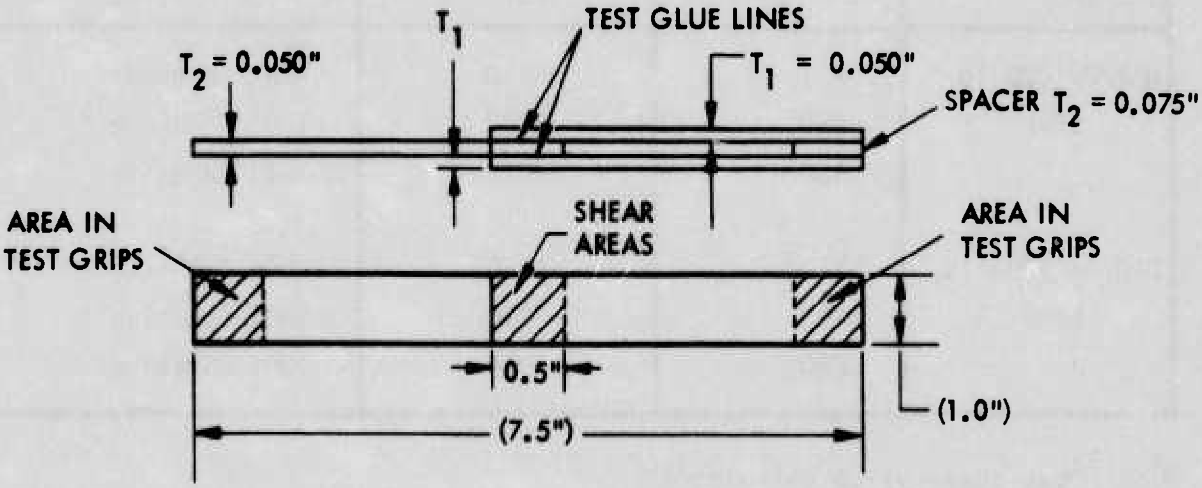


Figure 6. Double Lap-Shear Specimen

The test panels were cleaned, primed and processed using the specimen assembly shown in Figure 6 and the procedure previously described in Section 3.2.5. The double lap-shear panels were then machined and tested and the results are shown in Table IX. The room temperature lap-shear values for both adhesive systems increased significantly when tested in the double lap-shear configuration. However, the elevated temperature properties, were about the same as those observed for the single lap-shear panels. These results strongly support the original supposition that the resins are somewhat brittle at room temperature. On the basis of these results, double lap-shear specimens were selected for use in the stress durability determinations of Task III.

TABLE IX

PROPERTIES OF DOUBLE LAP-SHEAR PANELS

RESIN SYSTEM	TEST TEMP °F	LAP-SHEAR VALUE[1]	
		PSI	MODE OF FAILURE
DAB/85 ODB:15 BFGB	R.T.	3720	100% Cohesive
	450	2700	100% Cohesive
	550	2030	100% Cohesive
DAB/85 BPBG:15 BFGB	R.T.	4150	100% Cohesive
	450	2890	100% Cohesive
	550	1840	100% Cohesive

(1)Lap-shear value calculated

$$\text{Lap Shear Value} = \frac{\text{Breaking Load (lbs)}}{\text{Cross Sectional Area (sq in)}}$$

3.3 TASK III - DETAILED PROPERTY EVALUATION

It was the purpose of this task to evaluate the performance of the PPQ adhesive developed in Task II in key property areas that included stress durability under conditions of heat and humidity, peel strength, and suitability for preparing large area bonded specimens. The work conducted on this task is described in detail below.

3.3.1 Wedge Opening Test

Wedge opening specimens (see Figure 7) were fabricated using Turco 5578 cleaned Ti-6Al-4V adherends and the two CPPQ adhesive candidates, DAB/85 ODB:15 BFGB and DAB/85 BPGB:15 BFGB. The processing conditions employed were the same as those described in Section 3.2.5. The crack extension test consisted of inserting a wedge as shown in Figure 7, locating and marking the tip of the initial crack, exposing the specimen to 95-100% relative humidity in a chamber maintained at 160°F and then

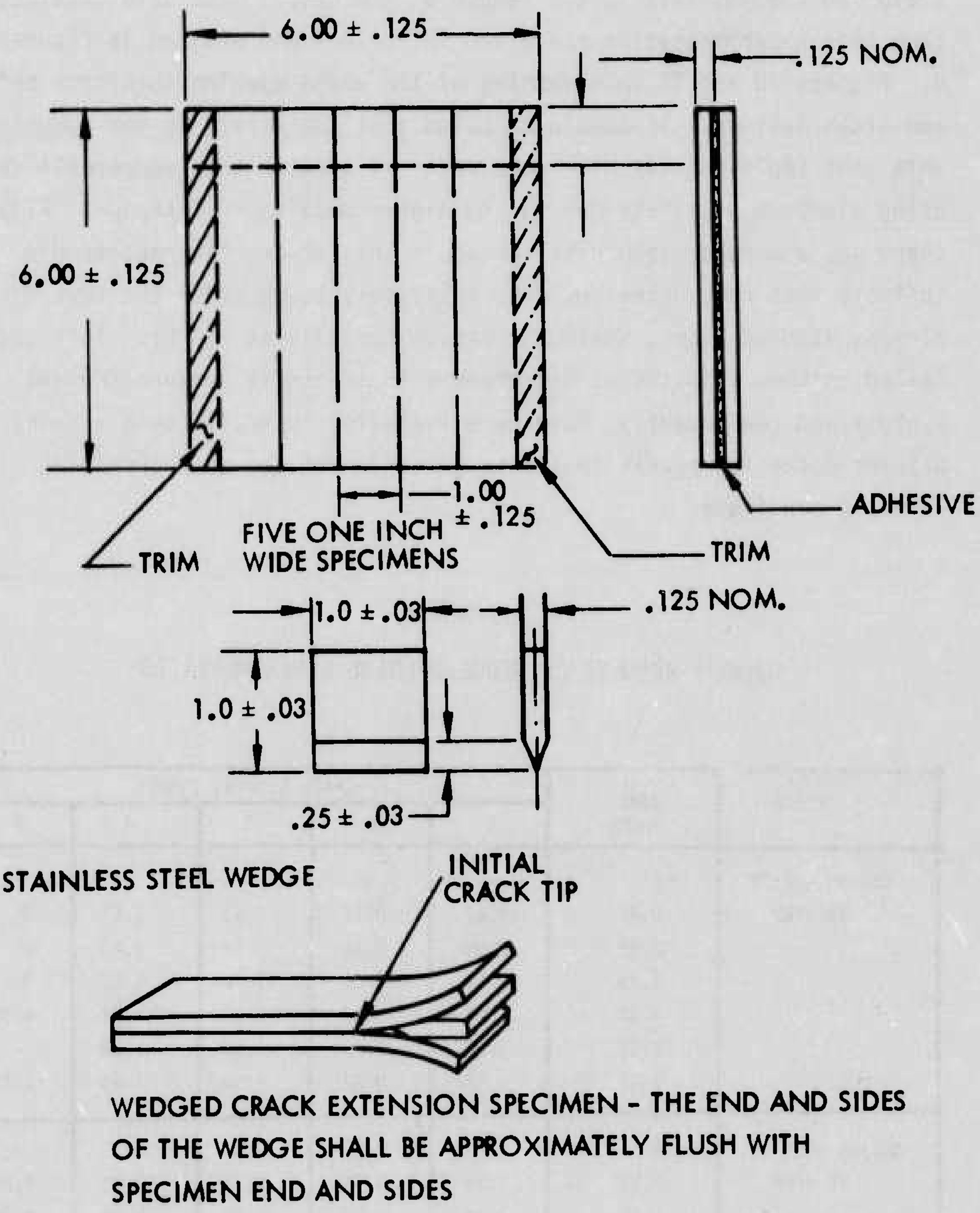


Figure 7. Wedge Opening Specimen

measuring the increase in the length of the crack. The data obtained from this experimentation are given in Table X and plotted in Figures 8 and 9. Figures 10 and 11 show samples of the wedge opening specimens before and after testing. It should be noted that the stress on the adhesive in this test employing titanium substrates is greater than comparable tests using aluminum substrate due to the higher modulus of titanium. Although there was a considerable data spread in this study, the results did indicate that both adhesives were relatively tough under the test conditions studied (i.e., 95-100% relative humidity at 160°F). This test failed to show significant differences in toughness between the two systems and consequently, both were evaluated in small (6-in x 6-in) blister detection panels to aid in selection of the most promising adhesive candidate.

TABLE X

SUMMARY RESULTS OF WEDGE OPENING EXPERIMENTATION

RESIN	TIME (HRS)	CRACK GROWTH, INCHES				
		1	2	3	4	5
DAB/85 ODB:15	0	-	-	-	-	-
15 BFGB	0.25	0.57	0.12	0.63	0.67	0
	0.50	0.90	0.16	0.92	0.83	0
	2.25	1.54	0.22	1.38	1.02	0
	4.00	1.60	0.28	1.50	1.02	0.35
	26.00	1.60	0.83	1.50	1.20	-
	72.00	1.60	0.83	1.50	1.20	0.35
DAB/85 BPBG:15	0	-	-	-	-	-
15 BFGB	0.25	1.24	0.65	0.11	0.03	0.20
	0.50	1.38	0.72	0.11	0.03	0.20
	2.25	1.50	1.08	0.11	0.33	0.20
	4.00	1.50	1.50	0.11	0.42	-
	26.00	1.50	1.50	0.11	0.42	-
	72.00	1.50	1.70	0.23	0.43	0.32

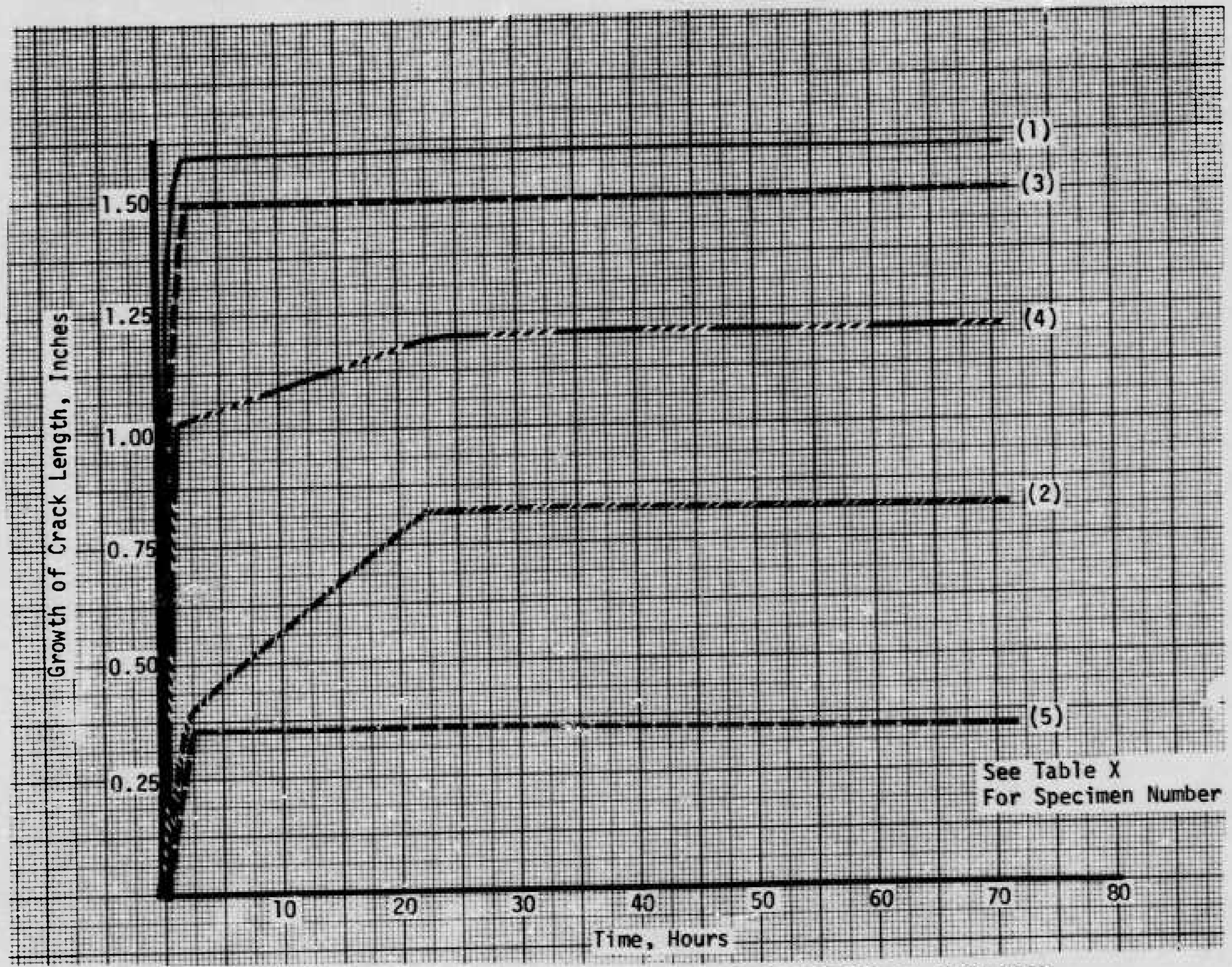


Figure 8. Crack Extension Plots of DAB/85 ODB:15 BFGB CPPQ

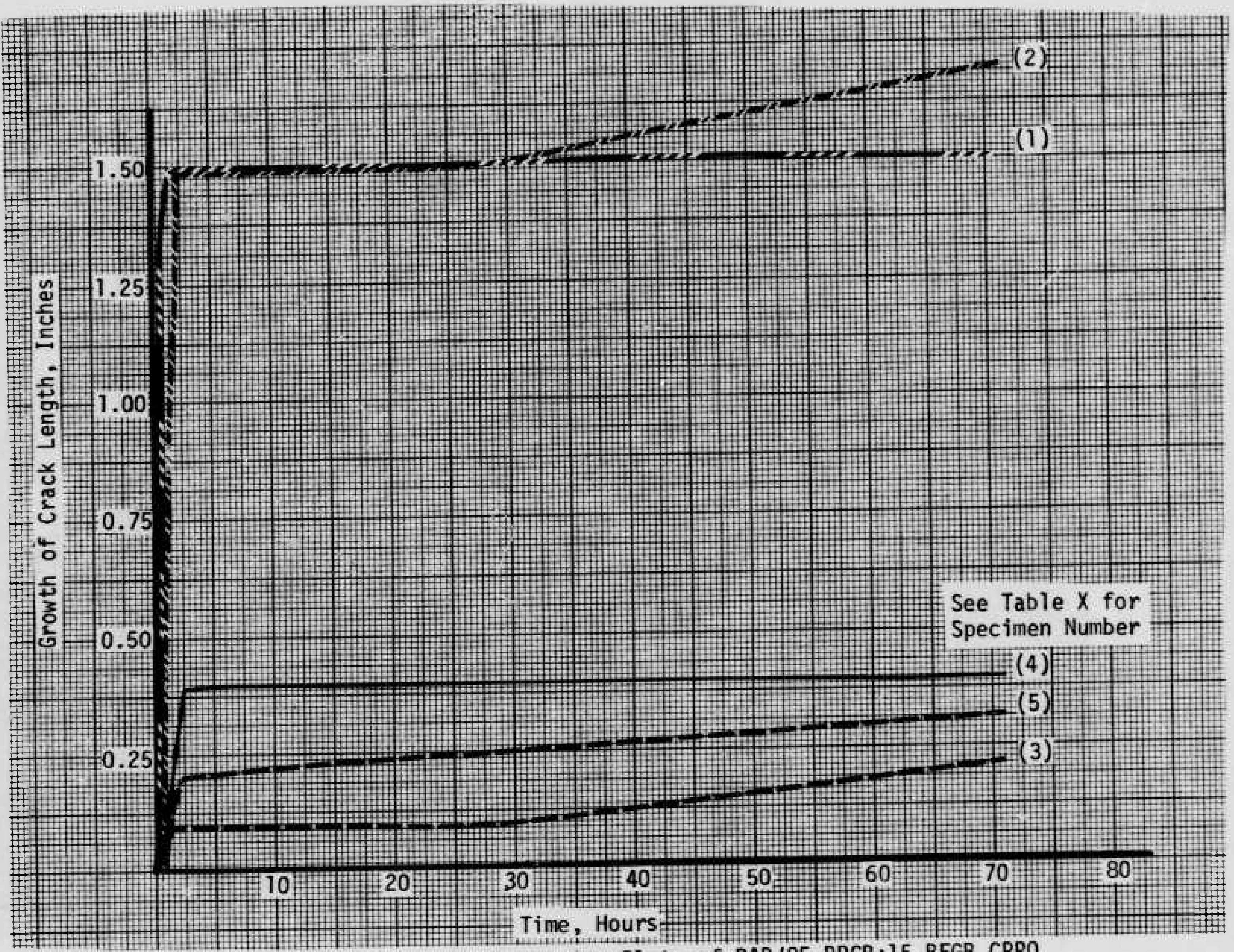


Figure 9. Crack Extension Plots of DAB/85 BPGB:15 BFGB CPPQ

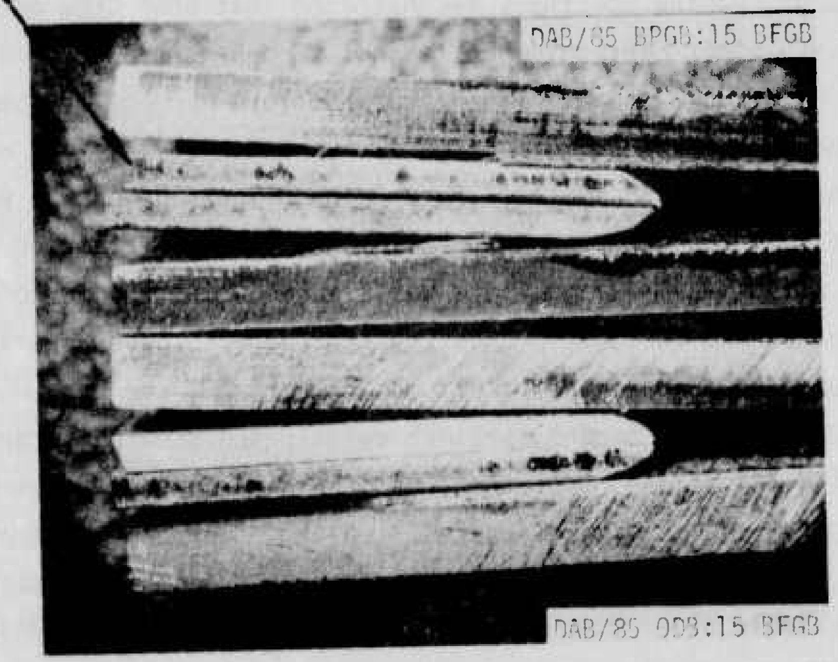

Aluminum Wedge 1" x .125"

Figure 10.

Wedge Opening Specimen After Wedge Insertion

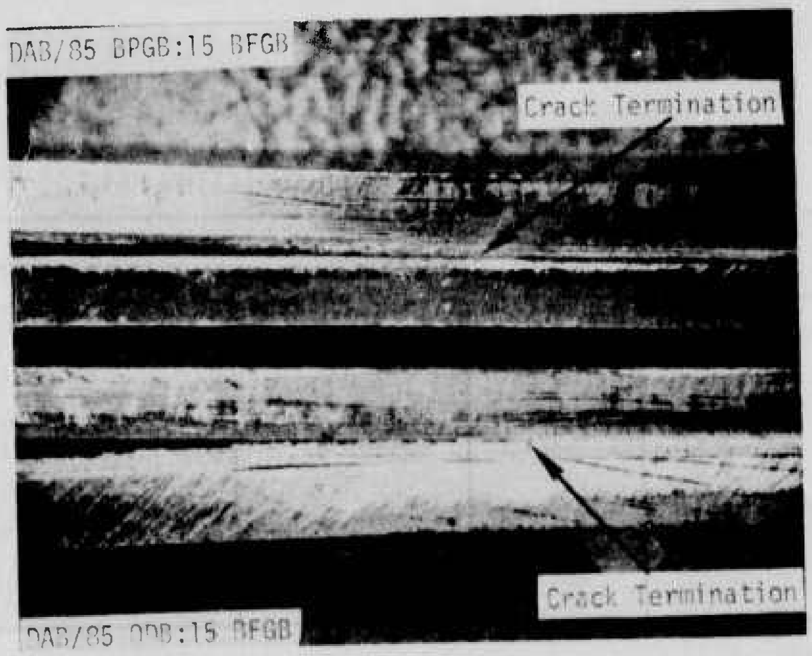


Figure 11.

Wedge Opening Specimen After Testing

3.3.2 Blister Detection Panels

The wedge opening specimens demonstrated that both CPPQ adhesive systems (i.e., ether containing resin and the non-ether containing resin) were tough adhesive systems. The primary failure mode of the wedge opening specimen was cohesive in nature. Consequently, it was decided to evaluate both systems in small (6-in x 6-in) blister detection panels before selecting a system for the remaining detailed evaluation studies. The 6-in x 6-in Ti-6Al-4V substrate was cleaned using the Turco 5578 cleaning method and the same processing procedure as described in Section 3.2.5 was used to prepare the panel. Upon machining the bonded panels, the DAB/85 ODB:15 BFGB bonded specimen delaminated showing strong evidence of blistering. A second panel then was fabricated, using the same adhesive system and it also blistered. On the other hand, the panel containing the DAB/85 BPGB:15 BFGB adhesive was successfully machined and tested (see Table XI). Based on these results the DAB/85 BPGB:15 BFGB resin formulation was selected as being the most promising adhesive. Further studies then were conducted which included peel strength determination and stress durability measurements using stressed aging specimens fabrication of large blister panels.

TABLE XI

PROPERTIES OF SMALL BLISTER DETECTION PANELS

RESIN SYSTEM	TEST TEMP °F	LAP-SHEAR VALUE(1)	
		PSI	MODE OF FAILURE
DAB/85 OOB:15 BFGB	R.T.	Delaminated	-
"	"	Delaminated	-
DAB/85 BPBG:15 BFGB	R.T.	1120	95% Adhesive
	450	2030	95% Cohesive
	550	2180	95% Cohesive

(1) Lap-shear value calculated:

$$\text{Lap-Shear Value} = \frac{\text{Breaking Load (lbs)}}{\text{Cross Sectional Area of Lap (sq in)}}$$

After the selection of DAB/85 BPGB:15 BFGB as the most promising adhesive resin, two large blister detection panels (10-in x 12-in) were fabricated; the first panel for testing in Task III and the second panel for delivery to AFML (see Table XII for test results).

TABLE XII

PROPERTIES OF LARGE BLISTER DETECTION PANEL

Resin System	Test Temp ^{o}F	Lap Shear Strength(1)	
		PSI	Failure mode
DAB/85	RT	1960	70% Cohesive
BPBG:15			
BFGB	450^{o}F	2440	100% Cohesive

(1) Lap Shear Strength Value calculated as follows:

$$\text{Lap Shear Strength Value} = \frac{\text{Breaking Load (lbs)}}{\text{Cross Sectional Area of Lap (sq. in.)}}$$

3.3.3 T-Peel Strength Determinations

Two smaller panels (9 in x 6 in) also were fabricated for obtaining T-Peel strength values. Thin Ti-6Al-4V foil (.010 in) was utilized in place of the thicker (.125 in) titanium alloy sheet used in the blister detection panels. The initial values (see Table XIII) are not outstanding but compare quite favorably with reported values of other high temperature polymers such as PBI (Imidite 850).

TABLE XIII

T-PEEL PROPERTIES OF CPPQ ADHESIVE

Resin System	Test Temp	T-Peel Values	
		lbs/in width	Failure Mode
DAB/85 BPBG:15 BFGB	RT	3 (1)	Cohesive
	RT	1.3 (2)	Adhesive

(1) Average of 4 specimens (1-in wide x 9-in length)

(2) Average of 3 specimens (1-in wide x 9-in length) aged 7 days at 450°F

3.3.4 Isothermal Aging of Double Lap Shear Specimens

Double lap shear test specimens were prepared from DAB/85 BPGB:15 BFGB CPPQ adhesive using the procedure described in Section 3.2.6 and were subjected to isothermal aging at 450°F and 550°F. The test specimens were aged in air circulating ovens with an air velocity of approximately 250 ft/minute and an air exchange rate of approximately 500 ft^3/minute. Specimens were withdrawn from the ovens after aging durations of 500 and 1000 hours and their lap-shear strengths determined at the aging temperature. The results of the aging study are given in Table IX and a plot of strength retention is shown in Figure 12. The 450°F aging data are somewhat misleading because the initial test properties of the double lap-shear specimens at both ambient and elevated temperature conditions were lower than previously observed for this adhesive system (Table IX). It was noted that DAB/85 BPBG:15 BFGB did maintain its 450°F properties throughout the 1000-hour exposure, whereas previous tests using single lap shear test specimens (see Figure 4) yielded approximately 50 percent strength retention.

TABLE XIV

RESULTS OF ISOTHERMAL AGING STUDY ON TI-6Al-4V DOUBLE LAP SHEAR SPECIMENS

Aging Temp °F	Aging Time Hours	Test Temp °F	Lap Shear Strength Properties		
			Ultimate (1) Strength (PSI)	Failure Mode	Strength Retention
—	—	RT	3040	90% Cohesive	—
450	.5	450	1420	90% Cohesive	47(2)
550	.5	550	830	75% Cohesive	27(2)
450	500	450	2240	60% Cohesive	158(3)
550	500	550	790	20% Cohesive	95(3)
450	1000	450	2040	50% Cohesive	144(3)
550	1000	550			

(1) Calculated: Load ÷ Bonded Area

(2) Calculated: $\frac{\text{Lap Shear Strength at Test Temp}}{\text{Lap Shear Strength of Control @ RT}} \times 100$

(3) Calculated: $\frac{\text{Lap Shear Strength at Test Temp}}{\text{Lap Shear Strength of Control @ Test Temp}} \times 100$

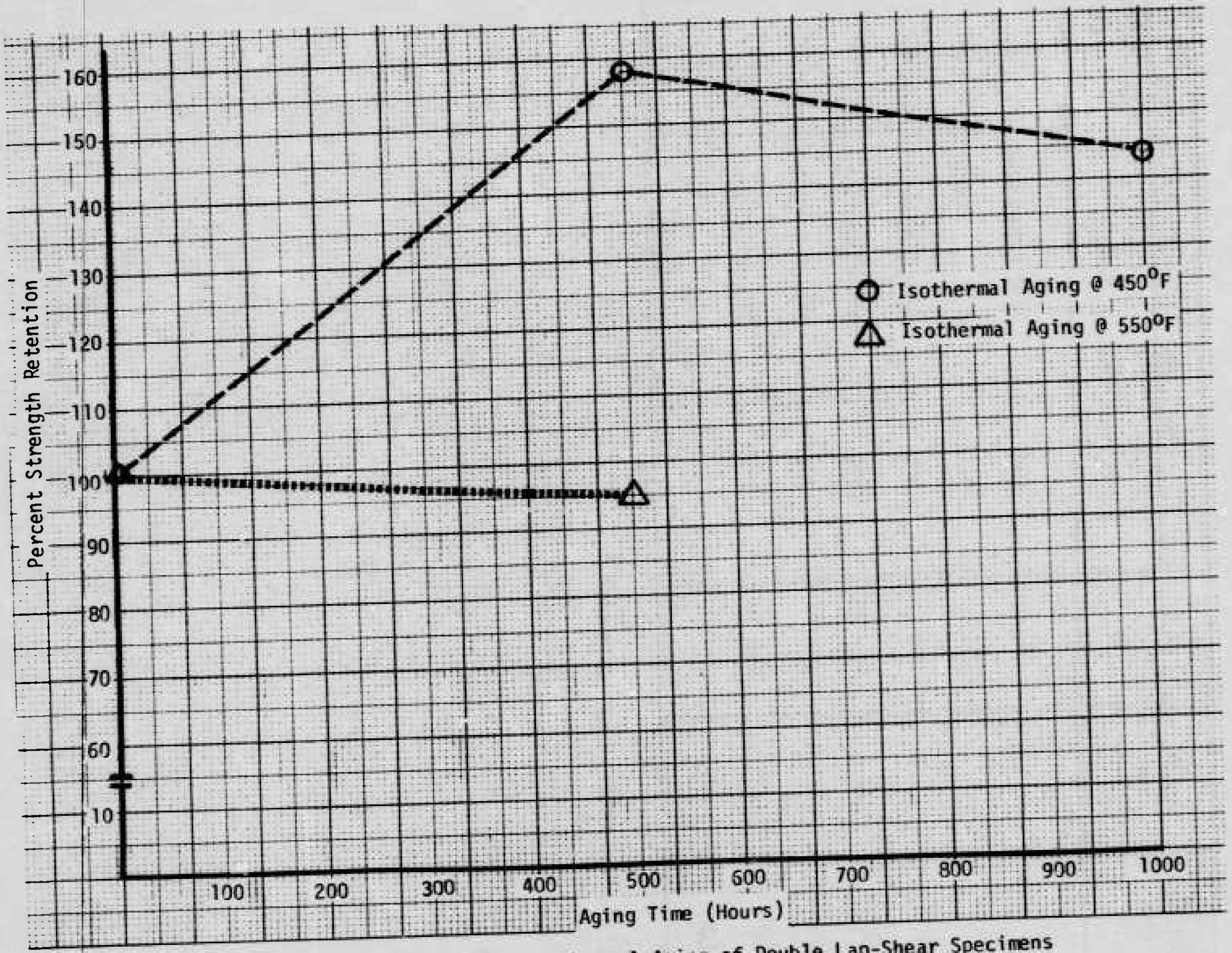


Figure 12. Isothermal Aging of Double Lap-Shear Specimens

3.3.5 Stress Durability Evaluations

Stress durability measurements were made on specimens exposed to two different environments, i.e., condensing humidity (160°F, 95% R.H.) and 450°F isothermal. The specimens were stressed at values of eighty, sixty, forty and twenty percent of the initial lap-shear value. Because the maximum loading capability of the stress durability test fixture was 1000 pounds load, the double lap-shear test specimen was adjusted to provide the desired stress level,i.e., the joint area was reduced by machining the overlap to the correct dimension. All specimens failed either initially or within less than 1.5 hours in the 160°F 95% R.H. environment. The results of the thermal aging specimens are reported in Table XV.

TABLE XV

SUMMARY OF STRESSED THERMAL AGING STUDIES FOR CPPQ ADHESIVE SYSTEM

Initial Shear Strength, RT psi	Shear Strength After Aging, RT psi	Strength Retention, %	Failure Time, hours	Stressed Thermal Aging Conditions		
				Test Load lbs	Test Shear Stress psi	Stress Level
3560	—	—	<1	880(2)	1760	80%
3560	—	—	1<1 1-950	660(2)	1320	60%
3560	1950	55	1-100 N.F.	880	880	40%
3300	2350	71	N.F.	440	440	20%

(1) $$\text{Strength Retention} = \frac{\text{Shear Stress @ RT After Aging}}{\text{Shear Stress @ RT Before Aging} \times 100}$$

(2) Specimen was machined to possess a bonded area of 0.5 sq. inch.

IV. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this effort to develop a crosslinked polyphenylquinoxaline (PPQ) resin for large area bonding of titanium alloys. Based on these findings, recommendations are given for further development activities.

4.1 CONCLUSIONS

- The pendant furan rings incorporated into linear PPQ resins offer a facile method for crosslinking PPQ's. The furan containing tetraketone, p-bis(2-furylglyoxalyl) benzene (BFGB), employed to introduce the furan rings is easily prepared in high purity by a non-selenium dioxide route.
- Low to medium molecular weight linear PPQ polymers were used to obtain sufficient flow to ensure full coverage of the bond line.
- Evaluation of the DAB/85 BPBG:15 BFGB indicated that the CPPQ system met the requirements of this program, i.e., thermally stable at 450°F, possessed adequate toughness and could be used to produce large bonded specimens. However, additional detailed development studies are necessary in order to obtain a thorough evaluation of this adhesive resin.
- Results from long-term thermal aging of joints bonded with CPPQ adhesive systems demonstrated the suitability of the systems for operation in 450°F thermal environments without significant degradation.

4.2 RECOMMENDATIONS

- Studies to evaluate tetraamines other than 3,3'-diaminobenzidine and 3,3',4,4'-tetraaminodiphenylether are warranted in order to provide 1) improved solubility and 2) a less brittle crosslinked resin.

- Studies to evaluate coupling agents and/or different carrier cloths are warranted in order to improve the overall performance of the adhesive. Failure modes observed in this program were almost always to the glass carrier.
- Additional studies to evaluate the effect of surface preparation of the titanium alloys also are warranted. The debonding phenomenon observed during isothermal aging appears to be related to the cleaning method and/or the solvent used (i.e., m-cresol).
- Further property evaluation studies of joints bonded with CPPQ adhesive systems are warranted to obtain detailed design information. Studies should include the determination of shear modulus, creep, fatigue strength and stressed thermal aging at operating temperature (i.e., 450°F) and at different stress levels.

APPENDIX A

The experimental procedures employed to prepare and/or purify the monomers used in this program are provide below.

A.1 Preparation of *p*-Bis(phenylglyoxalyl)benzene.

The method of Hoggat, et al, (Reference 1) was used with some minor modifications as described below.

A.1.1 Preparation of *p*-Phenylenediacetic Acid Chloride.

Two portions of diacid chloride were prepared as follows. A 100 g (0.51 mole) portion of *p*-phenylenediacetic acid was suspended in 150 ml dry benzene containing 1 ml dimethylformamide and then 150 g thionyl chloride was added. The reaction mixture was stirred for 40 hours at 40-50°C. Excess thionyl chloride and the benzene solvent were removed at reduced pressure. Hexane (250 ml) was added to the flask and the mixture was allowed to stand 16 hours. The diacid chloride was collected by filtration, washed with hexane and dried to give 98.4 g product (84% yield).

A.1.2 Preparation of 1,4-Bis(phenacyl)benzene.

To 282 g (2.1 mole) aluminum chloride suspended in 400 ml anhydrous benzene, was added dropwise with mechanical stirring a solution of 184 g (0.8 mole) *p*-phenylene diacetic acid chloride in 500 ml of anhydrous benzene. After completion of the addition, the mixture was stirred 16 hours at 48°C. The cooled reaction mixture was poured over 3 kg of crushed ice containing 400 ml concentrated hydrochloric acid. The precipitate was filtered, washed with water and dried, to give 195.9 g (78%) of product melting 204-208°C [lit m.p. 204-207°C (Reference 1)].

A.1.3 Preparation of 1,4-Bis(phenylglyoxalyl)benzene.

To a slurry of 133 g SeO_2 (1.2 mole)in 1000 ml acetic acid was added 188.6 g (0.6 mole) of 1,4-bis(phenacyl)benzene. The mixture was refluxed for 18 hours, filtered, and the yellow filtrate then was treated with carbon and refiltered. On cooling the bis(1,2-dicarbonyl) compound precipitated as yellow needles. The product was collected by filtration, dried, and then recrystallized from ethanol to afford 97.6 g (48%) of *p*-bis(phenylglyoxalyl)benzene, m.p. 122.5-124°C [lit m.p. 124.5-126°C (Reference 1)].

A.2 Preparation of *p,p*'-Oxydibenzil.

A.2.1 Preparation of *p,p*'-Di(phenylacetylphenyl)ether.

To a slurry of 270.6 g (2.1 mole) aluminum chloride in 1500 ml methylene chloride cooled to 0°C was added dropwise a mixture of 170 g (1 mole) diphenyl ether and 309 g (2 mole) phenylacetyl chloride over a 3-hour period. The reaction mixture was stirred for 18 hours at room temperature, then poured into 1 kg of ice containing 200 g concentrated hydrochloric acid. The resulting slurry was stirred for 4 hours and then allowed to stand for 36 hours. The water was decanted from the solid and the residue was air dried. The crude product was powdered and washed successively with dilute hydrochloric acid, water, 5% (w/v) aqueous sodium carbonate, and water. The off-white material was dried *in vacuo* and then recrystallized from DMF (3 l.) to afford 191 g (47%) of *p,p*'-di(phenylacetylphenyl)ether, m.p. 169-172°C [lit m.p. 169-171°C (Reference 1)].

A.2.2 Preparation of *p,p*'-Oxydibenzil.

To a heated slurry of 88.8 g (0.8 mole) selenium dioxide in 1000 ml glacial acetic acid was added 162.6 g (0.4 mole) *p,p*'-di(phenylacetylphenyl)ether. The mixture was refluxed for 16 hours. The black solution was filtered hot and the filtrate was treated with charcoal and refiltered. The oxydibenzil crystallized as a yellow mass. The product was collected by filtration and then recrystallized from ethanol to give 125 g (72%) of *p,p*'-oxydibenzil as yellow crystals, m.p. 105-106.5°C [lit m.p. 105-106.5°C (Reference 1)]. Overall yield was 28%.

A.3 Preparation of *p*-Bis(2-furylglyoxalyl)benzene (BFGB).

A.3.1 Preparation of *p*-Bis(2-furylglycolyl)benzene.

The BFGB precursor was prepared in three different runs. The products from the two smaller runs were used for recrystallization studies and the material obtained from the third run (double the first runs) was used directly in the oxidation reaction.

To a mixture of 67.1 g (0.5 mole) terephthalaldehyde and 96.09 g (1.0 mole) furfural (freshly distilled) in 800 ml of ethanol was added dropwise a solution of 50 g (0.76 mole) of potassium cyanide in 350 ml of water. (The mixture turned reddish-brown after the addition was started.) An exotherm was observed during the cyanide addition and a precipitate formed within 5 minutes from the start of the addition. After the cyanide addition was completed, the reaction mixture was refluxed for 2 hours and then cooled to room temperature. The precipitate was collected by filtration, washed with ethanol and dried to give 160 g (91%) crude product, m.p. 215-225°C. The brownish material was dissolved in 1200 ml of DMF, treated with charcoal and filtered. Ethanol was added to the hot filtrate until it became turbid. The mixture was allowed to stand for 48 hours, and then the precipitate was collected by filtration, washed with ethanol and dried to give 50 g (31%) of nearly colorless material, m.p. 230-233°C. A second crop (7 g) was obtained by removing solvent and cooling, m.p. 228-231°C. Total yield was 57 g (35%). Using pyridine as the recrystallization solvent, 65 g of material was obtained, m.p. 229-232°C.

A.3.2 Preparation of *p*-Bis(2-furylglyoxalyl)benzene.

A typical small scale oxidation using purified BFGB precursor is first described and then a large scale oxidation using crude precursor is described.

A 119.9 g (0.48 mole) portion of cupric sulfate pentahydrate was added to a mixture of 60 ml water and 140 ml pyridine. The mixture was heated to near reflux and then 39.12 g (0.12 mole) of *p*-bis(2-furylglycolyl)benzene was added. The mixture was refluxed for 5 hours and then allowed to cool. The mixture was poured into 1000 ml water and the precipitate was collected by filtration and washed with water. Recrystallization of the filter cake from acetone afforded 24 g (62%) of BFGB, m.p. 192-194°C. A second crop (5.5 g) was obtained by removing solvent. Total yield was 29.5 g (76%).

A 195.6 g (0.6 mole) sample of crude *p*-bis(2-furylglycolyl)benzene was oxidized in the same manner as above with 599 g (2.4 mole) cupric sulfate pentahydrate in a solvent mixture of 700 ml of pyridine and 300 ml water. The oxidation product was recrystallized from acetone (charcoal) to give 121 g (62%) of BFGB as bright yellow needles, m.p. 191-193°C. Overall yield based on the condensation reaction was 56%. Using purified precursor, the overall yield drops to 27%.

A.4 Purification of Tetraamines

A.4.1 3,3-Diaminobenzidine

The as received material was recrystallized from deoxygenated water (100g in 4-ℓ) containing a pinch of sodium dithionite under a nitrogen atmosphere. The dark brown solution was treated with charcoal, filtered through a diatomaceous earth filter bed and cooled. The light tan crystalline precipitate was collected by filtration and dried *in vacuo* over phosphorus pentoxide at 60°C to give 68 g (68% recovery) of tetraamine, m.p. 177.5-178°C [lit m.p. 179-180°C (Reference 4)].

A.4.2 3,3',4,4'-Tetraaminodiphenyl Ether

The tetraamine was recrystallized from deoxygenated water (100 g in 4-ℓ) containing a pinch of sodium dithionite under a nitrogen atmosphere. The solution was treated with charcoal, filtered and cooled. The off-white crystals were collected by filtration and dried over phosphorus pentoxide, *in vacuo*, at 80°C for 24 hours to give 80 g (80% recovery) of tetraamine, m.p. 149-151°C [lit. m.p. 150-151°C (Reference 5)].

A.5 Preparation of 1,3-Dimaleimidobenzene

To a solution of 196 g (2.0 mole) maleic anhydride in 450 ml of dimethylformamide was added a solution of 108 g (1.0 mole) m-phenylenediamine in 450 ml of dimethylformamide with cooling under a nitrogen atmosphere. To the reaction mixture were added 16.4 g (0.2 mole) sodium acetate and 204.2 g (2.0 mole) acetic anhydride and then the mixture was heated at 50°C for three hours. The imide was precipitated by adding the mixture to 6000 ml water with vigorous stirring. The crude product was collected by filtration and washed with water. The yellow filter cake was air dried and recrystallized from xylene and then from methyl ethyl ketone to give 186 g (69%) of bis(maleimide); mp. 195-197°C.

APPENDIX B.

POLYMER PREPARATION PROCEDURE

The following paragraph presents the experimental procedure employed to prepare the linear PPQ's. The procedure given is for the preparation of the lower molecular weight PPQ used to fabricate the test specimens in Task III.

To a slurry of 14.999 g (70 mmole) 3,3'-diaminobenzidine in 200 g of a 1:1 (w/w) mixture of *m*-cresol:xylene (both solvents freshly distilled) was added, during 10 minutes, a mixture of 20.778 g (60.69 mmole) *p-bis* (phenylglyoxalyl) benzene and 3.452 g (10.71 mmole) *p-bis*(2-furylglyoxalyl) benzene (finely powdered). The residual tetracarbonyl compounds were washed down with an additional 50 g of the solvent mixture. The reaction temperature was controlled by means of a water bath. The reaction mixture was stirred for 20 hours at ambient temperature to give an orange, viscous solution. A sample of the polymer was precipitated by pouring part of the varnish into methanol in a Waring blender. The fibrous yellow polymer was boiled twice in methanol and then dried at 140°C *in vacuo* for 8 hours.

APPENDIX C.

DETAILED PROCESSING PROCEDURES

C.1 PREPARATION OF TI-6AL-4V SUBSTRATE FOR BONDING

Step 1. Solvent clean faying surfaces with methyl ethyl ketone (MEK).

Step 2. Alkaline clean at 180°F for 15 minutes in solution of Turco HTC (90-120 g/liter).

Step 3. Rinse in hot tap water (150°F), then cold tap water (72°F).

Step 4. Immerse in an aqueous bath of Turco 5578 (479 g/liter distilled water) at 200°F for 20 minutes.

Step 5. Wash with 180°F distilled water.

Step 6. Dry in air circulating at 150°F.

Note: Panels fabricated for detailed testing included a step of rinsing in a solution of HNO_3 (5% v/v), followed by a 180°F distilled water rinse after the Turco 5578 etch.

C.2 PREPARATION OF ADHESIVE TAPE

To a 12 percent resin solids polyphenylquinoxaline varnish containing the crosslinking agent was added aluminum powder. The adhesive film was prepared by mounting style 112 A1100 glass scrim over a picture frame and coating the scrim with a 6% w/w PPQ resin in the xylene/m-cresol solvent mixture. The resultant film then was air dried 30 minutes at room temperature followed by 1-2 hours at 180°F. A second coating of the adhesive paste then was applied and dried in the same fashion. This process was repeated, alternating sides of the adhesive film until the desired quantity of adhesive paste had been applied. The adhesive tape was then dried for 16 hours at 180°F. (Drying should take place in a vented air circulating oven.)

C.3 PREPARATION OF BONDED TI-6AL-4V TEST SPECIMENS

Step 1. Prepare titanium alloy for bonding using the Turco 5578 cleaning method (see Section C.1).

Step 2. Using a 6% solution of the PPQ varnish in xylene/m-cresol (50/50 v/v), apply a thin coating, air dry 30 minutes and 16 hours at 180°F in a vented air circulating oven.

Step 3. Prepare adhesive film in accordance with procedure C-2 and apply to primed faying surface.

Step 4. Assemble specimen to be bonded onto a preheated assembly jig at 700°F and load into a preheated press. Apply 500 psig pressure and hold 60 minutes.

Note: When using DAB/850DB:15BFGB resin, the assembly jig and press were at 600°F instead of 700°F.

Step 5. Cool press to below 300°F prior to release of pressure.

Step 6. Remove bonded specimens from assembly jig and cool to room temperature.

Note: When bonding specimens with DAB/850DB:15BFGB resin system, the specimens were postcured at 650°F for 16 hours in an air circulating oven.

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